Developing motorway balancing ponds with long-term net ecological value

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Summary

The contamination of aqueous environments by metals of concern due to anthropogenic factors such as the use of motor vehicles is increasing at an alarming rate, with contaminants such as lead (Pb), copper (Cu), zinc (Zn) and cadmium (Cd) being carried into receiving waterbodies. The sources of vehicle pollution that contaminate these waterbodies through road runoff are reasonably well understood and the release of the most recognised metals of concern (Pb, Cu, Zn and Cd) are primarily as a result of vehicle abrasion or leaks. Current techniques to remediate motorway runoff, such as balancing ponds, are in place but have the potential to leave toxic residue with the associated removal costs often proving prohibitive.

This research focuses on the use of biochar and amended biochar as a remediator for the key metals of concern from motorway run off. The primary aims of this thesis are to: (i) investigate which amendments to biochar improve the immobilisation of Pb, Cu, Zn and Cd (ii) investigate the immobilisation capacities and immobilisation mechanisms of biochar and amended biochar (iii) investigate if amended biochar leaches nutrients harmful to aquatic environments and if so what treatment options are available to mitigate leaching without reducing the immobilisation of Pb, Cu, Zn and Cd, and (iv) to quantify the contact time required for amended biochar to immobilise key metals of concern.

Amendments to biochar, particularly wood ash, were found to significantly increase the immobilisation of Pb, Cu, Zn and Cd. Wood ash amended biochar had a maximum measured removal of 61.5 mg/g for Pb, 38.9 mg/g for Cu, 12.1 mg/g for Zn and 10.2 mg/g for Cd, around an order of magnitude greater than pristine biochar. Immobilisation was primarily as a result of precipitation, ion exchange and co-precipitation. When the wood ash was sintered to the biochar, ground to <3mm and rinsed with deionised water the leaching of nutrients, such as phosphates, sulphates and nitrates, fell to below Water Framework Directive thresholds without reducing immobilisation of the metal contaminants. Furthermore, once these treatments were undertaken, the fast removal performance of wood ash amended biochar was still evident with between 86 – 97% of metals being immobilised in the first minute due to precipitation and ion exchange which are key to early stage immobilisation. The results from this research clearly indicate that biochar, specifically wood ash amended biochar has the potential to be scaled up and used to immobilise Pb, Cu, Zn and Cd from motorway runoff as well as from other contaminated aqueous environments such as mine waters.

Declarations and statements

Declaration

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree

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Abbreviation

AADT:	Annual average daily traffic
BaP:	Benzo-a-pyrene (Benzo[pqr]tetraphene)
BC:	Pristine larch biochar
CAHB:	Charge assisted H-bonding
CEC:	Cation exchange capacity
DOM:	Dissolved organic matter
EC:	Electrical conductivity
EDA:	Electron donor acceptor
EU:	European Union
FTIR:	Fourier transform infrared spectroscopy
ICP-OES:	Inductively coupled plasma - optical emission spectroscopy
MP-AES:	Microwave plasma atomic emission spectroscopy
PAH:	Polyaromatic hydrocarbons
PZC:	Point of zero charge
SEM-EDX:	Scanning electron microscopy with energy dispersive x-ray
SSA:	Specific surface area
SuDS:	Sustainable drainage systems
WA:	Larch biochar cold mixed with wood ash
WAGr:	Larch biochar cold mixed with wood ash ground <3mm
WAR:	Larch biochar cold mixed with wood ash rinsed with deionised water
WAS:	Larch biochar sintered with wood ash
WASGr:	Larch biochar sintered with wood ash ground <3mm
WASR:	Larch biochar sintered with wood ash rinsed with deionised water
WFD:	Water framework directive
XRD:	X-ray powder diffraction
XPS:	X-ray photoelectron spectroscopy

Chapter 1. Introduction

1. Introduction

1.1 Motivation

Motor vehicles are recognised as a key source of pollution in modern society. As of December 2021, there were ~40 million licensed vehicles in the UK, a number that has been rising by ~544k per year since 1995 and by ~643k per year since 2013 (Gov.uk 2022). This escalating increase in traffic volume specifically annual average daily traffic (AADT) has been seen to directly correlate with an increase in contaminant input (Ewen et al., 2009; Hwang et al., 2016, 2018). Such an increase in vehicles also naturally necessitates a growth in impermeable urban roads, pavements and motorways. In highly developed areas these surfaces can account for up to 70% of the total surface creating an increase in the volume and velocity of runoff generated by precipitation (Budai and Clement 2011; Ladislas et al. 2015; Hwang et al. 2016). This runoff washes away the particles deposited by anthropogenic sources, such as motor vehicles, carrying the contaminants into receiving waterbodies (Zhang et al. 2012b; Ladislas et al. 2015). The combination of the growth of motor vehicle numbers and the increase in impermeable surfaces has led to rising amounts of pollution making traffic a major contributor of both organic and inorganic contaminants into the environment (Napier et al. 2008).

Both inorganic and organic contaminants entering waterways because of motor vehicles can lead to freshwater degradation, threaten local plants and organisms, and negatively affect human health. Whilst trace levels of metals are necessary for species to prosper, where metal levels accumulate and increase beyond acceptable levels, they become toxic (Mayer-Pinto et al. 2010). The exposure of aquatic organisms to metals of concern, such as Cd, Cu, Pb and Zn, can lead to their increased predation, changes in growth, reduced cellular health, reduced reproductive ability and increased mortality (Burrows and Whitton 1983; Napier et al. 2008; Cooper et al. 2009; Mayer-Pinto et al. 2010; Yi et al. 2011). Furthermore, the ingestion of these metals of concern by species that are primary aquatic food sources, such as shellfish and phytoplankton, allow metal contaminants to enter the food chain (Cooper et al. 2009). Humans are exposed to these metals via this food chain and freshwater leisure activities. This can lead to significant adverse health consequences such as reduced neurological function, reduced liver function, reduced fertility, kidney damage, lung damage, osteoporosis and mortality (Järup 2003; Ewen et al. 2009; Morais et al. 2012). Organic contaminants, particularly hydrocarbons and more specifically polycyclic aromatic hydrocarbons (PAHs) are also of concern due to their potential effects on biota and human health (Hilliges et al. 2013). PAHs are toxic with mutagenic and carcinogenic properties, are associated with cardiopulmonary diseases, cause liver damage, have developmental and reproductive effects and increased mortality (Martellini et al. 2012; Aziz et al. 2014; Public Health England 2018). As with metals of concern, human exposure is linked to direct contact (in this case through freshwater leisure activities) and the aquatic food chain (Public Health England 2018). Runoff can contain hundreds of hydrocarbon compounds therefore receivers of road runoff have to deal with a complex mixture of contaminants (Boxall and Maltby 1997), however there are some key PAHs which are of primary concern. Both the EU and US EPA cite several hydrocarbons as priority due to their high levels of toxicity (European Commission, 2008; United States Environmental Protection Agency, 2019), of these pyrene, benzo-a-pyrene (BaP) and acenapthene [or acenaphthylene] are particularly associated with vehicle and exhaust emissions (Kennedy et al. 2002; Crabtree et al. 2009; Martellini et al. 2012; Markiewicz et al. 2017; Hwang et al. 2018).

1.2 Road dust and runoff traffic contaminants

It is commonly accepted that road runoff is a major contributor to freshwater degradation through traffic related contaminants including metals of concern and hydrocarbons (Roger et al. 1998; Helmreich et al. 2010a; Kayhanian 2012; Klöckner et al. 2020). Although the key contaminants and sources are generally agreed upon, the concentrations of the polluted runoff are more contentious. Furthermore, whilst some fundamental principles can be held true, many studies return different findings on a country by country or even site by site basis due to factors such as traffic density, traffic flow, local composition of car parts, national legislation or climate.

The sources of vehicle runoff pollution are reasonably well understood and multiple studies have looked at the sources of vehicular contaminants. Vehicular pollution can be categorised into two main sections: exhaust and non-exhaust, to which must be added non vehicle runoff pollution such as road surface and signage.

Exhaust pollution

Although exhaust emissions are primarily associated with atmospheric pollution, the incomplete combustion of fuel is a significant source of inorganic and organic particulate matter (PM) pollution (Hwang et al. 2018). Particle emissions from uncombusted fuel fall into three categories: soot, soluble organic fraction and inorganic fraction (Reşitoglu et al. 2015). PM organic emissions of primary concern are hydrocarbons, most significantly PAHs such as pyrene, benzo(a)pyrene, acenaphthene and indeno(123-cd)pyrene (Kennedy et al. 2002; Zielinska et al. 2004; Martini and Larsen 2013; Zheng et al. 2017) and PM inorganic emissions of note include Cd and Mg (Ewen et al. 2009; Hwang et al. 2016; Markiewicz et al. 2017).

The methods to quantify the PM exhaust emissions vary significantly between papers with no standardised method. Methods used include laboratory tests (Zielinska et al. 2004; Martini and Larsen 2013), stationary road tunnel / road tests (Gertler et al. 2002) and portable emissions tests fitted to vehicles driving in real world situations (Zheng et al. 2017). The advantage of a laboratory method is that specific areas of concern can be addressed and analysed. Zielinska et al (2004) discuss how the age and mileage of vehicles impact emissions with older higher mileage vehicles producing more PAHs. However, this methodology doesn’t provide a real world perspective and can provide limited variables around driving style which also affect emissions. Road tunnel tests such as Gertler et al’s (2002) study overcome the restrictions of laboratory work but do not allow the characterisation of emissions from individual vehicles or categories of vehicles rather focus on measuring emission rates averaged over many vehicles. The most rounded methodology appears to be mobile portable emissions tests used by Zheng et al (2017) which combine real world conditions whilst enabling the characterisation of specific vehicles. These three different methods are partly as a result of how varied PM emissions are due to vehicle type and conditions with each method enabling focus on certain aspects of exhaust emissions. Emission variations result from a number of factors including engine technology (Zheng et al. 2017), climate (Kennedy et al. 2002), altitude, vehicle age and mileage (Zielinska et al. 2004). Depending on the area of focus of any given study different methods may be necessary.

The variation in emissions due to vehicle type and conditions lead to hundreds of thousands of PAH isomers being emitted resulting in two broad methods in reporting emissions: total PAH or individual PAHs. Kennedy et al (2002) highlight that the complexity of the combustion exhaust stream results in the potential for any compound permeation to be formed in the ever changing combustion conditions. To circumvent some of the difficulties that this presents Napier et al (2008) reported total PAH in their study rather than teasing out individual PAHs. However, this method ignores that different PAH species produce different toxicities resulting in different risk levels (Aryal et al. 2013). Reporting a combination of priority PAHs and total PAHs is more appropriate, a method used by several papers including Zheng et al (2017) and Aryal et al (2013).

Non exhaust pollution

Non exhaust vehicle sources are also significant emitters of road surface contaminants, generally through abrasive forces or leaks and include tyre wear, brake wear and motor oil. However, there is a lack of standardized sampling procedure and measurement techniques for these emission sources often leading to incomparable results and conclusions (Grigoratos and Martini 2015).

Tyre Wear

Tyre wear is recognised as being responsible for a number of key toxic contaminants both inorganic (primarily Zn and Cd) and organic (such as the PAHs pyrene and benzo[ghi]perylene and phthalates). These contaminants are released through vehicle use as the tyres wear down, and unlike exhaust emissions, are collected entirely on the road surface, around 90% of which is captured by runoff, and subsequently leach toxic compounds (Wik et al. 2009; Budai and Clement 2011; Markiewicz et al. 2017). The mass of each tyre that is released during its lifespan is estimated to be between 857 g (Legret and Pagotto 1999), 1kg (Markiewicz et al. 2017) and 1-1.5 kg (Goodwin et al. 2013), this lifespan being between 50,000 – 60,000 km or 4 years (Legret and Pagotto 1999; Goodwin et al. 2013; Markiewicz et al. 2017). Tyre wearing leads to ~460,000 tonnes of rubber being released in Europe annually (Wik et al. 2009).

Tyre wear has been demonstrated to be the main source of Zn found in road dust and is recognised as a source of Cd, Pb, Cu, Ni, Cr and Sb (Legret and Pagotto 1999; Hjortenkrans et al. 2007; Budai and Clement 2011). Tyres are strengthened using Zn to improve resistance to heat and abrasion and constitutes the consumption of 1.2 million tonnes of ZnO annually during tyre production (Hwang et al. 2016). Although tyres are the major emitter of Zn, Hjortenkrans et al (2007) believe that there is an overestimation of importance of Zn from tyres in some studies due to inclusion of the whole tyre composition in reporting rather than the fraction of the tyre that wears. Nonetheless Hjortenkrans et al (2007) still rank tyre debris as the primary source of Zn emissions.

Legret and Pagotto (1999) and Hjortenkrans et al (2007) assert that tyre wear is not just the primary source of Zn but of Cd as well, whereas Budai and Clement (2011) suggest that Cd emissions from brake wear is equal to that of tyre wear. This seemingly small disparity between papers highlights some of the issues in comparing many of these studies. Firstly, each of the three studies were undertaken in different countries: Legret and Pagotto, (1999) focused on France, Hjortenkrans et al, (2007) focused on Sweden and Budai and Clement, (2011) focused on Hungary. Tyre and brake composition are different in in each country as vehicle component make up varies depending on type, model and manufacturer, all of which are likely to vary dependent on location (Thorpe and Harrison 2008; Budai and Clement 2011). Furthermore, Hjortenkrans et al’s study in Sweden analysed tyres outside of the EU that were not subject to the same legislation as the EU countries in terms of composition. The age of the studies are also impacted by legislation surrounding tyre and brake composition; according to the directive of the European Parliament and Council after July 2003 materials and components of vehicles should not contain Pb, Hg, Cd or Cr(VI), with brake linings as an exception to these restrictions (Hjortenkrans et al. 2007). As such, the levels of Cd in tyre emissions should show a reduction between Legret and Pagotto’s 1999 study and Budai and Clements 2011 study, likely explaining the rise of importance of brake wear as a source of Cd. Finally, the methods used by each study vary, with potential to impact results. Legret and Pagotto (1999) look solely at motorway vehicle emissions, Budai and Clement used urban and motorway vehicle emissions, whereas Hjorkens et al (2007) analysed the composition of tyres and brakes and made calculations based on emission levels (mg/vkm) based on previous studies and national traffic volume (urban and motorway). Braking and tyre wear are dependent on several factors including driving style, acceleration and deceleration, amount of cornering and traffic speed, all of which would be different dependant on motorway or urban driving (Ewen et al. 2009; Budai and Clement 2011; Goodwin et al. 2013; Crosby et al. 2014; Markiewicz et al. 2017). Whilst it is pertinent to illustrate the potential for different contaminant concentrations or different priority ordering of contaminant sources between papers, there is an overarching consensus that tyres are responsible for a substantial amount of Zn and Cd pollution (as well as Pb, Cu, Ni, Cr and Sb).

Tyre wear is also considered to be the primary non exhaust emission source of hydrocarbons, primarily PAHs (such as pyrene, benzo[ghi]perylene, indeno(1,2,3cd)pyrene and coronene), phthalates and alkylphenols (Martellini et al. 2012; Aryal et al. 2013; Markiewicz et al. 2017; Hwang et al. 2018). Hydrocarbons are used in the production process of tyres to improve tyre performance and stability, however, since 2010 there has been EU legislation to remove the most toxic organic additions to the tyres in production such as the highly aromatic oils used as softeners (Markiewicz et al. 2017). Despite this Markiewicz et al’s study (2017) found that there was still a high number of tyres containing HA oils on roads due to a delay in tyre replacement, rubber recycling and international transport with the result that PAH contaminants have not reduced in the expected manner. This change in legislation again underscores the importance in study date and location in terms of pollution type and concentration.

Brake wear

Brake wear is recognised as being the primary source for inorganic contaminants such as Cu and Sb (Legret and Pagotto 1999; Hjortenkrans et al. 2007; Budai and Clement 2011; Goodwin et al. 2013) and to a lesser degree a source of organic contaminants such as PAHs, specifically benzo[a]pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene (Goodwin et al. 2013; Markiewicz et al. 2017). Brake wear has also been shown to contain significant quantities of inorganics of interest such as As, Cd, Cr, Pb and Zn (Legret and Pagotto 1999; Hjortenkrans et al. 2007; Budai and Clement 2011; Goodwin et al. 2013). Such brake wear is associated with Cu in particular with Hwang et al (2016) estimating that around 2400 tonnes of Cu was released by brake wear in Europe during 2000, representing 48% of Cu released from all sources. Manufacturer rationale for adding Cu to brake pads is to make the pads smoother when applied and to prevent shuddering (Hwang et al. 2016). In a similar fashion Sb is used as a lubricant (Hjortenkrans et al. 2007). PAHs are added to the brake lining as a protective coating (Rogge et al. 1993).

It is worth noting that legislation has changed the make-up of brake linings over the decades. Asbestos was a significant constituent of brake linings in the 1970s, used to increase friction. Unsurprisingly such a carcinogenic mix of minerals is no longer used in brake linings with the 1999 European Directive 98/12/EC enforcing asbestos-free brake pads for all road vehicles (Goodwin et al. 2013). Despite legislation around the use of Pb (for example as an additive in fuel), it is still used in car components. Goodwin et al (2013) detected Pb studies all be it at reduced concentrations in comparison to older studies such as that of Legret and Pagotto (1999). The continued use of Pb by manufacturers is facilitated by an exception to European legislation surrounding car component composition relating to brakes. In 2003, EU legislation stated that vehicles should not contain Pb, Hg, Cd or Cr(VI), however, brake linings were one of the components added in June 2002 to Appendix II of the directive as an exception to these restrictions (Hjortenkrans et al. 2007).

The brake wear that releases these components is generally reported in mg/vehicle/km and falls between the range of 7.5 – 20 mg/vehicle/km for passenger cars, 16.9 – 30 mg/vehicle/km for light goods vehicles and 40-80 mg/vehicle/km for heavy goods vehicles (Legret and Pagotto 1999; Napier et al. 2008; Budai and Clement 2011; Goodwin et al. 2013). The first explanation for disparity here revolves around whether the study focuses on urban driving, highway driving or mean values of both, as less braking is required during highway driving and therefore less emissions per vehicle are generated (Grigoratos and Martini 2015). Further reasons for differences include how the study defined the proportion of vehicles with back brakes or front brakes, as front brakes produce more debris (Goodwin et al. 2013), manufacturer and quality of brake lining (Thorpe and Harrison 2008).

Motor oil

Motor oil is also recognised as a major source of PAHs which contribute to pollution (Napier et al. 2008; Budai and Clement 2011; Aryal et al. 2013; Mummullage et al. 2016; Markiewicz et al. 2017). Other contaminants include Zn and to a lesser degree Pb and Cu, with PAHs being the key contaminant (Napier et al. 2008; Budai and Clement 2011). Studies vary in their priority ordering of PAH sources. Both Napier et al (2008) and Mummullage et al (2016) rank vehicle sources of PAH as Oil > exhaust > tyre, however Markiewicz et al (2017) assert the rank exhaust > tyre > oil > road wear > brakes. There appear to be two main reasons for this difference, the first of which again revolves around urban and highway driving. Oil loss usually occurs while the vehicle is standing, a situation more likely to occur in urban rather than highway situations (Budai and Clement 2011), Markiewicz et al (2017) focus on highway driving as opposed to Napier et al (2008) and Mummullage et al (2016). Secondly Markiewicz et al (2017) don’t use a purely volume based ranking unlike the other studies; they also designate priority to PAHs due to a list of factors including toxicity of the different types of PAH and expert judgements on the impact of each of the individual PAHs in addition to volume. Markiewicz et al (2017) specifically highlight benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3- c,d] pyrene and anthracene as problematic.

Road wear and signage corrosion

Outside of the key non exhaust sources of contaminants there are several sources, such as road wear and signage corrosion which also contribute to pollution (Brandt and de Groot 2001; Markiewicz et al. 2017).

Roads thus far have been considered as a repository for contaminants, but their composition and wear mean that they also function as a contributor. The composition of roads can again be disparate from area to area with typical structure including coal tar, bitumen, granite based, quartzite based or concrete (Gustafsson et al. 2009; Goodwin et al. 2013; Gustafsson 2018; Hwang et al. 2018). Nonetheless, broadly speaking roads normally have a rock ballast comprising around 90-95% and a bitumous binder comprising around 5-10%, however this bitumen content has been seen to be as high as 50% (Kennedy et al. 2002; Goodwin et al. 2013; Gustafsson 2018). Bitumen is primarily a mixture of high molecular weight hydrocarbons

(PAHs) with small quantities of nitrogen, sulphur and trace metals, a composition that is generally consistent worldwide (Kennedy et al. 2002; Hwang et al. 2018). The make-up of the surface is directly linked to the contaminants that are released by wear and dust generated from bitumen roads will naturally include a proportion of bitumen and therefore PAHs particles (Kennedy et al. 2002). Furthermore, Brandt and De Groot (2001) assert that PAHs leach from such bitumen surfaces and contribute to PAH contamination. Analysis has found key PAHs such as naphthalene, pyrene, benzo(g,h,i)perylene and fluoranthene within the bitumen with overall PAH concentrations between 9.2 and 15.2 mg/kg (Brandt and de Groot 2001; Kennedy et al. 2002). The amount of road wear is impacted by a number of factors such as vehicle speed, aggregate size within the road composite, weight of vehicles on the road and traffic density making motorways larger contributors of road wear than urban roads (Kennedy et al. 2002; Thorpe and Harrison 2008; Gustafsson et al. 2009).

The corrosion of safety barriers or road signage is also generally accepted as a contributor to Zn pollution. However, although multiple studies mention this corrosion most studies do not attempt to quantify its impact (Helmreich et al. 2010a; Budai and Clement 2011; Markiewicz et al. 2017). Legret and Pagotto (1999) are the exception to this point and argue that safety fences are responsible for 0.95 kg/km/year Zn**.** Whilst in itself the discussion around the emission of Zn from barriers / signage doesn’t seem to be of great significance it does demonstrate there are multiple sources of many contaminants and as such the direct linkage of any one contaminant concentration to any one source, e.g. Zn to tyres, has to be viewed with caution.

Road dust and runoff contaminants

Whilst there is broad consensus over the primary contaminants emitted by car components and a reasonably small range of values in which the wear takes place, studies attempting to conclusively link the source of contaminants to the concentration of contaminants seen in road dust or runoff are sparse. Linking a contaminant concentration directly to an individual source even with the use of tracer elements, fingerprinting approaches and links between component content and road dust or runoff is imperfect (Thorpe and Harrison, 2008; Taylor et al., 2014). Methods such as those undertaken by Apeagyei et al (2011) using a portable XRF to analyse tyres in the same area as road dust have been used but may not provide definitive links between source and road dust contaminant. As a result, it is pertinent not just to review potential sources of contamination, which form an important part of understanding how to remove contaminants, but also to review contaminant type and concentrations found directly in road dust, runoff and sediment.

	Road dust							
Author and Date	Cd	Cr	Cu	Ni	Pb	Zn	measurement	Location
Crosby et al. (2014)	12	175	337	31	227	1145	mg/g	London, UK
Aryal et al. (2017)	1	301	182	97	216	950	µg/g	Sydney, Australia
Duong and Lee (2011)	3.44		182	33	153	325	µg/g	South Korea
Zhao et al. (2010)	0.6	75.5	113	39.2	112	591	µg/g	Beijing, China
Apeagyei et al. (2011)		95	105		73	240	ppm	Massachusetts, USA

Table 1.1a: concentration and location of road dust contaminants

	Runoff																			
Author and Date	Mean Cd µg/l	Mean dissolved Cd %	Maximum dissolved Cd %	Mean Cr µg/l	Mean dissolved Cr %	Maximum dissolved Cr %	Mean Cu µg/l	Mean dissolved Cu %	Maximum dissolved Cu %	Mean Ni µg/l	Mean dissolved Ni %	Maximum dissolved Ni %	Mean Pb µg/l	Mean dissolved Pb %	Maximum dissolved Pb %	Mean Zn µg/l	Mean dissolved Zn %	Maximum dissolved Zn %	pH	Location
Zhao et al. (2010)	0.273	43		30.5	45		59.5	56		26.5	41		71	37		405.5	18			Beijing, China
Crabtree et al. (2003)	0.49			5.98			41	48		5.31			23.05			140.3	35		6.4 - 9	UK
Crabtree et al. (2009)	0.63						91.2	34								352.6	32			UK
MacKay et al. (2011)							62.6	36	100				6			155.3	40	93		Conneticut, USA
Zhang et al. (2013)								65.1	95				3.1	38.3	60.1	5.8	57.2	96.7	7.67 - 8.76	Chongqing, China
Hallberg & Renman (2008)	0.127	49					33.4	50								169	88		7.0 - 7.5	Stockholm, Sweden
Helmreich et al. (2010)	<0.5						191	21		55	17		56	0		847	27		6.2 - 8.3	Munich, Germany
Hilliges et al. (2017)	0.36		~100				67.1	28.3	~100				21.4	5	~100	311	23.5	~100	7.11 - 8.15	Ausberg, Germany

Table.1.1b: concentration and location of road runoff contaminants

Different studies focus on a different number of contaminants but generally encompass the key metals Cu, Pb and Zn and in most cases also Cd (Table 1.1a and 1.1b). As with the sources of contaminants, there are a number of reasons that can be attributed to differences between the concentrations of contaminants in studies. Legislative differences are a potential for variations often signified by location and age of study. A source of Pb in some American states is Pb wheel balancing weights, but these are not legal in other US states such as California or in Europe post 2005 (Hwang et al. 2016). Again, as with studies relating to the source of contaminants, the type of road (e.g. highway, urban or rural) and consequent average annual daily traffic (AADT) that is studied will impact road dust or runoff contaminant concentrations. High AADT as a result of the urban nature of the roads, such as that observed by Aryal et al. (2017), are more likely to produce higher concentrations than studies which incorporate more rural roads such as those observed by Apeagyi et al. (2011). This is borne out by Aryal et al. (2017) recording Pb concentrations at a factor of three higher than Apeagyi et al. (2011). Often the AADT is not specifically referenced in these papers forcing the reader to make assumptions on this variable based on the type of road studied (highway, rural etc); papers such as Zhang et al (2013) do specifically mention AADT values, whereas papers such as MacKay et al (2011) do not.

Sampling period also has the potential to create inconsistency between papers. Longer sampling periods will reduce the potential variation between results and as such studies that sample over longer periods are more likely to be representative (Crosby et al. 2014). Crabtree et al (2003) were able to undertake a five year study, with six sites all of which were monitored for at least a year with 10 rainfall events. Other studies were conducted over much shorter periods. In the case of Zhao et al (2010) studies were only conducted over three sites and two rainfall events. Crabtree et al (2003) show values of Pb and Zn three orders of magnitude lower than Zhao et al (2010), potentially in part due to the variability in study length. Other reasons for variations between papers can include variables that are not mentioned in papers such as antecedent dry period, temperature or the use of road sweepers (relevant for road dust). Although some papers do make reference to at least some of these factors (Crabtree et al. 2009; Aryal et al. 2017) many do not.

Although there are variations of several magnitudes in contaminant concentrations in road dust and road runoff between papers there does appear to be general consensus over which contaminants are present. As with papers focusing on the sources of contaminants the key inorganics found are Pb, Cu, Zn and Cd with Cr and Ni also being of relevance.

1.3 Road runoff remediation

Whilst there are remediation techniques that attempt to lessen the impact of particulate vehicle pollution these methods are not without issue both in terms of toxic residue and removal costs. There are three key processes currently used to remove contaminants: vegetated treatment processes, separation and sedimentation. Filtration via systems such as constructed wetlands are used to diminish contaminants, filtering polluted runoff through uniformly graded stone, soil or other such media. This can be effective in initially mitigating contaminants; however, the spent filter media can be classified as contaminated requiring expensive treatment and removal. Filters are often not replaced once their expected useful life has expired (Berhanu Desta et al. 2007; Hatt et al. 2011). Settlement tanks with baffle tanks, oil interceptors and petrol interceptors are also options that can be employed to reduce hydrocarbons from runoff, however these systems are considered expensive and as a result are adopted less infrequently (Meland 2016). In addition to initial cost, regular, expensive maintenance is required for these systems, without which capacity is quickly reached, rendering the device ineffective and releasing the hydrocarbons captured (Meland 2016). The removal of contaminants through sedimentation, using treatment systems such as balancing ponds, are a further tool used in the remediation of motorway runoff.

1.3.1 Balancing ponds

Currently attempts to mitigate metals of concern entering waterways as constituent parts of motorway runoff primarily involve sedimentation, the subsequent accumulation of which then require expensive treatment and extraction. Techniques such as balancing ponds capture sediment mitigating the flow of contaminants into waterways (Farm 2002; Starzec et al. 2005; Karlsson et al. 2010; Weinstein et al.

2010; Hilliges et al. 2013; Meland 2016). Studies have asserted that balancing ponds can initially reduce contaminants, such as metals of concern and PAHs, by significant amounts (Farm 2002; Starzec et al. 2005; Weinstein et al. 2010). Runoff is channelled from motorways through pipes and drains connected to the motorway (surface water drainage systems) to allow the runoff to flow into the balancing pond. As the motorway surface materials are effectively impermeable runoff is shed towards the edges of the motorway and into surface water drainage systems (Highways England 2020). There are several collection methods for runoff to be transported to the surface water drainage systems including combined kerb and drainage and linear drainage channels; different roadways will have different runoff collection methods dependant on road type and road age (Highways England 2020). Combined kerb and drainage methods comprise monolithic kerbs with internal drainage channels linked to openings in the kerb face whereas linear drainage channels are a closed profile hydraulic conduit with slots or holes located in the top that the runoff drains into (Highways England 2020). Linear drainage channels are currently in use on the M4 junctions three to twelve to collect runoff (Figure 1.1) As well as runoff collection methods differing, the stretch of road that is serviced by the balancing pond, the average daily traffic on that section of road, the outlet to the balancing pond, and the size of the balancing pond itself can vary from site to site (Starzec et al. 2005). For example the pond situated at Leatherhead, Surrey studied by Ladislas et al., (2015) collected water from a road section measuring ~13722 m^2 with two inlet pipes feeding the pond, the pond situated at Oxted, Surrey examined in the same study captured runoff from ~76160 m^2 of road and is drained from the motorway surface through a series of pipes and manholes that discharge into the pond whereas the pond studied by Barbosa & Hvitved-Jacobsen, (1999) collected water from 2500 m^2 of road with only one inlet pipe feeding the pond. Whilst the principle of collection of runoff from the road fed by inlet pipes to the pond is standard the area covered and design is site specific (Starzec et al. 2005). Once the runoff has been fed by pipe into the pond, particle sedimentation occurs immobilising metals such as Pb, Cu, Zn and Cd after which the water is then discharged into the natural environment through an outlet (Barbosa and Hvitved-Jacobsen 1999; Hares and Ward 1999; Farm 2002; Starzec et al. 2005; Ladislas et al. 2015)

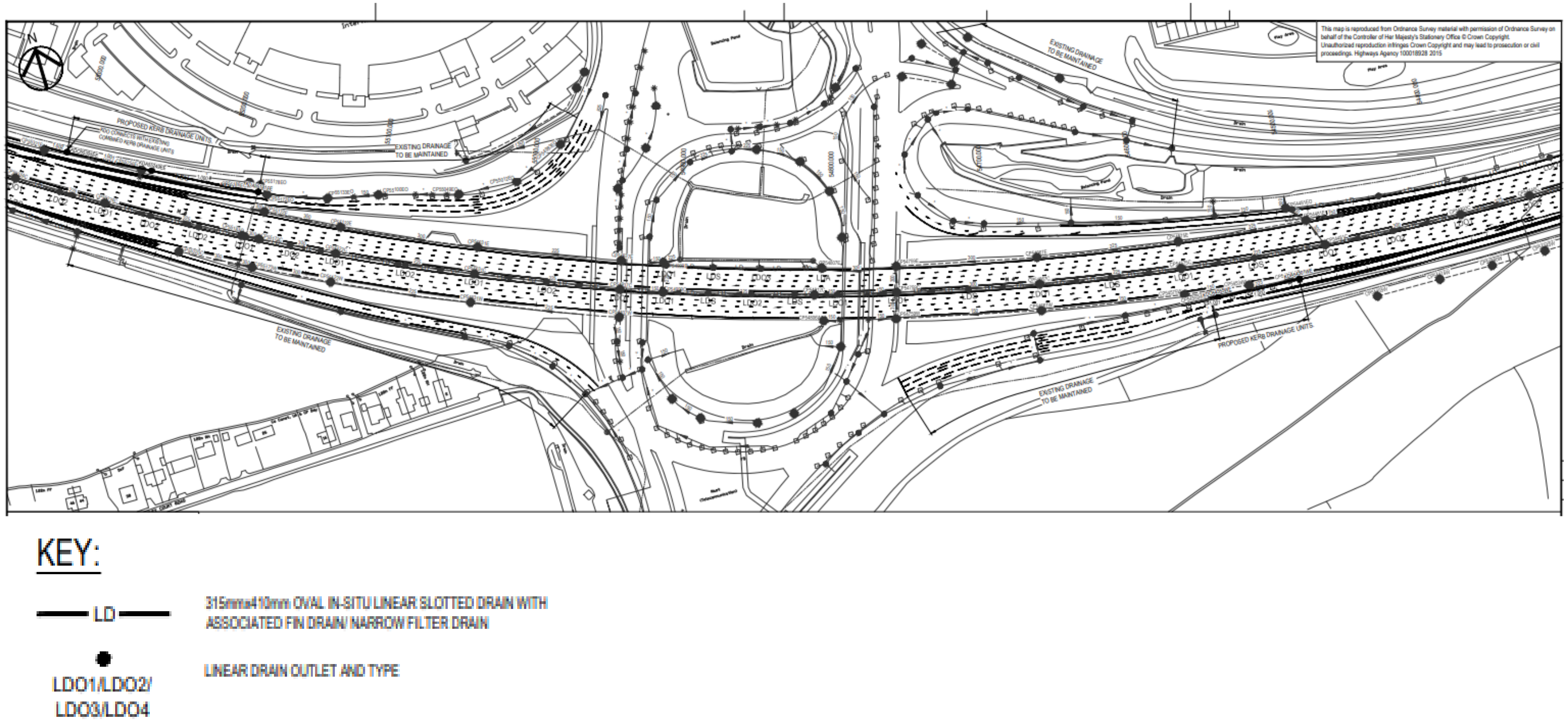

Figure 1.1: M4 junctions 3 – 12 drainage schematics highlighting the use of linear drainage channels to transport surface runoff to water drainage systems (Highways England, 2015)

Although balancing ponds can reduce contaminants, they do have issues in terms of longevity and removal of waste. Concentrations of PAH in Florida range from background levels in ponds that are less than one year old to 7g/kg in 30 year old ponds (Weinstein et al. 2010). Farm (2002) found that storm water passing through the balancing pond showed an average reduction rate of between 26% and 84% for metals of concern. Similarly, Crabtree et al (2006) demonstrated a reduction of metals of concern in the range of 0-70 %. However, this reduction of metals from the water results in the build up of a polluted sediment forming a toxic waste product that requires the pond to be dredged, a process that is exceptionally expensive and as a result is often neglected (Rulkens 2005; Weinstein et al. 2010; Meland 2016). Although balancing ponds initially reduce the influx of contaminants into freshwater systems, as the ponds sediment levels increase with age, remediation effectiveness reduces (Farm 2002; Starzec et al. 2005; Weinstein et al. 2010). Ponds can be as shallow as 800mm with annual sediment accrual of up to 50mm (Farm 2002; Karlsson et al. 2010).

Any complementary treatment processes designed to immobilise / capture metals in motorway runoff and reduce the sedimentation build up in balancing ponds must also consider the mobility of the metals in road runoff. If the mobility of metals in runoff can vary from 0% to ~100% (Table 1.1b) treatment options should aim to treat runoff prior to sedimentation occurring within the balancing pond to stop the build up of the expensive to treat toxic waste. The principal areas where this would be most effective would be in the pipe work that delivers the runoff from the motorway to the balancing pond and / or the area beneath the pipe work but before the runoff has flowed into the balancing pond (Figure 1.2).

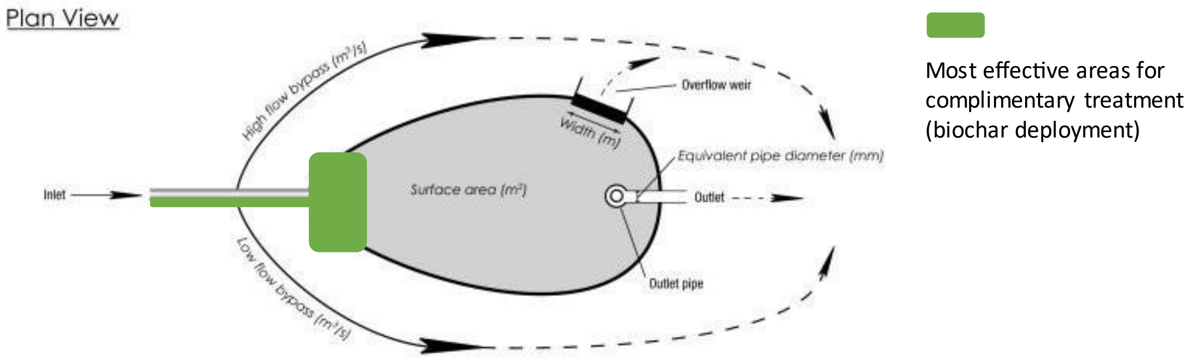

Figure 1.2: Balancing pond schematic with principle areas for the deployment of a complementary treatment (such as biochar) highlighted (Davis 2022)

An alternative option to current remediation practices is the deployment of biochar, the carbon rich product of the pyrolysis of biomass, which has the potential to be used as an easily removable, complementary method to removing both organic and inorganic contaminants from motorway runoff.

1.4 Engineered biochar as adsorbent for the removal of contaminants from aqueous medium

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Book chapter 22: Engineered Biochar: Fundamentals, Preparation, Characterization and Applications

1.4.1 Introduction

Biochar is defined as a porous, carbonaceous material that is produced by biomass pyrolysis at temperatures ranging from 350 - 1000°C under limited oxygen conditions (European Biochar Foundation 2016). During pyrolysis highly aromatic clusters are formed which are responsible for several key features of biochar, specifically its high chemical stability and high porosity. Biochar is reported to have several functions such as the ability to sequester carbon, enhance soil fertility and remediate environmental contaminants including the removal of contaminants from aqueous media (Inyang et al. 2016; Kätterer et al. 2019). The use of biochar in the remediation of inorganic and organic pollutants has been highlighted for various aqueous media such as road runoff (Cairns et al. 2020), mine waters (Bandara et al. 2020a), stormwater (Boehm et al. 2020), drinking water (Hu et al. 2019) and biologically treated wastewater (Hagemann et al. 2020). Its attractiveness is further enhanced due to its relatively low cost, simple production process and versatility in utilizing renewable raw material, including biomass waste materials (Ahmad et al., 2014; Zhang et al., 2015; European Biochar Foundation, 2016; Wang et al., 2018b; Xiao et al., 2018).

Biochar itself is a reasonably broad term which covers production from a vast number of different biomass raw materials produced at different pyrolytic temperatures yielding biochar with different characteristics. Essentially raw material, pyrolysis and modification such as the addition of minerals, activation or magnetisation alter the efficacy and the mechanisms of the biochar to remediate contaminants in aqueous media. Comparative studies primarily review either raw material, pyrolysis temperature or modified vs unmodified biochar to review sorption capacity or mechanisms (Table 1.2).

Feedstock category	Biochar raw materials	Pyrolysis temperature (°C)	Sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
Plant Biomass	Oak bark	400 and 450		As, Cd, Pb	ion exchange	Mohan *et al.*, 2007
	Pine bark			As, Cd, Pb		
	Oak wood			As, Cd, Pb		
	Pine wood			As, Cd, Pb		
	lucerne shoot	550		Cd, Cu	precipitation, complexation and electrostatic interaction	Bandara et al, 2020
	Norway spruce	450-500		Cd, Cu, Pb, Zn	electrostatic attraction	Cairns et al., 2020
	Norway spruce amended with wood ash	450-500		Cd, Cu, Pb, Zn	electrostatic attraction and precipitation	
	Norway spruce amended with basalt rock dust	450-500		Cd, Cu, Pb, Zn	electrostatic attraction and precipitation	
	Tobacco stem	300-700		Cd	cation-p interaction, precipitation	Zhou et al., 2018
				Cu	complexation	
				Pb	Precipitation	
	Canna indica	500	125.8	Cd	precipitates, cation exchange, binding to oxygen-containing groups	Cui et al., 2016
	Pennisetum purpureum Schum	500	119.3	Cd	precipitates, cation exchange and binding to oxygen-containing groups	
	KMnO4 modified hickory wood	600	28.1	Cd	surface adsorption	Wang *et al.*, 2015
			34.2	Cu	surface adsorption	
			153.1	Pb	surface adsorption	
	Miscanthus	300	11.4	Cd	surface sorption, precipitation	Kim et al, 2013
		400	11.99	Cd	surface sorption, precipitation	

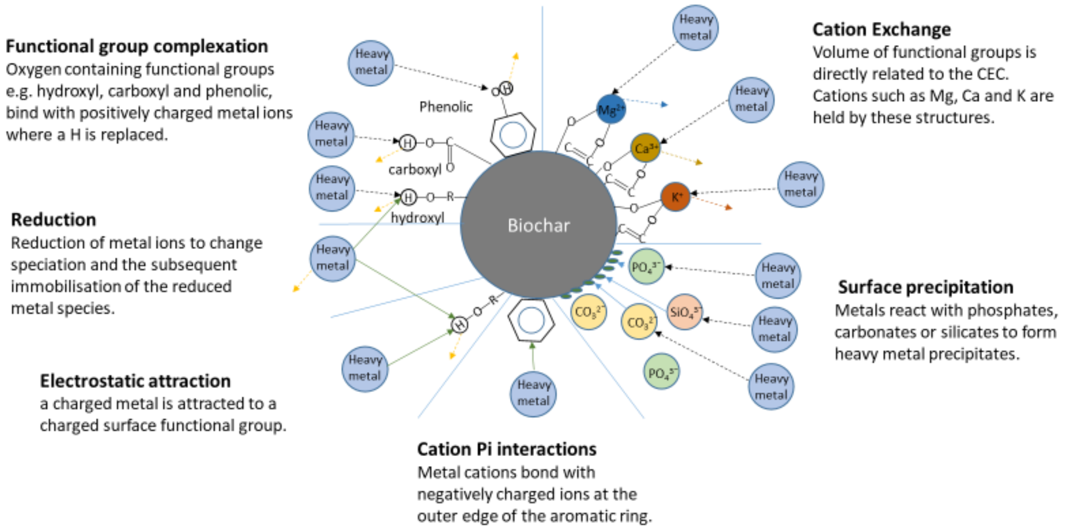
		500	13.24	Cd	surface sorption, precipitation	
		600	12.96	Cd	surface sorption, precipitation	
	honey mesquite	200, 300, 350, 550, 650		Cd, K	ion exchange, cation-pi bond	Harvey et al,. 2011
	cord- grass	200, 300, 350, 550		Cd, K	ion exchange, cation-pi bond	
	loblolly pine	200, 300, 350, 550		Cd, K	ion exchange, cation-pi bond	
	Anaerobically digested sugarcane bagasse	600		Cd, Cu, Pb, Ni	precipitation and surface adsorption	Inyang *et al.*, 2011
	Sugarcane bagasse	600		Cd, Cu, Pb, Ni	surface adsorption	
	Hardwood mix	450	12.52	Cu	H bonding	Chen *et al.*, 2011
			11	Zn	H bonding	
	Straw	600	6.79	Cu	H bonding	
			4.54	Zn	H bonding	
	Celery	500 and 350	288 - 304	Pb	precipitation, cation exchange and surface complexation	Zhang *et al.*, 2017
	Wheat straw pellets	550		Ni	cation exchange, electro- static adsorption and surface precipitation	Shen et al, 2017
	Acacia wood chip	550	4.02	Zn	precipitation, chelation (complexation)	Van Hien et al, 2020
Sewage / Manure	Dairy manure	350	7.28-15.68	Cd	complexation, precipitation	Xu, Cao and Zhao, 2013
			4.16-8.96	Cu	complexation, precipitation	
			13.45-28.98	Pb	complexation, precipitation	
			4.23-9.1	Zn	complexation, precipitation	
	Broiler litter	350 and 700		Cd, Cu, Ni, Pb	coordination by π electrons (CdC) of carbon and precipitation.	Uchimiya *et al.*, 2010

	Magnetised Sewage sludge	400	249	Pb	electrostatic attraction, ion exchange, complexation, precipitation	Ifthikar *et al.*, 2017
	Sewage sludge	550	30.88	Pb	coordination with organic hydroxyl and carboxyl functional groups, coprecipitation and complexation	Lu *et al.*, 2012
	Dairy manure	500	140.76	Pb	precipitation	Cao *et al.*, 2009
Food Waste	Nut shells	600		Cd, Pb	ion exchange	Trakal *et al.*, 2014
	Plum stones			Cd, Pb	ion exchange	
	Wheat straws			Cd, Pb	ion exchange	
	Grape stalks			Cd, Pb	ion exchange	
	Grape husks			Cd, Pb	ion exchange	
	Rice husk	350	>54.432	Cd	complexation, precipitation	Xu, Cao and Zhao, 2013
			>31.104	Cu	complexation, precipitation	
			>100.602	Pb	complexation, precipitation	
			>31.59	Zn	complexation, precipitation	
	peanut	400		Cr (III)	complexation	Pan et al., 2013
	soybean	400		Cr (III)		
	canola	400		Cr (III)		
	rice straw	400		Cr (III)		
	Sugar Beet Tailing	300	123	Cr (VI)	electrostatic attraction, reduction and complexation	Dong et al., 2011
Other	Sediment	400 and 500		Cd, Cu, Pb	cation–pi bond	Dong *et al.*, 2014

Table 1.2: Immobilisation mechanisms of inorganic contaminants by biochar produced from different raw materials

1.4.2 Immobilisation of inorganic contaminants

The key immobilization mechanisms for inorganic contaminants in aqueous media by biochar are: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and subsequent sorption, and precipitation (Figure 1.3). It is worth noting that these mechanisms do not work in isolation and often several mechanisms are relevant at the same time (Ramola et al 2020a).



Functional group complexation
Oxygen containing functional groups e.g. hydroxyl, carboxyl and phenolic, bind with positively charged metal ions where a H is replaced.

Reduction
Reduction of metal ions to change speciation and the subsequent immobilisation of the reduced metal species.

Electrostatic attraction
a charged metal is attracted to a charged surface functional group.

Cation Pi interactions
Metal cations bond with negatively charged ions at the outer edge of the aromatic ring.

Cation Exchange
Volume of functional groups is directly related to the CEC. Cations such as Mg, Ca and K are held by these structures.

Surface precipitation
Metals react with phosphates, carbonates or silicates to form heavy metal precipitates.

Figure 1.3: The six major mechanisms of heavy metal immobilization by biochar

1.4.2.1 Cation exchange

Cation exchange occurs most notably at early stage adsorption (Mohan et al. 2007; Uchimiya et al. 2010b; Ifthikar et al. 2017; Shen et al. 2017) . During cation exchange the biochar releases exchangeable cations such as alkali and alkaline earths, typically Mg, Na, K and Ca (Kumar et al. 2016). These cations are effectively replaced by heavier metal cations found in the aqueous media which bind to the biochar in their stead. Immobilisation mechanisms often do not work in isolation but rather work simultaneously or are intrinsically linked. Studies, such as (Mohan et al. 2007), cite several other mechanisms working alongside cation exchange in the remediation of inorganic contaminants i.e. precipitation and physical adsorption. In a similar vein cation exchange capacity (CEC) is recognised as being controlled by surface oxygen related functional groups (Trakal et al. 2014b; Ding et al. 2016), these functional groups also being of great importance in the remediation of inorganic contaminants through complexation.

1.4.2.2 Complexation

Several authors cite functional group complexation as a major mechanism of immobilization specifically of transition metals such as Cr, Cu and Cd and post transition metals such as Pb (Lu et al. 2012b; Pan et al. 2013; Cui et al. 2016c; Peng et al. 2017). Complexation occurs when a H ion is replaced in functional groups such as phenolic, carboxy or hydroxyl (Figure 1) (Xu et al. 2013a; Dong et al. 2014). Complexation is cited in studies with a variety of raw materials including sewage / manure (Zhang et al. 2020a), food waste such as millet bran (Qiu et al. 2019) and plant biomass (Wang et al., 2018a) (Table 1). Again, complexation is often described as working in conjunction with other mechanisms. Lv et al. (2018) reported complexation working alongside electrostatic interaction to remove Pb and Cu from aqueous solution.

1.4.2.3 Electrostatic interactions

Electrostatic interaction occurs between positively charged metals, such as Pb^{2+}, and the negatively charged surface of the biochar, particularly with a proliferation of oxygenated functional groups such as -COOH or -OH (Cui et al. 2015; Lv et al. 2018). Electrostatic attraction is a weaker process than precipitation or complexation and as a result metals immobilised via this mechanism are more susceptible to desorption (Bandara et al. 2020a). During their study Bandara et al., (2020) described the major mechanisms of Cd and Cu removal as electrostatic interaction with O-containing functional groups, surface complexation and precipitation. Ifthikar et al. (2017) also saw electrostatic attraction as being involved in the immobilisation of Pb alongside ion exchange, complexation and precipitation; electrostatic attraction was linked specifically to carboxyl groups. Cui et al. (2016) proposed that electrostatic interactions are likely the primary driving force for Cd sorption on wetland plant derived biochar, however even here it is indicated that electrostatic interaction is not the sole mechanism of Cd sorption with complexation playing a role. Ramola et al. (2020 b) found electrostatic interaction to be one of the important mechanisms between Pb ions and mineral groups i.e. bentonite and calcite present in biochar-bentonite composite and biochar-calcite composite respectively prepared at 700ºC.

1.4.2.4 Cation- π bonding

Cation- π bonding is a stabilizing electrostatic interaction of a cation with the polarizable π electron cloud of an aromatic ring. During the pyrolysis of biochar graphene sheets are formed with aromatic structures (Wang et al. 2020). Within these aromatic structures are electron rich domains on the edge of the aromatic structure which have been seen to attract inorganic contaminants such as Cd (Harvey et al. 2011b). (Uchimiya et al. 2010b) recognised the sorptive interactions between d-electrons of metals and aromatic π-electrons of the biochar as one of the primary mechanisms for the retention of Ni and Cd by broiler litter biochar. Xu et al. (2013) also found interactions between d-electrons of metals and aromatic π-electrons when using dairy manure derived biochar, however their study reported that this was important for Zn and Cd remediation but less so for Cu. Kim et al. (2013), Yuan et al. (2020) and Qiu et al. (2019) also recognised the positive impact of aromaticity on adsorption of Cd.

1.4.2.5 Precipitation

In dependence of pH, metals can react with anions including CO_3^{2-} , PO_4^{3-} and SiO_4^{3-} to form solid precipitates (Šráček and Zeman 2004). Again, raw material is critical to this process being the main driver of the availability of these mineral components (Lu et al. 2012b; Xu et al. 2013a). Ifthikar et al. (2017) found silica co-precipitation to be of importance in the remediation of Pb by sewage sludge biochar due to the abundance of silica in the sewage sludge raw material. Precipitation was also significant in celery derived biochar (Zhang et al. 2017b), however due to the characteristics of the raw material carbonate rather than silica co-precipitation was evident. The importance of raw material is further highlighted by Arán et al. (2017) who reiterated that the formation of metal carbonates and phosphate precipitates is favoured in biochar from mineral-rich raw material. Several studies assert that precipitation is the primary mechanism for immobilization (Cao and Harris 2010; Inyang et al. 2012; Lu et al. 2012b; Xu et al. 2013a). These studies typically use a raw material of sewage sludge / manure or an amended raw material which provides a high pH and high levels of phosphate and carbonate to be released to precipitate with metals (Inyang et al. 2012). However, precipitation is usually not the sole immobilization mechanism even when such mineral rich raw materials are used. Xu, Cao and Zhao (2013) demonstrated that where P rich dairy manure was used as a raw material, electrostatic attraction and precipitation were both seen to be the governing mechanisms for the removal of Pb, Cu, Zn and Cd. Similarly, van Hien et al. (2020) illustrated the importance of precipitation alongside complexation in the immobilization of Zn.

1.4.2.6 Reduction

Metals can be reduced by biochar enabling the reduced metal species to be immobilised. (Dong et al. 2011) reported that due to its high redox potential, Cr(VI) is easily reduced to Cr(III) under acidic conditions in the presence of organic matter. In Dong et al's (2011) study, the immobilisation of Cr occurred by electrostatic attraction of the negatively charged Cr(VI) to positively charged surface sections of a sugar beet biochar and reduction of Cr(VI) to Cr(III) facilitating complexation with functional groups. Cr(VI) reduction to Cr(III) was also reported by Mohan et al. (2011) in their study of oak biochar; by products of lignin pyrolysis such as catechol were seen to act as reducing agents as well as being important constituents of units that chelate Cr allowing the biochar to both reduce and bind Cr cations. Klüpfel et al. (2014) also highlight the importance of the pyrolysis process by demonstrating that new redox active moieties can be formed in the charring process. (Bogusz et al. 2015) assert that this reduction can happen in metals with a positive normal potential such as Cu but not with metals such as Cd and Zn that have a negative normal potential.

1.4.2.7 Key material properties for inorganic contaminant immobilization

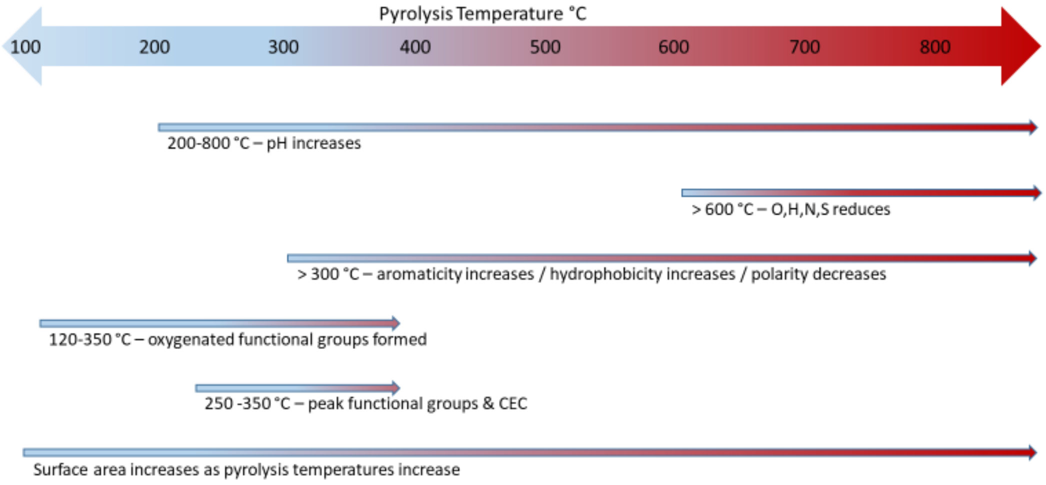


Figure 1.4: Biochar property changes as a result of pyrolysis temperature

Functional Groups

Surface functional groups of biochar are essential to several immobilisation mechanisms including cation exchange, electrostatic attraction and complexation. Ding et al. (2016) discuss the increase in cation exchange of the modified biochar as being resultant from the increase of oxygenated functional groups most notably carboxyl and hydroxyl groups. Other studies, such as Kharel et al. (2019) and Huff et al. (2018) acknowledge the role of functional groups in cation exchange and have specifically tried to increase carbonyl, carboxyl and hydroxyl groups to increase CEC. Functional groups such as carboxyl and phenolic groups also underpin electrostatic interactions as a charged surface to interact with a given contaminant (Cui *et al.*, 2015). Hydroxyl, carboxyl and phenolic groups also enable complexation to take place when a H ion is replaced by a metal (Trakal et al. 2014a; Wang et al. 2018a). The formation of these functional groups depends on raw material properties and pyrolysis temperature.

(Trakal et al. 2014a) suggest that differences in the relevance placed on functional groups can be explained by differences in pyrolysis temperature with studies around 350°C giving greater importance to functional groups and studies around 550-600°C attributing less significance to functional groups as the levels of O reduce. Oxygenated functional groups, such as carboxyl, carbonyl and hydroxyl, start to form at ~120°C in the first stages of pyrolysis where oxygen is more abundant and continue until around 350°C (figure 1.4) beyond which the O / C ratio is lowered (Lehmann and Joseph 2009). Studies such as Gray et al. (2014) and (Zhang et al. 2020b) have recorded a decrease in these oxygenated functional groups as pyrolysis temperatures rose, with Gray recording a decrease from 370 to 500°C and a further decrease to elimination from 500 °C to 620 °C. Similarly in a comparative study Chen et al. (2011) saw that pyrolysis of hardwood at 450 °C resulted in a larger number of functional groups and a higher O/C ratio than straw pyrolyzed at 600 °C. Although temperatures below 450 °C appear to be the best conditions for oxygenated functional groups, at pyrolysis temperatures as high as 600°C the adsorption by hickory wood biochar was still seen to be primarily driven by functional groups (Wang et al. 2015). Whilst raw material and pyrolysis temperature are the primary drivers of the abundance of functional groups they can also increase as a result of oxidation; such oxidation can be a due to natural aging or by chemical oxidation such as with HNO_3-H_2SO_4 or NaOH-H_2O_2 (Fan et al. 2018)

Cation Exchange Capacity

CEC is the key property for sorption through cation exchange. Raw material and pyrolysis temperature are key drivers of CEC (Trakal et al. 2014a). Studies show peak CEC to occur at pyrolysis temperatures of 250 – 350°C where functional groups are most abundant, and a diminishing of CEC as pyrolysis temperatures rise past this level (Figure 1.4), (Harvey et al. 2011a). (Mohanty et al. 2018) concur with the paradigm that low pyrolysis temperature (250–350 °C) lead to high CEC and suggest that this is as a result of the considerable volatile organic matter remaining on biochar rather than it being lost at higher temperatures. If a raw material has high levels of alkali and / or alkaline earths it has the potential for these elements to be available in the biochar for cation exchange. (Ifthikar et al. 2017) used sewage sludge as a biochar raw material which contained high levels of Ca and Mg, as a result the exchange of these alkaline earth metals was shown to be involved in the early stage adsorption of Pb. Similarly, the use of celery biomass as a raw material, which is rich in alkali and alkaline earth metals, resulted in cation exchange playing a significant role in adsorption (Zhang et al. 2017b). Conversely, in studies such as (Mantonanaki et al. 2016) or van Hien et al. (2020) where the raw material, such as coffee grounds or bamboo, have low levels of Ca, K or Mg, cation exchange is either not highlighted or is described as neither a driver nor a good predictor of adsorption.

Specific Surface Area

Specific surface area (SSA) is a property of biochar that is very often cited by authors due to its importance in the immobilisation of contaminants in aqueous media; the higher the SSA the more sites are available for sorption to occur. Ifthikar et al. (2017) in their study of magnetic sewage sludge biochar, described surface area as critical in the adsorption of Pb. When they compared magnetised and unmagnetised sewage sludge biochar an increase in surface area allowed access to a large number of active sites for remediation to take place increasing removal rates. In their study of oak bark and pine wood biochar, Mohan et al. (2007) also suggest that higher adsorption levels were at least partially due to the higher surface area of the oak bark biochar. It is worth noting that a higher surface area does not always result in higher rates of immobilisation particularly if chemisorption rather than physisorption is the driving factor. In studies where precipitation is the major immobilisation mechanism such as Cao and Harris, (2010) and Xu, Cao and Zhao, (2013) surface area is not a major factor. (Xu et al. 2013a) demonstrated that dairy manure biochar had lower surface areas than rice husk biochar (5.61m^2g^{-1} vs 27.8 m^2g^{-1}) but higher sorption (486 mmol kg^{-1} vs 65.5-140 mmol kg^{-1}) as a result of precipitation being the driving mechanism.

As with functional groups, surface area is primarily driven by raw material and pyrolysis temperature (figure 1.4). (Zhang et al. 2020b) describe a surface area increase as a result of temperature increase with rice straw biochar pyrolysed at 400°C having a surface area 0.367 m^2g^{-1} which increased to 51.105 m^2g^{-1} at 700°C. The largest surface area increase occurred between 600 to 700°C with an increase from 8.598 m^2g^{-1} to 51.105 m^2g^{-1}. Ahmad et al. (2012) report a surface area increase from 6m^2g^{-1} to 448m^2g^{-1} when temperatures increased from 300 to 700°C. Chen et al. (2018) demonstrate an increase from 1.26 m^2g^{-1} to 351 m^2g^{-1} with an increase in temperature from 300 to 900°C. As explained by Kercher and Nagle, (2003) SSA increases due to the condensation of biomass to graphene like carbon structures forming pyrogenic micro- and mesopores. Hale et al. (2016) describe the increase in

SSA at high temperatures as a result of amorphous components arranging into turboclastic chrystallites. Chen et al. (2011) and Ippolito et al. (2020) assert that it is raw material rather than pyrolysis temperatures play the major role in the SSA of biochar.

pH

The pH of biochar is usually alkaline (Lehmann and Joseph 2015) and as a result it increases and buffers its environments pH. These increases are dependent on raw material and pyrolysis temperatures (figure 1.4), (Fidel et al. 2017). Studies have shown that the solution pH which effects the metal speciation can be influenced by the pH of the biochar (Cairns et al. 2020), the increase in aqueous media pH can induce changes in metal speciation that are favourable for cationic metals such as Pb or Cd and unfavourable for anionic metalloids such as As. The pH of the aqueous solution is cited as one of the main variables affecting the sorption process influencing both the speciation of the metals and the surface charge of the sorbent (Kilic et al. 2013). pH is a key determinant of metal solubility and bioavailability; the more bioavailable a metal is, the more toxic it is to the surrounding ecosystem (Charters et al. 2016). Metals such as Pb and Cd are more mobile at low pH whereas metalloids such as As are more mobile at high pH and as a result the maximum sorption of these metals is seen at different pH (Mohan et al. 2007). Metals that are more mobile at low pH such as Cd, Co, Ni, Pb and Zn are removed best at pH of ~5-6, above pH levels where the metals are mobile (Chen et al. 2011; Lu et al. 2012b; Kilic et al. 2013; Trakal et al. 2014a). In contrast, the removal of metalloids that are more mobile at higher pH, such as As, fall when pH is above 8 and the metalloid is more mobile (Navarathna et al. 2019). In terms of cationic heavy metals Lu et al., (2012) cited surface charge as being the primary mechanism for Pb sorption and that higher surface charge was driven by increasing pH from 2 to 5. Increasing adsorption was attributed to deprotonation as pH increased. Chen et al. (2011) also saw an increase in adsorption until a pH of 5 due to competition between protons and metal cations for sorption sites, with a decrease over pH 5 due to the formation of hydroxide complexes. Despite pH 5 being suggested as the pH of maximum sorption by Lu et al. (2012) and Chen et al. (2011) most studies cite a pH of 6 as being ideal.

In their study of activated maple wood biochar Wang et al. (2018b) saw that with an increasing pH there was an increasing surface charge due to the deprotonation of functional groups up to a pH of 6, above which soluble hydroxyl complexes or surface precipitation formed. Kilic et al. (2013) reported similar findings in their study where they saw an increase in electrostatic charge from pH 2 to 6, improving Ni and Co interaction with binding sites. At above pH 6, formation of hydroxylated complexes which compete for active sites were again found. Tran et al. (2017) were also in agreement in their study where they investigated the effect of solution pH on the adsorption process of Cu(II) in solutions with pH values from 2.0 to 6.0. They found that up to pH 6 the negative charge of carboxyl groups increased improving adsorption of Cu. Studies also show pH to have an impact on co-precipitation with pH influencing the speciation of metals (Kilic et al. 2013). Inyang et al. (2011) suggests that the co-precipitation of Pb and CO_3^{2-} forming hydrocerrusite and cerrusite was as a result of high pH. Similarly, Cao and Harris, (2010) note that high pH (~pH 10) allows Pb co-precipitation with both phosphate and carbonate. Biochar pH is effected by pyrolysis temperatures with increases of pH demonstrated from 370 to 600°C (Gray et al. 2014), 350 to 750°C (Domingues et al. 2020) and 300 to 700°C (Yuan et al. 2011a; Ahmad et al. 2012). Ramola et al. (2020b) found a significant increase in adsorption capacity of biochar-calcite composite prepared at 700 ⁰C, with increase in pH from 3 to 9. This may be because calcite form stronger bond with Pb under alkaline conditions.

Modification

A number of papers study the effect of modifying biochar to enhance adsorption mechanisms of inorganic contaminants in aqueous media. These modifications generally take the form of activation (creating activated carbon / activated biochar), addition of minerals, or magnetisation.

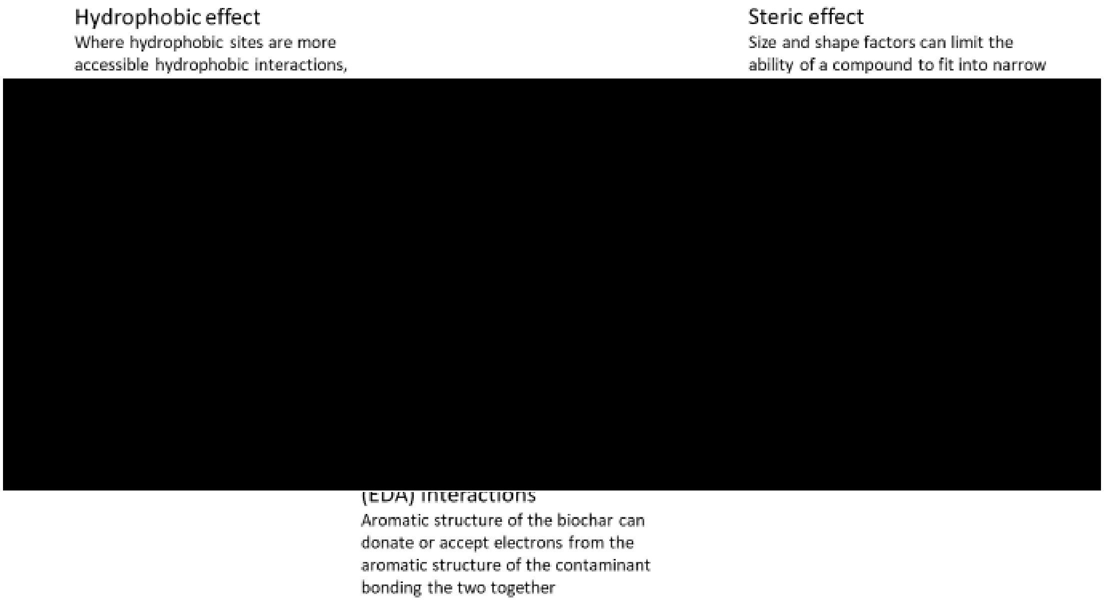
Several studies look to activate the pristine biochar, increasing sorption through an increase in specific surface area (SSA) and modifying surface chemistry, creating activated carbon from biomass sometimes referred to as activated biochar. Methods to chemically activate biochar include the addition of chemicals such as hydrogen peroxide (Wang et al., 2018a), sodium hydroxide (Ding et al. 2016) or zinc chloride (Ifthikar et al. 2017). Each of these studies demonstrated an increase in functional groups and surface area leading to an increase in sorption capacity. However, these methods do increase production costs and produce contaminated effluents during production (Hagemann et al. 2020). Physical rather than chemical methods using steam, oxygen or carbon dioxide are also used to increase SSA and remove contaminants (Uchimiya et al. 2010b; Grycová et al. 2016; Hagemann et al. 2020)

The addition of minerals to modify biochar commonly takes place pre pyrolysis such as in the Wang et al. (2015) study where potassium permanganate ($KMnO_4$) was added to increase oxygen functional groups. Under high temperature, $KMnO_4$ was converted to MnO_x particles onto the surface of the biochar which resulted in an increase in hydroxyl and carboxyl functional groups due to oxidising effect of $KMnO_4$. These modifications increased the sorption capacities of biochar by 2.1 times for Pb, 2.8 times for Cu and 5.9 times for Cd. Gan et al. (2015) used ZnO modification to adsorb Cr (VI) ions. Again, the raw material was pre-treated with ZnO prior to pyrolysis. The sorption of the modified biochar was 1.2-2 times greater than the sorption of the pristine biochar.

Magnetising biochar is a further direction investigated by Yuan et al, (2020) Mohan et al, (2014) and (Chang et al. 2006), who introduced Fe^{3+} and / or Fe^{2+} to the pristine biochar to increase the sorption of metals. Magnetisation was carried out with a variety of raw materials including sewage sludge (Ifthikar et al. 2017), oak wood and bark (Mohan et al. 2014) and chitosan (Chang et al. 2006). Each of these studies introduce Fe via solution that is mixed with the biochar and then oven dried to bind the Fe to the surface of the biochar. SSA has been reported to increase with magnetisation in some studies (Chang et al. 2006; Mohan et al. 2014; Ifthikar et al. 2017), however in Mohan et al. (2014) this was dependant on raw material with oak bark SSA decreasing with magnetisation but SSA increasing with oak wood magnetisation. Biochar loaded with Fe^{3+} increased the oxygen-containing functional groups and enhanced the ability of complexing Cd (Yuan et al. 2020). Ramola et al. (2014) observed that iron impregnated tyre biochar (FeTy) was able to remove Pb better than its pristine biochar. The maximum removal of Pb by FeTy was 95% that followed Temkin adsorption isotherm.

1.4.3 Immobilization of organic contaminants

As with inorganic contaminants in aqueous media several mechanisms have been documented in the removal of organic contaminants primarily H-bonding and charge assisted H-bonding (CAHB), π-π Electron Donor Acceptor (EDA) interaction, electrostatic interaction and steric effect. These are driven by the structure and properties of the biochar, in particular specific surface area (SSA), aromaticity which can be approximated by the molar H/C ratio and polarity which can be approximated by the molar O/C ratio. Sorption behaviour differs strongly between aromatic and aliphatic compounds, as well as neutral, polar, anionic, cationic and zwitterionic compounds (Hale et al. 2016; Sigmund et al. 2020). The types of organic contaminants found in aqueous media that have attracted the most concern and attention include pesticides, herbicides, polycyclic aromatic hydrocarbons, dyes, and antibiotics which are structurally diverse (Qiu et al., 2009, Beesley et al., 2010, Zheng et al., 2010, Teixidó et al., 2011, Xu et al., 2012).



[redacted]

Figure 1.5: The major mechanisms of organic contaminant immobilization by biochar

1.4.3.1 π-π Electron Donor Acceptor Interactions

π-π Electron Donor Acceptor (EDA) has been highlighted as one of the most important interactions in the adsorption of aromatic organic compounds to biochar in aqueous media. π-π EDA can occur between π-electron accepting moieties in the centre of the aromatic cluster within the biochar structure and π-electron donating compounds such as phenols or polyaromatic hydrocarbons (PAHs) (Zhu and Pignatello 2005). The π-π EDA mechanism has been reported as the major mechanism in organic contaminant removal for contaminants including PAHs such as phenanthrene, dibutyl phthalate, sulphides (sulfamethoxazole and sulfapyridine), carbaryl and atrazine (Zhang et al. 2013a; Jin et al. 2014; Xie et al. 2014). A study by Ahmed et al (2018) also determined that functionalized biochar can act both as π-electron-donor (sorbing phenanthrene) and π-electron-acceptors (sorbing dinitrobenzene). Therein the π-electron donating sites are located at the outer edges of the graphene like structures within the biochar. For polar contaminants π-π EDA is often reported in conjunction with H-bonding such as in the adsorption of tetracycline, estrone, 17β-estradiol, estriol, 17α-ethynylestradiol, bisphenol A and acetate (Saquing et al. 2016; Zhou et al. 2017; Ahmed et al. 2018). The strength of π bonds is in the realm of weak interactions comparable to H-bonds (Pignatello et al. 2017).

1.4.3.2 H-bonding

H-bonding occurs between a single proton covalently bound to more electronegative atoms and another electronegative atom bearing a lone pair of electrons. Such electronegative atoms can be found on the biochar surface (e.g. O-containing functional groups) (Gilli and Gilli 2010). Studies have highlighted the importance of H-bonding in the removal of several polar organic contaminants such as tetracycline (Jing et al. 2014; Tang et al. 2018), norflurazon and fluridone (Sun et al. 2011) and florfenicol (Zhao and Lang 2018). Charge assisted H bonding (CAHB) is a special type of H-bonding that occurs when the dissociation constant of the H donor and H acceptor groups are very similar (Δ pKa approaches 0) creating an exceptionally strong H-bond (Li et al. 2013). The formation of negative charge-assisted H bonds have also been reported by Ahmed et al. (2017) in the sorption of negative species (sulfonamide antibiotics) form aqueous media. Similarly at a pH of ~8 where deprotonation of the amino group and sulfamido were enhanced, sulfadimine (an antibiotic contaminant) converted to an anion state enabling a strong negative CAHB between sulfadimine and the carboxylate or phenolate functional groups on the biochar (Wan et al. 2020).

1.4.3.3 Electrostatic interactions

Electrostatic interactions refer to the attraction of oppositely charged groups. For example, negatively charged oxygenated functional groups can bind positively charged organic contaminants, such as methyl violet or methyl blue (Xu et al. 2011; Dawood et al. 2017). The charge of the biochar is heavily pH dependant, at pH below the point of zero charge (PZC) the surface charge is positive causing electrostatic repulsion of positively charged contaminants such as sulfadimidine (SMT^+) (Wan et al. 2020); as the pH of the biochar increases the ionization shifts depending on functional group and compound dissociation constants and the effect of the electrostatic repulsion declines.

1.4.3.4 Steric effects

Steric effects can influence sorption behaviour of organic compounds. Size and conformational factors may limit the ability of a molecule to fit into narrow pores (pore exclusion), or limit a molecule’s approach to sorption sites on the surface (Pignatello et al. 2017). Removal of organic contaminants from aqueous media by biochar must be considered in conjunction with the pore size of the biochar, the size of the organic contaminant and the shape of the organic contaminant.

Size exclusion was reported by Yang et al. (2018) in their study of wood chips, rice straw, bamboo chips, cellulose, lignin and chitin biochar. Organic molecules were seen to be restricted and could not access biochar pores smaller than the molecule diameter. Tang et al. (2018) also reported size exclusion in their study of the removal of tetracycline by sewage sludge biochar suggesting that adsorbent shows its best adsorption property when pore diameter is 1.7 – 3 times larger than that of the adsorbate molecule. (Schreiter et al. 2018) attributed the higher max sorption capacity for trichloroethylene (TCE) over tetrachloroethylene (PCE) to size exclusion with the smaller TCE molecules able to access a bigger portion of the pore volume of the biochar. Zhang et al. (2013) also conducted a bi-solute study about the removal of carbaryl and atrazine by pig manure biochar. In a similar manner to (Schreiter et al. 2018) the higher removal of atrazine was attributed to the smaller molecular size of atrazine compared to carbaryl (0.61 nm versus 0.71 nm). Kah et al. (2016) also highlighted size exclusion as a phenomenon in their study of a diverse series of sorbents pyrolyzed at different temperatures. Size exclusion was significant for plant derived materials but not so for biochar derived from sewage sludge or pig manure raw materials. These raw materials did not have a microporous structure and as a result did not develop the porosity associated with size exclusion when pyrolyzed. For small molecules, pore filling can occur which is dependent on pore geometry, pore volume and pore size distribution. When these factors are favourable for contaminant condensation in these pores, pore filling can play a dominant role in the immobilisation of organic contaminants (Nguyen et al. 2007; Zhu et al. 2014; Zhao and Lang 2018). Wang and Xing, (2007) studied the sorption of the hydrophobic compounds phenanthrene and naphthalene and noted that at low solute concentrations, sorption of phenanthrene and naphthalene by biopolymer biochar was dominated by the micropore-filling mechanism; however, with an increase in the solute concentration, immobilisation of these two compounds shifted to a surface-sorption-dominant process.

1.4.3.5 Key material properties for inorganic immobilization

Specific Surface area

Specific surface area (SSA) is a property of biochar that, as with inorganic immobilisation, is often cited as important for the sorption of organic contaminants as a larger SSA means access to more sorption sites. The larger the SSA, the more opportunity the contaminant has to be removed by the biochar from aqueous media (Prévoteau et al. 2016). SSA is cited as being a primary property in the removal of organic contaminants in aqueous media by many papers (Zhang et al. 2013a; Lattao et al. 2014; Wang et al. 2016; Zhao and Lang 2018). SSA is driven by pyrolysis temperature and raw material (figure 1.4). The role of raw material is discussed by Kah et al. (2016) who demonstrate that plant based raw materials can develop micropores, increasing SSA and pore filling potential, but animal waste or sewage based raw materials do not show evidence of such micropore structures. Similarly, Wang et al. (2016) highlight that the SSA of plant based biochar was significantly higher than animal based biochar with the result that there were positive correlations between SSA and removal of organic contaminants by wood dust biochar but no such correlations were apparent for swine manure biochar. In their meta data analysis review Ippolito et al. (2020) assert that although pyrolysis temperature is important in determining SSA, raw material has the largest influence on SSA with SSA being greatest in wood based biochar. Nonetheless pyrolysis temperatures are still an important tool to control SSA: at higher pyrolysis temperatures amorphous carbons condense to crystalline structures, more pores are formed and volatiles are removed causing a higher SSA (Chen et al. 2012; Zhang et al. 2013a; Wang et al. 2016).

Aromaticity

The molar H/C ratio is widely recognised as an index for the degree of aromaticity / carbonisation of biochar which is essential for π-π EDA and hydrophobic interactions. As pyrolysis temperatures increase and aromaticity increases stacks of graphene grow enabling the π-π mechanism to dominate in the removal of contaminants from aqueous media (Jin et al. 2014). Hydrophobic interactions which promote the immobilisation of non-polar / hydrophobic compounds, such as phenanthrene, are also possible where aromatic groups are more accessible (Sun et al. 2013). The hydrophobicity of a contaminant is generally described by the octanol water partition co-efficient (K_{ow}). The aromaticity of biochar is affected by pyrolysis temperature, above ~300°C an increase in pyrolysis temperature leads to greater carbonisation and an increase in aromatic compounds (figure 1.4) (Uchimiya et al. 2010a; Mukherjee et al. 2011; Lehmann and Joseph 2015; Lou et al. 2016). However, the degree of carbonisation in the biochar is also relevant to partitioning with the partitioning of organic contaminants occurring in the uncarbonized fraction of the biochar (Chen et al. 2018; Schreiter et al. 2018). At lower temperature pyrolysis (<400°C) removal of organic pollutants by biochar is dominated by partitioning due to the amorphous structure of the biochar making them effective media for the partitioning of more polar organic compounds (Chen et al. 2008; Sun et al. 2012).

Polarity

The O/C ratio is commonly accepted as an index for polarity and is intrinsically linked to the abundance of oxygenated functional groups. The higher the polarity, and therefore the higher the O/C ratio, the more negatively charged the biochar surface is with the associated benefits for the removal of cations / polar contaminants via H-bonding and electrostatic attraction (Xu et al. 2011; Qiao et al. 2018; Schreiter et al. 2018; Zhao and Lang 2018). However a high O/C ratio and resultant negative charge can also cause the electrostatic repulsion of anions and can cause water clusters to form around the O-groups repulsing non-polar / hydrophobic contaminants, further demonstrating the importance of the relationship between contaminant structure and properties with the biochar structure and properties (Zhu et al. 2005; Rajapaksha et al. 2015; Chen and Ni 2017; Schreiter et al. 2018). H. Zhang et al, (2017) also discussed the link between partitioning and the polarity of the contaminant with acetone, cyclohexane and toluene partition rates relating directly to polarity; hydrophilic / polar contaminants were adsorbed more easily by biochar that was less polar as the low pyrolysis temperatures lent themselves to the presence of noncarbonized organic matter where partitioning takes place. Polarity, indexed by the O/C ratio, is determined in the main by pyrolysis temperatures; at lower temperatures O is more abundant, and as such the biochar is more polar (figure 1.4), (Chen and Chen 2009; Zhang et al. 2017c).

Limitations

Whilst there is extensive literature on biochar and the removal of organic and inorganic pollutants more research should be conducted to bridge the gap between laboratory results and field work. The majority of research continues to revolve around laboratory findings rather than the use of biochar in the field or in simulated field conditions. Maximum sorption capacity is an important metric however, it represents sorption in perfect conditions such as ideal temperatures, pH, contaminant concentrations and flow. Single contaminant environments are often studied in laboratory batch experiments, yet these conditions are unlikely to be seen in the field where multiple contaminants exist together with dissolved organic matter affecting contaminant mobility, bioavailability and toxicity. The impact of changes in temperature, pH and contaminant concentrations have been studied providing useful insights but very rarely use the parameters as seen in aqueous media where biochar could potentially be deployed such as rivers, runoff or mine waters. Such laboratory findings are not fully transferrable to field conditions which limit their value when attempts are made to use these findings in practice. Whilst the use of simulated field conditions such as storm water, synthetic mine water or even collected mine water has been used to undertake studies in a laboratory setting this approach is far from prevalent.

1.4.4 Conclusion and future prospects

This chapter highlights the successful use of biochar as an adsorbent for the removal of contaminants from aqueous media. Biochar is a relatively low cost, sustainable product which has been demonstrated to be effective in the removal of both organic and inorganic contaminants. This has led to the study of biochar in relation to aqueous environments such as road runoff (Cairns et al. 2020), mine waters (Bandara et al. 2020a), stormwater (Boehm et al. 2020) drinking water (Hu et al. 2019) and biologically treated wastewater (Hagemann et al. 2020). This chapter reviews the key immobilisation mechanisms and underpinning material properties for both inorganic and organic contaminants.

The key immobilization mechanisms for inorganic contaminants in aqueous media by biochar are: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and subsequent sorption, and precipitation. These mechanisms do not work in isolation and it is common for several mechanisms to be relevant simultaneously. Key material properties for inorganic contaminant immobilization include surface functional groups, cation exchange capacity, specific surface area and pH. These material properties are primarily controlled by raw materials and / or pyrolysis temperatures. Surface functional groups of biochar are essential to cation exchange, electrostatic attraction and complexation and are affected by both raw material and pyrolysis temperature. Functional groups start to form at ~120°C in the first stages of pyrolysis where oxygen is more abundant and continue until around 350°C. CEC is the key property for sorption through cation exchange. Raw material and pyrolysis temperature are primary drivers of CEC with the lower pyrolysis temperatures allowing more functional groups and as such greater CEC. Specific surface area (SSA) is a further important property of biochar; the higher the SSA the more sites are available for sorption to occur. As opposed to functional groups and CEC, SSA is seen to increase as a result of an increase in pyrolysis temperature. Solution pH, which can be affected by the biochar, is also cited as one of the main variables affecting the sorption process influencing both the speciation of the metals and the surface charge of the sorbent.

Several mechanisms have been documented in the removal of organic contaminants from aqueous media, primarily: H-bonding and charge assisted H-bonding (CAHB), π-π Electron Donor Acceptor (EDA) interaction, electrostatic interaction and steric effect. These are driven by the structure and properties of the biochar, in particular specific surface area (SSA), aromaticity which can be approximated by the molar H/C ratio and polarity which can be approximated by the molar O/C ratio. Again, these material properties are primarily controlled by raw materials and / or pyrolysis temperatures. As with inorganic contaminants specific surface area (SSA) is an important property of biochar in relation to the immobilisation of organic contaminants. The molar H/C ratio is an index aromaticity / carbonisation of biochar which is essential for π-π EDA and hydrophobic interactions. Aromaticity increases with pyrolysis temperatures enabling the π-π mechanism to dominate in the removal of contaminants from aqueous media. Hydrophobic interactions which promote the immobilisation of non-polar / hydrophobic compounds are also possible where aromatic groups are more accessible. The O/C ratio, which is commonly accepted as an index for polarity is intrinsically linked to the abundance of oxygenated functional groups. The higher the O/C ratio, the more negatively charged the biochar surface is with the associated benefits for the removal of cations / polar contaminants via H-bonding and electrostatic attraction. However, a high O/C ratio and resultant negative charge can also cause the electrostatic repulsion of anions and can cause water clusters to form around the O-groups repulsing non-polar / hydrophobic contaminants. This highlights the importance of the relationship between contaminant structure and properties with the biochar structure and properties.

Studies reviewing the removal of contaminants from aqueous media by biochar in the field are scarce and as a result biochar onsite use in aqueous media necessitates further studies to systematically investigate the interplay of different environmental factors such as pH, dissolved organic matter (DOM) and the mix of contaminants seen in various real world sites. Fouling as a result of these environmental factors could lead to “caking” and the subsequent blocking of biochar surface and pores; such fouling is discussed in the activated carbon community but less so by biochar researchers. A transfer of knowledge between these research communities would help drive meaningful further developments in the field. Furthermore, key material properties of biochar relevant to field conditions are often not reported, including the previously discussed point of zero charge. Understanding the impact of the environmental pH on the charge of the biochar underpins a number of key immobilisation mechanisms and as such arguably should become standard to report bringing laboratory work and field study closer together.

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1.5 Biochar amendments (previous developmental work)

Biochar has been highlighted as a potential remediator of (post) transition metals in aqueous environments such as motorway runoff or mine impacted waters. To increase this remediation potential, biochar studies previous to this work were undertaken to understand the effect of amending biochar on the immobilisation of Pb, Cu, Zn and Cd. Wood ash (specifically fly ash) purchased from NPK Ltd (Orchard Way, Venlake, Uplyme, Lyme Regis, Dorset DT7 3SA), which in turn was sourced by NPK Ltd from a renewable energy plant in the UK, and ground basalt rock were studied as amendments to biochar to review the effect on metal immobilisation.

The biochar used in the column study by Cairns et al. (2020) used a feedstock of Norway spruce (*Picea abies* (L.) Karst.). The Norway spruce wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 450–500 °C, with a retention time of ~ 90 s. The resultant biochar was granulated (< 3 mm) to increase surface area and potentially increase sorption. Norway spruce, as a softwood, was chosen because of its greater number of pores and surface area for sorption to take place in comparison with hardwood (Mohanty et al. 2018). Amendments to the biochar were mixed dry at room temperature, at a ratio of 1:1, with a plasterer's whisk. Mixing the amendments at room temperature rather than at higher temperature immediately post pyrolysis had the potential for the amendments to not adhere to the biochar and be washed when subjected to water. Mixed wood ash was selected as an amendment due to its high pH, phosphorus (P) and alkaline earth content (Mg and Ca). Basaltic rock dust was used because of its high pH and alkaline earth content (Mg and Ca). Quartz sand was employed as a control due to its neutral pH, low levels of alkaline earth and low levels of heavy metal pollutants.

Four sets of four replicate water columns were used to study the immobilisation of Pb, Cu, Zn and Cd. Set 1 contained pristine biochar (BC), set 2 contained biochar amended with wood ash (WA), set 3 contained biochar amended with basaltic rock dust (BR) and set 4 containing the quartz sand control (QS). The first set of four replicate water columns had 90 g of biochar added and compressed with an aluminium rod to a height of 285 mm with a volume of ~ 450 mL. This volume was then used as a template for the sets of water columns holding WA, BR and QS. A column study with daily pulses of water spiked with Pb, Cu, Zn and Cd provided the opportunity to broadly mimic the sporadic nature of motorway runoff whilst approximating issues such as preferential flow paths within the biochar. Although determination of the precise immobilisation mechanisms was possible, it was beyond the scope of this study to investigate at greater depth (Cairns et al., 2020).

Sorption of Pb, Cu, Zn and Cd were shown to differ significantly between biochar (BC), biochar amended with wood ash (WA) and biochar amended with basaltic rock dust (BR) with amended biochar showed significantly more removal of all contaminants (WA> BR > BC). WA was the only study material that did not show signs of desorption in the eluate for any of the contaminants during the 36-day study. Pb, Cu, Zn and Cd removal showed strong correlations with pH and total P content indicating that metal speciation, surface charge and precipitation with P were the primary influence on immobilisation. CEC was seen to be relevant in Pb removal, of secondary importance in Cu and Zn removal and of weak or at best moderate importance in Cd removal.

1.6 Wood ash as an amendment to biochar

The study of biochar amendments by Cairns et al. (2020) demonstrates that wood ash amended biochar increases metal immobilisation and is a more effective amendment than basalt rock.

Wood ash in its own right, specifically fly ash and bottom ash from energy plants, has been the subject of numerous publications focusing on its chemistry, minerology and effectiveness as a remediator of contaminants. Fly ash and bottom ash are produced as a result of biomass combustion, typically involving the burning of wood and wood residues including bark, wood chip / pellet and sawdust (Nurmesniemi et al. 2012). This process of energy generation is considered to be a more environmentally friendly alternative to the more conventional use of fossil fuels due to the reduced CO_2 emissions from biomass energy generation (Nurmesniemi et al. 2012). However, the ash produced from the burning of wood can become a costly environmental problem if not repurposed as this potentially valuable waste product often ends up as expensive landfill occupying large areas of land and potentially damaging the surrounding ecosystem (Agrela et al. 2018; Park et al. 2020; Zhao et al. 2021).

There are two types of wood ash which are generated by energy plants, namely fly ash and bottom ash. Fly ash and bottom ash are captured at different points within the energy plant (Figure 1.6) resulting in differing elemental and chemical compositions (Demirbaş, 2005). Fly ash is a fine light ash collected from the air outside the combustion chamber in bag filters, whereas the bottom ash is collected as it falls from the furnace combustion grate at the bottom of the combustion system and resembles a fine natural dark sand (Park et al. 2012; Agrela et al. 2018; Park et al. 2020)

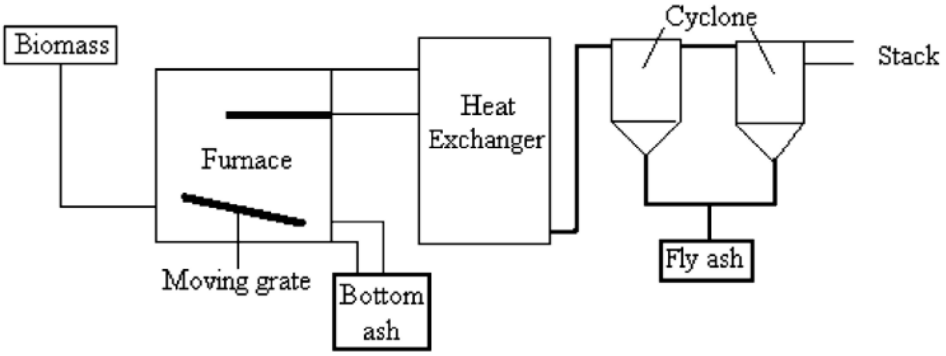

Figure 1.6: Biomass fired grate boiler schematic (Demirbaş 2005)

1.6.1 Wood ash chemistry and minerology

The mineral composition of wood ash is at least in part responsible for its considerable sorption capacity (Demirbaş 2005; Genty et al. 2012; Park et al. 2012). The concentration of minerals and metals in the ash is dependent on the characteristics of the biomass and the combustion conditions (Nurmesniemi et al. 2012; Agrela et al. 2018). However, when examining wood ash there are some consistent themes around composition, for example the most dominant feature of all wood ashes is a high Ca content (Steenari et al. 1999). Wood ashes are rich in Ca, K, Mg, Na and P (Etitgni and Campbell 1991; Demirbaş 2005; Park et al. 2012). The prevalent species of these minerals found in both fly ash and bottom ash are oxyhydroxides such as P_2O_5, K_2O, Na_2O, MgO and CaO, carbonates such as $CaCO_3$ and silicates such as SiO_2 and $CaSiO_3$, all of which are relevant to the immobilisation of metals of concern from aqueous environments (Demirbaş 2005; Nurmesniemi et al. 2012; Park et al. 2012; Vassilev et al. 2014; Agrela et al. 2018; Park et al. 2020). However, the concentration of Ca, Mg, P_2O_5, K_2O, and CaO has been found to be far greater in fly ash than bottom ash (Demirbaş 2005; Nurmesniemi et al. 2012; Park et al. 2020). Concentrations of S and N have also been found to be higher in fly ash as a result of volatile S and N components being burnt off and then condensing in the fly ash bag filters forming constituent parts of the ash (Nurmesniemi et al. 2012; Park et al. 2012).

Fly ash metal concentrations are also markedly higher than bottom ash metal concentrations (Table 1.3). Again, this indicates a high degree of volatisation and subsequent capture in the fly ash bag (Nurmesniemi et al., 2012).

Metal	Fly Ash concentration (mg/kg)	Bottom Ash concentration (mg/kg)	Author
Zn	5929	108	Park et al., 2012
	427	176	Park et al., 2020
	3360	720	Nurmesniemi et al., 2012
	668		Demirbas, 2005
Pb	44	0.5	Park et al., 2012
	9.14	7.02	Park et al., 2020
	33	<3.0	Nurmesniemi et al., 2012
	325		Demirbas, 2005
	107		Pederson, 2003
Cd	41	0.6	Park et al., 2012
			Park et al., 2020
	12	0.3	Nurmesniemi et al., 2012
	16.6		Demirbas, 2005
	27.8		Pederson, 2003
Cu	158	129	Park et al., 2012
	84.66	68.85	Park et al., 2020
	100	18	Nurmesniemi et al., 2012
	358		Demirbas, 2005
Mn	18500	17800	Park et al., 2012
	1162	750	Park et al., 2020
			Nurmesniemi et al., 2012
	90.5		Demirbas, 2005
Cr	120	46	Park et al., 2012
	57.34	60.7	Park et al., 2020
	69	39	Nurmesniemi et al., 2012
	76.2		Demirbas, 2005

Ni	21	23	Park et al., 2012
	27.6	20.56	Park et al., 2020
	38	16	Nurmesniemi et al., 2012
	34.6		Demirbas, 2005
	37.0		Pederson, 2003
As	4.4	1.2	Park et al., 2012
	20.2	7.5	Park et al., 2020
	<3.0	<3.0	Nurmesniemi et al., 2012
	16.9		Demirbas, 2005

Table 1.3: metal concentrations (mg/kg) in fly ash and bottom ash.

The pH values of fly ash are strongly alkaline whereas the pH values of bottom ash are slightly alkaline with fly ash generally having a higher pH. (Nurmesniemi et al. 2012; Park et al. 2020). Reported pH for fly ash has been between 12.7 to 13.3 and for bottom ash between 9.4 – 11.9 (Pedersen 2003; Nurmesniemi et al. 2012; Park et al. 2012; Park et al. 2020). The difference in pH can be accounted for by the higher mineral and elemental concentrations seen in fly ash e.g., Zn, K_2O and Na_2O. Dissolved metals, such as Zn, occur as basic metal salts, oxides or hydroxides increasing pH and alkali oxides such as CaO, K_2O and Na_2O are easily soluble in water which also increase the pH.(van Herck and Vandecasteele 2001; Pedersen 2003; Park et al. 2020). Where pH decreases the cause is likely due to the disappearance of alkaline minerals (Genty et al., 2012).

1.6.2 Wood ash remediation of metal contaminated effluents

The mineral composition of wood ash gives it considerable sorption potential for elements including Pb, Cu, Zn and Cd, whilst being much cheaper than other sorbents such as activated carbon (Vassilev et al. 2014). As with biochar, there are multiple sorption mechanisms which are relevant to metal immobilisation and several of these can occur at any one time (Genty et al. 2012). Mechanisms include precipitation, ion exchange, co-precipitation and electrostatic attraction (Genty et al. 2012; Vassilev et al. 2014; Rakotonimaro et al. 2016; Park et al. 2020). The different mineral and elemental composition of fly ash and bottom ash also create sorption differences both in terms of maximum measured immobilisation and sorption mechanisms in a given environment. In their study of the removal of Cd by wood ash J. H. Park et al., (2020) suggested that fly ash was ~ 7 times more effective than bottom ash. However, as a result of differing sorption mechanisms, J. H. Park et al., (2020) saw bottom ash to be more effective in the remediation of heavy metals from water at a pH range of 5-6. The primary immobilisation mechanism attributed to fly ash was precipitation, whereas the primary immobilisation mechanism attributed to bottom ash was ion exchange. For bottom ash at pH 5-6 H^+ ion concentration had reduced allowing sorption by active sites to become more prevalent (Park et al. 2020).

Precipitation has been cited as a primary immobilisation mechanism of metals by fly ash (Genty et al. 2012; Rakotonimaro et al. 2016; Park et al. 2020). Immobilisation via precipitation is at least partly due to the rise in aqueous pH caused by the dissolution of metal oxide in the fly ash and has been demonstrated to take the form of hydroxides (Rakotonimaro et al. 2016; Park et al. 2020). The high concentrations of minerals in fly ash is the driving factor behind this change in speciation. The importance of ion exchange in sorption is also relevant in the immobilisation of metals by fly ash. Studies such as Chirenje et al., (2006) and Kalak et al., (2021) assert that ion exchange was, in part, responsible for the immobilisation of Pb, Cu, Zn and Cd. As previously discussed in relation to biochar, the presence of functional groups and the resultant base cations such as Ca or Mg, enable this ion exchange to take place. FTIR was used by Kalak et al., (2021) to evidence a shift in peaks attributed to the interaction and binding of metal cations with oxygenated functional groups. Immobilisation of metals of concern by fly ash have been seen to take place within the first 5 min and the first 15 min, this is consistent with precipitation and ion exchange being recognised as early stage sorption mechanisms (Ifthikar et al. 2017; Park et al. 2020; Song et al. 2020; Kalak et al. 2021)

Ion exchange has also been seen to be a metal sorption mechanism for bottom ash. Both Vassilev et al., (2014) and J. H. Park et al., (2020) see this as the key factor for the sorption of metals by bottom ash as a result of the presence of oxygenated functional groups such as silanol, hydroxyl, phenolic and carboxyl. Aligned to this Vassilev et al,. (2014) highlight the importance of electrostatic attraction in the adsorption of metals by bottom ash. Some of the minerals in bottom ash under alkaline conditions exhibit a negative surface charge attracting positively charged metals that may be adsorbed (Vassilev et al. 2014).

1.7 Passive mine water treatment

Whilst balancing ponds are the focus of this research, remediation using biochar is also relevant for other aqueous environments contaminated by metals of concern such as metal mines. Both active and abandoned mines are a major source of contamination effecting both terrestrial and aquatic environments (Beane et al. 2016). Point sources e.g. mine adits and diffuse sources e.g. spoil heaps are both responsible for the contamination of aqueous environments (Rieuwerts et al. 2009). There are over 1300 mines which have a deleterious effect on over 700 km of river in Wales alone, all of which were closed and abandoned before 1999 (Environment Agency Wales 2002; Coal Authority 2020a). Metal mines are responsible for the pollution of rivers with metals of concern also seen in road runoff with Zn, Pb and Cu concentrations being elevated in waterways primarily as a result of Pb / Zn mining and smelting (Zhang et al. 2012a; Morgan et al. 2017). In areas where mine impacted water is present and above water framework directive thresholds remediation is important to improve the quality of the water and the surrounding environment. Mine impacted water can bioaccumulate in soils, flora, and fauna near the contaminated water and enter the foodchain (Sartorius et al. 2022).

There are three primary methods of remediating mine impacted water (i) diversion of water away from to mine (ii) active treatment of the mine impacted water e.g. chemical dosing or electrical coagulation (iii) passive treatment e.g. with vertical flow ponds or reed beds (Thisani et al. 2021). Remediation of mine impacted water in the UK has been limited due to regulatory framework, as no one is directly responsible for the contamination caused by mines and where remediation does take place it is often expensive and maintenance heavy (Wyatt et al. 2013; Rose et al. 2019). Where mine sites are closed it is passive treatment systems that are preferred as they use natural or waste materials to remediate and have low operating and maintenance costs due to simple installation and operation (Genty et al. 2012; Rakotonimaro et al. 2016). As closed mine sites are prevalent in countries such as Wales passive treatment systems are an important method in the remediation of mine impacted waters.

There are several key types of passive treatments to remove metals from mine impacted water, which can be broadly categorised into three types of system: inorganic media passive systems (IMPs), wetland type passive systems and subsurface flow bacterial sulphate reduction systems (Younger et al. 2002).

Inorganic media passive systems (IMPs)

IMPs are designed based on dissolution and / or precipitation; they raise pH, neutralise acidity and add alkalinity to mine impacted water (Younger et al. 2002). There are two principal types of IMP, the first being carbonate dissolution IMPS which include anoxic limestone drains, oxic limestone drains and closed system Zn removal reactors (Younger et al. 2002). Limestone drains are a widely used passive treatment used in the management of mine impacted water where the limestone dissolves having the effect of increasing pH and alkalinity leading to oxidation, hydrolysis and precipitation (ben Ali et al. 2019). Mn is one metal that favours precipitation in such limestone drains rather than aerobic passive systems such as wetlands (Opitz et al. 2022). Genty et al., (2012) asserted that wood ash from a biomass power plant was a feasible alternative to materials such as limestone or peat due to its neutralizing potential and metal removal qualities such as hydroxide precipitation.

The second type of IMP is a system using inorganic material, such as plastic or blast furnace slag, which provides surfaces to capture precipitates e.g. surface-catalysed oxidation of ferrous iron reactors (SCOOFI) (Younger et al. 2002). A SCOOFI reactor is a porous media with a high surface area which causes iron to precipitate on the surface of the media which in turn increases the rate at which the iron is immobilised (Moorhouse et al. 2013). Due to the continuous nature of this process, iron immobilisation will occur until the SCOOFI media is blocked (Moorhouse et al. 2013).

Wetland type passive systems

There are three key variants of wetland passive treatment systems namely aerobic wetlands, compost wetlands and reducing and alkalinity producing systems (RAPS).

Aerobic wetlands are ponds that are under 30 cm deep with or without wetland plants which slow down influent water and allows oxidation, hydrolysis and particle settling (Skousen et al. 2019). To further reduce flow rates flow diverting baffles are often used to improve efficacy (Skousen et al. 2019). Aerobic wetlands are often used as a polishing treatment in conjunction with other treatments such as sulphate reducing bioreactors (SRB) (Wang et al. 2022). Aerobic wetlands have been seen to reduce additional mining metal(oids) such as Pb, Cu, Zn and Cd but this has been primarily attributed to adsorption or complexation in wetland substrates or adsorption or co-precipitation with metal oxides including Fe, Al and Mn (Opitz et al. 2022). Aerobic wetlands are only to be used in net alkaline waters as if net acidic waters are subjected to oxidative hydrolysis in this type of wetland the pH will drop to a level of < 5 changing the speciation of metals into more mobile forms aerobic decrease pH of net acidic due to release of protons during hydrolysis of Fe^{3+} and Al^{3+} (Younger et al. 2002).

Compost wetlands or anaerobic wetlands are more commonly used in net acidic waters where the head is limiting (Younger et al. 2002). They have an anoxic substrate of compost creating an anaerobic environment where sulphate reducing bacteria thrives reducing sulphate to sulfide. That sulfide can then react with the free metal ions in the water to form insoluble metal sulphides (e.g. FeS and ZnS) that remain within the wetland (Batty and Younger 2004; Ettner 2007).

Reducing alkalinity producing systems (sometimes referred to as vertical flow ponds) are similar to compost wetlands but in addition they include a limestone gravel bed to maximise alkalinity generation, act as a source of sulphate reducing bacteria and remove metals through precipitation (Batty and Younger 2004). RAPS systems are said to be more efficient than compost wetlands and as a result require less land area to be effective, however, they need more head to function as the design necessitates the water to flow downwards through the system rather than just requiring a surface flow as per a compost wetland (Younger et al. 2002; Batty and Younger 2004). The RAPS system is generally not planted with reeds but rather an aerobic wetland reed bed is often included as a polishing treatment downstream (Batty and Younger 2004).

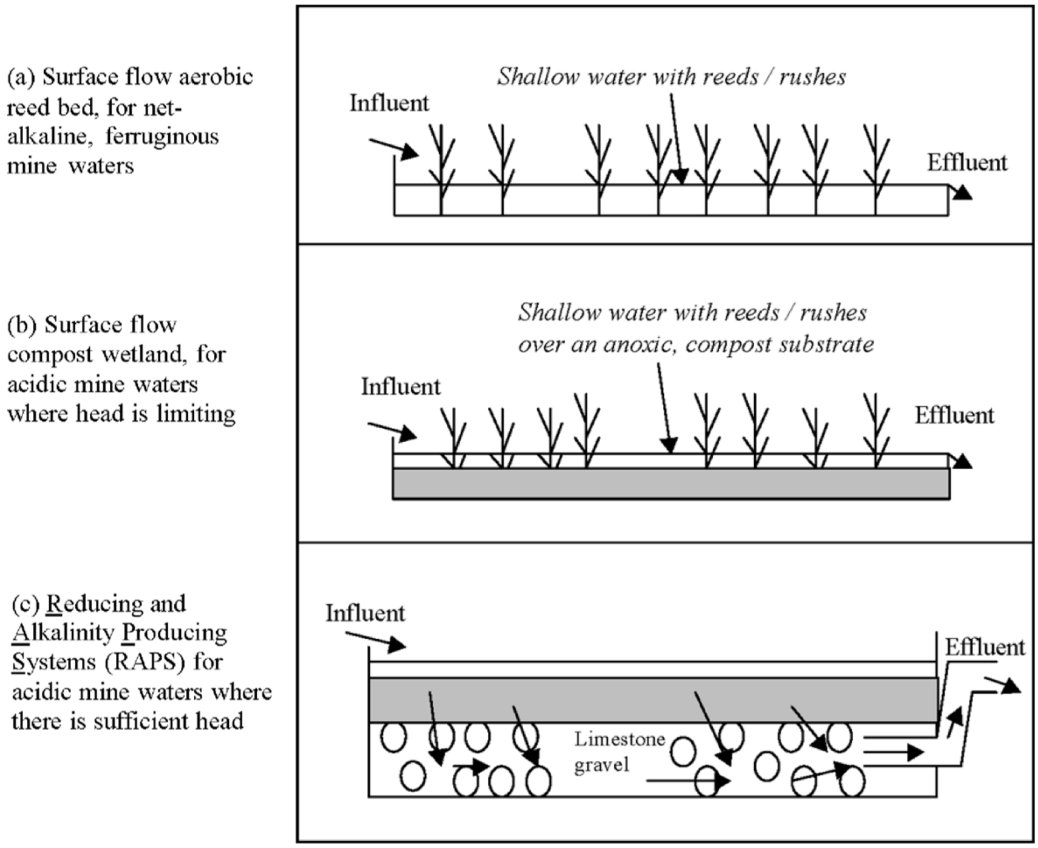

Figure 1.7: Schematic illustration of the three types of wetland: (a) aerobic wetland, (b) compost wetland and (c) reducing alkalinity producing systems (RAPS) (Younger et al. 2002)

Subsurface flow bacterial sulphate reduction systems (SFBs)

There are two types of SFBs, in situ permeable reactive barriers and SFBs constructed to treat mine water discharges. These are distinguished by their location but function without scientific difference (Younger et al. 2002). These systems employ an area of semi-permeable reactive media which is placed in the flow path of mine impacted water; this creates biogeochemical processes (e.g., precipitation, sorption, oxidation/reduction, fixation, degradation) which remove the contaminants (Batty and Younger 2004; ben Ali et al. 2019). There are highlighted issues with this system the most notable of which is that there is the potential for the water to flow around rather than through the barrier and that the barrier must be replenished / replaced due to exhaustion or clogging (Younger et al. 2002).

1.8 Research aims

The research aims of this work are to ascertain the efficacy of biochar as a remediator of inorganic pollutants from motorway runoff. In particular this will focus on Cu, Cd, Pb and Zn. This research has focused on these particular pollutants due to their ubiquitous nature and toxicity.

More specifically the research objectives are to study:

1. The effect of amendments on biochar’s sorption of metals of concern prevalent in motorway runoff (namely Pb, Cu, Zn and Cd).
2. The maximum measured immobilisation of biochar and amended biochars.
3. The mechanisms involved in the immobilisation of Pb, Cu, Zn and Cd.
4. The concentration of potentially harmful nutrients leached during remediation and treatments to mitigate this.
5. The contact time required to immobilise contaminants.

Chapter 2: Methods and materials

2. Methods and materials

The methods and materials used in each stage of this work are outlined in each chapter / publication. The principle aim of this materials and methods chapter is to expand on key aspects of the methods and to give the background to work that led to the development of the methods used. Several key instruments, methods and materials have been used several times, where this is the case the first time an instrument, method or material is outlined it is covered in detail with briefer descriptions thereafter.

2.1 Wood ash amended biochar for the removal of lead, copper, zinc and cadmium from aqueous solution

2.1.1 Biochar production

European larch (Larix decidua (L.) Karst.) wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 485-530°C, with a retention time of ~90s (Figure 2.1). The design of the pyrolysis unit is subject to intellectual property restriction and as such not all details can be discussed in this work. However, the unit has a kiln section with integrated feedstock intake. This feedstock intake delivers the feedstock (in this instance wood chip of <30mm and a moisture content of <20%) to the rotary hearth via an elevator. The rotary hearth can maintain temperatures of between 400°C and 550°C, for the purposes of this production run temperatures were between 485-530°C. Off-gases reach temperatures of 400-900°C and rise to the thermal oxidiser at the top of the kiln. Due to the counter flow of the gases air is restricted from entering the chamber. Once the feedstock has moved through the hearth the biochar is discharged into a receiving container. There is also a thermal oxidiser designed to ensure that there is full oxidation of the organic compounds; off gases are ducted from the kiln section of the unit past air controls to the thermal oxidiser chamber (Harries 2017). The conversion from feedstock to biochar takes ~90 seconds to complete. Once the biochar had been discharged into the receiving container it was transferred into a clean cement mixer whilst hot. To the freshly pyrolyzed still hot biochar, wood ash (specifically fly ash) purchased from

NPK Ltd (sourced by NPK Ltd from a renewable energy plant in the UK), was added on a 1:1 ratio. Due to commercial sensitivity the precise power plant that this wood ash was produced was not revealed to the consumer. Wood ash was chosen as an amendment due to its mineral fraction (including Ca, K, Mg, S, P and Si) and pH buffering capacity. The cement mixer mixed the wood ash and hot biochar for 15 minutes to sinter the wood ash to biochar and aid the retention of the wood ash. A second load of biochar was deposited into the receiving container and left to cool for 1 hour. This was then mixed with the wood ash in a 1:1 ratio at ambient temperature in the cement mixer for 15 minutes. A third and final load of biochar was deposited into the receiving container and was left as pristine biochar rather than amending it.

Half of each the wood ash sintered (WAS), wood ash mixed cold (WA) and pristine biochar (BC) was then granulated to <3mm with a Tria G1 granulator and half was left ungranulated. The pristine larch biochar, larch biochar cold mixed with wood ash and larch biochar sintered with wood ash are referred to as BC, WA, and WAS throughout the study. All characterisation was of the materials post pyrolysis rather than their constituent parts i.e., analysis revolved around characterising WAS, WA and BC rather than the wood ash or wood chips in isolation. Due to pyrolysis unit access, feedstock availability, wood ash availability, cost issues and the requirement for a large quantity of uniform biochar to be studied there was only one opportunity to undertake biochar / amended biochar production. As a result, it was not possible to investigate other parameters that may have an effect on sorption such as the ratio of wood ash used.

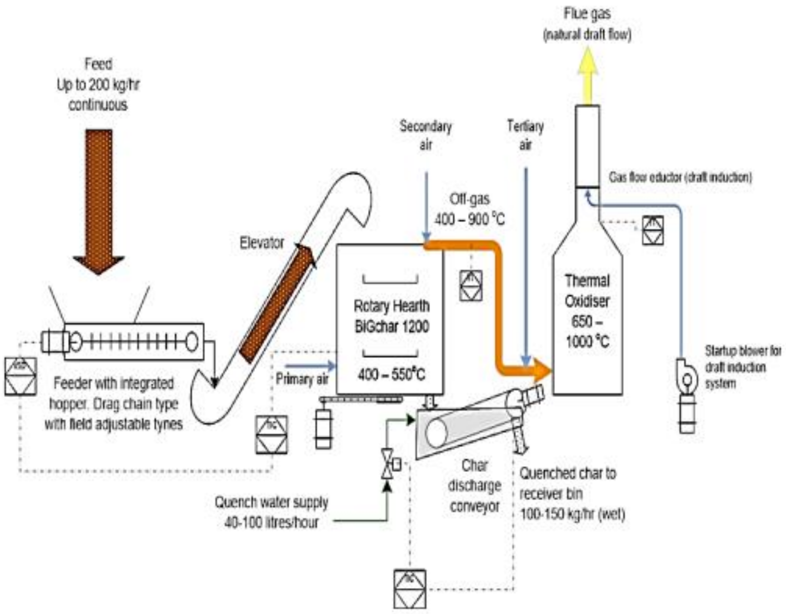

FIGURE 2.1: Schematic diagram of the Pyrocal BigChar 1000 which produced the biochar used for this work (Harries 2017)

2.1.2 Sorption experiments

Solution preparation

Sorption batch experiments were carried out using Pb, Cu, Zn and Cd to ascertain the maximum measured immobilisation of these contaminants in the conditions tested at five different concentrations between 10 mg/L and 150 mg/L (10 mg/L, 30 mg/L, 70 mg/L, 120 mg/L and 150 mg/L). These metal concentrations are higher than those studied in runoff (table 1.1b) but were necessary both to expose the biochar to a high enough concentration of metals to reach exhaustion thus enabling the quantification of a maximum measured immobilisation and to enable the MP-AES to measure the solution at concentrations above its limit of detection. All chemical reagents were of analytical grade and the five concentrations were obtained by preparing a stock solution (1000 mg/L) of $Pb(NO_3)_2$, $Cu(NO_3)_2{\bullet}xH_2O$, $Zn(NO_3)_2{\bullet}6H_2O$ and $Cd(NO_3)_2.4H_2O$ and diluting with deionised water. The pH of each of these five concentrations was adjusted to 4.7 with the dropwise addition of HNO_3 to achieve an equal pH between solutions that represented the closest to runoff pH possible using the instruments available. Previous methods had used NaOH to increase the pH of each solution to ~6, closer to the pH range found in road runoff which studies have shown range from ~pH 6 – 7.9 (Legret and Pagotto 1999; Dean et al. 2005; Helmreich et al. 2010b). However, Zn and Cu analysis by MP-AES suffered interference from Na which acted as a masking agent, producing inaccurate and imprecise results. As a result, the pH of the five solutions had to be lowered by HNO_3 to the lowest pH measured in each of the five solutions rather than increasing the pH to ~6. Once the pH was adjusted, 25 mL of each concentration was added to 40 mL polyethylene Falcon tubes.

Biochar preparation

The biochar and amended biochars (BC, WA and WAS), which had been granulated to <3 mm, were dried at 105°C for 24 hours to remove moisture and allow replicable weighing of the samples. Samples were weighed at 0.2 g, 0.1 g, 0.15 g, 0.05 g, 0.04 g, 0.03 g and 0.025 g on a polystyrene diamond shaped antistatic weighing boat. Biochar and amended biochar weights were changed rather than solution concentration as the pH of a higher concentration solution would be lower than the pH ~4.7 used in the rest of the sorption experiment. This would make comparisons at best less robust. The BC, WA and WAS were then added to the 40 mL polyethylene Falcon tubes. Two types of control experiments were included — biochar without contaminants, as well as contaminants without biochar. All experiments were performed in triplicates using a batch sorption equilibrium method (OECD 2000b).

Agitation and separation

Agitation was achieved on a Unitwist 400 Orbital Shaker for 48 h at∼280 rpm to reach equilibrium. Studies such as Uchimiya et al. (2011) prescribe contact of 24 h to reach equilibrium, but longer contact times have not shown significant changes in equilibrium concentration and ensure that the adsorption phase had reached equilibrium (Wang et al. 2018a). The solution was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000 rpm for 15 min (OECD, 2000).

Acidification and filtering

The supernatant was removed from the Falcon tubes and decanted into 25 mL borosilicate glass beakers. The pH was then measured using a Voltcraft pH meter which was calibrated with a two point calibration using buffer solutions with a pH of 4 and 7. The supernatant was then immediately acidified to<pH 2 with 1 mL of 70% HNO3 as per United States Environmental Protection Agency, (1994). Post acidification, filtration with a 0.45µm PTFE syringe filter for analysis was undertaken. Filtration was deemed to be an essential step in the process to ensure that no particulate matter was present in the supernatant which would have a detrimental effect on analytical instrumentation such as ICP-OES or MP-AES. Although acidification took place prior to filtration however, previous iterations of this method planned to acidify post filtration (Betts et al., 2013; Hilliges et al., 2017; Feng et al., 2018; Serra-Ventura, Vidal and Rigol, 2022). In this case, post filtration acidification was not possible as, in some cases, the 0.45 µm PTFE syringe filter became clogged. Whilst acidifying prior to filtration was a necessary step it is possible that it could have dissolved fine / colloidal metals suspended in the supernatant with the potential consequence that metal analysis potentially overestimated metal concentrations.

ICP-OES

Pb, Cu, Zn and Cd concentrations of the acidified supernatants were measured using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES 5110, Agilent Technologies Inc., USA). Sorbent loading (q) was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:

$q = (c_i – c_{aq})\ V / W$

where c_i is the initial concentration of metals in solution, c_{aq} is the final equilibrium concentration of metals in solution, V is the volume of solution and W is the weight of the biochar. Some of the decisions leading to the experimental design (including solution concentration pH of solution) were made based on the assumption that MP-AES rather than ICP-OES would be used for analysis. However, due to lack of laboratory access as a result of both COVID-19 and unplanned laboratory closure due to fire, samples were sent to the University of Austria for ICP-OES analysis to be undertaken.

Equilibrium sorption coefficients (Kd) were calculated as:

$$Kd=q / caq$$

where, Kd (L/kg) =amount of metal adsorbed onto biochar per L of water, q(mg/kg)= sorbent loading (metals adsorbed by biochar) and Caq (mg/L)=concentration in the aqueous phase .Kd is commonly used in estimating the potential sorption of dissolved metals by a solid phase with higher values indicating higher sorption potential

2.1.3 Biochar characterisation

Sorbents were characterised via Fourier transform infrared spectroscopy (FTIR), x-ray powder diffraction (XRD), surface area and pore size analyser and scanning electron microscopy with energy dispersive x-ray (SEM-EDX) analysis.

Fourier transform infrared spectroscopy (FTIR)

FTIR is a technique which is primarily used to identify the functional groups present in inorganic and organic compounds by measuring their absorption of infrared radiation over a specified range of wavelengths (Berna 2017). An interferogram of a sample is collected after which a mathematical algorithm named a Fourier transform is performed to obtain the infrared spectrum; for this work the spectra was obtained in absorption (Berna 2017). FTIR was undertaken using a Perkin Elmer Spectrum Two FTIR Spectrometer. Measurements are in the range of 400-4000 cm^{-1} to compare possible changes before and after sorbent loading with particular focus on oxygenated functional groups, phosphate and silicate. Post sorbent loading BC, WA and WAS were air dried in the Falcon tubes used for the sorption experiments. Each biochar and amended biochar were mixed with KBr at a ratio of 1:100 (W/W) (Merino et al. 2017). KBr was used as a carrier for the sample as it is optically transparent for the light in the range of IR measurement meaning that no interference in absorbance would occur. Each biochar was mixed with KBr in an agate pestle and mortar whilst gently ground (Johnston 2017). Prior to analysis a background scan was run without a sample present to remove interference such as carbon dioxide. Each BC, WA and WAS sample was placed on the FTIR and the clamp with horse shoe was tightened onto the sample before running the analysis. Data was returned via Spectrum TM 10 software.

X-ray powder diffraction (XRD)

XRD is a non-destructive technique which is used to provide information regarding crystallographic structure, chemical composition and physical properties of a material (Bothi and Mohamad 2022). XRD was used to identify possible crystalline precipitates formed on the surface of the sorbents. Comparisons were made pre and post sorption for BC, WA and WAS. Again, post sorbent loading BC, WA and WAS were air dried in the Falcon tubes used for the sorption experiments in a similar manner to Rakotonimaro et al. (2016) who dried their samples at 40 °C for 48 hours. It should be noted that whilst air drying in this manner is a recognised method there is the potential that precipitates may have dried onto the surface of the post test residue. XRD analysis was undertaken by Dr Tom Dunlop (SPECIFIC). Brief methods were that XRD patterns were obtained using a Bruker D8 Discover with a Copper source (40kV, 40mA) and a 1D detector. Powdered sorbents were pushed flat on a single signal silicate zero diffraction plate to minimise background interference. Scans themselves had a 0.5 second time per step and an increment of 0.02° over the range of 10-90 (Hasan Khan Tushar et al. 2012; Li et al. 2017b).

Surface area and pore size analyser

The surface area and pore analyser was used to measure surface area and pore size distribution in a non-destructive fashion. Specific surface area and pore volume distribution were determined from N_2 physisorption isotherms using the Brunauer–Emmett–Teller method and Barrett–Joyner– Halenda method respectively. The physisorption tubes were weighed followed by the samples of BA, WA and WAS being placed into physisorption tubes and weighed. The weight of the samples and tubes were subtracted from the weight of the tubes to give the sample weight. This was to stop any loss of sample when being transferred in and out of the physisorption tubes. Vacuum dried samples were degassed to remove contaminants at 105°C overnight. This degassing took place via a vacuum degassing using a pump system. After degassing samples were weighed again to give their decontaminated weight, a lower mass denoting that degassing has removed contaminants opening up the samples true surface area for measurement. Physisorption tubes were then loaded into the surface area analyser to be measured and the degassed weights of the samples were entered. Samples were initially measured with N_2 adsorption at the liquid nitrogen temperature of -196°C (77K) by a NOVA 2000e surface area and pore size analyser (Cao and Harris 2010). Due to the small pore size of BC, CO_2 was also used to determine pore size distribution because of microporosity and kinetic limitations with N_2 physisorption (Sigmund et al. 2017).

Scanning electron microscopy with energy dispersive x-ray (SEM-EDX)

Scanning electron microscopy (SEM) produces images by scanning the sample with an electron beam which emits electrons into a vacuum. As the electron beam interacts with the sample it knocks out secondary electrons from the sample which are used to build up a picture. In this study surface morphologies were examined by scanning electron microscopy (Hitachi TM3000 desktop microscope) comparing pre and post sorbent loaded BC, WA and WAS. Post sorbent loading BC, WA and WAS were air dried in the Falcon tubes used for the sorption experiments. Samples were mounted to aluminium SEM stubs using conductive double-sided carbon tape to enable examination of samples in an uncoated state (Eiblmeier et al. 2014). A working distance of 10mm and an acceleration voltage of 15kV were used and images were obtained using the in-built Hitachi TM3000 software. Elemental composition analysis was undertaken at the same surface locations by electron dispersive x-ray spectroscopy (EDX) attached to the Hitachi TM3000 desktop microscope. An EDX spectrum was produced after scanning the area of interest for ten minutes.

Water chemistry and metal speciation

Water chemistry was determined using ICP-OES, ion exchange chromatograph and TOC analyser. Speciation analysis of the solutions were carried out using Visual MINTEQ version 3.1. The change in base cations (Ca, K, Na, Na and Mg) was measured using the eluate from the sorption experiment at a concentration of 10 mg/L and analysed using the ICP-OES to review possible cation exchange. Similarly total P and Si were also measured from the sorption experiment eluate using the ICP-OES to review potential co-precipitation. The major anions (Cl^-, NO_3^{2-}, PO_4^{3-}, and SO_4^{2-}) were measured with an ion exchange chromatograph which also used the eluate from the sorption experiment. Speciation of C in the solid phase was measured using a multiphase carbon analyser RC-612 from LECO. All analysis was undertaken in triplicate. Samples were sent to the University of Austria for analysis to be undertaken.

2.2 Treatments of wood ash amended biochar to reduce nutrient leaching and immobilise lead, copper, zinc and cadmium in aqueous solution: column experiments

2.2.1 Biochar production and wood ash amendment

The amended biochar that was used was that described in (section 2.1.1). Briefly European larch (*Larix decidua* Mill.) wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 485-530°C, with a retention time of ~90s 28. Wood ash, purchased from NPK Ltd, was added to the biochar after pyrolysis via two alternative methods. For the first method, it was mixed with the freshly pyrolyzed, hot biochar at a ratio of 1:1 for 15 minutes in a cement mixer in order to sinter the materials (WAS). The sintering of the wood ash to the biochar was to promote particle bonding between the wood ash and the biochar to create a more stable matrix than when mixed cold. This was also designed to retain alkali and alkaline earth metals, P, N and S all of which are either relevant to contaminant immobilisation or nutrients that could be harmful to the wider ecosystem. For the second method the wood ash was mixed at a ratio of 1:1 with biochar that had been allowed to cool to ambient temperature for 15 minutes (WA). Wood ash was chosen as an amendment due to its high mineral and nutrient fraction, including Ca, K, Mg, S, P, N and Si and pH buffering capacity (Cairns et al. 2020). Half of WAS was granulated to <3mm with a Tria G1 granulator (WASGr) and half remained ungranulated (WAS). Similarly, half of WA was granulated to <3mm (WAGr) and half remained ungranulated (WA).

2.2.2 Biochar characterisation

Total metal concentrations for WA and WAS were determined using microwave assisted digestion. Approximately 20mg of each sample of biochar were digested in the presence of 6 mL HNO3, 2 mL HCl and 0.5 mL HF. The samples were digested using a microwave (Speedwave4, Berghof Products + Instruments GmbH, Germany), ramped up to 220°C for 30 minutes and then held at 220°C for 30 minutes before cooling in a water bath. 200mg of H_3BO_3 was then added as a complexation agent alongside 2mL of H_2O_2 and held at 160°C for 30 minutes. Deionised water was then added to bring the samples up to a volume of 50 mL. An aliquot of the sample was filtered through a 0.45µm cellulose acetate filter. Metal concentrations were measured in triplicate using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES 5110, Agilent Technologies Inc., USA). ICP-OES analysis was undertaken in the University of Austria. Total carbon, hydrogen, nitrogen and sulphur contents were determined in triplicate by elemental analyses (Vario MACRO CHNS elemental analyzer, Elementar Analysensysteme GmbH, Germany). Furnace temperatures were ramped up by 2°C per minute and then a dwell time of 750°C was maintained for 6 hours. Ash content was determined by heating the biochars in a muffle furnace. Total oxygen was calculated from C, H, N, S and ash content via mass balance (European Biochar Foundation 2016).

2.2.3 Biochar rinsing

Quartz sand, selected due to its neutral pH, low levels of alkaline earth and low levels of heavy metal pollutants, was washed with 1% HCl and rinsed with distilled water to remove impurities such as carbonates, silicates, CaO, MgO, Na_2O, K_2O and P_2O_5 (Xu et al. 1997; Anas Boussaa et al. 2017). Deionised water was used to dilute 36% HCl (analytical grade) to a 1% concentration. Sand was added to a 250 mL beaker in batches of 30 g. This was then washed with 100 mL of 1% HCl, stirred vigorously and left for three hours. The sand and HCl mix was then poured through a sieve was rinsed with 200 mL of DI four times. After rinsing the sand was dried at 100 °C for 20 hours before use (Thirunavukkarasu et al. 2001). The acid washed, dry sand (8 g) was added to the bottom of an open ended polypropylene column. The column had an internal diameter of 31 mm, a wall thickness of 1 mm and a length of 500 mm. The sand was added to help distribute the flow of deionised water and prevent the loss of biochar from the bottom of the column. An 80µm nylon mesh was attached to the bottom of the column to stabilise the column content and further prevent loss of sand and biochar as per Cairns et al. (2020). To the column and sand 5 g of the biochar treatment was added. The treatments used were larch biochar mixed cold with wood ash (WA), larch biochar mixed cold with wood ash and ground < 3 mm (WAGr), larch biochar sintered with wood ash (WAS) and larch biochar sintered with biochar and ground < 3 mm (WASGr). Each of these had been dried at 105°C for 24 hours to remove moisture and allow replicable weighing of the samples. Finally, 8 g of the acid washed sand was then added to the top of the column to help distribute the flow of the deionised water. Each treatment was rinsed by pumping deionised water downward through the column at flow rates of∼5.5 mL min−1with a peristaltic pump (Baoding peristaltic pump model YZ1515X). The biochar and amended biochar were each rinsed with 800 mL of deionised water equating to approximately one year of precipitation in England and Wales (Metoffice.gov.uk 2021). Each treatment was performed in triplicate and the eluates from the columns were captured at 25 mL intervals in a 50 mL Falcon tube. Pumping deionised water down through the column rather than up through the column was undertaken to mimic the flow that would go through the biochar if put in the pipe work that delivers motorway runoff to a balancing pond (figure 1.2). Several iterations of column size, quantity of biochar and sand were studied before choosing to top and bottom 5g of biochar with 8 g of acid washed sand. This configuration proved to result in the steady flow of deionised water without the water either overflowing from the top of the column or leaving the column dry for periods. This configuration also allowed the biochar to be at a depth of ~ 1 cm which was deep enough for the biochar to comfortably cover the internal diameter of the column where, ensuring that all of the eluate had been in contact with the biochar, but also not so deep as to restrict flow rates and cause the deionised water to back up and overflow.

2.2.4 Column eluate analysis

The eluate pH, eluate electrical conductivity (EC) and leaching of nutrients (PO_4^{3-}, SO_4^{2-} and NO_3^-) were studied for all rinsed biochars. The eluate from the rinsed biochars was pH tested in triplicate using a Voltcraft pH meter which was calibrated with a two point calibration using buffer solutions with a pH of 4 and 7. The EC was measured in triplicate using a Whatman CDM 400 Conductivity Meter which was calibrated with a two point calibration using a 1413 µs/cm solution and a 12880 µs/cm solution. Each eluate was then analysed in triplicate for phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and nitrate (NO_3^-) using an ion chromatograph (IC 930 Compact Flex, Metrohm, Switzerland). However, due to lack of available instrumentation in Swansea University samples were sent to the University of Austria for ion chromatograph analysis to be undertaken.

2.2.5 Lead, copper, zinc and cadmium immobilisation

The immobilisation of Pb, Cu, Zn and Cd was studied for each of the unrinsed biochars and the biochars rinsed with deionised water. Immobilisation batch experiments were carried out using Pb, Cu, Zn and Cd at a concentration of 10 mg/L for each metal. This concentration was chosen to enable the MP-AES to measure the solution at concentrations above its limit of detection whilst exposing the biochars to levels beyond those expected in road runoff which have been reported to be as high as 88 µg/L, 146 µg/L, 1544 µg/L and 4.2 µg/L for Pb, Cu, Zn and Cd respectively (Legret and Pagotto 1999; Crabtree et al. 2009; Zhao et al. 2010; MacKay et al. 2011; Zhang et al. 2013b). The solution was prepared as described previously by Cairns et al., (2021). All chemical reagents were of analytical grade and the five concentrations were obtained by preparing a stock solution (1000 mg/L) of $Pb(NO_3)_2$, $Cu(NO_3)_2{\bullet}xH_2O$, $Zn(NO_3)_2{\bullet}6H_2O$ and $Cd(NO_3)_2.4H_2O$ and diluting with deionised water. The pH of each of these five concentrations was adjusted to 4.7 with the dropwise addition of HNO_3 to achieve an equal pH between solutions that represented the closest to runoff pH possible using the instruments available. All rinsed and unrinsed biochars were oven dried at 105 °C for 24 h. Biochar (0.2g) was then added to 25 mL of the spiked aqueous solution in 50 mL polyethylene Falcon tubes and agitated for 48 h at 280 rpm on a Unitwist 400 Orbital Shaker to reach equilibrium. The solution was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000rpm for 15 minutes (OECD 2000b). The supernatant was removed and immediately acidified to <pH 2 with 1mL of 70% HNO3 before being filtered with a 0.45µm PTFE syringe filter for elemental analysis. Two types of control experiments were included: biochar without contaminants, as well as contaminants without biochar. All experiments were performed in triplicate using a batch sorption equilibrium method (OECD 2000b).

Pb, Cu, Zn and Cd concentrations of the acidified supernatants were measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200, Agilent).

Microwave Plasma Atomic Emission Spectroscopy (MP-AES) is an atomic emission technique for the analysis of elements in solution. It relies on the fact that once an atom of a specific element is excited it emits a light at wavelengths characteristic of certain elements (an emission spectrum) as it returns to its ground state. The source for atomic emission in the MP-AES is the microwave plasma which creates a high temperature source of ~5000 K. Magnetically coupling microwave energy is used to generate a self sustained atmospheric pressure plasma from nitrogen that has been extracted from compressed air. An aerosol is created from the liquid sample using a nebuliser which is then introduced to the centre of the hot nitrogen fuelled plasma. The light that is emitted as the sample returns to its ground state is then quantified by comparing its emission to that of known concentrations of the element(s) selected for analysis, which then in turn gives the concentration of the element(s) (Agilent 2021). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), which was used in chapter 2 for metal analysis, uses similar principals to the MP-AES to quantify elemental concentration in a much as a plasma is used to excite atoms of a liquid sample and measure the wavelengths of the light emitted as the atoms return to ground state. However, there are differences between the two instruments the key ones being that the ICP-OES has a wider range of elemental concentrations that can be measured with a lower limit of detection (LOD) than the MP-AES and the ICP-OES uses argon to fuel its plasma which is more expensive than the nitrogen that is extracted from air that the MP-AES uses (Agilent 2022). Both cost and LOD considerations needed to be taken into account with experimental set up.

To analyse the filtered batch experiment samples with the MP-AES, general quality control criteria used by routine analytical laboratories were undertaken (Marília Teodoro et al. 2013). The MP-AES was calibrated using a blank and multi element standard diluted to 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L (Marília Teodoro et al. 2013). These calibration concentrations were chosen to match the possible range of concentrations that could be seen in the samples resultant from the immobilisation experiment that started with a solution concentration of 10 mg/L. Calibration curves were run for Pb, Cu, Zn and Cd using these calibration solution concentrations. The acceptance criterion for calibration curve co-efficient is 0.999 with at least four calibration standards and the acceptance criterion for standards is ±10%, these criteria were met (Hettipathirana 2011). The calibration fit used for Pb and Cd was linear and the calibration fit used for Cu and Zn was rational (Hettipathirana 2011; Marília Teodoro et al. 2013). The MP-AES analysed each sample (including control samples) three times and produced a mean concentration for each.

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Sorbent loading (q) was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:

$$q = (c_i - c_{aq})\ V / W$$

where c_i is the initial concentration of metals in solution, c_{aq} is the final equilibrium concentration of metals in solution, V is the volume of solution and W is the weight of the biochar.

2.3 Treatment of mine water for the fast removal of zinc and lead by wood ash amended biochar

2.3.1 Biochar production

European larch (Larix decidua(L.) Mill.) wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 485–530°C, with a retention time of ~90 s. Wood ash, originating from a renewable energy plant in the UK and sold commercially by NPK Ltd, was added to the still hot biochar at a ratio of 1 : 1 and mixed for15 min in a cement mixer to sinter the materials and then granulated to <3 mm with a Tria G1 granulator (Cairns et al. 2021).Wood ash was selected as an amendment to the pristine biochar because of its mineral fraction (specifically Ca, K, Mg, S, P and Si) and pH buffering capacity. However, as a result of the mineral fraction the wood ash amended biochar (WAS) can potentially leach nutrients such as nitrates, phosphates and sulphates. Cairns et al. (2022)

demonstrated that rinsing wood ash amended biochar with 200 mL of water per 5 g biochar removes these unbound nutrients and reduces leaching to below water framework directive thresholds. To remove these unbound nutrients every 15 g of biochar was rinsed with 600 mL of deionised water. To rinse, the biochar was added to an open-ended polypropylene column with an internal diameter of 31 mm, a wall thickness of1 mm and a length of 500 mm. An 80mm mesh was used to stabilise the column content and further prevent loss of biomass (Cairns et al. 2020).

2.3.2 Sample collection and mine water characterisation

Water was obtained from the Deep Boat Level adit and Tributary1 at Nantymwyn lead mine and sub-divided into identical 1 L polyethylene terephthalate (PET) bottles. These bottles were each rinsed with sample water three times before filling, and stored at 4°C, in accordance with national guidelines (Environment Agency 2014).The pH, electrical conductivity, temperature, redox and dissolved oxygen levels were taken concurrently at each site with a calibrated Hanna Instruments HI98194 Multiparameter meter following national guidelines (Environment Agency 2014).

2.3.3 Sorption experiments

Batch sorption experiments were carried out to determine the effect of contact time on immobilisation using the Deep Boat Level adit and Tributary 1 water and to determine the maximum measured removal of Zn and Pb by biochar using Tributary 1 water. For both sorption batch experiments the sorbent was oven dried at 105°C for 24 h. To determine the effect of contact time on immobilisation, WAS (0.5 g with a particle size of <3mm) was added to 5 mL of deionised water in 50 mL polyethylene Falcon tubes and shaken for one hour to saturate the sorbent thus reducing the time needed for the mine water to saturate WAS. 0.5 g biochar was a larger quantity than previous studies to take into account the reduced immobilisation capacity of mine water compared to synthetic contaminated water. Mine water was then added (20 mL) to the biochar slurry and shaken for a known amount of time (1 min, 5 min,15 min, 30 min, 1 h and 24 h). To determine the maximum measured removal of Zn and Pb by biochar, a known amount of biochar (0.1 g, 0.05 g, 0.03 g, 0.02 g, 0.01 g, 0.006 g, 0.003 g and 0.002 g) was added to 40 mL of Tributary 1 mine water in 50 mL polyethylene Falcon tubes and shaken for 24 h. For both sorption batch experiments agitation was achieved on a Unitwist 400 Orbital Shaker at 280 rpm. The solution was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000 rpm for 15 min (OECD 2000b). The supernatant was then acidified to <pH 2 with 1 mL of 70% HNO_3 before being filtered with a 0.45mm PTFE syringe filter for analysis. All experiments were performed in triplicates using a batch sorption equilibrium method with biochar without mine water and mine water without biochar used as controls. Zn and Pb concentrations of the acidified supernatants were measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200, Agilent Technologies Inc., USA). For contact time sorption batch experiments the percentage of sorbent removal was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:

$$\%\text{ removal} = \left(\frac{c_i - c_{aq}}{c_{aq}}\right) \times 100$$

Where C_i is the initial concentration of metals in solution and C_{aq} is the final equilibrium concentration of metals in solution. For maximum measured removal experiments removal in mg/g was calculated as the difference between initial metal concentration and the final metal concentration in the aqueous phase:

$$\text{q} = (c_i - c_{aq})V/W$$

where q is the maximum measured removal, V is the volume of solution and W is the weight of the biochar.

Whilst typically sorption data would be presented with equilibrium data (mg/L) versus loading (mg/g) this was not possible in this study as different quantities of sorbent were used to determine maximum measured immobilisation. This was done as once studies had shown that sorbents hadn’t reached maximum immobilisation with 0.2g or sorbent and 150 mg/L of contaminated solution further data points were required. However, in light of the importance of pH more concentrated solutions were not mixed as the stronger concentration would have resulted in a lower pH hindering accurate sorption comparisons, rather a smaller quantity of sorbent was used.

2.3.4 Biochar properties

A range of biochar properties were determined to understand how they effected immobilisation. The release of base cations (Ca, K, Na and Mg) by the biochar were measured for biochar that had been agitated with deionised water and for biochar that had been agitated with mine water and compared to review possible cation exchange. This measurement was undertaken on MP-AES using the supernatant from the sorption experiments. The pH, EC and alkalinity of the biochar supernatant from the sorption experiments were measured prior to acidification using a calibrated Voltcraft pH Meter, a calibrated Whatman CDM 400 Conductivity Meter and a Hanna HI-3811 Alkalinity test kit respectively. Alkalinity is the capacity of a water sample to neutralise a given acid to a set pH. Sources of alkalinity can include hydroxide, carbonate, phosphates and silicates. In the determination of total alkalinity one drop of bromophenol blue indicator was added to 5 mL of sample and shaken to mix. A titration syringe was then filled, and titration solution was added dropwise until the solution turned yellow. The mL of titration solution added to the sample was then multiplied by 300 to obtain mg/L $CaCO_{3.}$ Fourier trans-form infrared spectroscopy (FTIR) was undertaken using a PerkinElmer Spectrum Two FTIR Spectrometer. Measurements in the range 400–4000 cm1were determined to compare possible changes to functional groups, minerals capable of precipitation and aromatic structures. As in previous chapters the solid biochar sample was air dried in the sorption experiment Falcon tube prior to analysis by FTIR. However, as opposed to chapter 2 the biochar was not mixed with KBr. As a part of the ongoing review of literature it became apparent that whilst some papers referred to the use of KBr not all of the methods described in more recent papers used KBr to aid with the visibility of the biochar (Cole et al. 2019; Keerthanan et al. 2020; Nair et al. 2020). The PerkinElmer supporting information also confirmed that not all configurations required the use of KBr (PerkinElmer 2022). As a result the method used in this work was amended to stop the use of KBr. Comparisons of the spectra were made for biochar before sorbent loading and at each timed stage of the sorption experiment. The air dried solid biochar sample was used to carry out x-ray photoelectron spectroscopy (XPS) analysis on a Kratos Axis Supra instrument using a monochromatic Al KaX-ray source at 225 W, with a 15mA emission current. Each sample had multiple wide scans at pass energy of 160 eV over the binding energy range of 1200–0 eV to identify all possible elements present, with a step size of1 eV.

High resolution spectra were scanned with a pass energy of40 eV, a step size of 0.01 eV and a multi sweep dwell time of 2000ms to improve the signal to noise ratios for the lower concentration elements of interest. The binding energy axis was charge correct to the C–C component of the carbon peak at 284.8 eV. Casa XPS (2.3.22PR1.0) was used to quantify the data using the Kratos sensitivity factor library, standard Shirley backgrounds and Gauss–Lorentz peak models. XPS analysis was conducted to identify the change in biochar characteristics, especially incomposite compounds, before and after sorption. XPS analysis was undertaken by Dr Tom Dunlop (SPECIFIC).

2.3.5 Metal speciation

Speciation analysis of the mine water and biochar supernatants were carried out using the pH redox equilibrium (PHREEQC) program (version 3.7.1) and the MINTEQV4 database (Parkhurst and Appelo 1999).The pH, redox, temperature and concentrations of base cations, metal contaminants, alkalinity and nutrients were used as model inputs. To confirm the PHREEQC modelling, the proportion of mobile Zn and Pb species in Tributary 1 were further investigated by comparing acidified and non-acidified Tributary 1 samples. One set of mine water samples were acidified to <pH 2 with 1 mL of 70% HNO_3 before being filtered with a 0.22mm PTFE syringe filter, a further set was not acidified and filtered with a 0.22mm PTFE syringe filter. All experiments were per-formed in triplicates and measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200, Agilent Technologies Inc., USA)

Chapter 3

Wood ash amended biochar for the removal of lead, copper, zinc and cadmium from aqueous solution

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3.1 Introduction

Heavy metals in aqueous environments have increased at an alarming rate over recent years. This increase has been primarily attributed to anthropogenic activities such as mining, waste disposal, industrial activities, agriculture, and the increase of motor vehicles use. As of September 2020, there are ~39 million vehicles registered in the UK, representing an increase of ~5 million vehicles in 10 years (Gov.uk 2022). This escalating increase in registered vehicles and the resultant increase in annual average daily traffic has been seen to directly correlate with an increase in pollutant input (Hwang et al. 2016). Such an increase in vehicles also naturally necessitates a growth in impermeable urban roads, pavements and motorways. In highly developed areas these surfaces can account for up to 70% of the total surface creating an increase in the volume and velocity of runoff (Budai and Clement 2011; Ladislas et al. 2015; Hwang et al. 2016). This runoff washes away contaminants from anthropogenic sources, such as motor vehicles, carrying the pollutants into receiving waterbodies (Ladislas et al. 2015). The combination of the growth of motor vehicle numbers and the increase in impermeable surfaces has led to rising amounts of pollution making traffic a major contributor of contaminants into the UK's environment (Ladislas et al. 2015).

The sources of vehicle runoff pollution are reasonably well understood and generally occur through abrasive forces or leaks and include tyre wear, brake wear and motor oil. Tyre wear is recognised primarily as a source for zinc (Zn), and to a lesser extent cadmium (Cd), lead (Pb) and copper (Cu) (Legret and Pagotto 1999; Budai and Clement 2011). Pollutants released through tyre wear, unlike exhaust emissions, are collected entirely on the road surface, around 90% of which is captured by runoff, and subsequently may leach toxic compounds (Budai and Clement 2011; Markiewicz et al. 2017). Each tyre releases ~1 kg of mass during its lifespan of 50,000 km (Legret and Pagotto 1999; Markiewicz et al. 2017); such wear leads to ~1,327,000 tonnes of rubber being released in Europe annually (Wagner et al. 2018). As a consequence, Zn has been measured at levels as high as 240 ppm in road dust and as high as 354 µg / L in road runoff (Legret and Pagotto 1999; Apeagyei et al. 2011). Brake wear is recognised as a primary source of Cu; it has also been shown to contain significant quantities of inorganic contaminants such as Cd, Pb, and Zn (Legret and Pagotto 1999; Budai and Clement 2011). Hwang et al (2016) estimate that around 2400 tonnes of Cu was released by brake wear in Europe during 2000. This has, in part, led to concentrations of Cu and Pb being as high as 105 ppm and 73 ppm, respectively in road dust and Cu, Pb, and Cd concentrations in runoff being as high as 45 µg / L, 58 µg / L, and 2.7 µg / L, respectively (Legret and Pagotto 1999; Farm 2002). Motor oil is also recognised as a contributor to inorganic pollution including Zn and to a lesser degree Pb and Cu (Budai and Clement 2011). Organic pollutants from sources such as tyre wear and motor oil are also of concern (Markiewicz et al. 2017). In addition to these sources exhaust emissions are a significant source of organic particulate matter (PM) such as polycyclic aromatic hydrocarbons (PAHs) and inorganic PM including metals (Agarwal 2007).

The primary inorganic pollutants found in motorway runoff can also be found in other polluted waters such as mine water, tailing ponds and industrial effluent in rivers. In these environments concentrations of pollutants are often reported to be even higher than in road dust / runoff. Abandoned metal mines are polluting waters with Pb, Cu and Zn at concentrations regularly over 1000 µg / L (Todd et al., 2021); metal pollution in mine tailing ponds have been recorded at levels of 150 ppm (Pb), 230 ppm (Cu) and 146 ppm (Zn) (Pagnanelli et al. 2004); and extensive industrial Pb, Cu, Zn, and Cd river pollution has been measured with Zn as high as 167.8 µg / L (Saha et al. 2017).

Heavy metal pollutants entering waterways can lead to freshwater degradation, threaten local plants and organisms, and negatively affect human health. Where metal levels accumulate and increase beyond acceptable concentrations they become toxic and as a result a significant environmental hazard for invertebrates and fish (Yi et al. 2011). Humans are exposed to these heavy metals via the food chain and freshwater leisure activities. This can lead to significant adverse health consequences such as reduced neurological function, reduced liver function, reduced fertility, kidney damage, lung damage, osteoporosis and mortality (Morais et al. 2012).

Although the impact of motorway runoff is recognised, current Sustainable Drainage Systems (SuDS) that attempt to lessen the consequences of vehicle pollution have the unintended consequence of filling with toxic residues with high removal costs. Presently attempts to mitigate heavy metals primarily involve sedimentation, the subsequent accumulation of which then require expensive treatment and extraction. SuDS such as balancing ponds (wet and dry), sedimentation tanks, grassed surface water channels and constructed wetlands capture sediment mitigating the flow of pollutants into waterways (Farm 2002; Meland 2016). Although these methods initially reduce the influx of pollutants into freshwater systems, as sediment levels increase with age, remediation effectiveness reduces (Farm 2002). The removal of this toxic sediment involves dredging which is prohibitively expensive (Meland 2016).

The use of biochar is a potential remediation technique for motorway runoff, as well as for mine waters and industrially polluted rivers, that could overcome the shortcomings and expense of current runoff sedimentation techniques. This study sets out to explore biochar and wood ash amended biochar in terms of the immobilisation of four key inorganic contaminants found in motorway runoff: Pb, Cu, Zn and Cd. Engineered biochar is defined as the carbon rich product obtained from the thermal decomposition of organic material under oxygen limited conditions (pyrolysis) at temperatures generally under 900°C (Lehmann and Joseph 2009). The use of biochar in the immobilisation of metals in aqueous media has been highlighted by a number of researchers with a view to remediate polluted waters (Bandara et al. 2020a; Cairns et al. 2020). Its attractiveness is enhanced due to its relatively low cost, availability and sustainability (Ahmad et al. 2014; Wang et al. 2018b). Pristine biochar immobilises inorganic contaminants via six key mechanisms: Cation exchange, change in speciation with subsequent precipitation, cation-π interactions, functional group complexation, electrostatic attraction, and reduction (Mohan et al. 2011; Ahmad et al. 2014; Bandara et al. 2020a).

Wood ash, a by-product of biomass power plants, can be used as an amendment to biochar with the potential to improve biochar’s immobilisation of inorganic contaminants due to its mineral fraction and pH buffering capacity. The major components of wood ash have been reported as Ca, K, Mg, S, P and Si (Cerrato et al. 2016). Ca, K and Mg play an important role in ion exchange. The presence of P and Si can induce the formation of phosphates, silicates and siloxane which can be important in forming precipitates. The chemical constituents of wood ash including alkali and alkaline earth metals, oxides and carbonates also have the potential to cause the amended biochar to increase and buffer its environments pH inducing changes in metal speciation that are favourable for the immobilisation of cationic metals such as Pb, Cu, Zn and Cd (Cerrato et al. 2016; Fidel et al. 2017). Cairns et al. (2020) demonstrate that the addition of wood ash as an amendment to pristine biochar can increase immobilisation of Pb, Cu, Zn and Cd. The process was driven by pH and P content, but detailed understanding of driving immobilisation mechanisms remained elusive.

The primary aim of this study is to ascertain if pristine larch biochar and / or wood ash amended biochar is effective as an alternative green remediator of inorganic vehicular pollutants found in motorway runoff specifically Pb, Cu, Zn and Cd. Such remediation would also be relevant for mine waters and industrially polluted rivers. The effect of biochar amendments on immobilisation capacities and mechanisms were investigated to understand if scaling up is plausible.

3.2 Methods:

3.2.1 Biochar production and wood ash amendment

European larch (*Larix decidua* (L.) Karst.) wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 485-530°C, with a retention time of ~90s. The biochar was granulated to <3mm with a Tria G1 granulator. Wood ash, originating from a renewable energy plant in the UK, was added to the biochar post pyrolysis via two methods. For the first method the wood ash was mixed at a ratio of 1:1 with biochar that had been allowed to cool to ambient temperature in a cement mixer for 15 minutes. For the second method, it was mixed with the freshly pyrolyzed, still hot biochar at a ratio of 1:1 for 15 minutes in a cement mixer to sinter the materials. Wood ash was chosen as an amendment due to its mineral fraction (including Ca, K, Mg, S, P and Si) and pH buffering capacity. The pristine larch biochar, larch biochar cold mixed with wood ash and larch biochar sintered with wood ash are referred to as BC, WA, and WAS throughout the study.

3.2.2 Biochar Characterisation

Sorbents were characterised via surface area and pore size analyser, Fourier transform infrared spectroscopy (FTIR), x-ray powder diffraction (XRD) and scanning electron microscopy with energy dispersive x-ray (SEM-EDX) analysis. FTIR was undertaken using a Perkin Elmer Spectrum Two FTIR Spectrometer. Measurements are in the range of 400-4000 cm^{-1} to compare possible changes before and after sorbent loading. Pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) were each mixed with KBr at a ratio of 1:100 (W/W) (Merino et al. 2017). XRD was used to identify possible crystalline precipitates formed on the surface of the sorbents. XRD patterns were obtained using a Bruker D8 Discover with a Copper source (40kV, 40mA) and a 1D detector. Powdered sorbents were pushed flat on a single signal silicate zero diffraction plate to minimise background interference. Scans themselves had a 0.5 second time per step and an increment of 0.02° over the range of 10-90 (Hasan Khan Tushar et al. 2012; Li et al. 2017b). Specific surface area and pore volume distribution were determined from N_2 physisorption isotherms using the Brunauer–Emmett–Teller method and Barrett–Joyner– Halenda method respectively. Vacuum dried samples were degassed at 105°C overnight and initially measured with N_2 adsorption at the liquid nitrogen temperature of -196°C (77K) by a NOVA 2000e surface area and pore size analyser (Cao and Harris 2010). Due to the small pore size of the pristine biochar, CO_2 was also used to determine pore size distribution because of microporosity and kinetic limitations with N_2 physisorption (Sigmund et al. 2017). Surface morphologies were examined by scanning electron microscopy (Hitachi TM3000 desktop microscope). A working distance of 10mm and an acceleration voltage of 15kV were used and images were obtained using the in-built Hitachi TM3000 software. Elemental composition analysis was undertaken at the same surface locations by electron dispersive x-ray spectroscopy (EDX) attached to the Hitachi TM3000 desktop microscope. An EDX spectrum was produced after scanning the area of interest for ten minutes. Samples were mounted to aluminium SEM stubs using conductive double-sided carbon tape to enable examination of samples in an uncoated state (Eiblmeier et al. 2014).

3.2.3 Sorption Experiments

Sorption batch experiments were carried out using Pb, Cu, Zn and Cd at five different concentrations in the range of 10 mg/L to 150 mg/L applying different sorbent to solution ratio to increase the range of measured sorbent loading. This range included scenarios to stress the sorbents beyond what could be reasonably expected in road runoff and oversaturate them (Crabtree et al. 2009; Zhao et al. 2010). All chemical reagents were of analytical grade and the five concentrations were obtained by preparing a stock solution (1000 mg/L) of the metals, using lead (II) nitrate (N_2O_6Pb) copper (II) nitrate hydrate ($CuH_2N_2O_7$), Zinc nitrate hexahydrate ($H_{12}N_2O_{12}Zn$) and cadmium nitrate tetrahydrate ($CdH_8N_2O_{10}$) and diluting with deionized water. The pH was adjusted to ~4.7 with the dropwise addition of HNO_3 to achieve an equal pH between solutions that represented the closest to runoff conditions before precipitation occurred for those metals. Two types of control experiments were included – biochar without contaminants, as well as contaminants without biochar. All experiments were performed in triplicates using a batch sorption equilibrium method (OECD 2000b)

All sorbents were oven dried at 105 °C for 24 h. A known amount of biochar (particle size of < 3mm) was added to 25 mL of aqueous solution in 40 mL polyethylene Falcon tubes. Agitation was achieved on a Unitwist 400 Orbital Shaker for 48 hrs at ~280 rpm to reach equilibrium. Studies such as Uchimiya et al. (2011) prescribe contact of 24 hours to reach equilibrium, but longer contact times haven't shown significant changes in equilibrium concentration and ensure that the adsorption phase had reached equilibrium (Wang et al. 2018b). The solution was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000 rpm for 15 minutes (OECD 2000b). The supernatant was removed, pH measured using a calibrated Voltcraft pH Meter and immediately acidified to < pH 2 with 1mL of 70% HNO_3 before being filtered with a 0.45 µm PTFE syringe filter for analysis.

Pb, Cu, Zn and Cd concentrations of the acidified supernatants were measured using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES 5110, Agilent Technologies Inc., USA). Sorbent loading (q) was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:

$q = (c_i – c_{aq})\ V / W$

where c_i is the initial concentration of metals in solution, c_{aq} is the final equilibrium concentration of metals in solution, V is the volume of solution and W is the weight of the biochar.Equilibrium sorption coefficients (Kd) were calculated as:

$Kd = q/c_{aq}$

where, Kd (L/kg) = amount of metal adsorbed onto biochar per L of water, q (mg/kg) = sorbent loading (metals adsorbed by biochar) and C_{aq} (mg/L) = concentration in the aqueous phase.

Kd is commonly used in estimating the potential sorption of dissolved metals by a solid phase with higher values indicating higher sorption potential (Pourret and Houben 2018),

The contaminant loaded sorbents were further analysed via FTIR, XRD, SEM-EDX to detect changes before and after sorption.

3.2.4 Water chemistry and metal speciation

For speciation determination, samples with and without contaminants at a selected concentration of 10 mg/L were analysed for other water chemistry parameters. These included (i) base cation analysis (Ca, K, Na, and Mg) using ICP-OES, (ii) major anions (Cl^-, NO_3^{2-}, $PO_4^{3-}$and SO_4^{2-}) using an ion exchange chromatograph (IC 930 Compact Flex, Metrohm, Switzerland) and (iii) dissolved organic carbon using TOC analyser (Shimadzu, TOC-L series), measuring non-purgeable organic carbon (NPOC). Speciation analysis of the solutions were carried out using Visual MINTEQ version 3.1. Base cation analysis was also used to review possible cation exchange. Total P and Si in the above solutions were measured via ICP-OES. Together with PO_4^{3-} analysis, these parameters were used to check for their involvements in the immobilization process. Speciation of C in the solid phase was measured using a multiphase carbon analyzer RC-612 from LECO.

3.3. Results and discussion

3.3.1 Contaminant removal by biochar and wood ash amended biochars

Analysis of the aqueous phase shows that wood ash amended biochar, both cold mixed with wood ash (WA) and sintered with wood ash (WAS), removed significantly more metals than pristine larch biochar (BC) (SI 3.1 A, B, C, D). Metals were removed in the order of Pb>Cu>Zn>Cd by all three sorbents. The removal of Pb by BC was the lowest amongst the sorbents with a maximum measured removal of 7.8 ± 0.1 mg/g (SI 3.1 A and E). The maximum measured removal of Pb by WA was 61.5 ± 3.1 mg/g and by WAS was 54.6 ± 3.3 mg/g (SI 3.1 A and E). Maximum measured removal of Cu by BC was again the lowest amongst the materials at 3.5 ± 0.1 mg/g (SI 3.1 B and E). WA and WAS showed similar patterns and quantities of Cu removal to each other, however WA showed a greater maximum measured removal at 38.9 ± 2.4 mg/g with WAS at 33.8 ± 2.3 mg/g (SI 3.1 B and E). The maximum measured removal of Zn by

BC at 0.8 ± 0.1 mg/g was significantly lower than both WA and WAS (SI 3 C and E). WA and WAS were very similar to each other in terms of Zn removal but, again, the maximum measured removal by WA was higher at 12.1 ± 0.2 mg/g than WAS at 11.2 ± 0.1 mg/g (SI 3.1 C and E). Cd was the metal that had the lowest measured removal by each of the materials. At 0.7 ± 0.1 mg/g the maximum measured removal of Cd by BC was again significantly lower than both WA and WAS (SI 3.1 D and E). The removal of Cd and Zn show very similar removal behaviour in contrast with Cu and Pb which both had a significantly higher maximum measured removal (SI 3.1 A, B, C, D). WA and WAS show very similar Cd removal; however, WA with a maximum measured removal of 10.2 ± 0.2 mg/g did outperform WAS with a maximum measured removal of 9.3 ± 0.1 mg/g (SI 3.1 D and E). Removal was measured within a multi metal solution where the presence of competing metal ions in the solution for the same sorption sites can reduce the removal rate (Mantonanaki et al. 2016) which impacts Zn and Cd removal rates more than Pb and Cu (Xu and Zhao, 2013).

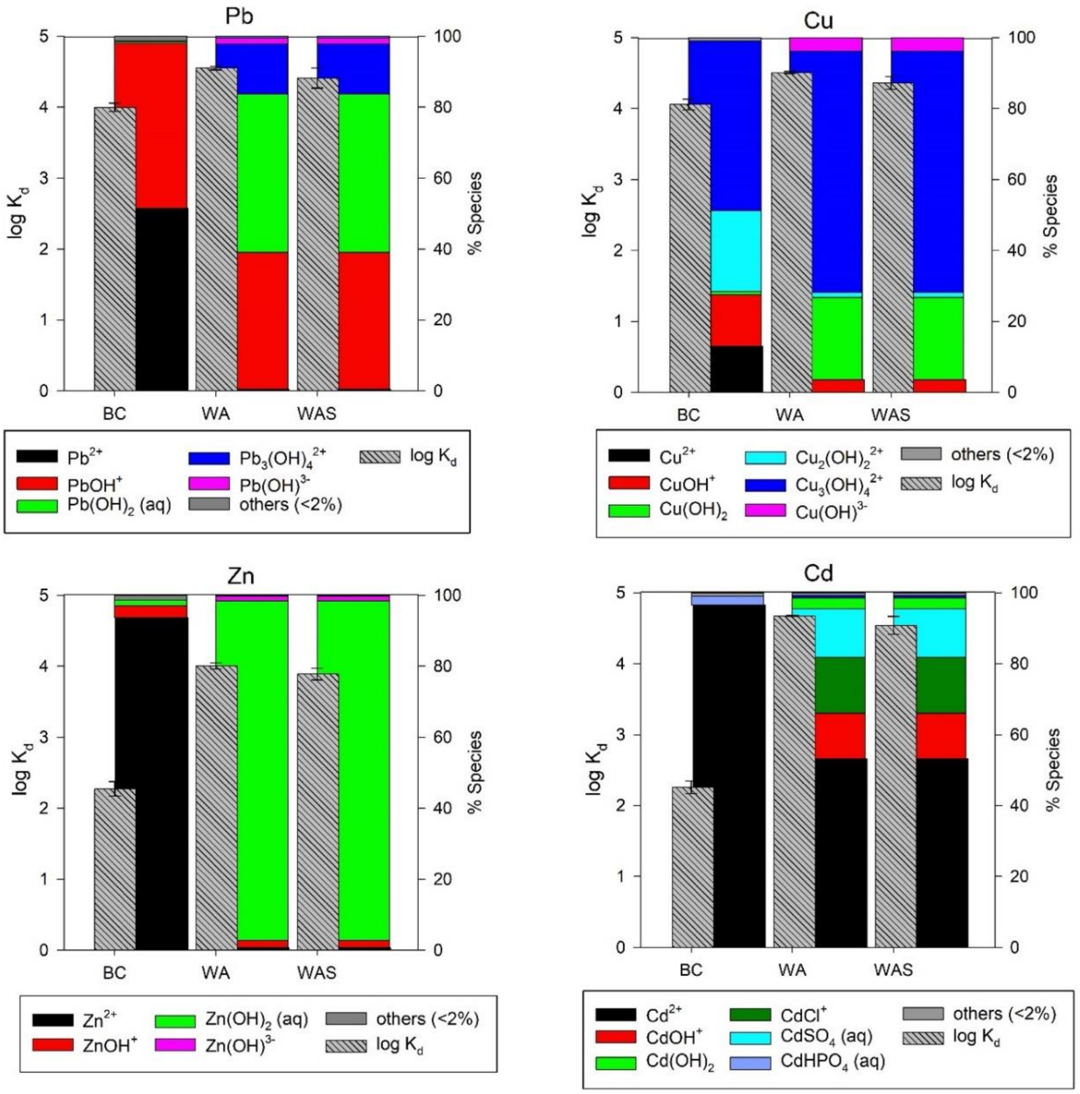


Figure 3.1: Bar graph showing the equilibrium distribution coefficients (Kd) of Pb, Cu, Zn and Cd with pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) at 10 mg/L, and stacked bars in the background showing metal aqueous species distributions. Error bars show ± SD (n = 3).

3.3.2 Aqueous phase chemistry – immobilization via precipitation and ion exchange

Speciation plots across pH show that the distribution shifts from their divalent forms to hydroxyl forms as the pH increases (SI 3.3). As shown in Figure 3.1, the existence of these metal species in different hydroxyl forms is accompanied by increased sorption affinities (K$_d$ values). Addition of anions such as PO_4^{3-}, Cl^- and SO_4^{2-} into solution can lead to the formation of mineral precipitates. This combination of increased pH and presence of dissolved anions from wood ash drives immobilization of the metals, due to oversaturation with certain mineral forms, especially for Cd and Zn. Modeled saturation indices (SI 3.3A and 3.3B) indicate the possibility of formation of precipitates such as $Cd_4(OH)_6SO_4$, $Zn(OH)_2$ and ZnO, being more prominent for wood ash amended chars. Also, multiple phosphate containing phases, such as $Pb_5(PO_4)_3Cl$, $Cd_3(PO_4)_2$, $Pb_3(PO_4)_2$ are seen to be oversaturated. From MINTEQ modeling (SI 3.3) it was determined that 99.5% and 99.9% of Pb and Cu, respectively, can be precipitated. Wood ash amendments further allowed 99.4% Cd and 98.5% Zn to precipitate. Additionally, 99% and 73% of PO_4^{3-} can form precipitates in BC and WA/WAS systems, respectively.

In addition to modelling, differences in the total P, PO_4^{3-} and Si levels in the solutions with and without the metals for the different materials (Figure 3.2) provide further evidence of precipitation. For all three materials, total P in solution was significantly reduced and PO_4^{3-} levels fall below the limit of quantification for all solutions with metals in contrast to solutions without metals. This implies that some of the metal ions in solution are complexing with PO_4^{3-} and precipitating onto the biochar surface, or co-precipitating with PO_4^{3-}. For WA and WAS, Si levels were also reduced from 2.53 mg/L to 2.06 mg/L and from 2.44 mg/L to 2.01 mg/L in the presence of the metals. From these results, it is implied that Si in the form of silicates on the sorbent surfaces might be playing a role in the immobilization process for wood ash amended biochars as seen in previous studies by Lu et al. (2012) and Gao et al. (2019). Carbonate containing metal phases were not accounted and modelled for. However, C speciation analysis of the solid phase using the carbon analyzer showed that WA and WAS had 0.97% and 0.79% of inorganic C present, respectively. Thus, it is expected that the metals can also be immobilized through formation of carbonates.

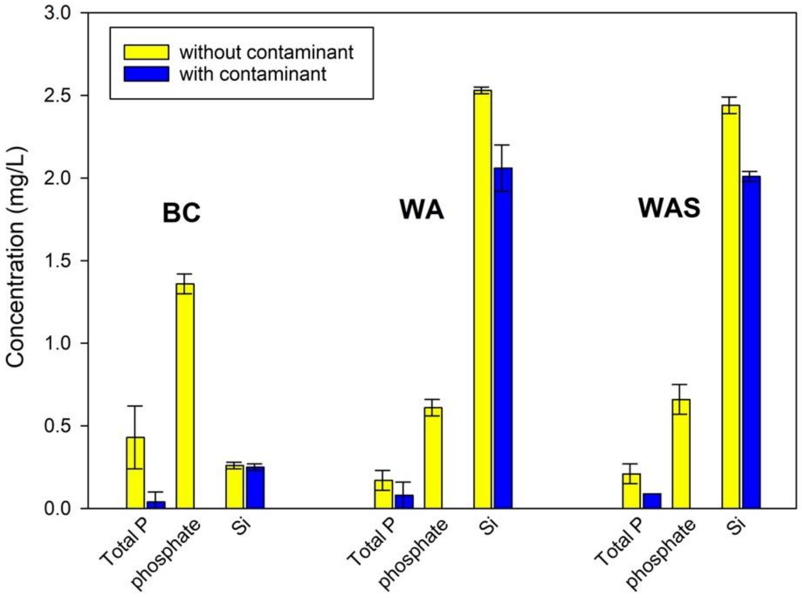


Figure 3.2: Concentration of Total P, phosphate (PO_4^{3-}) and Si in solution in the presence of different sorbents without and with metals (n=3). Concentration of solution with contaminants was 10 mg/L.

All three sorbents also affect the water chemistry by adding base cations such as Ca^{2+}, Mg^{2+}, K^+ and Na^+. Increased cation release in the presence of metals can indicate cation exchange processes occurring on the surface of biochar (Uchimiya et al. 2010a). If cation exchange is one of the driving mechanisms for immobilization, the target divalent metal contaminants will tend to replace divalent cations on the surface of the biochar, such as Ca^{2+} and Mg^{2+} rather than monovalent ones. For this purpose, we investigated base cations released from the sorbents, with and without 10 mg/L of metals present (Figure 3.3). For BC, small increases in concentration of the base cations Mg^{2+}, Na^+ and K^+ were observed from 0.72 ± 0.2 mg/L to 1.33 ± 0.1 mg/L, from 1.05 ± 0.0 mg/L to 1.41± 0.1 mg/L and from 11.19 ± 1.1 mg/L to 17.20 ± 0.8 mg/L, respectively. This indicates that cation exchange may be important in metal immobilisation by BC. For the wood ash amended biochars, a marked two-fold increase in Ca^{2+} concentration in the presence of metals was observed (Figure 3.3). For WA and WAS, Ca^{2+} increased from 8.7 ± 0.7 mg/L to 22.3 ± 4.1 mg/L and from 10.4 ± 1.0 mg/L to 20.7 ± 2.1 mg/L respectively. Increased levels of divalent Mg^{2+} were also observed for the wood ash amended chars. For WA Mg^{2+} increased from 0.63 ± 0.0 mg/L without metals to 1.23 ± 0.3 mg/L with contaminants. For WAS, this was not as apparent with a concentration increase from 1.11 ± 0.1 mg/L to 1.32 ± 0.2 mg/L.

This increased release of base cations in the presence of the metals with the wood ash treatments indicates that cation exchange plays a role in the immobilization process. Such ion exchange is seen to be a key immobilisation mechanism for Pb, Cu, Zn and Cd by several studies but is secondary to precipitation (Lu et al. 2012a; Gao et al. 2019).

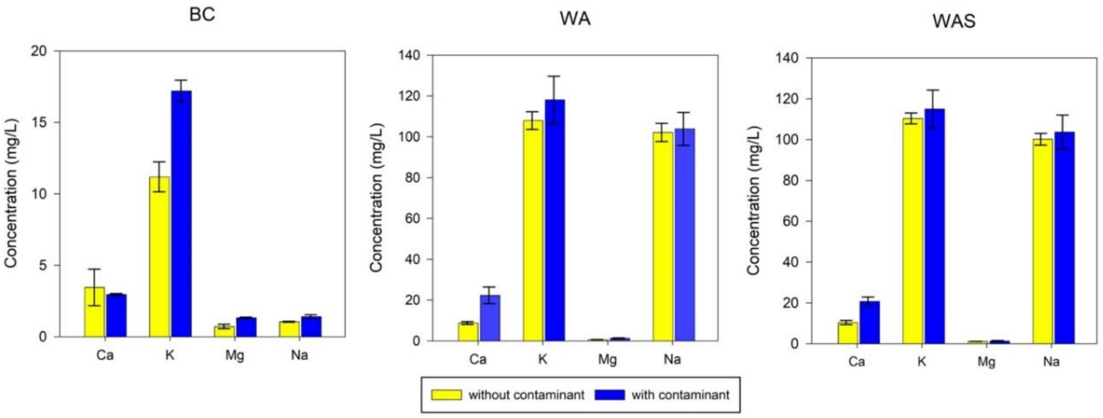


Figure 3.3: Concentration of base cations in solution in the presence of the different sorbents without and with metals (n=3)

The pH of solution showed increases for each of the sorbents, with wood ash amended biochars increasing pH significantly more than BC (SI 3.4A). Rises in pH were greater at lower concentrations of Pb, Cu, Zn and Cd. There is strong correlation between rises in solution pH and immobilisation (SI 3.4B). For all of the sorbents such correlation is likely, at least in part, as a result of ion exchange increasing with pH driving the increase in negative charge of functional groups allowing alkali and alkaline earth metals to be exchanged more easily (Silber et al. 2010). For wood ash amended biochars, but not for BC, the correlation of immobilisation and pH is also a result of the increase in pH driving precipitation. The pH buffering ability of the wood ash amended biochars raises the solution pH making it alkaline enough for (i) metal hydroxide precipitation (SI 3.3A and 3.3B) (Chen et al. 2015), and (ii) precipitation with phosphates and silicates (Uchimiya et al. 2010a).

3.3.3 Solid Phase Analysis - immobilisation via precipitation and ion exchange

The following pre and post immobilisation solid phase analysis (FTIR, SEM-EDX, and XRD) were implemented to further investigate the mechanisms of each sorbent in the immobilisation of Pb, Cu, Zn and Cd alongside the measurement of surface area. FTIR was used to identify functional groups to denote ion exchange, minerals capable of precipitation and aromatic structures for BC, WA and WAS. WA and WAS follow very similar pattern of peaks within the FTIR spectra pre-adsorption of the metal solution (Figure 3.4). Whilst BC also shows similarities to WA and WAS in peaks above 1500 cm^{1} pre-adsorption, key differences between wood ash amended biochar and BC are evident below 1500 cm^{1}. Below 1500 cm^{1} peaks for both WA and WAS are seen which are attributed to phosphate (Uchimiya et al. 2010b; Han et al. 2017), siloxane (Gao et al. 2019) as well as oxygenated functional groups (Iqbal et al. 2009); phosphate and siloxane peaks, important for precipitation, are not evident in the FTIR spectra of BC.

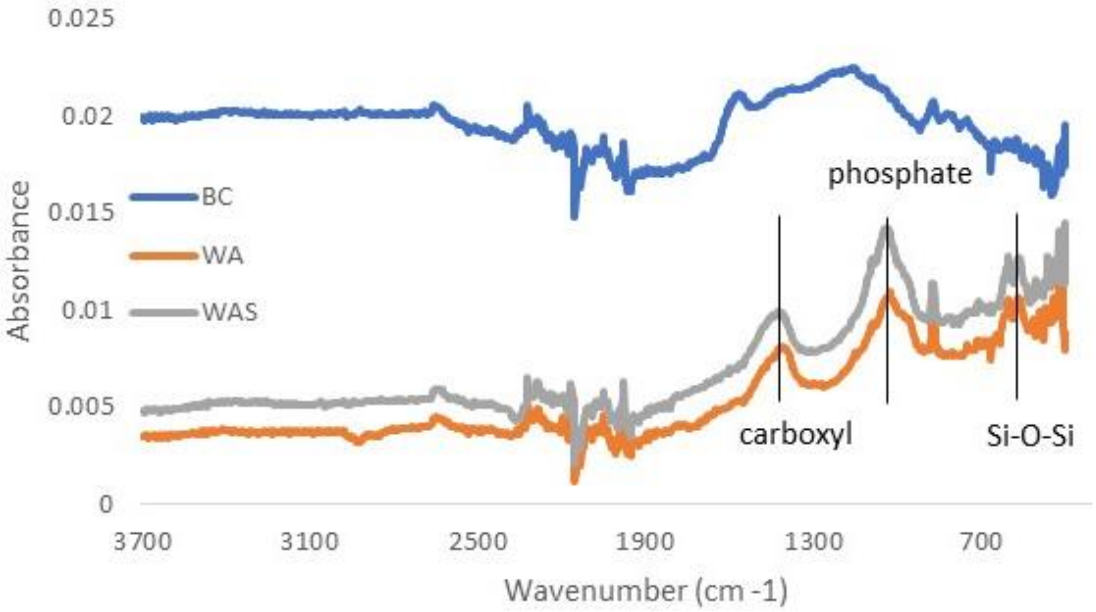


Figure 3.4: FTIR spectra of pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) before immobilisation of Pb, Cu, Zn and Cd.

The FTIR results for BC pre and post adsorption of Cd, Cu, Pb and Zn show increases in the intensity of wavelengths attributed to carbonyl and carboxyl surface functional groups again indicating that ion exchange is taking place (Li et al. 2014). However, BC's spectra show no indication of precipitation (figure 3.5A). The FTIR results for WA and WAS pre and post adsorption of Cd, Cu, Pb and Zn show shifts and a flattening of peaks attributed to carboxyl surface functional groups also indicating ion exchange (figures 3.5B and 3.5C). These shifts may be attributed to changes in the counterions associated with carboxylate anions (Iqbal et al. 2009).

Studies have shown such shifts to demonstrate ion exchange for Pb, Cu, Zn and Cd (Iqbal et al. 2009; Bandara et al. 2020a). Studies have also shown the ion exchange of carboxyl to be stronger for Pb and Cu than that of Cd resulting in lower levels of Cd adsorption agreeing with the sorption ordering of this study further pointing to the role of ion exchange for all of the sorbents studied (Xu and Zhao 2013). WA FTIR spectra show a shift and increase in intensity for peaks assigned to both phosphate and Si-O-Si, WAS spectra also show a peak shift for both phosphate and Si-O-Si. Xu et al. (2013) attributed similar shifts in peaks to the formation of metal precipitates.

FTIR analysis indicates that ion exchange is an immobilisation mechanism for all three sorbents but only demonstrates precipitation with phosphate and Si-O-Si for wood ash amended biochars. This difference is likely to partially account for the difference in removal between BC and wood ash amended biochars.

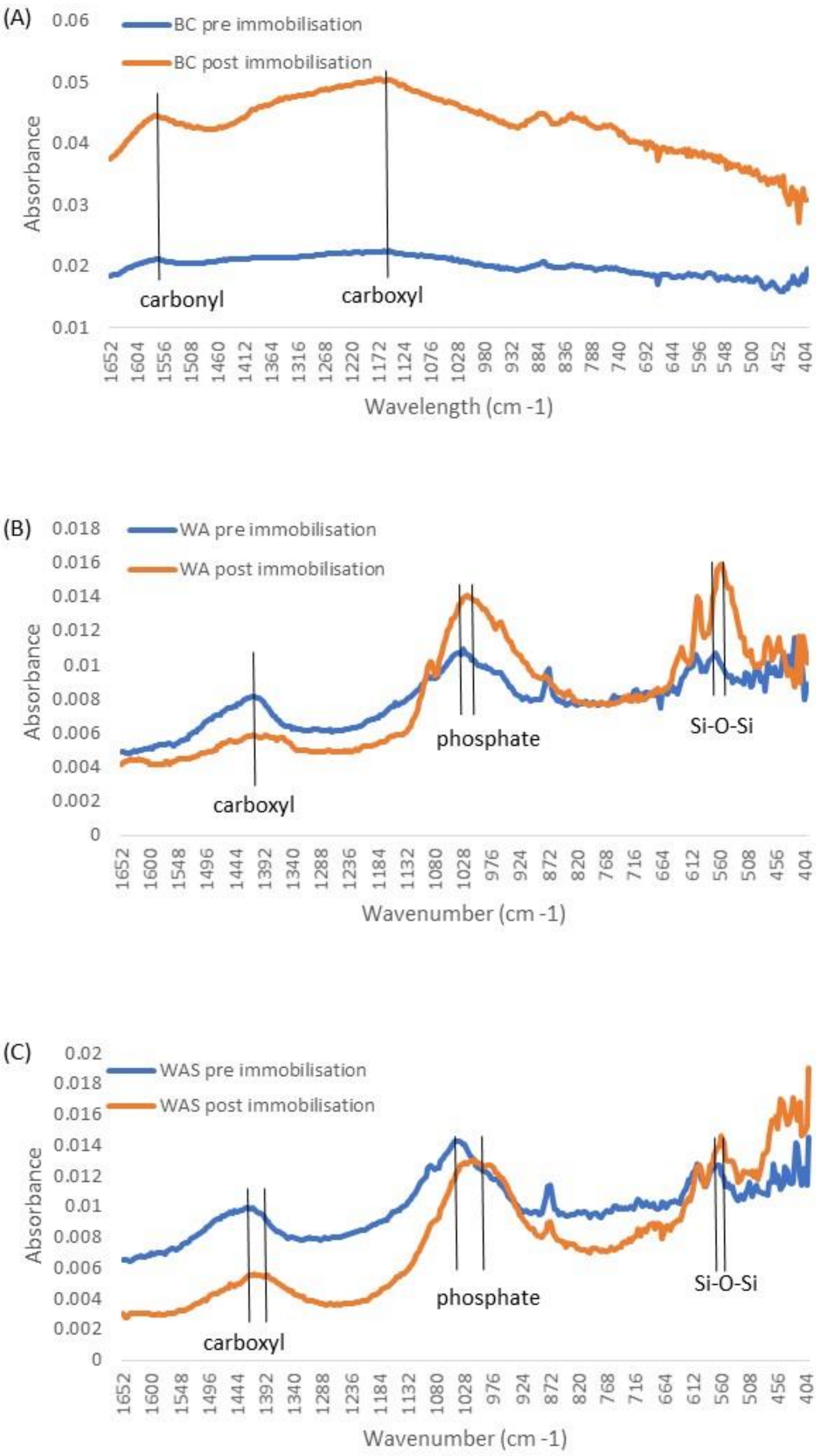
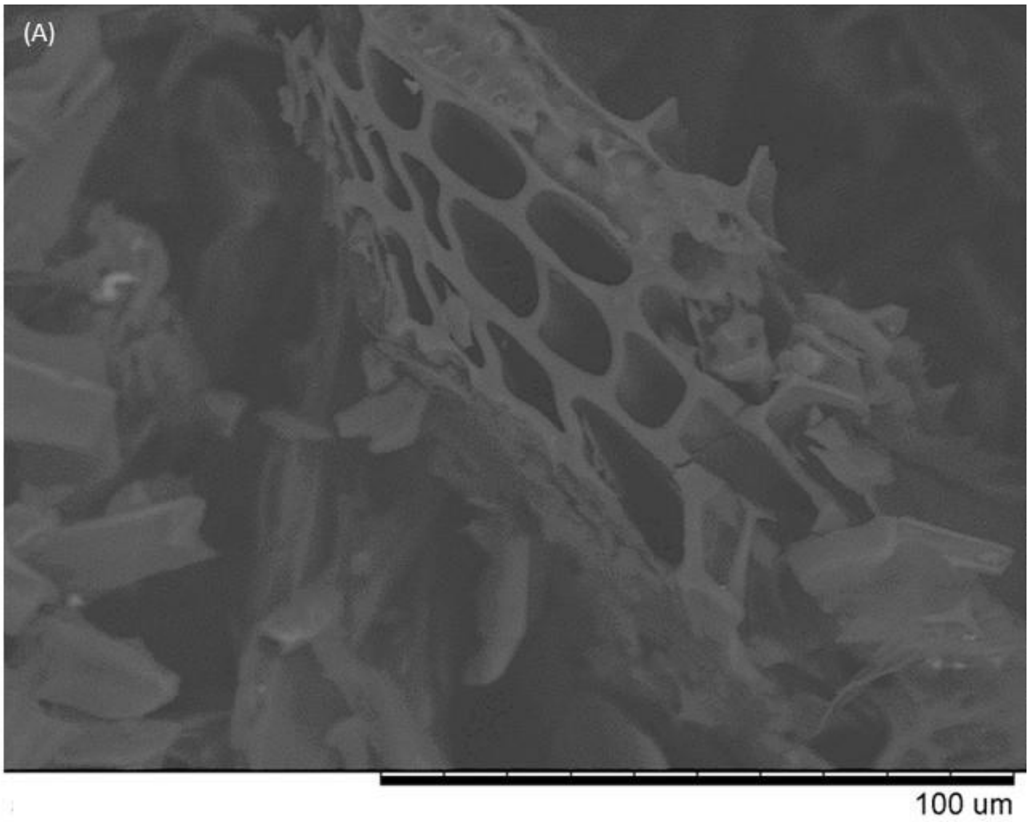


Figure 3.5: (A) FTIR spectra of larch biochar (BC) pre and post immobilisation of Pb, Cu, Zn and Cd (B) FTIR spectra of larch biochar cold mixed with wood ash (WA) pre

and post immobilisation of Pb, Cu, Zn and Cd (C) FTIR spectra of larch biochar sintered with wood ash (WAS) pre and post immobilisation of Pb, Cu, Zn and Cd

SEM-EDX analysis was used to observe the morphology and structure of the sorbents and to ascertain the elemental composition and distribution including the presence of immobilised Pb, Cu, Zn and Cd. For BC SEM-EDX did not show signs of precipitation such as high levels of P or Si or bright areas on the surface of the char. In contrast, SEM images of WAS post adsorption did show bright areas on the surface of the char (SI 3.9A) which are Pb rich phases (Lu et al. 2012a). The EDX spectrum associated with this SEM image demonstrates the presence of P, O, Cl and C alongside Pb, Cu and Zn (SI 3.10A). SEM images of WA post adsorption also showed the bright areas associated with Pb alongside high levels of P, O, Si, C, Cl, Cu and Zn seen in the corresponding EDX spectra (SI 3.9B and SI 3.10B). Again, Cd was not present in this zone. In addition to the elemental results of EDX, XRD analysis indicated the presence of carbonates, siloxane and phosphates in both WA and WAS (SI 3.11). Where metals are seen in the presence of high levels of minerals such as P or Si precipitation between these metals and minerals should be expected (Trakal et al. 2014a) and as such precipitation should again be considered a mechanism in the immobilisation of metals by wood ash amended biochars, a mechanism not evidenced for BC. SEM images of BC post adsorption did not show large bright areas or crystalline structures which would indicate precipitation (SI 3.9 C). EDX elemental data showed that Cu, Zn and Cd were not detected at all and that Pb is present in this zone but in small quantities when compared to wood ash amended biochars (0.51%) (SI 3.10 A, B, C). P, Cl and Si were all undetected, but K was evidenced in this zone again indicating the potential for ion exchange (SI 3.10 C). There is also no evidence of carbonates, siloxane or phosphates for BC within the XRD analysis making precipitation unlikely as an important mechanism.

The dominant mechanism for Pb, Cu, Zn and Cd removal by wood amended biochars is precipitation with ion exchange also playing a role. However, these mechanisms do not correlate to surface area. Although BC had the lowest measured removal of each contaminant its surface area (409 m^2/g) is significantly higher than the surface area of WA (34.5 m^2/g) or WAS (26.5 m^2/g). Pore size distribution for WA and WAS follow similar patterns to each other both with a high concentration of pores with 41 Å diameter (SI 3.12 A and B). BC however shows a high concentration of smaller pores with 31 Å diameter (SI 3.12 C). SEM-EDX images show BC to have an unblocked honeycomb structure with 98% C (figure 3.6A). Although WA has a similar structure the pores are blocked with only 29% C due to the presence of other elements such as P, Si, K and Na (Figure 3.6B). Despite the addition of the wood ash being seen to reduce surface area by more than an order of magnitude this does not impact negatively on immobilisation. The wood ash amendment and resultant pH, mineral and functional group increases have proven to be more important than surface area. WA and WAS pores are blocked by the minerals added with the wood ash, such pore blocking has been seen by Hu et al. (2015) in their study of iron impregnated biochar whereby the iron clogged pore openings on the biochar surface whilst increasing metal removal from solution. Although surface area is often seen as an important physical property for contaminant sorption, comparative studies have shown that when surface area of a char is lower but immobilisation is higher, as seen in this study, chemical processes such as ion exchange or more importantly precipitation supersede the importance of surface area (Wang et al., 2018).


(A)
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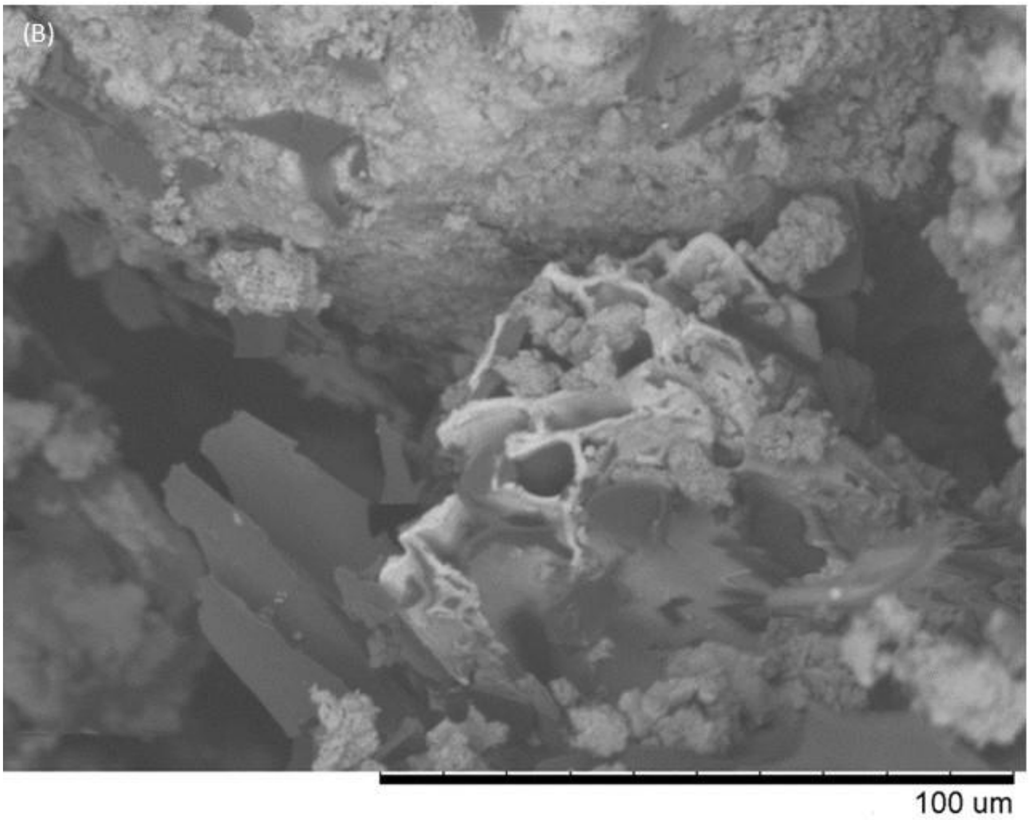
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Figure 3.6: (A) SEM image of the honeycomb structure of the pristine larch biochar (BC) (B) SEM image of the honeycomb structure of the larch biochar cold mixed with wood ash (WA) which is blocked with P, Si, K and Na.

3.4 Conclusion

This study investigated if pristine larch biochar (BC) or wood ash amended biochar was effective as an alternative and green remediator of the inorganic vehicular pollutants Pb, Cu, Zn and Cd found in motorway runoff, mine waters and industrially polluted rivers. It also set out to investigate why BC, larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) immobilised these contaminants and understand differences between wood ash amended biochar and BC in terms of contaminant removal and immobilisation mechanisms. Maximum measured removal of Pb, Cu, Zn and Cd by WA and WAS were significantly higher than BC alone. This difference was the result of the wood ash amendment increasing pH, thus shifting metal species, and increasing the presence of minerals such as PO_4^{3-} causing immobilization of the metals through precipitation. The proportion of hydroxides modelled for BC is far less than for wood ash amended biochars likely resulting in precipitation accounting for less immobilisation of the contaminants. Although precipitation with phosphate and silicates, was found to be an immobilisation mechanism for WA and WAS, precipitation with silicates was not observed for BC further highlighting differences in removal between wood ash amended biochars and BC. Ion exchange contributed to the immobilisation of the contaminants for all three sorbents. Surface area was not seen to be a dominant factor for metal removal with precipitation and ion exchange superseding its importance.

Sustainability of feedstock, maximum measured removal (61.5 mg/g, 38.9 mg/g, 12.1 mg/g and 10.2 mg/g for Pb, Cu, Zn and Cd respectively) and low feedstock / production costs indicate that wood ash amended biochar is a viable option to immobilise Pb, Cu, Zn and Cd from motorway runoff.

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Chapter 4

Treatments of wood ash amended biochar to reduce nutrient leaching and immobilise lead, copper, zinc and cadmium in aqueous solution: column experiments

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4.1 Introduction

The pollution of aqueous environments by heavy metals has continued to increase considerably in recent years. Anthropogenic activities have been the principle cause of this rise through activities including, but not limited to, mining, waste disposal, industrial activities and the escalating use of motor vehicles. Globally, vehicle numbers are predicted to be as high as 2.8 billion by 2050, with an anticipated increase in road length of at least 25 million km (Laurance et al. 2014; van der Ree et al. 2015). The pollution and significant ecological effect associated with this vast and growing infrastructure extends outwards even further into the adjacent landscape in an area described as the "road-effect zone" (Richard et al. 2000). The reach of this pollution is significant in the UK, with only 6% of land escaping its impact and 25% of land being within 80m of a road (Phillips et al. 2021).

Vehicular and road pollution types can include heavy metals, particulate matter, $NO_{x,}$ polycyclic aromatic hydrocarbons (PAHs), road salts, light and noise. (Hilliges et al. 2017; Phillips et al. 2021). Of these pollutants, heavy metals are a group considered to be of great concern as they cannot be decomposed by micro-organisms and exhibit long term toxicity for plants, animals and humans (Werkenthin et al. 2014). Road runoff also carries pollutants such as heavy metals into rivers, tributaries and lakes leading to the pollution of ecosystems. This pollution causes significant impact on aquatic life, enters the food chain and cause human exposure to these heavy metals (Reddy et al. 2014; Withanachchi et al. 2018). Such exposure has been shown to have a detrimental impact on health such as cancer, weakened immunological responses, impairment of neurological functions and cardiovascular disease (Rai et al. 2019).

The most recognised metals in roadside environments include Pb, Cu, Zn and Cd; whilst there are other metals and metalloids of importance, such as Ni, Cr and Sb the metals Pb, Cu, Zn and Cd remain among the most examined (Werkenthin et al. 2014). The vehicular pollutants found in road runoff, notably Pb, Cu, Zn and Cd, generally occur through abrasive forces or leaks such as tyre wear, brake wear and motor oil leaks (Budai and Clement 2011; Klöckner et al. 2020; Ma et al. 2021). The concentrations of these pollutants are directly linked to traffic density (Du et al. 2019); driving style, with more aggressive speeds and breaking resulting in greater brake and tyre wear (Werkenthin et al. 2014); manufacturer and time of component production, with compositions of tyres and brakes varying considerably (Budai and Clement 2011); vehicle type, with weight, engine power and state of maintenance being of import (Napier et al. 2008; Wagner et al. 2018); and road composition (Duong and Lee 2011). As a result of these factors Pb, Cu, Zn and Cd contamination is pervasive in the UK. Phillips et al. (2021) argue that the proportion of land in the UK affected by road pollution is as high as 6.86% for Zn, 7.09% for Cu, 14.50% for Cd and 18.29% for Pb.

Alongside the increase in inorganic vehicular pollutants anthropogenic sources of contamination such as metal mines, waste disposal and industrial activities are also considered major sources of metal pollution in aqueous environments (Beane et al. 2016; Hussein et al. 2021; Sharma and Kumar 2021). In Wales alone, there are over 1300 metal mines affecting over 700km of river with primary contaminants including Pb and Zn (Environment Agency Wales 2002; Coal Authority 2020b) . Waste disposal, particularly landfilling, also poses a significant pressure on the environment through the leaching of heavy metals such as Cd and Pb exerting toxic effects (Hussein et al. 2021) and industrial effluent is known to contain large quantities of hazardous metals, such as Pb, Cu, Zn and Cd, which are contaminating water resources.

With growing anthropogenic contamination, methods to minimise pollution which are environmentally stable are key. Regulatory measures to combat the impact of pollution, such as the ban on leaded petrol, are often negated by the significant and continuing growth in the sources of contamination such as worldwide traffic and road networks (Werkenthin et al. 2014). As a result, novel engineered techniques have a role to play in tackling this pollution. Biochar is one material that has been studied to ascertain its potential as a novel remediator that could be scaled up to deal with contaminated runoff and other anthropogenic sources of contamination (Hasan et al. 2020). Biochar is defined as a porous, carbonaceous material produced by biomass pyrolysis at temperatures ranging from 350 - 1000°C under limited oxygen conditions (European Biochar Foundation 2016). During pyrolysis, highly aromatic clusters are formed responsible for biochar’s high chemical stability and porosity (Yang et al. 2018b). The key functions of biochar include the ability to sequester carbon, improve soil fertility and remove environmental contaminants from aqueous media (Inyang et al. 2016; Kätterer et al. 2019; Cairns et al. 2020). Cairns et al. (2021) found that the removal from aqueous media of the key vehicular inorganic contaminants, Pb, Cu, Zn and Cd, by biochar increased by an order of magnitude with the addition of wood ash. Precipitation and ion exchange were found to be the dominant immobilisation mechanisms as a result of the increased pH and addition of minerals associated with the wood ash amendment.

Whilst biochar has the potential to reduce contaminated runoff, studies also need to explore the potential for the biochar itself to leach nutrients, such as phosphate (PO_4^{3}), sulphate (SO_4^{2-}) and nitrate (NO_3^{-}), which are constituent parts of its biomass. The leaching of these nutrients could be harmful to the ecosystem the biochar would be deployed to remediate particularly in nutrient deficient (oligotrophic) ecosystems. The potential for biochar to leach nutrients such as N and P was recognised by Wu et al. Wu et al. (2011) who studied biochar from a feedstock of mallee wood and saw reductions in N and P proportions in the biochar as a result of exposure to water, indicating that leaching was occurring to some degree. Liang et al. (2014) also recognised the potential leaching of P from dairy manure biochar rich in nutrients and highlighted that this could pose a risk of surface and groundwater impairment if P release was too high. The potential loss of N and P as a result of biochars exposure to aqueous environments is also relevant to biochar amended with wood ash which is also rich with nutrients such as P, N and S. Whilst these nutrients aid immobilisation of metal contaminants and their chemical derivatives such as phosphates and nitrates are an important element in plant growth, their release in high levels is considered one of the key factors in eutrophication and poses risks to aquatic ecosystems (Smith et al. 1999; Cui et al. 2016a). It is these concerns that have led to European Union (EU) directives such as the Nitrates Directive 91/676/EEC, Directive 91/271/EEC concerning urban waste-water treatment and the Water Framework Directive 2008/105/EC.

This study builds on previous work that demonstrates the effectiveness of wood ash amended biochar in the removal of Pb, Cu, Zn and Cd (Cairns et al. 2021) to understand whether the leaching of P, N and S in the form of phosphates, nitrates and sulphates is apparent, and if so what treatment options are available to mitigate leaching this without reducing the immobilisation of Pb, Cu, Zn and Cd.

4.2 Methods

4.2.1 Biochar production and wood ash amendment

European larch (*Larix decidua* Mill.) wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 485-530°C, with a retention time of ~90s (Cairns et al. 2021). Wood ash, purchased from NPK Ltd, was added to the biochar after pyrolysis via two alternative methods. For the first method, it was mixed with the freshly pyrolyzed, hot biochar at a ratio of 1:1 for 15 minutes in a cement mixer in order to sinter the materials (WAS). The sintering of the wood ash to the biochar was to promote particle bonding between the wood ash and the biochar to create a more stable matrix than when mixed cold. This was also designed to retain alkali and alkaline earth metals, P, N and S all of which are either relevant to contaminant immobilisation or nutrients that could be harmful to the wider ecosystem. For the second method the wood ash was mixed at a ratio of 1:1 with biochar that had been allowed to cool to ambient temperature for 15 minutes (WA). Wood ash was chosen as an amendment due to its high mineral and nutrient fraction, including Ca, K, Mg, S, P, N and Si (SI 4.1) and pH buffering capacity (Cairns et al. 2020). Half of WAS was granulated to <3mm with a Tria G1 granulator (WASGr) and half remained ungranulated (WAS). Similarly, half of WA was granulated to <3mm (WAGr) and half remained ungranulated (WA).

4.2.2 Biochar characterisation

Total metal concentrations were determined using microwave assisted digestion. Approximately 20mg of each sample of biochar were digested in the presence of 6 mL HNO_3, 2 mL HCl and 0.5 mL HF. The samples were digested using a microwave (Speedwave4, Berghof Products + Instruments GmbH, Germany), ramped up to 220°C for 30 minutes and then held at 220°C for 30 minutes before cooling in a water bath. 200mg of H_3BO_3 was then added as a complexation agent alongside 2mL of H_2O_2 and held at 160°C for 30 minutes. Deionised water was then added to bring the samples up to a volume of 50mL. An aliquot of the sample was filtered through a

0.45µm cellulose acetate filter. Metal concentrations were measured in triplicate using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES 5110, Agilent Technologies Inc., USA).

Total carbon, hydrogen, nitrogen and sulphur contents were determined in triplicate by elemental analyses (Vario MACRO CHNS elemental analyzer, Elementar Analysensysteme GmbH, Germany). Furnace temperatures were ramped up by 2°C per minute and then a dwell time of 750°C was maintained for 6 hours. Ash content was determined by heating the biochars in a muffle furnace. Total oxygen was calculated from C, H, N, S and ash content via mass balance (European Biochar Foundation 2016).

4.2.3 Biochar rinsing

Each biochar treatment was rinsed with deionised water to quantify the concentration of PO_4^{3-}, SO_4^{2-} and nitrate NO_3^- leached from the biochar. Using a sieve, sand was washed with 1% HCl, rinsed with deionised water and dried. Each treatment (5g of WA, WAGr, WAS and WASGr) was added to an open-ended polypropylene column with an internal diameter of 31mm, a wall thickness of 1mm and a length of 500mm. The acid washed sand (8g; 1% HCl) was placed at the top and bottom of each column to help distribute the flow of deionised water and prevent loss of biochar. An 80 µm nylon mesh was used to stabilise the column content and further prevent loss of biochar. Each treatment was rinsed by pumping deionised water downward through the column at flow rates of ~5.5mL/min with a peristaltic pump (Baoding peristaltic pump model YZ1515X). Each treatment was rinsed with either 200mL (WA200, WAGr200, WAS200, WASGr200) or 800 mL of deionised water (WA800, WAGr800, WAS800, WASGr800); 800mL equating to approximately one year of precipitation in England and Wales (Metoffice.gov.uk 2021). Each treatment was performed in triplicate and the eluates from the columns were captured at 25mL intervals in a 50mL Falcon tube.

4.2.4 Eluate analysis

The eluate pH, eluate electrical conductivity (EC) and leaching of nutrients (PO_4^{3-}, $SO_4^{2-}$and NO_3^-) were studied for all rinsed biochars. The eluate from the rinsed biochars was pH tested in triplicate using a calibrated Voltcraft pH Meter and the EC was measured in triplicate using a calibrated Whatman CDM 400 Conductivity Meter. Each eluate was then analysed in triplicate for phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and nitrate (NO_3^-) using an ion chromatograph (IC 930 Compact Flex, Metrohm, Switzerland).

4.2.5 Lead, copper, zinc and cadmium immobilisation

The immobilisation of Pb, Cu, Zn and Cd was studied for each of the unrinsed biochars and the biochars rinsed with deionised water. Immobilisation batch experiments were carried out using Pb, Cu, Zn and Cd at a concentration of 10 mg/L for each metal. This concentration was chosen to expose the biochars to levels beyond those expected in road runoff which have been reported to be as high as 88 µg/L, 146 µg/L, 1544 µg/L and 4.2 µg/L for Pb, Cu, Zn and Cd respectively (Legret and Pagotto 1999; Crabtree et al. 2009; Zhao et al. 2010; MacKay et al. 2011; Zhang et al. 2013b). The solution was prepared as described previously by Cairns et al. (2021). Analytical-grade chemical reagents were used to prepare a stock solution (1000 mg/L) of $Pb(NO_3)_2$, $Cu(NO_3)_2$•xH_2O, $Zn(NO_3)_2$•$6H_2O$ and $Cd(NO_3)_2.4H_2O$. The pH was adjusted to ~4.7 by dropwise addition of concentrated HNO_3 to equalise the pH between solutions to represent the closest to runoff conditions before precipitation occurred for those metals.

All rinsed and unrinsed biochars were oven dried at 105 °C for 24 h. Biochar (0.2g) was then added to 25 mL of the spiked aqueous solution in 50 mL polyethylene Falcon tubes and agitated for 48 hrs at 280 rpm on a Unitwist 400 Orbital Shaker to reach equilibrium. The solution was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000rpm for 15 minutes (OECD 2000a). The supernatant was removed and immediately acidified to <pH 2 with 1mL of 70% HNO_3 before being filtered with a 0.45µm PTFE syringe filter for elemental analysis. Two types of control experiments were included: biochar without contaminants, as well as contaminants without biochar. All experiments were performed in triplicate using a batch sorption equilibrium method (OECD 2000b). Pb, Cu, Zn and Cd

concentrations of the acidified supernatants were measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200, Agilent). Sorbent loading (q) was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:

$$q = (c_i - c_{aq})V/W$$

where c_i is the initial concentration of metals in solution, c_{aq} is the final equilibrium concentration of metals in solution, V is the volume of solution and W is the weight of the biochar.

4.3 Results and discussion

Wood ash amended biochar has been demonstrated to remove the key motorway runoff contaminants Pb, Cu, Zn and Cd from aqueous solution (Cairns et al. 2020; Cairns et al. 2021). These previous studies have shown that immobilisation of these metals is as a result of precipitation due to increased pH caused by the increase of alkali and alkaline earth metals associated with the wood ash; ion exchange, due to the increase in carboxyl oxygenated functional groups and resultant exchange of heavy metals with the alkali and alkaline earth metals held by these functional groups (Cairns et al. 2021). However, in a field setting the components of wood ash that cause immobilisation could have the potential to be leached from the biochar adding phosphate, nitrate and sulphate into the wider system resulting in potential environmental impacts such as eutrophication. (Tulonen et al. 2002; Vassilev et al. 2013; Bogush et al. 2018).

Different treatments, including mixing wood ash hot with to larch biochar (sintering), mixing wood ash cold with biochar and granulating biochar, were studied in this work. The treatments were assessed to ascertain their effect on the elemental composition of the biochars; the leaching of phosphate, nitrate and sulphate; and the immobilisation of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}.

4.3.1 Biochar properties: unrinsed and rinsed with deionised water

Unrinsed larch biochar mixed cold with wood ash (WA) and larch biochar sintered with wood ash (WAS) contained similar concentrations (mg/g) of alkali and alkaline earth metals overall. WA had a higher concentration of K and Na whilst WAS had higher concentration of Ca with Mg concentrations being comparable between the biochars (Figure 4.1). Although concentrations of alkali and alkaline earth metals were similar between the unrinsed biochars, once they were rinsed with deionised water WAS retained a greater concentration of Ca, K, Mg and Na than WA. Furthermore, once WAS was rinsed with deionised water the concentration for each of the alkali and alkaline earth metals increased (Figure 4.1). This indicates that these minerals are not only retained better when the wood ash amendment is sintered to the biochar than when it is cold mixed, but also that they are retained better than other constituent parts of the biochar.

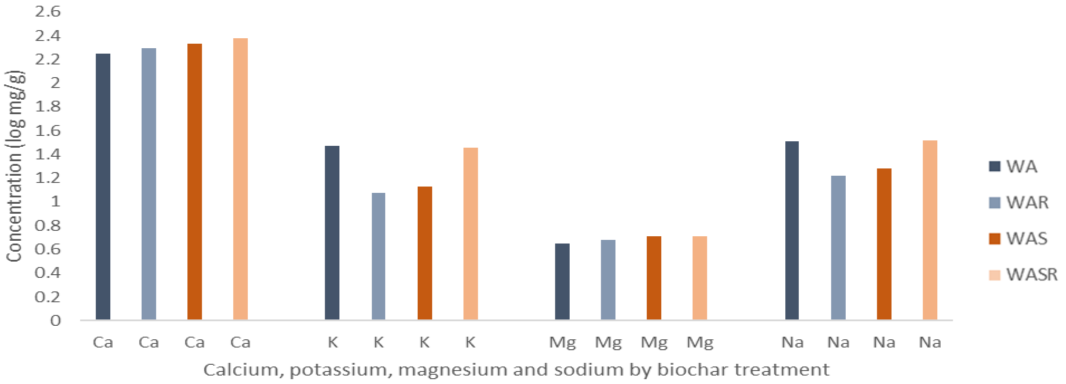

Figure 4.1: Log concentration of calcium, potassium, magnesium and sodium for larch biochar mixed cold with wood ash (WA), larch biochar mixed cold with wood ash and rinsed with deionised water (WAR), larch biochar sintered with wood ash (WAS) and larch biochar sintered with wood ash and rinsed with deionised water (WASR)

Alkali and alkaline earths are key in the immobilisation of Pb, Cu, Zn and Cd and as such the greater retention of Ca, K, Mg and Na by WAS is important to ongoing immobilisation. This importance is due to the role of alkali and alkaline earth metals in increasing aqueous pH, which is directly related to immobilisation through precipitation (Cairns et al. 2021). This increase in pH will also drive the increase of negative charge of the functional groups because the anionic forms will dominate when $pH > pK_a$ allowing alkali and alkaline earth metals to be exchanged more easily (Silber et al. 2010). The retention of alkali and alkaline earth metals alongside the retention of the oxygenated functional groups that hold these metals as part of their structure are fundamental to ion exchange (SI 4.3). During deployment in the environment, the longer WAS can retain Ca, K, Mg and Na when rinsed the longer the immobilisation mechanisms associated with these elements have the potential to continue. During thermal process such as sintering, heat will drive the decomposition process (e.g., decomposition of mineral phases, charring or biomass) which changes the solid and especially the surface which is key for nutrient or pollutant retention. At the same time, any volatile material will be lost from the outer surface of the solid by evaporation. For the materials under study here, the volatile matter will be volatile organic carbon, CO_2 and water. This means that the hot, as-sintered solids will be decarboxylated and dehydrated which will increase interparticle bonding because the respective surfaces are effectively unsaturated. The surfaces will also be free of any surface adsorbed material to increase the sorption of ions from solution. However, as the material is allowed to cool, it will inevitably adsorb CO_2 and water from the ambient air to create a more saturated (carboxylated and hydrated) surface and hence the uptake of solutes decreases. The increased retention as a result of the higher temperature of sintering the wood ash to the biochar promoting particle bonding and creating a more stable matrix than mixing the wood ash cold has previously been observed (Astrup et al. 2016). In addition, X-ray diffraction shows the presence of carbonate (calcite, kalicinite) and phosphate (hydroxyapatite) in the wood ash (SI 4.4). Hence, these are entirely compatible with the uptake of carbonate and phosphate anions (and charge balancing cations) from solution.

Unrinsed WAS had a higher concentration of P and S than WA with the concentration of N being similar between the biochars (Figure 4.2). Once rinsed with deionised water the concentration of P increased for both biochars, with P in WA increasing by 15.9% and P in WAS increasing by 17.4% (Figure 4.2). However, S decreased by 55% and 59% for WA and WAS respectively once rinsed with deionised water. This demonstrates that P is retained better when the wood ash amendment is sintered to the biochar, however P and N are well retained by both treatments in comparison to other elements. S is susceptible to significant loss due to rinsing with deionised water.

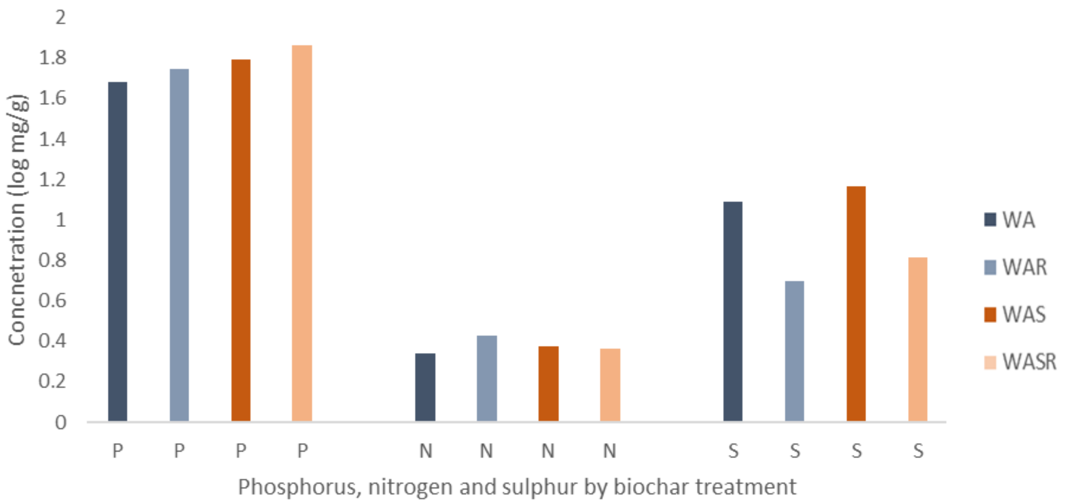

Figure 4.2: Log concentration of phosphorus, nitrogen and sulphur for larch biochar mixed cold with wood ash (WA), larch biochar mixed cold with wood ash and rinsed with deionised water (WAR), larch biochar sintered with wood ash (WAS) and larch biochar sintered with wood ash and rinsed with deionised water (WASR)

Co-precipitation is facilitated by minerals such as P and S (Fouladi Tajar et al. 2009; Zarga et al. 2013; Cairns et al. 2021). Of these elements P, and its most prevalent naturally occurring its chemical derivative phosphate, are particularly associated with the immobilisation of Pb, Cu, Zn and Cd through co-precipitation (Cairns et al. 2021). With its greater initial concentrations of P and greater increases in concentrations of P once rinsed with deionised water, WAS has a greater potential to immobilise Pb, Cu, Zn and Cd over longer periods than WA. As well as the importance of P, N and S for immobilisation, they are also constituent elements of nutrients of concern such as phosphates, nitrates and sulphates. The retention of these elements is important not just to the continued immobilisation of contaminants but also to the prevention of leaching nutrients into the aqueous system due to their potentially harmful effects (Smith et al. 1999; Anderson et al. 2002).

4.3.2 Eluate analysis

The initial concentration (mg/L) of eluate phosphate for all treatment types was above the Water Framework Directive (WFD) threshold for groundwater and / or drinking water (The Water Framework Directive 2015). However, during rinsing with deionised water eluate concentrations of phosphate immediately showed a pattern of steep decline followed by a flattening of the curve to a consistent concentration (Figure 4.3A). As a result, it is apparent that rinsing is necessary for all treatment types to remove unbound phosphate that is susceptible to leaching. The eluate of larch biochar sintered with wood ash and granulated to <3mm (WASGr) and larch biochar mixed cold with wood ash and granulated to <3mm (WAGr) were the only treatments that reduced phosphates measured to below detection limits when rinsed with deionised water. Due to this reduction in phosphate concentrations these are the only treatments that should be considered as candidates for upscaling for use in the field.

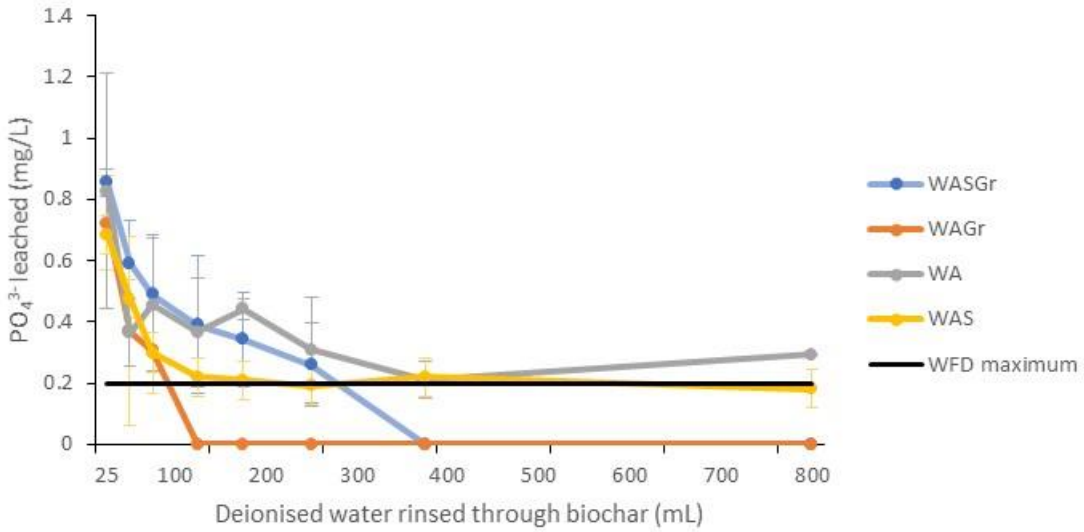

Figure 4.3: Concentration of phosphate leached from wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr). Concentrations are compared to WFD phosphate thresholds.

Sulphates initially leached from the biochar treatments at concentrations above 200mg/L for each treatment type (Figure 4.4). This reflects the mg/g loss of S demonstrated by the analysis of the biochar properties. The initially high concentrations of sulphate in the eluates reduce within 100mL of rinsing with deionised water to concentrations below the WFD thresholds (The Water Framework Directive 2015). Once more, this demonstrates that rinsing with deionised water of all treatments would be necessary prior to deployment in a field situation.

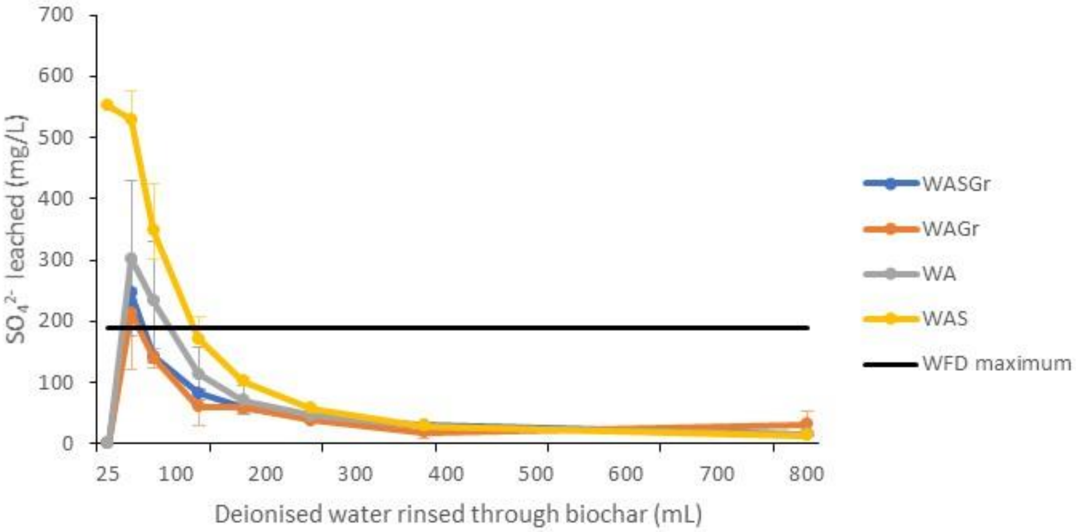

Figure 4.4: Concentration of sulphate leached from wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr). Concentrations are compared to WFD sulphate thresholds.

The concentration of nitrates in WASGr, WAGr and WA eluate are also initially above the WFD thresholds (The Water Framework Directive 2015) at over 40mg/L but reduce to ~0mg/L for each treatment within 200mL of rinsing with deionised water (Figure 4.5). This further demonstrates the need for each treatment to be rinsed before deployment in the field.

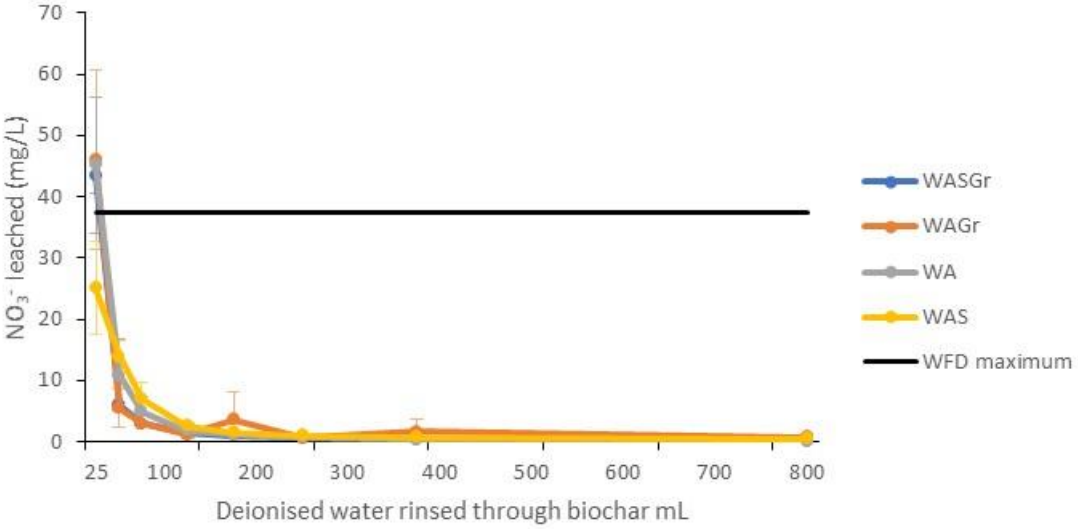

Figure 4.5: Concentration of nitrate leached from wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr). Concentrations are compared to WFD nitrate thresholds.

All of the treatments increased eluate pH for the duration of rinsing with deionised water (SI 4.6). Eluate pH did not fall below 8 for any treatment and the Δ pH for all treatments remained between 0.6 and 2.9. With pH in this range Pb, Cu, Zn and Cd are less mobile and are more likely to precipitate (Pourbaix 1966). Cairns et al. (2021) modelled that the distribution of divalent forms of Pb, Cu, Zn and Cd shift to hydroxyl forms at these pH levels and that when accompanied by anions such as PO_4^{3-} and SO_4^{2-} led to the formation of precipitates immobilising Pb, Cu, Zn and Cd (Figure 4.6 A, B, C and D). Surface charge is also strongly influenced by pH. Several previous studies have also shown that pH in the range of this study to be above the point of zero charge (PZC) (Yuan et al. 2011b; Yin et al. 2019; Maneechakr and Mongkollertlop 2020). When pH is greater than the PZC biochar is negatively charged and binds to metal cations (Li et al. 2017a). Eluate pH remaining above 8 even after rinsing with 800mL of deionised water, or the equivalent of one year’s rainfall, indicates that these treatments have the potential to immobilise Pb, Cu, Zn and Cd over longer periods as a result of precipitation and electrostatic attraction.

The potential of such continued immobilisation is reinforced by the strong retention of key minerals, nutrients and oxygenated functional groups associated with ion exchange and co-precipitation (Figure 4.1, Figure 4.2, SI 4.5).

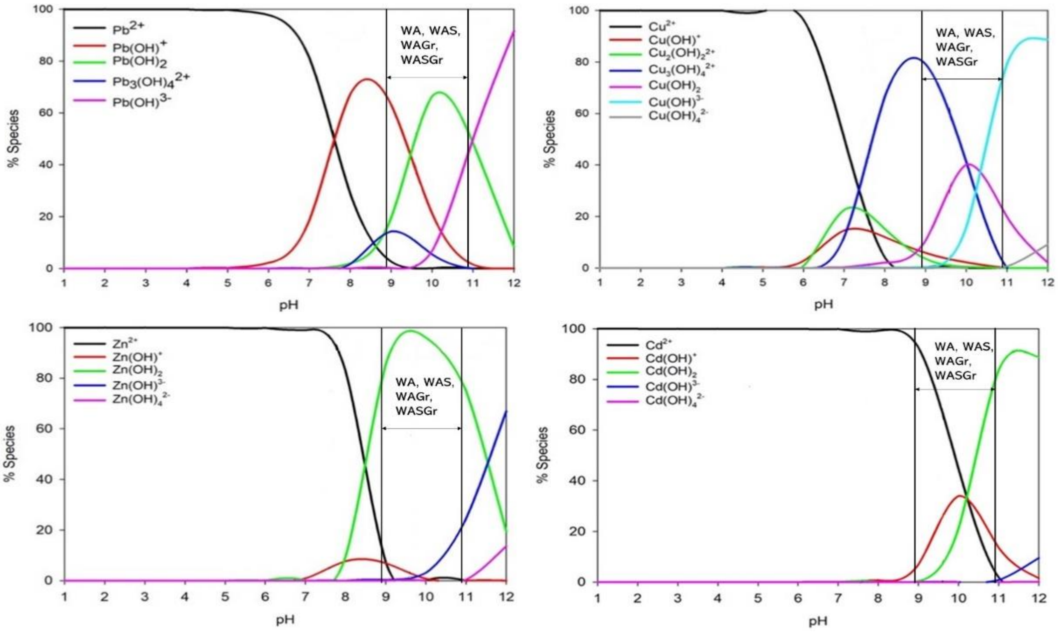

Figure 4.6: Speciation plots of (A) Pb, (B) Cu, (C) Zn, and (D) Cd across pH. Reference lines indicate pH range of wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr). Adapted from Cairns et al. (2021)

4.3.3 Lead, copper, zinc and cadmium immobilisation

Rinsing with deionised water did not reduce the immobilisation of Pb, Cu, Zn and Cd by any of the biochar treatments with each treatment removing between 97% and 100% of each contaminant when rinsed with the maximum 800mL (SI 4.8). This demonstrates that when the biochar treatments are rinsed with deionised water to reduce the leaching of phosphates, sulphates and nitrates to below WFD thresholds immobilisation of Pb, Cu, Zn and Cd continues.

The high degree of immobilisation of Pb, Cu, Zn and Cd (97 - 100%) when rinsed by 800mL of deionised water, the equivalent of one year of rainfall, demonstrates that the biochars did not reach exhaustion during this study. The treatments studied have the potential to immobilise Pb, Cu, Zn and Cd over longer periods. Such immobilisation is as a result of increased eluate pH, the retention of alkali and alkaline earths and the retention of P important to precipitation, ion exchange and co-precipitation. These mechanisms are particularly evident for treatments where the wood ash was sintered rather than mixed cold.

4.4 Conclusion

Wood ash sintered larch biochar granulated <3mm (WASGr) and wood ash cold mixed with larch biochar granulated <3mm (WAGr) are both viable options to immobilise Pb, Cu, Zn and Cd from motorway runoff, with WASGr having the greatest potential to immobilise these contaminants over longer periods. WAS retains Ca, K, Mg, Na and P better than WA when rinsed with deionised water. The retention of these minerals and nutrients are key to the immobilisation of Pb, Cu, Zn and Cd. The increased retention is as a result of the higher temperature of sintering the wood ash to the biochar promoting particle bonding and creating a more stable matrix than mixing the wood ash cold (Astrup et al. 2016). Despite the retention of key elements such as P and N, when rinsed with deionised water the biochars all initially leach phosphates, sulphates and nitrates at concentrations (mg/L) above the Water Framework Directive (WFD) threshold for groundwater and / or drinking water (The Water Framework Directive 2015). However, when WASGr and WAGr were rinsed with deionised water the concentrations of phosphates, sulphates and nitrates fell below WFD thresholds. The rinsing with deionised water required to lower the concentrations of phosphates, sulphates and nitrates did not reduce the high degree of immobilisation of Pb, Cu, Zn and Cd (97 - 100%) demonstrated by WASGr and WAGr. As a result, WASGr rinsed with deionised water has the potential to be scaled up and deployed to immobilise Pb, Cu, Zn and Cd from motorway runoff without a negative impact on the concentration of nutrients in the surrounding waters.

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Chapter 5.

Treatment and Fast Removal of Zinc and Lead from Mine Water by Wood Ash Amended Biochar

Stuart Cairns, Aaron Todd, Iain Robertson, Patrick Byrne, Tom Dunlop

Submitted

5.1 Introduction

Active and abandoned mines are a major source of contamination for both terrestrial and aquatic environments (Beane et al. 2016). Water pollution from these mines can originate from point sources such as mine adits, or diffuse sources such as spoil heaps (Rieuwerts et al. 2009). In the UK, the potential contamination by mines is compounded by the fact that owners of mines abandoned before 1999 bear no responsibility for their impacts. In Wales, there are over 1300 such mines affecting over 700km of river all of which were abandoned pre-1999 (Environment Agency Wales 2002; Coal Authority 2020a). Pb / Zn mining and smelting are seen as some of the primary sources of environmental (post)-transition metal contamination with Pb and Zn mines having resulted in major water contamination (Zhang et al. 2012a).

Both Zn and Pb concentrations that are above European Union Water Framework Directive (WFD) standards have the potential to cause harm to the environment and to human health. Metals such as Zn and Pb can enter the food chain harming plants, herbivores, carnivores and humans (Kumar et al. 2020; Shi et al. 2020). High concentrations of Pb can have effects on the central nervous system and kidneys, interfere with brain development and adversely affect both male and female reproduction (Needleman 2004). Exposure to Zn at higher concentrations can cause nausea, vomiting, epigastric pain, lethargy, and fatigue (Fosmire 1990).

Where polluted mine water is evident remediation is important not just to improve the quality of the water but also to improve the surrounding environment. Indirectly this improvement in water quality can improve usable farmland and restrict the intake of metals into plants, animals, and eventually humans. Currently there are three basic methods of water remediation or improving water quality: (i) diversion of the water away from the mine so that metals are not leached into rivers and streams; (ii) active treatment of the polluted water e.g. with chemical dosing or electrical coagulation; and (iii) passive treatment e.g. with settling ponds or reed beds (Thisani et al. 2021). As each site has different issues due to water chemistry, underground workings, physical space and access, remediation should be tailored on an individual site basis. Current remediation of metal mines in the UK has been limited due to the regulatory framework, as no one holds direct responsibility for the mines and resultant pollution and where it does occur it is often expensive, requires significant maintenance and creates potentially toxic waste products (Wyatt et al. 2013; Rose et al. 2019).

Water diversion is one of the remediation techniques that can be seen at Frongoch Mine, Wales, UK, an abandoned Pb-Zn mine with subterranean connections to Wemyss Pb-Zn mine. Frongoch has a large area of spoil mounds suitable for reprofiling and capping, and a single entry point for the majority of the water flowing into the mine. These site conditions make it possible for water in Frongoch to be diverted from entering the mine. The channel the diverted water follows has been lined with concrete cloth to reduce contact with spoil, and the largest spoil heaps have been recontoured and capped with either 300+ mm of clay or a geotechnical clay liner, covered with 100 mm of topsoil (Edwards et al. 2016). While the mine continues to fail environmental quality standards, the Zn load in the stream was reduced from 23.0 t p.a. to 7.4 t p.a. (Edwards et al. 2016). This approach will however only be possible where site conditions allow stream diversion.

An example of a passive mine water treatment scheme can be seen at Force Crag Mine in Cumbria, a Zn / Pb mine that was abandoned in 1991, which adversely affects 60 km of river. Since 2014 the mine effluent has been captured by two parallel Vertical Flow Pond compost bioreactors followed by a small wetland, removing 95-99% of the Zn (Bailey et al. 2016). It is estimated however that the substrate will require replacing after 10 years of use, and the disposal alone of this is almost the same as the capital expenditure for building the system (Bailey et al. 2016). A similar but larger system has been in use in West Fork Pb mine in Missouri, treating 76 L/s of water and reducing the Zn concentration by 75%, with a design life of 12 years (Gusek and Clarke-Whistler 2005).

Active treatment systems, such as those employed at Wheal Jane in Cornwall, require less land area for the system, but ongoing dosing of chemicals; 2,000 t of hydrated lime and 7 t of anionic flocculant, averaging £1.5M annually (Wyatt et al. 2013). The Wheal Jane active treatment system removes up to 99.2% of the metals, resulting in 600 t of metal contaminated sludge to dispose of annually.

A cost-effective alternative to these remediation techniques is the use of biochar to remove environmental contaminants from aqueous media. Biochar is a porous, carbonaceous material produced by biomass pyrolysis at temperatures ranging from

350–1000 °C under limited oxygen conditions (European Biochar Foundation 2016). In addition to the removal of contaminants from aqueous media studies have also highlighted several other benefits of biochar including carbon sequestration and enhancing soil fertility (Inyang et al. 2016; Kätterer et al. 2019). Its appeal is heightened as a result of its relatively low cost, simple production process and the ability to use a vast number of locally sourced feedstocks including sustainable and waste materials (Ahmad et al. 2014; Zhang et al. 2015; European Biochar Foundation 2016; Wang et al. 2018c; Xiao et al. 2018; Fosso-Kankeu et al. 2019).

Biochar has six key immobilization mechanisms for inorganic contaminants in aqueous media namely: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and subsequent sorption, and precipitation (Cairns et al. 2022b) (Figure 5.1). Several mechanisms can be relevant in any given biochar and these mechanisms can remove contaminants at different rates. Initial fast stage adsorption can be attributed to mechanisms such as electrostatic attraction and ion exchange whereas rate limiting steps have been seen to mainly involve chemical processes such as inner sphere complexation and co-precipitation (Ifthikar et al. 2017). The fast removal performance of biochar has been highlighted as a necessity for a successful adsorbent (Zhou et al. 2018); if the required contact time between sorbent and sorbate to remediate a contaminated water is too long then the use of that sorbent becomes impractical. This is particularly true in systems with a continuous flow where contact time between biochar and contaminant is limited.

Wood ash, a waste product of biomass power plants, has been used as an amendment to biochar to improve immobilisation of metals (Cairns et al. 2020). The increased rates of immobilisation are as a result of the wood ash mineral fraction and pH buffering capacity (Cairns et al. 2021). The alkali and alkaline earth metals added are central to ion exchange as well as increasing the pH of its environment inducing changes in metal speciation favourable to the immobilisation of Zn and Pb (Cerrato et al. 2016; Fidel et al. 2017). P and Si added to the biochar by the wood ash are also key in the formation of phosphates and silicates important in forming co-precipitates.

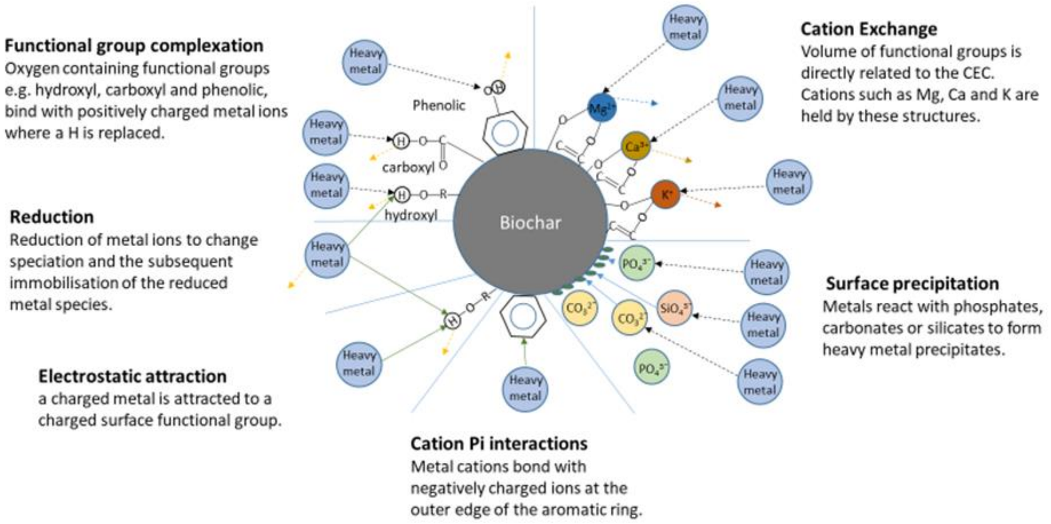


Figure 5.1: immobilisation mechanisms of inorganic contaminants in aqueous media (Cairns et al. 2022b)

Research has demonstrated that biochar can be successful in the removal of key mine water contaminants such as Zn and Pb from aqueous solution (Cairns et al. 2020). Most biochar studies do not focus on the scalability and practicality of the use of biochar which are essential considerations in moving to the end goal of industry-scale application. The required contact time for remediation is often overlooked. When considering practical use of biochar in a field setting the minimum contact time in which biochar can reach equilibrium is an important factor. This factor is particularly relevant in systems with continual flow, such as streams or rivers, where contact time between aqueous contaminant and sorbent is much shorter than in stagnant systems, such as ponds. Synthetic single contaminant solutions are often used rather than complex waters such as mine water. The adoption of single contaminant solutions neglects the fact that contaminants like Zn or Pb often co-exist with other pollutants, such as Fe, Al or SO_4^{3-} causing competition for sorption sites effecting sorption (Li et al. 2017a; Bandara et al. 2020b). Furthermore, the biochars studied are often produced on a laboratory scale rather than on a large or industrial scale putting further steps in the process to move toward scaled up production (Ahmed et al. 2016; Zhang et al. 2016).

The overall aim of this study is to determine if the use of wood ash amended biochar is a viable option to remediate mine water contaminated with Zn and Pb. The following objectives have been devised to meet this aim using wood ash amended biochar produced by an industry scale pyrolysis gasification kiln: (i) to quantify the contact time required for WAS to immobilise Zn and Pb (ii) to quantify the maximum measured removal of Zn and Pb by WAS (iii) to identify the mechanisms key to Zn and Pb immobilisation.

5.2 Experimental

5.2.1 Study site

Nantymwyn Pb mine is one of a number of mines accessing the mineral veins of Mid Wales which cross the site in a north easterly direction carrying galena (PbS) and sphalerite (ZnS) (Al-Atia and Barnes 1975). The mine (Figure 5.2) (52°5'12" N; 3°46'20" W) was worked sporadically over centuries by a variety of methods as technologies progressed, leaving a complex hydrogeological system, scarcely mapped when in operation and now complicated further by 90 years of degradation since closure (Hughes 1992). Records detailing quantities of ore recovered are limited, but in the final four months of full scale operation in 1930, 168 t of Pb and 548 t of Zn concentrates were recovered (Hughes 1992). Nantymwyn causes the River Tywi to fail European Union Water Framework Directive (WFD) standards for Zn for up to 69 km (Coal Authority 2020a). The River Tywi also provides drinking water to Swansea and Carmarthen from an intake at Nantgaredig. However, the substantially larger flow of the Tywi means that metals from Nantymwyn are diluted (Brown 1986; Welsh Water 2019). Much of the mine site is now a forestry plantation, but the main spoil heaps remain bare. The site is intersected by two streams; firstly, to the north the Nant y Bai flows through the main Nantymwyn spoil heaps and areas where the more recent surface operations were carried out (Hall 2011). The Nant y Bai receives diffuse polluted water from spoil run off, including over 30% of its Zn load from Tributary 1, which flows through spoil and tailings before joining the Nant y Bai, as well as subterranean sources (Todd et al. 2021). The second stream to the south is the smaller Nant y Mwyn, which does not flow through any visible surface spoil but receives point source input from the Pannau adit and the Deep Boat Level, both of which drain the mine workings. Zn and Pb WFD standards of 0.0129 mg/L and 0.014 mg/L respectively are both widely exceeded at Nantymwyn; this is apparent at both the Deep Boat Level and Tributary 1 (The Water Framework Directive 2015; Natural Resources Wales 2021).

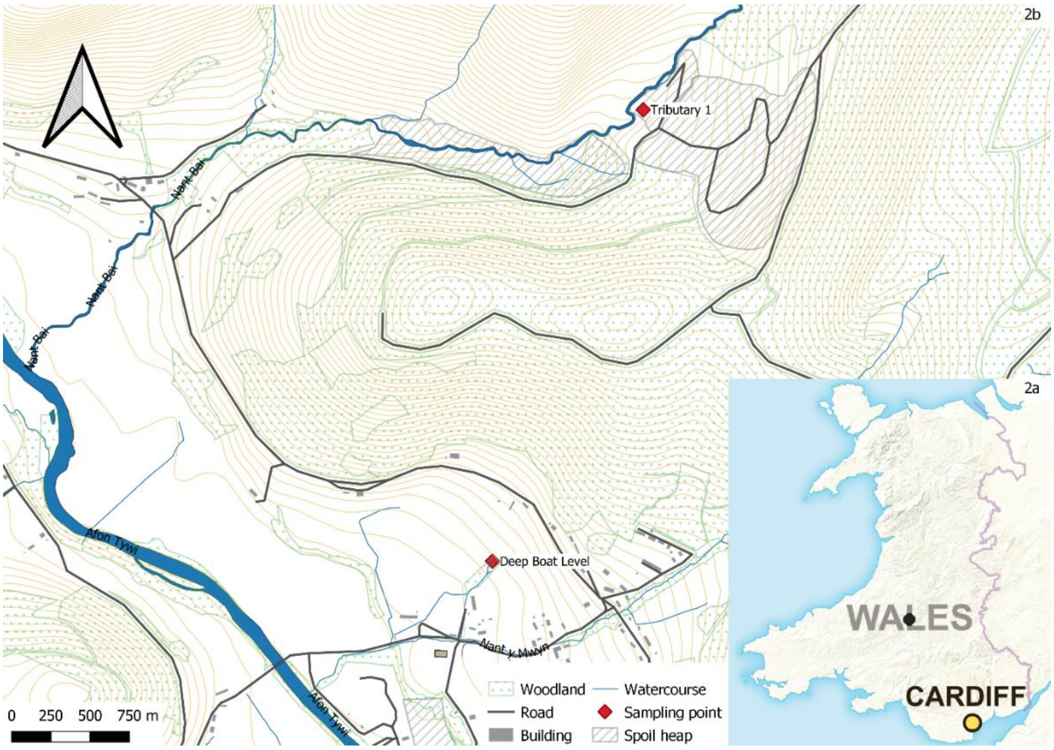


Figure 5.2: (a) Nantymwyn within Wales, (b) sample point locations (Ordnance Survey 2013, 2020)

5.2.2 Biochar production

European larch (*Larix decidua* (L.) Mill.) wood chips were pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a temperature of 485–530 °C, with a retention time of ~90 s. Wood ash, originating from a renewable energy plant in the UK, was added to the still hot biochar at a ratio of 1:1 and mixed for 15 min in a cement mixer to sinter the materials and then granulated to <3 mm with a Tria G1 granulator (Cairns et al. 2021). Wood ash was selected as an amendment to the pristine biochar because of its mineral fraction (specifically Ca, K, Mg, S, P and Si) and pH buffering capacity. However, as a result of the mineral fraction the wood ash amended biochar (WAS) can potentially leach nutrients such as nitrates, phosphates and sulphates (Liang et al. 2014). Cairns et al. (2022) demonstrated that rinsing wood ash amended biochar with 200 mL of water per 5 g biochar removes these unbound nutrients and reduces leaching to below water framework directive thresholds. To remove these unbound nutrients every 15 g of biochar was rinsed with 600 mL of deionised water. To rinse, the biochar was added to an open-ended polypropylene column with an internal diameter of 31 mm, a wall thickness of 1 mm and a length of 500 mm. An 80 µm mesh was used to stabilise the column content and further prevent loss of biomass (Cairns et al. 2020).

5.2.3 Sample collection and mine water characterisation

Water was obtained from the Deep Boat Level adit and Tributary 1 at Nantymwyn lead mine (Figure 4.2b) and sub-divided into five identical 1 L polyethylene terephthalate (PET) bottles. These bottles were each rinsed with sample water three times before filling, and stored at 4 °C, in accordance with national guidelines (Environment Agency 2014). The pH, electrical conductivity, temperature, redox and dissolved oxygen levels were taken concurrently at each site with a calibrated Hanna Instruments HI98194 Multiparameter meter following national guidelines (Environment Agency 2014).

5.2.4 Sorption Experiments

Batch sorption experiments were carried out to determine the effect of contact time on immobilisation using the Deep Boat Level adit and Tributary 1 water and to determine the maximum measured removal of Zn and Pb by biochar using Tributary 1 water. For both sorption batch experiments the sorbent was oven dried at 105 °C for 24 h. To determine the effect of contact time on immobilisation, biochar (0.5 g with a particle size of <3 mm) was added to 5 mL of deionised water in 50 mL polyethylene Falcon tubes and shaken for one hour to saturate the sorbent. Mine water was then added (20 mL) to the biochar slurry and shaken for a known amount of time (1 min, 5 min, 15 min, 30 min, 1 h and 24 h). To determine the maximum measured removal of Zn and Pb by biochar a known amount of biochar was added to a known amount of Tributary 1 mine water in 50 mL polyethylene Falcon tubes and shaken for 24 h. For both sorption batch experiments agitation was achieved on a Unitwist 400 Orbital Shaker at ~280 rpm. The solution was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000 rpm for 15 min (OECD 2000b). The supernatant was then acidified to < pH 2 with 1 mL of 70% HNO_3 before being filtered with a 0.45 µm PTFE syringe filter for analysis. All experiments were performed in triplicates using a batch sorption equilibrium method with biochar without mine water and mine water without biochar used as controls (OECD 2000b).

Zn and Pb concentrations of the acidified supernatants were measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200, Agilent Technologies Inc., USA). For contact time sorption batch experiments the percentage of sorbent removal was calculated from the difference between initial metal concentration and final metal concentrations in the aqueous phase:

$$\%\ \text{removal} = \left(\frac{c_i - c_{aq}}{c_i}\right) \times 100$$

where *Ci* is the initial concentration of metals in solution and *Caq* is the final equilibrium concentration of metals in solution. For maximum measured removal experiments removal in mg/g was calculated as the difference between initial metal concentration and the final metal concentration in the aqueous phase:

$$\text{q} = (c_i - c_{aq})V/W$$

where q is the maximum measured removal, *V* is the volume of solution and *W* is the weight of the biochar.

5.2.5 Biochar properties

A range of biochar properties were determined to understand how they effected immobilisation. The release of base cations (Ca, K, Na and Mg) by the biochar were measured for biochar that had been agitated with deionised water and for biochar that had been agitated with mine water and compared to review possible cation exchange. The pH, EC and alkalinity of the biochar supernatant from the sorption experiments were measured prior to acidification using a calibrated Voltcraft pH Meter, a calibrated Whatman CDM 400 Conductivity Meter and a Hanna HI-3811 Alkalinity test kit respectively. Fourier transform infrared spectroscopy (FTIR) was undertaken using a Perkin Elmer Spectrum Two FTIR Spectrometer. Measurements in the range 400-4000 cm^{-1} were determined to compare possible changes to functional groups, minerals capable of precipitation and aromatic structures. Comparisons of the spectra were made for biochar before sorbent loading and at each timed stage of the sorption experiment. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis Supra instrument using a monochromatic Al Kα X-Ray source at 225W, with a 15mA emission current. Each sample had multiple wide scans at pass energy of 160eV over the binding energy range of 1200-0eV to identify all possible elements present, with a step size of 1eV. High resolution spectra were scanned with a pass energy of 40eV, a step size of 0.01eV and a multi sweep dwell time of 2000ms to improve the signal to noise ratios for the lower concentration elements of interest. The binding energy axis was charge correct to the C-C component of the carbon peak at 284.8eV. Casa XPS (2.3.22PR1.0) was used to quantify the data using the Kratos sensitivity factor library, standard Shirley backgrounds and Gauss-Lorentz peak models. XPS analysis was conducted to identify the change in biochar characteristics, especially in composite compounds, before and after sorption.

5.2.6 Metal speciation

Speciation analysis of the mine water and biochar supernatants were carried out using the PHREEQC code (version 3.7.1) and the MINTEQV4 database (Parkhurst and Appelo 1999). The pH, redox, temperature and concentrations of base cations, metal contaminants, alkalinity and nutrients were used as model inputs. To confirm the PHREEQC modelling, the proportion of mobile Zn and Pb species in Tributary 1 were further investigated by comparing acidified and non-acidified Tributary 1 samples. One set of mine water samples were acidified to < pH 2 with 1 mL of 70% HNO_3 before being filtered with a 0.22 µm PTFE syringe filter, a further set was not acidified and filtered with a 0.22 µm PTFE syringe filter. All experiments were performed in triplicates and measured using Microwave Plasma Atomic Emission Spectroscopy (MP-AES 4200, Agilent Technologies Inc., USA).

5.3 Results and Discussion

5.3.1 Mine water chemistry

The Deep Boat Level was sampled 12 times during 2019-2020 and average metal concentration were calculated. It was characterised by a high Zn concentration of 12.7 mg/L, a Pb concentration of 0.2 mg/L, a pH of 7.0 and a flow of 24 L/s (Natural Resources Wales 2021).Tributary 1 had Zn concentrations of 9.8 mg/L, Pb concentrations of 3.8 mg/L, a pH of 6.4 and a flow of 3.4 L/s, again from 12 samples taken 2019-2020 (Natural Resources Wales 2021). The Zn and Pb concentrations for both Deep Boat Level and Tributary 1 are substantially above the WFD standards for dissolved Zn and Pb in the River Tywi which are 0.0129 mg/L and 0.014 mg/L respectively (The Water Framework Directive 2015).

5.3.2 Contaminant removal time-scales

The time in which biochar can immobilise contaminants from aqueous media is an important aspect of remediation with flowing water, as contaminant contact time with any sorbent is limited (Yang et al. 2014; Zhou et al. 2018). Mechanisms such as precipitation and ion exchange have been seen to be important in early stage immobilisation whereas mechanisms such as co-precipitation have been seen to take longer and as such be seen as rate limiting factors (Ifthikar et al. 2017).

The immobilisation of Zn from both the Deep Boat Level and Tributary 1 was a relatively fast process with 97% of mine water Zn removed in the first minute and equilibrium and complete removal achieved around 1 h (Figure 5.3a and b). The immobilisation of Pb from Tributary 1 was also a relatively fast process with 86% of mine water Pb removed in the first minute and an equilibrium of 92% removal again achieved around 1 h. Pb concentration in the Deep Boat Level mine water was below the limit of detection (<0.1 mg/L) and as such removal was not quantified.

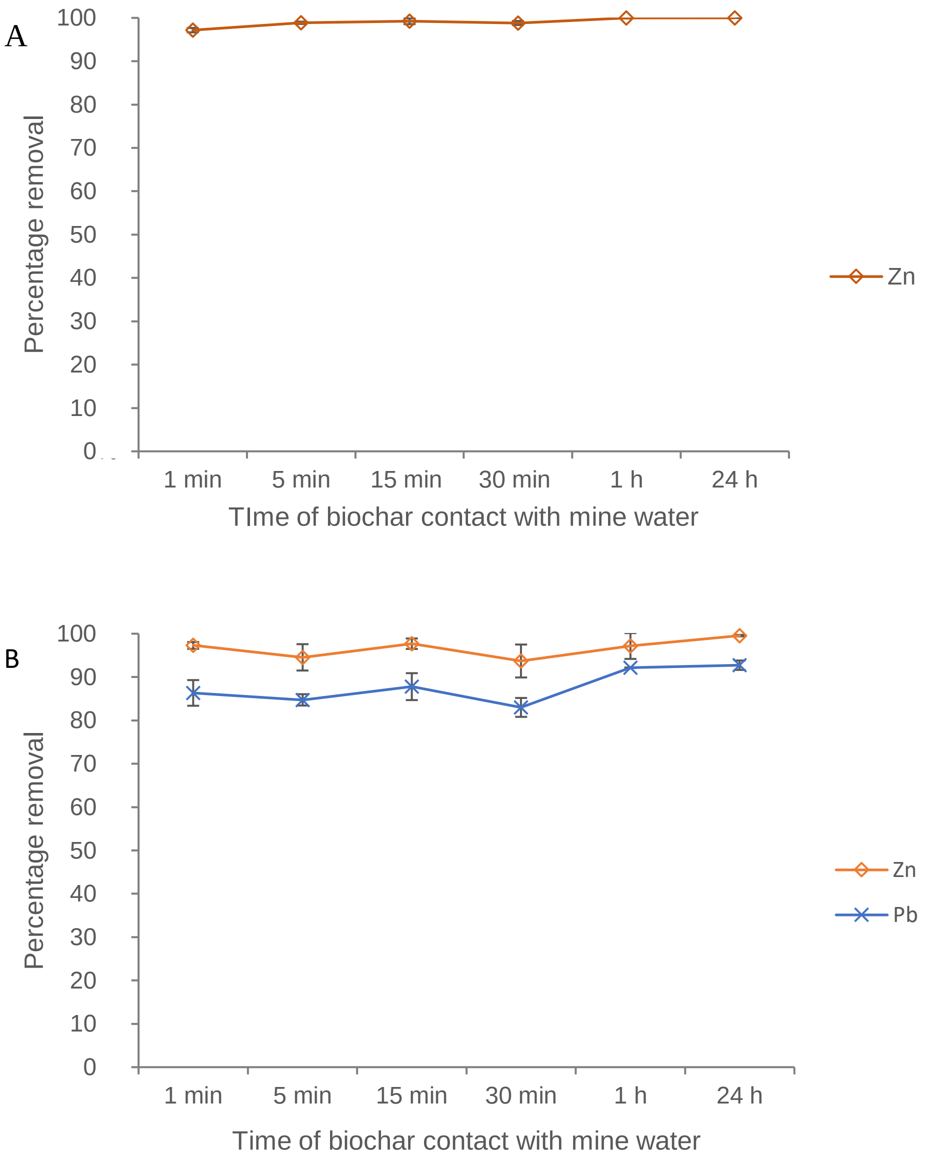


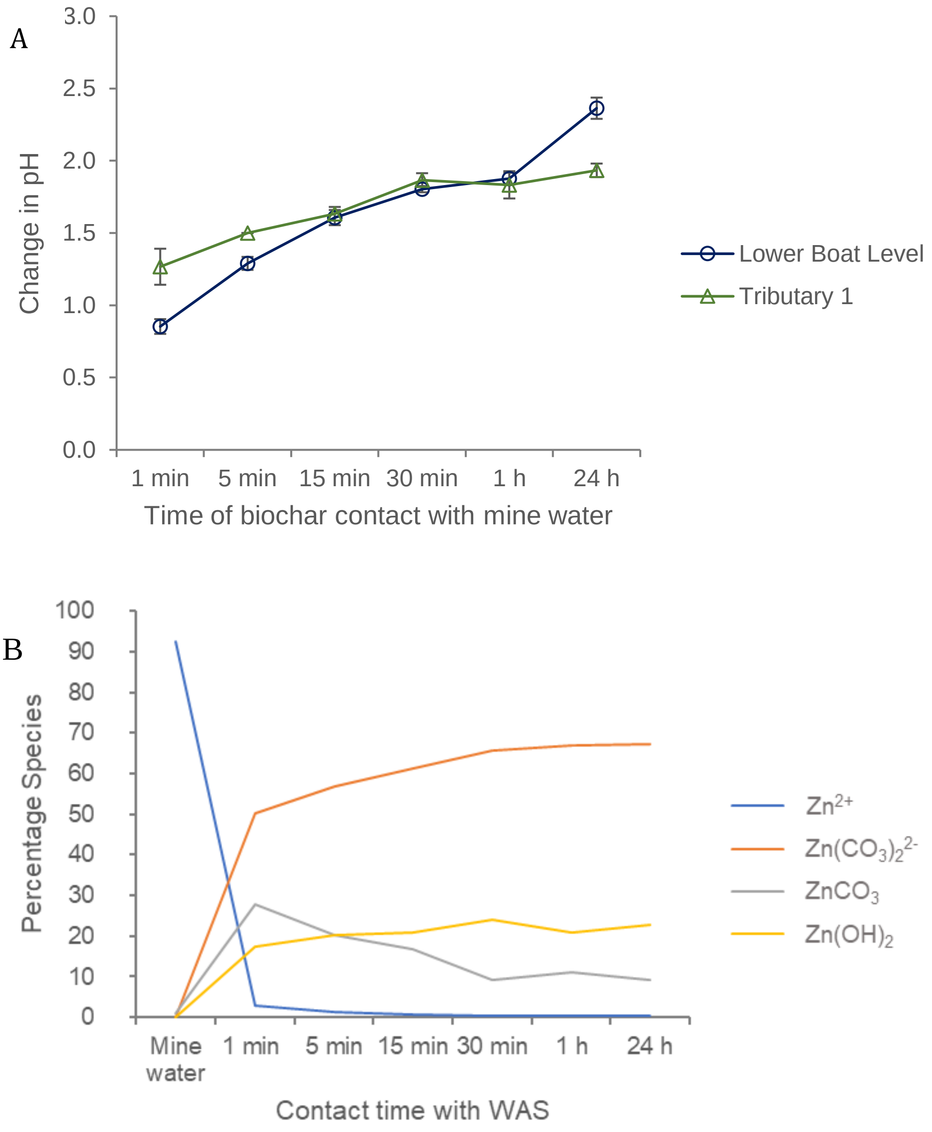
Figure 5.3: (a) percentage of zinc removed from the Deep Boat Level mine water by contact time with wood ash amended biochar. Lead concentrations in the Deep Boat Level being below detection limits (<0.1 mg/L); (b) percentage of zinc and lead removed from Tributary 1 mine water by contact time with wood ash amended biochar

5.3.3 Immobilization mechanisms

The pH of both the Deep Boat Level and Tributary 1 mine water was increased as a result of contact with the wood ash amended biochar (WAS) leading to early stage Zn and Pb immobilisation and capture via precipitation (Figure 5.4 b). An increase in media pH can be instrumental to changes in metal speciation that are favourable for the immobilisation of metals such as Zn and Pb (Cairns et al. 2020). After a contact time of 1 min with WAS the Deep Boat Level mine water increased in pH to 8.2 and after 1 h increased to a pH of 9.2 where equilibrium was reached. After a contact time of 1 min with the WAS the Tributary 1 mine water pH increased to 8.9 and after 1 h it increased to a pH of 9.4 at which point equilibrium was reached.

Speciation modelling of Zn and Pb ions was conducted using PHREEQC software (Palumbo-Roe et al. 2009). According to the PHREEQC calculations with the environmental conditions and pH observed in the mine water of Tributary 1 before the addition of WAS, 92% of Zn would be in mobile divalent forms (Figure 5.4 b). This proportion of mobile Zn was confirmed by a comparison of Tributary 1 acidified (pH <2) and non-acidified samples. Mobile species were captured in the filtered eluate whereas immobile species were filtered out of the eluate. Once WAS had been applied for 1 min, the PHREEQC modelling demonstrated that Zn mobile divalent forms only constitute 3% of Zn species (Figure 5.3 b). This change was caused by WAS promoting the formation of immobile carbonates and hydroxides such as $ZnCO_3$. Divalent forms of Zn dropped to close to 0% when WAS had been added for between 15 min and 24 h. The distribution shifts from Zn^{2+} to immobile zinc carbonate and hydroxide forms, forming mineral precipitates which were captured on the surface of WAS. The capture of $ZnCO_3$ modelled by PHREEQC on the surface of the biochar was demonstrated by XPS analysis where peaks attributed to $ZnCO_3$ were observed only when WAS had been in contact with the Tributary 1 mine water (Figure 5.5 a and b).

PHREEQC results also showed that before the addition of WAS, 44% of the Pb in the mine water of Tributary 1 would be in mobile divalent forms (Figure 5.4 c). Again, that a proportion of Pb was mobile was confirmed by the comparison of filtered acidified and non-acidified Tributary 1 mine water. According to PHREEQC modelling, once WAS had been applied to the mine water for 1 min, the divalent Pb concentration was reduced to close to 0%; this proportion remained constant for the 24 h period of this study. Mobile divalent Pb species shift to immobile lead carbonate and hydroxide forms which dominate speciation causing Pb precipitation and capture by WAS. The formation of lead carbonates, such as $Pb(CO_3)$ modelled by PHREEQC, have been seen to be related to the high alkalinity of the biochar and soluble carbonate, sulphate and phosphate anions (Chen et al. 2016; Zhang et al. 2017b). Regular sampling of Nantymywn has shown sulphate concentration to be as high as 11 mg/L adding substantially more anions into the system possibly playing a role in Zn and Pb speciation and further increasing the formation of precipitates (Dean et al. 2005; Natural Resources Wales 2021). Given the right conditions, as the addition of WAS to the Nantymwyn system provides, precipitation is a rapid process. This, in part, explains the speed of Zn and Pb removal by WAS.



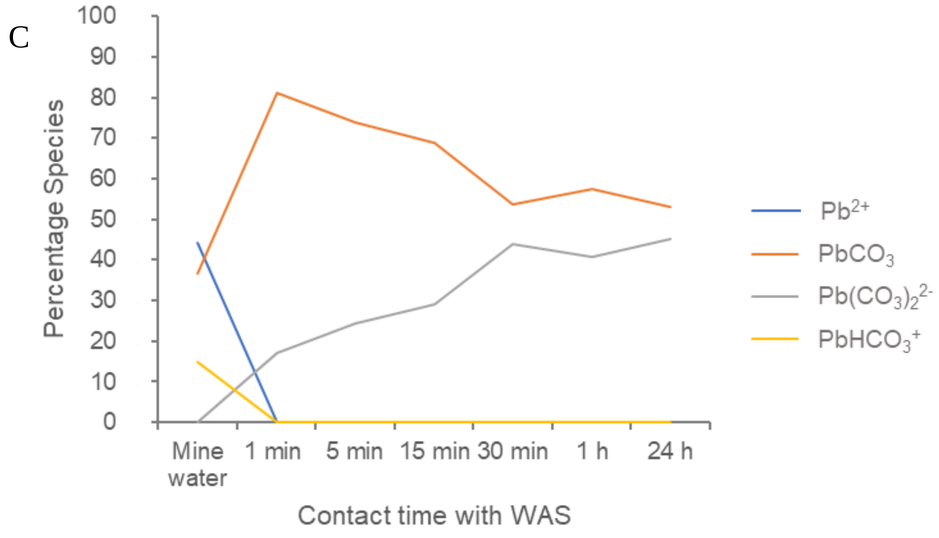


Figure 5.4: (a) change in Deep Boat Level and Tributary 1 mine water pH by contact time with wood ash amended biochar; (b) speciation plots of Zn in Tributary 1 mine water across contact time with wood ash amended biochar; (c) speciation plots of Pb in Tributary 1 mine water across contact time with wood ash amended biochar

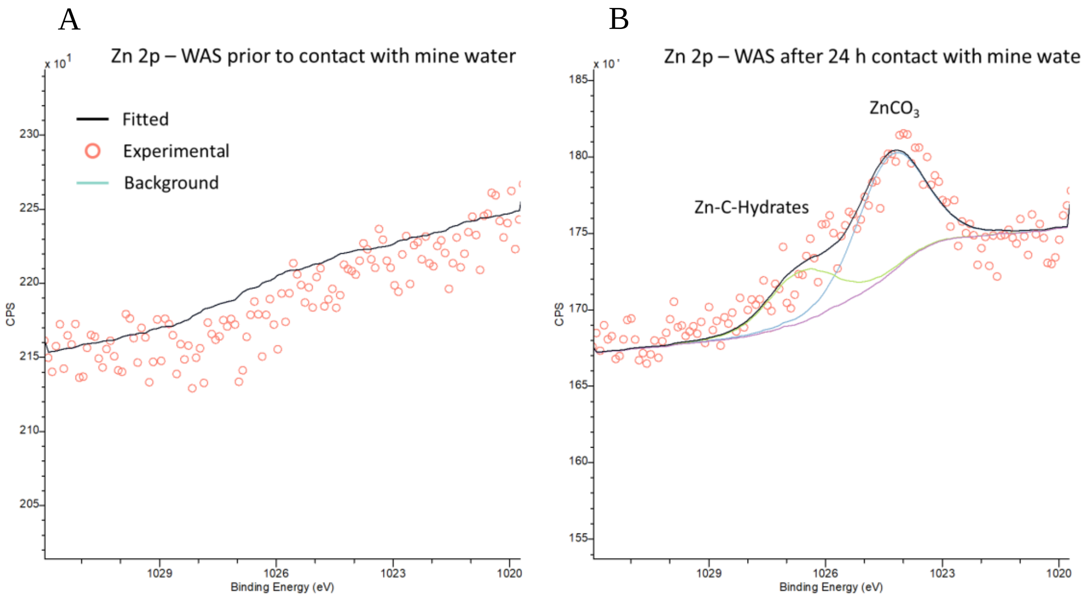


Figure 5.5: XPS region scans and peak fitting for wood ash amended biochar (a) Zn peaks prior to contact with Tributary 1 mine water (b) Zn peaks after 24 hours contact time with Tributary 1 mine water

Ion exchange was also seen to play a role in early stage sorption of Zn and Pb by WAS. A rise in base cation release in the presence of metals can signify ion exchange on the surface of the biochar as the divalent contaminants replace the divalent cations such as Ca^{2+} and Mg^{2+} (Uchimiya et al. 2010a). In this study concentrations of Ca and / or Mg in solution increased within the first minute of the experiment and remained broadly steady for the 24 h sampling period indicating that cation exchange played an early role in sorption of Zn and Pb and continued to be of importance for the duration of the study (Figure 5.6 a and b). Early stage sorption of Zn and Pb have been ascribed to ion exchange in several previous studies often alongside electrostatic attraction, with Ca and Mg being cited as the ions most important in the exchange, which is consistent with the findings of this study (Ifthikar et al. 2017; Song et al. 2020).

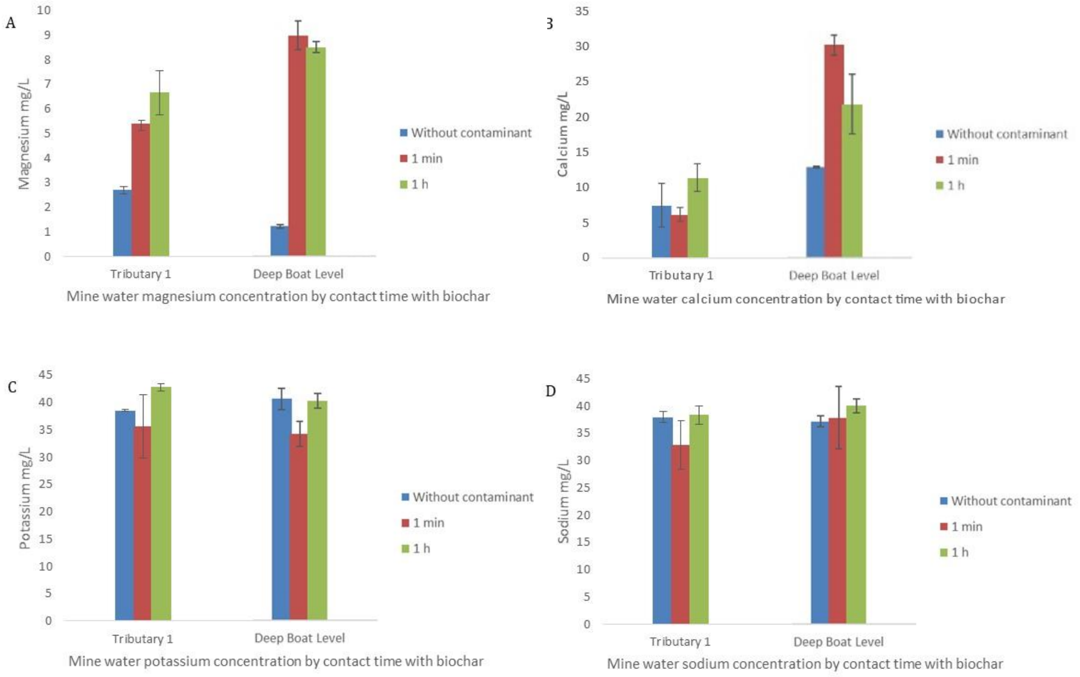


Figure 5.6: (a) changes in magnesium concentrations by contact time with wood ash amended biochar for Tributary 1 and Deep Boat Level (b) changes in calcium

concentrations by contact time with wood ash amended biochar for Tributary 1 and Deep Boat Level (c) changes in potassium concentrations by contact time with wood ash amended biochar for Tributary 1 and Deep Boat Level (d) changes in sodium concentrations by contact time with wood ash amended biochar for Tributary 1 and Deep Boat Level

5.3.4 Maximum measured Zn and Pb removal and late stage immobilisation mechanisms

The maximum measured removal of Zn and Pb by wood ash amended biochar (WAS) was 14.8 mg/g and 23.7 mg/g respectively. Immobilisation of Pb continued at 84% even as the proportion of Zn immobilised dropped to 3% demonstrating that WAS affinity with Pb is stronger than with Zn and that Pb removal can continue even once the capacity of WAS to remove Zn is exhausted. The key mechanisms that drive the removal of Zn and Pb through to maximum measured removal remained precipitation, and subsequent capture by WAS, and ion exchange.

PHREEQC modelling demonstrated that as the proportion of immobile Zn species reduced so too did the proportion of Zn immobilised by WAS with a strong correlation ($r = 0.91$; $p<0.01$) illustrating the importance of precipitation to Zn removal (SI 5.11). The modelling also shows that immobile Pb species remains as high as 92% even when Zn immobile species reduces to 20%. This partly explains why WAS continues to remove Pb beyond Zn exhaustion.

Cation exchange with Ca and Mg is also a relevant mechanism in the ongoing removal of the metals of concern by WAS. As the removal of Zn decreases the concentration of Ca, and to a lesser extent Mg, also decrease indicating that these base cations have been replaced by Zn and reducing the sites left available for Zn (Figure 5.7a). There is a strong correlation between Ca concentration and Zn removal ($r = 0.85$; $p<0.01$) as well as a strong correlation between Mg concentration and Zn removal ($r = 0.77$; $p<0.01$). FTIR analysis further demonstrates the importance of ion exchange in the removal of metals of concern (Figure 5.7b). The FTIR peak at 1418 is assigned to the carboxyl surface functional group (Iqbal et al. 2009; Cairns et al. 2021); when immobilisation of Zn by WAS is as high as 99% this peak is strong. However, as immobilisation of Zn decreases to exhaustion this peak diminishes considerably. This, in conjunction with the correlation between Zn immobilisation and Ca and Mg concentrations, shows that ion exchange plays an important role in the immobilisation of metals of concern from the mine water from initial immobilisation to exhaustion.

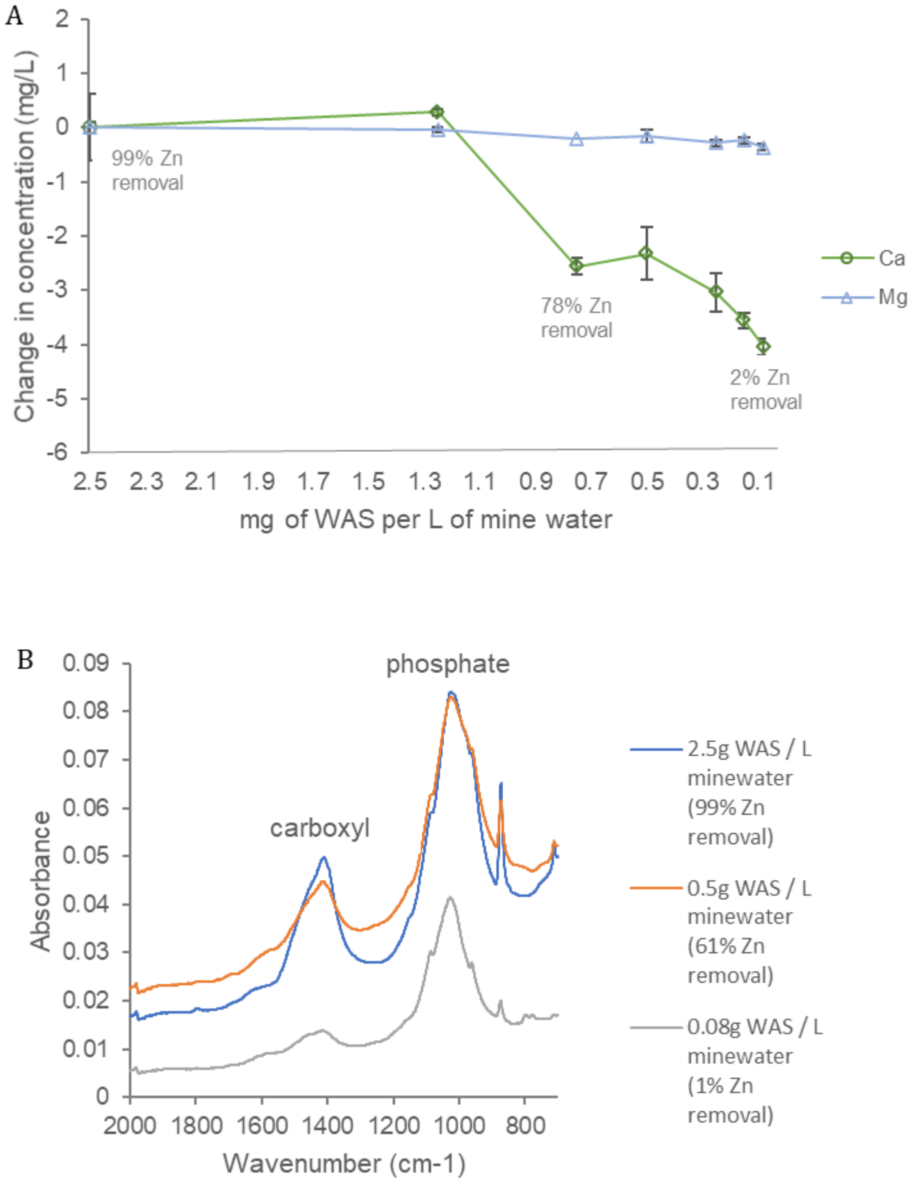


Figure 5.7: (a) The change in concentration (mg/L) of Calcium and Magnesium in the presence of different quantities of wood ash amended biochar (WAS) in a litre of mine water. (b) FTIR spectra of wood ash amended biochar (WAS) before maximum measured removal of Zn (2.5 mg WAS / L mine water), maximum

measured removal of Zn (0.5 g WAS / L mine water) and at exhaustion of Zn (0.08 g WAS / L mine water)

5.4 Conclusion

On a global scale, mine sites are a major source of contamination of aqueous environments. This study investigated if wood ash amended biochar (WAS) could immobilise Zn and Pb with a short enough contact time to be viable as a green remediator. The fast removal performance of biochar is necessary for it to be successful; if the required contact time between sorbent and sorbate to remediate a contaminated water is too long, then the use of that sorbent becomes impractical. This is particularly true in continuous flow systems where contact time between biochar and contaminant is limited such as in streams and rivers contaminated by mine water. This study used mine impacted waters from the Deep Boat Level and Tributary 1 areas of the Nantymwyn mine which flow into tributaries of the River Tywi to investigate Zn and Pb immobilisation. These waterways displayed Zn concentrations as high as 12.1 mg/L and Pb concentrations as high as 1.7 mg/L, both considerably above WFD standards of 0.0129 mg/L for Zn and 0.014 mg/L for Pb in the River Tywi. WAS removed 97% of Zn and 86% of Pb within the first minute of contact time with the mine water, with a maximum measured removal of 14.8 mg/g for Zn and 23.7 mg/g for Pb.

The fast removal of Pb and Zn was primarily caused by precipitation, and subsequent capture by WAS, and ion exchange. Both of these mechanisms are key to early stage immobilisation. Elevated pH and the presence of minerals shifted metal species to carbonates, such as $Pb(CO_3)$ and $Zn(CO_3)$ and hydroxides such as $Zn(OH)_2$. Under these conditions, these metal species are more susceptible to precipitation. The resultant capture of the species modelled by PHREEQC on the surface of the biochar was demonstrated by XPS. Ion exchange was demonstrated between the metal contaminants and base cations specifically Ca and Mg. The fast removal performance due to these mechanisms demonstrate the potential for the practical application of WAS.

Early stage immobilization mechanisms, maximum measured removal, sustainability of feedstock and low production costs when aligned to the industrial scale production of WAS makes wood ash amended biochar a viable option to pursue in the remediation of polluted waters. Although the findings of this study demonstrate the benefits of WAS at Nantymwyn they have wider significance than treatment at one site. Potentially WAS could be deployed at thousands of mine sites in the UK and abroad. Furthermore, these findings are not just restricted to mine waters but are also relevant to other contaminated aquatic environments including but not limited to motorway runoff balancing ponds, drinking water, industrially polluted rivers and paddy fields.

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Chapter 6.

General Discussion

The results from each chapter are discussed in depth at the end of each chapter / publication. The principle aim of this discussion chapter is to summarise the key findings of the thesis, articulate the links and progression between each chapter / publication, discuss them in a wider context and suggest the direction that future work should take. The experimental work in this thesis aimed to investigate: (i) the effect of amendments on biochar's sorption of metals of concern prevalent in motorway runoff (namely Pb, Cu, Zn and Cd); (ii) the maximum measured immobilisation of biochar and amended biochars; (iii) the mechanisms involved in the immobilisation of Pb, Cu, Zn and Cd; (iv) the concentration of potentially harmful nutrients leached during remediation and treatments to mitigate this; (v) the contact time required to immobilise contaminants.

6.1 Vehicular pollution of waterbodies

The contamination of aqueous environments as a result of metals of concern emitted by vehicles is a sizeable issue. In the UK there are over 40 million registered vehicles, a number which is increasing year on year (Gov.uk 2022). The volume of vehicles directly correlates to increases in contaminant input (Ewen et al. 2009). Tyre wear, brake wear and contamination from motor oil causes Pb, Cu, Zn and Cd to be deposited on roads and subsequently washed into receiving waterbodies by runoff (Budai and Clement 2011; Ladislas et al. 2015; Hwang et al. 2016; Markiewicz et al. 2017). There are remediation techniques already in place to lessen the impact of particulate vehicle pollution, including motorway balancing ponds, but these methods are flawed. Whilst they initially reduce contaminants, such as the Pb, Cu, Zn and Cd that are emitted by vehicles, they result in a build up of polluted sediment that is extremely expensive to remove. As a result of this expense the removal of this polluted sediment is often neglected reducing the effectiveness of the balancing ponds in the removal of contaminants (Rulkens 2005; Weinstein et al. 2010; Meland 2016). To combat this new, innovative, sustainable remediation methods need to be investigated with the potential to act as a cost effective alternative or complementary technique to existing processes. One such option is the deployment of biochar.

6.2 Key biochar material properties and immobilisation mechanisms

Biochar has been recognised as having the potential to remediate aqueous environments such as motorway balancing ponds (Cairns et al. 2020) by immobilising metals of concern through six key mechanisms (Figure 1.3). Critical to the findings of this work these six mechanisms include co-precipitation and ion exchange. These mechanisms are strongly influenced by the material properties of the biochar, as is metal speciation. Metals, such as Pb, Cu, Zn and Cd, are more mobile, bioavailable and toxic at low pH (Pourbaix 1966; Mohan et al. 2007; Charters et al. 2016). Cairns et al. (2020) demonstrated that solution pH, a key driver of metal speciation, can be influenced by the pH of the biochar, leading to metal precipitation and subsequent capture by biochar. Ion exchange is driven by the presence of functional groups, particularly carboxyl and hydroxyl groups, on the surface of the biochar (Ding et al. 2016). During cation exchange the biochar replaces base cations, typically Mg, Na, K and Ca, which are replaced by heavier metals, such as Pb, Cu, Zn or Cd, which then bind to the biochar (Kumar et al. 2016). The properties of biochar that are essential for co-precipitation include the presence of CO_3^{2-} , PO_4^{3-} or SiO_4^{3}. In dependence of pH Pb, Cu, Zn or Cd can react with these nutrients to form solid precipitates (Šráček and Zeman 2004). These nutrients are available as a result of the raw material which comprises the constituent parts of the biochar (Xu et al., 2013). In order to positively control these material properties for the immobilisation of Pb, Cu, Zn and Cd amending the biochar in a cost effective way, using sustainable materials and without the need for chemical activation was investigated.

6.3 Wood ash amended biochar immobilisation mechanisms and maximum measured removal of metals of concern

Amending biochar with wood ash increased immobilisation as compared to pristine biochar by an order of magnitude (SI 3.1 A, B, C and D). This difference was primarily due to the wood ash amendment increasing solution pH (SI 3.4 A and C), the increased proportion of oxygenated functional groups (Figure 3.4) and the increased presence of $3.2PO_4^{3-}$ and Si (Figure 3.2). These material changes led to an increase in precipitation, ion exchange and co-precipitation respectively.

Speciation plots across pH show that the distribution of metal species shifts from their divalent forms to hydroxyl forms as the pH increases (SI 3.3). The move from more mobile species to hydroxyl forms is accompanied by an increase in immobilization as the pH and dissolved anions from the wood ash drive metal precipitation and subsequent capture by the biochar (Figure 3.1). This capture subsequent to precipitation was evidenced several times throughout this work both as a result of XRD and XPS analysis. The method used required air drying of the post sorption biochar to be analysed by XRD and XPS as per Rakotonimaro et al. (2016). There is the possibility that this method could have led to precipitates that were in solution being dried onto the surface of the biochar during air drying rather than being captured as part of the sorption processes, this has the potential to overestimate the metals held by the biochar. The increase in solution pH seen as a result of the addition of wood ash amended biochar was anticipated due to the strongly alkaline properties of the wood ash (Nurmesniemi et al. 2012; Park et al. 2012). These strongly alkaline properties are directly related to the high alkai and alkaline earth content of the wood ash particularly the high Ca content (Steenari et al. 1999). The change in the speciation of the metals of concern from divalent forms to hydroxide forms such as $Pb(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$ or $Cd(OH)_2$ (figure 3.1, figure 5.4b and figure 5.4c) has also been seen in the study of metal removal by wood fly ash where the change in speciation to $Cd(OH)_2$ and resultant precipitation has been highlighted as the primary immobilization mechanisms (Park et al. 2020). Precipitation has been cited as a primary immobilisation mechanism of metals by fly ash, with high concentrations of minerals in fly ash being the driving factor behind this change in speciation further confirming its importance in the immobilisation of metals by wood ash amended biochar (Genty et al. 2012; Rakotonimaro et al. 2016; Park et al. 2020). Modelling by both MINTEQ and PHREEQC have highlighted the role of precipitation in the immobilisation of Pb, Cu, Zn and Cd. However, the method to prepare batch work supernatant for analysis by ICP-OES and MP-AES (the basis for some of the modelling variables) acidified and then filtered batch samples which could have had the impact of dissolving particulate matter that didn't respond to centrifugation and thus analysis may have been testing the supernatants for dissolved plus particulate. This could have had the consequence of redissolving precipitated metals of concern and other particulate matter; analysis would then underestimate the maximum immobilisation of the biochar and wood ash amended biochars and cause the MINTEQ modelling results to show supersaturation. However, it must also be noted that the species modelled in this work are also seen in similar modelling using similar sorbents and parameters (Frišták et al., 2015; J. H. Park et al., 2020; Xu, Cao, Zhao, et al., 2013; Xu et al., 2014). The increase in carboxyl functional groups as a result of the wood ash amendment facilitated increased ion exchange.

Ion exchange was also evidenced as an immobilization mechanism for the pristine biochar both through an increase in base cation release when in the presence of metals of concern and through the flattening of oxygenated functional group peaks post immobilization (figure 3.3 and 3.5a). Ion exchange has been reported to be a relevant factor in several studies that have examined the sorption of metals of concern by biochar (Mohan et al. 2007; Uchimiya et al. 2010a; Harvey et al. 2011b; Kołodyńska et al. 2012; Cui et al. 2016b; Komkiene and Baltrenaite 2016). However, the evidence of ion exchange is increased when the biochar was amended with wood ash specifically exchange with Ca and Mg (figure 3.3), an increase in oxygenated functional groups (figure 3.4) and a shift / flattening of peaks associated with oxygenated functional groups denoting ion exchange (figure 3.5 b and c). Increased cation release in the presence of metals can indicate ion exchange processes occurring on the surface of biochar (Uchimiya et al. 2010a). When considered in conjunction with the increase in carboxyl functional groups increased ion exchange due to the addition of the wood ash is demonstrated. Ion exchange has also been highlighted as an important mechanism for the removal of metals from aqueous solution by Chirenje et al. (2006) and Kalak et al. (2021), again underlining the importance of the wood ash as an amendment to the biochar. The pH value is also a relevant parameter to consider when discussing ion exchange. In order for base cations, such as Ca or Mg, to be released from the biochar and partition into water the charge on the surface site left behind needs to be balanced. If the pH is more acidic e.g. at 4.7 as with this work rather than above 6 as often seen in balancing ponds / runoff, dissolution is more likely and could contribute to the Ca and Mg release rather than it being solely related to ion exchange. Nonetheless the analysis does still point to the relevance of ion exchange as an important sorption mechanism behind the principal mechanism of precipitation.

Co-precipitation, implied by a change in concentration of Total P and phosphate (PO_4^{3-}) when metals of concern were added to solution, was also seen to be of relevance in both pristine biochar and wood ash amended biochar (figure 3.2). However, co-precipitation with Si was only demonstrated with wood ash amended biochar (figure 3.2), again as a result of the wood ash itself. Si is prevalent within wood ash, facilitating the occurrence of co-precipitation as indicated by the change in concentration of Si when metals of concern were added to solution (Vassilev et al. 2013; Agrela et al. 2018). Metals such as Pb, Zn and Cd have been seen to be immobilised by co-precipitation onto the surface of wood ash further asserting the importance of role of the wood ash amendment to the biochar (Genty et al. 2012)

Maximum measured immobilisation of up to 61.5 mg/g meant that wood ash amended biochar compared favourably with pristine or unactivated biochars investigated in other studies with similar pyrolysis temperatures and feedstocks such as hardwood, straw, woodchip, dairy manure or sewage sludge (Chen et al. 2011; Lu et al. 2012a; Xu et al. 2013b; van Hien et al. 2020). Although, studies show that activated carbon immobilises contaminants at a higher rate than wood ash amended biochar, activated carbon production is energy intensive, expensive and has a higher environmental impact e.g. acidification potential, human toxicity and fresh water ecotoxicity (Hjaila et al. 2013; Thompson et al. 2016; Alhashimi and Aktas 2017). Cost and environmental impact are two important criteria in any attempts to scale up and deploy biochar as an aquatic remediator again making biochar a viable option to consider. Although the wood ash amended biochar had demonstrated a stronger immobilisation of Pb, Cu, Zn and Cd than pristine biochar due to an increase of minerals and nutrients further research was necessary to understand if these additions could have a negative impact on the environment that they were deployed to remediate.

6.4 Potential leaching of nutrients from amended biochar and treatments to mitigate

Whilst biochar mechanistic and maximum measured removal studies demonstrate that wood ash amended biochar has the potential to reduce metals of concern from runoff, investigations were required to explore the potential for the amended biochar itself to leach potentially environmentally harmful nutrients. The leaching of nutrients has been highlighted in biochars that use a feedstock with high concentrations of N and P such as biochar with a manure feedstock (Wu et al. 2011; Liang et al. 2014). The addition of nutrients and minerals to the biochar which are associated with the wood ash are important in the immobilisation of metals of concern (Figure 4.2 and 4.3) but have potential to leach in a similar manner to manure biochar with high concentrations of P. As a result, mineral and nutrient retention was an important aspect of developing an effective and scalable remediator of aqueous environments. Column studies were undertaken to quantify the concentrations of phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and nitrate (NO_3^-) leached from the biochar itself when rinsed with deionised water. These nutrients were studied due to both the potential for them to cause environmental harm but also due to the prevalence of P, S and N in wood ash (Vassilev et al. 2013). Concentrations of nutrients leached were considered in relation to European Union Water Framework Directive (WFD) thresholds (The Water Framework Directive 2015). Different treatment options were used to investigate how to mitigate any potential leaching of nutrients and minerals without reducing immobilisation of the metals of concern. Wood ash was firstly sintered to biochar by mixing the two when the biochar was removed from the pyrolysis unit and still hot. The second method to mix the wood ash with the biochar was to mix when the biochar had cooled post pyrolysis. The hypothesis being that sintering the wood ash to the biochar would promote particle bonding between the wood ash and the biochar to create a more stable matrix than when mixed cold (Astrup et al. 2016). This stable matrix would mean the retention of material properties key to immobilisation namely alkali and alkaline earth metals, P and S. As hypothesised sintering the wood ash to the biochar retained more key material properties than when mixed cold (Figure 4.1 and 4.2). This combined with rinsing and granulating the wood ash amended biochar reduced leaching of nutrients to below European Union Water Framework Directive thresholds (The Water Framework Directive 2015) (Figure 4.3, 4.4 and 4.5). The immobilisation of Pb, Cu, Zn and Cd remained at between 97% - 100% once the wood ash amended biochar (all treatments) had been rinsed (SI 4.8). In order to successfully upscale and deploy biochar production would ideally be as simple and therefore as cost effective as possible. Nevertheless, the steps of sintering, granulating and rinsing the wood ash amended biochar with water are necessary to make the scaling up of wood ash amended biochar viable. Once maximum removal capacities, immobilisation mechanisms and treatments to reduce leaching had been investigated using a synthetic solution a study into how quickly contaminants were immobilised by wood ash amended biochar in a more complex real-world environment was also necessary.

6.5 Implications of high pH effluent

Whilst the leaching of nutrients has been addressed by this work the potential effect of a higher pH effluent should be considered and form part of future work. Whilst balancing ponds are man made rather than natural environments, they still host aquatic life such as benthic macroinvertebrate communities (Shutes et al. 1999) and they flow into the wider aqueous system both of which could be affected by pH changes. Polluted sediments, as seen in untreated balancing ponds, pose a serious environmental risk for human beings and ecosystems (Rulkens 2005). Benthic macroinvertebrate, amphibians, flora and fauna can all be negatively affected by contaminated sediment as seen in balancing ponds (Shutes et al. 1999; Rulkens 2005; Peng et al. 2009). Nonetheless, although the application of wood ash amended biochar to motorway runoff is designed to alleviate the issues surrounding water and sediment contamination there needs to be careful consideration as to whether the use of this material and the potential for a subsequent rise in pH will have detrimental as well as beneficial impacts. Shifts in pH can be damaging to aquatic life; O'Brien & DeNoyelles, (1972) cite a change in pH from 10.8 to 11.2 as being harmful to zooplankton. In this work metal bearing supernatant pH during batch experiments increased from an initial pH of ~4.7 to between 5.7 and 9.7 (SI 3.4C) dependant on biochar to solution ratio and metal concentration. During batch experiments with the same methodology using mine water with a starting pH of ~7.3 and ~7.6 post sorption supernatant never rose above 9.7, pH values in the column experiments also followed this pattern (SI 5.2) suggesting a maximum buffering capacity. Even without the addition of wood ash amended biochar studies have shown the pH of runoff to be as high as ~8.6, close to the buffering capacity of the wood ash amended biochar (Apul et al. 2010; Helmreich et al. 2010b; Hilliges et al. 2013). It is also worth noting that the maximum pH recorded as a result of the use of wood ash amended biochar is lower than other work that has studied the removal of heavy metal from road runoff using materials such as alumina, dolomite or lignite where post sorption pH has risen to as high as 10.9 (Huber et al. 2016). Whilst biochar does increase solution pH post sorption, runoff would flow into the balancing pond once it had come into contact with the biochar diluting the runoff, conceptually reducing the pH and mitigating any potential issues associate with a sharp increase in environmental pH. Despite this, further trials would need to be undertaken, potentially on a site by site basis, to fully understand the changes that runoff pH would make to the larger balancing pond, the buffering capacities of the ponds in question and the pH of the balancing ponds themselves.

6.6 Fast removal of contaminants in a complex mine water system

Aqueous environments such as motorway balancing ponds fed by runoff and rivers contaminated by mine water or industrial effluent are more complex than the synthetic contaminated water often studied (Vijayaraghavan et al. 2009). In road runoff or mine water contaminants, such as Pb, Cu, Zn or Cd, often co-exist with other pollutants such as Fe, Al or SO_4^{3-} which cause competition for sorption sites impacting immobilisation mechanisms and maximum removal capacities which are not taken into account in studies using synthetic water (Li et al., 2017; Bandara et al., 2020b). Whilst studies using synthetically contaminated water are of use to understand maximum removal capacities, immobilisation mechanisms and biochars effect on eluate, they need to progress towards real world water samples to fully understand how biochar will remediate when deployed. The removal of Zn and Pb by wood ash amended biochar was studied using mine water. Mine water was chosen as an environment that had similar contaminants to road run off in a site that was readily accessible.

Investigations into wood ash amended biochar using synthetic road runoff had demonstrated that the key mechanisms to immobilise Pb, Cu, Zn and Cd are precipitation, ion exchange and co-precipitation (Cairns et al. 2020; Cairns et al. 2021). Immobilisation mechanisms for Pb, Cu, Zn and Cd when wood ash amended biochar was studied using real world mine water were primarily precipitation facilitated by pH change (Figure 5.4) and ion exchange (Figure 5.5 and 5.6). Mine water was also used to study how quickly wood ash amended biochar removed Zn and Pb. In order for the biochar to be viable, scalable and deployable the contact time required between contaminated water and the wood ash amended biochar needs to be short enough to remediate systems with a continuous flow otherwise it becomes impractical for dealing with runoff, streams or rivers (Zhou et al. 2018). Fast immobilisation is advantageous and offers more possibilities when biochar deployment systems are designed (Vijayaraghavan et al. 2009). Both the primary immobilisation mechanisms of precipitation and ion exchange are considered early stage immobilisation mechanisms (Ifthikar et al. 2017) and as a result 97% of Zn and 86% of Pb were removed within the first minute of contact time (Figure 5.3). This fast removal performance further points to wood ash amended biochar being a viable option to be scaled up and used in continuous flow systems such runoff or mine water contaminated rivers.

6.7 Recommendations for further work

1) Future studies require a stronger focus on real world contaminated water and field studies. Whilst this work indicates that wood ash amended biochar is a viable option to treat aqueous environments such as motorway runoff or mine impacted water more research should be conducted to bridge the gap between laboratory results and field work. Studies investigating the immobilisation of inorganic and organic contaminants from aqueous media by biochar using real world contaminated water rather than synthetic water is not prevalent and studies in a field setting are even more scare. Due to this field studies using sites such as balancing ponds or motorway runoff receiving waters are essential to methodically investigate the interplay of different environmental factors including pH, dissolved organic matter, dissolved organic carbon and the mix of contaminants seen in various real world sites but not in synthetically contaminated water. Furthermore, the use of field sites in studies is essential to mitigate or prevent secondary pollution caused by the biochar. Studies relating to the potential of biochar to leach potentially harmful constituent parts as a result of biochar composition or modification are limited but available (Wu et al. 2011; Liang et al. 2014). However, these are generally under laboratory conditions again ignoring the complex combination of components seen in a field setting but also failing to review the potential of secondary pollution when biochar is deployed on a large scale (Wang et al. 2019).

2) In order to successfully investigate the efficacy of wood ash amended biochar needs to be produced and then studied on a larger scale. Although this work used biochar produced in large quantities in an industrial sized pyrolysis kiln, studies relating directly to the scaling of biochar with the end goal of industry-scale application are generally sparse. The majority of published studies rely on biochars produced in small kilns or biochars that are laboratory prepared; in these studies, the goal of producing a biochar with consistent characteristics on a commercial scale is lacking (Zhang et al. 2016). With the aim of using biochar to remediate motorway runoff the use of appropriate field sites must be accompanied by the deployment of increasing quantities of biochar which is produced at an industrial scale.

3) In tandem with increasing the quantities of biochar future studies also need to investigate the method of deploying biochar on a larger scale to remediate balancing ponds. There are a number of practical considerations and potential limitations that need to be explored before engineering a system that could successfully deploy biochar. Any deployment method would need to consider parameters such as particulate matter loss and resultant secondary pollution, the impact of biochar on runoff flow rates, contact time required for large scale remediation, potential for fouling or caking of the biochar and ease of biochar removal once removal capacity has been reached.

   Whilst the deployment method is out of scope for this work some key aspects to be considered when developing a deployment method have been touched upon. The immobilisation by wood ash amended biochar have been seen to primarily be as a result of precipitation and ion exchange, both of which are key to early stage immobilisation. Fast paced immobilisation such as this provides the opportunity to remediate systems with flow, thus increasing options for deployment. As the mobility of metals in motorway runoff can vary from 0 – 100% (table 1.1b) one of the goals of the remediation of motorway runoff must be to immobilise and capture metals, both mobile and immobile, before they reach the balancing pond. Once the runoff has reached the balancing pond there it becomes more difficult to remove these metals before sedimentation occurs causing the build-up of an expensive to treat toxic waste (Rulkens 2005; Weinstein et al. 2010; Meland 2016). To this end, it would seem sensible for investigations into deployment should take place in the pipe work that delivers the runoff from the motorway to the balancing pond and / or the area beneath the pipework where the runoff falls before reaching the balancing pond (figure 1.2).

4) More work is also required to understand the potential for regeneration and recycling of biochar as well as the release and reuse of metals from biochar that has reached removal capacity. Both processes are key to biochars scalability and commercial viability to remediate balancing ponds and other aqueous environments (Poonam et al. 2018). One of the rationales for the use of biochar as a remediator for motorway runoff is that current methods, such as balancing ponds, create toxic sediments that are expensive to remove (Rulkens 2005; Karlsson et al. 2010; Meland 2016). An advantage of biochar is that the heavy metals are contained on the surface of the biochar and the biochar itself is easily removed from situ potentially making it more cost effective to remove contaminants. However, unless the biochars can be recycled and contaminants can be recovered for reuse, a waste product will still be created. The reuse of the biochar as part of this process is also critical to reduce the quantity of biomass required to remediate a given aqueous environment and to improve its economic viability (Gan et al. 2015a). The quantity of biomass required for full scale treatment of individual mine discharges has been raised as an issue (Perkins 2016), but successful regeneration of the sorbent for reuse would considerably reduce this as a concern. With metal precipitation as a result of changes in pH proven to be a primary mechanism for metal immobilisation by wood ash amended biochar, research into remobilising captured metals with acid washes would be where investigations should begin (Wang et al. 2019). However, studies into using a green solvent or remobilisation via an enzyme process would potentially be a more environmentally friendly option. From here metals could be eluted, separated into single element solutions, and reused.

Chapter 7.

Conclusions

This thesis set out to establish if biochar was an affordable remediator for the key metals of concern from motorway runoff. This research shows that amending pristine biochar increases the immobilisation of the key inorganic contaminants in motorway runoff, namely Pb, Cu, Zn and Cd. Amending biochar with wood ash specifically increased immobilisation of these contaminants by an order of magnitude. This difference was the result of the wood ash amendment increasing pH, thus shifting metal species, and increasing the presence of minerals such as PO_4^{3-} causing immobilization of the metals through precipitation and the increase in oxygenated functional groups facilitating ion exchange. These mechanisms resulted in maximum measured removal by wood ash amended biochar of 61.5 mg/g for Pb, 38.9 mg/g for Cu, 12.1 mg/g for Zn and 10.2 mg/g for Cd, comparing favourably with other biochars.

Wood ash added minerals and nutrients to the biochar some of which were key to the immobilisation of inorganic contaminants seen in motorway runoff, namely Pb, Cu, Zn and Cd. These nutrients had the potential to leach from the wood ash amended biochar in the form of phosphates, nitrates and sulphates which could be harmful to the ecosystem the biochar would be deployed to remediate. However, treatments such as sintering the wood ash to the biochar, granulating and rinsing with deionised water reduced the leaching of phosphates, sulphates and nitrates to below European Union Water Framework Directive thresholds without a loss of immobilisation capacity of Pb, Cu, Zn and Cd.

Wood ash amended biochar which had been sintered, granulated and rinsed also demonstrated strong immobilisation in mine impacted water as well as in synthetic water. In mine impacted water wood ash amended biochar was seen to have fast removal performance with 97% of Zn and 86% of Pb immobilised within the first minute of contact time with the mine water.

This thesis demonstrates that biochar amended with wood ash is a viable option to remediate key inorganic contaminants from road runoff as well as other contaminated aqueous environments such as mine impacted water. Removal capacities, immobilisation mechanisms lending themselves to fast removal capacity and treatments that mitigate the leaching of nutrients all show that wood ash amended biochar has the potential to be scaled up and deployed to immobilise Pb, Cu, Zn and Cd.

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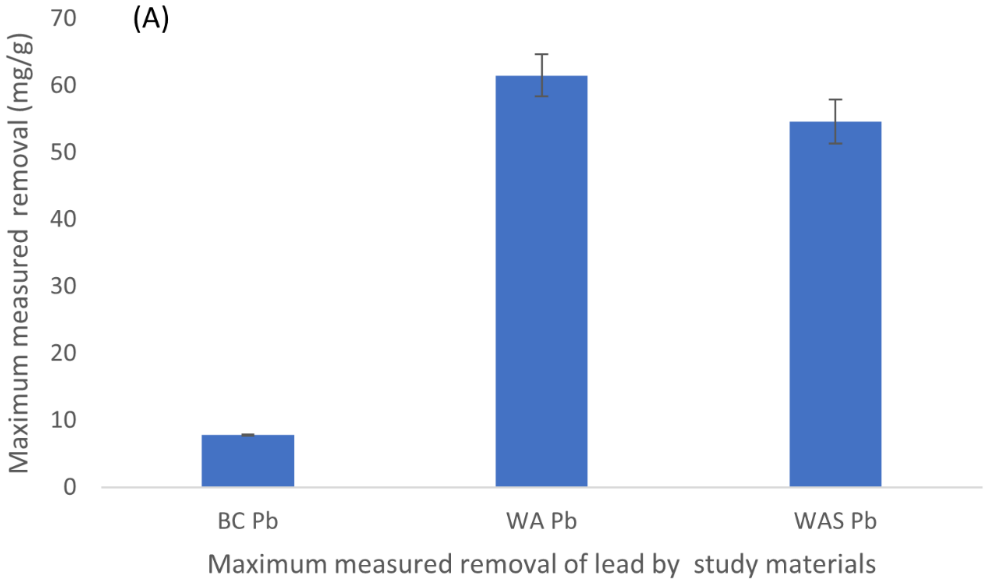
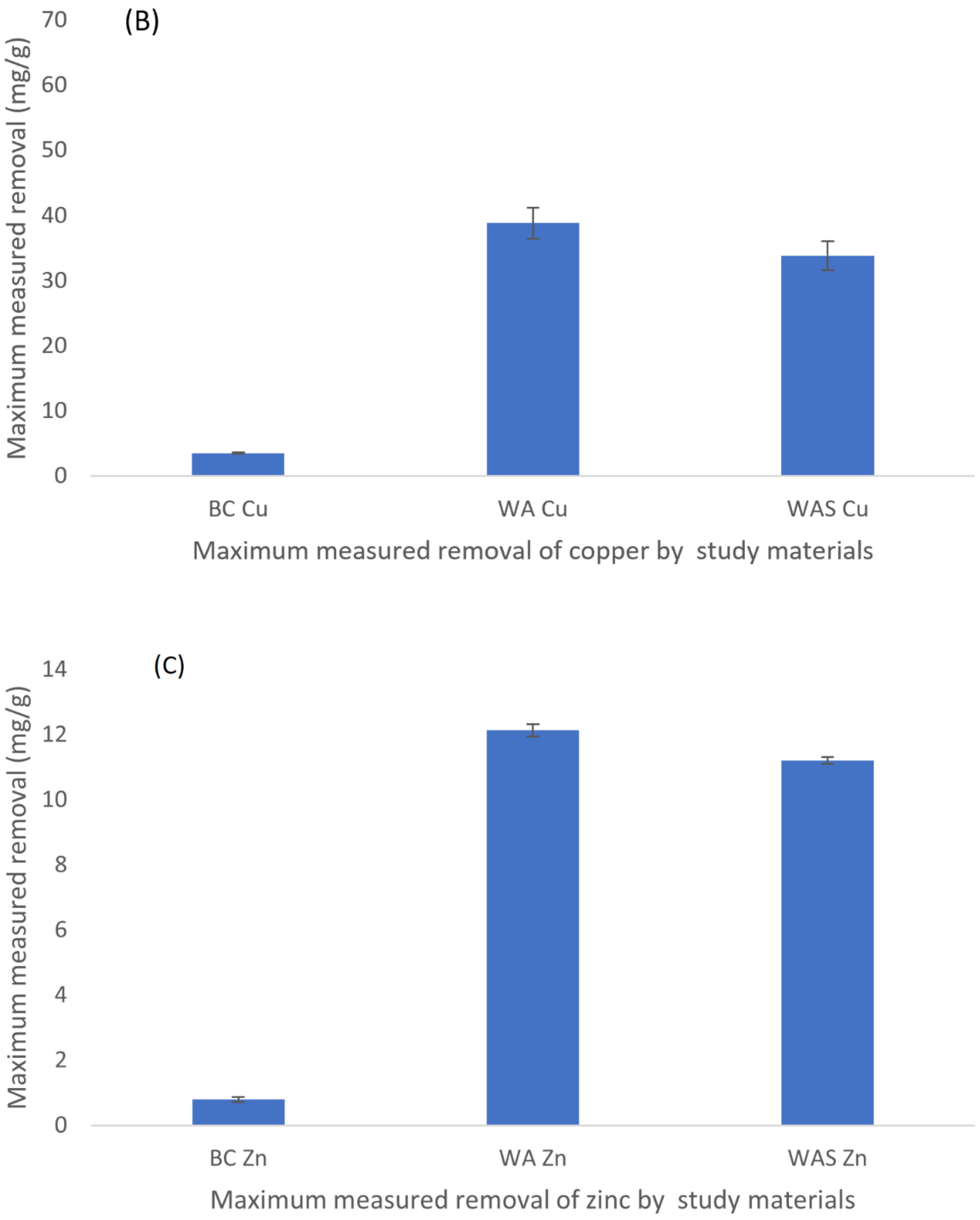
Appendices

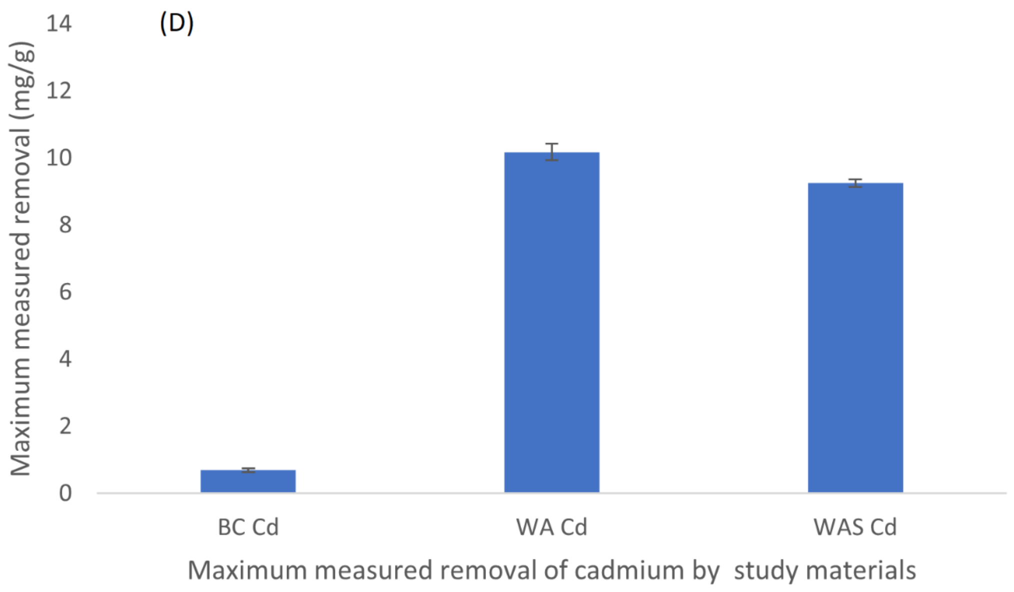
This section provides supplementary information either referred to in the peer reviewed publications or data which has been used to support the discussion in these papers / chapters. The presentation of the data is in the same order in which the data is discussed in the body of each paper / chapter and as a result follow the same structure as each of these papers / chapters to enable ease of use. Where further detail around the data or figures are required, more information is provided.

i) Supplementary material: Chapter 3

SI 3.3.1 Contaminant removal by biochar and wood ash amended biochars




(B)
Maximum measured removal (mg/g)
0
10
20
30
40
50
60
70
BC Cu
WA Cu
WAS Cu
Maximum measured removal of copper by study materials
(C)
Maximum measured removal (mg/g)
0
2
4
6
8
10
12
14
BC Zn
WA Zn
WAS Zn
Maximum measured removal of zinc by study materials

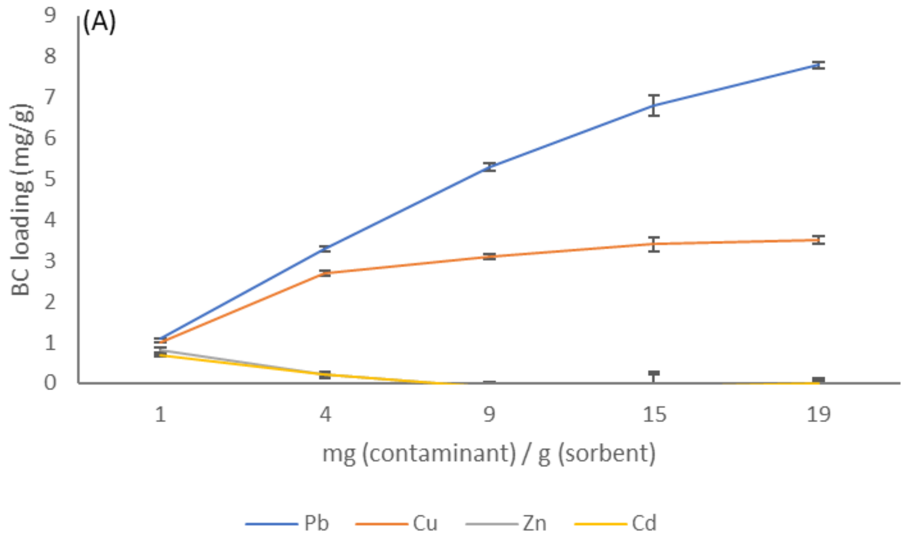


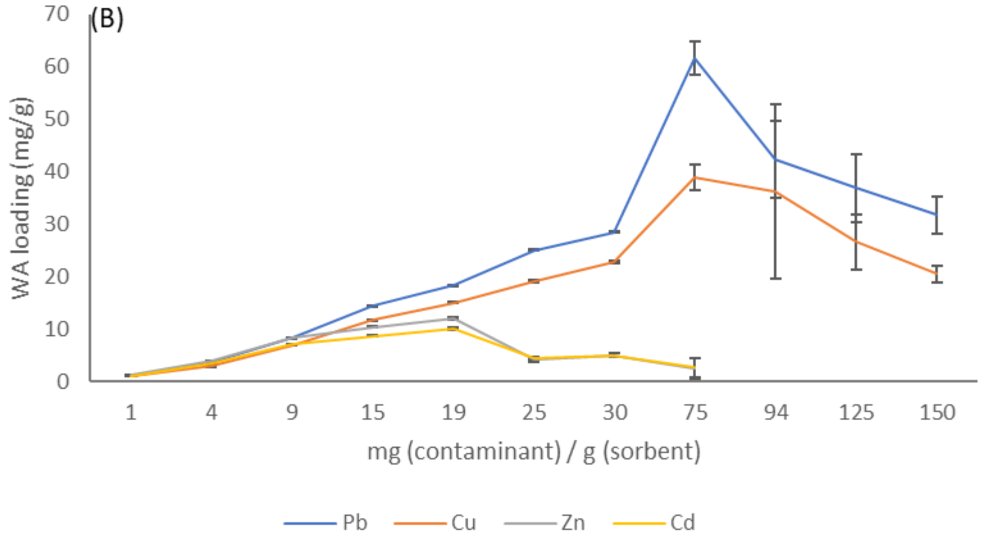
SI 3.1: Bar graph showing the maximum measured removal for pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) of (A) lead (B) copper (C) zinc (D) cadmium. Error bars show ± SD (n=3).

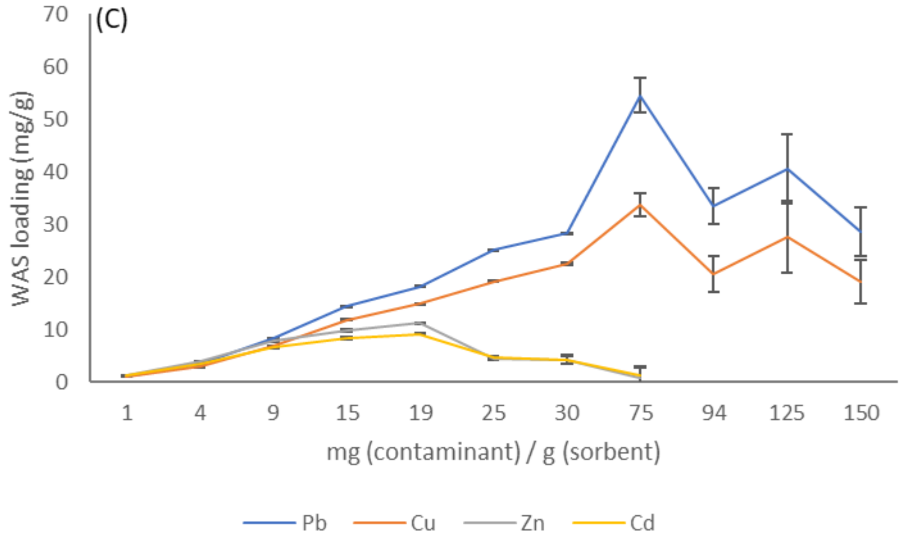
SI 3.1A, 2.1B, 2.1C and 2.1D are referred to in section 3.3.1 (results and discussion section of chapter 3) whilst discussing the maximum measured immobilisation of each metal of concern by BC, WA and WAS. They are also referred to in section 6.3 (discussion chapter) in the discussion around immobilisation mechanisms and maximum measured removal of contaminants.

	solution (mL)	sorbent quantity (g)	mg/L	mg contaminant per g of sorbent	Pb	Pb standard deviation (mg/g)	Pb correlation (mg contaminant per g sorbent and loading)	Cu	Cu standard deviation (mg/g)	Cu correlation (mg contaminant per g sorbent and loading)	Zn	Zn standard deviation (mg/g)	Zn correlation (mg contaminant per g sorbent and loading)	Cd	Cd standard deviation (mg/g)	Cd correlation (mg contaminant per g sorbent and loading)
BC 0.2g 10 mg/L	25	0.200	10	1.25	1.1	0.00		1.0	0.00		0.8	0.07		0.7	0.06	
BC 0.2g 30 mg/L	25	0.200	30	3.75	3.3	0.06		2.7	0.06		0.2	0.07		0.2	0.06	
BC 0.2g 70 mg/L	25	0.200	70	8.75	5.3	0.09		3.1	0.05		-0.1	0.12		-0.1	0.10	
BC 0.2g 120 mg/L	25	0.200	120	15.00	6.8	0.25		3.4	0.18		-0.1	0.39		-0.1	0.33	
BC 0.2g 150 mg/L	25	0.200	150	18.75	7.8	0.08	0.97	3.5	0.09	0.83	-0.1	0.16	-0.79	0.0	0.13	-0.75
WA 0.2g 10 mg/L	25	0.200	10	1.25	1.1	0.00		1.0	0.00		1.3	0.00		1.2	0.00	
WA 0.2g 30 mg/L	25	0.200	30	3.75	3.7	0.01		3.1	0.01		4	0.01		3.6	0.00	
WA 0.2g 70 mg/L	25	0.200	70	8.75	8.3	0.01		7.0	0.00		8.4	0.11		7.2	0.09	
WA 0.2g 120 mg/L	25	0.200	120	15.00	14.5	0.02		11.9	0.03		10.4	0.13		8.7	0.11	
WA 0.2g 150 mg/L	25	0.200	150	18.75	18.4	0.02		15.1	0.02		12.1	0.19		10.2	0.25	
WA 0.15g 150 mg/L	25	0.150	150	25.00	25	0.12		19.1	0.30		4.2	0.34		4.5	0.32	
WA 0.1g 120 mg/L	25	0.100	120	30.00	28.5	0.13		22.8	0.14		5.1	0.42		5.0	0.37	
WA 0.05g 150 mg/L	25	0.050	150	75.00	61.5	3.14		38.9	2.38		2.5	2.02		2.7	1.75	
WA 0.04g 150 mg/L	25	0.040	150	93.75	42.4	7.29		36.2	16.69							
WA 0.03g 150 mg/L	25	0.030	150	125.00	36.9	6.44		26.6	5.20							
WA 0.025g 150 mg/L	25	0.025	150	150.00	31.8	3.55	0.69	20.5	1.65	0.67			-0.23			-0.18
WAS 0.2g 10 mg/L	25	0.200	10	1.25	1.1	0.00		1.0	0.00		1.3	0.00		1.2	0.00	
WAS 0.2g 30 mg/L	25	0.200	30	3.75	3.6	0.01		3.0	0.01		4	0.02		3.5	0.01	
WAS 0.2g 70 mg/L	25	0.200	70	8.75	8.3	0.01		7.0	0.01		7.8	0.12		6.6	0.14	
WAS 0.2g 120 mg/L	25	0.200	120	15.00	14.5	0.03		11.9	0.03		9.9	0.28		8.3	0.28	
WAS 0.2g 150 mg/L	25	0.200	150	18.75	18.2	0.14		14.9	0.14		11.2	0.11		9.2	0.11	
WAS 0.15g 150 mg/L	25	0.150	150	25.00	25.2	0.03		19.2	0.06		4.5	0.07		4.8	0.10	
WAS 0.1g 120 mg/L	25	0.100	120	30.00	28.4	0.10		22.5	0.27		4.3	0.91		4.3	0.79	
WAS 0.05g 150 mg/L	25	0.050	150	75.00	54.6	3.30		33.8	2.27		0.9	1.90		1.3	1.65	
WAS 0.04g 150 mg/L	25	0.040	150	93.75	33.6	3.42		20.5	3.40							
WAS 0.03g 150 mg/L	25	0.030	150	125.00	40.5	6.57		27.7	6.89							
WAS 0.025g 150 mg/L	25	0.025	150	150.00	28.7	4.58	0.70	19.1	4.25	0.66			-0.35			-0.31

SI 3.1E: Table outlining the sorption of Pb, Cu, Zn and Cd by pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) for each concentration of contaminants, each volume of sorbent and by mg of contaminant per g of sorbent.


(A)
BC loading (mg/g)
0
1
2
3
4
5
6
7
8
9
1
4
9
15
19
mg (contaminant) / g (sorbent)
Pb
Cu
Zn
Cd


(B)
WA loading (mg/g)
0
10
20
30
40
50
60
70
1
4
9
15
19
25
30
75
94
125
150
mg (contaminant) / g (sorbent)
Pb
Cu
Zn
Cd


(C)
WAS loading (mg/g)
0
10
20
30
40
50
60
70
1
4
9
15
19
25
30
75
94
125
150
mg (contaminant) / g (sorbent)
Pb
Cu
Zn
Cd

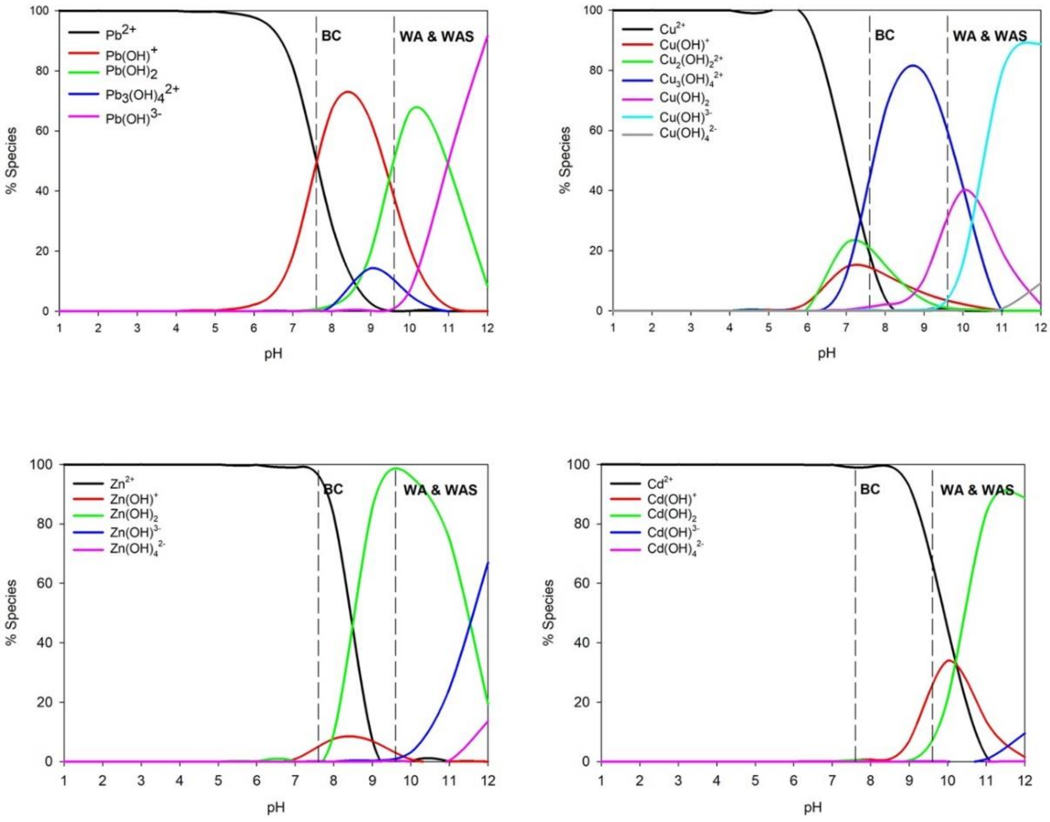
SI 3.2: (A) immobilisation of Pb, Cu, Zn and Cd by pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) at known concentrations of contaminant and known quantities of sorbent. SD (n=3). Due to various sorbent quantities being used in the batch experiments mg (contaminant) / g (sorbent) has also been included. This enables correlation analysis of sorbent loading and contaminant quantity to be undertaken.

(B) The loading of Pb, Cu, Zn and Cd onto pristine larch biochar (BC) by contaminant quantity. (C) The loading of Pb, Cu, Zn and Cd onto larch biochar cold mixed with wood ash (WA) by contaminant quantity. (D) The loading of Pb, Cu, Zn and Cd onto larch biochar sintered with wood ash (WAS) by contaminant quantity.

SI 3.2A, is the data used to underpin the maximum measured immobilisation referred to in section 3.3.1 (results and discussion section of chapter 3) whilst discussing the maximum measured immobilisation of each metal of concern by BC, WA and WAS. It is also discussed in relation to adsorption mechanisms in section 6.3 (discussion chapter). SI 3.2A, 3.2B and 3.2C are the visualisation of the sorbent loading and the contaminant quantity.

Whilst typically sorption data would be presented with equilibrium data (mg/L) versus loading (mg/g) this was not possible in this study as different quantities of sorbent were used to determine maximum measured immobilisation. This was done as once studies had shown that sorbents hadn’t reached maximum immobilisation with 0.2g of sorbent and 150 mg/L of contaminated solution further data points were required. However, in light of the importance of pH more concentrated solutions were not mixed as the stronger concentration would have resulted in a lower pH hindering accurate sorption comparisons, rather a smaller quantity of sorbent was used.

SI 3.3.2 Aqueous phase chemistry – immobilization via precipitation and ion exchange



SI 3.3: Speciation plots of Pb, Cu, Zn, and Cd across pH (reference lines indicate pH of BC, WA, WAS)

Mineral	log IAP	Saturation Index	Stoichiometry and mineral components									
Chloropyromorphite(c)	-57.90	26.53	5	Pb+2	3	PO4-3	1	Cl-1				
Chloropyromorphite(soil)	-57.90	22.50	5	Pb+2	3	PO4-3	1	Cl-1				
Hydroxylpyromorphite	-45.84	16.95	5	Pb+2	3	PO4-3	1	H2O	-1	H+1		
Pb3(PO4)2(s)	-34.07	9.46	3	Pb+2	2	PO4-3						
Tsumebite	-1.33	8.46	-3	H+1	2	Pb+2	1	Cu+2	1	PO4-3	6	H2O
Brochantite	21.70	6.47	4	Cu+2	6	H2O	-6	H+1	1	SO4-2		
Langite	21.70	4.21	-6	H+1	4	Cu+2	7	H2O	1	SO4-2		
Zn3(PO4)2:4H2O(s)	-31.79	3.63	3	Zn+2	2	PO4-3	4	H2O				
Tenorite(c)	10.44	2.80	1	Cu+2	-2	H+1	1	H2O				
Cu3(PO4)2(s)	-34.34	2.51	3	Cu+2	2	PO4-3						
Antlerite	11.26	2.47	3	Cu+2	4	H2O	-4	H+1	1	SO4-2		
Pb(OH)2(s)	10.53	2.38	-2	H+1	1	Pb+2	2	H2O				
Tenorite(am)	10.44	1.95	1	Cu+2	1	H2O	-2	H+1				
PbHPO4(s)	-22.30	1.51	1	Pb+2	1	H+1	1	PO4-3				
Atacamite	8.83	1.43	2	Cu+2	3	H2O	-3	H+1	1	Cl-1		
Larnakite	0.99	1.43	-2	H+1	2	Pb+2	1	SO4-2	1	H2O		
Cu(OH)2(s)	10.44	1.15	1	Cu+2	2	H2O	-2	H+1				
Pb4(OH)6SO4(s)	22.05	0.95	-6	H+1	4	Pb+2	1	SO4-2	6	H2O		
Cu2(OH)3NO3(s)	10.19	0.94	2	Cu+2	3	H2O	-3	H+1	1	NO3-1		
Pb3O2SO4(s)	11.52	0.84	-4	H+1	3	Pb+2	1	SO4-2	2	H2O		
Cu3(PO4)2:3H2O(s)	-34.34	0.78	3	Cu+2	2	PO4-3	3	H2O				
Pb2(OH)3Cl(s)	9.00	0.21	-3	H+1	2	Pb+2	3	H2O	1	Cl-1		
Pb4O3SO4(s)	22.05	0.18	-6	H+1	4	Pb+2	1	SO4-2	3	H2O		
Cd3(PO4)2(s)	-32.46	0.14	3	Cd+2	2	PO4-3						
Zincite	11.29	0.06	1	Zn+2	1	H2O	-2	H+1				

SI 3.3A: Modelled Saturation Indices of possible mineral phases under given aqueous conditions for biochar

Mineral	log IAP	Saturation Index	Stoichiometry and mineral components									
Chloropyromorphite(c)	-61.25	23.18	5	Pb+2	3	PO4-3	1	Cl-1				
Chloropyromorphite(soil)	-61.25	19.15	5	Pb+2	3	PO4-3	1	Cl-1				
Hydroxylpyromorphite	-49.16	13.63	5	Pb+2	3	PO4-3	1	H2O	-1	H+1		
Brochantite	25.20	9.98	4	Cu+2	6	H2O	-6	H+1	1	SO4-2		
Tsumebite	-0.38	9.41	-3	H+1	2	Pb+2	1	Cu+2	1	PO4-3	6	H2O
Cd4(OH)6SO4(s)	37.38	8.98	-6	H+1	4	Cd+2	6	H2O	1	SO4-2		
Langite	25.20	7.71	-6	H+1	4	Cu+2	7	H2O	1	SO4-2		
Pb4(OH)6SO4(S)	27.70	6.60	-6	H+1	4	Pb+2	1	SO4-2	6	H2O		
Pb3(PO4)2s	-36.93	6.60	3	Pb+2	2	PO4-3						
PB4O2SO4(s)	27.71	5.83	-6	H+1	4	Pb+2	1	SO4-2	3	H2O		
Anterite	13.35	4.56	3	Cu+2	4	H2O	-4	H+1	1	SO4-2		
Pb3O2SO4(s)	15.23	4.54	-4	H+1	3	Pb+2	1	SO4-2	2	H2O		
Pb(OH)2(s)	12.48	4.33	-2	H+1	1	Pb+2	2	H2O				
Atacamite	11.61	4.22	2	Cu+2	3	H2O	-3	H+1	1	Cl-1		
Tenorite(c)	11.85	4.21	1	Cu+2	-2	H+1	1	H2O				
PB2(OH)3Cl(s)	12.87	4.07	-3	H+1	2	Pb+2	3	H2O	1	Cl-1		
Tenorite(am)	11.85	3.36	1	Cu+2	1	H2O	-2	H+1				
Larnakite	2.75	3.19	-2	H+1	2	Pb+2	1	SO4-2	1	H2O		
Cd3(PO4)2(s)	-29.68	2.92	3	Cd+2	2	PO4-3						
Zn5(OH)8Cl2(s)	41.14	2.64	-8	H+1	5	Zn+2	8	H2O	2	Cl-1		
Cu(OH)2(s)	11.85	2.56	1	Cu+2	2	H2O	-2	H+1				
Zincite	13.06	1.83	1	Zn+2	1	H2O	-2	H+1				
Cu2(OH)3NO3(s)	10.98	1.73	2	Cu+2	3	H2O	-3	H+1	1	NO3-1		
Zn4(OH)6SO4(s)	30.05	1.65	-6	H+1	4	Zn+2	6	H2O	1	SO4-2		
Zn(OH)2(epsilon)	13.06	1.53	1	Zn+2	2	H2O	-2	H+1				
Zn(OH)2(gamma)	13.06	1.33	1	Zn+2	2	H2O	-2	H+1				
Zn(OH)2(beta)	13.06	1.31	1	Zn+2	2	H2O	-2	H+1				
Cd(OH)2(s)	14.89	1.25	1	Cd+2	2	H2O	-2	H+1				
Zn(OH)2(delta)	13.06	1.22	1	Zn+2	-2	H+1	2	H2O				
Zn(OH)2(am)	13.06	0.59	1	Zn+2	2	H2O	-2	H+1				
Zn3(PO4)2:4H2)(s)	-35.18	0.24	3	Zn+2	2	PO4-3	4	H2O				

SI 3.3B: Modelled Saturation Indices of possible mineral phases under given aqueous conditions for wood ash amended sorbents (WA and WAS)

Note: Modelling was done inputting the mineral components which are seen to be oversaturated from Table SI 2A and 2B. Sorption % is not considered since biochar surface is very heterogeneous and it is not possible to precisely attribute specific sorption sites.

	Component	% dissolved	% precipitated
BC	Cd+2	100.00	0.00
	Cu+2	0.05	99.96
	Pb+2	0.41	99.59
	PO4-3	0.00	100.00
	Zn+2	100.00	0.00
WA and WAS	Component	% dissolved	% precipitated
	Cd+2	0.57	99.43
	Cu+2	0.0	100.00
	Pb+2	0.00	100.00
	PO4-3	27.25	72.76
	SO4-2	99.03	0.97
	Zn+2	1.47	98.53

SI 3.3C: Modelled percentage of dissolved and precipitated components under given aqueous conditions for BC and wood ash amended chars (WA and WAS)

SI 3.3, 3.3A, 3.3B and 3.3C are referred to in section 3.3.2 (results and discussion section of chapter 3) whilst discussing the importance of changes in speciation relating to precipitation.

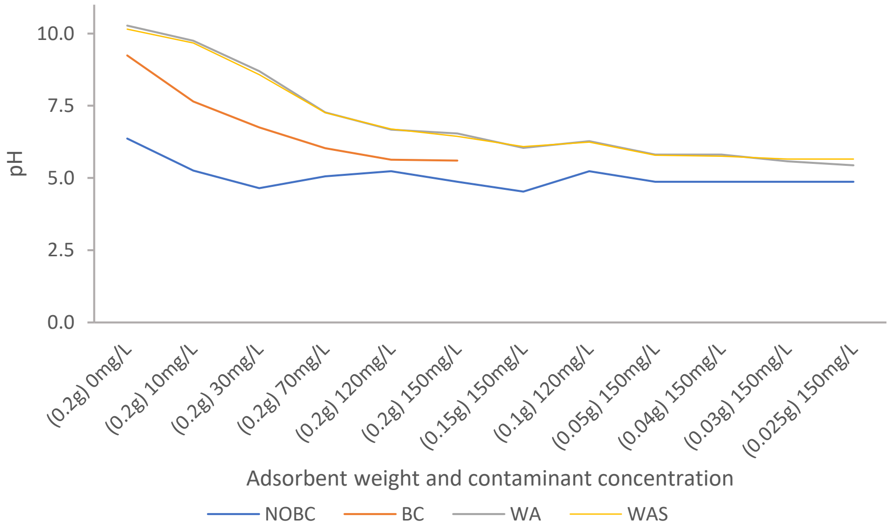
	Supernatant Δ pH											
	0mg/L	(0.2g) 10mg/L	(0.2g) 30mg/L	(0.2g) 70mg/L	(0.2g) 120mg/L	(0.2g) 150mg/L	(0.15g) 150mg/L	(0.1g) 120mg/L	(0.05g) 150mg/L	(0.04) 150mg/L	(0.03) 150mg/L	(0.025) 150mg/L
BC1		2.47	2.19	0.97	0.29	0.71						
BC2		2.38	2.06	0.95	0.43	0.75						
BC3		2.3	2.06	1.00	0.47	0.74						
WA1		4.37	3.95	2.19	1.38	1.63	1.42	1.04	0.93	0.87	0.68	0.59
WA2		4.53	4.07	2.19	1.47	1.69	1.49	1.01	0.91	0.98	0.69	0.50
WA3		4.57	4.14	2.25	1.47	1.69	1.63	1.05	0.97	0.96	0.74	0.62
WAS1		4.6	3.96	2.20	1.50	1.60	1.55	1.03	0.95	0.89	0.74	0.69
WAS2		4.35	3.92	2.17	1.43	1.57	1.58	1.03	0.91	0.89	0.84	0.89
WAS3		4.29	3.91	2.22	1.43	1.55	1.56	0.96	0.90	0.88	0.78	0.78

SI 3.4 A: Δ pH for pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS), column headings detail both concentration of metal solution and amount of biochar.

Study Material	Pb Correlation	Cu Correlation	Zn Correlation	Cd Correlation
BC	97%	98%	72%	73%
WA			82%	85%
WAS			85%	87%
WA >70 mg/l	75%	79%		
WAS>70 mg/L	74%	78%		

Pearson's correlation coefficient $p<0.001$

SI 3.4 B: – correlation between Δ pH for pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) and Pb, Cu, Zn, Cd



SI 3.4C: Measurements of pH for pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA), larch biochar sintered with wood ash (WAS) and deionised water not subjected to biochar or amended biochar (NO BC). Measurements were taken with a known quantity of BC, WA or WAS with a known concentration of Pb, Cu, Zn and Cd.

SI 3.4A, 3.4B, and 3.4C are referred to in section 3.3.2 (results and discussion section of chapter 3) and 6.3 whilst discussing the importance of changes in pH relating to precipitation. SI 3.4C is also referred to in section 6.5 (discussion chapter) in the discussion around the implications of high effluent pH.

	Total P (mg/L)	Total P standard deviation	Si (mg/L)	Si standard deviation	Phosphate (mg/L)	Phosphate standard deviation
BC1	0.42		0.27		1.30	
BC2	0.45		0.24		1.40	
BC3	0.42		0.27		1.39	
BC		0.01		0.01		0.05
BC_10ppm1	0.06		0.27		0.00	
BC_10ppm2	0.03		0.24		0.00	
BC_10ppm3	0.03		0.24		0.00	
BC_10ppm		0.01		0.01		-
WA1	0.15		2.52		0.58	
WA2	0.18		2.55		0.67	
WA3	0.18		2.52		0.59	
WA		0.01		0.01		0.04
WA_10ppm1	0.06		1.92		0.00	
WA_10ppm2	0.09		2.07		0.00	
WA_10ppm3	0.09		2.19		0.00	
WA_10ppm		0.01		0.11		-
WAS1	0.24		2.49		0.76	
WAS2	0.18		2.43		0.59	
WAS3	0.21		2.40		0.62	
WAS		0.02		0.04		0.07
WAS_10ppm1	0.09		1.98		0.00	
WAS_10ppm2	0.09		2.01		0.00	
WAS_10ppm3	0.09		2.04		0.00	

WAS_10ppm		0.00		0.02		-

SI 3.5: Concentration of Total P, phosphate (PO_4^{3-}) and Si in solution in the presence of different sorbents without and with metals

SI 3.5 is referred to in section 3.3.2 (results and discussion section of chapter 3) to indicate the importance of co-precipitation as a mechanism.

	Ca	Ca standard deviation	K	K standard deviation	Mg	Mg standard deviation	Na	Na standard deviation
BC1	4.62		10.43		0.88		1.08	
BC2	2.07		12.39		0.55		1.05	
BC3	3.66		10.76		0.72		1.01	
BC		1.05		0.86		0.13		0.03
BC_10ppm1	2.95		18.05		1.38		1.55	
BC_10ppm2	3.02		16.89		1.32		1.36	
BC_10ppm3	2.91		16.65		1.29		1.32	
BC_10ppm		0.05		0.61		0.04		0.10
WA1	9.00		105.17		0.64		97.24	
WA2	7.97		105.80		0.59		103.35	
WA3	9.31		112.94		0.65		105.92	
WA		0.57		3.53		0.03		3.64
WA_10ppm1	18.86		108.28		0.99		101.80	
WA_10ppm2	21.31		115.18		1.51		97.06	
WA_10ppm3	26.78		130.87		1.18		112.82	
WA_10ppm		3.31		9.45		0.21		6.60
WAS1	9.39		109.79		1.06		103.00	
WAS2	10.43		108.07		1.11		97.30	
WAS3	11.45		113.29		1.16		100.29	
WAS		0.84		2.17		0.04		2.33
WAS_10ppm1	18.34		107.59		1.43		99.37	
WAS_10ppm2	22.27		112.12		1.47		98.33	
WAS_10ppm3	21.72		125.42		1.06		113.36	
WAS_10ppm		1.74		7.57		0.19		6.85

SI 3.6: Concentration of base cations in solution in the presence of the different sorbents without and with metals (n=3)

SI 3.6 is referred to in section 3.3.2 (results and discussion section of chapter 3) to indicate the importance of ion exchange as a mechanism.

SI 3.3.3 Solid Phase Analysis - immobilisation via precipitation and ion exchange

cm-1	BC pre immobilisation	WA pre immobilisation	WAS pre immobilisation
4000	0.020179	0.003488	0.004804
3996	0.020224	0.003576	0.00476
3992	0.020224	0.003576	0.00476
3988	0.020179	0.003532	0.00476
3984	0.020179	0.003532	0.00476
3980	0.020179	0.003532	0.004804
3976	0.020088	0.003488	0.00476
3972	0.020179	0.003532	0.00476
3968	0.020224	0.003576	0.004848
3964	0.020315	0.003576	0.004892
3960	0.02027	0.003488	0.004804
3956	0.02027	0.003576	0.004804
3952	0.020361	0.003663	0.004804
3948	0.020315	0.003576	0.004804
3944	0.02027	0.003576	0.004848
3940	0.02027	0.00362	0.004892
3936	0.02027	0.003663	0.004935
3932	0.020224	0.00362	0.004804
3928	0.020224	0.003576	0.004804
3924	0.020224	0.003532	0.004848
3920	0.02027	0.003532	0.004848
3916	0.02027	0.003576	0.004935
3912	0.02027	0.003576	0.004848
3908	0.020315	0.00362	0.004848
3904	0.02027	0.00362	0.004848
3900	0.020361	0.003532	0.004892
3896	0.02027	0.003532	0.00476
3892	0.020315	0.003488	0.00476
3888	0.020315	0.003488	0.004935
3884	0.020361	0.003576	0.004935
3880	0.02027	0.003488	0.004892
3876	0.02027	0.003488	0.004892
3872	0.020315	0.003576	0.004892
3868	0.020452	0.003576	0.004979
3864	0.020315	0.003488	0.004848
3860	0.020224	0.003532	0.004804
3856	0.020452	0.003401	0.004979
3852	0.020497	0.003532	0.004979

3848	0.02027	0.003576	0.004935
3844	0.02027	0.00362	0.004935
3840	0.020406	0.003488	0.004892
3836	0.020406	0.003532	0.004892
3832	0.02027	0.003576	0.004935
3828	0.02027	0.00362	0.004935
3824	0.020361	0.003576	0.004979
3820	0.02027	0.003532	0.004935
3816	0.020315	0.00362	0.004979
3812	0.020315	0.00362	0.004935
3808	0.020224	0.003576	0.004892
3804	0.020315	0.003532	0.004892
3800	0.020361	0.003532	0.004979
3796	0.020179	0.003576	0.004848
3792	0.020133	0.003663	0.004892
3788	0.020133	0.003663	0.004848
3784	0.020179	0.003663	0.004935
3780	0.020133	0.003576	0.004935
3776	0.020179	0.003707	0.005023
3772	0.020179	0.003663	0.005023
3768	0.02027	0.00362	0.004979
3764	0.020179	0.003663	0.004892
3760	0.02027	0.003707	0.005023
3756	0.020224	0.00362	0.005023
3752	0.020361	0.003488	0.004979
3748	0.020452	0.003488	0.005111
3744	0.020497	0.00362	0.005199
3740	0.020224	0.00362	0.004892
3736	0.020179	0.003488	0.00476
3732	0.020042	0.003445	0.004804
3728	0.020179	0.003576	0.004848
3724	0.020088	0.003576	0.004892
3720	0.019951	0.003488	0.004935
3716	0.019997	0.003576	0.005023
3712	0.020179	0.00362	0.004979
3708	0.020042	0.003576	0.004892
3704	0.019951	0.003488	0.004804
3700	0.019997	0.003532	0.004804
3696	0.019815	0.003488	0.004716
3692	0.019815	0.003488	0.00476
3688	0.019951	0.003488	0.004804
3684	0.019951	0.00362	0.004935
3680	0.01986	0.003488	0.004804
3676	0.019906	0.003445	0.004804
3672	0.020088	0.003532	0.004935

3668	0.019906	0.003488	0.004848
3664	0.019815	0.003532	0.004804
3660	0.019906	0.003663	0.004892
3656	0.019951	0.00362	0.004892
3652	0.020042	0.003445	0.004935
3648	0.020042	0.003401	0.004979
3644	0.019906	0.003532	0.004804
3640	0.01986	0.003576	0.00476
3636	0.019951	0.003532	0.004804
3632	0.020042	0.003532	0.004892
3628	0.020088	0.003401	0.004979
3624	0.019951	0.003532	0.004804
3620	0.01986	0.003488	0.004804
3616	0.019951	0.003576	0.004892
3612	0.019951	0.003401	0.004892
3608	0.020042	0.003532	0.004935
3604	0.019997	0.00362	0.004848
3600	0.01986	0.003576	0.004848
3596	0.019906	0.003576	0.004848
3592	0.019997	0.00362	0.004892
3588	0.019997	0.003532	0.004892
3584	0.019906	0.003576	0.004892
3580	0.019815	0.003488	0.004892
3576	0.01986	0.003576	0.004935
3572	0.019906	0.003663	0.004935
3568	0.019997	0.003576	0.004979
3564	0.019997	0.003532	0.004979
3560	0.019906	0.00362	0.004979
3556	0.019906	0.00362	0.005067
3552	0.019906	0.003576	0.005067
3548	0.019997	0.00362	0.005023
3544	0.020042	0.003663	0.005023
3540	0.019951	0.003663	0.005067
3536	0.019951	0.00362	0.004979
3532	0.019997	0.003663	0.005023
3528	0.020088	0.003751	0.005155
3524	0.020088	0.003707	0.005155
3520	0.020042	0.003751	0.005067
3516	0.019997	0.003751	0.005111
3512	0.019997	0.003663	0.005067
3508	0.019997	0.003663	0.005111
3504	0.020088	0.003707	0.005155
3500	0.019997	0.003663	0.005111
3496	0.020042	0.003663	0.005067
3492	0.020042	0.003707	0.005067

3488	0.020042	0.003795	0.005155
3484	0.020133	0.003751	0.005199
3480	0.020088	0.003663	0.005155
3476	0.020088	0.003795	0.005199
3472	0.020088	0.003751	0.005155
3468	0.020042	0.003663	0.005067
3464	0.020179	0.003795	0.005243
3460	0.020179	0.003751	0.005287
3456	0.020133	0.003751	0.005199
3452	0.020224	0.003795	0.005243
3448	0.020179	0.003795	0.005243
3444	0.020179	0.003795	0.005199
3440	0.020133	0.003707	0.005199
3436	0.020042	0.003707	0.005199
3432	0.020179	0.003751	0.005243
3428	0.02027	0.003839	0.005331
3424	0.020224	0.003795	0.005243
3420	0.02027	0.003839	0.005243
3416	0.020315	0.003883	0.005331
3412	0.02027	0.003795	0.005287
3408	0.020315	0.003839	0.005243
3404	0.02027	0.003839	0.005331
3400	0.02027	0.003795	0.005375
3396	0.020315	0.003839	0.005331
3392	0.02027	0.003795	0.005287
3388	0.020224	0.003795	0.005243
3384	0.02027	0.003751	0.005243
3380	0.020315	0.003751	0.005287
3376	0.020315	0.003839	0.005287
3372	0.02027	0.003795	0.005287
3368	0.02027	0.003795	0.005287
3364	0.020315	0.003795	0.005287
3360	0.020315	0.003751	0.005287
3356	0.020315	0.003751	0.005287
3352	0.020224	0.003751	0.005243
3348	0.020224	0.003751	0.005287
3344	0.020224	0.003751	0.005287
3340	0.020179	0.003795	0.005243
3336	0.02027	0.003751	0.005243
3332	0.02027	0.003707	0.005243
3328	0.020224	0.003707	0.005199
3324	0.020179	0.00362	0.005243
3320	0.020224	0.003707	0.005243
3316	0.020315	0.003839	0.005331
3312	0.02027	0.003795	0.005331

3308	0.020179	0.003751	0.005243
3304	0.020179	0.003751	0.005243
3300	0.020179	0.003751	0.005287
3296	0.020179	0.003751	0.005287
3292	0.020133	0.003707	0.005287
3288	0.020224	0.003751	0.005287
3284	0.020133	0.003663	0.005243
3280	0.020133	0.003707	0.005243
3276	0.020224	0.003751	0.005243
3272	0.020224	0.003751	0.005287
3268	0.02027	0.003795	0.005287
3264	0.020224	0.003751	0.005243
3260	0.020088	0.003751	0.005243
3256	0.020133	0.003751	0.005287
3252	0.020224	0.003751	0.005287
3248	0.020088	0.003751	0.005243
3244	0.020179	0.003795	0.005199
3240	0.020224	0.003663	0.005243
3236	0.020088	0.003663	0.005243
3232	0.020088	0.003795	0.005243
3228	0.020088	0.003751	0.005155
3224	0.020088	0.003707	0.005199
3220	0.020179	0.003751	0.005199
3216	0.020133	0.003707	0.005111
3212	0.020133	0.003751	0.005155
3208	0.020088	0.003707	0.005199
3204	0.020133	0.003795	0.005243
3200	0.020133	0.003751	0.005155
3196	0.020088	0.003795	0.005155
3192	0.020088	0.003751	0.005155
3188	0.020179	0.003707	0.005199
3184	0.020133	0.003751	0.005155
3180	0.020179	0.003795	0.005199
3176	0.020088	0.003663	0.005155
3172	0.020133	0.003707	0.005155
3168	0.020179	0.003839	0.005199
3164	0.020088	0.003751	0.005155
3160	0.020133	0.003751	0.005155
3156	0.020133	0.003795	0.005111
3152	0.020088	0.003795	0.005199
3148	0.020042	0.003751	0.005155
3144	0.020179	0.003839	0.005155
3140	0.020133	0.003751	0.005111
3136	0.020088	0.003751	0.005111
3132	0.020088	0.003707	0.005111

3128	0.020133	0.003795	0.005155
3124	0.020133	0.003751	0.005111
3120	0.020088	0.003707	0.005155
3116	0.020042	0.003751	0.005111
3112	0.020088	0.003795	0.005111
3108	0.020042	0.003751	0.005111
3104	0.020042	0.003751	0.005155
3100	0.019997	0.003707	0.005111
3096	0.020088	0.003795	0.005111
3092	0.020088	0.003663	0.005111
3088	0.020088	0.003751	0.005155
3084	0.020042	0.003707	0.005155
3080	0.020042	0.003751	0.005111
3076	0.020179	0.003795	0.005199
3072	0.020133	0.003795	0.005199
3068	0.020042	0.003751	0.005199
3064	0.020133	0.003795	0.005287
3060	0.020179	0.003795	0.005199
3056	0.020133	0.003707	0.005199
3052	0.020133	0.003751	0.005155
3048	0.020133	0.003795	0.005067
3044	0.020088	0.003707	0.005155
3040	0.020133	0.003795	0.005155
3036	0.020179	0.003751	0.005199
3032	0.020179	0.003839	0.005199
3028	0.020179	0.003795	0.005155
3024	0.020179	0.003751	0.005155
3020	0.020133	0.003751	0.005199
3016	0.020088	0.003795	0.005243
3012	0.020042	0.003795	0.005199
3008	0.020088	0.003751	0.005199
3004	0.020179	0.003795	0.005199
3000	0.020179	0.003795	0.005199
2996	0.020179	0.003839	0.005243
2992	0.020179	0.003751	0.005199
2988	0.020179	0.003839	0.005243
2984	0.020224	0.003839	0.005287
2980	0.02027	0.003839	0.005287
2976	0.020133	0.003663	0.005199
2972	0.020088	0.00362	0.005199
2968	0.019997	0.003532	0.005155
2964	0.020088	0.003532	0.005243
2960	0.020088	0.003445	0.005155
2956	0.020133	0.003488	0.005243
2952	0.020042	0.003488	0.005243

2948	0.020133	0.003488	0.005287
2944	0.020088	0.003445	0.005287
2940	0.020179	0.003401	0.005287
2936	0.020224	0.003269	0.005243
2932	0.020224	0.003182	0.005243
2928	0.020315	0.003226	0.005199
2924	0.020361	0.003226	0.005243
2920	0.02027	0.003269	0.005243
2916	0.020224	0.003313	0.005243
2912	0.020179	0.003401	0.005243
2908	0.020179	0.003488	0.005287
2904	0.020224	0.003532	0.005287
2900	0.020179	0.00362	0.005287
2896	0.020179	0.003532	0.005287
2892	0.020224	0.003663	0.005375
2888	0.020179	0.00362	0.005287
2884	0.020088	0.003576	0.005287
2880	0.020133	0.00362	0.005375
2876	0.020133	0.003576	0.005331
2872	0.020133	0.003532	0.005375
2868	0.020179	0.003576	0.005375
2864	0.020133	0.003532	0.005375
2860	0.020042	0.003488	0.005375
2856	0.020179	0.003488	0.005375
2852	0.020224	0.003532	0.005331
2848	0.020224	0.00362	0.005419
2844	0.020179	0.003707	0.005419
2840	0.020133	0.003707	0.005375
2836	0.020088	0.003707	0.005331
2832	0.020133	0.003751	0.005287
2828	0.020088	0.003795	0.005375
2824	0.020088	0.003839	0.005375
2820	0.020088	0.003795	0.005331
2816	0.020088	0.003839	0.005331
2812	0.020179	0.003839	0.005331
2808	0.020179	0.003883	0.005375
2804	0.020179	0.003883	0.005375
2800	0.020133	0.003839	0.005375
2796	0.020133	0.003883	0.005419
2792	0.020133	0.003839	0.005375
2788	0.020088	0.003795	0.005375
2784	0.020133	0.003883	0.005419
2780	0.020133	0.003926	0.005375
2776	0.020179	0.003926	0.005463
2772	0.020133	0.003883	0.005375

2768	0.020133	0.003883	0.005331
2764	0.020179	0.00397	0.005375
2760	0.020179	0.00397	0.005375
2756	0.020133	0.00397	0.005331
2752	0.020224	0.003926	0.005375
2748	0.020179	0.003926	0.005419
2744	0.020224	0.00397	0.005419
2740	0.020224	0.00397	0.005419
2736	0.020224	0.004058	0.005463
2732	0.020179	0.004014	0.005419
2728	0.020133	0.003926	0.005331
2724	0.020179	0.00397	0.005375
2720	0.020133	0.00397	0.005375
2716	0.020179	0.00397	0.005419
2712	0.020133	0.00397	0.005419
2708	0.020179	0.004014	0.005419
2704	0.020179	0.004014	0.005419
2700	0.020224	0.004058	0.005463
2696	0.020224	0.004014	0.005463
2692	0.02027	0.004014	0.005463
2688	0.020224	0.004014	0.005463
2684	0.020133	0.004014	0.005463
2680	0.020179	0.004014	0.005463
2676	0.020224	0.004058	0.005463
2672	0.020224	0.004102	0.005463
2668	0.020224	0.004102	0.005507
2664	0.020361	0.004233	0.005683
2660	0.020543	0.004409	0.005815
2656	0.020543	0.004409	0.005903
2652	0.020588	0.004496	0.005947
2648	0.020497	0.004496	0.005903
2644	0.020497	0.004409	0.005903
2640	0.020497	0.004453	0.005947
2636	0.020406	0.004453	0.005903
2632	0.020406	0.004409	0.005859
2628	0.020315	0.004409	0.005903
2624	0.020224	0.004277	0.005771
2620	0.020133	0.004233	0.005683
2616	0.020133	0.004277	0.005683
2612	0.019951	0.004189	0.005639
2608	0.019906	0.004102	0.005463
2604	0.019906	0.004189	0.005551
2600	0.019906	0.004146	0.005507
2596	0.01986	0.004058	0.005507
2592	0.019769	0.004014	0.005463

2588	0.019769	0.004058	0.005551
2584	0.019815	0.004058	0.005419
2580	0.019815	0.004058	0.005507
2576	0.019678	0.00397	0.005419
2572	0.019588	0.00397	0.005331
2568	0.019588	0.004014	0.005375
2564	0.019588	0.003926	0.005375
2560	0.019724	0.004014	0.005419
2556	0.019633	0.003926	0.005375
2552	0.019542	0.003839	0.005287
2548	0.019497	0.003926	0.005243
2544	0.019406	0.003926	0.005243
2540	0.019406	0.003883	0.005155
2536	0.019451	0.003883	0.005111
2532	0.019179	0.003663	0.005111
2528	0.019406	0.003926	0.005243
2524	0.01936	0.003926	0.005155
2520	0.01936	0.003839	0.005023
2516	0.019406	0.003839	0.005199
2512	0.019497	0.003926	0.005287
2508	0.019451	0.003926	0.005199
2504	0.019315	0.003839	0.005155
2500	0.01927	0.003707	0.005155
2496	0.019406	0.003839	0.005243
2492	0.01936	0.003926	0.005199
2488	0.01927	0.003883	0.005155
2484	0.019224	0.003751	0.005155
2480	0.019315	0.003839	0.005199
2476	0.019224	0.003795	0.005155
2472	0.01927	0.003883	0.005155
2468	0.019224	0.003839	0.005155
2464	0.01927	0.003839	0.005243
2460	0.019224	0.003795	0.005155
2456	0.019406	0.003883	0.005243
2452	0.01936	0.003926	0.005243
2448	0.01927	0.003883	0.005243
2444	0.019224	0.003839	0.005111
2440	0.01927	0.003795	0.005111
2436	0.019179	0.003839	0.005023
2432	0.019179	0.003707	0.005067
2428	0.018952	0.00362	0.004935
2424	0.018997	0.003707	0.004979
2420	0.018952	0.003663	0.005023
2416	0.019088	0.003707	0.004935
2412	0.019088	0.003751	0.004979

2408	0.019043	0.003663	0.004979
2404	0.018952	0.003576	0.004935
2400	0.018907	0.00362	0.004935
2396	0.018952	0.003751	0.004935
2392	0.018997	0.003707	0.004892
2388	0.018907	0.003532	0.004848
2384	0.018907	0.003576	0.004716
2380	0.018816	0.003488	0.004496
2376	0.018771	0.003576	0.004453
2372	0.018952	0.003576	0.004496
2368	0.018861	0.003576	0.004321
2364	0.018952	0.003576	0.004277
2360	0.019315	0.003926	0.004496
2356	0.019088	0.003751	0.004453
2352	0.019043	0.003663	0.004496
2348	0.01936	0.00397	0.00454
2344	0.01936	0.004058	0.004672
2340	0.019451	0.004146	0.004979
2336	0.019451	0.004102	0.005023
2332	0.01927	0.00397	0.005067
2328	0.019633	0.004365	0.005331
2324	0.020634	0.005287	0.00652
2320	0.019951	0.004716	0.005903
2316	0.019906	0.004628	0.005683
2312	0.019633	0.004496	0.005551
2308	0.019588	0.004453	0.005639
2304	0.019542	0.004365	0.005551
2300	0.019678	0.00454	0.005639
2296	0.019724	0.004584	0.005727
2292	0.019815	0.00476	0.006079
2288	0.019997	0.004979	0.006343
2284	0.019906	0.004979	0.006255
2280	0.019588	0.004716	0.005947
2276	0.019406	0.004321	0.005727
2272	0.019179	0.004189	0.005463
2268	0.019633	0.00454	0.005859
2264	0.01927	0.004233	0.005639
2260	0.019179	0.004277	0.005595
2256	0.019133	0.004233	0.005595
2252	0.018816	0.00397	0.005331
2248	0.018952	0.004102	0.005375
2244	0.019088	0.00397	0.005683
2240	0.018861	0.004146	0.005727
2236	0.018771	0.004014	0.005155
2232	0.01868	0.00397	0.005419

2228	0.018907	0.004058	0.005595
2224	0.018408	0.003926	0.005375
2220	0.018589	0.004014	0.005199
2216	0.018816	0.003883	0.005199
2212	0.018861	0.00397	0.005331
2208	0.018499	0.003751	0.005243
2204	0.01868	0.00397	0.005199
2200	0.019088	0.004496	0.005507
2196	0.018952	0.004321	0.005683
2192	0.018453	0.004102	0.005551
2188	0.018816	0.003926	0.005639
2184	0.018771	0.003795	0.004935
2180	0.018091	0.003357	0.004584
2176	0.018317	0.00397	0.005067
2172	0.018408	0.003751	0.005155
2168	0.019224	0.00454	0.006211
2164	0.018952	0.004058	0.005771
2160	0.018408	0.003883	0.005287
2156	0.014843	0.001218	0.002133
2152	0.015968	0.001697	0.00292
2148	0.016644	0.002745	0.003883
2144	0.016599	0.002439	0.003488
2140	0.017231	0.003007	0.003839
2136	0.01678	0.00257	0.003313
2132	0.016329	0.002046	0.00292
2128	0.017006	0.002832	0.003795
2124	0.017412	0.003051	0.004365
2120	0.017729	0.003357	0.004453
2116	0.018046	0.00362	0.004804
2112	0.018363	0.003926	0.004935
2108	0.018181	0.003883	0.004979
2104	0.018136	0.003926	0.005067
2100	0.018046	0.003488	0.004935
2096	0.017684	0.003445	0.00476
2092	0.017774	0.003357	0.00454
2088	0.018091	0.00362	0.004892
2084	0.018091	0.003926	0.005111
2080	0.018272	0.004058	0.005331
2076	0.018363	0.00397	0.005287
2072	0.018272	0.00397	0.005067
2068	0.018091	0.003839	0.005067
2064	0.018091	0.003707	0.005199
2060	0.018181	0.003926	0.005023
2056	0.018181	0.004146	0.005375
2052	0.018997	0.004628	0.005815

2048	0.018408	0.004189	0.005375
2044	0.018091	0.00362	0.005111
2040	0.018	0.00362	0.005287
2036	0.018272	0.003926	0.005331
2032	0.017638	0.003182	0.00454
2028	0.017774	0.003313	0.004365
2024	0.017457	0.00292	0.004409
2020	0.017322	0.003401	0.004628
2016	0.017322	0.003357	0.004584
2012	0.017412	0.003226	0.004409
2008	0.01687	0.002614	0.004189
2004	0.016915	0.003182	0.003926
2000	0.017277	0.002876	0.004409
1996	0.017774	0.00292	0.004321
1992	0.01791	0.00362	0.004892
1988	0.017141	0.003532	0.004935
1984	0.017548	0.003839	0.005595
1980	0.018634	0.004409	0.006299
1976	0.017186	0.002963	0.004189
1972	0.016509	0.003051	0.004014
1968	0.016735	0.003094	0.004058
1964	0.016148	0.002614	0.003839
1960	0.016238	0.00257	0.003751
1956	0.016193	0.002526	0.003532
1952	0.016554	0.002832	0.00397
1948	0.01678	0.003357	0.004628
1944	0.016825	0.003094	0.004365
1940	0.017186	0.003313	0.004365
1936	0.01696	0.003182	0.004409
1932	0.01696	0.003357	0.004277
1928	0.016915	0.002963	0.004233
1924	0.017096	0.003269	0.004365
1920	0.017277	0.003313	0.004628
1916	0.01696	0.003182	0.004496
1912	0.01696	0.003313	0.004496
1908	0.017051	0.003269	0.004628
1904	0.017051	0.003488	0.00476
1900	0.017096	0.003357	0.004716
1896	0.017322	0.003707	0.004892
1892	0.017096	0.003357	0.004672
1888	0.017231	0.003488	0.004892
1884	0.017141	0.003488	0.004935
1880	0.017277	0.003751	0.005023
1876	0.017277	0.003751	0.004935
1872	0.017006	0.003532	0.004804

1868	0.017186	0.00362	0.005023
1864	0.017231	0.003795	0.005067
1860	0.017186	0.003707	0.004892
1856	0.017096	0.003707	0.004935
1852	0.017231	0.003751	0.005111
1848	0.017231	0.003707	0.005023
1844	0.017141	0.003576	0.005111
1840	0.017006	0.003663	0.004979
1836	0.017141	0.003751	0.004979
1832	0.017186	0.003795	0.005243
1828	0.017141	0.003795	0.005155
1824	0.017231	0.003839	0.005243
1820	0.017141	0.003751	0.005111
1816	0.017051	0.003707	0.004979
1812	0.017141	0.003839	0.005111
1808	0.017322	0.003883	0.005287
1804	0.017322	0.00397	0.005419
1800	0.017277	0.004058	0.005507
1796	0.017231	0.004014	0.005551
1792	0.017367	0.004102	0.005639
1788	0.017457	0.004058	0.005595
1784	0.017367	0.004102	0.005551
1780	0.017367	0.004102	0.005595
1776	0.017322	0.004058	0.005551
1772	0.017231	0.004102	0.005595
1768	0.017367	0.004102	0.005639
1764	0.017367	0.004146	0.005727
1760	0.017412	0.004058	0.005727
1756	0.017457	0.004102	0.005771
1752	0.017367	0.00397	0.005727
1748	0.017457	0.004058	0.005771
1744	0.017638	0.004014	0.005859
1740	0.017684	0.00397	0.005859
1736	0.017593	0.004014	0.005859
1732	0.017638	0.004058	0.005903
1728	0.017638	0.004058	0.005947
1724	0.017638	0.004058	0.005991
1720	0.017774	0.004146	0.005991
1716	0.017729	0.004014	0.005903
1712	0.017774	0.004146	0.005991
1708	0.017819	0.004233	0.006035
1704	0.017865	0.004277	0.006079
1700	0.017774	0.004233	0.006035
1696	0.018	0.004365	0.006079
1692	0.018046	0.004409	0.006079

1688	0.017865	0.004365	0.006167
1684	0.01791	0.004453	0.006255
1680	0.017955	0.00454	0.006299
1676	0.017955	0.004584	0.006299
1672	0.01791	0.004496	0.006255
1668	0.018091	0.004584	0.006343
1664	0.018046	0.004628	0.006343
1660	0.018181	0.00476	0.006387
1656	0.018272	0.004672	0.006432
1652	0.018544	0.004935	0.006564
1648	0.018589	0.004935	0.006564
1644	0.01868	0.004848	0.00652
1640	0.018771	0.004848	0.006476
1636	0.018952	0.004848	0.006564
1632	0.019224	0.004935	0.006652
1628	0.019406	0.004979	0.006696
1624	0.019588	0.004935	0.00674
1620	0.019769	0.004979	0.006784
1616	0.019951	0.004979	0.00674
1612	0.020179	0.005067	0.00674
1608	0.020361	0.005067	0.006828
1604	0.020406	0.005067	0.006784
1600	0.020588	0.005155	0.007005
1596	0.020634	0.005111	0.006917
1592	0.020816	0.005243	0.006961
1588	0.020816	0.005199	0.006961
1584	0.020953	0.005287	0.007005
1580	0.021044	0.005331	0.007005
1576	0.021044	0.005287	0.006917
1572	0.021135	0.005331	0.007049
1568	0.021135	0.005375	0.007137
1564	0.021181	0.005375	0.007226
1560	0.021044	0.005331	0.007226
1556	0.021044	0.005243	0.007181
1552	0.020862	0.005375	0.00727
1548	0.02077	0.005375	0.007402
1544	0.02077	0.005551	0.007579
1540	0.02077	0.005551	0.007667
1536	0.020543	0.005639	0.007667
1532	0.020452	0.005639	0.007712
1528	0.020588	0.005903	0.007933
1524	0.020452	0.005991	0.008021
1520	0.020497	0.006035	0.00811
1516	0.020497	0.006079	0.008198
1512	0.020497	0.006211	0.008287

1508	0.020497	0.006343	0.008331
1504	0.020497	0.006432	0.008508
1500	0.020543	0.006608	0.008641
1496	0.020543	0.006696	0.008774
1492	0.020588	0.006828	0.008863
1488	0.020588	0.006784	0.008996
1484	0.020588	0.006961	0.009129
1480	0.020725	0.007049	0.009217
1476	0.020679	0.007093	0.009217
1472	0.02077	0.007093	0.009395
1468	0.020862	0.007226	0.00935
1464	0.020862	0.007314	0.009484
1460	0.020953	0.007446	0.009528
1456	0.021089	0.007491	0.009661
1452	0.020953	0.007446	0.009572
1448	0.021135	0.007535	0.00975
1444	0.021044	0.007535	0.009706
1440	0.021181	0.007712	0.00975
1436	0.021226	0.007756	0.009794
1432	0.021272	0.0078	0.009883
1428	0.021226	0.007933	0.009972
1424	0.021272	0.008065	0.009972
1420	0.021272	0.008021	0.009883
1416	0.021317	0.00811	0.009928
1412	0.021226	0.008154	0.009883
1408	0.021272	0.00811	0.009661
1404	0.021317	0.008065	0.009572
1400	0.021363	0.008021	0.009528
1396	0.021409	0.007933	0.00935
1392	0.021363	0.007844	0.009173
1388	0.021363	0.007623	0.008996
1384	0.021363	0.007446	0.008863
1380	0.021363	0.007226	0.008641
1376	0.021454	0.007093	0.008552
1372	0.021409	0.006961	0.008375
1368	0.021409	0.006828	0.008331
1364	0.021409	0.006696	0.008242
1360	0.021363	0.006564	0.008198
1356	0.021409	0.00652	0.008065
1352	0.021363	0.006432	0.007933
1348	0.021409	0.006432	0.008021
1344	0.021409	0.006387	0.008021
1340	0.021409	0.006255	0.008021
1336	0.021454	0.006299	0.007933
1332	0.0215	0.006255	0.007933

1328	0.0215	0.006255	0.007844
1324	0.0215	0.006211	0.007844
1320	0.021546	0.006123	0.007889
1316	0.021546	0.006123	0.007889
1312	0.021591	0.006167	0.007977
1308	0.021591	0.006167	0.007933
1304	0.021637	0.006211	0.007933
1300	0.021683	0.006211	0.007889
1296	0.021728	0.006211	0.007889
1292	0.021683	0.006211	0.007844
1288	0.021728	0.006167	0.007933
1284	0.021865	0.006167	0.007977
1280	0.021865	0.006167	0.007933
1276	0.021865	0.006123	0.007933
1272	0.021957	0.006211	0.008021
1268	0.021911	0.006079	0.008021
1264	0.022048	0.006167	0.008021
1260	0.022048	0.006167	0.008021
1256	0.022094	0.006123	0.008021
1252	0.022094	0.006167	0.008065
1248	0.022094	0.006123	0.008065
1244	0.022185	0.006211	0.008198
1240	0.022231	0.006211	0.008198
1236	0.022185	0.006255	0.008242
1232	0.022276	0.006299	0.008287
1228	0.022231	0.006299	0.008375
1224	0.022231	0.006343	0.008375
1220	0.022231	0.006387	0.00842
1216	0.022276	0.006432	0.008464
1212	0.022276	0.00652	0.008464
1208	0.022276	0.006564	0.008552
1204	0.022276	0.006696	0.008685
1200	0.022231	0.006696	0.008774
1196	0.022414	0.006828	0.008818
1192	0.022322	0.006784	0.008863
1188	0.022322	0.006873	0.008951
1184	0.022368	0.006917	0.00904
1180	0.022414	0.007049	0.00904
1176	0.022368	0.007049	0.009084
1172	0.022368	0.007137	0.009129
1168	0.022414	0.00727	0.009306
1164	0.022459	0.007402	0.009439
1160	0.022551	0.007535	0.009617
1156	0.022414	0.007535	0.009661
1152	0.022505	0.007844	0.009794

1148	0.022368	0.007667	0.009794
1144	0.022276	0.007756	0.009928
1140	0.022231	0.007844	0.010017
1136	0.022094	0.007844	0.010105
1132	0.022094	0.007933	0.010328
1128	0.022094	0.008065	0.010506
1124	0.021957	0.00811	0.010684
1120	0.022002	0.008242	0.010862
1116	0.022002	0.008375	0.01104
1112	0.022002	0.008552	0.011396
1108	0.021819	0.008508	0.011575
1104	0.021865	0.008863	0.011798
1100	0.021728	0.008863	0.011976
1096	0.021957	0.009217	0.012468
1092	0.021957	0.00935	0.012736
1088	0.021774	0.009217	0.012602
1084	0.021774	0.009306	0.012423
1080	0.021591	0.009173	0.012468
1076	0.021637	0.009306	0.012512
1072	0.021637	0.009572	0.013004
1068	0.021546	0.009617	0.013183
1064	0.021546	0.009794	0.013363
1060	0.0215	0.009972	0.013497
1056	0.021409	0.01015	0.013811
1052	0.021454	0.010283	0.013945
1048	0.021409	0.010461	0.014214
1044	0.021272	0.010595	0.014214
1040	0.021363	0.010728	0.014214
1036	0.021089	0.010684	0.014214
1032	0.021044	0.010595	0.01408
1028	0.021135	0.010951	0.014035
1024	0.020862	0.010728	0.013676
1020	0.020907	0.010595	0.013318
1016	0.020862	0.010506	0.013228
1012	0.020862	0.010328	0.013049
1008	0.020816	0.010328	0.012736
1004	0.020634	0.010061	0.012557
1000	0.020452	0.009972	0.012512
996	0.020406	0.009928	0.012334
992	0.020452	0.009883	0.012289
988	0.020361	0.009928	0.0122
984	0.02027	0.009794	0.012066
980	0.020088	0.00975	0.011887
976	0.020179	0.009706	0.011798
972	0.020088	0.009572	0.011798

968	0.020088	0.009528	0.011753
964	0.019997	0.009528	0.011486
960	0.019951	0.009528	0.011352
956	0.019997	0.00935	0.011218
952	0.019678	0.009129	0.010951
948	0.019724	0.009084	0.010684
944	0.019633	0.008685	0.010461
940	0.019724	0.008685	0.010328
936	0.019633	0.008464	0.010194
932	0.019542	0.008287	0.010017
928	0.019497	0.008198	0.009883
924	0.01936	0.00811	0.009794
920	0.01927	0.007977	0.009661
916	0.019542	0.008021	0.00975
912	0.019678	0.008154	0.009706
908	0.019678	0.007933	0.009572
904	0.019769	0.007889	0.009706
900	0.019769	0.007933	0.009661
896	0.020042	0.007977	0.009661
892	0.020042	0.007933	0.009484
888	0.020224	0.007933	0.009572
884	0.020406	0.008154	0.009928
880	0.020543	0.008818	0.010639
876	0.020679	0.009528	0.011352
872	0.02077	0.009794	0.011396
868	0.020406	0.008951	0.010328
864	0.020179	0.008242	0.009839
860	0.020042	0.008154	0.009794
856	0.019951	0.007889	0.009484
852	0.019815	0.007977	0.009528
848	0.019769	0.0078	0.009572
844	0.01986	0.007844	0.009395
840	0.01986	0.007667	0.009395
836	0.019951	0.007712	0.009439
832	0.020088	0.0078	0.009484
828	0.020133	0.0078	0.009484
824	0.020224	0.007756	0.009617
820	0.020224	0.007667	0.009706
816	0.020133	0.007756	0.009528
812	0.020088	0.007756	0.009661
808	0.020088	0.007844	0.009617
804	0.020042	0.007889	0.009528
800	0.019906	0.007667	0.009306
796	0.019769	0.007712	0.009484
792	0.019815	0.0078	0.009528

788	0.019724	0.0078	0.009528
784	0.019678	0.007623	0.009395
780	0.019406	0.007667	0.009306
776	0.019497	0.0078	0.009484
772	0.019542	0.007756	0.009661
768	0.019678	0.007756	0.00975
764	0.019724	0.007667	0.009661
760	0.019815	0.007844	0.009706
756	0.019633	0.008065	0.010017
752	0.019906	0.008242	0.010017
748	0.019588	0.008065	0.009839
744	0.019724	0.008021	0.009972
740	0.019497	0.008065	0.009883
736	0.019406	0.007977	0.009928
732	0.019406	0.007977	0.009839
728	0.01927	0.007977	0.009928
724	0.019179	0.00811	0.010061
720	0.019179	0.00811	0.009883
716	0.018997	0.008464	0.010328
712	0.019043	0.008508	0.010506
708	0.018952	0.008331	0.010283
704	0.018816	0.008287	0.010061
700	0.018816	0.008198	0.01015
696	0.018861	0.00842	0.010283
692	0.018634	0.008375	0.010061
688	0.018634	0.008331	0.010061
684	0.018589	0.008375	0.010194
680	0.018453	0.008198	0.009972
676	0.018589	0.008508	0.009839
672	0.018544	0.008287	0.009928
668	0.017141	0.007446	0.010328
664	0.018634	0.008331	0.010194
660	0.018589	0.008375	0.009928
656	0.018589	0.008331	0.010194
652	0.018725	0.008597	0.010328
648	0.018634	0.008774	0.010328
644	0.018227	0.008464	0.010372
640	0.018272	0.008641	0.010283
636	0.018227	0.008287	0.010194
632	0.018499	0.008863	0.010639
628	0.018453	0.009173	0.01104
624	0.018317	0.00935	0.011174
620	0.018544	0.009794	0.011798
616	0.018589	0.00975	0.011575
612	0.018816	0.009883	0.012244

608	0.018363	0.009928	0.012155
604	0.018771	0.010595	0.012825
600	0.01868	0.010461	0.01211
596	0.018363	0.010105	0.011753
592	0.018408	0.009617	0.01153
588	0.018227	0.009883	0.011352
584	0.018499	0.009617	0.011887
580	0.018861	0.010239	0.0122
576	0.018907	0.010372	0.012423
572	0.018816	0.010417	0.012602
568	0.01868	0.010728	0.012736
564	0.018272	0.01055	0.012691
560	0.017865	0.010105	0.01211
556	0.018227	0.010061	0.011887
552	0.018317	0.009706	0.011352
548	0.018091	0.009572	0.011486
544	0.018499	0.009306	0.011263
540	0.018091	0.009395	0.011307
536	0.018046	0.008996	0.010817
532	0.017729	0.009129	0.010461
528	0.017865	0.009217	0.010372
524	0.018136	0.00904	0.010728
520	0.01791	0.00904	0.010461
516	0.017865	0.008907	0.010728
512	0.018227	0.009572	0.011218
508	0.018317	0.009484	0.011619
504	0.017593	0.008685	0.010684
500	0.017684	0.008818	0.010906
496	0.017593	0.009661	0.011441
492	0.018181	0.009972	0.010995
488	0.018046	0.009572	0.010951
484	0.017593	0.009084	0.010862
480	0.01696	0.009262	0.010817
476	0.016374	0.008464	0.010728
472	0.016825	0.01015	0.011619
468	0.01678	0.009528	0.011619
464	0.017593	0.009528	0.012825
460	0.017277	0.009839	0.011575
456	0.01669	0.00935	0.012066
452	0.016464	0.009395	0.011174
448	0.015923	0.00935	0.011441
444	0.016013	0.010684	0.012647
440	0.016599	0.010328	0.012289
436	0.016329	0.009528	0.011619
432	0.017277	0.010506	0.011486

428	0.017412	0.009661	0.011575
424	0.018453	0.011575	0.01417
420	0.017322	0.010328	0.01399
416	0.017051	0.011352	0.011932
412	0.017684	0.011129	0.011396
408	0.018771	0.009217	0.012468
404	0.017457	0.007977	0.011441
400	0.019588	0.008907	0.014574

SI 3.7: FTIR spectra of pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) before immobilisation of Pb, Cu, Zn and Cd.

SI 3.7 is referred to in section 3.3.3 (results and discussion section of chapter 3) to compare the characteristics of each sorbent, namely: oxygenated functional groups, phosphate and siloxane. This data is plotted in figure 3.4.

cm-1	BC pre immob.	WA pre immob.	WAS pre immob.	BC post immob.	WA post immob.	WAS post immob.
1652	0.018544	0.004935	0.006564	0.0376	0.0042	0.003
1648	0.018589	0.004935	0.006564	0.038	0.0043	0.0028
1644	0.01868	0.004848	0.00652	0.0383	0.0043	0.0028
1640	0.018771	0.004848	0.006476	0.0387	0.0044	0.003
1636	0.018952	0.004848	0.006564	0.039	0.0045	0.003
1632	0.019224	0.004935	0.006652	0.0393	0.0044	0.003
1628	0.019406	0.004979	0.006696	0.0399	0.0044	0.003
1624	0.019588	0.004935	0.00674	0.0404	0.0044	0.003
1620	0.019769	0.004979	0.006784	0.0407	0.0045	0.003
1616	0.019951	0.004979	0.00674	0.0412	0.0044	0.003
1612	0.020179	0.005067	0.00674	0.0417	0.0044	0.003
1608	0.020361	0.005067	0.006828	0.042	0.0043	0.003
1604	0.020406	0.005067	0.006784	0.0424	0.0043	0.003
1600	0.020588	0.005155	0.007005	0.0428	0.0042	0.0029
1596	0.020634	0.005111	0.006917	0.0431	0.0042	0.0029
1592	0.020816	0.005243	0.006961	0.0435	0.0042	0.0029
1588	0.020816	0.005199	0.006961	0.0438	0.0042	0.003
1584	0.020953	0.005287	0.007005	0.044	0.0042	0.0029
1580	0.021044	0.005331	0.007005	0.0441	0.0042	0.0029
1576	0.021044	0.005287	0.006917	0.0444	0.0042	0.0029
1572	0.021135	0.005331	0.007049	0.0446	0.0043	0.003
1568	0.021135	0.005375	0.007137	0.0445	0.0043	0.003

1564	0.021181	0.005375	0.007226	0.0445	0.0042	0.003
1560	0.021044	0.005331	0.007226	0.0443	0.0043	0.003
1556	0.021044	0.005243	0.007181	0.0443	0.0043	0.0031
1552	0.020862	0.005375	0.00727	0.0443	0.0044	0.0032
1548	0.02077	0.005375	0.007402	0.044	0.0045	0.0032
1544	0.02077	0.005551	0.007579	0.0437	0.0045	0.0032
1540	0.02077	0.005551	0.007667	0.0438	0.0045	0.0032
1536	0.020543	0.005639	0.007667	0.0434	0.0045	0.0033
1532	0.020452	0.005639	0.007712	0.0434	0.0045	0.0034
1528	0.020588	0.005903	0.007933	0.0433	0.0045	0.0034
1524	0.020452	0.005991	0.008021	0.0432	0.0046	0.0036
1520	0.020497	0.006035	0.00811	0.0432	0.0046	0.0037
1516	0.020497	0.006079	0.008198	0.0429	0.0047	0.0037
1512	0.020497	0.006211	0.008287	0.0431	0.0047	0.0038
1508	0.020497	0.006343	0.008331	0.0429	0.0048	0.0039
1504	0.020497	0.006432	0.008508	0.0427	0.0048	0.004
1500	0.020543	0.006608	0.008641	0.0426	0.0048	0.0039
1496	0.020543	0.006696	0.008774	0.0428	0.0049	0.0041
1492	0.020588	0.006828	0.008863	0.0426	0.0049	0.0042
1488	0.020588	0.006784	0.008996	0.0425	0.0049	0.0043
1484	0.020588	0.006961	0.009129	0.0424	0.005	0.0043
1480	0.020725	0.007049	0.009217	0.0424	0.005	0.0043
1476	0.020679	0.007093	0.009217	0.0424	0.0052	0.0045
1472	0.02077	0.007093	0.009395	0.0424	0.0052	0.0045
1468	0.020862	0.007226	0.00935	0.0424	0.0054	0.0046
1464	0.020862	0.007314	0.009484	0.0424	0.0054	0.0047
1460	0.020953	0.007446	0.009528	0.0426	0.0055	0.0047
1456	0.021089	0.007491	0.009661	0.0428	0.0056	0.005
1452	0.020953	0.007446	0.009572	0.0427	0.0056	0.0049
1448	0.021135	0.007535	0.00975	0.0429	0.0055	0.0048
1444	0.021044	0.007535	0.009706	0.0429	0.0055	0.005
1440	0.021181	0.007712	0.00975	0.0431	0.0055	0.005
1436	0.021226	0.007756	0.009794	0.0434	0.0056	0.0051
1432	0.021272	0.0078	0.009883	0.0434	0.0056	0.0052
1428	0.021226	0.007933	0.009972	0.0436	0.0057	0.0053
1424	0.021272	0.008065	0.009972	0.0437	0.0058	0.0055
1420	0.021272	0.008021	0.009883	0.044	0.0058	0.0055
1416	0.021317	0.00811	0.009928	0.0442	0.0058	0.0055
1412	0.021226	0.008154	0.009883	0.0443	0.0059	0.0056
1408	0.021272	0.00811	0.009661	0.0446	0.0058	0.0055
1404	0.021317	0.008065	0.009572	0.045	0.0058	0.0055
1400	0.021363	0.008021	0.009528	0.0455	0.0057	0.0055
1396	0.021409	0.007933	0.00935	0.0455	0.0057	0.0054
1392	0.021363	0.007844	0.009173	0.0457	0.0058	0.0055
1388	0.021363	0.007623	0.008996	0.0461	0.0059	0.0055

1384	0.021363	0.007446	0.008863	0.046	0.0058	0.0053
1380	0.021363	0.007226	0.008641	0.0461	0.0057	0.0052
1376	0.021454	0.007093	0.008552	0.0463	0.0057	0.0052
1372	0.021409	0.006961	0.008375	0.0462	0.0057	0.0051
1368	0.021409	0.006828	0.008331	0.0462	0.0056	0.005
1364	0.021409	0.006696	0.008242	0.0465	0.0057	0.0049
1360	0.021363	0.006564	0.008198	0.0468	0.0057	0.0048
1356	0.021409	0.00652	0.008065	0.0469	0.0057	0.0047
1352	0.021363	0.006432	0.007933	0.047	0.0056	0.0046
1348	0.021409	0.006432	0.008021	0.0474	0.0055	0.0045
1344	0.021409	0.006387	0.008021	0.0473	0.0054	0.0045
1340	0.021409	0.006255	0.008021	0.0475	0.0052	0.0043
1336	0.021454	0.006299	0.007933	0.0477	0.0051	0.0042
1332	0.0215	0.006255	0.007933	0.0475	0.005	0.0042
1328	0.0215	0.006255	0.007844	0.0477	0.005	0.0041
1324	0.0215	0.006211	0.007844	0.0477	0.005	0.0041
1320	0.021546	0.006123	0.007889	0.0477	0.005	0.004
1316	0.021546	0.006123	0.007889	0.0478	0.005	0.0039
1312	0.021591	0.006167	0.007977	0.0479	0.005	0.0039
1308	0.021591	0.006167	0.007933	0.0479	0.0049	0.0039
1304	0.021637	0.006211	0.007933	0.048	0.0049	0.0039
1300	0.021683	0.006211	0.007889	0.0481	0.0049	0.0038
1296	0.021728	0.006211	0.007889	0.0481	0.0049	0.0038
1292	0.021683	0.006211	0.007844	0.0482	0.0049	0.0037
1288	0.021728	0.006167	0.007933	0.0481	0.0049	0.0037
1284	0.021865	0.006167	0.007977	0.0484	0.0049	0.0036
1280	0.021865	0.006167	0.007933	0.0485	0.0049	0.0036
1276	0.021865	0.006123	0.007933	0.0487	0.005	0.0037
1272	0.021957	0.006211	0.008021	0.0487	0.005	0.0037
1268	0.021911	0.006079	0.008021	0.0487	0.0049	0.0036
1264	0.022048	0.006167	0.008021	0.049	0.0049	0.0036
1260	0.022048	0.006167	0.008021	0.0489	0.0049	0.0037
1256	0.022094	0.006123	0.008021	0.0491	0.0049	0.0036
1252	0.022094	0.006167	0.008065	0.0491	0.0049	0.0037
1248	0.022094	0.006123	0.008065	0.0492	0.0049	0.0037
1244	0.022185	0.006211	0.008198	0.0493	0.005	0.0037
1240	0.022231	0.006211	0.008198	0.0494	0.0049	0.0037
1236	0.022185	0.006255	0.008242	0.0493	0.005	0.0037
1232	0.022276	0.006299	0.008287	0.0494	0.0049	0.0037
1228	0.022231	0.006299	0.008375	0.0495	0.005	0.0038
1224	0.022231	0.006343	0.008375	0.0496	0.0051	0.0038
1220	0.022231	0.006387	0.00842	0.0496	0.005	0.0038
1216	0.022276	0.006432	0.008464	0.0497	0.0051	0.0039
1212	0.022276	0.00652	0.008464	0.0499	0.0052	0.0039
1208	0.022276	0.006564	0.008552	0.0499	0.0052	0.0039

1204	0.022276	0.006696	0.008685	0.0499	0.0052	0.004
1200	0.022231	0.006696	0.008774	0.0499	0.0052	0.0041
1196	0.022414	0.006828	0.008818	0.05	0.0052	0.0042
1192	0.022322	0.006784	0.008863	0.0501	0.0053	0.0042
1188	0.022322	0.006873	0.008951	0.0502	0.0053	0.0043
1184	0.022368	0.006917	0.00904	0.0503	0.0054	0.0044
1180	0.022414	0.007049	0.00904	0.0503	0.0055	0.0046
1176	0.022368	0.007049	0.009084	0.0506	0.0055	0.0047
1172	0.022368	0.007137	0.009129	0.0505	0.0055	0.0048
1168	0.022414	0.00727	0.009306	0.0506	0.0056	0.0048
1164	0.022459	0.007402	0.009439	0.0505	0.0057	0.005
1160	0.022551	0.007535	0.009617	0.0503	0.0058	0.0051
1156	0.022414	0.007535	0.009661	0.0504	0.0058	0.0052
1152	0.022505	0.007844	0.009794	0.0505	0.0059	0.0054
1148	0.022368	0.007667	0.009794	0.0504	0.0059	0.0054
1144	0.022276	0.007756	0.009928	0.0503	0.0059	0.0056
1140	0.022231	0.007844	0.010017	0.0501	0.0059	0.0056
1136	0.022094	0.007844	0.010105	0.0498	0.006	0.0058
1132	0.022094	0.007933	0.010328	0.0496	0.0061	0.0059
1128	0.022094	0.008065	0.010506	0.0497	0.0062	0.0062
1124	0.021957	0.00811	0.010684	0.0496	0.0064	0.0063
1120	0.022002	0.008242	0.010862	0.0491	0.0067	0.0066
1116	0.022002	0.008375	0.01104	0.0491	0.007	0.0069
1112	0.022002	0.008552	0.011396	0.0488	0.0074	0.0071
1108	0.021819	0.008508	0.011575	0.0486	0.0079	0.0074
1104	0.021865	0.008863	0.011798	0.0486	0.0083	0.0077
1100	0.021728	0.008863	0.011976	0.0485	0.0088	0.0081
1096	0.021957	0.009217	0.012468	0.0483	0.0094	0.0084
1092	0.021957	0.00935	0.012736	0.0482	0.0099	0.0088
1088	0.021774	0.009217	0.012602	0.0482	0.0102	0.0089
1084	0.021774	0.009306	0.012423	0.048	0.0101	0.0091
1080	0.021591	0.009173	0.012468	0.0478	0.0094	0.0091
1076	0.021637	0.009306	0.012512	0.0477	0.0095	0.0093
1072	0.021637	0.009572	0.013004	0.0475	0.0102	0.0098
1068	0.021546	0.009617	0.013183	0.0474	0.0107	0.0101
1064	0.021546	0.009794	0.013363	0.0472	0.0111	0.0104
1060	0.0215	0.009972	0.013497	0.0471	0.0116	0.0108
1056	0.021409	0.01015	0.013811	0.0471	0.012	0.0112
1052	0.021454	0.010283	0.013945	0.0468	0.0123	0.0116
1048	0.021409	0.010461	0.014214	0.0468	0.0127	0.0118
1044	0.021272	0.010595	0.014214	0.0469	0.0128	0.0121
1040	0.021363	0.010728	0.014214	0.0468	0.0132	0.0124
1036	0.021089	0.010684	0.014214	0.0467	0.0135	0.0127
1032	0.021044	0.010595	0.01408	0.0464	0.0137	0.0128
1028	0.021135	0.010951	0.014035	0.0465	0.0139	0.0129

1024	0.020862	0.010728	0.013676	0.0461	0.014	0.0128
1020	0.020907	0.010595	0.013318	0.0458	0.0141	0.013
1016	0.020862	0.010506	0.013228	0.0459	0.0139	0.013
1012	0.020862	0.010328	0.013049	0.0458	0.0139	0.0131
1008	0.020816	0.010328	0.012736	0.0457	0.0138	0.0129
1004	0.020634	0.010061	0.012557	0.0453	0.0138	0.0129
1000	0.020452	0.009972	0.012512	0.0453	0.0136	0.0128
996	0.020406	0.009928	0.012334	0.0452	0.0134	0.0127
992	0.020452	0.009883	0.012289	0.045	0.0133	0.0126
988	0.020361	0.009928	0.0122	0.0453	0.0133	0.0127
984	0.02027	0.009794	0.012066	0.0448	0.0131	0.0127
980	0.020088	0.00975	0.011887	0.0447	0.0128	0.0127
976	0.020179	0.009706	0.011798	0.0446	0.0128	0.0125
972	0.020088	0.009572	0.011798	0.0441	0.0123	0.0122
968	0.020088	0.009528	0.011753	0.0445	0.0121	0.0121
964	0.019997	0.009528	0.011486	0.0441	0.0124	0.012
960	0.019951	0.009528	0.011352	0.044	0.0125	0.0119
956	0.019997	0.00935	0.011218	0.0438	0.0123	0.0117
952	0.019678	0.009129	0.010951	0.0435	0.0119	0.0114
948	0.019724	0.009084	0.010684	0.0437	0.0116	0.0111
944	0.019633	0.008685	0.010461	0.0432	0.0114	0.0108
940	0.019724	0.008685	0.010328	0.0432	0.0114	0.0105
936	0.019633	0.008464	0.010194	0.0429	0.0109	0.01
932	0.019542	0.008287	0.010017	0.043	0.0108	0.0098
928	0.019497	0.008198	0.009883	0.0429	0.0106	0.0095
924	0.01936	0.00811	0.009794	0.0429	0.0105	0.0093
920	0.01927	0.007977	0.009661	0.0427	0.0103	0.0091
916	0.019542	0.008021	0.00975	0.043	0.0101	0.0089
912	0.019678	0.008154	0.009706	0.0431	0.0101	0.0087
908	0.019678	0.007933	0.009572	0.043	0.0097	0.0086
904	0.019769	0.007889	0.009706	0.0437	0.0097	0.0086
900	0.019769	0.007933	0.009661	0.0437	0.0094	0.0083
896	0.020042	0.007977	0.009661	0.044	0.0094	0.0081
892	0.020042	0.007933	0.009484	0.0441	0.0093	0.0081
888	0.020224	0.007933	0.009572	0.0444	0.0092	0.008
884	0.020406	0.008154	0.009928	0.0448	0.0092	0.0082
880	0.020543	0.008818	0.010639	0.045	0.0094	0.0084
876	0.020679	0.009528	0.011352	0.045	0.0093	0.0089
872	0.02077	0.009794	0.011396	0.0449	0.0091	0.009
868	0.020406	0.008951	0.010328	0.0446	0.0089	0.0083
864	0.020179	0.008242	0.009839	0.0441	0.0088	0.0081
860	0.020042	0.008154	0.009794	0.0434	0.0087	0.0078
856	0.019951	0.007889	0.009484	0.0433	0.0085	0.0078
852	0.019815	0.007977	0.009528	0.0433	0.0084	0.0077
848	0.019769	0.0078	0.009572	0.0434	0.0084	0.0077

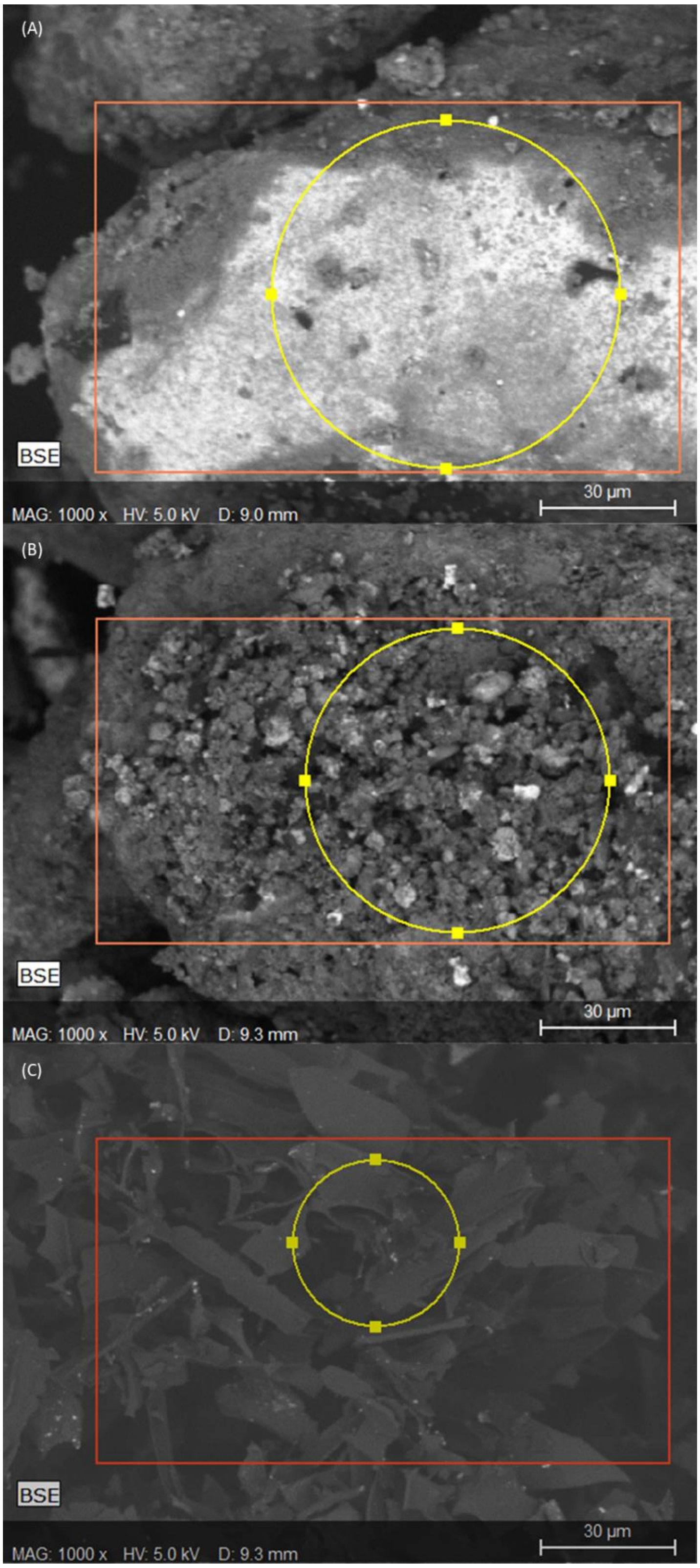
844	0.01986	0.007844	0.009395	0.0436	0.0081	0.0074
840	0.01986	0.007667	0.009395	0.0439	0.0083	0.0076
836	0.019951	0.007712	0.009439	0.0438	0.0085	0.0075
832	0.020088	0.0078	0.009484	0.0441	0.0082	0.0075
828	0.020133	0.0078	0.009484	0.0447	0.0081	0.0075
824	0.020224	0.007756	0.009617	0.0448	0.0079	0.0073
820	0.020224	0.007667	0.009706	0.0442	0.0079	0.0073
816	0.020133	0.007756	0.009528	0.0443	0.0078	0.0072
812	0.020088	0.007756	0.009661	0.0441	0.0078	0.0072
808	0.020088	0.007844	0.009617	0.0439	0.0078	0.0072
804	0.020042	0.007889	0.009528	0.0438	0.0077	0.0071
800	0.019906	0.007667	0.009306	0.0441	0.0077	0.007
796	0.019769	0.007712	0.009484	0.0436	0.0076	0.0073
792	0.019815	0.0078	0.009528	0.0434	0.0077	0.0073
788	0.019724	0.0078	0.009528	0.0431	0.0077	0.0073
784	0.019678	0.007623	0.009395	0.0428	0.0077	0.0072
780	0.019406	0.007667	0.009306	0.0427	0.0077	0.0071
776	0.019497	0.0078	0.009484	0.0426	0.0078	0.0072
772	0.019542	0.007756	0.009661	0.0426	0.0077	0.0071
768	0.019678	0.007756	0.00975	0.0428	0.0077	0.0071
764	0.019724	0.007667	0.009661	0.0431	0.0076	0.0072
760	0.019815	0.007844	0.009706	0.0428	0.0078	0.0074
756	0.019633	0.008065	0.010017	0.043	0.0077	0.0072
752	0.019906	0.008242	0.010017	0.0431	0.0077	0.0073
748	0.019588	0.008065	0.009839	0.0427	0.0078	0.0074
744	0.019724	0.008021	0.009972	0.0426	0.0078	0.0074
740	0.019497	0.008065	0.009883	0.0422	0.0079	0.0076
736	0.019406	0.007977	0.009928	0.0415	0.0081	0.0077
732	0.019406	0.007977	0.009839	0.0419	0.008	0.0076
728	0.01927	0.007977	0.009928	0.041	0.0082	0.0079
724	0.019179	0.00811	0.010061	0.0411	0.0079	0.0077
720	0.019179	0.00811	0.009883	0.0404	0.0079	0.008
716	0.018997	0.008464	0.010328	0.0404	0.0081	0.0081
712	0.019043	0.008508	0.010506	0.0405	0.0082	0.0086
708	0.018952	0.008331	0.010283	0.0404	0.0079	0.0081
704	0.018816	0.008287	0.010061	0.0402	0.0082	0.0085
700	0.018816	0.008198	0.01015	0.0401	0.008	0.0086
696	0.018861	0.00842	0.010283	0.04	0.008	0.0084
692	0.018634	0.008375	0.010061	0.0402	0.0081	0.0088
688	0.018634	0.008331	0.010061	0.0392	0.0083	0.0088
684	0.018589	0.008375	0.010194	0.0402	0.0082	0.0089
680	0.018453	0.008198	0.009972	0.0401	0.0085	0.0086
676	0.018589	0.008508	0.009839	0.0393	0.0084	0.0089
672	0.018544	0.008287	0.009928	0.0396	0.0086	0.0088
668	0.017141	0.007446	0.010328	0.0374	0.0085	0.0079

664	0.018634	0.008331	0.010194	0.0389	0.0084	0.0085
660	0.018589	0.008375	0.009928	0.0393	0.0086	0.0087
656	0.018589	0.008331	0.010194	0.0394	0.0086	0.0087
652	0.018725	0.008597	0.010328	0.0388	0.0088	0.0085
648	0.018634	0.008774	0.010328	0.0392	0.0091	0.0089
644	0.018227	0.008464	0.010372	0.0392	0.0097	0.0089
640	0.018272	0.008641	0.010283	0.0386	0.0101	0.0091
636	0.018227	0.008287	0.010194	0.0386	0.0104	0.0091
632	0.018499	0.008863	0.010639	0.0388	0.0107	0.0094
628	0.018453	0.009173	0.01104	0.039	0.011	0.0101
624	0.018317	0.00935	0.011174	0.0386	0.0104	0.0102
620	0.018544	0.009794	0.011798	0.0391	0.0102	0.0106
616	0.018589	0.00975	0.011575	0.0379	0.01	0.0104
612	0.018816	0.009883	0.012244	0.0391	0.0104	0.0111
608	0.018363	0.009928	0.012155	0.0381	0.0113	0.0118
604	0.018771	0.010595	0.012825	0.0386	0.0132	0.0126
600	0.01868	0.010461	0.01211	0.0388	0.014	0.0127
596	0.018363	0.010105	0.011753	0.0381	0.0137	0.0123
592	0.018408	0.009617	0.01153	0.0382	0.0121	0.0113
588	0.018227	0.009883	0.011352	0.0387	0.0116	0.0114
584	0.018499	0.009617	0.011887	0.0377	0.0118	0.012
580	0.018861	0.010239	0.0122	0.0382	0.0119	0.0127
576	0.018907	0.010372	0.012423	0.038	0.0128	0.0128
572	0.018816	0.010417	0.012602	0.0383	0.014	0.0134
568	0.01868	0.010728	0.012736	0.0374	0.0145	0.0138
564	0.018272	0.01055	0.012691	0.0381	0.0156	0.014
560	0.017865	0.010105	0.01211	0.037	0.0158	0.0146
556	0.018227	0.010061	0.011887	0.0379	0.0159	0.0142
552	0.018317	0.009706	0.011352	0.0372	0.0154	0.0131
548	0.018091	0.009572	0.011486	0.0373	0.0149	0.013
544	0.018499	0.009306	0.011263	0.0359	0.0145	0.013
540	0.018091	0.009395	0.011307	0.0368	0.0145	0.013
536	0.018046	0.008996	0.010817	0.0361	0.0137	0.0128
532	0.017729	0.009129	0.010461	0.0366	0.0133	0.0121
528	0.017865	0.009217	0.010372	0.0365	0.0128	0.0116
524	0.018136	0.00904	0.010728	0.0366	0.012	0.0118
520	0.01791	0.00904	0.010461	0.0358	0.0116	0.0123
516	0.017865	0.008907	0.010728	0.0354	0.0116	0.0122
512	0.018227	0.009572	0.011218	0.0362	0.0107	0.0122
508	0.018317	0.009484	0.011619	0.0354	0.0105	0.0121
504	0.017593	0.008685	0.010684	0.0361	0.0109	0.0123
500	0.017684	0.008818	0.010906	0.0352	0.0102	0.012
496	0.017593	0.009661	0.011441	0.0351	0.0099	0.0123
492	0.018181	0.009972	0.010995	0.0358	0.01	0.0118
488	0.018046	0.009572	0.010951	0.0349	0.0099	0.0124

484	0.017593	0.009084	0.010862	0.034	0.0101	0.0134
480	0.01696	0.009262	0.010817	0.0343	0.0101	0.0134
476	0.016374	0.008464	0.010728	0.0345	0.0111	0.0137
472	0.016825	0.01015	0.011619	0.0334	0.0116	0.0146
468	0.01678	0.009528	0.011619	0.0341	0.011	0.0156
464	0.017593	0.009528	0.012825	0.0344	0.0103	0.0155
460	0.017277	0.009839	0.011575	0.0336	0.0107	0.0159
456	0.01669	0.00935	0.012066	0.0343	0.0109	0.0151
452	0.016464	0.009395	0.011174	0.0345	0.0116	0.017
448	0.015923	0.00935	0.011441	0.0331	0.0108	0.0167
444	0.016013	0.010684	0.012647	0.0347	0.0108	0.0161
440	0.016599	0.010328	0.012289	0.0321	0.0103	0.0154
436	0.016329	0.009528	0.011619	0.0308	0.0094	0.0155
432	0.017277	0.010506	0.011486	0.0301	0.0098	0.0163
428	0.017412	0.009661	0.011575	0.033	0.0096	0.0171
424	0.018453	0.011575	0.01417	0.031	0.0087	0.0163
420	0.017322	0.010328	0.01399	0.0323	0.0091	0.0156
416	0.017051	0.011352	0.011932	0.0272	0.0117	0.0168
412	0.017684	0.011129	0.011396	0.0304	0.009	0.0146
408	0.018771	0.009217	0.012468	0.0328	0.0117	0.0148
404	0.017457	0.007977	0.011441	0.0309	0.0112	0.0153
400	0.019588	0.008907	0.014574	0.0309	0.0101	0.019

SI 3.8: FTIR spectra of larch biochar (BC) pre and post immobilisation of Pb, Cu, Zn and Cd, FTIR spectra of larch biochar cold mixed with wood ash (WA) pre and post immobilisation of Pb, Cu, Zn and Cd, FTIR spectra of larch biochar sintered with wood ash (WAS) pre and post immobilisation of Pb, Cu, Zn and Cd.

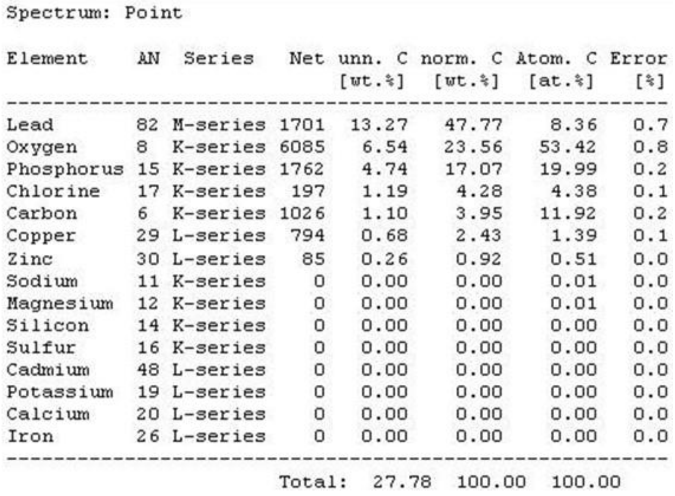
SI 3.8 is referred to in section 3.3.3 (results and discussion section of chapter 3) to indicate the importance of co-precipitation and ion exchange as mechanisms for each sorbent. These data are plotted in figure 3.5A, B and C.



SI 3.9: (A) SEM photograph of larch biochar sintered with wood ash (WAS) post immobilisation of Pb, Cu, Zn and Cd (B) SEM photograph larch biochar cold mixed with wood ash (WA) post immobilisation of Pb, Cu, Zn and Cd (C) SEM photograph larch biochar (BC) post immobilisation of Pb, Cu, Zn and Cd

SI 3.9A, 3.9B and 3.9C are referred to in section 3.3.3 (results and discussion section of chapter 3) whilst the bright areas seen on 3.7A and B but not C which denote the presence of metal rich phases.

A



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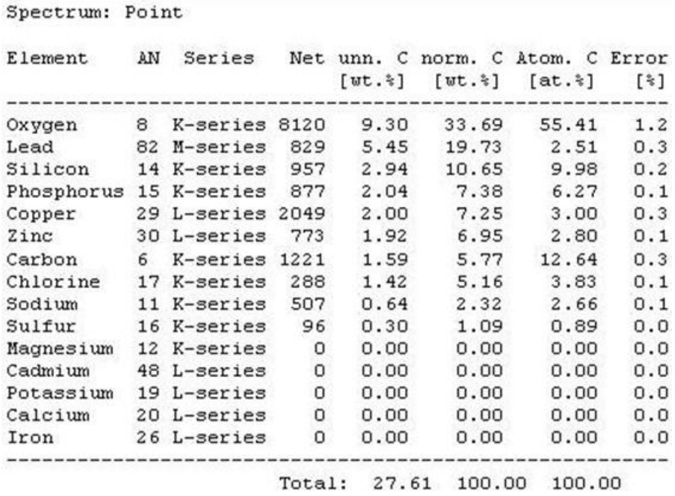
Spectrum: Point

Element    AN  Series   Net unn. C norm. C Atom. C Error
                            [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------------------
Lead       82 M-series 1701  13.27   47.77    8.36   0.7
Oxygen     8  K-series 6085   6.54   23.56   53.42   0.8
Phosphorus 15 K-series 1762   4.74   17.07   19.99   0.2
Chlorine   17 K-series  197   1.19    4.28    4.38   0.1
Carbon     6  K-series 1026   1.10    3.95   11.92   0.2
Copper     29 L-series  794   0.68    2.43    1.39   0.1
Zinc       30 L-series   85   0.26    0.92    0.51   0.0
Sodium     11 K-series    0   0.00    0.00    0.01   0.0
Magnesium  12 K-series    0   0.00    0.00    0.01   0.0
Silicon    14 K-series    0   0.00    0.00    0.00   0.0
Sulfur     16 K-series    0   0.00    0.00    0.00   0.0
Cadmium    48 L-series    0   0.00    0.00    0.00   0.0
Potassium  19 L-series    0   0.00    0.00    0.00   0.0
Calcium    20 L-series    0   0.00    0.00    0.00   0.0
Iron       26 L-series    0   0.00    0.00    0.00   0.0
--------------------------------------------------------
                       Total:  27.78  100.00  100.00
```

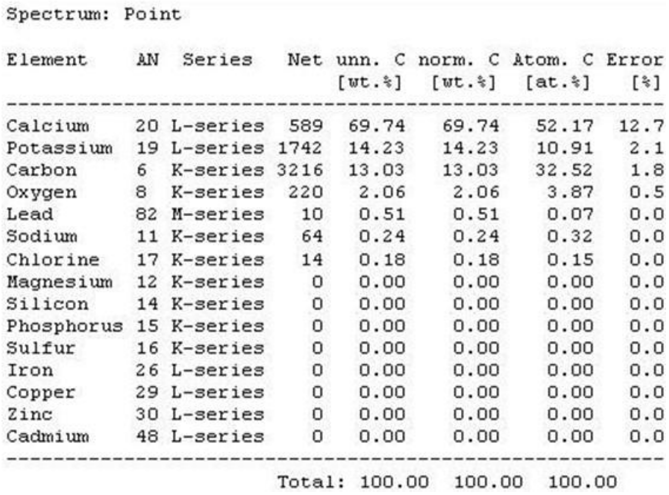
B



```
Spectrum: Point

Element    AN  Series   Net unn. C norm. C Atom. C Error
                            [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------------------
Oxygen     8  K-series 8120   9.30   33.69   55.41   1.2
Lead       82 M-series  829   5.45   19.73    2.51   0.3
Silicon    14 K-series  957   2.94   10.65    9.98   0.2
Phosphorus 15 K-series  877   2.04    7.38    6.27   0.1
Copper     29 L-series 2049   2.00    7.25    3.00   0.3
Zinc       30 L-series  773   1.92    6.95    2.80   0.1
Carbon     6  K-series 1221   1.59    5.77   12.64   0.3
Chlorine   17 K-series  288   1.42    5.16    3.83   0.1
Sodium     11 K-series  507   0.64    2.32    2.66   0.1
Sulfur     16 K-series   96   0.30    1.09    0.89   0.0
Magnesium  12 K-series    0   0.00    0.00    0.00   0.0
Cadmium    48 L-series    0   0.00    0.00    0.00   0.0
Potassium  19 L-series    0   0.00    0.00    0.00   0.0
Calcium    20 L-series    0   0.00    0.00    0.00   0.0
Iron       26 L-series    0   0.00    0.00    0.00   0.0
--------------------------------------------------------
                       Total:  27.61  100.00  100.00
```

C

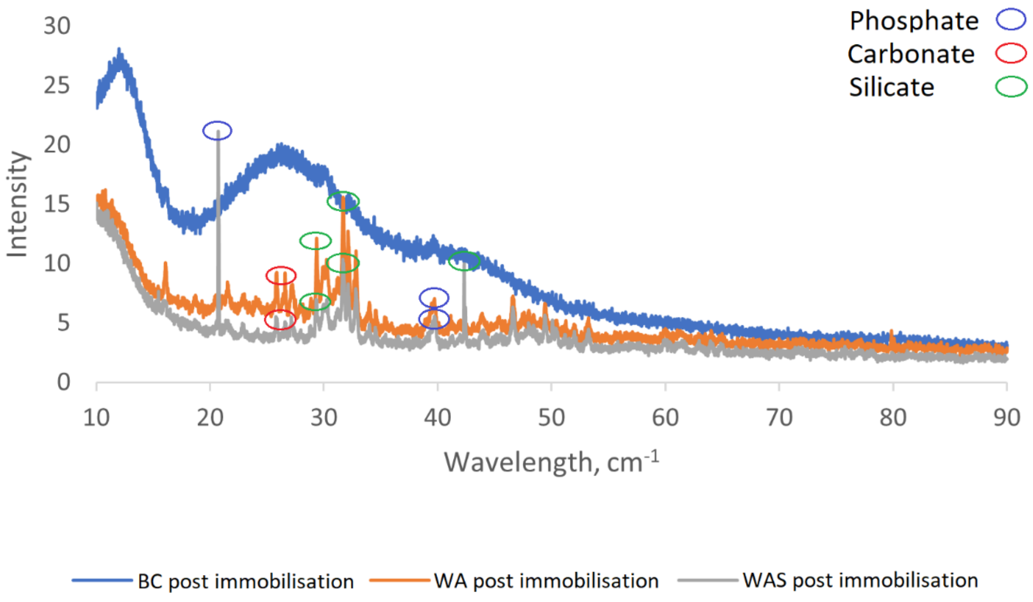


```
Spectrum: Point

Element     AN  Series    Net  unn. C  norm. C  Atom. C  Error
                              [wt.%]   [wt.%]   [at.%]    [%]
--------------------------------------------------------------
Calcium     20 L-series   589   69.74    69.74    52.17   12.7
Potassium   19 L-series  1742   14.23    14.23    10.91    2.1
Carbon      6  K-series  3216   13.03    13.03    32.52    1.8
Oxygen      8  K-series   220    2.06     2.06     3.87    0.5
Lead        82 M-series    10    0.51     0.51     0.07    0.0
Sodium      11 K-series    64    0.24     0.24     0.32    0.0
Chlorine    17 K-series    14    0.18     0.18     0.15    0.0
Magnesium   12 K-series     0    0.00     0.00     0.00    0.0
Silicon     14 K-series     0    0.00     0.00     0.00    0.0
Phosphorus  15 K-series     0    0.00     0.00     0.00    0.0
Sulfur      16 K-series     0    0.00     0.00     0.00    0.0
Iron        26 L-series     0    0.00     0.00     0.00    0.0
Copper      29 L-series     0    0.00     0.00     0.00    0.0
Zinc        30 L-series     0    0.00     0.00     0.00    0.0
Cadmium     48 L-series     0    0.00     0.00     0.00    0.0
--------------------------------------------------------------
                      Total:  100.00   100.00   100.00
```

SI 3.10 A: EDX elemental data of larch biochar (BC) post immobilisation of Pb, Cu, Zn and Cd, B: EDX elemental data of larch biochar cold mixed with wood ash (WA) post immobilisation of Pb, Cu, Zn and Cd and C: EDX elemental data of larch biochar sintered with wood ash (WAS) post immobilisation of Pb, Cu, Zn and Cd

SI 3.10A, 3.10B and 3.10C are referred to in section 3.3.3 (results and discussion section of chapter 3) to demonstrate the presence of metals of concern in the presence of P and Si indicating co-precipitation.



SI 3.11: XRD pattern of larch biochar (BC) post immobilisation of Pb, Cu, Zn, larch biochar cold mixed with wood ash (WA) post immobilisation of Pb, Cu, Zn and Cd and larch biochar sintered with wood ash (WAS) post immobilisation of Pb, Cu, Zn and Cd

SI 3.11 are referred to in section 3.3.3 (results and discussion section of chapter 3) to indicate the presence of carbonates, siloxane and phosphates in relation to co-precipitation.

	BC post removal	WA post removal	WAS post removal
10.0001	24.39583	15.3125	14.71875
10.01973	24.38542	15.13542	14.57292
10.03935	23.89583	15.46875	15.08333
10.05898	23.78125	15.67708	13.76042
10.07861	23.10417	15.47917	14.16667
10.09824	24.10417	15.16667	14.09375
10.11786	24.04167	15.69792	14.51042
10.13749	23.8125	15.23958	14.07292
10.15712	23.45833	15.78125	14.23958
10.17674	23.91667	15.48958	13.625
10.19637	24.42708	14.90625	13.67708
10.216	24.89583	15.20833	13.40625
10.23562	24.75	15.25	13.45833
10.25525	23.70833	15.22917	13.57292
10.27488	24.05208	15.73958	14.27083
10.29451	25.40625	15.39583	14.07292
10.31413	24.84375	15.1875	13.84375
10.33376	24.22917	14.98958	13.96875
10.35339	24	15.16667	14.04167
10.37301	24.88542	15.57292	14.45833
10.39264	24.05208	15.73958	14
10.41227	24.46875	15.44792	13.9375
10.43189	24.60417	15.61458	13.20833
10.45152	23.625	15.72917	14.32292
10.47115	24.6875	14.5	14.22917
10.49078	23.9375	15.13542	13.84375
10.5104	24.86458	15.73958	14.02083
10.53003	25.17708	15.125	13.94792
10.54966	24.67708	14.65625	13.89583
10.56928	24.4375	16.125	13.64583
10.58891	25.05208	14.5	13.17708

10.60854	24.60417	15.25	14.09375
10.62816	25.5625	15.46875	13.54167
10.64779	24.80208	15.02083	13.23958
10.66742	24.05208	15.26042	13.59375
10.68705	24.86458	15.61458	14.28125
10.70667	24.9375	15.21875	13.25
10.7263	25.47917	15.4375	13.58333
10.74593	24.33333	15.75	13.21875
10.76555	25.42708	15.55208	13.48958
10.78518	25	15.44792	14.10417
10.80481	24.97917	16.21875	14.36458
10.82443	24.96875	15.02083	13.9375
10.84406	25.78125	15.36458	13.3125
10.86369	25.5625	15.02083	12.84375
10.88332	25.45833	14.44792	13.35417
10.90294	25.23958	14.60417	13.9375
10.92257	24.625	14.70833	13.10417
10.9422	25.16667	14.21875	13.34375
10.96182	24.875	14.63542	13.42708
10.98145	25.14583	14.66667	14.5
11.00108	24.88542	14.36458	13.34375
11.0207	25.5625	14.30208	13.4375
11.04033	25.875	14.69792	14.375
11.05996	26.09375	14.79167	14.28125
11.07959	24.86458	15.01042	12.51042
11.09921	26.05208	14.83333	13.14583
11.11884	25.51042	14.27083	13.60417
11.13847	25.59375	14.77083	13.41667
11.15809	26.14583	14.54167	13.11458
11.17772	26.97917	14.80208	13.375
11.19735	25.92708	14.375	13.01042
11.21697	25.69792	13.78125	13.33333
11.2366	25.94792	15.04167	12.41667
11.25623	26.4375	13.97917	13.59375
11.27586	25.6875	14.64583	13.07292
11.29548	25.41667	14.0625	13.34375
11.31511	25.76042	15.21875	13.15625
11.33474	26.67708	13.48958	12.73958
11.35436	25.36458	14.5	13.21875
11.37399	25.9375	14.625	12.75
11.39362	25.83333	15.375	12.65625
11.41324	25.72917	14.39583	13.70833
11.43287	26.01042	14.40625	13.20833
11.4525	26.29167	14.08333	12.91667
11.47213	25.83333	13.96875	13.17708

11.49175	26.52083	13.9375	12.83333
11.51138	26.125	14.73958	12.78125
11.53101	25.65625	14.11458	11.96875
11.55063	26.5625	14.61458	13.13542
11.57026	26.52083	12.85417	12.8125
11.58989	27.29167	13.52083	13.13542
11.60951	25.90625	14.47917	12.59375
11.62914	26.71875	13.85417	13.01042
11.64877	26.01042	13.58333	13.02083
11.6684	26.20833	14.30208	12.875
11.68802	26.13542	13.65625	12.25
11.70765	26.27083	13.91667	12.47917
11.72728	27.05208	14.08333	12.17708
11.7469	26.42708	14.35417	12.44792
11.76653	26.51042	14.16667	12.09375
11.78616	27.13542	13.07292	12.3125
11.80578	26.69792	13.625	12.3125
11.82541	26.4375	13.88542	12.76042
11.84504	26.76042	13.95833	12
11.86467	27.14583	13.36458	12.25
11.88429	26.84375	13.66667	11.73958
11.90392	27.10417	13.6875	12.02083
11.92355	27.19792	13.61458	11.78125
11.94317	27.53125	13.66667	11.65625
11.9628	26.30208	14.19792	11.40625
11.98243	27.29167	13.90625	12.3125
12.00205	28.08333	13.48958	12.09375
12.02168	26.47917	13.98958	11.58333
12.04131	27.0625	13.75	11.83333
12.06094	27.27083	13.42708	12.0625
12.08056	26.83333	13.59375	11.875
12.10019	27.05208	13.09375	12.21875
12.11982	26.95833	13.08333	12.22917
12.13944	26.4375	13.15625	11.45833
12.15907	26.40625	12.67708	11.67708
12.1787	27.30208	12.55208	11.16667
12.19832	26.5625	12.94792	11.90625
12.21795	26.46875	13.28125	11.47917
12.23758	27.125	13.51042	11.61458
12.25721	27.625	13.08333	11.19792
12.27683	27.46875	13.48958	10.78125
12.29646	26.90625	13.05208	11.04167
12.31609	26.69792	12.55208	11.11458
12.33571	26.8125	12.92708	11.58333
12.35534	27.16667	12.92708	10.55208

12.37497	26.66667	12.51042	10.80208
12.39459	26.69792	12.16667	11.90625
12.41422	26.125	13.03125	10.76042
12.43385	26.82292	12.92708	11.38542
12.45348	26.45833	13.09375	10.14583
12.4731	26.8125	13.33333	11.47917
12.49273	26.66667	12.625	11.17708
12.51236	25.73958	12	11.14583
12.53198	26.63542	12.5625	10.63542
12.55161	26.86458	12.32292	10.69792
12.57124	26.85417	12.42708	10.91667
12.59087	27.05208	11.96875	10.67708
12.61049	26.375	12.34375	10.63542
12.63012	26.51042	12.59375	10.41667
12.64975	26.04167	12.84375	10.95833
12.66937	26.19792	12.34375	10.69792
12.689	25.83333	11.58333	10.20833
12.70863	26.60417	12.625	10.375
12.72825	24.71875	12	10.48958
12.74788	26.32292	11.375	10.29167
12.76751	26.40625	11.73958	9.958333
12.78714	26.72917	11.52083	10.32292
12.80676	25.77083	11.47917	10
12.82639	25.125	11.53125	9.75
12.84602	26.21875	11.625	9.8125
12.86564	25.64583	11.76042	10.20833
12.88527	25.36458	11.625	10.16667
12.9049	25.16667	11.02083	9.927083
12.92452	25.75	10.97917	9.614583
12.94415	25.51042	11.17708	10.15625
12.96378	25.92708	10.82292	9.552083
12.98341	25.4375	10.90625	9.854167
13.00303	25.19792	11.16667	10.15625
13.02266	25.82292	11.08333	9.28125
13.04229	25.80208	10.875	10.30208
13.06191	26.41667	11.32292	9.791667
13.08154	24.97917	10.47917	10.03125
13.10117	25.90625	11.44792	9.28125
13.12079	24.36458	11.57292	9.46875
13.14042	25.19792	10.8125	9.53125
13.16005	24.45833	10.8125	9.104167
13.17968	25.61458	9.927083	8.885417
13.1993	24.26042	10.79167	9.0625
13.21893	25.58333	9.885417	9.177083
13.23856	24.9375	10.71875	9.177083

13.25818	25.33333	10.75	8.697917
13.27781	24.83333	10.98958	9.125
13.29744	24.11458	10.35417	8.614583
13.31706	25.39583	10.3125	9.5625
13.33669	24.13542	10.92708	9.197917
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13.37595	24.54167	10.30208	8.916667
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13.4152	24.23958	10.36458	9.03125
13.43483	24.625	10.55208	8.729167
13.45445	24.23958	10.14583	8.864583
13.47408	24.5625	10.07292	8.65625
13.49371	24.45833	9.8125	8.46875
13.51333	24.71875	9.760417	8.375
13.53296	23.79167	9.833333	8.895833
13.55259	23.5625	10.28125	8.072917
13.57222	23.10417	9.916667	8.541667
13.59184	23.83333	10.19792	8.395833
13.61147	23.3125	10.35417	8.604167
13.6311	23.58333	10.11458	8.510417
13.65072	23.60417	10.30208	8.541667
13.67035	22.8125	9.84375	8.666667
13.68998	22.9375	9.927083	7.875
13.7096	23.25	9.979167	8.6875
13.72923	22.96875	9.583333	8.135417
13.74886	22.44792	10.20833	8.302083
13.76849	22.65625	10.04167	8.760417
13.78811	23.28125	9.84375	8.78125
13.80774	22.26042	9.875	7.71875
13.82737	22.59375	9.947917	8.166667
13.84699	22.625	9.5	8.208333
13.86662	22.41667	10.04167	7.59375
13.88625	21.94792	9.375	7.9375
13.90587	23.625	9.072917	7.791667
13.9255	21.73958	9.427083	7.552083
13.94513	22.16667	9.46875	7.6875
13.96476	22.59375	8.958333	8.03125
13.98438	21.96875	9.25	7.5625
14.00401	22.14583	9.635417	7.520833
14.02364	21.5625	8.75	7.572917
14.04326	22.27083	8.739583	7.802083
14.06289	22.17708	9.270833	7.854167
14.08252	22.0625	8.552083	7.458333
14.10214	22.20833	8.895833	7.479167
14.12177	22.60417	9.041667	7.677083

14.1414	21.86458	8.9375	7.145833
14.16103	21.22917	8.9375	7.458333
14.18065	21.79167	8.78125	7.8125
14.20028	21.11458	8.53125	7.177083
14.21991	22.02083	8.270833	7.135417
14.23953	21.28125	8.59375	7.541667
14.25916	21.97917	8.78125	7.708333
14.27879	21.23958	9.041667	6.833333
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14.31804	21.33333	7.78125	7.541667
14.33767	20.21875	9.0625	7.208333
14.3573	20.30208	8.427083	7.125
14.37692	20.63542	8.145833	7.125
14.39655	20.57292	8.322917	7.197917
14.41618	21.09375	8.625	7.03125
14.4358	19.78125	8.15625	7.229167
14.45543	19.9375	7.947917	6.583333
14.47506	20.25	8.53125	7.416667
14.49468	19	8.458333	6.697917
14.51431	19.80208	8.1875	7.479167
14.53394	20.01042	8.197917	7.21875
14.55357	20.60417	8.53125	6.916667
14.57319	19.80208	7.875	6.375
14.59282	20.10417	8.229167	7.09375
14.61245	19.9375	8.041667	7.28125
14.63207	19	8.260417	6.864583
14.6517	20.4375	7.614583	6.625
14.67133	19.38542	8.302083	7
14.69095	19.51042	8.375	6.885417
14.71058	19.17708	8.5	7.197917
14.73021	19.29167	8.03125	7
14.74984	19.39583	7.541667	6.666667
14.76946	18.9375	7.520833	7.166667
14.78909	19.07292	7.958333	6.75
14.80872	18.72917	7.96875	6.46875
14.82834	19.5625	7.65625	6.552083
14.84797	18.57292	8.041667	6.375
14.8676	17.88542	7.520833	7.1875
14.88722	18.71875	7.958333	6.59375
14.90685	18.61458	7.5625	6.5
14.92648	19.03125	8.229167	6.3125
14.94611	17.98958	8.135417	6.083333
14.96573	18.5625	7.5625	6.5625
14.98536	18.4375	8.25	6.447917
15.00499	18.4375	7.4375	6.635417

15.02461	17.39583	8.260417	6.197917
15.04424	18.3125	7.8125	6.520833
15.06387	17.78125	7.677083	6.197917
15.08349	18.32292	7.96875	6.4375
15.10312	17.88542	7.479167	6.145833
15.12275	18.15625	7.208333	6.125
15.14238	18.23958	7.875	5.958333
15.162	18.09375	7.614583	6.395833
15.18163	18.11458	7.739583	6.010417
15.20126	17.875	7.447917	6.833333
15.22088	17.79167	7.177083	6.197917
15.24051	17.19792	7.416667	6.791667
15.26014	18	7.708333	6.041667
15.27976	17.35417	7.416667	5.802083
15.29939	17.33333	7.885417	6.364583
15.31902	17.16667	7.53125	6.489583
15.33865	16.91667	7.354167	6.208333
15.35827	17.5	7.5625	6.9375
15.3779	16.07292	7.385417	6.875
15.39753	17.44792	7.802083	6.5625
15.41715	16.88542	7.854167	6.40625
15.43678	17.53125	8.114583	6.427083
15.45641	16.65625	7.416667	6.729167
15.47604	17.32292	8	7.666667
15.49566	17.77083	7.125	6.65625
15.51529	16.3125	7.583333	6.78125
15.53492	16.71875	7.802083	6.34375
15.55454	16.33333	7.354167	6
15.57417	16.60417	7.145833	6.010417
15.5938	16.67708	7.09375	6.083333
15.61342	15.59375	7.0625	6.135417
15.63305	15.60417	7.104167	5.947917
15.65268	15.92708	7.239583	5.916667
15.67231	16.30208	7.020833	5.9375
15.69193	16.02083	7.75	6.145833
15.71156	16.1875	7.697917	6.572917
15.73119	15.89583	7.354167	6.583333
15.75081	15.1875	7.65625	6.427083
15.77044	16.34375	7.489583	5.791667
15.79007	16.13542	7.666667	6.291667
15.80969	14.82292	7.177083	6.416667
15.82932	15.83333	7.427083	6.166667
15.84895	15.71875	7.552083	6.010417
15.86858	15.22917	7.583333	6.864583
15.8882	16.17708	7.458333	6.645833

15.90783	15.375	7.5	6.53125
15.92746	15.10417	8.395833	6.604167
15.94708	15.73958	8.229167	6.416667
15.96671	15.26042	8.5625	6.895833
15.98634	15.77083	8.3125	6.635417
16.00596	15.98958	8.802083	6.59375
16.02559	16.36458	8.84375	6.5
16.04522	15.79167	9.333333	6.875
16.06485	16.39583	9.489583	6.760417
16.08447	16.15625	10.08333	6.65625
16.1041	15.79167	9.625	6.802083
16.12373	16.04167	9.739583	6.364583
16.14335	16.28125	9.354167	6.447917
16.16298	16.11458	9.333333	6.53125
16.18261	15.90625	8.25	6.6875
16.20223	15.85417	8.427083	5.625
16.22186	16.0625	8.072917	6.104167
16.24149	15.9375	7.6875	6.0625
16.26112	16.22917	7.510417	5.760417
16.28074	15.19792	7.958333	5.96875
16.30037	15.5625	7.75	5.947917
16.32	14.84375	7.1875	5.65625
16.33962	14.70833	6.833333	6.020833
16.35925	14.8125	7.46875	5.71875
16.37888	14.71875	7.34375	5.510417
16.3985	14.20833	7.427083	6.052083
16.41813	14.39583	7.052083	5.6875
16.43776	13.79167	7.15625	5.6875
16.45739	14.76042	6.645833	5.822917
16.47701	14.82292	7.21875	5.760417
16.49664	14.41667	7.260417	6.177083
16.51627	14.58333	7.34375	5.385417
16.53589	14.48958	6.708333	5.6875
16.55552	13.84375	7.145833	5.364583
16.57515	14.79167	7.28125	5.729167
16.59477	14.1875	6.708333	5.458333
16.6144	14.375	6.885417	5.302083
16.63403	14.11458	7.239583	5.489583
16.65366	14.3125	6.677083	5.541667
16.67328	14.30208	7.208333	5.34375
16.69291	14.59375	7	5.291667
16.71254	14	6.833333	5.177083
16.73216	14.02083	6.833333	5.270833
16.75179	14.45833	7.03125	5.489583
16.77142	13.52083	7.135417	5.375

16.79104	14.58333	6.96875	5.677083
16.81067	14.4375	7.177083	5.739583
16.8303	14.22917	6.947917	5.4375
16.84993	13.625	6.802083	4.885417
16.86955	14.16667	6.8125	5.510417
16.88918	14.05208	6.760417	5.197917
16.90881	13.38542	7.104167	5.385417
16.92843	13.69792	7.114583	5.635417
16.94806	13.64583	7.114583	5.572917
16.96769	13.91667	7.125	5.5625
16.98731	14.1875	6.833333	5.302083
17.00694	13.96875	7.072917	5.552083
17.02657	14.55208	6.645833	5.458333
17.0462	13.42708	6.708333	5.427083
17.06582	14.05208	6.885417	5.5
17.08545	13.85417	6.614583	5.59375
17.10508	14.07292	7.104167	5.114583
17.1247	14.35417	7.135417	5.65625
17.14433	13.58333	6.53125	5.447917
17.16396	14.3125	6.75	5.291667
17.18358	13.5	7.28125	5.239583
17.20321	14.34375	6.28125	5.177083
17.22284	13.875	6.260417	5
17.24247	13.71875	6.40625	4.8125
17.26209	13.70833	6.489583	5.1875
17.28172	13.13542	6.5625	4.75
17.30135	13.66667	6.770833	5.197917
17.32097	13.54167	6.4375	5.364583
17.3406	13.9375	6.739583	5.125
17.36023	13.30208	6.541667	5.177083
17.37985	13.1875	6.635417	5.0625
17.39948	13.41667	6.833333	4.5
17.41911	13.53125	6.40625	5.0625
17.43874	13.47917	6.427083	4.4375
17.45836	13.90625	6.78125	5.135417
17.47799	13.52083	6.583333	5.072917
17.49762	13.375	6.552083	5.4375
17.51724	13.34375	6.770833	4.84375
17.53687	13.82292	6.489583	4.791667
17.5565	14.40625	6.75	5.020833
17.57612	13.14583	7.15625	5.135417
17.59575	13.80208	6.541667	5.4375
17.61538	13.58333	6.5625	5.177083
17.63501	13.72917	7.03125	5.15625
17.65463	13.55208	6.729167	5.177083

17.67426	12.57292	7.145833	5.104167
17.69389	12.60417	7	4.770833
17.71351	13.97917	6.677083	5
17.73314	13.34375	6.5625	4.75
17.75277	13.5625	7.072917	4.90625
17.77239	13.01042	6.71875	5.34375
17.79202	13.27083	6.395833	4.71875
17.81165	12.94792	6.90625	4.96875
17.83128	13.20833	6.645833	4.697917
17.8509	13.38542	6.666667	5.270833
17.87053	13.875	6.1875	4.947917
17.89016	14.30208	6.802083	4.947917
17.90978	13.51042	6.40625	4.78125
17.92941	13.35417	6.53125	5.104167
17.94904	13.64583	6.625	4.96875
17.96866	13.60417	6.447917	4.84375
17.98829	13.5	6.885417	4.84375
18.00792	13.5	6.395833	5.239583
18.02755	14.36458	6.364583	4.854167
18.04717	13.70833	6.34375	4.4375
18.0668	13.30208	6.322917	5.114583
18.08643	13.48958	6.28125	4.78125
18.10605	13.59375	6.729167	4.427083
18.12568	14.0625	6.791667	4.729167
18.14531	13.82292	6.53125	4.895833
18.16493	13	6.208333	4.46875
18.18456	13.875	5.760417	4.9375
18.20419	13	5.96875	4.739583
18.22382	13.13542	6.020833	4.75
18.24344	13.4375	6.46875	5.114583
18.26307	13.82292	6.083333	4.8125
18.2827	14.09375	6.052083	4.75
18.30232	13.26042	6.09375	4.958333
18.32195	13.40625	6.5	4.78125
18.34158	13.47917	6.489583	4.666667
18.36121	12.9375	6.135417	4.854167
18.38083	12.875	6.53125	4.4375
18.40046	12.82292	6.072917	4.75
18.42009	13.75	5.9375	4.53125
18.43971	13.875	6.135417	4.666667
18.45934	13.80208	6.46875	4.875
18.47897	12.94792	6.229167	4.708333
18.49859	13.83333	6.53125	4.5625
18.51822	14.66667	6.572917	4.9375
18.53785	13.32292	6.854167	5.083333

18.55748	13.59375	6.635417	4.8125
18.5771	13.58333	6.75	4.958333
18.59673	13.22917	7.166667	5.09375
18.61636	12.875	6.520833	5.03125
18.63598	12.98958	6.625	5.09375
18.65561	12.875	6.864583	5.291667
18.67524	13.36458	7.208333	4.875
18.69486	13.70833	6.875	4.739583
18.71449	13.86458	7.333333	5.125
18.73412	12.59375	7.083333	4.645833
18.75375	13.69792	7.270833	4.8125
18.77337	13.42708	7.010417	5.177083
18.793	13.70833	6.927083	4.958333
18.81263	13.6875	6.40625	4.96875
18.83225	14.0625	6.666667	4.541667
18.85188	13.90625	6.8125	4.822917
18.87151	13.0625	6.739583	4.510417
18.89113	13.46875	6.78125	4.854167
18.91076	13.29167	6.375	4.635417
18.93039	13.89583	6.427083	5.041667
18.95002	13.59375	6.625	4.75
18.96964	13.67708	6.65625	4.510417
18.98927	13.59375	6.052083	4.739583
19.0089	13.33333	5.885417	4.864583
19.02852	13.54167	6.09375	4.96875
19.04815	13.63542	6.072917	4.552083
19.06778	13.13542	5.822917	4.260417
19.0874	13.1875	6.104167	4.65625
19.10703	13.52083	6.572917	4.729167
19.12666	12.51042	6.010417	4.520833
19.14629	13.40625	6.1875	4.510417
19.16591	13.94792	6.177083	4.510417
19.18554	13.42708	6.46875	4.25
19.20517	13.46875	6.28125	4.458333
19.22479	13.9375	6.614583	4.40625
19.24442	13.11458	6.541667	4.458333
19.26405	13.53125	6.0625	4.46875
19.28367	13.30208	6.864583	4.4375
19.3033	13.78125	6.489583	4.5625
19.32293	13.22917	6.645833	4.520833
19.34256	14.125	6.40625	4.197917
19.36218	13.77083	5.833333	4.427083
19.38181	13.91667	6.395833	4.03125
19.40144	14.08333	5.78125	4.0625
19.42106	13.38542	5.46875	4.229167

19.44069	13.76042	6.395833	4.15625
19.46032	14.15625	6.40625	4.65625
19.47994	13.21875	6.09375	4.291667
19.49957	14.04167	5.90625	4.208333
19.5192	14.60417	5.71875	4.447917
19.53883	14.3125	6.479167	4.635417
19.55845	14.23958	6.239583	4.583333
19.57808	13.58333	6.125	4.40625
19.59771	13.86458	6.020833	3.885417
19.61733	13.84375	5.71875	4.25
19.63696	13.85417	5.895833	4.427083
19.65659	14.05208	6.125	4.729167
19.67621	14.32292	5.666667	4.229167
19.69584	14.22917	6.302083	4.520833
19.71547	13.57292	5.96875	4.489583
19.7351	13.96875	6.4375	4.270833
19.75472	13.96875	5.927083	4.15625
19.77435	13.96875	6.177083	3.854167
19.79398	14.05208	6.166667	4.197917
19.8136	13.97917	6.46875	4.458333
19.83323	14.58333	6.072917	4.270833
19.85286	14.54167	5.927083	4.59375
19.87248	14.23958	5.822917	4.354167
19.89211	13.92708	6.03125	4.125
19.91174	14.16667	5.78125	4.333333
19.93137	14.27083	6.375	4.25
19.95099	14.1875	5.947917	4.072917
19.97062	13.77083	6.03125	4.416667
19.99025	14.0625	5.84375	4.302083
20.00987	14.1875	6.385417	4.25
20.0295	14.40625	6.21875	4.583333
20.04913	14.1875	6.020833	4.458333
20.06875	14.14583	6.125	4.302083
20.08838	14.3125	6.34375	4.15625
20.10801	13.71875	6.458333	4.333333
20.12764	14.5625	6.020833	4.28125
20.14726	14.48958	6.364583	4.520833
20.16689	13.91667	6.354167	4.489583
20.18652	14.46875	6.3125	4.614583
20.20614	13.89583	6.583333	4.1875
20.22577	14.61458	6.041667	4.583333
20.2454	14.0625	6.239583	4.729167
20.26502	14.08333	6.427083	4.645833
20.28465	14.33333	6.583333	4.645833
20.30428	13.69792	6.125	4.53125

20.32391	13.91667	6.572917	4.270833
20.34353	14.59375	6.614583	4.0625
20.36316	13.85417	6.979167	4.6875
20.38279	14.26042	6.5	4.65625
20.40241	14.32292	6.8125	4.666667
20.42204	15.25	7.25	4.395833
20.44167	14.88542	7.083333	4.447917
20.46129	15.01042	7.041667	4.75
20.48092	14.70833	6.927083	4.46875
20.50055	14.40625	7	4.864583
20.52018	14.6875	7.364583	4.958333
20.5398	14.35417	6.552083	5.114583
20.55943	14.51042	6.729167	4.864583
20.57906	14.82292	7.322917	4.520833
20.59868	14.47917	6.78125	5.21875
20.61831	14.04167	6.583333	4.916667
20.63794	14.85417	6.302083	4.895833
20.65756	14.51042	6.666667	5.229167
20.67719	15.46875	6.427083	5.458333
20.69682	14.96875	6.583333	8.572917
20.71645	14.23958	6.447917	20.78125
20.73607	14.58333	6.520833	17.69792
20.7557	14.34375	6.604167	10.54167
20.77533	14.78125	6.21875	13.70833
20.79495	14.55208	6.635417	8.90625
20.81458	14.63542	6.520833	5.739583
20.83421	14.09375	7.177083	4.604167
20.85383	14.8125	7.125	4.59375
20.87346	14.15625	6.541667	4.020833
20.89309	15.17708	6.354167	4.020833
20.91272	14.84375	6.3125	4.229167
20.93234	14.26042	6.65625	4.46875
20.95197	14.91667	6.208333	4.520833
20.9716	15.44792	6.427083	4.666667
20.99122	14.625	6.59375	4.135417
21.01085	14.875	6.5625	4.09375
21.03048	15.6875	7.239583	4.010417
21.0501	15.59375	7.302083	4.875
21.06973	15	6.739583	4.84375
21.08936	15.40625	6.84375	4.302083
21.10899	15.0625	6.96875	4.208333
21.12861	14.78125	6.833333	4.84375
21.14824	15.40625	7.083333	4.614583
21.16787	15.54167	6.90625	4.697917
21.18749	15.61458	6.833333	4.5

21.20712	15.4375	6.8125	4.125
21.22675	15.51042	7.0625	4.697917
21.24637	15.23958	7.145833	4.416667
21.266	14.98958	6.989583	4.302083
21.28563	15.33333	6.864583	4.447917
21.30526	14.5625	6.520833	4.625
21.32488	15.61458	6.947917	4.541667
21.34451	15.51042	7.34375	4.5
21.36414	16.26042	7.177083	4.520833
21.38376	15.53125	6.697917	5.229167
21.40339	15.29167	7.208333	4.916667
21.42302	16.69792	7.15625	4.572917
21.44265	15.15625	7.708333	4.770833
21.46227	15.5625	7.739583	5.135417
21.4819	15.85417	7.614583	5
21.50153	14.6875	7.854167	4.895833
21.52115	16.39583	8.458333	5
21.54078	16.04167	8.0625	5.041667
21.56041	15.44792	7.84375	4.635417
21.58003	15.85417	7.864583	5.21875
21.59966	16.28125	8.21875	4.666667
21.61929	15.70833	7.479167	5.010417
21.63892	15.52083	7.78125	4.8125
21.65854	15.32292	7.364583	4.3125
21.67817	16.36458	7.4375	4.75
21.6978	15.75	7.125	4.489583
21.71742	15.16667	7.3125	4.479167
21.73705	16.40625	7.166667	4.427083
21.75668	15.11458	6.666667	4.864583
21.7763	15.30208	6.6875	4.46875
21.79593	15.47917	7.010417	4.541667
21.81556	15.875	6.375	4.135417
21.83519	16.09375	6.729167	4.21875
21.85481	15.63542	6.802083	4.25
21.87444	16.76042	7.083333	4.614583
21.89407	15.80208	6.208333	4.104167
21.91369	15.59375	6.645833	4.229167
21.93332	15.64583	6.729167	4.177083
21.95295	16	6.302083	4
21.97257	15.89583	6.46875	4.4375
21.9922	15.82292	6.3125	3.9375
22.01183	15.36458	6.677083	3.90625
22.03146	15.65625	6.229167	4.15625
22.05108	16.29167	6.520833	3.895833
22.07071	16.51042	6.385417	4.229167

22.09034	16.375	6.229167	3.75
22.10996	16.51042	6.385417	3.666667
22.12959	16.10417	5.958333	3.916667
22.14922	15.71875	6.583333	3.75
22.16884	15.79167	6.125	3.78125
22.18847	16.71875	6.072917	4.03125
22.2081	16.5	6.645833	4.25
22.22773	16.39583	5.90625	4.083333
22.24735	16.86458	6.114583	3.822917
22.26698	15.79167	6.166667	4.135417
22.28661	16.20833	6.572917	3.75
22.30623	16.26042	5.895833	3.75
22.32586	16.47917	6.3125	3.947917
22.34549	15.96875	5.96875	3.677083
22.36511	16.89583	6.0625	3.822917
22.38474	16.13542	6.135417	3.833333
22.40437	16.03125	5.96875	3.885417
22.424	16.61458	5.760417	3.916667
22.44362	16.07292	5.96875	4.020833
22.46325	16.6875	6.0625	3.833333
22.48288	16.44792	6.697917	3.708333
22.5025	17.34375	6.177083	4.083333
22.52213	16.32292	5.979167	3.822917
22.54176	16.17708	6.541667	3.84375
22.56138	16.875	6.177083	4.041667
22.58101	17.02083	6.0625	3.854167
22.60064	16.38542	6.3125	3.875
22.62027	16.83333	6.375	3.84375
22.63989	17.5625	6.3125	3.947917
22.65952	16.15625	6.416667	3.875
22.67915	16.41667	6.510417	4.1875
22.69877	16.23958	6.78125	4.229167
22.7184	16.63542	6.71875	3.958333
22.73803	17.08333	6.916667	4.572917
22.75765	17.17708	6.75	4.583333
22.77728	16.36458	6.979167	4.260417
22.79691	17	7.125	4.21875
22.81654	16.57292	6.479167	4.197917
22.83616	16.70833	6.9375	4.96875
22.85579	16.94792	7.072917	4.40625
22.87542	16.13542	7.395833	4.416667
22.89504	16.58333	7.0625	4.729167
22.91467	16.59375	7.208333	4.520833
22.9343	16.98958	7.416667	4.572917
22.95392	17.23958	7.270833	4.895833

22.97355	17.35417	7.302083	4.322917
22.99318	16.83333	7.21875	4.416667
23.01281	15.96875	7.447917	4.09375
23.03243	17.03125	6.729167	4.40625
23.05206	16.42708	6.885417	4.0625
23.07169	16.88542	6.927083	3.791667
23.09131	16.86458	6.385417	4.104167
23.11094	16.94792	6.239583	4.21875
23.13057	16.66667	6.53125	3.802083
23.15019	17.15625	6.895833	3.895833
23.16982	17.17708	6.635417	4.15625
23.18945	17.82292	6.260417	3.854167
23.20908	17.9375	6.375	4.020833
23.2287	17.20833	6.447917	4.291667
23.24833	17.38542	6.416667	3.770833
23.26796	17.5	6.302083	4.041667
23.28758	16.30208	6.270833	3.6875
23.30721	17.67708	5.84375	3.75
23.32684	16.80208	5.90625	3.78125
23.34646	18.36458	6.21875	3.770833
23.36609	17.61458	6.145833	3.833333
23.38572	17.85417	6.28125	4.020833
23.40535	17.125	6.1875	4.041667
23.42497	16.96875	5.979167	3.864583
23.4446	17.55208	6.760417	3.625
23.46423	17.82292	6.09375	3.53125
23.48385	17.13542	6.322917	3.864583
23.50348	17.125	6.072917	3.854167
23.52311	17.5625	6.395833	3.90625
23.54273	17.14583	6.114583	3.791667
23.56236	17.64583	5.947917	3.9375
23.58199	17.83333	6.25	4.010417
23.60162	17.53125	6.010417	3.583333
23.62124	17.42708	6.395833	3.770833
23.64087	18.05208	5.791667	3.520833
23.6605	17.80208	6.3125	3.833333
23.68012	17.54167	6.25	3.958333
23.69975	17.90625	6.302083	4.052083
23.71938	17.39583	5.90625	3.65625
23.739	17.71875	6.25	3.5
23.75863	17.41667	5.635417	3.927083
23.77826	18.35417	6.770833	3.854167
23.79789	17.84375	6.541667	3.59375
23.81751	17.27083	6.21875	3.46875
23.83714	17.72917	6	3.65625

23.85677	17.91667	5.96875	4.0625
23.87639	18.10417	6.052083	3.65625
23.89602	17.39583	6.770833	3.989583
23.91565	17.6875	6.208333	4.0625
23.93527	17.5	6.604167	4.166667
23.9549	17.86458	6.614583	3.760417
23.97453	17.46875	6.375	4.114583
23.99416	18.79167	6.53125	3.760417
24.01378	17.875	7.208333	4.114583
24.03341	17.6875	6.84375	4.052083
24.05304	18.63542	7.052083	4.229167
24.07266	18.20833	7.0625	4.083333
24.09229	17.26042	6.729167	4.3125
24.11192	17.5	6.635417	4.020833
24.13154	18.35417	6.90625	3.9375
24.15117	18.09375	6.416667	3.989583
24.1708	18.28125	6.885417	3.854167
24.19043	17.95833	6.96875	4.510417
24.21005	17.66667	6.541667	3.833333
24.22968	18.78125	6.8125	3.927083
24.24931	17.98958	6.96875	3.96875
24.26893	18.25	7.010417	4.083333
24.28856	18.3125	6.822917	4.0625
24.30819	17.94792	6.25	3.864583
24.32782	18.14583	6.385417	3.791667
24.34744	17.9375	6.479167	3.677083
24.36707	18.14583	6.458333	3.958333
24.3867	17.92708	6.145833	3.760417
24.40632	19.07292	6.75	3.729167
24.42595	18.16667	6.208333	3.635417
24.44558	17.72917	6.416667	3.635417
24.4652	18.28125	6.03125	3.989583
24.48483	17.71875	5.989583	3.708333
24.50446	18.34375	6.145833	3.6875
24.52409	17.75	6.03125	3.489583
24.54371	18.5	5.822917	3.552083
24.56334	17.89583	6.34375	3.84375
24.58297	18.69792	6.010417	3.8125
24.60259	18.08333	6.385417	3.833333
24.62222	18.61458	6.166667	3.864583
24.64185	18.44792	6.15625	3.6875
24.66147	19.09375	6.364583	3.395833
24.6811	18.54167	5.864583	3.364583
24.70073	18.66667	6.083333	4.114583
24.72036	18.51042	5.854167	4.104167

24.73998	18.85417	6.104167	4.208333
24.75961	19	6.15625	3.791667
24.77924	19.09375	6.114583	4
24.79886	19.05208	6.020833	3.510417
24.81849	17.71875	6.333333	3.572917
24.83812	17.66667	6.0625	3.822917
24.85774	18.03125	6.09375	3.739583
24.87737	18.11458	5.645833	3.604167
24.897	18.08333	6.354167	4.083333
24.91663	18.10417	5.9375	3.697917
24.93625	19.0625	5.760417	4.145833
24.95588	18.25	6.114583	3.708333
24.97551	18.78125	6.114583	3.71875
24.99513	18.79167	6.40625	3.635417
25.01476	18.51042	6.020833	3.739583
25.03439	18.58333	6.614583	4.03125
25.05401	19.125	6.21875	3.59375
25.07364	18.79167	6.041667	3.604167
25.09327	18.84375	5.927083	3.666667
25.1129	18.91667	5.854167	3.583333
25.13252	18.625	6.239583	3.447917
25.15215	19.11458	5.96875	4.0625
25.17178	18.60417	5.864583	3.385417
25.1914	18.92708	5.8125	4.083333
25.21103	19.375	6.229167	3.541667
25.23066	19.08333	6	3.90625
25.25028	18.19792	6.083333	3.729167
25.26991	18.42708	6.3125	3.489583
25.28954	18.83333	5.958333	4
25.30917	18.63542	6.041667	3.635417
25.32879	18.125	6.291667	4.114583
25.34842	18.3125	6.479167	3.729167
25.36805	18.60417	5.53125	3.625
25.38767	19.60417	6.145833	4.010417
25.4073	18.9375	5.822917	3.520833
25.42693	18.45833	5.760417	3.479167
25.44655	19	6.0625	3.65625
25.46618	18.95833	5.770833	3.802083
25.48581	18.97917	6.177083	3.895833
25.50544	18.26042	6.3125	3.479167
25.52506	19.28125	6.739583	3.864583
25.54469	18.75	6.333333	4.010417
25.56432	18.13542	6.208333	3.5
25.58394	18.4375	6.4375	3.59375
25.60357	18.19792	6.0625	4.21875

25.6232	19.03125	6.416667	4.135417
25.64282	18.63542	6.46875	3.822917
25.66245	18.95833	6.333333	3.8125
25.68208	19.35417	6.989583	4.020833
25.70171	19.30208	6.708333	4.322917
25.72133	18.55208	6.770833	4.291667
25.74096	19.03125	7.041667	4.760417
25.76059	19.28125	8.177083	4.520833
25.78021	18.98958	7.802083	5.53125
25.79984	18.28125	9	5.072917
25.81947	19.3125	9.197917	5.291667
25.83909	19.19792	9.15625	5.447917
25.85872	18.83333	9.260417	5.28125
25.87835	18.55208	8.552083	5.375
25.89798	19.71875	7.833333	4.958333
25.9176	18.9375	7.90625	5.010417
25.93723	20.03125	7.666667	4.333333
25.95686	18.86458	7.21875	4.1875
25.97648	19.40625	6.885417	4.21875
25.99611	19.04167	6.572917	4.1875
26.01574	18.86458	6.5625	4.114583
26.03536	19.0625	6.4375	3.520833
26.05499	19.02083	5.9375	3.90625
26.07462	19.14583	6.34375	3.895833
26.09425	19.38542	6.510417	3.760417
26.11387	19.80208	6.125	3.5625
26.1335	19.66667	6.5	3.666667
26.15313	18.625	6.28125	3.791667
26.17275	19.375	6.25	3.947917
26.19238	19.41667	6.25	3.729167
26.21201	19.61458	6.46875	3.75
26.23163	19.55208	5.96875	4.177083
26.25126	18.38542	6.375	3.822917
26.27089	20.09375	6.270833	3.947917
26.29052	19.09375	6.354167	3.84375
26.31014	19.20833	6.541667	4.114583
26.32977	19.41667	7.052083	4.052083
26.3494	18.92708	6.552083	4.104167
26.36902	19.53125	6.71875	4.291667
26.38865	18.88542	7.15625	4.333333
26.40828	18.98958	7.239583	4.5
26.4279	19.16667	7.489583	4.46875
26.44753	19.04167	7.15625	4.510417
26.46716	19.75	6.666667	3.78125
26.48679	18.85417	7.260417	4.239583

26.50641	18.67708	7.09375	4.645833
26.52604	18.44792	7.052083	4.3125
26.54567	19.71875	6.8125	4.427083
26.56529	19.73958	7.895833	4.760417
26.58492	19.88542	9.197917	5.104167
26.60455	19.35417	8.770833	4.427083
26.62417	19.34375	7.416667	4.427083
26.6438	19.17708	7.5	4.489583
26.66343	18.8125	7.697917	4.96875
26.68306	18.76042	6.802083	4.291667
26.70268	19.20833	6.28125	3.989583
26.72231	18.28125	6.083333	3.9375
26.74194	19.75	6.416667	3.78125
26.76156	19.02083	6.427083	4.010417
26.78119	19.02083	6.104167	3.791667
26.80082	18.30208	5.645833	3.729167
26.82044	19.46875	6.072917	3.65625
26.84007	19.375	6.302083	4.104167
26.8597	19.84375	6.552083	4.010417
26.87933	18.75	5.729167	3.947917
26.89895	18.53125	6.34375	4.166667
26.91858	18.96875	5.65625	4.458333
26.93821	19.125	6.28125	4.020833
26.95783	18.30208	6.395833	3.90625
26.97746	19.51042	6.322917	4.208333
26.99709	18.07292	6.885417	4.052083
27.01671	18.67708	6.864583	3.916667
27.03634	19.53125	6.791667	4.5
27.05597	18.8125	7.09375	4.708333
27.0756	19.13542	7.083333	4.791667
27.09522	18.45833	7.645833	4.583333
27.11485	19.54167	7.96875	4.802083
27.13448	19.11458	8.177083	5.5
27.1541	18.16667	8.166667	4.59375
27.17373	18.55208	7.927083	5.114583
27.19336	19.10417	8.15625	4.854167
27.21299	18.875	7.958333	4.885417
27.23261	18.38542	8.239583	4.958333
27.25224	18.53125	8.166667	4.84375
27.27187	19.70833	7.854167	4.479167
27.29149	18.88542	7.583333	4.479167
27.31112	18.83333	7.739583	4.677083
27.33075	19.39583	7.166667	4.697917
27.35037	18.73958	7.322917	3.895833
27.37	18.55208	6.989583	4.552083

27.38963	19.14583	7.010417	4.260417
27.40926	18.58333	6.28125	4.40625
27.42888	19.02083	6.614583	4.135417
27.44851	18.89583	6.729167	4.375
27.46814	18.82292	6.65625	4.114583
27.48776	18.10417	6.125	3.791667
27.50739	18.66667	6.96875	3.885417
27.52702	18.04167	6.135417	3.604167
27.54664	18.72917	5.6875	3.90625
27.56627	19.125	6.177083	4.072917
27.5859	18.72917	5.947917	4.072917
27.60553	19.53125	6.072917	3.666667
27.62515	18.61458	5.395833	3.760417
27.64478	18.52083	5.9375	3.645833
27.66441	17.73958	5.71875	3.947917
27.68403	19.28125	5.96875	3.385417
27.70366	18.26042	5.479167	3.770833
27.72329	18.16667	6.03125	3.739583
27.74291	18.29167	5.71875	3.791667
27.76254	19.03125	5.708333	3.583333
27.78217	17.95833	5.875	3.552083
27.8018	18.01042	6.25	3.90625
27.82142	18.79167	5.979167	3.864583
27.84105	18.27083	6.479167	4.114583
27.86068	18.875	6.416667	3.947917
27.8803	18.63542	5.864583	4.145833
27.89993	19.15625	6.510417	4.270833
27.91956	18.23958	6.625	3.947917
27.93918	18.625	6.604167	4.09375
27.95881	18.48958	6.3125	4.291667
27.97844	18.04167	6.4375	4.416667
27.99807	18.42708	6.427083	3.78125
28.01769	17.77083	6.510417	3.989583
28.03732	18.76042	6.09375	3.947917
28.05695	18.57292	6.239583	3.96875
28.07657	18.41667	5.96875	3.854167
28.0962	19.45833	6.072917	4.052083
28.11583	18.07292	6.302083	3.958333
28.13545	18.75	6.104167	4.010417
28.15508	17.97917	6.59375	3.65625
28.17471	18.21875	5.635417	3.947917
28.19434	17.86458	5.90625	4.010417
28.21396	18.45833	5.520833	3.541667
28.23359	18.67708	5.604167	3.5625
28.25322	17.58333	5.083333	3.333333

28.27284	17.82292	5.364583	3.71875
28.29247	17.95833	5.114583	3.489583
28.3121	18.69792	5.822917	3.322917
28.33172	18.53125	5.854167	3.8125
28.35135	17.95833	5.677083	3.666667
28.37098	18.80208	5.322917	3.958333
28.39061	18.35417	5.572917	3.510417
28.41023	18.21875	6.229167	3.677083
28.42986	18.3125	5.40625	3.6875
28.44949	17.48958	5.447917	3.354167
28.46911	17.45833	5.479167	3.895833
28.48874	18.23958	5.489583	3.510417
28.50837	18.29167	5.65625	3.40625
28.52799	18.53125	5.8125	4.010417
28.54762	17.58333	5.770833	3.416667
28.56725	17.61458	5.385417	3.822917
28.58688	18.125	5.791667	3.645833
28.6065	17.10417	5.677083	3.520833
28.62613	17.59375	6.114583	3.489583
28.64576	17.79167	5.8125	3.666667
28.66538	18.55208	5.395833	3.625
28.68501	18.17708	5.729167	4.0625
28.70464	17.77083	6.104167	3.729167
28.72426	18.44792	5.5625	4.03125
28.74389	17.52083	6.020833	4.677083
28.76352	18	6.21875	3.875
28.78315	17.61458	6.375	4.333333
28.80277	17.67708	6.322917	4.395833
28.8224	17.45833	6.760417	4.770833
28.84203	18.13542	6.9375	3.885417
28.86165	17.3125	7.083333	4.208333
28.88128	17.96875	6.770833	4.479167
28.90091	17.07292	6.520833	4.177083
28.92053	17.33333	6.166667	4.458333
28.94016	17.67708	6.34375	4.520833
28.95979	17.41667	6.260417	4.041667
28.97942	17.95833	6.052083	4.40625
28.99904	17.5625	6.34375	4.333333
29.01867	17.94792	6.208333	4.270833
29.0383	18.20833	6.072917	4.34375
29.05792	17.38542	6.09375	3.9375
29.07755	17	5.791667	4.229167
29.09718	17.72917	6.322917	4.166667
29.1168	18.27083	6.6875	4.270833
29.13643	17.3125	6.729167	4.114583

29.15606	17.39583	6.197917	4.364583
29.17569	17.65625	6.885417	3.864583
29.19531	18.13542	6.635417	4.25
29.21494	16.66667	6.520833	4.708333
29.23457	16.95833	6.916667	5.625
29.25419	17.01042	7.28125	5.34375
29.27382	17.21875	7.729167	5.697917
29.29345	17.51042	9	5.791667
29.31307	17.03125	10.33333	6.958333
29.3327	17.33333	10.89583	6.697917
29.35233	16.53125	12.11458	6.28125
29.37196	17.91667	11.84375	6.916667
29.39158	17.71875	11.125	6.145833
29.41121	17.30208	10.25	5.40625
29.43084	17.90625	9.53125	5.489583
29.45046	16.92708	9.322917	5.5625
29.47009	17.98958	8.708333	5.291667
29.48972	18.33333	7.854167	5.354167
29.50934	17.57292	8.583333	5.09375
29.52897	17.47917	7.989583	5.052083
29.5486	17.40625	8.03125	5.125
29.56823	18.07292	7.4375	4.760417
29.58785	17.35417	7.729167	4.78125
29.60748	17.80208	7.03125	4.520833
29.62711	17.53125	6.78125	4.4375
29.64673	18.09375	6.989583	4.739583
29.66636	17.16667	7.03125	4.75
29.68599	16.5625	7.010417	4.958333
29.70561	17.52083	7.208333	4.708333
29.72524	17.9375	6.9375	5.4375
29.74487	16.90625	7.510417	4.916667
29.7645	17.76042	7.791667	5.427083
29.78412	17.51042	8	5.364583
29.80375	18.21875	8.354167	5.260417
29.82338	17.28125	8.364583	5.354167
29.843	17.5625	8.927083	5.583333
29.86263	17.97917	9.03125	6.1875
29.88226	16.72917	9.677083	6.302083
29.90188	17.65625	9.53125	5.916667
29.92151	17.26042	9.208333	6.458333
29.94114	17.03125	9.40625	6.072917
29.96077	17.11458	9.760417	6.572917
29.98039	17.72917	9.333333	6.40625
30.00002	17.3125	9.291667	6.385417
30.01965	17.20833	9.21875	6.25

30.03927	17.4375	9.010417	5.979167
30.0589	18.1875	8.8125	6.28125
30.07853	17.39583	8.729167	6.0625
30.09816	17.20833	8.916667	6.041667
30.11778	17.33333	8.96875	6
30.13741	17.65625	9.59375	6.3125
30.15704	17.41667	9.177083	6.010417
30.17666	17.46875	9.239583	6.614583
30.19629	17.11458	9.885417	6.125
30.21592	17.21875	9.895833	6.572917
30.23554	17.17708	10.34375	6.729167
30.25517	17.21875	10.09375	6.989583
30.2748	17.95833	10.33333	6.760417
30.29443	16.98958	10.21875	6.166667
30.31405	17.79167	9.635417	5.78125
30.33368	16.85417	9.229167	5.885417
30.35331	16.88542	8.9375	6.46875
30.37293	16.57292	8.645833	5.510417
30.39256	16.86458	8.65625	5.458333
30.41219	17.21875	8.104167	5.25
30.43181	17.02083	8.09375	5.510417
30.45144	16.57292	8.125	5.020833
30.47107	16.78125	7.635417	4.989583
30.4907	16.23958	7.53125	4.833333
30.51032	16.07292	7.135417	4.541667
30.52995	15.80208	7.135417	5.03125
30.54958	17.02083	7.395833	4.65625
30.5692	15.58333	7.166667	4.520833
30.58883	16.44792	7.166667	5.1875
30.60846	15.73958	6.645833	4.75
30.62808	16.4375	6.770833	4.78125
30.64771	15.98958	7.416667	4.46875
30.66734	17.3125	7.03125	4.697917
30.68697	16.30208	6.645833	4.8125
30.70659	16.72917	7.416667	4.96875
30.72622	16.5625	6.697917	4.479167
30.74585	16.60417	7.125	4.739583
30.76547	15.95833	6.5625	4.541667
30.7851	16.60417	7.229167	4.833333
30.80473	15.96875	6.760417	5.072917
30.82435	16.53125	7.354167	5.020833
30.84398	16.125	7.03125	5.010417
30.86361	16.20833	7.416667	4.760417
30.88324	16.63542	7.833333	4.520833
30.90286	16.48958	7.625	4.84375

30.92249	15.86458	7.229167	5.041667
30.94212	16.41667	7.166667	5.072917
30.96174	15.65625	7.135417	5.239583
30.98137	16.03125	7.010417	4.75
31.001	15.83333	7.770833	5.552083
31.02062	16.07292	7.854167	5.28125
31.04025	16.13542	7.822917	5.489583
31.05988	15.84375	7.479167	5.447917
31.07951	16.125	7.59375	5.895833
31.09913	15.78125	7.6875	5.583333
31.11876	15.05208	8.166667	5.479167
31.13839	15.53125	8.135417	5.46875
31.15801	15.89583	8.6875	5.802083
31.17764	15.85417	8.65625	6.09375
31.19727	15.38542	8.375	6.114583
31.21689	16.14583	8.604167	6.208333
31.23652	15.59375	8.833333	5.9375
31.25615	15.875	8.28125	5.739583
31.27578	15.73958	8.041667	5.53125
31.2954	15.10417	7.916667	5.458333
31.31503	15.29167	7.71875	5.833333
31.33466	15.45833	7.916667	5.46875
31.35428	15.72917	7.78125	5.40625
31.37391	15.78125	7.458333	5.395833
31.39354	15.76042	7.541667	5.40625
31.41316	15.17708	7.583333	5.229167
31.43279	15.72917	7.520833	5.229167
31.45242	15.4375	7.822917	5.260417
31.47205	14.72917	8.197917	5.739583
31.49167	15.54167	8.40625	6.135417
31.5113	15.17708	8.479167	5.979167
31.53093	15.02083	9.125	6.072917
31.55055	15.5	9.739583	6.833333
31.57018	15.23958	10.15625	7.416667
31.58981	15.51042	10.90625	8.083333
31.60943	15.53125	11.92708	8.354167
31.62906	15.09375	12.89583	9.052083
31.64869	15.3125	13.90625	9.520833
31.66832	15.44792	15.46875	10.375
31.68794	15.08333	15.60417	9.71875
31.70757	15.30208	15.51042	10.0625
31.7272	14.63542	14.80208	10.04167
31.74682	15.16667	13.17708	9.239583
31.76645	15.38542	11.79167	8.354167
31.78608	14.85417	10.84375	8.5

31.8057	14.95833	10.4375	8.21875
31.82533	15.41667	9.916667	6.96875
31.84496	14.86458	8.666667	6.604167
31.86459	15.21875	7.96875	6.385417
31.88421	14.89583	8.25	5.854167
31.90384	15.0625	8.229167	5.385417
31.92347	15.13542	8.020833	5.760417
31.94309	14.95833	7.697917	5.260417
31.96272	14.97917	7.604167	5.364583
31.98235	14.27083	7.916667	6.0625
32.00197	15.03125	8.1875	5.625
32.0216	15.67708	8.604167	6.114583
32.04123	15	9.427083	6.541667
32.06086	15.09375	9.927083	6.78125
32.08048	14.8125	11.20833	6.854167
32.10011	15.54167	11.42708	7.375
32.11974	14.625	12.69792	8.041667
32.13936	15.10417	12.375	8.28125
32.15899	15.83333	12.02083	7.625
32.17862	15.79167	11.26042	7.052083
32.19824	15.15625	11.41667	7.25
32.21787	15.88542	10.33333	6.354167
32.2375	15.57292	9.875	6.020833
32.25713	14.94792	9.885417	6.260417
32.27675	14.55208	8.677083	5.59375
32.29638	14.44792	8.125	5.333333
32.31601	15.26042	7.510417	5.302083
32.33563	15.39583	7.229167	4.583333
32.35526	14.76042	7.427083	4.40625
32.37489	15.47917	7.010417	4.854167
32.39451	15.30208	6.864583	4.739583
32.41414	14.94792	6.5	4.4375
32.43377	15.125	6.6875	4.447917
32.4534	14.59375	6.239583	4.427083
32.47302	14.38542	6.9375	4.270833
32.49265	13.89583	6.208333	4.395833
32.51228	14.61458	6.791667	4.5
32.5319	15.09375	6.270833	4.458333
32.55153	14.48958	7.135417	4.427083
32.57116	14.04167	7.447917	4.4375
32.59078	14.875	7.489583	4.5625
32.61041	13.95833	7.416667	4.770833
32.63004	14.875	8.03125	5.104167
32.64967	13.82292	8.53125	5.322917
32.66929	15.23958	7.822917	4.885417

32.68892	14.5	8.625	5.625
32.70855	14.85417	8.510417	6.302083
32.72817	14.15625	8.489583	6.25
32.7478	14.48958	9.625	6.791667
32.76743	14.13542	10.625	6.541667
32.78705	14.01042	10.15625	7.864583
32.80668	13.72917	10.26042	7.5
32.82631	13.84375	11.0625	7.197917
32.84594	13.94792	9.635417	7.645833
32.86556	14.28125	9.958333	7.145833
32.88519	13.67708	9.59375	7.0625
32.90482	13.89583	9.010417	6.854167
32.92444	13.28125	8.197917	6.145833
32.94407	14.17708	7.614583	5.833333
32.9637	13.84375	6.84375	5.53125
32.98333	14.33333	6.666667	5.34375
33.00295	13.63542	6	5.145833
33.02258	14.69792	5.53125	4.302083
33.04221	13.55208	5.53125	4.1875
33.06183	13.34375	5.479167	3.895833
33.08146	13.28125	5.3125	3.71875
33.10109	13.57292	5.770833	3.895833
33.12071	14.01042	4.78125	3.729167
33.14034	13.57292	5.135417	3.885417
33.15997	14.33333	5.25	3.947917
33.1796	13.57292	5.489583	3.4375
33.19922	13.63542	5.010417	3.53125
33.21885	13.59375	5.0625	3.34375
33.23848	13.63542	4.864583	3.65625
33.2581	13.30208	5.052083	3.260417
33.27773	12.86458	5.020833	3.84375
33.29736	13.60417	4.875	3.427083
33.31698	13.01042	4.791667	3.520833
33.33661	13.54167	4.697917	3.645833
33.35624	13.28125	4.458333	3.333333
33.37587	13.19792	5.104167	3.65625
33.39549	13.85417	4.760417	3.520833
33.41512	13.65625	5.197917	3.572917
33.43475	13.44792	4.760417	3.322917
33.45437	13.59375	4.989583	3.479167
33.474	13.66667	4.979167	3.697917
33.49363	12.51042	4.875	3.395833
33.51325	13.125	5.145833	3.364583
33.53288	13.57292	4.666667	3.395833
33.55251	12.67708	4.864583	3.416667

33.57214	13.3125	4.4375	3.833333
33.59176	12.58333	5.333333	3.40625
33.61139	12.72917	5.166667	3.447917
33.63102	13.14583	4.770833	3.84375
33.65064	12.79167	5.177083	3.53125
33.67027	13.44792	5.1875	4.09375
33.6899	13.65625	5.510417	3.635417
33.70952	12.5	5.229167	3.875
33.72915	13.05208	5.083333	4.041667
33.74878	12.95833	5.645833	3.989583
33.76841	13.15625	5.4375	4.270833
33.78803	13.07292	5.114583	3.84375
33.80766	13.19792	5.208333	3.979167
33.82729	13.47917	5.864583	3.885417
33.84691	12.94792	5.302083	3.822917
33.86654	12.77083	5.395833	4.166667
33.88617	13.6875	5.354167	3.864583
33.90579	12.9375	5.5	4.15625
33.92542	13.4375	5.8125	4.166667
33.94505	12.90625	6.3125	4.302083
33.96468	13.13542	6.46875	4.520833
33.9843	12.5625	6.739583	4.864583
34.00393	12.625	6.479167	4.895833
34.02356	13.125	6.5625	4.666667
34.04318	12.88542	6.385417	4.25
34.06281	12.79167	5.854167	4.197917
34.08244	12.64583	5.947917	4.03125
34.10206	12.97917	5.729167	4.21875
34.12169	12.57292	5.729167	3.635417
34.14132	12.64583	4.947917	4
34.16095	13.19792	5.052083	3.8125
34.18057	12.38542	5.072917	3.9375
34.2002	12.53125	5.166667	3.552083
34.21983	12.19792	5.28125	3.28125
34.23945	12.61458	4.739583	3.625
34.25908	13.07292	4.71875	3.833333
34.27871	13.13542	4.96875	3.322917
34.29833	12.5	4.333333	3.15625
34.31796	12.19792	4.864583	3.333333
34.33759	12.9375	4.739583	3.604167
34.35722	12.97917	5.21875	3.71875
34.37684	12.4375	4.71875	3.59375
34.39647	13.17708	4.979167	3.65625
34.4161	13.94792	5.041667	3.729167
34.43572	12.82292	4.760417	3.604167

34.45535	12.51042	4.708333	3.8125
34.47498	12.44792	5.03125	4.125
34.4946	11.90625	5.354167	4.645833
34.51423	12.19792	6.072917	4.583333
34.53386	12.9375	5.489583	4
34.55349	12.29167	5.625	3.885417
34.57311	13.02083	5.71875	4.427083
34.59274	12.3125	6.0625	4.166667
34.61237	12.47917	5.645833	3.822917
34.63199	11.71875	5.541667	3.635417
34.65162	13	5.03125	3.364583
34.67125	12.5625	5.302083	3.572917
34.69087	12.51042	4.875	3.645833
34.7105	12.41667	5.010417	3.604167
34.73013	12.97917	4.864583	3.791667
34.74976	12.70833	5.03125	3.302083
34.76938	12.375	4.572917	3.458333
34.78901	11.80208	4.864583	3.40625
34.80864	12.6875	4.53125	3.46875
34.82826	12.69792	4.4375	3.447917
34.84789	11.88542	4.6875	3.1875
34.86752	12.45833	4.677083	3.53125
34.88714	12.41667	3.927083	3.260417
34.90677	12.04167	4.385417	3.083333
34.9264	12.14583	4.3125	3.208333
34.94603	11.73958	4.541667	3.09375
34.96565	12.94792	4.78125	3.177083
34.98528	12.48958	4.489583	3.270833
35.00491	11.94792	4.15625	3.114583
35.02453	12.13542	4.46875	3.208333
35.04416	12.47917	4.479167	3
35.06379	12.90625	4.84375	3.229167
35.08341	11.95833	4.708333	3.322917
35.10304	12.30208	4.697917	3.260417
35.12267	11.8125	4.510417	2.979167
35.1423	11.23958	4.270833	3.6875
35.16192	11.72917	4.416667	3.447917
35.18155	11.69792	4.6875	3.427083
35.20118	11.98958	4.5625	3.291667
35.2208	12.4375	4.427083	3.427083
35.24043	12.29167	4.75	3.375
35.26006	12.03125	4.65625	3.614583
35.27968	11.98958	4.885417	3.833333
35.29931	12.27083	4.979167	3.5625
35.31894	12.125	5.375	3.520833

35.33857	11.5	5.510417	3.489583
35.35819	12.27083	5.28125	3.75
35.37782	11.98958	5.03125	3.697917
35.39745	11.75	5.354167	3.541667
35.41707	12.14583	5.229167	4.0625
35.4367	12.5625	5.3125	3.458333
35.45633	11.72917	5.427083	3.385417
35.47595	12.30208	4.770833	3.270833
35.49558	11.9375	4.53125	3.364583
35.51521	12.125	4.447917	3.489583
35.53484	12.3125	4.989583	3.3125
35.55446	11.70833	5.09375	3.385417
35.57409	12.40625	4.416667	3.614583
35.59372	11.9375	4.739583	3.083333
35.61334	12.02083	4.458333	3.229167
35.63297	12.71875	4.760417	3.1875
35.6526	11.9375	4.822917	3.041667
35.67222	11.89583	4.458333	3.3125
35.69185	11.52083	4.854167	3.552083
35.71148	11.71875	4.302083	3.59375
35.73111	12.125	4.375	3.427083
35.75073	11.82292	4.739583	3.552083
35.77036	11.86458	4.645833	3.447917
35.78999	11.89583	4.583333	3.208333
35.80961	11.78125	4.510417	3.614583
35.82924	11.53125	4.552083	3.53125
35.84887	11.54167	4.40625	3.510417
35.86849	12	4.65625	3.145833
35.88812	11.85417	4.71875	3.25
35.90775	12.3125	4.489583	3.458333
35.92738	11.3125	4.958333	3.458333
35.947	11.30208	5	3.583333
35.96663	11.76042	4.625	3
35.98626	11.88542	4.552083	3.125
36.00588	11.3125	4.697917	3.28125
36.02551	11.8125	4.65625	3.53125
36.04514	11.6875	4.645833	3.25
36.06477	11.44792	4.6875	3.34375
36.08439	11.67708	4.1875	3.145833
36.10402	11.6875	4.125	3.333333
36.12365	11.73958	4.197917	3.416667
36.14327	11.4375	4.09375	3.479167
36.1629	11.82292	4.166667	3.260417
36.18253	11.58333	4.072917	3.333333
36.20215	11.36458	4.46875	3.260417

36.22178	12.04167	4.104167	3.572917
36.24141	11.65625	4.447917	3.270833
36.26104	11.53125	4.229167	3.09375
36.28066	11.58333	4.114583	3.302083
36.30029	12.27083	4.34375	3.302083
36.31992	11.91667	4.15625	3.052083
36.33954	11.6875	4.041667	3.375
36.35917	11.40625	4.270833	2.875
36.3788	10.9375	3.8125	3.270833
36.39842	12.32292	4.145833	3.09375
36.41805	11.20833	4.21875	3.447917
36.43768	11.25	3.958333	3.604167
36.45731	11.16667	4.583333	3.541667
36.47693	12.02083	4.177083	3.854167
36.49656	12.01042	4.40625	3.322917
36.51619	12.10417	4.541667	3.40625
36.53581	11.75	4.239583	3.895833
36.55544	12.11458	4.416667	3.104167
36.57507	12.03125	4.583333	3.28125
36.59469	12.48958	4.427083	3.3125
36.61432	11.29167	4.479167	3.03125
36.63395	11.44792	4.458333	3.083333
36.65358	12.23958	4.114583	3.625
36.6732	11.5	4.5625	3.010417
36.69283	11.80208	4.489583	3.375
36.71246	11.41667	4.40625	3.197917
36.73208	11.54167	4.708333	3.354167
36.75171	11.44792	4.260417	3.083333
36.77134	11.17708	4.5	3.052083
36.79096	11.78125	4.75	3.166667
36.81059	11.61458	4.15625	3.302083
36.83022	11.64583	4.020833	3.395833
36.84985	11.22917	4.447917	3.041667
36.86947	11.1875	4.416667	3.104167
36.8891	11.14583	4.78125	3.364583
36.90873	11.70833	4.125	2.90625
36.92835	11.35417	4.677083	3.333333
36.94798	11.4375	4.135417	2.927083
36.96761	11.94792	4.666667	3.302083
36.98723	11.58333	4.375	3.09375
37.00686	11.11458	4.458333	3.364583
37.02649	10.22917	4.322917	3.333333
37.04612	11.23958	4.21875	2.989583
37.06574	11.82292	4.40625	3.395833
37.08537	10.64583	4.21875	3.427083

37.105	10.96875	4.15625	3.3125
37.12462	11.15625	4.677083	3.302083
37.14425	11.11458	4.614583	3.604167
37.16388	11.30208	4.84375	3.4375
37.1835	11.80208	4.708333	3.677083
37.20313	11.16667	4.729167	3.385417
37.22276	10.90625	4.166667	3.270833
37.24239	11.05208	4.416667	3.458333
37.26201	11.42708	4.65625	3.5
37.28164	11.26042	4.635417	3.208333
37.30127	11.60417	4.78125	3.520833
37.32089	11.88542	4.708333	3.020833
37.34052	11.26042	4.53125	3.291667
37.36015	10.65625	4.510417	3.302083
37.37977	10.96875	4.802083	3.458333
37.3994	11.58333	4.1875	3.395833
37.41903	10.86458	4.270833	3.177083
37.43866	10.8125	4.166667	3.09375
37.45828	11.65625	4.604167	3.260417
37.47791	11.88542	4.291667	3.625
37.49754	11.25	4.395833	2.979167
37.51716	10.98958	4.802083	3.125
37.53679	11.25	4.40625	2.71875
37.55642	10.77083	4.0625	3.177083
37.57604	11.15625	4.354167	2.875
37.59567	10.52083	4.291667	3.197917
37.6153	11.11458	4.145833	3.34375
37.63493	11.01042	4.239583	3.46875
37.65455	11.625	4.083333	3.15625
37.67418	11.10417	4.572917	3.15625
37.69381	10.69792	4.208333	2.958333
37.71343	11.22917	4.3125	3.21875
37.73306	11.21875	4.114583	3.208333
37.75269	10.96875	4.354167	3.020833
37.77231	11.52083	4.114583	3.3125
37.79194	11.30208	4.479167	2.885417
37.81157	11.48958	3.822917	3.0625
37.8312	10.97917	4.010417	3.708333
37.85082	11.27083	4.03125	2.885417
37.87045	10.57292	4.15625	3.322917
37.89008	10.44792	4.354167	3.125
37.9097	11.22917	4.322917	3.302083
37.92933	11.85417	4.458333	3.135417
37.94896	11.63542	4.4375	3.197917
37.96858	11.57292	4.385417	3.208333

37.98821	11.36458	4.302083	3.041667
38.00784	11.30208	4.614583	3.364583
38.02747	11.55208	3.9375	3.604167
38.04709	10.23958	4.697917	3.4375
38.06672	10.86458	4.125	3.510417
38.08635	10.75	4.635417	3.791667
38.10597	11.07292	4.354167	3.427083
38.1256	10.80208	4.739583	3.708333
38.14523	11.375	4.6875	3.427083
38.16485	12.25	4.802083	3.28125
38.18448	11.10417	4.854167	3.5625
38.20411	11.23958	4.572917	3.53125
38.22374	11.125	4.666667	3.25
38.24336	10.875	4.21875	3.3125
38.26299	10.85417	4.21875	3.46875
38.28262	11.38542	4.510417	3.020833
38.30224	11.29167	4.552083	3.40625
38.32187	11.61458	4.53125	3.166667
38.3415	10.78125	3.90625	3.15625
38.36112	10.9375	4.104167	3.041667
38.38075	10.88542	3.822917	3.625
38.40038	11.04167	4.135417	3.1875
38.42001	11.54167	4.354167	3.25
38.43963	11.67708	4.5	3.104167
38.45926	11.1875	4.5	3.114583
38.47889	12.01042	4	2.90625
38.49851	10.92708	4.083333	3.208333
38.51814	11.45833	4.635417	3.177083
38.53777	11.04167	4.395833	3.291667
38.55739	10.88542	3.791667	3.239583
38.57702	11.11458	4.114583	3.354167
38.59665	11.10417	4.260417	3.135417
38.61628	11.44792	4.427083	3.03125
38.6359	10.79167	4.729167	3.15625
38.65553	10.5	3.916667	3.458333
38.67516	11.14583	4.489583	3.354167
38.69478	10.41667	4.416667	3.135417
38.71441	11.3125	4.427083	3.520833
38.73404	10.875	4.34375	3.572917
38.75366	11.35417	4.447917	3.520833
38.77329	11.01042	4.583333	3.177083
38.79292	10.97917	4.895833	3.260417
38.81255	11.21875	4.40625	3.510417
38.83217	10.54167	4.666667	3.260417
38.8518	10.61458	4.760417	3.28125

38.87143	10.71875	5.3125	3.395833
38.89105	11	5.270833	3.729167
38.91068	11.5	5.052083	3.4375
38.93031	11.125	5.020833	3.645833
38.94994	11.5	4.989583	3.458333
38.96956	10.9375	5.104167	3.84375
38.98919	10.65625	4.895833	3.84375
39.00882	10.9375	4.729167	3.53125
39.02844	10.44792	5.239583	3.4375
39.04807	10.73958	5.395833	3.729167
39.0677	11.11458	4.916667	3.677083
39.08732	11.77083	4.78125	3.427083
39.10695	11.05208	4.947917	3.84375
39.12658	10.89583	5.1875	4.166667
39.14621	10.57292	4.84375	3.96875
39.16583	11.29167	5.104167	3.791667
39.18546	11.27083	5.145833	3.645833
39.20509	11.40625	5.322917	3.979167
39.22471	10.75	5.25	4.104167
39.24434	11.51042	5.59375	3.520833
39.26397	11.70833	5.083333	3.489583
39.28359	11.3125	5.25	4.270833
39.30322	11.38542	5.916667	4.114583
39.32285	10.94792	5.625	4.125
39.34248	10.67708	5.739583	4.322917
39.3621	11.14583	6.322917	4.25
39.38173	11.1875	5.90625	4.229167
39.40136	11.4375	6.354167	4.770833
39.42098	11.625	6.0625	4.177083
39.44061	11.98958	6.65625	4.395833
39.46024	11.22917	6.59375	4.572917
39.47986	10.875	6.479167	4.40625
39.49949	11.10417	6.666667	4.385417
39.51912	11.94792	5.864583	4.239583
39.53875	11.84375	6.177083	5.145833
39.55837	11.40625	6.135417	4.614583
39.578	11.88542	6.40625	4.760417
39.59763	12.375	6.635417	5.104167
39.61725	11.98958	6.3125	4.552083
39.63688	11.35417	6.427083	5.28125
39.65651	11.64583	6.895833	5.3125
39.67613	11.23958	6.8125	5.364583
39.69576	11.22917	6.59375	5.572917
39.71539	10.95833	7.052083	5.239583
39.73502	11.55208	6.708333	5.541667

39.75464	12.0625	6.427083	5.09375
39.77427	11.77083	6.166667	5.40625
39.7939	11.8125	6.375	4.833333
39.81352	11.14583	6.166667	4.8125
39.83315	11.44792	5.864583	4.947917
39.85278	11.5	5.270833	4.583333
39.8724	11.47917	5.520833	4.385417
39.89203	11.46875	4.989583	4.052083
39.91166	11.89583	4.895833	3.729167
39.93129	11.04167	5.041667	3.822917
39.95091	10.84375	5.0625	3.666667
39.97054	11.04167	4.802083	3.479167
39.99017	11.10417	4.708333	3.625
40.00979	10.69792	4.395833	3.53125
40.02942	11.58333	4.697917	3.322917
40.04905	11.01042	4.6875	3.395833
40.06867	10.92708	4.666667	3.770833
40.0883	10.64583	5.041667	3.416667
40.10793	10.82292	4.541667	3.3125
40.12756	10.84375	4.322917	3.552083
40.14718	11.04167	4.770833	3.354167
40.16681	10.98958	4.135417	2.770833
40.18644	11.125	4.364583	3.427083
40.20606	10.15625	4.541667	2.958333
40.22569	10.04167	4.541667	3.53125
40.24532	10.5625	4.364583	3.0625
40.26494	10.78125	4.385417	3.291667
40.28457	11.16667	4.6875	3.4375
40.3042	10.5625	4.385417	3.46875
40.32383	10.41667	4.364583	3.59375
40.34345	10.69792	4.364583	2.9375
40.36308	10.5625	4.510417	3.541667
40.38271	11.30208	4.447917	3.260417
40.40233	11.01042	4.427083	3.520833
40.42196	10.88542	4.510417	3.25
40.44159	10.52083	4.385417	3.447917
40.46121	11.5	4.03125	3.375
40.48084	10.75	4.052083	3.25
40.50047	11.14583	4.229167	3.177083
40.5201	10.04167	4.09375	3.072917
40.53972	10.84375	4.104167	2.96875
40.55935	11.17708	4.010417	3.270833
40.57898	11.34375	4.333333	3.322917
40.5986	10.64583	4.385417	2.96875
40.61823	10.875	4.333333	3.041667

40.63786	10.41667	4.270833	2.96875
40.65748	10.61458	4.1875	3.5625
40.67711	11.07292	4.052083	3.260417
40.69674	11.05208	4.34375	3.083333
40.71637	10.53125	4.520833	3.21875
40.73599	11.04167	4.395833	3.416667
40.75562	11.26042	4.416667	3.03125
40.77525	11.33333	4.3125	3.197917
40.79487	10.94792	4.53125	2.958333
40.8145	10.54167	4.59375	3.302083
40.83413	11.08333	4.270833	3.28125
40.85375	11.1875	4.5	3.385417
40.87338	10.78125	4.083333	3.25
40.89301	10.38542	4.552083	2.895833
40.91264	10.78125	4.03125	3.291667
40.93226	10.88542	4.84375	3.1875
40.95189	11.25	4.6875	3.375
40.97152	11.27083	4.364583	3.291667
40.99114	11.14583	4.489583	3.270833
41.01077	10.36458	4.625	3.104167
41.0304	10.92708	4.635417	3.166667
41.05002	10.66667	4.572917	3.458333
41.06965	11.20833	5.166667	3.760417
41.08928	10.75	4.708333	3.71875
41.10891	10.58333	4.635417	3.802083
41.12853	11.51042	5	3.5
41.14816	11.19792	5.635417	3.708333
41.16779	10.5	4.677083	3.666667
41.18741	10.70833	4.875	3.520833
41.20704	11.48958	4.46875	3.333333
41.22667	10.83333	4.645833	3.46875
41.24629	10.47917	5.15625	3.572917
41.26592	10.89583	4.864583	3.489583
41.28555	11.22917	5.041667	3.96875
41.30518	10.66667	4.65625	3.40625
41.3248	11.21875	4.770833	3.614583
41.34443	10.90625	4.479167	3.739583
41.36406	11.1875	4.958333	3.5625
41.38368	10.59375	4.447917	3.489583
41.40331	10.52083	4.677083	3.3125
41.42294	10.79167	4.447917	3.333333
41.44256	10.91667	4.885417	3.145833
41.46219	10.8125	4.59375	3.177083
41.48182	10.77083	4.822917	3.0625
41.50145	10.625	4.6875	3.072917

41.52107	10.6875	4.395833	3.260417
41.5407	11.05208	4.3125	3.15625
41.56033	10.32292	4.78125	3.364583
41.57995	10.52083	4.166667	3.395833
41.59958	10.95833	4.5625	3.28125
41.61921	10.41667	4.3125	3.354167
41.63883	10.78125	4.677083	3.229167
41.65846	10.44792	4.583333	3.458333
41.67809	10.59375	4.489583	3.291667
41.69772	10.04167	4.354167	3.46875
41.71734	10.55208	4.3125	3.239583
41.73697	10.69792	4.572917	3.677083
41.7566	10.875	4.520833	3.479167
41.77622	10.47917	4.75	3.5
41.79585	10.89583	4.8125	3.458333
41.81548	10.38542	5.041667	3.520833
41.83511	11.19792	4.479167	3.635417
41.85473	10.82292	4.635417	3.791667
41.87436	10.80208	5.15625	3.729167
41.89399	11.09375	5	3.802083
41.91361	10.91667	4.822917	3.75
41.93324	11.23958	5.052083	3.833333
41.95287	10.47917	4.8125	4.041667
41.97249	10.96875	5.072917	3.572917
41.99212	10.96875	5.145833	3.854167
42.01175	10.39583	5.25	3.489583
42.03138	10.51042	4.979167	3.854167
42.051	10.65625	4.604167	3.822917
42.07063	10.40625	4.666667	3.395833
42.09026	10.53125	4.40625	3.875
42.10988	11.28125	4.520833	3.375
42.12951	10.45833	4.552083	3.583333
42.14914	10.59375	4.864583	3.604167
42.16876	10.40625	4.541667	3.375
42.18839	10.58333	4.354167	3.416667
42.20802	10.64583	4.53125	3.5
42.22765	10.70833	4.614583	4
42.24727	10.69792	4.75	3.916667
42.2669	10.72917	4.666667	4.041667
42.28653	10.3125	4.760417	6.010417
42.30615	10.17708	4.635417	9.479167
42.32578	10.65625	5.21875	9.947917
42.34541	10.59375	4.697917	6.6875
42.36503	10.14583	4.6875	4.833333
42.38466	11.23958	4.65625	4.4375

42.40429	10.44792	4.864583	5.53125
42.42392	10.73958	5.333333	6.34375
42.44354	10.48958	5.010417	6.15625
42.46317	10.46875	4.958333	4.8125
42.4828	10.27083	4.364583	3.635417
42.50242	11.13542	4.729167	4.125
42.52205	10.30208	4.927083	3.708333
42.54168	10.34375	4.395833	3.375
42.5613	10.3125	4.770833	3.15625
42.58093	10.35417	4.40625	3.364583
42.60056	10.89583	4.510417	3.40625
42.62019	10.55208	4.666667	3.458333
42.63981	10.36458	4.625	3.3125
42.65944	10.125	4.375	3.083333
42.67907	10.25	4.229167	2.979167
42.69869	10.11458	4.072917	3.520833
42.71832	10.33333	4.1875	3.177083
42.73795	10.66667	4.46875	3
42.75757	10.61458	4.53125	3.197917
42.7772	10.44792	4.28125	3.333333
42.79683	10.28125	4.354167	3.552083
42.81646	9.5625	4.28125	2.989583
42.83608	10.46875	4.53125	3.21875
42.85571	10.38542	4.239583	3.260417
42.87534	10.02083	4.416667	3.28125
42.89496	10.85417	4.364583	3.28125
42.91459	10.67708	4.354167	3.364583
42.93422	10.61458	4.4375	3.125
42.95384	10.44792	4.03125	3.416667
42.97347	10.27083	4.5	3.40625
42.9931	10.0625	4.541667	3.208333
43.01273	10.35417	4.416667	3.416667
43.03235	10.26042	4.875	3.270833
43.05198	10.02083	4.552083	3.479167
43.07161	10.21875	4.9375	3.458333
43.09123	10.45833	4.510417	3.510417
43.11086	10.39583	4.854167	3.572917
43.13049	9.447917	4.625	3.21875
43.15011	9.958333	5.010417	3.635417
43.16974	10.52083	4.5	3.083333
43.18937	10.0625	4.302083	3.385417
43.209	10.83333	4.677083	3.541667
43.22862	9.822917	4.322917	3.177083
43.24825	10.27083	4.65625	3.34375
43.26788	9.552083	4.40625	3.125

43.2875	10.73958	4.614583	3.552083
43.30713	10.29167	4.520833	3.354167
43.32676	10.63542	4.666667	3.125
43.34638	10.78125	4.3125	3.395833
43.36601	9.864583	4.322917	3.375
43.38564	10.66667	4.416667	3.333333
43.40527	10.40625	4.6875	3.166667
43.42489	10.78125	4.395833	3.166667
43.44452	9.760417	4.416667	3.291667
43.46415	10.41667	4.458333	3.229167
43.48377	9.947917	4.510417	3.166667
43.5034	9.666667	4.895833	3.104167
43.52303	10.91667	4.75	3.322917
43.54265	10.15625	4.927083	2.875
43.56228	10.84375	5	3.322917
43.58191	9.729167	4.270833	3.520833
43.60154	10.47917	5	3.645833
43.62116	10.15625	4.489583	2.8125
43.64079	10.29167	4.864583	3.427083
43.66042	10.01042	4.90625	3.84375
43.68004	10.0625	5.135417	3.625
43.69967	10.625	5.03125	3.552083
43.7193	10.59375	5.333333	3.75
43.73892	10.47917	4.958333	3.90625
43.75855	10.13542	5.541667	4.145833
43.77818	10.57292	5.489583	3.645833
43.79781	10.05208	5.260417	3.947917
43.81743	9.927083	5.697917	4.177083
43.83706	10.08333	5.333333	4.145833
43.85669	10.05208	5.239583	4.229167
43.87631	10.0625	5.479167	3.75
43.89594	10.05208	5.822917	4.322917
43.91557	10.625	5.8125	4.354167
43.93519	10.35417	5.46875	3.916667
43.95482	9.885417	5.5625	4.083333
43.97445	9.552083	5.5	4.1875
43.99408	10.3125	5.354167	3.927083
44.0137	10.48958	5.34375	4.4375
44.03333	9.947917	5.40625	3.875
44.05296	9.875	4.895833	3.739583
44.07258	10.14583	5.3125	3.822917
44.09221	9.614583	4.854167	3.885417
44.11184	10.10417	5.260417	3.916667
44.13146	10.01042	5.125	3.875
44.15109	10.14583	4.84375	3.645833

44.17072	9.6875	4.729167	4.09375
44.19035	10.04167	4.75	3.84375
44.20997	9.864583	4.708333	3.489583
44.2296	9.96875	4.645833	3.458333
44.24923	9.802083	4.96875	3.302083
44.26885	9.729167	4.489583	3.447917
44.28848	9.958333	4.59375	3.833333
44.30811	9.958333	5.072917	3.395833
44.32773	9.895833	4.822917	3.65625
44.34736	9.927083	4.989583	3.572917
44.36699	10.14583	4.583333	3.375
44.38662	10.46875	4.34375	3.260417
44.40624	10.01042	4.645833	3.8125
44.42587	9.84375	4.78125	3.291667
44.4455	10.25	3.979167	3.3125
44.46512	9.78125	4.489583	3.322917
44.48475	9.270833	4.59375	3.3125
44.50438	10.19792	4.34375	3.40625
44.524	9.541667	4.25	3.479167
44.54363	9.75	4.34375	3.364583
44.56326	9.75	4.458333	3.21875
44.58289	9.729167	4.4375	2.947917
44.60251	10.03125	4.520833	3.15625
44.62214	9.875	4.583333	3.5625
44.64177	9.875	4.5625	3.09375
44.66139	9.0625	4.354167	3.104167
44.68102	9.510417	5.010417	3.104167
44.70065	9.802083	4.541667	3.020833
44.72028	9.385417	4.583333	3.208333
44.7399	9.71875	4.59375	3.28125
44.75953	9.927083	4.75	3.354167
44.77916	9.604167	4.427083	3.802083
44.79878	9.052083	4.71875	3.15625
44.81841	9.666667	4.677083	3.333333
44.83804	9.489583	4.510417	3.166667
44.85766	9.375	4.885417	3.541667
44.87729	9.208333	4.71875	3.3125
44.89692	9.291667	4.791667	3.541667
44.91655	9.229167	4.458333	3.427083
44.93617	9.114583	4.510417	3.3125
44.9558	9.354167	4.729167	3.59375
44.97543	9.40625	4.708333	3.385417
44.99505	9.697917	4.625	3.604167
45.01468	9.416667	4.947917	3.927083
45.03431	9.739583	4.90625	3.322917

45.05393	9.229167	4.96875	3.5625
45.07356	9.625	4.666667	3.21875
45.09319	10.20833	4.645833	3.645833
45.11282	8.947917	4.979167	3.5625
45.13244	9.697917	4.791667	3.895833
45.15207	9.239583	5.020833	4.083333
45.1717	8.96875	4.822917	3.625
45.19132	9.40625	4.614583	3.5
45.21095	9.489583	5.15625	3.760417
45.23058	9.270833	5.114583	3.791667
45.2502	8.958333	4.979167	3.645833
45.26983	9.302083	5.427083	3.864583
45.28946	9.229167	5.3125	3.770833
45.30909	8.979167	5.125	3.979167
45.32871	9.614583	5.010417	3.34375
45.34834	9.177083	5.333333	3.6875
45.36797	9.302083	5.322917	3.802083
45.38759	9.385417	5.3125	3.739583
45.40722	9.020833	5.552083	3.875
45.42685	9.041667	5.270833	3.989583
45.44647	8.979167	4.989583	3.75
45.4661	9.104167	4.916667	3.927083
45.48573	9.145833	5.010417	3.84375
45.50536	9.239583	5.125	3.916667
45.52498	8.822917	5.145833	3.729167
45.54461	9.09375	4.916667	4.135417
45.56424	8.96875	4.520833	3.958333
45.58386	9.25	4.635417	3.677083
45.60349	8.9375	4.697917	3.75
45.62312	9.40625	4.302083	3.947917
45.64274	8.697917	4.4375	3.4375
45.66237	9.833333	4.96875	3.760417
45.682	8.552083	5.1875	3.1875
45.70163	9.197917	4.510417	3.25
45.72125	9.020833	4.541667	3.15625
45.74088	8.59375	4.604167	3.927083
45.76051	8.541667	4.833333	3.25
45.78013	9.447917	5.072917	3.708333
45.79976	8.8125	4.479167	3.427083
45.81939	9.052083	4.604167	3.458333
45.83901	8.6875	4.333333	3.447917
45.85864	8.947917	4.625	3.177083
45.87827	8.947917	4.78125	3.885417
45.8979	8.958333	4.958333	3.395833
45.91752	9.010417	5.1875	3.3125

45.93715	8.677083	4.572917	3.75
45.95678	8.708333	4.78125	3.25
45.9764	8.90625	4.1875	3.697917
45.99603	8.635417	4.84375	3.40625
46.01566	8.770833	4.333333	3.260417
46.03528	8.84375	4.53125	3.135417
46.05491	8.71875	4.114583	3.3125
46.07454	9.229167	4.34375	3.46875
46.09417	8.447917	4.416667	3.71875
46.11379	8.489583	4.270833	3.666667
46.13342	8.645833	4.822917	3.5
46.15305	8.770833	4.21875	3.541667
46.17267	9.0625	4.28125	3.520833
46.1923	8.6875	4.5625	3.395833
46.21193	8.885417	4.90625	3.302083
46.23155	8.645833	4.75	3.552083
46.25118	8.958333	4.395833	3.75
46.27081	8.947917	4.552083	3.458333
46.29044	9.15625	4.854167	3.791667
46.31006	8.916667	5.208333	3.510417
46.32969	8.802083	5.020833	4.09375
46.34932	8.947917	5.135417	4.239583
46.36894	8.947917	5.291667	4.125
46.38857	8.708333	5.1875	4.020833
46.4082	8.979167	5.239583	4.197917
46.42782	8.677083	5.791667	4.75
46.44745	8.15625	5.59375	4.302083
46.46708	8.84375	5.979167	4.416667
46.48671	8.708333	6.395833	4.625
46.50633	8.34375	6.333333	4.479167
46.52596	8.3125	7.114583	5.697917
46.54559	8.583333	6.708333	5.885417
46.56521	9.166667	6.989583	5.989583
46.58484	8.364583	7.072917	6.34375
46.60447	8.197917	7.270833	6.15625
46.62409	8.625	7.03125	5.9375
46.64372	8.4375	6.65625	6.041667
46.66335	8.489583	7.010417	5.822917
46.68298	8.479167	6.916667	5.583333
46.7026	7.885417	5.9375	5.541667
46.72223	8.708333	6.25	5.489583
46.74186	8.145833	6.177083	5.40625
46.76148	8.375	5.802083	4.90625
46.78111	8.479167	5.9375	4.635417
46.80074	8.645833	5.822917	4.604167

46.82036	8.260417	5.135417	3.90625
46.83999	7.9375	4.875	3.885417
46.85962	7.427083	4.822917	4.385417
46.87925	8.5	4.458333	3.9375
46.89887	8.479167	4.666667	3.802083
46.9185	8.604167	4.708333	3.5625
46.93813	7.875	4.8125	3.96875
46.95775	8.5	4.708333	3.489583
46.97738	8.083333	4.197917	3.5
46.99701	8.03125	4.635417	3.447917
47.01663	8.145833	4.697917	3.75
47.03626	8.104167	4.822917	3.53125
47.05589	7.958333	4.395833	3.614583
47.07552	8.375	4.833333	4.0625
47.09514	8.416667	5.020833	3.28125
47.11477	7.9375	4.5625	3.729167
47.1344	8.145833	5.010417	3.739583
47.15402	8.645833	4.979167	3.833333
47.17365	8.447917	5.083333	3.822917
47.19328	8.395833	4.979167	3.729167
47.2129	8.28125	4.947917	3.708333
47.23253	7.989583	4.625	3.885417
47.25216	8.604167	4.6875	3.802083
47.27179	7.958333	4.875	3.9375
47.29141	8	5.291667	4.03125
47.31104	8.614583	4.708333	4.177083
47.33067	8.072917	5.1875	3.989583
47.35029	8.145833	5.333333	3.979167
47.36992	7.75	5.25	4.114583
47.38955	7.854167	5.447917	3.760417
47.40917	8.052083	5.34375	3.979167
47.4288	7.635417	5.791667	4.135417
47.44843	8.052083	5.302083	4.041667
47.46806	8.1875	5.21875	3.6875
47.48768	7.802083	5.28125	3.822917
47.50731	7.416667	5.25	4
47.52694	8.0625	5.333333	3.989583
47.54656	7.9375	4.916667	3.916667
47.56619	8.416667	5.760417	4.114583
47.58582	7.833333	5.895833	4.072917
47.60545	8.020833	5.0625	4
47.62507	8.135417	5.604167	3.96875
47.6447	8.197917	4.791667	3.822917
47.66433	7.78125	4.833333	3.979167
47.68395	7.239583	5.104167	4.416667

47.70358	7.989583	5.03125	4.041667
47.72321	8.104167	4.96875	4.010417
47.74283	7.447917	4.8125	4.135417
47.76246	7.802083	4.885417	4.020833
47.78209	7.364583	5.1875	4.177083
47.80172	8.0625	4.520833	3.96875
47.82134	7.979167	5.020833	4.28125
47.84097	7.979167	5.15625	4.291667
47.8606	7.71875	5.333333	4.09375
47.88022	8.03125	5.677083	4.197917
47.89985	8.083333	5.25	4.427083
47.91948	7.427083	5.885417	4.302083
47.9391	8.229167	5.583333	4.614583
47.95873	7.760417	5.5625	5.020833
47.97836	8.072917	6.03125	4.604167
47.99799	8.041667	6.0625	4.28125
48.01761	7.729167	5.958333	4.895833
48.03724	8.53125	5.645833	4.552083
48.05687	8.364583	5.84375	4.333333
48.07649	7.760417	5.78125	4.770833
48.09612	7.854167	5.09375	4.229167
48.11575	7.697917	5.364583	4.010417
48.13537	7.375	5.104167	4.322917
48.155	7.4375	5.333333	4.385417
48.17463	7.552083	5.458333	4.625
48.19426	7.760417	5.177083	4.114583
48.21388	8.010417	4.96875	4.166667
48.23351	7.71875	4.739583	4.03125
48.25314	8.020833	5.083333	4.135417
48.27276	7.520833	5.270833	4.333333
48.29239	7.708333	5.03125	4.21875
48.31202	7.625	5.020833	4.375
48.33164	7.90625	5.395833	3.833333
48.35127	7.208333	5.479167	3.9375
48.3709	7.427083	5.28125	3.979167
48.39053	6.770833	5.59375	4.072917
48.41015	7.239583	5.708333	4.822917
48.42978	7.5	5.552083	4.322917
48.44941	7.427083	5.645833	4.5
48.46903	7.03125	5.395833	4.5625
48.48866	7.385417	5.135417	4.364583
48.50829	7.96875	5.229167	4.583333
48.52791	8	5.208333	4.260417
48.54754	7.09375	5.197917	3.833333
48.56717	7.458333	4.78125	4.0625

48.5868	7.364583	4.833333	4.104167
48.60642	7.375	4.770833	3.6875
48.62605	7.635417	5.052083	4.322917
48.64568	6.96875	4.979167	3.5625
48.6653	7.5	4.770833	3.625
48.68493	7.791667	5.020833	3.708333
48.70456	7.5	4.697917	4.34375
48.72418	7.541667	4.927083	3.572917
48.74381	7.854167	5	3.479167
48.76344	7.5	4.864583	3.791667
48.78307	6.635417	5.072917	3.447917
48.80269	7.479167	4.989583	3.552083
48.82232	7.135417	5.010417	3.677083
48.84195	6.875	5.083333	3.677083
48.86157	7.229167	4.947917	3.916667
48.8812	7.270833	4.885417	3.229167
48.90083	7.260417	4.78125	3.916667
48.92045	7.135417	4.9375	3.416667
48.94008	6.979167	5.177083	3.927083
48.95971	7.458333	5.166667	4.052083
48.97934	7.145833	4.666667	4.083333
48.99896	7.322917	5.083333	4.03125
49.01859	7.322917	5.40625	3.854167
49.03822	7.229167	5.0625	3.708333
49.05784	7.125	4.916667	3.802083
49.07747	7.34375	4.770833	3.770833
49.0971	7.46875	4.989583	3.760417
49.11672	7.541667	4.697917	3.458333
49.13635	7.270833	4.864583	3.604167
49.15598	7.645833	4.510417	3.40625
49.17561	7.604167	4.833333	3.875
49.19523	7.364583	5.104167	3.947917
49.21486	7.395833	5.020833	3.739583
49.23449	7.291667	4.65625	3.947917
49.25411	7.458333	4.71875	3.6875
49.27374	7.177083	5.104167	4.0625
49.29337	7.260417	5.0625	4.5
49.31299	6.916667	5.40625	4.260417
49.33262	7.354167	5.333333	4.802083
49.35225	7.1875	5.958333	4.833333
49.37188	7.010417	6.395833	5.416667
49.3915	7.041667	6.645833	5.65625
49.41113	7.09375	6.5625	5.552083
49.43076	7.09375	6.552083	5.510417
49.45038	7.40625	6.385417	5.291667

49.47001	6.833333	6.583333	5.5
49.48964	7.0625	6.0625	5.052083
49.50926	7.229167	6.260417	4.708333
49.52889	7.09375	5.697917	4.8125
49.54852	6.552083	5.75	4.604167
49.56815	7.125	5.541667	4.625
49.58777	7.354167	5.1875	4.104167
49.6074	7.333333	5.21875	3.989583
49.62703	7.322917	5.3125	3.989583
49.64665	7.333333	4.84375	3.802083
49.66628	7.322917	4.614583	3.416667
49.68591	7.239583	4.65625	3.65625
49.70553	7.5	4.645833	3.729167
49.72516	7.239583	4.583333	3.40625
49.74479	6.5	4.645833	3.447917
49.76442	7.177083	4.489583	3.65625
49.78404	6.927083	4.802083	3.8125
49.80367	6.729167	4.739583	3.791667
49.8233	7.260417	4.84375	3.583333
49.84292	7.229167	4.895833	3.833333
49.86255	7.302083	5.052083	3.458333
49.88218	6.989583	4.53125	3.697917
49.9018	7	4.333333	3.5625
49.92143	7.3125	4.28125	3.489583
49.94106	7.239583	4.229167	3.53125
49.96069	6.65625	4.572917	3.854167
49.98031	6.791667	4.40625	3.697917
49.99994	6.791667	4.677083	3.84375
50.01957	6.770833	4.364583	4.333333
50.03919	6.697917	4.916667	4.729167
50.05882	7.625	4.5625	5.135417
50.07845	6.979167	4.635417	5.239583
50.09807	6.666667	4.6875	4.489583
50.1177	6.625	4.21875	3.90625
50.13733	6.864583	4.90625	4.302083
50.15696	6.822917	4.90625	4.197917
50.17658	6.927083	4.53125	4.666667
50.19621	6.458333	4.479167	4.229167
50.21584	6.96875	4.541667	4.354167
50.23546	7.052083	4.885417	4.46875
50.25509	6.729167	4.6875	3.614583
50.27472	6.5625	4.760417	3.833333
50.29434	6.770833	5.166667	4.197917
50.31397	6.510417	4.854167	4.09375
50.3336	6.15625	5.135417	3.947917

50.35323	6.635417	5.052083	3.979167
50.37285	7	5.145833	4.552083
50.39248	7.395833	5.229167	4.010417
50.41211	6.302083	5.15625	4.3125
50.43173	6.552083	5.03125	4.5
50.45136	6.708333	5.229167	4.0625
50.47099	6.666667	5.010417	4.010417
50.49062	5.989583	4.791667	4.052083
50.51024	6.385417	4.979167	4.270833
50.52987	6.770833	4.677083	4.083333
50.5495	6.802083	4.5625	3.947917
50.56912	6.177083	4.489583	3.71875
50.58875	6.520833	4.416667	3.78125
50.60838	6.354167	4.385417	3.229167
50.628	6.6875	3.9375	3.541667
50.64763	6.71875	4.083333	3.479167
50.66726	6.697917	4.572917	3.114583
50.68689	6.458333	4.34375	3.520833
50.70651	6.625	3.958333	3.302083
50.72614	6.510417	4.052083	3.15625
50.74577	6.666667	4.052083	3.416667
50.76539	6.520833	4.010417	3.479167
50.78502	7.145833	3.979167	3.25
50.80465	7.34375	4.458333	2.947917
50.82427	6.71875	4.1875	3.125
50.8439	6.4375	4.385417	3.291667
50.86353	6.21875	3.979167	3.0625
50.88316	6.572917	4.6875	3.197917
50.90278	6.708333	4.125	3.208333
50.92241	6.458333	4.0625	3.28125
50.94204	6.677083	3.8125	3.104167
50.96166	6.197917	4.40625	3.21875
50.98129	6.25	3.895833	3.552083
51.00092	6.864583	4.28125	3.604167
51.02054	6.5	4.708333	3.708333
51.04017	6.354167	4.145833	3.354167
51.0598	6.260417	4.333333	3.333333
51.07943	6.520833	4.708333	3.5625
51.09905	6.083333	4.25	3.15625
51.11868	6.229167	4.541667	3.46875
51.13831	6.5	4.302083	4.03125
51.15793	6.3125	4.854167	3.802083
51.17756	6.0625	4.760417	3.614583
51.19719	5.958333	4.583333	3.3125
51.21681	6.708333	4.5	4.020833

51.23644	6.197917	5.0625	3.291667
51.25607	5.802083	5.197917	3.5
51.2757	6.333333	4.791667	3.375
51.29532	5.9375	4.520833	3.416667
51.31495	6.5	4.197917	3.645833
51.33458	5.833333	4.03125	3.572917
51.3542	6.395833	4.15625	3.28125
51.37383	6.052083	3.885417	3.34375
51.39346	6.1875	4.447917	3.197917
51.41308	6.135417	3.65625	2.885417
51.43271	6.458333	4.083333	3.260417
51.45234	6.145833	3.854167	3.552083
51.47197	6.489583	4.270833	2.979167
51.49159	6.25	3.916667	3.239583
51.51122	6.333333	3.604167	3.104167
51.53085	6.4375	3.958333	3.03125
51.55047	6.166667	4.270833	3.71875
51.5701	6.166667	3.979167	3.364583
51.58973	6.46875	3.791667	3.145833
51.60935	6.0625	4.145833	2.875
51.62898	6.416667	4.09375	3.333333
51.64861	6.708333	3.895833	3.34375
51.66824	5.895833	4.239583	2.989583
51.68786	6.21875	4.34375	3.041667
51.70749	6.229167	4.34375	3.15625
51.72712	6.552083	4.166667	3.208333
51.74674	6.166667	3.96875	2.989583
51.76637	6.541667	4.177083	3.552083
51.786	6.333333	4.270833	3.052083
51.80562	6.322917	4.052083	3.416667
51.82525	6.395833	4.34375	3.541667
51.84488	6.260417	4.291667	3.53125
51.86451	6.333333	4.59375	3.59375
51.88413	5.625	4.510417	3.614583
51.90376	6.270833	4.395833	3.322917
51.92339	6.458333	4.041667	3.96875
51.94301	6.145833	4.614583	3.583333
51.96264	5.84375	4.895833	4
51.98227	5.979167	4.84375	3.864583
52.00189	6.447917	4.760417	4.302083
52.02152	6.083333	4.3125	4
52.04115	6.041667	4.822917	3.645833
52.06078	6.489583	4.802083	3.770833
52.0804	6	4.479167	3.510417
52.10003	6.291667	4.21875	3.520833

52.11966	5.833333	4.40625	3.760417
52.13928	5.927083	4.375	3.0625
52.15891	6.145833	4.291667	3.78125
52.17854	6.833333	4.40625	3.3125
52.19816	5.9375	4.072917	3.197917
52.21779	5.895833	4.020833	3.25
52.23742	5.90625	3.822917	3.041667
52.25705	6.083333	3.947917	3.21875
52.27667	6.083333	3.708333	3.09375
52.2963	6.052083	3.864583	3
52.31593	6	3.916667	2.8125
52.33555	6.302083	3.510417	3.052083
52.35518	6.072917	3.947917	3.041667
52.37481	6.833333	3.739583	2.96875
52.39443	6.083333	3.416667	3.25
52.41406	6.1875	3.885417	2.71875
52.43369	5.916667	3.78125	3.114583
52.45332	5.96875	3.75	2.729167
52.47294	5.885417	3.75	2.854167
52.49257	5.927083	3.78125	2.604167
52.5122	6.53125	3.760417	2.822917
52.53182	5.666667	3.5	2.895833
52.55145	6.416667	3.927083	2.65625
52.57108	5.822917	3.96875	3.208333
52.5907	6.0625	4.052083	3.020833
52.61033	5.9375	4.260417	2.71875
52.62996	6.416667	3.625	2.708333
52.64959	6.166667	3.65625	3.25
52.66921	5.375	4.145833	2.916667
52.68884	6.09375	3.395833	3.041667
52.70847	6.072917	4.072917	3.041667
52.72809	6.1875	3.59375	3.104167
52.74772	5.864583	3.614583	2.583333
52.76735	6.041667	3.78125	2.90625
52.78697	5.895833	3.791667	2.770833
52.8066	6.489583	3.6875	3.0625
52.82623	5.854167	3.802083	2.989583
52.84586	6.041667	3.791667	3.395833
52.86548	6.010417	3.875	3.4375
52.88511	6.84375	3.958333	3.447917
52.90474	6.083333	4.1875	3.28125
52.92436	5.96875	4.135417	3.239583
52.94399	5.78125	4.458333	3.197917
52.96362	5.96875	4.625	3.270833
52.98324	5.885417	4.510417	3.479167

53.00287	6.15625	4	3.166667
53.0225	5.71875	4.28125	3.260417
53.04213	5.864583	4.5	3.666667
53.06175	6.25	4.614583	3.364583
53.08138	5.760417	4.65625	3.90625
53.10101	5.979167	4.958333	3.979167
53.12063	6.5	4.6875	4.104167
53.14026	6.520833	4.614583	3.958333
53.15989	5.895833	4.96875	3.666667
53.17951	6.4375	5.1875	4.166667
53.19914	5.958333	4.947917	3.59375
53.21877	5.8125	4.947917	4.375
53.2384	6.364583	5.4375	4.479167
53.25802	6.197917	5.0625	4.072917
53.27765	5.59375	4.34375	3.770833
53.29728	6.645833	4.916667	4.145833
53.3169	6.145833	4.833333	3.510417
53.33653	6.541667	4.697917	3.59375
53.35616	5.729167	4.697917	3.3125
53.37578	6.270833	4.4375	3.489583
53.39541	6.177083	4.34375	3.260417
53.41504	6.364583	4.520833	3.25
53.43467	5.833333	4.364583	3.677083
53.45429	5.71875	4.447917	3.21875
53.47392	6.177083	4.114583	3.125
53.49355	5.947917	4.3125	3.114583
53.51317	6.020833	4.125	2.75
53.5328	5.96875	3.604167	2.84375
53.55243	6.072917	3.75	2.979167
53.57206	5.9375	3.572917	2.8125
53.59168	5.447917	3.989583	3.020833
53.61131	6.21875	3.854167	2.958333
53.63094	5.666667	3.864583	2.927083
53.65056	6.666667	3.854167	3.072917
53.67019	5.864583	3.90625	2.59375
53.68982	5.875	3.583333	2.864583
53.70944	6	3.927083	2.75
53.72907	6.09375	4.083333	2.947917
53.7487	5.645833	3.75	2.625
53.76833	6.09375	3.364583	3.09375
53.78795	5.833333	3.6875	2.927083
53.80758	5.65625	3.625	3.239583
53.82721	5.354167	3.90625	2.854167
53.84683	5.84375	3.854167	2.770833
53.86646	6.114583	3.885417	3.052083

53.88609	5.604167	3.53125	3.09375
53.90571	6.114583	3.416667	2.885417
53.92534	5.697917	3.6875	2.697917
53.94497	6.041667	3.854167	2.979167
53.9646	5.541667	4.104167	2.90625
53.98422	5.708333	3.75	2.989583
54.00385	5.375	3.90625	3.020833
54.02348	5.802083	3.583333	2.71875
54.0431	5.635417	3.625	3.145833
54.06273	5.53125	3.635417	2.9375
54.08236	5.697917	4.083333	2.90625
54.10198	5.302083	4.15625	2.864583
54.12161	5.270833	3.614583	2.697917
54.14124	5.885417	3.697917	2.979167
54.16087	5.8125	3.65625	2.583333
54.18049	5.71875	3.479167	2.59375
54.20012	5.541667	3.541667	2.645833
54.21975	5.6875	3.541667	2.75
54.23937	5.46875	3.572917	2.885417
54.259	5.614583	3.364583	3.052083
54.27863	5.729167	3.739583	2.604167
54.29825	5.614583	3.802083	2.864583
54.31788	5.739583	3.25	2.75
54.33751	5.510417	3.541667	2.822917
54.35714	5.739583	3.604167	2.729167
54.37676	5.572917	3.927083	2.572917
54.39639	5.46875	3.645833	3.1875
54.41602	5.541667	3.75	2.90625
54.43564	5.59375	4.010417	2.854167
54.45527	5.9375	3.4375	2.947917
54.4749	5.833333	3.520833	2.864583
54.49452	5.791667	3.645833	2.635417
54.51415	5.5625	3.927083	2.625
54.53378	5.645833	3.96875	2.979167
54.55341	5.5	3.90625	3.010417
54.57303	6.03125	3.96875	2.802083
54.59266	5.572917	3.895833	2.71875
54.61229	5.520833	3.833333	2.895833
54.63191	5.979167	3.5625	2.895833
54.65154	5.614583	3.927083	2.697917
54.67117	6.072917	3.458333	2.958333
54.69079	5.729167	3.447917	3.083333
54.71042	6.010417	3.46875	2.927083
54.73005	5.90625	3.677083	3.020833
54.74968	5.541667	4.145833	2.791667

54.7693	5.78125	3.979167	2.833333
54.78893	5.90625	3.895833	2.770833
54.80856	5.583333	3.989583	2.822917
54.82818	5.5625	3.864583	2.989583
54.84781	5.489583	3.864583	2.958333
54.86744	5.541667	3.666667	2.84375
54.88706	5.302083	4.041667	2.677083
54.90669	5.541667	3.666667	3.03125
54.92632	5.552083	3.59375	2.65625
54.94595	5.520833	3.520833	2.979167
54.96557	5.552083	3.5	2.666667
54.9852	5.53125	3.84375	2.9375
55.00483	5.552083	3.8125	2.84375
55.02445	5.375	3.572917	2.479167
55.04408	5.447917	3.572917	2.6875
55.06371	6.010417	3.520833	2.791667
55.08333	5.864583	3.3125	3.052083
55.10296	5.666667	3.614583	3.052083
55.12259	5.177083	3.8125	2.78125
55.14222	5.260417	3.895833	2.75
55.16184	5.90625	3.697917	2.510417
55.18147	5.791667	3.583333	3
55.2011	5.71875	3.802083	2.958333
55.22072	5.520833	3.739583	2.822917
55.24035	5.614583	3.4375	2.677083
55.25998	5.78125	3.625	2.802083
55.2796	5.854167	3.25	2.583333
55.29923	6.239583	3.354167	2.739583
55.31886	5.354167	3.8125	2.90625
55.33849	5.302083	3.4375	2.979167
55.35811	5.5	3.604167	2.729167
55.37774	5.572917	3.770833	2.885417
55.39737	5.385417	3.427083	2.666667
55.41699	5.489583	3.9375	2.583333
55.43662	5.760417	3.59375	2.760417
55.45625	5.760417	3.791667	3.083333
55.47587	5.489583	3.895833	2.78125
55.4955	5.666667	3.78125	3.083333
55.51513	5.739583	3.71875	2.96875
55.53476	5.5625	4.270833	2.9375
55.55438	5.760417	3.947917	3.020833
55.57401	5.010417	3.864583	3.03125
55.59364	5.729167	3.9375	2.802083
55.61326	5.572917	3.583333	2.8125
55.63289	4.947917	3.885417	2.666667

55.65252	5.427083	3.791667	3.229167
55.67214	5.5	3.9375	2.947917
55.69177	5.5	4.09375	3.104167
55.7114	5.802083	4.21875	3.020833
55.73103	5.260417	4.072917	3.052083
55.75065	4.875	4.010417	3.21875
55.77028	5.229167	4.145833	2.90625
55.78991	5.625	3.96875	3.114583
55.80953	5.510417	3.833333	3.46875
55.82916	5.53125	3.875	3
55.84879	5.302083	3.708333	3.010417
55.86841	5.78125	3.71875	2.760417
55.88804	5.5	3.84375	3.114583
55.90767	5.5	3.833333	3.145833
55.9273	5.46875	3.75	2.572917
55.94692	5.59375	3.833333	2.864583
55.96655	5.354167	3.9375	2.770833
55.98618	5.385417	4.020833	3.125
56.0058	5.541667	3.6875	2.833333
56.02543	5.020833	4.25	3.145833
56.04506	5.572917	3.197917	2.947917
56.06468	5.583333	3.895833	2.90625
56.08431	5.385417	3.96875	2.9375
56.10394	5.416667	4.010417	3.041667
56.12357	5.270833	3.5625	2.770833
56.14319	5.489583	3.864583	2.875
56.16282	5.479167	3.708333	2.84375
56.18245	5.4375	3.625	2.854167
56.20207	5.083333	3.40625	2.864583
56.2217	5.84375	3.479167	3.0625
56.24133	5.041667	3.5	2.989583
56.26095	5.40625	3.927083	2.739583
56.28058	5.375	3.572917	2.791667
56.30021	5.375	3.604167	3.166667
56.31984	5.322917	3.916667	3.041667
56.33946	5.09375	3.791667	2.90625
56.35909	5.458333	3.666667	2.989583
56.37872	5.21875	3.895833	2.75
56.39834	5.333333	3.833333	3.083333
56.41797	4.989583	4.177083	3.072917
56.4376	5.364583	3.927083	3
56.45723	5.833333	3.947917	2.833333
56.47685	5.708333	4.03125	3.239583
56.49648	5.927083	3.625	2.916667
56.51611	5.552083	4.177083	2.833333

56.53573	5.40625	3.989583	3.166667
56.55536	5.135417	4.229167	2.927083
56.57499	5.28125	4.052083	3.135417
56.59461	5.625	4.0625	3.072917
56.61424	5.239583	4.177083	2.770833
56.63387	5.260417	4.0625	2.802083
56.6535	5.46875	3.75	3.125
56.67312	5.21875	3.75	2.822917
56.69275	5.260417	3.65625	2.958333
56.71238	5.53125	4	2.8125
56.732	5.135417	4	2.635417
56.75163	5.104167	3.9375	3.09375
56.77126	5.333333	3.989583	2.895833
56.79088	5.135417	3.885417	3.364583
56.81051	5.208333	3.96875	3.072917
56.83014	5.28125	4.041667	3.135417
56.84977	5.270833	4.03125	3.135417
56.86939	5.59375	4.010417	2.885417
56.88902	5.5	4.104167	3.25
56.90865	5.697917	3.8125	2.75
56.92827	5.145833	3.625	3.114583
56.9479	5.239583	4.135417	3.083333
56.96753	5.28125	3.552083	3
56.98715	4.916667	3.9375	3.260417
57.00678	5.208333	4.145833	3.020833
57.02641	5.395833	4.145833	3
57.04604	5.520833	4.125	3.302083
57.06566	5.53125	3.5	2.875
57.08529	4.96875	4.208333	3.15625
57.10492	5.802083	4.260417	3.291667
57.12454	5.28125	3.958333	3.104167
57.14417	5.125	3.854167	3.197917
57.1638	5.239583	4.03125	3.260417
57.18342	5.145833	3.885417	2.875
57.20305	5.666667	3.541667	3.135417
57.22268	4.979167	3.645833	3.083333
57.24231	5.041667	4.104167	3.041667
57.26193	5.145833	3.677083	3.010417
57.28156	5.354167	4.010417	3.197917
57.30119	5.302083	3.697917	2.895833
57.32081	5.729167	3.583333	3.114583
57.34044	4.96875	3.572917	3.1875
57.36007	5.510417	3.677083	3
57.37969	5.552083	3.635417	3.041667
57.39932	5.40625	3.875	2.947917

57.41895	5.395833	3.885417	2.9375
57.43858	5.270833	4.083333	2.958333
57.4582	5.0625	4.041667	3.239583
57.47783	5.166667	3.864583	2.802083
57.49746	5.010417	3.760417	2.927083
57.51708	5.072917	3.364583	3.322917
57.53671	5.166667	4.09375	2.8125
57.55634	5.333333	3.822917	2.875
57.57596	5.322917	4.145833	2.947917
57.59559	4.90625	3.8125	2.947917
57.61522	5.416667	3.552083	2.979167
57.63485	5	3.90625	2.96875
57.65447	5.34375	4.03125	3.09375
57.6741	4.927083	3.8125	3.145833
57.69373	5.166667	3.84375	3
57.71335	5.614583	3.989583	3.354167
57.73298	5.083333	4.03125	3.072917
57.75261	5.5	3.677083	2.770833
57.77223	4.833333	3.572917	2.9375
57.79186	5.458333	3.96875	3.09375
57.81149	5.239583	3.833333	2.854167
57.83112	5.302083	3.947917	2.916667
57.85074	5.28125	3.697917	3.197917
57.87037	5.03125	3.34375	3
57.89	4.958333	3.635417	2.916667
57.90962	4.75	4.020833	3.010417
57.92925	5.614583	3.40625	3.072917
57.94888	5.083333	3.697917	2.84375
57.9685	5.114583	3.895833	3.03125
57.98813	5.208333	3.479167	3.0625
58.00776	5.760417	3.697917	2.895833
58.02739	5.03125	3.927083	3.09375
58.04701	5.104167	3.604167	2.708333
58.06664	5.333333	3.802083	2.90625
58.08627	4.947917	3.75	2.677083
58.10589	5.229167	3.875	3.083333
58.12552	4.958333	3.458333	2.729167
58.14515	5.0625	3.864583	2.875
58.16477	5.208333	3.572917	2.791667
58.1844	5.125	3.75	2.979167
58.20403	5.364583	3.510417	2.5
58.22366	5.729167	3.635417	2.927083
58.24328	5.3125	3.760417	3.03125
58.26291	5.083333	3.96875	2.697917
58.28254	5.041667	3.416667	2.541667

58.30216	5.458333	3.583333	2.697917
58.32179	5.291667	3.625	2.895833
58.34142	4.71875	3.447917	2.583333
58.36104	5.229167	3.5	2.9375
58.38067	5.333333	3.875	2.739583
58.4003	4.989583	3.5	2.791667
58.41993	4.979167	3.479167	3.114583
58.43955	5.145833	3.375	2.833333
58.45918	5.09375	3.5625	3.166667
58.47881	5.083333	3.895833	2.8125
58.49843	5.302083	3.364583	2.854167
58.51806	4.84375	3.729167	2.25
58.53769	4.614583	3.385417	2.71875
58.55731	4.96875	3.552083	2.84375
58.57694	4.802083	3.71875	2.677083
58.59657	4.979167	3.177083	2.666667
58.6162	5.21875	3.770833	2.677083
58.63582	4.90625	2.979167	2.822917
58.65545	5.1875	3.458333	2.666667
58.67508	5.1875	3.458333	2.84375
58.6947	5.104167	3.34375	3
58.71433	5.46875	3.885417	3.020833
58.73396	5	3.229167	2.875
58.75358	4.989583	3.59375	3.09375
58.77321	5.09375	3.708333	3.072917
58.79284	5.625	3.5	2.958333
58.81247	4.802083	3.166667	2.84375
58.83209	5.333333	3.479167	3.041667
58.85172	5.3125	3.333333	2.96875
58.87135	5.5	3.635417	2.625
58.89097	5.270833	3.697917	2.791667
58.9106	4.958333	3.791667	2.708333
58.93023	5.333333	3.729167	2.885417
58.94985	4.875	3.854167	2.895833
58.96948	4.947917	3.770833	2.625
58.98911	5.09375	3.71875	2.885417
59.00874	4.84375	3.791667	3.041667
59.02836	4.864583	3.927083	2.927083
59.04799	5.1875	3.416667	2.916667
59.06762	4.927083	3.364583	2.729167
59.08724	5.09375	3.9375	2.96875
59.10687	4.916667	3.885417	2.90625
59.1265	4.96875	3.510417	2.5625
59.14612	5.604167	3.5625	2.5
59.16575	5.072917	3.53125	2.854167

59.18538	4.9375	3.520833	2.895833
59.20501	5.072917	3.572917	2.802083
59.22463	5.322917	3.53125	3
59.24426	4.947917	3.59375	2.833333
59.26389	4.614583	3.75	2.8125
59.28351	5.010417	3.583333	2.90625
59.30314	5.1875	3.333333	2.8125
59.32277	5.208333	3.46875	2.9375
59.3424	4.927083	3.802083	2.71875
59.36202	5.479167	3.479167	2.927083
59.38165	5.177083	3.020833	3.09375
59.40128	4.84375	3.635417	2.802083
59.4209	5.020833	3.854167	2.635417
59.44053	5.03125	3.739583	2.8125
59.46016	5.052083	3.520833	2.791667
59.47978	4.875	3.666667	2.833333
59.49941	5.072917	3.75	2.833333
59.51904	5.5625	3.552083	2.5625
59.53867	5.03125	3.760417	2.802083
59.55829	5.114583	3.572917	2.708333
59.57792	5.333333	4.15625	2.96875
59.59755	5.3125	3.447917	2.802083
59.61717	5.125	3.625	3
59.6368	5.354167	4.03125	3.041667
59.65643	4.833333	3.958333	2.666667
59.67605	5.260417	3.854167	2.729167
59.69568	5	3.625	3.125
59.71531	4.916667	4.125	2.875
59.73494	4.979167	3.833333	3.197917
59.75456	5.28125	3.854167	3.083333
59.77419	4.947917	4.166667	3.1875
59.79382	4.989583	4.239583	3.260417
59.81344	4.90625	3.8125	3.354167
59.83307	4.729167	4.416667	3.572917
59.8527	4.479167	4.34375	3.34375
59.87232	4.958333	4.395833	3.572917
59.89195	4.927083	4.3125	3.354167
59.91158	5.052083	4.447917	3.09375
59.93121	4.90625	4.354167	3.302083
59.95083	4.9375	4.166667	3.427083
59.97046	5.177083	4.302083	3.604167
59.99009	5.46875	4.53125	3.5625
60.00971	5.25	4.28125	3.354167
60.02934	4.739583	4.114583	3.479167
60.04897	4.71875	4.145833	3.322917

60.06859	4.875	4.229167	3.072917
60.08822	5.177083	4.447917	3.53125
60.10785	4.895833	4.114583	3.354167
60.12748	5.25	3.802083	3.072917
60.1471	4.5625	4.3125	3.583333
60.16673	5.083333	3.78125	2.666667
60.18636	5.072917	4.260417	2.9375
60.20598	4.791667	3.875	3.052083
60.22561	5.510417	4.0625	3.270833
60.24524	5.208333	4.239583	3
60.26486	4.875	3.979167	3.09375
60.28449	4.875	3.65625	3.114583
60.30412	5.020833	3.864583	3.114583
60.32375	4.895833	3.958333	3.260417
60.34337	4.791667	3.802083	3.28125
60.363	5	3.770833	3.447917
60.38263	4.645833	3.5	3.166667
60.40225	4.947917	4.010417	3.145833
60.42188	4.927083	3.739583	3.03125
60.44151	5.40625	4.104167	3.25
60.46113	4.90625	3.708333	2.895833
60.48076	5.291667	3.875	3.302083
60.50039	4.864583	3.90625	2.614583
60.52002	4.625	3.614583	2.791667
60.53964	5.260417	3.666667	2.895833
60.55927	4.489583	3.9375	2.802083
60.5789	4.979167	3.645833	2.885417
60.59852	5.21875	3.416667	2.875
60.61815	4.802083	3.729167	3.114583
60.63778	4.760417	4.21875	3.041667
60.6574	4.78125	3.760417	2.90625
60.67703	4.885417	4.052083	2.989583
60.69666	4.71875	3.083333	2.885417
60.71629	5.114583	3.875	3.072917
60.73591	4.8125	3.822917	2.770833
60.75554	4.71875	3.833333	3.052083
60.77517	5.322917	3.770833	3.15625
60.79479	4.875	3.885417	2.5625
60.81442	4.791667	4.125	2.822917
60.83405	4.84375	3.958333	2.895833
60.85367	4.802083	3.71875	2.677083
60.8733	4.78125	3.822917	2.802083
60.89293	4.84375	3.739583	2.833333
60.91256	4.510417	3.864583	3.302083
60.93218	4.78125	3.895833	3.28125

60.95181	4.989583	3.8125	2.791667
60.97144	4.791667	3.9375	2.979167
60.99106	5.34375	3.625	2.822917
61.01069	4.958333	3.729167	2.864583
61.03032	5	4.40625	3.177083
61.04994	5.177083	4.260417	2.927083
61.06957	4.84375	4.03125	2.96875
61.0892	4.78125	4.010417	3.333333
61.10883	4.90625	4.354167	3.145833
61.12845	4.666667	3.833333	3.03125
61.14808	4.822917	3.84375	3.104167
61.16771	5.364583	4.114583	3.125
61.18733	4.65625	4.010417	3.083333
61.20696	4.979167	4.177083	3.270833
61.22659	4.510417	4.270833	2.947917
61.24621	4.864583	4.052083	3.041667
61.26584	4.833333	4.03125	3.34375
61.28547	4.572917	4.010417	3.03125
61.3051	5	4.364583	3.229167
61.32472	4.75	4.333333	3.364583
61.34435	4.739583	4.052083	3.083333
61.36398	4.854167	4.010417	3.0625
61.3836	5.020833	4.125	3.1875
61.40323	4.78125	3.9375	3.34375
61.42286	5.03125	4.166667	3.177083
61.44248	4.916667	4.041667	3.541667
61.46211	4.802083	4.041667	3.333333
61.48174	4.822917	3.875	3.25
61.50137	5.364583	4.104167	3.125
61.52099	4.5625	4.229167	3.125
61.54062	5.21875	4.166667	2.916667
61.56025	5.1875	4.145833	3.114583
61.57987	4.916667	4.145833	3.40625
61.5995	4.770833	4.041667	3.125
61.61913	4.770833	3.833333	3.1875
61.63875	5.291667	4	3.447917
61.65838	4.770833	3.791667	3.479167
61.67801	4.84375	3.885417	3.020833
61.69764	4.604167	3.614583	3.15625
61.71726	4.822917	3.385417	3.072917
61.73689	4.802083	3.854167	3.072917
61.75652	4.8125	3.927083	2.791667
61.77614	5.104167	4.020833	2.895833
61.79577	4.729167	3.65625	2.583333
61.8154	4.552083	3.833333	3.052083

61.83502	4.458333	3.447917	3.260417
61.85465	4.90625	3.604167	2.59375
61.87428	4.489583	3.729167	2.947917
61.89391	5.083333	3.385417	2.8125
61.91353	4.645833	3.489583	2.645833
61.93316	4.635417	3.46875	2.697917
61.95279	5.28125	3.708333	2.916667
61.97241	4.65625	3.479167	2.614583
61.99204	4.625	3.9375	2.71875
62.01167	4.59375	3.354167	2.802083
62.03129	4.59375	3.5625	2.572917
62.05092	4.927083	3.291667	2.65625
62.07055	4.364583	3.833333	2.46875
62.09018	4.78125	3.34375	2.833333
62.1098	4.875	3.604167	2.520833
62.12943	5.229167	3.677083	2.541667
62.14906	4.791667	3.572917	2.666667
62.16868	4.427083	3.59375	2.802083
62.18831	4.75	3.40625	2.5625
62.20794	4.25	3.28125	2.5
62.22757	5.03125	3.3125	2.572917
62.24719	4.9375	3.989583	2.666667
62.26682	4.34375	3.65625	2.760417
62.28645	4.375	3.552083	2.625
62.30607	4.458333	3.5625	2.552083
62.3257	5.0625	3.604167	2.541667
62.34533	4.9375	3.333333	2.729167
62.36495	4.479167	3.34375	2.541667
62.38458	4.34375	3.447917	2.697917
62.40421	4.395833	3.416667	2.78125
62.42384	4.6875	3.40625	2.416667
62.44346	4.802083	3.458333	2.645833
62.46309	4.875	3.333333	2.802083
62.48272	4.75	3.302083	2.822917
62.50234	4.572917	3.625	2.510417
62.52197	4.875	3.21875	2.40625
62.5416	4.541667	3.239583	2.510417
62.56122	4.697917	3.4375	2.416667
62.58085	5.03125	3.864583	2.625
62.60048	4.760417	3.302083	2.541667
62.62011	4.802083	3.166667	2.479167
62.63973	4.541667	3.572917	2.645833
62.65936	5	3.583333	2.958333
62.67899	4.739583	3.46875	2.739583
62.69861	4.697917	3.90625	2.9375

62.71824	4.958333	3.572917	2.708333
62.73787	4.8125	3.552083	2.802083
62.75749	4.583333	3.739583	3.125
62.77712	4.770833	3.604167	3.104167
62.79675	4.604167	3.90625	2.760417
62.81638	4.708333	3.65625	2.760417
62.836	4.666667	3.822917	2.958333
62.85563	4.697917	3.989583	3.302083
62.87526	5	3.947917	3.25
62.89488	4.5	4.125	3.15625
62.91451	4.520833	4.052083	3.28125
62.93414	4.96875	4.052083	2.96875
62.95376	5.072917	3.583333	3.53125
62.97339	4.84375	3.96875	3.25
62.99302	4.583333	3.583333	3.15625
63.01265	4.614583	3.739583	2.875
63.03227	4.364583	3.53125	2.96875
63.0519	4.541667	3.989583	2.9375
63.07153	4.697917	3.4375	3.145833
63.09115	4.958333	3.958333	2.885417
63.11078	4.59375	3.875	2.739583
63.13041	5.104167	3.833333	2.645833
63.15003	4.895833	3.65625	2.864583
63.16966	4.697917	3.59375	2.708333
63.18929	4.65625	3.40625	2.822917
63.20892	4.75	3.489583	2.854167
63.22854	4.041667	3.53125	2.739583
63.24817	4.84375	3.479167	2.71875
63.2678	4.9375	3.28125	3.0625
63.28742	4.71875	3.385417	2.583333
63.30705	4.729167	3.395833	2.583333
63.32668	4.46875	3.479167	2.916667
63.3463	4.197917	3.895833	2.729167
63.36593	4.677083	3.677083	2.84375
63.38556	4.666667	3.614583	2.510417
63.40519	4.666667	3.4375	2.802083
63.42481	4.739583	3.53125	2.6875
63.44444	4.239583	3.447917	2.885417
63.46407	4.322917	3.760417	2.708333
63.48369	4.697917	3.229167	2.979167
63.50332	4.458333	4.104167	2.802083
63.52295	4.802083	3.052083	2.375
63.54257	4.8125	3.34375	2.322917
63.5622	4.583333	3.03125	2.729167
63.58183	4.604167	3.583333	2.520833

63.60146	4.458333	3.333333	2.489583
63.62108	4.40625	3.072917	2.625
63.64071	4.489583	3.479167	2.6875
63.66034	4.541667	3.385417	2.291667
63.67996	4.489583	3.6875	2.65625
63.69959	4.5625	3.802083	2.59375
63.71922	4.5625	3.5	2.229167
63.73884	4.697917	3.333333	2.875
63.75847	4.84375	3.572917	2.708333
63.7781	5.104167	3.260417	2.489583
63.79773	4.520833	3.875	3.020833
63.81735	4.666667	3.5	2.791667
63.83698	4.895833	3.6875	2.53125
63.85661	4.71875	3.947917	2.947917
63.87623	4.78125	3.760417	3.166667
63.89586	4.6875	4	3.333333
63.91549	4.489583	3.947917	3.010417
63.93511	4.635417	4	3.5
63.95474	4.302083	3.6875	3.25
63.97437	4.65625	4	3.34375
63.994	4.479167	4.145833	3.114583
64.01362	4.395833	4.375	3.364583
64.03325	4.875	3.916667	3.260417
64.05288	4.260417	4.239583	3.229167
64.0725	4.25	3.979167	3.28125
64.09213	4.645833	4.145833	3.208333
64.11176	4.552083	3.989583	2.833333
64.13138	4.40625	3.895833	3.166667
64.15101	4.552083	3.90625	3.28125
64.17064	4.541667	3.65625	3.1875
64.19027	4.34375	3.802083	3.104167
64.20989	4.322917	3.5625	2.552083
64.22952	4.552083	3.229167	2.979167
64.24915	4.229167	3.84375	2.96875
64.26877	4.291667	3.614583	2.885417
64.2884	4.291667	3.71875	2.885417
64.30803	4.364583	3.21875	2.291667
64.32765	4.635417	3.447917	2.427083
64.34728	4.572917	3.21875	2.479167
64.36691	4.53125	3.114583	2.6875
64.38654	4.895833	3.291667	2.291667
64.40616	4.8125	3.375	2.385417
64.42579	4.270833	3.270833	2.479167
64.44542	4.520833	3.354167	2.802083
64.46504	4.614583	3.25	2.729167

64.48467	4.34375	3.53125	2.541667
64.5043	4.510417	3.6875	2.75
64.52392	4.572917	3.635417	2.697917
64.54355	5.041667	3.46875	2.333333
64.56318	4.5	3.364583	2.541667
64.58281	4.052083	3.59375	2.729167
64.60243	4.65625	3.34375	2.510417
64.62206	4.427083	3.552083	2.21875
64.64169	4.53125	3.6875	2.375
64.66131	4.71875	3.635417	3.010417
64.68094	4.208333	3.375	2.9375
64.70057	4.177083	3.78125	2.572917
64.72019	4.270833	3.958333	2.75
64.73982	4.583333	3.84375	2.645833
64.75945	4.46875	3.84375	2.9375
64.77908	4.5	3.677083	2.677083
64.7987	4.479167	3.395833	2.791667
64.81833	4.520833	3.833333	2.9375
64.83796	4.09375	3.552083	3.3125
64.85758	4.354167	3.375	3.114583
64.87721	4.447917	3.635417	3.114583
64.89684	4.09375	3.541667	3.15625
64.91646	4.8125	3.854167	2.854167
64.93609	4.25	3.572917	3.21875
64.95572	4.135417	3.75	3.21875
64.97535	4.479167	4.125	2.854167
64.99497	4.8125	3.5	2.979167
65.0146	4.416667	3.364583	3.020833
65.03423	4.322917	3.791667	3.197917
65.05385	4.427083	3.291667	2.885417
65.07348	4.71875	3.854167	2.84375
65.09311	4.25	3.46875	2.729167
65.11274	4.260417	3.78125	2.947917
65.13236	4.270833	3.604167	2.614583
65.15199	4.09375	3.447917	2.572917
65.17162	4.40625	3.541667	2.375
65.19124	4.354167	3.822917	2.697917
65.21087	4.125	3.09375	2.53125
65.2305	4.3125	3.5	2.666667
65.25012	4.46875	2.96875	2.375
65.26975	4.322917	3.208333	2.666667
65.28938	4.572917	3.270833	2.729167
65.30901	4.53125	3.104167	2.5
65.32863	4.229167	3.375	2.447917
65.34826	4.59375	3.09375	2.395833

65.36789	4.104167	3.552083	2.364583
65.38751	4.604167	3.3125	2.25
65.40714	4.458333	3.416667	2.416667
65.42677	4.270833	3.15625	2.364583
65.44639	4.239583	3.135417	2.21875
65.46602	4.260417	3.1875	2.6875
65.48565	4.395833	3.083333	2.489583
65.50528	4.666667	3	2.270833
65.5249	4.5	3.291667	2.489583
65.54453	4.489583	3.3125	2.364583
65.56416	4.75	3.041667	2.822917
65.58378	4.572917	3.09375	2.291667
65.60341	4.385417	3.333333	2.479167
65.62304	4.791667	3.333333	2.46875
65.64266	4.333333	3.34375	2.666667
65.66229	4.479167	3.322917	2.65625
65.68192	4.395833	3.052083	2.59375
65.70155	4.3125	3.15625	2.3125
65.72117	4.1875	3.427083	2.5
65.7408	4.458333	2.979167	2.208333
65.76043	4.447917	3.010417	2.46875
65.78005	4.552083	3.208333	2.395833
65.79968	4.270833	3.333333	2.416667
65.81931	3.770833	3.21875	2.604167
65.83893	4.604167	3.083333	2.270833
65.85856	4.489583	2.979167	2.572917
65.87819	4.583333	3.53125	2.354167
65.89782	4.677083	3.229167	2.4375
65.91744	4.197917	3.28125	2.65625
65.93707	4.333333	3	2.59375
65.9567	4.395833	3.020833	2.5625
65.97632	4.458333	3.427083	2.53125
65.99595	4.614583	3.114583	2.583333
66.01558	4.729167	3.09375	2.666667
66.0352	4.020833	3.21875	2.34375
66.05483	4.40625	3.104167	2.583333
66.07446	4.083333	3.229167	2.239583
66.09409	4.3125	3.395833	2.541667
66.11371	4.041667	3.114583	2.270833
66.13334	4.239583	3.322917	2.53125
66.15297	4.760417	3.125	2.354167
66.17259	4.458333	3.03125	3
66.19222	4.84375	3.385417	2.458333
66.21185	4.645833	3.229167	2.604167
66.23147	4.46875	3.385417	2.395833

66.2511	4.46875	3.166667	2.78125
66.27073	4.322917	3.166667	2.645833
66.29036	4.71875	3.5	2.770833
66.30998	4.270833	3.729167	2.802083
66.32961	3.854167	3.65625	2.645833
66.34924	4.541667	3.177083	2.552083
66.36886	4.145833	3.6875	2.697917
66.38849	4.208333	2.958333	2.614583
66.40812	4.25	3.552083	2.614583
66.42774	3.885417	3.114583	2.666667
66.44737	4.59375	3.197917	2.4375
66.467	4.3125	3.21875	2.447917
66.48663	4.135417	2.979167	2.291667
66.50625	4.177083	3.375	2.65625
66.52588	4.46875	3.21875	2.614583
66.54551	4.03125	3.15625	2.552083
66.56513	4.385417	3.4375	2.46875
66.58476	4.427083	3.052083	2.510417
66.60439	4.21875	2.833333	2.395833
66.62401	4.583333	3.34375	2.34375
66.64364	4.395833	3.302083	2.46875
66.66327	4.302083	3.572917	2.34375
66.6829	4.052083	3.072917	2.625
66.70252	4.020833	2.989583	2.479167
66.72215	4.666667	3.739583	2.3125
66.74178	4.697917	3.604167	2.177083
66.7614	4.34375	3.34375	2.322917
66.78103	4.208333	3.1875	2.1875
66.80066	4.28125	3.708333	2.40625
66.82028	3.96875	3.145833	2.947917
66.83991	4.21875	3.3125	2.583333
66.85954	4.15625	3.364583	2.46875
66.87917	4.041667	3.239583	2.708333
66.89879	4.28125	3.166667	2.28125
66.91842	4.135417	3.28125	2.697917
66.93805	4.052083	3.3125	2.5625
66.95767	4.354167	3.260417	2.427083
66.9773	4.1875	3.510417	2.5625
66.99693	3.989583	3.604167	2.4375
67.01655	4.239583	3.375	2.739583
67.03618	4.46875	3	2.635417
67.05581	3.916667	3.260417	2.604167
67.07544	4.1875	3.260417	2.520833
67.09506	3.96875	3.458333	2.427083
67.11469	4.458333	3.375	2.40625

67.13432	4.21875	3.135417	2.84375
67.15394	4.135417	3.041667	2.520833
67.17357	4.395833	3.3125	2.458333
67.1932	4.0625	3.3125	2.739583
67.21282	4.135417	3.21875	2.40625
67.23245	4.1875	3.333333	2.354167
67.25208	4.229167	3.427083	2.614583
67.27171	4.333333	3.46875	2.416667
67.29133	4.208333	3.125	2.510417
67.31096	4.03125	3.114583	2.395833
67.33059	4.291667	3.270833	2.53125
67.35021	3.854167	3.583333	2.520833
67.36984	4.46875	3.09375	2.3125
67.38947	4.135417	3.197917	2.53125
67.40909	4.572917	3.135417	2.354167
67.42872	3.885417	3.604167	2.145833
67.44835	4.3125	2.989583	2.364583
67.46798	4.166667	3.322917	2.760417
67.4876	4.322917	3.177083	2.697917
67.50723	4.364583	3.447917	2.53125
67.52686	4.302083	3.239583	2.3125
67.54648	4.479167	3.03125	2.458333
67.56611	4.114583	3.520833	2.510417
67.58574	4.041667	3.447917	2.479167
67.60536	4.59375	2.9375	2.354167
67.62499	3.875	3.135417	2.364583
67.64462	4.46875	3.333333	2.166667
67.66425	3.885417	3.135417	2.572917
67.68387	4.354167	3.09375	2.75
67.7035	4.302083	3.697917	2.4375
67.72313	4.302083	3.0625	2.395833
67.74275	4.1875	3.395833	2.552083
67.76238	4.5	2.802083	2.59375
67.78201	4.364583	3.291667	2.40625
67.80163	4.416667	3.510417	2.46875
67.82126	4.114583	3.21875	2.583333
67.84089	4.145833	3.125	2.760417
67.86052	4.291667	3.364583	2.364583
67.88014	3.8125	3.34375	2.604167
67.89977	3.760417	3.375	2.239583
67.9194	3.791667	3.09375	2.375
67.93902	3.864583	3.510417	2.489583
67.95865	4.427083	3.354167	2.552083
67.97828	4.385417	3.46875	2.510417
67.99791	3.947917	3.302083	2.3125

68.01753	4.28125	3.572917	2.510417
68.03716	4.114583	3.375	2.3125
68.05679	4.385417	3.229167	2.572917
68.07641	4.583333	3.28125	2.833333
68.09604	3.9375	3.5	2.25
68.11567	3.833333	3.291667	2.479167
68.13529	4.041667	3.520833	2.3125
68.15492	4.447917	3.4375	2.46875
68.17455	4.135417	3.260417	2.583333
68.19418	3.979167	3.604167	2.458333
68.2138	4.4375	3.510417	2.5625
68.23343	4.21875	2.885417	2.28125
68.25306	4.270833	3.625	2.489583
68.27268	4.427083	3.197917	2.5
68.29231	3.614583	3.479167	2.333333
68.31194	4.166667	3.25	2.21875
68.33156	4.604167	3.4375	2.239583
68.35119	4.239583	3.364583	2.28125
68.37082	4.572917	3.385417	2.666667
68.39045	3.802083	3.40625	2.541667
68.41007	4.635417	3.135417	2.541667
68.4297	4.052083	2.885417	2.572917
68.44933	4.0625	3.322917	2.697917
68.46895	4.385417	3.28125	2.427083
68.48858	3.96875	3.333333	2.5
68.50821	3.979167	3.25	2.5
68.52783	3.625	3.354167	2.625
68.54746	4.3125	2.791667	2.395833
68.56709	4.270833	2.958333	2.4375
68.58672	4.125	3.020833	2.25
68.60634	4.40625	3.229167	2.260417
68.62597	4.135417	3.270833	2.1875
68.6456	4.09375	3.145833	2.3125
68.66522	4.052083	3.177083	2.6875
68.68485	3.979167	3.083333	2.541667
68.70448	3.927083	3.010417	2.260417
68.7241	3.895833	3.46875	2.28125
68.74373	4.291667	3.302083	2.291667
68.76336	4.239583	3.03125	2.520833
68.78299	3.708333	3.15625	2.729167
68.80261	3.854167	2.833333	2.385417
68.82224	3.8125	3.010417	2.40625
68.84187	3.833333	3.1875	2.270833
68.86149	4.333333	3.520833	2.052083
68.88112	4.072917	3.177083	2.6875

68.90075	4.09375	3.145833	2.3125
68.92037	4.072917	2.802083	2.364583
68.94	3.916667	2.729167	2.291667
68.95963	4.09375	3.46875	2.364583
68.97926	4.354167	3.270833	2.354167
68.99888	4.375	3.34375	2.3125
69.01851	3.739583	3.229167	2.572917
69.03814	4.135417	3.302083	2.479167
69.05776	4.03125	3.239583	2.4375
69.07739	3.677083	3.072917	2.03125
69.09702	4.114583	3.1875	1.9375
69.11664	3.833333	3.15625	2.59375
69.13627	4.21875	2.989583	2.364583
69.1559	4.020833	3.197917	2.635417
69.17553	4.40625	3.583333	2.447917
69.19515	4.229167	3.125	2.34375
69.21478	3.84375	3.197917	2.708333
69.23441	4.4375	3.322917	2.333333
69.25403	3.677083	3.166667	2.520833
69.27366	4.34375	3.302083	2.21875
69.29329	3.927083	3.041667	2.40625
69.31291	3.9375	3.489583	2.166667
69.33254	3.9375	3.395833	2.364583
69.35217	3.895833	3.125	2.614583
69.3718	4.197917	3.197917	2.375
69.39142	3.854167	3.270833	2.677083
69.41105	4.083333	3.322917	2.333333
69.43068	3.770833	3.072917	2.4375
69.4503	3.989583	3.166667	2.458333
69.46993	4.166667	3.104167	2.677083
69.48956	4.208333	3.052083	2.3125
69.50918	3.677083	3.447917	2.416667
69.52881	3.833333	2.5625	2.302083
69.54844	3.75	2.916667	2.489583
69.56807	4.21875	3.239583	2.375
69.58769	3.697917	3.291667	2.458333
69.60732	4.020833	3.15625	2.40625
69.62695	4.166667	2.8125	2.489583
69.64657	3.989583	3.333333	2.510417
69.6662	4	3.145833	2.364583
69.68583	4.1875	2.947917	2.416667
69.70545	4.21875	2.927083	2.458333
69.72508	3.885417	2.979167	2.354167
69.74471	4.145833	3.125	2.239583
69.76434	4.416667	3.395833	2.53125

69.78396	3.947917	3.333333	2.229167
69.80359	4.229167	3	2.385417
69.82322	4.135417	3.072917	2.802083
69.84284	3.8125	3.145833	2.739583
69.86247	3.96875	2.84375	2.489583
69.8821	4.010417	2.979167	2.46875
69.90172	4.25	3.052083	2.34375
69.92135	4	3.135417	2.427083
69.94098	4.239583	2.9375	2.385417
69.96061	4.1875	3.041667	2.270833
69.98023	4.208333	3.697917	2.635417
69.99986	4.333333	3.083333	2.364583
70.01949	4.114583	3.302083	2.291667
70.03911	4.020833	3.520833	2.416667
70.05874	3.9375	3.177083	2.416667
70.07837	3.802083	2.760417	2.104167
70.09799	4.010417	2.989583	2.520833
70.11762	3.739583	3.125	2.072917
70.13725	3.739583	3.1875	2.729167
70.15688	3.625	3.239583	2.46875
70.1765	4.020833	3.46875	2.229167
70.19613	3.604167	3.083333	2.583333
70.21576	4.1875	3.416667	2.6875
70.23538	3.90625	3.333333	2.541667
70.25501	4.020833	3.375	2.666667
70.27464	3.78125	3	2.697917
70.29426	3.958333	3.145833	2.614583
70.31389	3.885417	3.322917	2.416667
70.33352	4.239583	3.3125	2.46875
70.35315	3.71875	3.395833	2.427083
70.37277	4.135417	3.3125	2.510417
70.3924	4.302083	3.21875	2.354167
70.41203	3.854167	3.083333	2.447917
70.43165	3.75	3.03125	2.645833
70.45128	4.197917	3.260417	2.416667
70.47091	4.020833	3.40625	2.40625
70.49053	3.979167	3.3125	2.239583
70.51016	3.875	3.208333	2.416667
70.52979	3.822917	3.135417	2.5625
70.54942	4.135417	3.010417	2.197917
70.56904	3.833333	3.125	2.197917
70.58867	3.96875	3.21875	2.21875
70.6083	3.770833	3.135417	2.427083
70.62792	3.989583	3.4375	2.65625
70.64755	4.104167	3.104167	2.583333

70.66718	3.875	3.479167	2.572917
70.6868	3.96875	3.1875	2.354167
70.70643	3.916667	3.302083	2.541667
70.72606	4.125	3.21875	2.322917
70.74569	4.0625	3.666667	2.135417
70.76531	4.583333	3.125	2.666667
70.78494	3.833333	2.885417	2.666667
70.80457	3.885417	3.145833	2.4375
70.82419	3.614583	3.197917	2.3125
70.84382	3.364583	2.802083	2.447917
70.86345	3.75	3	2.541667
70.88307	4.229167	3.177083	2.53125
70.9027	3.854167	3.385417	2.40625
70.92233	3.791667	3.177083	2.333333
70.94196	3.90625	3.145833	2.177083
70.96158	3.96875	2.833333	2.635417
70.98121	3.78125	3.208333	2.020833
71.00084	3.979167	3.322917	2.354167
71.02046	3.979167	3.260417	2.21875
71.04009	4.135417	3.15625	2.270833
71.05972	4.020833	3.125	2.0625
71.07935	3.760417	3.229167	2.583333
71.09897	3.604167	2.958333	2.53125
71.1186	4.1875	3.270833	2.677083
71.13823	3.927083	3.395833	2.541667
71.15785	3.53125	3.3125	2.572917
71.17748	3.979167	3.385417	2.125
71.19711	3.71875	3.645833	2.583333
71.21673	3.78125	3.291667	2.760417
71.23636	3.833333	3.21875	2.447917
71.25599	4.197917	2.916667	2.083333
71.27562	3.697917	3.260417	2.541667
71.29524	3.947917	3.583333	2.28125
71.31487	3.53125	3.270833	2.78125
71.3345	3.614583	3.010417	2.6875
71.35412	3.802083	3.354167	2.635417
71.37375	3.989583	3.020833	2.96875
71.39338	3.8125	3.083333	2.708333
71.413	3.833333	3.197917	2.458333
71.43263	3.864583	3	2.90625
71.45226	4.0625	3.677083	2.635417
71.47189	4.125	3.427083	2.604167
71.49151	3.78125	3.395833	2.40625
71.51114	3.90625	3.46875	2.739583
71.53077	3.927083	3.604167	2.864583

71.55039	4.145833	3.135417	2.833333
71.57002	3.84375	3.385417	2.84375
71.58965	3.833333	3.28125	2.4375
71.60927	3.572917	3.333333	2.6875
71.6289	4.114583	3.614583	2.75
71.64853	3.760417	3.427083	2.635417
71.66816	3.96875	3.229167	2.8125
71.68778	4.052083	3.53125	2.96875
71.70741	3.947917	3.416667	2.520833
71.72704	4.229167	3.416667	2.583333
71.74666	3.84375	3.666667	2.572917
71.76629	3.604167	3.34375	2.59375
71.78592	3.739583	3.552083	2.510417
71.80554	3.739583	3.375	2.65625
71.82517	3.697917	3.677083	2.4375
71.8448	4.385417	3.145833	2.822917
71.86443	3.760417	3.729167	2.604167
71.88405	3.958333	3.489583	2.375
71.90368	3.854167	3.3125	2.822917
71.92331	4.125	3.375	2.541667
71.94293	3.989583	3.5625	2.520833
71.96256	3.96875	3.322917	2.677083
71.98219	4.145833	3.458333	2.71875
72.00181	3.8125	3.572917	2.885417
72.02144	3.625	3.46875	2.989583
72.04107	3.604167	3.291667	2.333333
72.0607	3.729167	3.416667	2.46875
72.08032	3.989583	3.416667	2.864583
72.09995	4.020833	3.614583	2.739583
72.11958	3.90625	3.71875	2.6875
72.1392	3.666667	3.416667	2.489583
72.15883	4.010417	3.40625	2.791667
72.17846	4.072917	3.395833	2.791667
72.19808	3.635417	3.666667	2.583333
72.21771	3.864583	3.28125	2.614583
72.23734	3.927083	3.1875	2.375
72.25697	3.875	3.479167	2.572917
72.27659	3.833333	3.15625	2.541667
72.29622	4.197917	3.03125	2.583333
72.31585	4.03125	3.125	2.645833
72.33547	3.958333	3.270833	2.354167
72.3551	3.84375	3.583333	2.427083
72.37473	4.0625	3	2.166667
72.39435	3.947917	3.135417	2.666667
72.41398	3.697917	3.354167	2.333333

72.43361	3.8125	3.28125	2.666667
72.45324	3.989583	3.010417	2.447917
72.47286	4	2.885417	2.854167
72.49249	3.489583	3.052083	2.40625
72.51212	3.552083	2.96875	2.28125
72.53174	3.572917	3.208333	2.166667
72.55137	3.645833	3.25	2.427083
72.571	3.71875	3.385417	2.333333
72.59062	3.989583	3.208333	2.59375
72.61025	3.8125	3.052083	2.427083
72.62988	3.8125	3.15625	2.364583
72.64951	3.864583	3.197917	2.197917
72.66913	3.885417	3.0625	2.46875
72.68876	3.333333	3.0625	2.322917
72.70839	3.958333	3.114583	2.229167
72.72801	3.666667	2.885417	1.875
72.74764	3.9375	3.052083	2.479167
72.76727	3.895833	3.395833	2.552083
72.78689	3.885417	3.5625	2.354167
72.80652	3.8125	3.4375	2.479167
72.82615	3.947917	3.229167	2.666667
72.84578	3.53125	3.072917	2.760417
72.8654	3.90625	3.1875	2.46875
72.88503	3.729167	3.291667	2.385417
72.90466	3.822917	3.020833	2.354167
72.92428	3.75	3.041667	2.364583
72.94391	3.802083	3.072917	2.229167
72.96354	3.895833	3.072917	2.65625
72.98316	3.510417	3.197917	2.177083
73.00279	4.052083	3.302083	2.260417
73.02242	3.875	3.604167	2.385417
73.04205	3.6875	3.083333	2.25
73.06167	3.8125	3.15625	2.666667
73.0813	4.208333	3.260417	2.239583
73.10093	3.822917	3.291667	2.65625
73.12055	3.53125	2.864583	2.34375
73.14018	4.135417	3.104167	2.208333
73.15981	4.041667	3.125	2.46875
73.17943	3.854167	3.135417	2.489583
73.19906	3.510417	2.895833	2.40625
73.21869	3.71875	3.15625	2.135417
73.23832	4.052083	3.291667	2.75
73.25794	4.197917	3.1875	2.145833
73.27757	3.90625	3.21875	2.5
73.2972	3.541667	2.947917	2.447917

73.31682	3.666667	3.229167	2.354167
73.33645	3.541667	3.0625	2.3125
73.35608	4.020833	3.1875	2.65625
73.3757	3.770833	2.947917	2.447917
73.39533	3.854167	3.28125	2.645833
73.41496	3.927083	3.34375	2.322917
73.43459	4.302083	3.322917	2.21875
73.45421	3.96875	3.197917	2.520833
73.47384	3.885417	3.479167	2.5
73.49347	3.885417	2.875	2.6875
73.51309	3.875	3.03125	2.59375
73.53272	4.010417	3.104167	2.385417
73.55235	4.09375	3.15625	2.291667
73.57197	4.1875	3.145833	2.489583
73.5916	3.90625	3.208333	2.364583
73.61123	3.947917	3.104167	2.614583
73.63086	3.75	2.927083	2.65625
73.65048	3.75	3.375	2.635417
73.67011	3.645833	2.958333	2.489583
73.68974	3.78125	3.25	2.4375
73.70936	3.9375	3.083333	2.302083
73.72899	3.65625	3.010417	2.760417
73.74862	3.947917	3.125	2.635417
73.76824	3.6875	2.947917	2.71875
73.78787	3.895833	3.083333	2.3125
73.8075	3.979167	3.583333	2.427083
73.82713	3.59375	3.15625	2.645833
73.84675	3.822917	3.322917	2.510417
73.86638	3.885417	3.510417	2.645833
73.88601	3.760417	3.416667	2.458333
73.90563	3.875	3.239583	2.583333
73.92526	3.75	3.270833	2.53125
73.94489	3.666667	3.104167	2.65625
73.96452	3.40625	3.541667	2.53125
73.98414	3.885417	3.395833	2.21875
74.00377	3.916667	3.385417	2.385417
74.0234	3.541667	3.260417	2.416667
74.04302	3.760417	3.291667	2.260417
74.06265	3.645833	3.239583	2.28125
74.08228	3.572917	2.9375	2.15625
74.1019	3.5625	3.177083	2.364583
74.12153	3.90625	3.427083	2.166667
74.14116	3.927083	3.270833	2.333333
74.16079	3.958333	2.947917	2.364583
74.18041	4.052083	3.041667	2.34375

74.20004	3.90625	2.90625	2.34375
74.21967	3.875	3.010417	2.229167
74.23929	3.625	3.322917	2.125
74.25892	3.864583	3	2.09375
74.27855	3.583333	3.333333	2.125
74.29817	3.739583	3.041667	2.395833
74.3178	3.75	2.666667	1.979167
74.33743	3.6875	3.15625	2.541667
74.35706	3.71875	2.53125	2.25
74.37668	3.895833	2.572917	2.145833
74.39631	3.9375	2.90625	2.354167
74.41594	3.541667	2.833333	2.229167
74.43556	3.65625	3.114583	2.166667
74.45519	3.697917	2.854167	2.270833
74.47482	3.625	3.291667	1.90625
74.49444	3.979167	3.072917	2.104167
74.51407	3.875	3.104167	2.395833
74.5337	3.604167	2.96875	2.270833
74.55333	3.604167	3.125	2.145833
74.57295	3.65625	3.052083	2.447917
74.59258	3.84375	2.96875	2.270833
74.61221	3.822917	3.09375	2.3125
74.63183	3.916667	2.875	2.072917
74.65146	3.291667	2.895833	2.447917
74.67109	3.53125	2.947917	2.052083
74.69071	3.635417	3.208333	2.302083
74.71034	3.447917	2.958333	2.3125
74.72997	3.520833	3.166667	2.114583
74.7496	3.947917	3.03125	2.34375
74.76922	3.854167	3	2.114583
74.78885	3.958333	3.65625	2.291667
74.80848	3.40625	2.895833	2.3125
74.8281	3.729167	3.125	2.15625
74.84773	3.927083	3.145833	1.979167
74.86736	3.979167	3.302083	2.479167
74.88698	3.916667	2.979167	2.479167
74.90661	3.6875	3.041667	2.260417
74.92624	3.427083	3.125	2.260417
74.94587	3.760417	2.864583	2.135417
74.96549	3.677083	3.0625	2.354167
74.98512	3.4375	3.104167	1.90625
75.00475	3.59375	3.010417	2.5
75.02437	4.145833	2.96875	2.71875
75.044	4.03125	2.96875	2.0625
75.06363	3.833333	3	2.5

75.08325	3.791667	2.78125	2.177083
75.10288	4.03125	2.989583	2.197917
75.12251	3.53125	3.364583	2.1875
75.14214	3.791667	2.916667	2.3125
75.16176	3.479167	3.0625	2.1875
75.18139	3.479167	3.020833	2.395833
75.20102	3.770833	3.291667	2.3125
75.22064	3.71875	3.09375	2.25
75.24027	3.416667	3.322917	2.479167
75.2599	3.645833	3.052083	2.28125
75.27952	3.854167	3.364583	2.3125
75.29915	3.583333	3.0625	2.208333
75.31878	3.5	2.979167	2.229167
75.33841	3.854167	3.333333	2.302083
75.35803	3.75	3.4375	2.177083
75.37766	3.541667	3.208333	2.1875
75.39729	3.84375	3.302083	2.197917
75.41691	3.697917	3.15625	2.416667
75.43654	4.21875	3.4375	2.135417
75.45617	3.96875	3.041667	2.541667
75.47579	3.875	3.135417	2.822917
75.49542	3.572917	3	2.385417
75.51505	3.833333	3.447917	2.5625
75.53468	4.010417	3.635417	2.4375
75.5543	3.9375	3.135417	2.416667
75.57393	3.895833	3.3125	2.541667
75.59356	3.875	3.375	2.552083
75.61318	3.854167	3.364583	2.739583
75.63281	3.84375	3.177083	2.447917
75.65244	4.229167	3.395833	2.489583
75.67206	3.46875	3.291667	2.260417
75.69169	3.59375	2.84375	2.302083
75.71132	3.791667	3.3125	2.666667
75.73095	3.885417	3.145833	2.34375
75.75057	4.09375	3.260417	3.041667
75.7702	3.489583	3.40625	2
75.78983	3.854167	2.979167	2.322917
75.80945	3.729167	3.28125	2.510417
75.82908	3.53125	3.104167	2.4375
75.84871	3.864583	3.020833	2.4375
75.86833	3.90625	2.927083	2.5625
75.88796	3.71875	3.125	2.625
75.90759	3.604167	3.135417	2.510417
75.92722	3.572917	3.072917	2.78125
75.94684	3.760417	2.958333	2.416667

75.96647	4.145833	3.375	2.416667
75.9861	3.78125	3.53125	2.635417
76.00572	3.802083	3.072917	2.520833
76.02535	3.65625	3.208333	2.53125
76.04498	3.729167	3.09375	2.395833
76.0646	4.28125	3.395833	2.34375
76.08423	3.9375	3.208333	2.4375
76.10386	3.9375	3.364583	2.322917
76.12349	4.197917	3.135417	2.447917
76.14311	3.614583	2.875	2.1875
76.16274	3.645833	3.260417	2.34375
76.18237	3.927083	2.875	2.447917
76.20199	3.864583	3.208333	2.28125
76.22162	3.604167	3.145833	2.447917
76.24125	3.53125	2.96875	2.6875
76.26087	3.947917	3.21875	2.322917
76.2805	3.697917	3.0625	2.40625
76.30013	4	2.96875	2.791667
76.31976	3.4375	3.041667	2.625
76.33938	3.552083	3.197917	2
76.35901	3.833333	3.229167	2.177083
76.37864	4.020833	3.260417	2.385417
76.39826	3.4375	3.020833	2.229167
76.41789	3.739583	3.114583	2.166667
76.43752	3.8125	2.947917	2.34375
76.45714	4.052083	2.96875	2.479167
76.47677	3.8125	3.197917	2.28125
76.4964	3.5625	3.1875	2.364583
76.51603	3.739583	3.260417	2.5
76.53565	3.84375	3.104167	2.010417
76.55528	3.364583	3.15625	2.125
76.57491	3.364583	3.291667	2.239583
76.59453	4.020833	3.354167	2.114583
76.61416	3.322917	3.145833	2.177083
76.63379	3.666667	2.854167	2.489583
76.65341	3.5625	3.416667	2.354167
76.67304	4.072917	3.322917	2.479167
76.69267	3.895833	3.395833	2.583333
76.7123	3.5	3.34375	2.270833
76.73192	3.59375	3.197917	2.427083
76.75155	3.75	3.333333	2.291667
76.77118	3.46875	3.114583	2.34375
76.7908	3.40625	2.958333	2.260417
76.81043	3.958333	3.5	2.333333
76.83006	3.791667	3.354167	2.354167

76.84969	3.552083	3.104167	2.604167
76.86931	3.822917	3.1875	2.520833
76.88894	3.354167	3.21875	2.520833
76.90857	3.708333	3.229167	2.645833
76.92819	3.552083	3.145833	2.53125
76.94782	3.46875	3.572917	2.427083
76.96745	3.645833	3.302083	2.479167
76.98707	3.854167	3.15625	2.75
77.0067	3.645833	3.291667	2.479167
77.02633	3.84375	3.291667	2.4375
77.04596	3.614583	3.34375	2.385417
77.06558	3.645833	3.21875	2.645833
77.08521	3.375	3.302083	2.770833
77.10484	3.739583	3.364583	2.552083
77.12446	3.8125	3.145833	2.489583
77.14409	4.177083	3.614583	2.447917
77.16372	3.739583	2.864583	2.489583
77.18334	3.53125	3.65625	2.5
77.20297	3.895833	3.1875	2.5
77.2226	4.15625	3.479167	2.385417
77.24223	3.489583	2.833333	2.40625
77.26185	3.5625	2.916667	2.729167
77.28148	3.822917	3.1875	2.291667
77.30111	3.9375	3.25	2.34375
77.32073	4	3.375	2.65625
77.34036	3.447917	2.9375	2.479167
77.35999	3.552083	3.03125	2.260417
77.37961	3.677083	3.125	2.416667
77.39924	3.770833	2.9375	2.46875
77.41887	4	2.947917	2.3125
77.4385	3.75	2.916667	2.291667
77.45812	3.739583	2.927083	2
77.47775	3.614583	2.6875	1.9375
77.49738	3.604167	3.072917	2.302083
77.517	3.197917	3.15625	2.375
77.53663	3.770833	3.010417	2.083333
77.55626	3.708333	2.697917	2.166667
77.57588	3.8125	3.208333	2.010417
77.59551	3.6875	2.552083	2.354167
77.61514	3.46875	2.895833	2.510417
77.63477	3.416667	3	1.96875
77.65439	3.604167	2.947917	2.270833
77.67402	3.666667	3.114583	2.385417
77.69365	3.822917	3.145833	2.34375
77.71327	3.697917	3.28125	2.34375

77.7329	3.375	3.302083	2.635417
77.75253	3.552083	3.114583	2.291667
77.77215	3.479167	3	2.541667
77.79178	3.583333	2.9375	2.447917
77.81141	3.6875	3	2.270833
77.83104	3.6875	3.125	2.15625
77.85066	3.895833	2.770833	2.46875
77.87029	3.479167	2.989583	2.1875
77.88992	3.4375	3.197917	2.229167
77.90954	3.927083	2.916667	2.375
77.92917	3.697917	3.291667	2.177083
77.9488	4.083333	3.083333	2.645833
77.96842	3.75	2.864583	2.291667
77.98805	3.635417	3.125	2.260417
78.00768	4.03125	3.166667	2.427083
78.02731	3.885417	2.885417	2.75
78.04693	3.760417	3.03125	2.729167
78.06656	3.96875	3.041667	2.302083
78.08619	3.458333	3.15625	2.395833
78.10581	3.854167	3.0625	2.4375
78.12544	3.822917	2.989583	2.322917
78.14507	3.583333	3.177083	2.645833
78.16469	3.71875	3.010417	2.302083
78.18432	3.635417	2.770833	2.333333
78.20395	3.6875	3.010417	2.510417
78.22358	3.40625	3.1875	2.5
78.2432	3.71875	3.21875	2.708333
78.26283	3.71875	2.989583	2.1875
78.28246	3.78125	3.104167	2.375
78.30208	3.78125	3.520833	2.4375
78.32171	3.854167	3.145833	2.125
78.34134	3.770833	3.0625	2.375
78.36096	3.65625	3.03125	2.166667
78.38059	3.614583	2.885417	2.208333
78.40022	3.833333	3.21875	2.1875
78.41985	3.416667	2.739583	2.21875
78.43947	3.041667	2.895833	2.447917
78.4591	3.416667	2.979167	2.177083
78.47873	3.458333	3.135417	2.104167
78.49835	3.916667	2.8125	1.927083
78.51798	3.59375	2.78125	2.270833
78.53761	3.458333	3.09375	2.09375
78.55723	3.333333	2.760417	2.270833
78.57686	3.927083	3.114583	1.979167
78.59649	3.6875	2.614583	2.020833

78.61612	3.8125	3.166667	2.114583
78.63574	3.427083	3.09375	1.708333
78.65537	3.614583	2.625	2.114583
78.675	3.927083	2.729167	2.28125
78.69462	4.010417	2.791667	1.989583
78.71425	3.541667	2.854167	2
78.73388	3.489583	2.96875	2.135417
78.7535	3.520833	2.895833	2.21875
78.77313	3.625	2.90625	2.166667
78.79276	3.645833	2.666667	2.083333
78.81239	3.708333	2.75	2.1875
78.83201	3.239583	2.90625	2.21875
78.85164	3.770833	2.90625	1.854167
78.87127	3.604167	2.78125	2.166667
78.89089	3.677083	3.197917	1.90625
78.91052	3.708333	2.916667	1.989583
78.93015	3.5	2.760417	2.104167
78.94977	3.46875	3.09375	2.083333
78.9694	3.59375	2.78125	2.28125
78.98903	3.770833	2.791667	2.1875
79.00866	3.46875	3.145833	1.979167
79.02828	3.260417	3.125	1.802083
79.04791	3.729167	2.697917	1.979167
79.06754	3.65625	2.875	1.9375
79.08716	3.46875	2.697917	2.34375
79.10679	3.864583	2.78125	2.15625
79.12642	4.208333	3.125	2.1875
79.14604	3.791667	2.78125	2.229167
79.16567	3.927083	2.635417	2.09375
79.1853	3.645833	2.916667	2.34375
79.20493	3.65625	2.635417	2.270833
79.22455	3.614583	2.989583	2.145833
79.24418	3.572917	2.75	1.979167
79.26381	3.6875	2.697917	1.96875
79.28343	3.75	2.9375	1.895833
79.30306	3.885417	3.083333	2.229167
79.32269	3.46875	2.864583	2.15625
79.34231	3.739583	2.989583	2.21875
79.36194	3.708333	3.041667	2.020833
79.38157	3.78125	2.885417	2.1875
79.4012	3.885417	2.9375	2
79.42082	3.083333	2.875	1.947917
79.44045	3.604167	2.697917	2.260417
79.46008	3.541667	2.3125	2.34375
79.4797	3.96875	2.583333	2.083333

79.49933	3.927083	2.885417	2.197917
79.51896	4.09375	2.770833	2.052083
79.53858	3.947917	2.5625	1.979167
79.55821	3.8125	2.927083	2.260417
79.57784	3.864583	2.854167	2.239583
79.59747	3.760417	2.958333	1.96875
79.61709	3.833333	2.791667	2.0625
79.63672	3.677083	2.96875	2.135417
79.65635	3.854167	2.729167	2.0625
79.67597	3.770833	2.9375	2.104167
79.6956	3.552083	2.9375	2.239583
79.71523	3.572917	3.166667	2.072917
79.73486	3.708333	3.03125	1.895833
79.75448	3.708333	2.8125	2.114583
79.77411	3.895833	2.802083	2.041667
79.79374	3.833333	3.385417	2.083333
79.81336	3.697917	3.677083	2.072917
79.83299	3.625	3.802083	2.291667
79.85262	3.677083	4.364583	2.5
79.87224	3.03125	3.791667	2.458333
79.89187	3.822917	3.520833	2.322917
79.9115	3.322917	3.322917	2.520833
79.93113	3.322917	2.854167	2.229167
79.95075	3.71875	2.90625	2.208333
79.97038	3.635417	3.083333	2.114583
79.99001	3.864583	2.645833	2.3125
80.00963	3.833333	3.322917	1.947917
80.02926	3.8125	3.270833	2.385417
80.04889	3.604167	3.125	2.104167
80.06851	3.802083	3.427083	2.239583
80.08814	3.645833	3.71875	2.354167
80.10777	3.604167	3.145833	2.3125
80.1274	3.677083	3.354167	2.145833
80.14702	3.541667	3.166667	1.791667
80.16665	3.510417	2.666667	2.083333
80.18628	3.6875	3.020833	2
80.2059	3.833333	2.552083	1.822917
80.22553	3.78125	2.791667	1.979167
80.24516	3.885417	3.1875	2.3125
80.26478	3.729167	2.78125	2.15625
80.28441	3.541667	2.895833	2.0625
80.30404	3.53125	2.895833	2.197917
80.32367	3.40625	2.958333	2.166667
80.34329	3.625	2.958333	2.145833
80.36292	3.34375	2.614583	2.020833

80.38255	3.59375	2.78125	2.177083
80.40217	3.510417	2.822917	2.1875
80.4218	3.65625	2.697917	2.114583
80.44143	3.760417	2.770833	2.25
80.46105	3.895833	2.791667	1.989583
80.48068	3.552083	3.208333	2.447917
80.50031	3.479167	2.59375	1.895833
80.51994	4	2.5	2.104167
80.53956	3.364583	2.583333	2.041667
80.55919	3.614583	2.895833	1.84375
80.57882	3.635417	2.854167	2.052083
80.59844	3.09375	2.791667	2.03125
80.61807	3.708333	2.84375	2.3125
80.6377	4.21875	2.71875	1.947917
80.65732	3.427083	2.5625	2.083333
80.67695	3.645833	2.71875	2.072917
80.69658	3.458333	2.833333	2.270833
80.71621	3.708333	2.65625	1.927083
80.73583	3.791667	3.03125	2.083333
80.75546	3.479167	2.770833	2.125
80.77509	3.677083	3.09375	2.104167
80.79471	3.541667	3.0625	2.364583
80.81434	3.71875	2.947917	1.96875
80.83397	3.614583	2.760417	2.3125
80.85359	3.635417	2.78125	1.916667
80.87322	3.604167	2.322917	2.03125
80.89285	3.75	2.791667	2.083333
80.91248	3.895833	3.145833	1.9375
80.9321	3.802083	2.65625	2.135417
80.95173	3.625	3.010417	2.3125
80.97136	3.75	2.8125	1.947917
80.99098	3.520833	3.1875	2.322917
81.01061	3.885417	3	2.208333
81.03024	3.635417	2.916667	2.09375
81.04986	3.6875	2.9375	2.072917
81.06949	3.354167	3.197917	1.979167
81.08912	3.583333	2.90625	2.34375
81.10875	3.489583	2.770833	2.114583
81.12837	3.395833	2.5	2.25
81.148	3.625	2.90625	2.46875
81.16763	3.458333	2.989583	2.416667
81.18725	3.697917	2.947917	2.4375
81.20688	3.447917	2.989583	2.145833
81.22651	3.395833	2.927083	2.697917
81.24613	3.21875	2.989583	2.072917

81.26576	3.65625	3.197917	2.25
81.28539	3.458333	3.145833	2.28125
81.30502	3.489583	3.010417	2.489583
81.32464	3.666667	3.447917	2.166667
81.34427	3.4375	3.239583	2.520833
81.3639	3.4375	2.770833	2.135417
81.38352	3.729167	2.8125	2.28125
81.40315	3.395833	3.166667	2.270833
81.42278	3.552083	2.854167	2.302083
81.4424	3.895833	3.03125	2.229167
81.46203	3.427083	3	2.4375
81.48166	3.375	2.84375	2.302083
81.50129	3.520833	3.083333	2.15625
81.52091	3.635417	3	2.229167
81.54054	3.614583	2.958333	2.25
81.56017	3.416667	3.385417	2.395833
81.57979	3.375	2.9375	2.3125
81.59942	3.75	3.322917	2.052083
81.61905	3.625	3.322917	2.333333
81.63867	3.3125	3.3125	2.1875
81.6583	3.427083	2.854167	2.28125
81.67793	3.322917	2.947917	2.197917
81.69756	3.708333	3.135417	2.46875
81.71718	3.71875	3.197917	2.322917
81.73681	3.59375	2.927083	2.3125
81.75644	3.552083	2.8125	2.489583
81.77606	3.927083	3	2.416667
81.79569	3.541667	2.677083	2.072917
81.81532	3.572917	2.625	2.375
81.83494	3.84375	2.989583	2.270833
81.85457	3.34375	3.041667	2.375
81.8742	3.520833	3.083333	2.125
81.89383	3.510417	2.677083	2.291667
81.91345	3.625	2.791667	1.989583
81.93308	3.625	2.614583	2.25
81.95271	3.822917	2.958333	2.114583
81.97233	3.458333	2.770833	2.270833
81.99196	3.53125	3.208333	2.145833
82.01159	3.677083	3.322917	2.229167
82.03121	3.510417	2.604167	2.291667
82.05084	3.541667	2.90625	2.34375
82.07047	3.385417	3.083333	2.072917
82.0901	3.447917	2.958333	2.34375
82.10972	3.458333	3.166667	2.125
82.12935	3.895833	2.84375	2.083333

82.14898	3.34375	2.947917	2.229167
82.1686	3.427083	2.8125	2.25
82.18823	3.739583	3.0625	2.322917
82.20786	3.65625	2.927083	1.84375
82.22748	3.520833	2.78125	2.239583
82.24711	3.625	2.84375	2.0625
82.26674	3.4375	3.020833	2.072917
82.28637	3.53125	2.822917	2.197917
82.30599	3.833333	3.020833	2.114583
82.32562	3.84375	2.9375	2.302083
82.34525	3.5	2.916667	2.427083
82.36487	3.458333	3.354167	2.40625
82.3845	3.666667	3	2.135417
82.40413	3.458333	3.0625	2.239583
82.42375	3.572917	2.989583	2.177083
82.44338	3.59375	2.864583	1.916667
82.46301	3.229167	2.96875	2.145833
82.48264	3.510417	2.802083	2.447917
82.50226	3.3125	3.052083	1.947917
82.52189	3.208333	2.864583	2.09375
82.54152	3.614583	3.083333	2.135417
82.56114	3.708333	2.697917	2.09375
82.58077	3.479167	2.927083	2
82.6004	3.666667	3.03125	2.072917
82.62003	3.489583	2.8125	2.010417
82.63965	3.083333	2.822917	2.020833
82.65928	3.666667	3	2.09375
82.67891	3.260417	2.739583	2.34375
82.69853	3.260417	3.010417	1.989583
82.71816	3.427083	3.083333	1.916667
82.73779	3.552083	2.96875	2.135417
82.75741	3.489583	2.875	2.020833
82.77704	3.864583	2.625	2.3125
82.79667	3.3125	2.78125	2.166667
82.8163	3.302083	2.46875	2.302083
82.83592	3.395833	2.71875	2.25
82.85555	3.125	2.802083	2.21875
82.87518	3.520833	2.8125	2.322917
82.8948	3.03125	2.822917	2.40625
82.91443	3.375	2.854167	1.958333
82.93406	3.333333	2.916667	2.395833
82.95368	3.604167	2.78125	1.78125
82.97331	3.708333	2.572917	2.125
82.99294	3.322917	2.625	2.375
83.01257	3.46875	2.645833	2.15625

83.03219	3.25	2.979167	2.145833
83.05182	3.447917	3.145833	2.0625
83.07145	3.458333	2.895833	2.302083
83.09107	3.59375	2.822917	2.25
83.1107	3.677083	2.947917	2.4375
83.13033	3.90625	2.875	2.083333
83.14995	3.270833	3.270833	2.010417
83.16958	3.614583	3.25	2.395833
83.18921	3.385417	2.885417	2.4375
83.20884	3.364583	3.135417	2.21875
83.22846	3.385417	2.822917	2.229167
83.24809	3.708333	2.760417	2.395833
83.26772	3.427083	3.083333	2.333333
83.28734	3.510417	2.791667	2.21875
83.30697	3.46875	2.90625	1.833333
83.3266	3.5625	3.15625	1.895833
83.34622	3.333333	2.854167	2.020833
83.36585	3.5625	2.84375	2.010417
83.38548	3.3125	3.125	2.364583
83.40511	3.4375	2.71875	2.020833
83.42473	3.0625	2.822917	1.9375
83.44436	3.21875	2.875	2.489583
83.46399	3.364583	2.833333	2.229167
83.48361	3.270833	2.833333	2.395833
83.50324	3.145833	3.177083	2.072917
83.52287	3.208333	2.84375	2.020833
83.54249	3.479167	3.208333	2.270833
83.56212	3.5625	2.75	1.90625
83.58175	3.46875	2.739583	2.145833
83.60138	3.604167	3.03125	2.28125
83.621	3.354167	2.78125	2.125
83.64063	3.635417	2.583333	2.072917
83.66026	3.479167	2.864583	2.104167
83.67988	3.385417	2.822917	2.09375
83.69951	3.322917	2.947917	2.145833
83.71914	3.34375	3.072917	2.260417
83.73876	3.166667	2.96875	2.197917
83.75839	3.229167	2.78125	2.010417
83.77802	3.5	2.802083	2.041667
83.79765	3.5	2.958333	2.041667
83.81727	3.5	2.864583	2.239583
83.8369	3.427083	2.71875	2.09375
83.85653	3.302083	3.052083	2.135417
83.87615	3.291667	3.010417	2.166667
83.89578	3.833333	2.770833	2.072917

83.91541	3.1875	3	2.416667
83.93503	3.739583	2.666667	2.3125
83.95466	3.260417	2.614583	2.385417
83.97429	3.177083	3.03125	2.125
83.99392	3.333333	3.21875	1.895833
84.01354	3.34375	2.947917	2.28125
84.03317	3.322917	3.114583	1.864583
84.0528	3.260417	2.614583	2.40625
84.07242	3.489583	2.96875	2.322917
84.09205	3.4375	2.78125	2.15625
84.11168	3.260417	2.770833	2.177083
84.1313	2.947917	3.0625	2.416667
84.15093	3	2.90625	2.197917
84.17056	3.520833	3	1.9375
84.19019	3.3125	3.166667	2.125
84.20981	3.010417	3.416667	2.302083
84.22944	3.291667	3.21875	2.333333
84.24907	3.208333	3.020833	2.135417
84.26869	3.28125	2.84375	1.947917
84.28832	3.166667	2.71875	2.354167
84.30795	2.875	2.697917	1.927083
84.32757	3.40625	2.427083	2.28125
84.3472	3.65625	2.833333	2.28125
84.36683	3.3125	2.739583	2.072917
84.38646	3.53125	2.614583	2.239583
84.40608	3.21875	2.916667	2.15625
84.42571	2.96875	3.020833	2.1875
84.44534	3.364583	2.875	1.989583
84.46496	3.114583	2.916667	2.114583
84.48459	3.114583	2.59375	2.135417
84.50422	3.291667	2.895833	2.114583
84.52384	3.03125	2.53125	2.197917
84.54347	3.5	2.5	2.208333
84.5631	3.125	2.520833	2.09375
84.58273	3.177083	2.90625	2.125
84.60235	3.291667	2.65625	2.052083
84.62198	3.458333	2.78125	2.197917
84.64161	3.197917	2.75	2.229167
84.66123	3.385417	2.6875	1.822917
84.68086	2.833333	2.9375	2.270833
84.70049	2.989583	2.802083	2.208333
84.72011	3.1875	3.21875	1.84375
84.73974	3.5	2.9375	2.25
84.75937	3.489583	3.239583	2.34375
84.779	3.34375	2.583333	2.229167

84.79862	2.979167	2.895833	1.9375
84.81825	3.083333	2.59375	2.197917
84.83788	3.583333	2.697917	2.104167
84.8575	3.135417	2.770833	2.375
84.87713	3.145833	2.729167	1.979167
84.89676	3.541667	2.65625	2.15625
84.91638	3.427083	2.71875	2.1875
84.93601	3.53125	2.822917	1.947917
84.95564	3.364583	2.65625	2.072917
84.97527	3.177083	2.552083	2.375
84.99489	3.302083	2.833333	1.9375
85.01452	3.572917	2.75	2.020833
85.03415	3.083333	2.625	2.197917
85.05377	3.322917	2.375	1.864583
85.0734	3.104167	2.604167	2.072917
85.09303	3.427083	2.625	2.0625
85.11265	3.229167	2.90625	2.09375
85.13228	3.40625	2.760417	2.270833
85.15191	3.302083	2.895833	1.927083
85.17154	3.166667	2.489583	2.072917
85.19116	2.802083	2.833333	2.34375
85.21079	3.34375	2.625	1.989583
85.23042	3.15625	2.802083	2.135417
85.25004	3.177083	2.916667	2.09375
85.26967	3.458333	2.84375	2
85.2893	3.489583	2.645833	2.072917
85.30892	3.3125	2.458333	2.177083
85.32855	3.291667	2.729167	1.947917
85.34818	3.072917	2.84375	2.28125
85.36781	3.364583	2.71875	1.958333
85.38743	2.854167	3.020833	2.333333
85.40706	3.479167	2.416667	2.166667
85.42669	3.239583	2.708333	2.15625
85.44631	3.302083	2.583333	1.697917
85.46594	3.416667	2.46875	2.052083
85.48557	3.052083	2.875	1.947917
85.5052	3.697917	3.010417	2.104167
85.52482	3.4375	2.625	1.895833
85.54445	3.291667	3.083333	2.09375
85.56408	3.489583	2.78125	1.916667
85.5837	3.291667	2.989583	1.8125
85.60333	3.3125	3.03125	2.052083
85.62296	3.177083	2.96875	2.25
85.64258	3.166667	3.125	1.729167
85.66221	3.166667	2.791667	2.135417

85.68184	3.21875	2.885417	1.875
85.70147	3.375	2.708333	1.770833
85.72109	3.53125	2.666667	2.104167
85.74072	3.104167	2.885417	1.947917
85.76035	3.447917	2.875	2.083333
85.77997	3.395833	2.822917	2.072917
85.7996	3.479167	2.677083	1.9375
85.81923	3.40625	2.802083	1.96875
85.83885	3.4375	2.760417	1.78125
85.85848	3.322917	2.84375	1.8125
85.87811	3.052083	2.25	1.979167
85.89774	3.34375	2.802083	1.677083
85.91736	3.21875	2.822917	2.010417
85.93699	3.25	2.708333	1.822917
85.95662	3.15625	2.6875	2
85.97624	2.989583	2.458333	1.9375
85.99587	3.270833	2.90625	1.989583
86.0155	3.46875	2.510417	1.958333
86.03512	3.041667	2.427083	1.895833
86.05475	2.833333	2.572917	1.875
86.07438	3.041667	2.541667	2.3125
86.09401	3.302083	2.364583	2
86.11363	3.197917	2.625	2.125
86.13326	3.260417	2.489583	1.635417
86.15289	3.0625	2.572917	1.78125
86.17251	3.572917	2.71875	2.020833
86.19214	3.270833	2.479167	1.895833
86.21177	3.322917	2.645833	2.072917
86.23139	3.59375	2.583333	2.239583
86.25102	3.177083	2.6875	2.21875
86.27065	3.072917	2.791667	2.041667
86.29028	2.958333	2.645833	1.75
86.3099	3.197917	2.677083	1.84375
86.32953	3.291667	2.541667	1.947917
86.34916	3.197917	2.6875	1.885417
86.36878	2.9375	2.447917	1.78125
86.38841	3.21875	2.75	1.895833
86.40804	3.104167	2.822917	1.760417
86.42766	3.145833	2.5625	1.895833
86.44729	3.333333	2.9375	1.739583
86.46692	3.395833	2.875	1.708333
86.48655	2.96875	2.958333	2.010417
86.50617	3.15625	3.09375	1.916667
86.5258	3.239583	2.666667	2.208333
86.54543	3.354167	2.479167	1.989583

86.56505	3.25	2.666667	1.84375
86.58468	2.791667	2.885417	1.958333
86.60431	3.114583	2.65625	2.09375
86.62393	3.572917	2.770833	2.041667
86.64356	3.489583	2.677083	1.854167
86.66319	3.270833	2.416667	2.145833
86.68282	3.0625	2.572917	2.166667
86.70244	3.114583	2.895833	2.052083
86.72207	3.15625	2.59375	2.229167
86.7417	3.333333	2.708333	2.020833
86.76132	3.208333	3.0625	1.9375
86.78095	3.229167	2.822917	1.895833
86.80058	3.3125	2.59375	2.177083
86.8202	3.302083	2.510417	1.989583
86.83983	3.40625	2.53125	2.177083
86.85946	2.96875	2.520833	2.020833
86.87909	3.447917	2.708333	2.208333
86.89871	3.010417	2.708333	1.84375
86.91834	3.260417	2.65625	2.104167
86.93797	2.958333	2.833333	2.010417
86.95759	3.197917	2.572917	1.864583
86.97722	3.1875	2.697917	1.833333
86.99685	2.84375	2.614583	2
87.01647	3.375	2.864583	1.833333
87.0361	2.864583	2.770833	2.010417
87.05573	2.78125	2.760417	1.916667
87.07536	3.270833	3.135417	2.208333
87.09498	3.09375	2.78125	2.229167
87.11461	3.083333	2.8125	2.03125
87.13424	3.052083	2.927083	2.260417
87.15386	3.125	2.760417	2.09375
87.17349	3.020833	3.15625	2.020833
87.19312	3.125	2.875	2.510417
87.21274	3.145833	2.96875	2.28125
87.23237	3.229167	2.9375	2.270833
87.252	3.21875	2.75	2.208333
87.27163	3.34375	2.739583	2.197917
87.29125	2.822917	3.09375	2
87.31088	3.427083	2.833333	2.208333
87.33051	3.135417	3.010417	2.3125
87.35013	3.03125	2.854167	2.260417
87.36976	3.1875	2.895833	2.21875
87.38939	3.583333	2.833333	2.447917
87.40901	3.291667	2.9375	2.104167
87.42864	3.197917	2.739583	2.427083

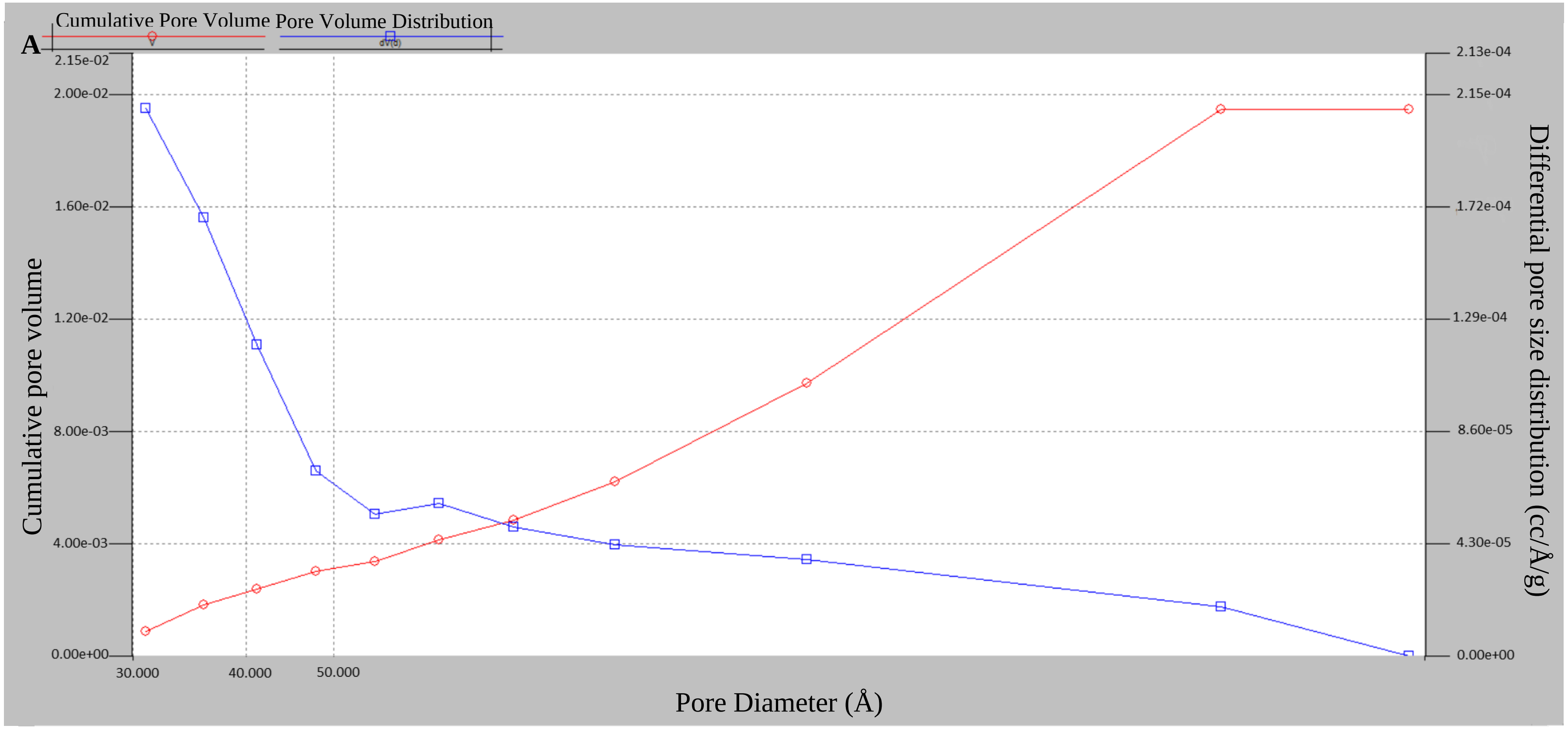
87.44827	3.072917	2.770833	2.041667
87.4679	3.114583	2.854167	2.4375
87.48752	3.3125	2.6875	2.21875
87.50715	2.822917	2.9375	2.125
87.52678	3.302083	2.75	1.770833
87.5464	2.875	2.65625	2.197917
87.56603	3.447917	2.9375	1.979167
87.58566	2.875	3.020833	2.239583
87.60528	2.989583	2.708333	2.322917
87.62491	3.260417	2.666667	2.145833
87.64454	3.166667	2.677083	1.927083
87.66417	2.916667	2.864583	1.90625
87.68379	3.354167	2.645833	2.1875
87.70342	3.208333	2.802083	2.229167
87.72305	3.145833	2.541667	1.8125
87.74267	3.15625	3.104167	2.25
87.7623	3.260417	2.989583	2.177083
87.78193	3.322917	2.989583	2.322917
87.80155	3.145833	2.5625	2.1875
87.82118	3.510417	3.041667	2.15625
87.84081	3.40625	2.625	2.145833
87.86044	3.072917	2.645833	2.354167
87.88006	3.354167	2.479167	2.25
87.89969	3.145833	2.541667	2.3125
87.91932	2.9375	2.854167	2.125
87.93894	3.0625	2.604167	2.010417
87.95857	3.25	3.104167	1.885417
87.9782	2.697917	3.114583	2.166667
87.99782	3.03125	2.9375	2.125
88.01745	3.0625	3	1.979167
88.03708	3	2.895833	1.75
88.05671	3.020833	3.260417	2.052083
88.07633	3	2.979167	1.989583
88.09596	3.041667	2.854167	2.229167
88.11559	3.229167	2.697917	2.322917
88.13521	3.354167	2.895833	2.03125
88.15484	3.364583	2.864583	2.15625
88.17447	3.072917	3.0625	2.104167
88.19409	3.083333	2.958333	1.989583
88.21372	3.25	2.979167	2.114583
88.23335	3.083333	2.708333	2.291667
88.25298	3.020833	2.916667	2.28125
88.2726	3.395833	2.96875	1.979167
88.29223	3.083333	2.875	2.322917
88.31186	3.197917	3.104167	2.302083

88.33148	3.260417	2.666667	2.239583
88.35111	2.572917	2.979167	2.385417
88.37074	2.677083	2.604167	2.15625
88.39036	2.90625	3.145833	2.083333
88.40999	2.833333	3.208333	2.072917
88.42962	3.010417	2.78125	2.166667
88.44925	3.239583	2.5	2.072917
88.46887	2.96875	3.010417	2.322917
88.4885	3.135417	2.864583	2.395833
88.50813	3.260417	2.916667	2.385417
88.52775	3.052083	2.677083	2.177083
88.54738	2.59375	2.8125	1.989583
88.56701	3.333333	2.895833	2.125
88.58664	3.072917	2.979167	2.177083
88.60626	2.75	2.59375	2.0625
88.62589	2.708333	2.6875	2.15625
88.64552	3.260417	2.53125	2.041667
88.66514	3.041667	2.770833	1.84375
88.68477	3.1875	2.625	1.90625
88.7044	3.0625	2.677083	2.197917
88.72402	2.854167	2.645833	2.09375
88.74365	3.229167	2.479167	1.927083
88.76328	2.739583	2.729167	1.84375
88.78291	3.458333	2.416667	1.989583
88.80253	3.375	2.59375	1.90625
88.82216	3.104167	2.364583	1.84375
88.84179	3.3125	2.708333	1.9375
88.86141	3.052083	2.552083	1.760417
88.88104	3.03125	2.4375	2.364583
88.90067	3.135417	2.5	1.833333
88.92029	2.864583	2.614583	1.979167
88.93992	2.854167	2.364583	1.78125
88.95955	2.916667	2.895833	2.125
88.97918	2.854167	2.385417	1.75
88.9988	3.25	2.302083	1.791667
89.01843	3.083333	3.208333	1.979167
89.03806	2.822917	2.552083	1.822917
89.05768	3.114583	2.65625	1.947917
89.07731	2.84375	2.604167	1.96875
89.09694	2.854167	2.583333	2.114583
89.11656	2.760417	2.739583	2.010417
89.13619	2.989583	2.760417	1.791667
89.15582	3.0625	2.927083	2.104167
89.17545	2.96875	2.635417	2
89.19507	3.177083	2.052083	1.9375

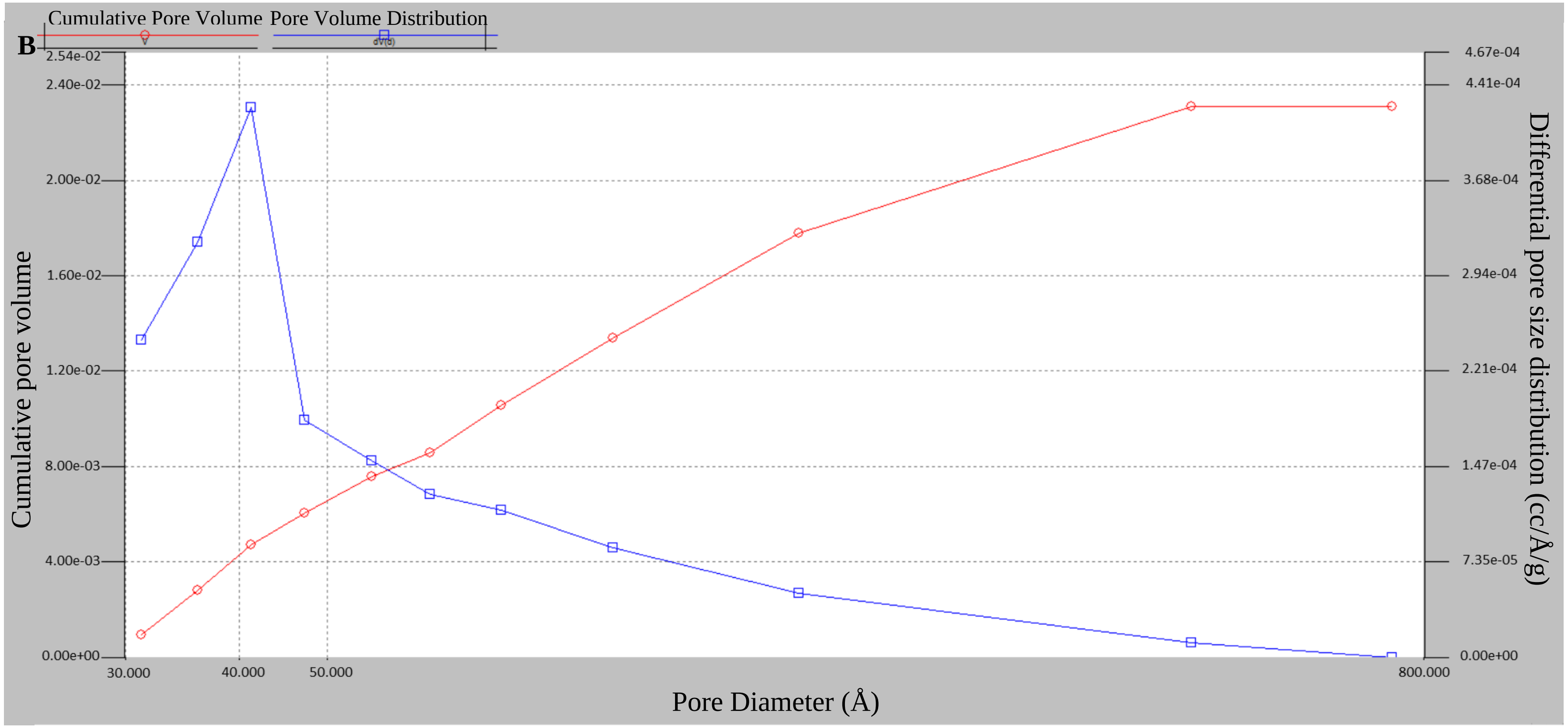
89.2147	2.979167	2.885417	2.25
89.23433	3.15625	2.552083	2.010417
89.25395	3.25	2.708333	2.010417
89.27358	3.15625	2.4375	1.958333
89.29321	2.833333	2.96875	1.802083
89.31283	3.114583	3.125	2.052083
89.33246	3.145833	2.8125	2.104167
89.35209	3.197917	2.333333	2.010417
89.37172	2.71875	2.802083	1.96875
89.39134	2.770833	2.520833	1.916667
89.41097	3.208333	2.4375	2.239583
89.4306	2.927083	2.84375	1.916667
89.45022	2.625	2.75	1.822917
89.46985	2.864583	2.697917	1.90625
89.48948	2.770833	2.552083	2.03125
89.5091	3.072917	2.46875	1.854167
89.52873	3.28125	2.385417	1.864583
89.54836	3.208333	2.416667	1.739583
89.56799	3.03125	2.677083	2.09375
89.58761	3.114583	2.927083	2.125
89.60724	3.177083	2.354167	1.989583
89.62687	3	2.625	2.03125
89.64649	2.885417	2.510417	1.9375
89.66612	2.90625	2.583333	2.15625
89.68575	3.239583	2.6875	2.010417
89.70537	3.052083	2.739583	1.947917
89.725	3.041667	2.541667	2.09375
89.74463	3.145833	2.572917	1.979167
89.76426	2.875	2.739583	1.885417
89.78388	3	2.65625	1.75
89.80351	3.020833	2.447917	2.291667
89.82314	3.041667	2.416667	2.083333
89.84276	2.947917	2.510417	1.885417
89.86239	2.875	2.458333	1.822917
89.88202	2.854167	2.604167	1.895833
89.90164	2.8125	2.572917	1.9375
89.92127	2.864583	2.5625	1.979167
89.9409	3.385417	2.541667	2.041667
89.96053	3.020833	2.645833	1.9375
89.98015	2.927083	2.552083	1.947917
89.99978	3.145833	2.895833	1.958333

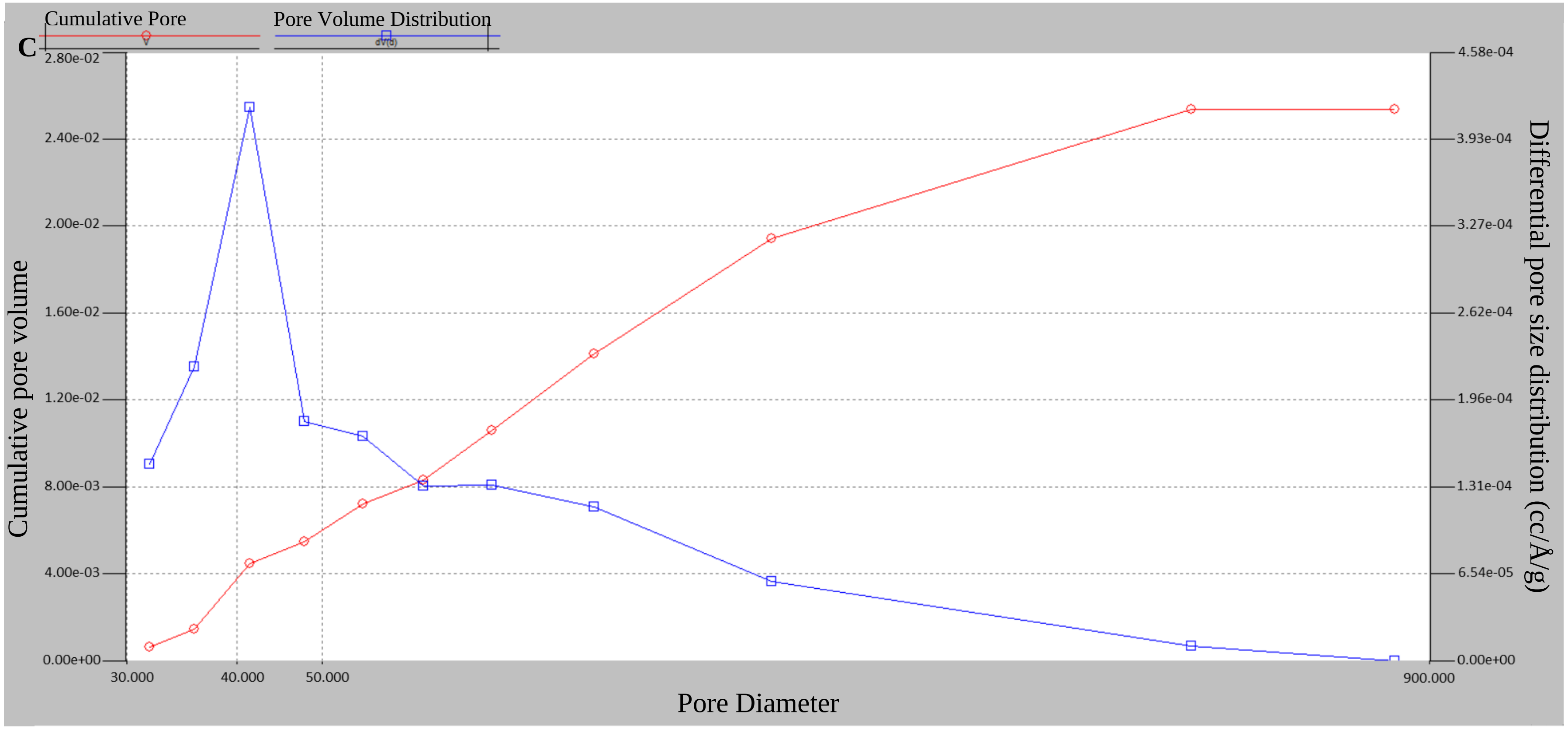
SI 3.11A: XRD peaks for for pristine larch biochar (BC),larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) post immobilisation of Pb, Cu, Zn and Cd

SI 3.11A is the data underpinning the XRD figure (3.9) which is referred to in section 3.3.3 (results and discussion section of chapter 3) to indicate the presence of carbonates, siloxane and phosphates in relation to co-precipitation.


A
Cumulative Pore Volume
Pore Volume Distribution
dV(d)
Cumulative pore volume
2.15e-02
2.00e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
Differential pore size distribution (cc/Å/g)
2.13e-04
2.15e-04
1.72e-04
1.29e-04
8.60e-05
4.30e-05
0.00e+00
30.000
40.000
50.000
Pore Diameter (Å)

B


Cumulative Pore Volume
Pore Volume Distribution
dV(d)
2.54e-02
2.40e-02
2.00e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
Cumulative pore volume
4.67e-04
4.41e-04
3.68e-04
2.94e-04
2.21e-04
1.47e-04
7.35e-05
0.00e+00
Differential pore size distribution (cc/Å/g)
30.000
40.000
50.000
800.000
Pore Diameter (Å)


C
Cumulative Pore
Pore Volume Distribution
dV(d)
2.80e-02
2.40e-02
2.00e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
Cumulative pore volume
4.58e-04
3.93e-04
3.27e-04
2.62e-04
1.96e-04
1.31e-04
6.54e-05
0.00e+00
Differential pore size distribution (cc/Å/g)
30.000
40.000
50.000
900.000
Pore Diameter

SI 3.12 A: Cumulative pore volume and pore size distribution for pristine larch biochar (BC), B: larch biochar cold mixed with wood ash (WA) and C: larch biochar sintered with wood ash (WAS).

SI 3.12 A, B and C underpin the argument that although surface area is often seen as an important physical property for contaminant sorption, comparative studies have shown that when surface area of a char is lower but immobilisation is higher, as seen in this study, chemical processes such as ion exchange or more importantly precipitation supersede the importance of surface area in section 3.3.3 (results and discussion section of chapter 3).

BC Diameter	BC Pore Vol	BC Pore Surf Area	BC dV(d)	BC dS(d)	BC dV(logd)	BC dS(logd)
31.5696	2.92E-03	3.70E+00	5.88E-04	7.45E-01	4.26E-02	5.40E+01
36.041	5.18E-03	6.21E+00	5.70E-04	6.32E-01	4.72E-02	5.24E+01
41.4372	7.58E-03	8.52E+00	3.51E-04	3.39E-01	3.34E-02	3.23E+01
47.61	8.04E-03	8.91E+00	8.38E-05	7.04E-02	9.18E-03	7.71E+00
55.4385	8.78E-03	9.44E+00	7.29E-05	5.26E-02	9.28E-03	6.70E+00
64.722	9.13E-03	9.66E+00	4.20E-05	2.59E-02	6.25E-03	3.86E+00
79.5005	9.74E-03	9.97E+00	2.89E-05	1.45E-02	5.25E-03	2.64E+00
102.2861	1.01E-02	1.01E+01	1.28E-05	5.02E-03	3.01E-03	1.18E+00
154.4637	1.06E-02	1.02E+01	7.06E-06	1.83E-03	2.46E-03	6.36E-01
572.4216	1.15E-02	1.03E+01	1.20E-06	8.39E-05	1.32E-03	9.20E-02
1211.431	1.15E-02	1.03E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00

WA Diameter	WA Pore Vol	WA Pore Surf Area	WA dV(d)	WA dS(d)	WA dV(logd)	WA dS(logd)
31.466	0.000613	0.77984	0.000185	0.23492	0.013377	17.005
36.0815	0.002291	2.6394	0.000284	0.31457	0.023522	26.076
41.3963	0.00423	4.5134	0.000411	0.39719	0.039139	37.818
47.9654	0.005541	5.6068	0.000156	0.12985	0.017153	14.305
55.5289	0.006414	6.2353	0.00013	0.093712	0.016613	11.967
64.2825	0.007777	7.0834	0.000126	0.078524	0.018635	11.595
77.8026	0.009452	7.9444	0.000103	0.053021	0.018408	9.464
101.9471	0.012036	8.9584	8.06E-05	0.031639	0.018772	7.3655
162.6079	0.016639	10.091	5.16E-05	0.012684	0.018812	4.6275
450.2628	0.022124	10.578	1.13E-05	0.001003	0.010459	0.92912
761.8332	0.022164	10.58	2.88E-07	1.51E-05	0.000503	0.026411

WAS Diameter	WAS Pore Vol	WAS Pore Surf Area	WAS dV(d)	WAS dS(d)	WAS dV(logd)	WAS dS(logd)
31.8529	6.09E-04	7.65E-01	1.48E-04	1.86E-01	1.08E-02	1.36E+01
35.8382	1.46E-03	1.72E+00	2.21E-04	2.47E-01	1.82E-02	2.04E+01
41.3679	4.46E-03	4.62E+00	4.16E-04	4.03E-01	3.96E-02	3.82E+01
47.7398	5.46E-03	5.45E+00	1.80E-04	1.51E-01	1.98E-02	1.66E+01
55.6606	7.20E-03	6.70E+00	1.69E-04	1.21E-01	2.16E-02	1.55E+01
65.0658	8.31E-03	7.39E+00	1.31E-04	8.07E-02	1.96E-02	1.21E+01
77.9605	1.06E-02	8.56E+00	1.32E-04	6.79E-02	2.37E-02	1.21E+01
101.7596	1.41E-02	9.94E+00	1.16E-04	4.55E-02	2.69E-02	1.06E+01
161.4965	1.94E-02	1.13E+01	5.95E-05	1.47E-02	2.16E-02	5.34E+00
483.3617	2.54E-02	1.17E+01	1.07E-05	8.87E-04	1.05E-02	8.68E-01
821.1512	2.54E-02	1.17E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00

SI 2.16: Pore size distribution for pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS)

SI 3.12 D is the data for SI 3.12 A, B and C that underpins the argument that although surface area is often seen as an important physical property for contaminant sorption, comparative studies have shown that when surface area of a char is lower but immobilisation is higher, as seen in this study, chemical processes such as ion exchange or more importantly precipitation supersede the importance of surface area in section 3.3.3 (results and discussion section of chapter 3).

ii) Supplementary material: Chapter 4

Biochar properties: unrinsed and rinsed with deionised water

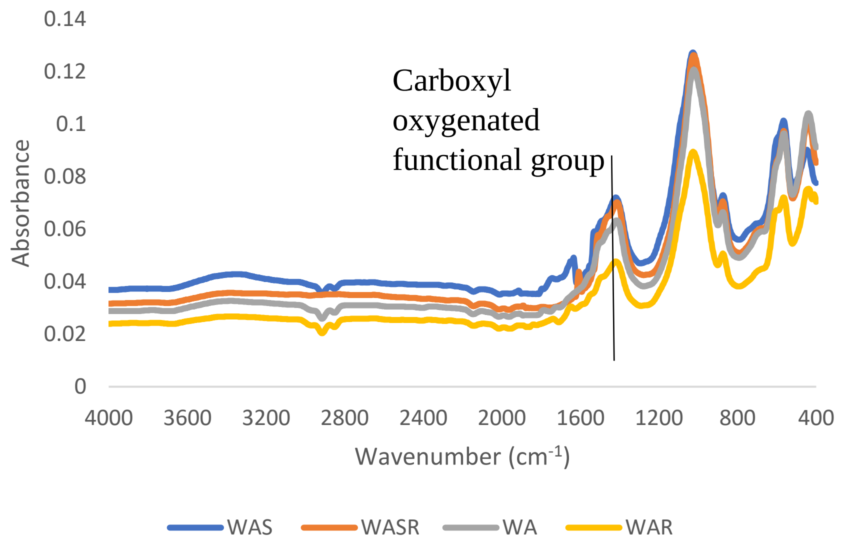
Metal	Sorbent	Sorbent Weight (mg)	Volume of solution (mL)	Volume of sample (mL)	Total volume (mL)	Dilution factor (-)	Measured Concentration (mg/L)	Actual concentration (mg/L)	Absolute concentration (mg)	Mass per unit mass of sorbent (g/kg)
Ca	WA	24.5	50	0.5	5	10	8.50	85.03	4.25	173.53
Ca	WAS	25.6	50	0.5	5	10	10.74	107.39	5.37	209.75
Ca	WA	24.5	50	5.0	5	1	87.17	87.17	4.36	177.90
Ca	WAS	25.6	50	5.0	5	1	110.07	110.07	5.50	214.98
K	WA	24.5	50	0.5	5	10	1.31	13.11	0.66	26.75
K	WAS	25.6	50	0.5	5	10	0.62	6.18	0.31	12.06
K	WA	24.5	50	5.0	5	1	14.49	14.49	0.72	29.57
K	WAS	25.6	50	5.0	5	1	6.92	6.92	0.35	13.51
Mg	WA	24.5	50	0.5	5	10	0.23	2.33	0.12	4.76
Mg	WAS	25.6	50	0.5	5	10	0.28	2.80	0.14	5.47
Mg	WA	24.5	50	5.0	5	1	2.20	2.20	0.11	4.49
Mg	WAS	25.6	50	5.0	5	1	2.61	2.61	0.13	5.10
Na	WA	24.5	50	0.5	5	10	1.50	15.02	0.75	30.66
Na	WAS	25.6	50	0.5	5	10	0.88	8.77	0.44	17.13
Na	WA	24.5	50	5.0	5	1	15.77	15.77	0.79	32.18
Na	WAS	25.6	50	5.0	5	1	9.74	9.74	0.49	19.01
P	WA	24.5	50	0.5	5	10	2.74	27.39	1.37	55.90
P	WAS	25.6	50	0.5	5	10	3.64	36.42	1.82	71.13
P	WA	24.5	50	5.0	5	1	23.40	23.40	1.17	47.75
P	WAS	25.6	50	5.0	5	1	31.73	31.73	1.59	61.96
Si	WA	24.5	50	0.5	5	10	2.06	20.63	1.03	42.10
Si	WAS	25.6	50	0.5	5	10	2.31	23.07	1.15	45.05
Si	WA	24.5	50	5.0	5	1	18.65	18.65	0.93	38.07
Si	WAS	25.6	50	5.0	5	1	20.69	20.69	1.03	40.40

SI 4.1: concentrations of alkali and alkaline earths, phosphorus and silicates for larch biochar mixed cold with wood ash (WA) and sintered with wood ash (WAS)

Metal	Sorbent	Mass per unit mass of sorbent (g/kg)	log scale
P	WA	47.7	1.7
P	WAS	62.0	1.8
P	WAR	55.4	1.7
P	WASR	72.8	1.9
N	WA	2.2	0.3
N	WAS	2.4	0.4
N	WAR	2.7	0.4
N	WASR	2.3	0.4
S	WA	12.3	1.1
S	WAS	14.6	1.2
S	WAR	5.0	0.7
S	WASR	6.5	0.8
Ca	WA	177.9	2.3
Ca	WAS	215.0	2.3
Ca	WAR	196.1	2.3
Ca	WASR	238.1	2.4
K	WA	29.6	1.5
K	WAS	13.5	1.1
K	WAR	11.9	1.1
K	WASR	28.8	1.5
Mg	WA	4.5	0.7
Mg	WAS	5.1	0.7
Mg	WAR	4.8	0.7
Mg	WASR	5.2	0.7
Na	WA	32.2	1.5
Na	WAS	19.0	1.3
Na	WAR	16.7	1.2
Na	WASR	33.0	1.5

SI 4.2: Metal characterisation of larch biochar sintered with wood ash before rinsing with deionised water (WAS) and after rinsing with 800mL of deionised water (WASR) and larch biochar mixed cold with wood ash before rinsing with deionised water (WA) and after rinsing with deionised water data (WAR)

SI 4.2 is the data used to populate figures 4.1 and 4.2 with attendant discussion (results and discussion section of chapter 4).



SI 4.3: FTIR spectra of larch biochar sintered with wood ash before rinsing with deionised water (WAS) and after rinsing with 800mL of deionised water (WASR) and larch biochar mixed cold with wood ash before rinsing with deionised water (WA) and after rinsing with deionised water (WAR)

SI 4.3 figure is referred to in section 4.3.1 (results and discussion section of chapter 4) in reference to the presence of oxygenated functional groups and their role in ion exchange.

Peak Position	Peak Intensity	Mineral Form
10.767	202.578	Hydroxylapatite
22.959	245.070	Calcite
24.178	82.342	Kalcinite
25.776	457.372	Hydroxylapatite
28.833	160.632	Hydroxylapatite
29.303	1562.754	Calcite
30.314	379.947	Kalcinite
31.640	1906.377	Hydroxylapatite
32.082	744.380	Hydroxylapatite
32.767	750.094	Hydroxylapatite
33.954	309.787	Hydroxylapatite
38.107	75.415	Hydroxylapatite
39.333	264.000	Calcite
39.666	237.138	Hydroxylapatite
43.064	234.498	Calcite
44.263	127.316	Kalcinite
46.578	304.190	Hydroxylapatite
47.392	160.475	Calcite
48.425	256.860	Calcite
49.371	407.789	Hydroxylapatite
50.345	127.410	Hydroxylapatite
53.131	111.245	Hydroxylapatite
56.435	65.076	Calcite
57.347	76.356	Calcite

SI 4.4: XRD peaks and intensities of hydroxylapatite, calcite and kalcinite for larch biochar sintered with wood ash (WAS)

SI 4.4 data are referred to in section 4.3.1 (results and discussion section of chapter 4) in reference to the presence of carbonate and phosphate anions and the resultant uptake of charge balancing cations.

	Biochar sintered with wood ash	Biochar mixed cold with wood ash
10.0001	22.54167	17.41667
10.01973	22.61458	17.02083
10.03935	23.46875	17.29167
10.05898	21.96875	16.5625
10.07861	21.53125	17.13542
10.09824	23.09375	17.42708
10.11786	21.9375	17.13542
10.13749	22.60417	17.76042
10.15712	22.64583	16.9375
10.17674	22.22917	17.25
10.19637	21.85417	17.45833
10.216	22.66667	17.67708
10.23562	23.22917	16.85417
10.25525	23.34375	18.10417
10.27488	23.8125	17.77083
10.29451	23.61458	16.63542
10.31413	22.78125	17.53125
10.33376	23.03125	17.46875
10.35339	22.85417	17.61458
10.37301	22.88542	17.26042
10.39264	24.42708	17.23958
10.41227	22.54167	17.69792
10.43189	23.125	17.71875
10.45152	23.60417	16.96875
10.47115	23.59375	17.33333
10.49078	23.23958	16.94792
10.5104	24.07292	18.08333
10.53003	23.70833	17.8125
10.54966	24.15625	17.51042
10.56928	23.94792	16.85417
10.58891	24.88542	17.13542
10.60854	24.15625	16.8125
10.62816	24.63542	17.05208
10.64779	23.98958	17.15625
10.66742	24.55208	18.11458
10.68705	24.6875	18.28125
10.70667	24.66667	18.46875
10.7263	24.90625	18.44792

10.74593	24.9375	18.73958
10.76555	25.875	19.05208
10.78518	25.52083	19.20833
10.80481	24.76042	19.5
10.82443	25.125	18.54167
10.84406	24.28125	18.54167
10.86369	24.15625	18.10417
10.88332	24.125	18.71875
10.90294	24.34375	18.5
10.92257	23.35417	18.21875
10.9422	23.60417	18.08333
10.96182	24.52083	17.92708
10.98145	24.90625	18.09375
11.00108	24.8125	18.375
11.0207	25.0625	18.20833
11.04033	24.70833	17.05208
11.05996	23.90625	17.51042
11.07959	24.09375	17.16667
11.09921	25.19792	17.65625
11.11884	24.55208	17.13542
11.13847	24.54167	17.71875
11.15809	24.36458	18.04167
11.17772	25.07292	17.64583
11.19735	26.03125	18.16667
11.21697	24.58333	18.34375
11.2366	25.16667	17.90625
11.25623	24.61458	18.33333
11.27586	24.79167	18.02083
11.29548	24.9375	18.05208
11.31511	25.29167	19.07292
11.33474	24.77083	17.77083
11.35436	25.82292	17.51042
11.37399	25.14583	17.79167
11.39362	25.73958	17.625
11.41324	25.78125	18.84375
11.43287	25.64583	17.97917
11.4525	25.19792	18.25
11.47213	25.17708	18.05208
11.49175	25.67708	18.04167
11.51138	25.29167	17.94792
11.53101	25.21875	17.63542
11.55063	26.21875	17.77083
11.57026	25.57292	18.66667
11.58989	25.03125	18.22917
11.60951	25.41667	18.17708

11.62914	25.52083	18.9375
11.64877	25.08333	18.65625
11.6684	25.32292	18.45833
11.68802	25.78125	17.67708
11.70765	25.67708	18.70833
11.72728	25.625	18.33333
11.7469	25.70833	17.72917
11.76653	26.15625	18.44792
11.78616	26.4375	18.94792
11.80578	24.5625	18.76042
11.82541	25.32292	19.14583
11.84504	25.20833	18.53125
11.86467	25.89583	18.125
11.88429	26.10417	18.22917
11.90392	26.40625	18.375
11.92355	26.19792	18.36458
11.94317	25.41667	18.07292
11.9628	25.76042	17.64583
11.98243	25.22917	18.21875
12.00205	25.625	18.75
12.02168	26.10417	18.55208
12.04131	25.4375	19
12.06094	26.05208	18.625
12.08056	25.85417	18.97917
12.10019	26.0625	18.77083
12.11982	26.69792	18.44792
12.13944	26.39583	18.23958
12.15907	26.35417	17.83333
12.1787	25.4375	18.83333
12.19832	25.92708	17.61458
12.21795	26.14583	19.07292
12.23758	25.52083	17.45833
12.25721	26.34375	17.59375
12.27683	26.79167	18.9375
12.29646	26.35417	18.14583
12.31609	25.89583	18.61458
12.33571	25.22917	18.61458
12.35534	27.05208	17.40625
12.37497	26.27083	18.16667
12.39459	26.02083	18.16667
12.41422	25.53125	18.16667
12.43385	25.625	18.5
12.45348	25.34375	18.5
12.4731	25.9375	18.35417
12.49273	25.85417	17.52083

12.51236	26.22917	18.02083
12.53198	25.60417	18.39583
12.55161	26.07292	19.21875
12.57124	25.66667	18.23958
12.59087	25.27083	18.05208
12.61049	25.38542	17.96875
12.63012	25.16667	17.45833
12.64975	25.35417	18.38542
12.66937	26.05208	18.63542
12.689	25.67708	18.14583
12.70863	25.14583	18.13542
12.72825	25.4375	19.375
12.74788	25.41667	18.35417
12.76751	25.28125	18.63542
12.78714	25.45833	17.46875
12.80676	25.65625	17.48958
12.82639	25.17708	17.69792
12.84602	24.54167	17.86458
12.86564	24.46875	17.59375
12.88527	25.54167	17.57292
12.9049	23.80208	17.61458
12.92452	25.3125	17.9375
12.94415	25.29167	18.19792
12.96378	24.94792	16.79167
12.98341	25.75	17.4375
13.00303	24.28125	18.16667
13.02266	25.92708	18.01042
13.04229	25.14583	16.89583
13.06191	24.90625	17.0625
13.08154	23.67708	17.05208
13.10117	24.16667	18.16667
13.12079	25.98958	16.70833
13.14042	24.22917	17.78125
13.16005	23.375	17.5
13.17968	24.13542	17.05208
13.1993	24.40625	17.65625
13.21893	23.76042	17.40625
13.23856	24.17708	17.27083
13.25818	23.34375	16.625
13.27781	23.95833	16.88542
13.29744	23.70833	16.98958
13.31706	24.86458	17.07292
13.33669	24.73958	17
13.35632	24.40625	17.09375
13.37595	23.96875	18.125

13.39557	23.35417	16.875
13.4152	22.95833	16.78125
13.43483	23.78125	17.17708
13.45445	22.8125	17.05208
13.47408	23.96875	16
13.49371	23.71875	16.94792
13.51333	22.77083	17.08333
13.53296	23.54167	17.11458
13.55259	23.73958	16.53125
13.57222	23.3125	15.70833
13.59184	23.61458	16.59375
13.61147	23.30208	16.05208
13.6311	24.625	16.5625
13.65072	23.90625	16.16667
13.67035	23.61458	17.54167
13.68998	24.0625	16.76042
13.7096	23.26042	17.59375
13.72923	23.88542	16.16667
13.74886	23.36458	17.85417
13.76849	23.17708	17.125
13.78811	21.96875	16.98958
13.80774	23.05208	17.34375
13.82737	22.41667	16.35417
13.84699	22.51042	16.22917
13.86662	20.79167	16.32292
13.88625	22.13542	15.76042
13.90587	22.09375	15.29167
13.9255	21.25	16.10417
13.94513	21.76042	15.55208
13.96476	21.67708	15.44792
13.98438	21.04167	15.17708
14.00401	21.25	15.39583
14.02364	20.78125	15.0625
14.04326	21.26042	14.58333
14.06289	20.98958	15.16667
14.08252	21.64583	14.82292
14.10214	20.55208	14.75
14.12177	20.35417	14.9375
14.1414	21.14583	14.20833
14.16103	20.72917	15.09375
14.18065	20.39583	15.60417
14.20028	20.92708	15.0625
14.21991	19.94792	14.72917
14.23953	20.17708	13.77083
14.25916	19.88542	14.38542

14.27879	21.53125	14.40625
14.29841	20.4375	14.04167
14.31804	21.10417	14.27083
14.33767	20.54167	14.57292
14.3573	19.97917	14.36458
14.37692	20.02083	14.13542
14.39655	20.35417	13.57292
14.41618	20.20833	13.72917
14.4358	19.95833	14.14583
14.45543	19.54167	14.19792
14.47506	19.07292	12.84375
14.49468	19.82292	13.69792
14.51431	19.3125	13.72917
14.53394	19.16667	13.26042
14.55357	18.625	13.70833
14.57319	18.76042	13.8125
14.59282	19.47917	13.52083
14.61245	19.35417	13.46875
14.63207	19.30208	13.3125
14.6517	18.65625	13.61458
14.67133	18.04167	13.39583
14.69095	18.625	13.29167
14.71058	19.375	12.83333
14.73021	18.96875	13.05208
14.74984	18.07292	11.82292
14.76946	18.23958	12.86458
14.78909	18.15625	13.125
14.80872	18.96875	12.55208
14.82834	18.88542	12.40625
14.84797	17.88542	12.92708
14.8676	18.33333	12.48958
14.88722	17.94792	12.53125
14.90685	17.44792	12.58333
14.92648	17.32292	12.17708
14.94611	18.4375	12.51042
14.96573	18.45833	11.67708
14.98536	17.98958	12.9375
15.00499	17.64583	12.23958
15.02461	17.34375	12.64583
15.04424	17.36458	12.10417
15.06387	17.8125	11.8125
15.08349	17.04167	12
15.10312	17.125	12.60417
15.12275	16.91667	11.35417
15.14238	16.8125	11.30208

15.162	16.59375	11.58333
15.18163	17.13542	11.77083
15.20126	16.57292	11.59375
15.22088	16.45833	11.94792
15.24051	16.65625	11.91667
15.26014	16.63542	11.77083
15.27976	16.40625	11.26042
15.29939	16.16667	11.39583
15.31902	16.01042	11.66667
15.33865	16.27083	11.54167
15.35827	15.63542	11.39583
15.3779	15.90625	11.92708
15.39753	15.86458	11.23958
15.41715	15.76042	11.125
15.43678	16.25	10.70833
15.45641	16	11.75
15.47604	16.86458	10.97917
15.49566	15.23958	11.38542
15.51529	15.55208	11.5625
15.53492	15.86458	10.46875
15.55454	14.69792	11.10417
15.57417	16.23958	10.375
15.5938	15.04167	10.57292
15.61342	15.875	10.94792
15.63305	14.69792	11.27083
15.65268	15.30208	10.64583
15.67231	14.76042	10.63542
15.69193	15.52083	10.34375
15.71156	15.19792	10.33333
15.73119	14.80208	10.69792
15.75081	14.40625	10.20833
15.77044	14.60417	10.27083
15.79007	14.6875	9.864583
15.80969	14.63542	9.5
15.82932	14.70833	10.20833
15.84895	15.11458	10.35417
15.86858	14.58333	10.48958
15.8882	14.1875	10.3125
15.90783	14.95833	10.35417
15.92746	14.83333	10.16667
15.94708	14.41667	10.13542
15.96671	13.70833	10.44792
15.98634	13.83333	9.739583
16.00596	14.10417	9.364583
16.02559	14.28125	9.822917

16.04522	14.41667	9.989583
16.06485	13.6875	9.760417
16.08447	13.54167	9.395833
16.1041	14.02083	10.22917
16.12373	13.33333	9.34375
16.14335	13.52083	9.34375
16.16298	13.4375	9.322917
16.18261	13.25	9.270833
16.20223	13.80208	9.28125
16.22186	12.96875	9.177083
16.24149	13.09375	8.9375
16.26112	12.41667	9.1875
16.28074	12.51042	8.333333
16.30037	13.35417	9.760417
16.32	12.40625	9.333333
16.33962	12.52083	8.90625
16.35925	12.48958	8.958333
16.37888	12.5	8.885417
16.3985	12.125	9.65625
16.41813	12.79167	8.90625
16.43776	12.61458	8.5
16.45739	12.42708	9.052083
16.47701	12.02083	8.760417
16.49664	12.44792	8.739583
16.51627	12.29167	8.510417
16.53589	11.94792	8.510417
16.55552	11.83333	8.447917
16.57515	11.46875	8.71875
16.59477	11.86458	8.75
16.6144	11.41667	8.375
16.63403	11.30208	8.354167
16.65366	12.39583	8.34375
16.67328	11.98958	8.447917
16.69291	12.02083	8.333333
16.71254	11.78125	8.520833
16.73216	11.44792	8.635417
16.75179	12.03125	9.135417
16.77142	11.39583	8.833333
16.79104	11.48958	8.760417
16.81067	12.11458	8.5625
16.8303	11.13542	8.239583
16.84993	11.10417	8.010417
16.86955	10.65625	7.916667
16.88918	11.11458	7.84375
16.90881	10.8125	7.84375

16.92843	11.38542	8.208333
16.94806	10.3125	7.770833
16.96769	10.3125	7.666667
16.98731	11.27083	8.03125
17.00694	11.44792	8.364583
17.02657	10.84375	8.114583
17.0462	10.9375	8.1875
17.06582	10.14583	8.197917
17.08545	10.54167	8.364583
17.10508	10.51042	7.489583
17.1247	10.45833	7.552083
17.14433	10.05208	7.395833
17.16396	10.46875	7.40625
17.18358	10.14583	7.375
17.20321	9.9375	7.4375
17.22284	9.364583	7.197917
17.24247	10.04167	7.114583
17.26209	10.14583	7.572917
17.28172	9.875	7.239583
17.30135	9.21875	7.645833
17.32097	10.125	7.552083
17.3406	9.208333	7.395833
17.36023	9.53125	7.135417
17.37985	9.864583	6.979167
17.39948	9.270833	6.572917
17.41911	9.364583	7.447917
17.43874	9.15625	6.802083
17.45836	9.552083	7.34375
17.47799	9.0625	7.041667
17.49762	9.104167	7.010417
17.51724	9.03125	7.09375
17.53687	8.854167	6.614583
17.5565	9.125	6.875
17.57612	8.59375	6.697917
17.59575	8.333333	6.510417
17.61538	8.197917	6.614583
17.63501	9.239583	7.104167
17.65463	8.6875	6.458333
17.67426	8.614583	6.5
17.69389	9.15625	6.135417
17.71351	8.34375	6.447917
17.73314	8.572917	6.75
17.75277	8.197917	6.416667
17.77239	8.6875	6.90625
17.79202	8.28125	6.552083

17.81165	8.65625	6.041667
17.83128	8.427083	6.5
17.8509	8.3125	6.354167
17.87053	8.427083	6.072917
17.89016	8.552083	6.458333
17.90978	8.71875	6.302083
17.92941	8.135417	6.395833
17.94904	8.635417	6.625
17.96866	8.072917	6.229167
17.98829	7.6875	6.59375
18.00792	8.375	6.177083
18.02755	7.989583	6.21875
18.04717	7.833333	6.34375
18.0668	7.09375	6.260417
18.08643	7.791667	5.979167
18.10605	7.5625	5.708333
18.12568	7.625	5.916667
18.14531	7.354167	6.21875
18.16493	8.145833	5.885417
18.18456	7.479167	5.770833
18.20419	7.760417	5.958333
18.22382	7.395833	5.677083
18.24344	7.395833	6.052083
18.26307	7.53125	6.09375
18.2827	7.447917	5.927083
18.30232	8.229167	6.09375
18.32195	7.802083	6.145833
18.34158	7.03125	6.1875
18.36121	7.458333	5.864583
18.38083	7.75	6.104167
18.40046	7.479167	6.270833
18.42009	7.541667	6.03125
18.43971	7.979167	6.15625
18.45934	7.885417	6.020833
18.47897	8.479167	5.989583
18.49859	8.291667	6.239583
18.51822	8.520833	6.5
18.53785	8.510417	7.0625
18.55748	8.520833	7.302083
18.5771	8.53125	7.875
18.59673	8.9375	8.364583
18.61636	8.5	7.84375
18.63598	7.65625	7.135417
18.65561	7.270833	7.6875
18.67524	7.71875	7.177083

18.69486	7.989583	6.395833
18.71449	7.3125	6.760417
18.73412	6.958333	6.5625
18.75375	6.895833	6.635417
18.77337	6.9375	6.15625
18.793	6.802083	5.885417
18.81263	6.09375	6.53125
18.83225	6.739583	5.78125
18.85188	6.625	5.604167
18.87151	6.614583	5.822917
18.89113	6.375	5.5625
18.91076	6.15625	5.375
18.93039	6.541667	6.010417
18.95002	6.041667	5.8125
18.96964	5.947917	5.416667
18.98927	5.895833	5.291667
19.0089	5.9375	6
19.02852	6.5	5.34375
19.04815	6.15625	5.208333
19.06778	5.9375	5.3125
19.0874	6.25	5.40625
19.10703	5.864583	5.4375
19.12666	6.34375	5.458333
19.14629	6.34375	4.927083
19.16591	5.71875	5.21875
19.18554	5.916667	5.03125
19.20517	5.729167	5.3125
19.22479	5.78125	5.270833
19.24442	5.645833	5.104167
19.26405	5.78125	5.354167
19.28367	5.822917	4.5
19.3033	5.895833	4.802083
19.32293	5.197917	4.96875
19.34256	6.010417	4.979167
19.36218	5.78125	4.84375
19.38181	5.5625	5.291667
19.40144	5.614583	4.8125
19.42106	5.583333	5.010417
19.44069	5.416667	4.770833
19.46032	5.614583	5
19.47994	5.864583	4.885417
19.49957	5.71875	4.864583
19.5192	5.614583	5.458333
19.53883	6	4.75
19.55845	5.90625	4.760417

19.57808	5.15625	4.760417
19.59771	5.09375	5.104167
19.61733	5.34375	4.84375
19.63696	5.34375	5.114583
19.65659	6.177083	4.979167
19.67621	5.354167	5.09375
19.69584	5.510417	5.010417
19.71547	5.895833	4.84375
19.7351	5.395833	4.958333
19.75472	5.177083	5.114583
19.77435	4.59375	4.40625
19.79398	5.208333	4.59375
19.8136	5.0625	4.604167
19.83323	5.166667	5
19.85286	5.40625	4.90625
19.87248	5.208333	4.6875
19.89211	4.885417	4.666667
19.91174	5.270833	4.71875
19.93137	5.364583	4.947917
19.95099	5.177083	4.760417
19.97062	5.229167	4.552083
19.99025	4.916667	4.739583
20.00987	5.083333	4.989583
20.0295	5.28125	4.677083
20.04913	5.625	4.71875
20.06875	4.864583	5.135417
20.08838	5.28125	4.364583
20.10801	5.541667	5.052083
20.12764	5.010417	4.6875
20.14726	5.1875	4.78125
20.16689	5.291667	4.916667
20.18652	5.5	4.75
20.20614	4.822917	4.833333
20.22577	5.666667	4.760417
20.2454	5.072917	4.78125
20.26502	4.885417	4.5625
20.28465	5.4375	4.4375
20.30428	5.364583	4.9375
20.32391	5.052083	4.770833
20.34353	4.927083	5.135417
20.36316	4.90625	4.708333
20.38279	5.260417	4.572917
20.40241	5.260417	4.458333
20.42204	4.864583	4.541667
20.44167	4.802083	4.739583

20.46129	5.09375	4.739583
20.48092	4.625	4.3125
20.50055	4.9375	4.604167
20.52018	5.125	4.125
20.5398	5.145833	4.3125
20.55943	5.020833	4.447917
20.57906	5.010417	4.166667
20.59868	4.25	4.28125
20.61831	4.708333	4.458333
20.63794	4.833333	4.375
20.65756	5.291667	4.375
20.67719	4.864583	4.260417
20.69682	5.479167	4.322917
20.71645	5.927083	4.90625
20.73607	5.666667	5
20.7557	6.0625	4.416667
20.77533	5.71875	4.802083
20.79495	5.458333	4.8125
20.81458	5.354167	4.510417
20.83421	5.59375	4.145833
20.85383	5.166667	4.635417
20.87346	5.104167	4.729167
20.89309	5.041667	4.21875
20.91272	4.677083	4.416667
20.93234	5.479167	4.9375
20.95197	5.625	4.8125
20.9716	5.489583	4.291667
20.99122	6.052083	5.135417
21.01085	5.770833	4.645833
21.03048	6.15625	5.145833
21.0501	5.6875	5.4375
21.06973	5.822917	5.604167
21.08936	5.645833	5.666667
21.10899	5.302083	5.333333
21.12861	5.291667	5.864583
21.14824	4.552083	5.25
21.16787	4.614583	4.541667
21.18749	4.885417	4.760417
21.20712	4.697917	4.604167
21.22675	4.8125	4.84375
21.24637	4.1875	4.40625
21.266	4.260417	4.135417
21.28563	4.833333	4.552083
21.30526	4.322917	4.052083
21.32488	4.114583	4.25

21.34451	4.708333	3.75
21.36414	4.208333	4.677083
21.38376	4.333333	3.875
21.40339	4.65625	4.114583
21.42302	4.5	3.90625
21.44265	4.291667	3.78125
21.46227	4.635417	4.697917
21.4819	4.489583	4.09375
21.50153	4.9375	4.0625
21.52115	4.3125	4.583333
21.54078	4.958333	4.395833
21.56041	5.375	4.6875
21.58003	5.489583	4.25
21.59966	5.84375	4.65625
21.61929	6.416667	4.333333
21.63892	5.895833	5.09375
21.65854	6.15625	5.135417
21.67817	6.177083	5.552083
21.6978	5.885417	5.604167
21.71742	5.458333	5.53125
21.73705	5.21875	5.3125
21.75668	4.583333	5.510417
21.7763	4.739583	4.854167
21.79593	4.677083	4.645833
21.81556	4.770833	4.375
21.83519	4.822917	4.53125
21.85481	4.5625	4.385417
21.87444	4.427083	3.989583
21.89407	4.739583	4.270833
21.91369	4.635417	4.1875
21.93332	4.239583	4.447917
21.95295	4.229167	4.375
21.97257	4.677083	4.5625
21.9922	4.59375	4.427083
22.01183	4.65625	4.28125
22.03146	4.333333	4.052083
22.05108	4.135417	4.208333
22.07071	4.395833	4.125
22.09034	4.21875	4.197917
22.10996	4.302083	4.15625
22.12959	4.166667	3.916667
22.14922	3.6875	3.947917
22.16884	4.739583	3.96875
22.18847	4.25	3.927083
22.2081	4.09375	4.052083

22.22773	3.8125	4
22.24735	4.104167	4.041667
22.26698	4.302083	4.03125
22.28661	4.364583	3.375
22.30623	4.510417	4.166667
22.32586	4.104167	4.166667
22.34549	4.552083	4.114583
22.36511	3.833333	3.739583
22.38474	3.96875	3.927083
22.40437	4.34375	3.979167
22.424	4.364583	3.979167
22.44362	4.083333	4.083333
22.46325	3.760417	3.96875
22.48288	4.40625	4.083333
22.5025	4.645833	4.177083
22.52213	4.25	4.0625
22.54176	4.21875	4.197917
22.56138	4.0625	4.15625
22.58101	4.375	3.916667
22.60064	4.854167	4.354167
22.62027	4.71875	4.083333
22.63989	4.71875	4.520833
22.65952	4.947917	4.5625
22.67915	5.71875	4.395833
22.69877	5.979167	4.364583
22.7184	5.927083	4.71875
22.73803	6.3125	4.947917
22.75765	6.0625	4.864583
22.77728	6.635417	5.666667
22.79691	6.166667	5.5625
22.81654	6.520833	6.15625
22.83616	6.4375	6.052083
22.85579	7.09375	6
22.87542	6.875	5.8125
22.89504	6.760417	6.458333
22.91467	6.958333	5.989583
22.9343	7.166667	6.302083
22.95392	7.010417	6.552083
22.97355	7.15625	6.802083
22.99318	6.96875	6.979167
23.01281	5.84375	7.447917
23.03243	6.0625	6.9375
23.05206	5.739583	6.895833
23.07169	5.0625	6.25
23.09131	5.25	5.760417

23.11094	4.958333	5.3125
23.13057	4.75	4.479167
23.15019	4.604167	4.791667
23.16982	5.208333	4.697917
23.18945	4.395833	4.729167
23.20908	4.583333	4.729167
23.2287	4.625	4.572917
23.24833	4.53125	3.958333
23.26796	4.90625	4.333333
23.28758	4.46875	4.145833
23.30721	4.40625	3.833333
23.32684	4.385417	3.5625
23.34646	4.479167	3.791667
23.36609	4.21875	3.625
23.38572	4.28125	3.916667
23.40535	4.46875	3.84375
23.42497	4.3125	3.916667
23.4446	4.385417	3.9375
23.46423	4.28125	4.104167
23.48385	4.28125	3.822917
23.50348	3.916667	4.208333
23.52311	4.3125	3.864583
23.54273	4.125	3.708333
23.56236	4.041667	3.635417
23.58199	4.270833	4.104167
23.60162	4.364583	3.979167
23.62124	3.885417	3.947917
23.64087	3.833333	4.114583
23.6605	3.875	3.90625
23.68012	4.0625	3.645833
23.69975	4.177083	4.291667
23.71938	4.145833	3.8125
23.739	4.333333	4.09375
23.75863	4.052083	3.635417
23.77826	4.583333	3.520833
23.79789	4.958333	4.177083
23.81751	4.833333	4.208333
23.83714	4.84375	4.270833
23.85677	5.197917	4.416667
23.87639	5.46875	4.395833
23.89602	6.354167	4.479167
23.91565	7.041667	5.09375
23.93527	6.25	5.1875
23.9549	6.083333	5.71875
23.97453	5.770833	6.46875

23.99416	5.71875	6.25
24.01378	4.979167	6.0625
24.03341	4.520833	5.677083
24.05304	4.625	5.229167
24.07266	4.46875	4.708333
24.09229	4.65625	4.46875
24.11192	4.729167	4.385417
24.13154	4.15625	4.458333
24.15117	4.875	4.197917
24.1708	5.041667	4.260417
24.19043	4.9375	4.583333
24.21005	4.708333	4.3125
24.22968	4.645833	4.541667
24.24931	4.875	4.302083
24.26893	4.5625	4.489583
24.28856	4.364583	4.541667
24.30819	4.239583	4.34375
24.32782	3.791667	4.3125
24.34744	3.895833	4.166667
24.36707	4.0625	4.0625
24.3867	3.885417	4.15625
24.40632	4.052083	4.104167
24.42595	3.927083	3.614583
24.44558	4.125	3.6875
24.4652	4.010417	3.9375
24.48483	4.135417	3.822917
24.50446	4.375	3.822917
24.52409	4.1875	3.822917
24.54371	4.364583	3.895833
24.56334	3.927083	3.822917
24.58297	4.5	4.15625
24.60259	4.041667	3.625
24.62222	3.65625	3.65625
24.64185	3.53125	3.8125
24.66147	3.885417	3.71875
24.6811	3.875	3.78125
24.70073	3.78125	3.729167
24.72036	4.020833	3.552083
24.73998	3.53125	3.802083
24.75961	3.802083	3.291667
24.77924	3.916667	3.739583
24.79886	3.989583	3.822917
24.81849	4.072917	3.625
24.83812	3.958333	3.791667
24.85774	3.697917	3.447917

24.87737	4.21875	3.895833
24.897	4.197917	3.604167
24.91663	3.979167	3.520833
24.93625	3.489583	3.729167
24.95588	3.572917	3.541667
24.97551	3.635417	3.854167
24.99513	3.364583	3.489583
25.01476	3.635417	3.520833
25.03439	3.71875	3.75
25.05401	3.947917	3.395833
25.07364	4.135417	3.760417
25.09327	4.1875	3.625
25.1129	3.739583	3.541667
25.13252	3.916667	3.864583
25.15215	3.6875	3.53125
25.17178	3.979167	3.354167
25.1914	4.083333	3.697917
25.21103	4.125	3.927083
25.23066	4.15625	3.71875
25.25028	4.135417	3.697917
25.26991	3.96875	3.677083
25.28954	4.0625	4.010417
25.30917	4.291667	3.916667
25.32879	3.958333	4.15625
25.34842	4.322917	3.989583
25.36805	3.84375	3.5625
25.38767	3.979167	3.947917
25.4073	3.947917	3.770833
25.42693	3.989583	3.864583
25.44655	3.40625	3.885417
25.46618	4.010417	3.947917
25.48581	3.96875	3.333333
25.50544	3.979167	3.552083
25.52506	4.104167	3.510417
25.54469	4.135417	4.40625
25.56432	4.510417	4.052083
25.58394	4.583333	3.989583
25.60357	5.041667	4
25.6232	5.416667	3.979167
25.64282	5.5625	4.552083
25.66245	6.145833	4.604167
25.68208	6.71875	4.958333
25.70171	6.9375	5.291667
25.72133	7.5625	5.666667
25.74096	8.583333	6.53125

25.76059	8.5625	6.979167
25.78021	8.854167	7.510417
25.79984	8.677083	8.145833
25.81947	8.364583	8.364583
25.83909	8.3125	8.791667
25.85872	6.78125	9.15625
25.87835	6.541667	8.65625
25.89798	5.708333	8.135417
25.9176	5.40625	7.416667
25.93723	5.4375	5.96875
25.95686	4.645833	5.552083
25.97648	4.59375	4.9375
25.99611	4.572917	4.552083
26.01574	4.125	4.541667
26.03536	3.875	4.09375
26.05499	3.854167	4.177083
26.07462	3.791667	3.90625
26.09425	4.0625	4.0625
26.11387	3.6875	3.90625
26.1335	3.583333	3.875
26.15313	3.90625	3.864583
26.17275	3.697917	3.3125
26.19238	3.760417	3.895833
26.21201	3.822917	3.65625
26.23163	3.927083	3.583333
26.25126	3.78125	3.458333
26.27089	3.6875	3.520833
26.29052	3.75	3.645833
26.31014	3.8125	3.864583
26.32977	3.770833	3.802083
26.3494	4.125	4.020833
26.36902	4.125	3.791667
26.38865	3.958333	4.010417
26.40828	4.052083	3.645833
26.4279	4.71875	3.770833
26.44753	4.458333	3.989583
26.46716	4.6875	3.875
26.48679	4.927083	4.072917
26.50641	5.864583	4.385417
26.52604	6.6875	4.59375
26.54567	7.833333	5.302083
26.56529	7.364583	4.770833
26.58492	5.697917	6.072917
26.60455	6.302083	7.21875
26.62417	5.166667	7.947917

26.6438	4.71875	7.6875
26.66343	4.125	6.677083
26.68306	4.010417	6.177083
26.70268	3.677083	5.71875
26.72231	3.895833	5.135417
26.74194	4.072917	4.5
26.76156	4	4.208333
26.78119	4.052083	4.291667
26.80082	4.260417	3.96875
26.82044	4.354167	4.0625
26.84007	3.958333	3.427083
26.8597	4.447917	4.083333
26.87933	4.40625	4.197917
26.89895	4.65625	3.958333
26.91858	4.760417	3.729167
26.93821	4.96875	4.010417
26.95783	5.208333	4.15625
26.97746	5.895833	4.25
26.99709	6.3125	4.770833
27.01671	6.65625	4.958333
27.03634	7.520833	5.572917
27.05597	7.916667	5.677083
27.0756	7.916667	6.916667
27.09522	7.114583	6.9375
27.11485	6.5	7.541667
27.13448	6.0625	7.947917
27.1541	6.03125	7.4375
27.17373	5.28125	6.854167
27.19336	4.822917	6.416667
27.21299	4.541667	5.677083
27.23261	4.927083	4.697917
27.25224	5.333333	4.84375
27.27187	4.666667	4.5625
27.29149	4.625	4.520833
27.31112	4.59375	4.333333
27.33075	4.302083	3.78125
27.35037	3.895833	4.010417
27.37	3.9375	4.375
27.38963	3.770833	4.302083
27.40926	4.239583	4.15625
27.42888	3.625	4.291667
27.44851	3.458333	3.916667
27.46814	3.645833	3.666667
27.48776	3.645833	3.395833
27.50739	3.395833	3.6875

27.52702	3.583333	3.614583
27.54664	3.604167	3.90625
27.56627	3.458333	3.822917
27.5859	3.916667	3.40625
27.60553	3.791667	3.84375
27.62515	3.375	3.197917
27.64478	3.875	3.604167
27.66441	3.375	3.895833
27.68403	3.427083	3.427083
27.70366	3.541667	3.604167
27.72329	3.65625	3.4375
27.74291	3.8125	3.427083
27.76254	4.135417	3.479167
27.78217	4.041667	3.5625
27.8018	4.208333	3.572917
27.82142	4.552083	3.552083
27.84105	4.625	4.145833
27.86068	4.5625	4.135417
27.8803	4.5625	4.09375
27.89993	4.395833	4.145833
27.91956	4.864583	4.21875
27.93918	4.875	4.520833
27.95881	4.947917	4.770833
27.97844	5.020833	4.760417
27.99807	4.96875	4.833333
28.01769	5.03125	4.6875
28.03732	4.510417	4.416667
28.05695	4.802083	4.677083
28.07657	4.635417	4.729167
28.0962	4.885417	4.25
28.11583	4.520833	4.427083
28.13545	4.760417	4.708333
28.15508	4.25	4.427083
28.17471	4.395833	4.552083
28.19434	4.395833	4.822917
28.21396	3.895833	4.416667
28.23359	3.8125	4.166667
28.25322	3.96875	3.895833
28.27284	3.708333	4.552083
28.29247	3.53125	3.947917
28.3121	3.9375	3.875
28.33172	3.770833	4.46875
28.35135	3.78125	4.083333
28.37098	3.645833	4.239583
28.39061	3.833333	3.697917

28.41023	3.770833	4.09375
28.42986	3.458333	3.65625
28.44949	3.5625	4.041667
28.46911	3.9375	3.8125
28.48874	3.760417	3.875
28.50837	3.708333	3.635417
28.52799	3.854167	3.708333
28.54762	3.90625	3.59375
28.56725	3.802083	3.447917
28.58688	4.072917	3.760417
28.6065	3.822917	3.71875
28.62613	4.197917	3.885417
28.64576	4.364583	3.65625
28.66538	4.114583	3.833333
28.68501	4.770833	3.791667
28.70464	5.072917	4.145833
28.72426	4.895833	4.510417
28.74389	4.916667	4.260417
28.76352	5.645833	4.520833
28.78315	5.46875	4.625
28.80277	6.333333	5.145833
28.8224	5.489583	5.072917
28.84203	6	5.541667
28.86165	5.145833	5.458333
28.88128	5.15625	5.375
28.90091	5.479167	5.697917
28.92053	4.770833	5.583333
28.94016	4.645833	5.177083
28.95979	5.25	5.15625
28.97942	4.572917	5.052083
28.99904	4.625	5.1875
29.01867	4.625	4.729167
29.0383	5.135417	4.375
29.05792	5.166667	4.666667
29.07755	5.177083	5.229167
29.09718	5.21875	4.875
29.1168	5.833333	4.770833
29.13643	6.489583	4.96875
29.15606	7.072917	5.010417
29.17569	8.333333	5.239583
29.19531	10.03125	5.770833
29.21494	11.86458	5.90625
29.23457	15.0625	6.854167
29.25419	18.15625	8.125
29.27382	19.92708	9.447917

29.29345	20.1875	11.52083
29.31307	20.64583	15.65625
29.3327	19.73958	19.01042
29.35233	18.6875	22.04167
29.37196	17.13542	21.75
29.39158	14.91667	20.65625
29.41121	13.36458	19.19792
29.43084	10.8125	17.875
29.45046	9.479167	16.21875
29.47009	8.447917	13.75
29.48972	7.947917	10.73958
29.50934	7.260417	10.30208
29.52897	6.197917	8.5
29.5486	5.916667	7.322917
29.56823	5.239583	6.520833
29.58785	5.0625	6.385417
29.60748	5.260417	5.59375
29.62711	4.78125	5.052083
29.64673	4.25	4.833333
29.66636	4.010417	4.666667
29.68599	4.385417	4.5
29.70561	3.854167	4.125
29.72524	4	3.895833
29.74487	3.958333	3.947917
29.7645	4	3.697917
29.78412	3.9375	3.354167
29.80375	3.958333	3.510417
29.82338	3.864583	3.645833
29.843	3.864583	3.6875
29.86263	3.385417	3.46875
29.88226	3.1875	3.447917
29.90188	3.65625	3.260417
29.92151	3.583333	3.802083
29.94114	3.416667	3.46875
29.96077	3.416667	3.5
29.98039	3.333333	3.25
30.00002	3.395833	3.572917
30.01965	3.322917	3.104167
30.03927	3.375	3.145833
30.0589	3.28125	3.208333
30.07853	3.333333	3.166667
30.09816	3.625	3.020833
30.11778	3.864583	3.34375
30.13741	3.552083	2.84375
30.15704	3.885417	3.208333

30.17666	3.59375	3.333333
30.19629	4.15625	3.385417
30.21592	5.739583	3.104167
30.23554	6.458333	3.416667
30.25517	6.020833	3.666667
30.2748	6.260417	3.833333
30.29443	7.572917	4.010417
30.31405	7.583333	3.65625
30.33368	7.3125	4.822917
30.35331	6.34375	5.697917
30.37293	6.15625	5.989583
30.39256	5.28125	5.4375
30.41219	4.791667	4.78125
30.43181	4.302083	4.770833
30.45144	3.739583	4.614583
30.47107	3.65625	4.447917
30.4907	3.708333	3.791667
30.51032	3.645833	3.614583
30.52995	3.458333	3.260417
30.54958	3.541667	3.28125
30.5692	3.53125	3.239583
30.58883	3.447917	3.270833
30.60846	3.739583	3.5
30.62808	3.875	3.260417
30.64771	3.78125	3.15625
30.66734	4.104167	3.458333
30.68697	3.729167	3.8125
30.70659	4.010417	3.739583
30.72622	3.8125	3.520833
30.74585	4.072917	3.322917
30.76547	4.270833	3.802083
30.7851	4.177083	3.822917
30.80473	4.395833	3.697917
30.82435	4.041667	3.59375
30.84398	3.854167	3.927083
30.86361	3.520833	3.708333
30.88324	3.625	3.5625
30.90286	3.65625	3.625
30.92249	3.9375	3.677083
30.94212	3.822917	3.5
30.96174	4.114583	3.572917
30.98137	4.291667	3.395833
31.001	4.322917	3.46875
31.02062	4.510417	3.5625
31.04025	4.447917	3.65625

31.05988	5.197917	3.635417
31.07951	5.489583	3.770833
31.09913	5.59375	4.010417
31.11876	6.270833	4.34375
31.13839	6.072917	3.979167
31.15801	6.8125	5.625
31.17764	7.34375	5.479167
31.19727	7.4375	6.083333
31.21689	7.46875	6.552083
31.23652	7.572917	6.041667
31.25615	8	6.552083
31.27578	7.84375	6.583333
31.2954	8.510417	6.385417
31.31503	8.96875	6.375
31.33466	10.11458	7.125
31.35428	10.95833	7.21875
31.37391	10.88542	7.958333
31.39354	10.57292	8.989583
31.41316	10.54167	11.32292
31.43279	10.85417	13.71875
31.45242	9.979167	13.47917
31.47205	10.23958	10.70833
31.49167	11.66667	9.770833
31.5113	12.1875	10.97917
31.53093	14.02083	11.22917
31.55055	16.51042	10.85417
31.57018	20.76042	10.08333
31.58981	24.13542	11.65625
31.60943	24.02083	12.75
31.62906	22.96875	14.69792
31.64869	25.47917	16.82292
31.66832	24.375	18.69792
31.68794	19.84375	18.02083
31.70757	16.88542	19.4375
31.7272	15.8125	19.02083
31.74682	13.42708	17.38542
31.76645	10.22917	15.52083
31.78608	9.822917	13.32292
31.8057	8.552083	11.36458
31.82533	7.21875	10.45833
31.84496	6.958333	9.197917
31.86459	6.729167	8.072917
31.88421	6.333333	6.895833
31.90384	6.229167	6.875
31.92347	6.458333	5.84375

31.94309	7.072917	6.083333
31.96272	6.947917	6.104167
31.98235	7.239583	5.46875
32.00197	8.59375	6.197917
32.0216	10.25	6.635417
32.04123	10.48958	7.40625
32.06086	12.29167	7.916667
32.08048	12	8.916667
32.10011	12.51042	9.583333
32.11974	11.69792	10.59375
32.13936	10.85417	12.61458
32.15899	9.020833	12.94792
32.17862	8	11.35417
32.19824	7.364583	9.895833
32.21787	6.177083	9.645833
32.2375	5.729167	8.3125
32.25713	5.083333	7.072917
32.27675	4.479167	6.104167
32.29638	4.385417	4.916667
32.31601	3.802083	4.489583
32.33563	4.0625	4.625
32.35526	3.5	4.28125
32.37489	3.875	4.458333
32.39451	4.354167	3.895833
32.41414	4.416667	3.927083
32.43377	4.375	3.802083
32.4534	4.145833	3.947917
32.47302	4.166667	3.65625
32.49265	4.885417	4.135417
32.51228	5.229167	3.8125
32.5319	5.28125	4.125
32.55153	5.65625	4.125
32.57116	6.21875	4.40625
32.59078	6.4375	4.875
32.61041	6.614583	5.447917
32.63004	7.28125	5.322917
32.64967	8.145833	5.895833
32.66929	9.177083	5.958333
32.68892	9.104167	6.34375
32.70855	9.833333	6.979167
32.72817	10.8125	7.75
32.7478	11.41667	8.46875
32.76743	11.73958	9
32.78705	11.32292	9.84375
32.80668	10.79167	10.35417

32.82631	10.25	11.16667
32.84594	9.28125	10.88542
32.86556	8.739583	11.90625
32.88519	7.875	10.36458
32.90482	7.03125	9.458333
32.92444	6.677083	8.385417
32.94407	5.875	7.9375
32.9637	5.40625	7.4375
32.98333	5.010417	6.375
33.00295	4.625	5.5625
33.02258	4.833333	5.020833
33.04221	4.364583	5.21875
33.06183	3.96875	4.28125
33.08146	4.572917	4.072917
33.10109	4.104167	3.895833
33.12071	3.916667	3.614583
33.14034	3.895833	4.072917
33.15997	3.677083	3.8125
33.1796	3.6875	3.833333
33.19922	3.635417	3.46875
33.21885	3.458333	3.604167
33.23848	3.302083	3.1875
33.2581	3.1875	3.09375
33.27773	3.302083	3.416667
33.29736	3.072917	3.083333
33.31698	3.3125	3.125
33.33661	3.4375	3.083333
33.35624	3.145833	3.21875
33.37587	3.541667	3.479167
33.39549	3.1875	3.364583
33.41512	3.270833	3.010417
33.43475	3.458333	3.072917
33.45437	3.635417	3.28125
33.474	3.270833	3.072917
33.49363	3.84375	3.447917
33.51325	3.927083	2.895833
33.53288	4.322917	3.239583
33.55251	4.635417	3.25
33.57214	4.260417	3.322917
33.59176	4.1875	4.072917
33.61139	4.635417	4.125
33.63102	4.697917	3.8125
33.65064	5.260417	4.489583
33.67027	4.989583	4.677083
33.6899	4.572917	4.90625

33.70952	4.583333	4.145833
33.72915	4.208333	4.427083
33.74878	4.458333	4.583333
33.76841	4.333333	4.208333
33.78803	4.552083	4.541667
33.80766	4.65625	3.760417
33.82729	4.1875	4.46875
33.84691	5.177083	4.25
33.86654	5.625	4.208333
33.88617	5.625	3.90625
33.90579	6.010417	4.833333
33.92542	7.03125	4.489583
33.94505	6.489583	4.895833
33.96468	6.916667	5.604167
33.9843	6.5625	6.229167
34.00393	6.385417	6.572917
34.02356	5.364583	7.020833
34.04318	5.145833	5.979167
34.06281	4.802083	5.75
34.08244	3.979167	5.333333
34.10206	3.989583	5.052083
34.12169	3.8125	4.71875
34.14132	3.3125	3.885417
34.16095	3.125	3.947917
34.18057	3.229167	3.197917
34.2002	3.270833	3.197917
34.21983	2.885417	3.291667
34.23945	3.333333	2.96875
34.25908	2.864583	3.28125
34.27871	3.125	3.052083
34.29833	3.208333	2.927083
34.31796	2.875	2.864583
34.33759	3.34375	2.90625
34.35722	3.895833	2.84375
34.37684	3.333333	2.96875
34.39647	3.5	2.729167
34.4161	3.625	3.135417
34.43572	4.03125	3.145833
34.45535	4.239583	3.229167
34.47498	4.260417	3.25
34.4946	4.145833	3.645833
34.51423	4.46875	3.822917
34.53386	4.104167	4.09375
34.55349	3.90625	4
34.57311	3.927083	3.9375

34.59274	3.927083	4.114583
34.61237	3.5625	4.229167
34.63199	3.3125	4.104167
34.65162	3.447917	3.447917
34.67125	3.072917	3.520833
34.69087	2.770833	3.020833
34.7105	2.916667	2.958333
34.73013	2.822917	2.958333
34.74976	3.25	2.885417
34.76938	3.208333	2.875
34.78901	3.072917	2.708333
34.80864	3.083333	2.875
34.82826	3.104167	2.75
34.84789	3.28125	2.75
34.86752	3.5	2.864583
34.88714	3.53125	2.864583
34.90677	3.020833	2.84375
34.9264	3.5625	2.979167
34.94603	2.958333	2.5625
34.96565	3.270833	2.4375
34.98528	3.03125	2.604167
35.00491	3.15625	2.604167
35.02453	3.21875	2.5625
35.04416	2.979167	2.822917
35.06379	2.729167	2.885417
35.08341	3.197917	2.364583
35.10304	3.3125	2.895833
35.12267	3.041667	2.4375
35.1423	3.260417	2.8125
35.16192	3.291667	2.947917
35.18155	3.604167	2.625
35.20118	3.020833	2.552083
35.2208	3.166667	3.15625
35.24043	3.4375	2.666667
35.26006	3.614583	3.166667
35.27968	3.46875	2.739583
35.29931	3.364583	3.197917
35.31894	3.0625	3.229167
35.33857	3.645833	2.885417
35.35819	3.635417	3.15625
35.37782	3.541667	3.416667
35.39745	3.510417	3.21875
35.41707	3.354167	3.385417
35.4367	3.125	3.25
35.45633	2.9375	3.427083

35.47595	3.166667	3.135417
35.49558	3.166667	2.791667
35.51521	3.15625	3.020833
35.53484	3.40625	3.083333
35.55446	3.645833	2.833333
35.57409	3.510417	3.010417
35.59372	3.427083	2.895833
35.61334	3.166667	3.53125
35.63297	2.947917	3.020833
35.6526	3.5625	3.010417
35.67222	3.260417	2.96875
35.69185	3.46875	2.833333
35.71148	3.291667	3.03125
35.73111	3.729167	2.989583
35.75073	3.802083	3.333333
35.77036	3.489583	2.895833
35.78999	4.041667	3.083333
35.80961	4.239583	3.208333
35.82924	4.3125	3.364583
35.84887	4.791667	3.59375
35.86849	4.53125	3.760417
35.88812	4.666667	3.885417
35.90775	4.760417	4.197917
35.92738	4.479167	4.802083
35.947	4.364583	4.114583
35.96663	3.833333	3.96875
35.98626	3.760417	4.489583
36.00588	3.447917	4.09375
36.02551	3.364583	3.729167
36.04514	3.572917	3.760417
36.06477	3.739583	3.510417
36.08439	3.09375	3.520833
36.10402	3.072917	3.145833
36.12365	2.739583	2.947917
36.14327	2.5	3.166667
36.1629	3.020833	2.979167
36.18253	2.96875	2.989583
36.20215	2.489583	2.791667
36.22178	2.40625	2.864583
36.24141	2.9375	2.4375
36.26104	2.739583	2.708333
36.28066	2.864583	2.645833
36.30029	2.708333	2.645833
36.31992	2.822917	2.6875
36.33954	3.03125	2.552083

36.35917	3.010417	2.791667
36.3788	3.229167	2.395833
36.39842	2.791667	2.427083
36.41805	3.208333	2.729167
36.43768	3.083333	3.083333
36.45731	3.135417	2.635417
36.47693	3.40625	3
36.49656	3.177083	2.9375
36.51619	2.979167	2.927083
36.53581	2.895833	2.958333
36.55544	3.208333	3.302083
36.57507	2.708333	2.854167
36.59469	2.96875	2.635417
36.61432	3.25	2.666667
36.63395	3.072917	2.770833
36.65358	3.395833	2.885417
36.6732	3.166667	2.927083
36.69283	3.15625	2.510417
36.71246	3.3125	2.697917
36.73208	3.197917	3.208333
36.75171	3.270833	2.739583
36.77134	2.854167	2.739583
36.79096	2.916667	2.78125
36.81059	3.03125	2.84375
36.83022	3.072917	2.885417
36.84985	2.90625	3.041667
36.86947	2.708333	2.96875
36.8891	2.447917	2.40625
36.90873	2.520833	2.78125
36.92835	3	2.354167
36.94798	2.333333	2.15625
36.96761	2.864583	2.322917
36.98723	2.572917	2.40625
37.00686	2.5625	2.458333
37.02649	2.520833	2.645833
37.04612	2.614583	2.520833
37.06574	2.5625	2.5625
37.08537	2.895833	2.322917
37.105	2.708333	2.395833
37.12462	2.625	2.479167
37.14425	2.760417	2.65625
37.16388	2.645833	2.427083
37.1835	2.614583	2.34375
37.20313	2.791667	2.59375
37.22276	2.989583	2.729167

37.24239	2.59375	2.1875
37.26201	3.041667	2.59375
37.28164	2.833333	2.6875
37.30127	2.791667	2.395833
37.32089	2.729167	2.885417
37.34052	2.885417	2.395833
37.36015	2.625	2.416667
37.37977	3	2.59375
37.3994	2.708333	2.5
37.41903	2.708333	2.28125
37.43866	2.791667	2.854167
37.45828	2.770833	2.59375
37.47791	2.645833	2.645833
37.49754	2.375	2.447917
37.51716	2.6875	2.40625
37.53679	2.447917	2.21875
37.55642	2.479167	2.760417
37.57604	2.760417	2.583333
37.59567	2.364583	2.489583
37.6153	2.416667	2.489583
37.63493	2.635417	2.510417
37.65455	2.666667	2.395833
37.67418	2.364583	2.385417
37.69381	2.614583	2.052083
37.71343	2.604167	2.166667
37.73306	2.479167	2.21875
37.75269	2.375	2.322917
37.77231	2.46875	2.604167
37.79194	2.541667	2.270833
37.81157	2.510417	2.21875
37.8312	2.385417	2.052083
37.85082	2.40625	2.208333
37.87045	2.5	2.302083
37.89008	2.34375	2.28125
37.9097	2.28125	2.427083
37.92933	2.385417	2.46875
37.94896	2.71875	2.0625
37.96858	2.5625	2.291667
37.98821	2.989583	2.239583
38.00784	3.083333	2.625
38.02747	3.239583	2.40625
38.04709	2.958333	2.885417
38.06672	2.75	2.625
38.08635	3.34375	2.854167
38.10597	3.333333	2.5625

38.1256	3.25	2.760417
38.14523	3.34375	2.958333
38.16485	3.322917	2.552083
38.18448	2.927083	2.96875
38.20411	3.208333	2.760417
38.22374	2.833333	2.958333
38.24336	2.489583	2.9375
38.26299	2.75	2.572917
38.28262	2.739583	2.729167
38.30224	2.6875	2.479167
38.32187	2.40625	2.40625
38.3415	2.447917	2.5
38.36112	2.510417	2.375
38.38075	2.604167	2.427083
38.40038	2.59375	2.041667
38.42001	2.770833	2.177083
38.43963	2.75	2.197917
38.45926	2.947917	2.604167
38.47889	3.229167	2.34375
38.49851	3.041667	3.052083
38.51814	3.260417	2.729167
38.53777	3.03125	2.625
38.55739	2.864583	2.885417
38.57702	2.854167	2.802083
38.59665	2.604167	2.21875
38.61628	2.802083	2.59375
38.6359	2.572917	2.604167
38.65553	2.645833	2.40625
38.67516	2.645833	2.40625
38.69478	2.604167	2.583333
38.71441	2.96875	2.385417
38.73404	2.614583	2.3125
38.75366	2.59375	2.25
38.77329	2.791667	2.614583
38.79292	3.052083	2.291667
38.81255	2.90625	2.458333
38.83217	2.489583	2.5
38.8518	2.9375	2.770833
38.87143	2.708333	2.53125
38.89105	2.75	2.447917
38.91068	2.729167	2.635417
38.93031	2.916667	2.572917
38.94994	2.947917	2.364583
38.96956	3.1875	2.8125
38.98919	3.260417	2.53125

39.00882	3.0625	2.65625
39.02844	3.510417	2.875
39.04807	3.552083	3.03125
39.0677	3.5625	2.96875
39.08732	3.375	3.010417
39.10695	3.552083	2.822917
39.12658	3.729167	2.958333
39.14621	4.020833	3.510417
39.16583	3.729167	3.5
39.18546	3.729167	3.541667
39.20509	3.96875	3.666667
39.22471	4.729167	3.770833
39.24434	4.885417	3.677083
39.26397	5.03125	3.854167
39.28359	5.677083	4.260417
39.30322	5.75	4.041667
39.32285	5.90625	4.375
39.34248	5.947917	4.770833
39.3621	5.71875	5.65625
39.38173	5.40625	5.3125
39.40136	5.260417	5.260417
39.42098	4.927083	5
39.44061	4.770833	5.135417
39.46024	4.989583	4.822917
39.47986	4.458333	4.489583
39.49949	4.489583	4.458333
39.51912	4.885417	4.0625
39.53875	4.65625	4.46875
39.55837	4.75	3.614583
39.578	4.989583	4.03125
39.59763	5.177083	4.104167
39.61725	5.177083	4.0625
39.63688	5.322917	4.177083
39.65651	5.708333	4.083333
39.67613	5.458333	4.520833
39.69576	5.4375	4.895833
39.71539	5	4.927083
39.73502	4.979167	5.375
39.75464	4.572917	4.729167
39.77427	4.8125	4.791667
39.7939	4.28125	3.8125
39.81352	3.864583	4.3125
39.83315	3.739583	3.78125
39.85278	3.5	3.78125
39.8724	3.229167	3.8125

39.89203	2.947917	3.260417
39.91166	3.291667	3.364583
39.93129	2.875	3.104167
39.95091	2.78125	3.1875
39.97054	3.083333	2.677083
39.99017	3.083333	2.489583
40.00979	2.65625	2.8125
40.02942	3.083333	2.520833
40.04905	2.916667	2.9375
40.06867	2.802083	2.447917
40.0883	2.65625	2.5625
40.10793	2.78125	2.364583
40.12756	2.458333	2.239583
40.14718	2.5	2.614583
40.16681	2.447917	2.614583
40.18644	2.729167	2.760417
40.20606	2.291667	2.375
40.22569	2.645833	2.364583
40.24532	2.833333	2.5625
40.26494	2.552083	2.447917
40.28457	2.34375	2.697917
40.3042	2.59375	2.270833
40.32383	2.34375	2.385417
40.34345	2.59375	2.552083
40.36308	2.53125	2.708333
40.38271	2.489583	2.635417
40.40233	2.5625	2.791667
40.42196	2.46875	2.635417
40.44159	2.9375	2.760417
40.46121	2.625	2.53125
40.48084	2.447917	2.708333
40.50047	2.416667	2.635417
40.5201	2.447917	2.4375
40.53972	2.614583	2.53125
40.55935	2.375	2.260417
40.57898	2.552083	2.447917
40.5986	2.666667	2.479167
40.61823	2.645833	2.5625
40.63786	2.416667	2.416667
40.65748	2.291667	2.354167
40.67711	2.291667	2.270833
40.69674	2.625	2.21875
40.71637	2.395833	2.291667
40.73599	2.416667	2.197917
40.75562	2.09375	2.239583

40.77525	2.541667	2.354167
40.79487	2.375	2.25
40.8145	2.447917	2.479167
40.83413	2.708333	2.0625
40.85375	2.322917	2.302083
40.87338	2.3125	2.15625
40.89301	2.291667	2.135417
40.91264	2.645833	2.583333
40.93226	2.40625	2.208333
40.95189	2.260417	2.375
40.97152	2.375	2.364583
40.99114	2.333333	2.239583
41.01077	2.46875	2.46875
41.0304	2.510417	1.958333
41.05002	2.583333	2.072917
41.06965	2.6875	2.364583
41.08928	2.5	2.260417
41.10891	2.645833	2.3125
41.12853	2.708333	2.5
41.14816	2.791667	2.375
41.16779	2.927083	2.822917
41.18741	2.71875	2.416667
41.20704	2.458333	2.416667
41.22667	2.604167	2.541667
41.24629	2.729167	2.416667
41.26592	2.708333	2.65625
41.28555	2.71875	2.708333
41.30518	2.677083	2.604167
41.3248	2.385417	2.583333
41.34443	2.5625	2.177083
41.36406	2.78125	2.510417
41.38368	2.59375	2.510417
41.40331	2.75	2.25
41.42294	2.489583	2.375
41.44256	2.239583	2.333333
41.46219	2.21875	2.125
41.48182	2.333333	2.427083
41.50145	2.145833	2.354167
41.52107	2.229167	2.229167
41.5407	2.291667	1.9375
41.56033	2.53125	2.166667
41.57995	2.604167	2.072917
41.59958	2.46875	2.083333
41.61921	2.4375	2.427083
41.63883	2.28125	2.28125

41.65846	2.541667	2.291667
41.67809	2.677083	2.427083
41.69772	2.645833	2.260417
41.71734	2.947917	2.697917
41.73697	2.96875	2.53125
41.7566	3.020833	2.645833
41.77622	3.03125	2.375
41.79585	3.104167	2.322917
41.81548	3.166667	2.572917
41.83511	3.34375	2.729167
41.85473	3.25	2.697917
41.87436	3.166667	2.614583
41.89399	3.479167	3.09375
41.91361	3.447917	2.958333
41.93324	3.322917	3.125
41.95287	3.114583	3.3125
41.97249	2.989583	2.895833
41.99212	3.375	3.28125
42.01175	3.208333	2.864583
42.03138	3.208333	3.229167
42.051	3.104167	2.958333
42.07063	3.34375	3.041667
42.09026	3.25	2.791667
42.10988	3.03125	2.916667
42.12951	3.229167	2.875
42.14914	3.166667	2.479167
42.16876	3.40625	3.083333
42.18839	3.09375	3.3125
42.20802	3.3125	2.78125
42.22765	3.0625	3.270833
42.24727	2.947917	2.78125
42.2669	3.135417	3.052083
42.28653	3.5625	3.0625
42.30615	3.25	3.010417
42.32578	3	3
42.34541	2.927083	2.5625
42.36503	2.65625	2.635417
42.38466	2.760417	2.65625
42.40429	2.708333	2.447917
42.42392	2.78125	2.927083
42.44354	2.291667	2.552083
42.46317	2.302083	2.21875
42.4828	2.84375	2.364583
42.50242	2.666667	2.479167
42.52205	2.71875	2.604167

42.54168	2.458333	2.322917
42.5613	2.59375	2.375
42.58093	2.447917	2.208333
42.60056	2.572917	2.5625
42.62019	2.385417	2.21875
42.63981	2.114583	2.229167
42.65944	2.291667	2.21875
42.67907	2.375	2.28125
42.69869	2.541667	1.989583
42.71832	2.333333	2.166667
42.73795	2.208333	2.302083
42.75757	2.291667	2.166667
42.7772	2.34375	2.322917
42.79683	2.677083	2.291667
42.81646	2.770833	2.541667
42.83608	2.614583	2.458333
42.85571	2.75	2.21875
42.87534	2.770833	2.614583
42.89496	2.71875	2.583333
42.91459	3.3125	2.489583
42.93422	3.1875	2.75
42.95384	3.125	2.59375
42.97347	3.583333	2.78125
42.9931	3.635417	2.8125
43.01273	4.614583	2.927083
43.03235	4.572917	2.875
43.05198	4.84375	3.125
43.07161	5.072917	4.020833
43.09123	4.4375	4.135417
43.11086	4.375	4.416667
43.13049	4.395833	4.479167
43.15011	4.447917	3.958333
43.16974	4.020833	4.0625
43.18937	4.104167	3.90625
43.209	3.5625	4.15625
43.22862	3.260417	3.71875
43.24825	3.34375	3.083333
43.26788	3.302083	3.125
43.2875	3.010417	2.927083
43.30713	2.875	3.15625
43.32676	2.71875	2.822917
43.34638	2.75	2.6875
43.36601	2.46875	2.541667
43.38564	2.34375	2.645833
43.40527	2.520833	2.375

43.42489	2.458333	2.5
43.44452	2.5	2.40625
43.46415	2.395833	2.0625
43.48377	2.427083	2.385417
43.5034	2.46875	2.40625
43.52303	2.291667	2.260417
43.54265	2.635417	2.21875
43.56228	2.614583	2.458333
43.58191	2.239583	2.21875
43.60154	2.395833	2.239583
43.62116	2.677083	2.34375
43.64079	2.5	2.53125
43.66042	2.614583	2.4375
43.68004	2.729167	2.677083
43.69967	2.864583	2.40625
43.7193	2.75	2.177083
43.73892	3.010417	2.6875
43.75855	2.770833	2.583333
43.77818	3.104167	2.5625
43.79781	2.8125	2.791667
43.81743	2.510417	2.75
43.83706	2.895833	3
43.85669	2.552083	2.947917
43.87631	2.583333	2.59375
43.89594	2.697917	2.395833
43.91557	2.552083	2.645833
43.93519	2.291667	2.5
43.95482	2.5	2.354167
43.97445	2.34375	2.447917
43.99408	2.145833	2.520833
44.0137	2.385417	2.416667
44.03333	2.208333	2.135417
44.05296	2.479167	2.15625
44.07258	2.40625	2.375
44.09221	2.4375	2.604167
44.11184	2.864583	2.208333
44.13146	2.59375	2.03125
44.15109	2.989583	2.416667
44.17072	3.635417	2.635417
44.19035	3.677083	2.416667
44.20997	4.40625	2.729167
44.2296	4.09375	2.979167
44.24923	3.770833	3.208333
44.26885	3.770833	3.385417
44.28848	3.59375	3.5625

44.30811	3.520833	3.583333
44.32773	3.895833	3.375
44.34736	3.104167	2.833333
44.36699	2.854167	3.020833
44.38662	3.354167	3.041667
44.40624	2.833333	2.8125
44.42587	3.010417	2.697917
44.4455	2.520833	2.84375
44.46512	2.604167	2.479167
44.48475	2.552083	2.541667
44.50438	2.28125	2.333333
44.524	2.40625	2.270833
44.54363	2.291667	2.177083
44.56326	2.229167	2.354167
44.58289	2.1875	2.125
44.60251	2.239583	2.427083
44.62214	2.1875	2.302083
44.64177	2.15625	2.083333
44.66139	2.364583	2.364583
44.68102	2.28125	2.385417
44.70065	2.15625	2.083333
44.72028	2.427083	2.09375
44.7399	2.395833	2.270833
44.75953	2.520833	2.21875
44.77916	2.25	2.197917
44.79878	2.677083	2.322917
44.81841	2.75	2.09375
44.83804	2.520833	2.302083
44.85766	2.489583	2.145833
44.87729	2.354167	2
44.89692	2.052083	2.03125
44.91655	2.625	2.302083
44.93617	2.208333	2.416667
44.9558	2.1875	2.302083
44.97543	2.614583	2.34375
44.99505	2.5	2.385417
45.01468	2.34375	2.197917
45.03431	2.25	2.302083
45.05393	2.510417	2.135417
45.07356	2.427083	2.510417
45.09319	2.96875	2.354167
45.11282	2.770833	2.333333
45.13244	2.90625	2.354167
45.15207	3.239583	2.46875
45.1717	3.09375	2.895833

45.19132	2.895833	2.6875
45.21095	3.260417	2.677083
45.23058	3.333333	3.302083
45.2502	3.291667	3.083333
45.26983	4.21875	3.15625
45.28946	4.375	3.020833
45.30909	5.90625	3.333333
45.32871	6.28125	3.40625
45.34834	7.03125	4.072917
45.36797	6.739583	3.875
45.38759	4.916667	4.708333
45.40722	4.697917	4.583333
45.42685	4.666667	4.21875
45.44647	4.28125	3.40625
45.4661	4.322917	3.3125
45.48573	4.6875	3.239583
45.50536	3.947917	3.40625
45.52498	2.96875	3.177083
45.54461	2.416667	3.520833
45.56424	2.572917	2.625
45.58386	2.270833	2.666667
45.60349	2.125	2.416667
45.62312	2.416667	2.583333
45.64274	2.40625	2.197917
45.66237	2.583333	2.333333
45.682	2.21875	2.322917
45.70163	2.135417	2.239583
45.72125	2.239583	2.09375
45.74088	2.114583	2.385417
45.76051	1.958333	2.333333
45.78013	2.270833	2.53125
45.79976	2.583333	2.239583
45.81939	2.239583	2.40625
45.83901	2.3125	2.135417
45.85864	2.177083	2.083333
45.87827	2.166667	2.177083
45.8979	2.520833	2.229167
45.91752	2.135417	2.0625
45.93715	2.114583	2.416667
45.95678	2.354167	2.03125
45.9764	2.052083	2.40625
45.99603	2.364583	2
46.01566	2.15625	2.104167
46.03528	2.125	2.083333
46.05491	2.1875	2.5

46.07454	2.427083	2.375
46.09417	2.375	2.197917
46.11379	2.385417	1.90625
46.13342	2.34375	2.114583
46.15305	2.479167	2.020833
46.17267	2.96875	2.28125
46.1923	2.447917	2.229167
46.21193	2.552083	2.322917
46.23155	2.5625	2.177083
46.25118	2.583333	2.21875
46.27081	2.604167	2.291667
46.29044	2.75	2.395833
46.31006	2.78125	2.28125
46.32969	2.770833	2.229167
46.34932	2.697917	2.354167
46.36894	3.229167	2.604167
46.38857	3.739583	2.5625
46.4082	3.59375	2.833333
46.42782	4.375	2.739583
46.44745	4.541667	2.645833
46.46708	4.6875	2.958333
46.48671	5.5	3.177083
46.50633	5.427083	3.875
46.52596	5.635417	4.03125
46.54559	6.09375	4.59375
46.56521	6.260417	4.760417
46.58484	6.354167	5.1875
46.60447	6.15625	5.291667
46.62409	5.84375	5.5625
46.64372	5.364583	5.333333
46.66335	5.489583	5.364583
46.68298	5.3125	5.28125
46.7026	4.5	4.75
46.72223	4.666667	4.5625
46.74186	4.489583	4.520833
46.76148	3.947917	4.458333
46.78111	3.489583	4.010417
46.80074	3.770833	3.489583
46.82036	3.875	3.416667
46.83999	3.447917	3.479167
46.85962	3.145833	3.15625
46.87925	3.270833	3.15625
46.89887	3.322917	2.96875
46.9185	3.59375	3.020833
46.93813	3.104167	2.802083

46.95775	3.34375	2.78125
46.97738	3.427083	2.833333
46.99701	3.760417	3.09375
47.01663	3.385417	2.979167
47.03626	3.15625	3.104167
47.05589	3.614583	2.927083
47.07552	3.4375	2.90625
47.09514	3.572917	3.197917
47.11477	3.21875	3.645833
47.1344	3.479167	3.375
47.15402	3.427083	3.135417
47.17365	3.479167	3.1875
47.19328	3.104167	3.09375
47.2129	3.489583	2.885417
47.23253	2.958333	3.333333
47.25216	3.708333	2.989583
47.27179	3.71875	3.291667
47.29141	3.677083	3.5
47.31104	4.34375	3.010417
47.33067	4.59375	3.385417
47.35029	4.489583	3.489583
47.36992	4.947917	3.71875
47.38955	4.989583	3.770833
47.40917	4.833333	4.270833
47.4288	4.677083	4.645833
47.44843	4.729167	4.4375
47.46806	4.583333	4.114583
47.48768	4.25	4.385417
47.50731	4.197917	4.291667
47.52694	3.78125	4.1875
47.54656	3.677083	3.96875
47.56619	3.645833	3.885417
47.58582	3.59375	3.677083
47.60545	3.3125	3.760417
47.62507	2.96875	3.072917
47.6447	2.96875	3.104167
47.66433	3.177083	3
47.68395	3.03125	2.71875
47.70358	2.739583	2.697917
47.72321	3.041667	2.510417
47.74283	2.75	2.645833
47.76246	2.677083	2.40625
47.78209	3.1875	2.489583
47.80172	2.895833	2.197917
47.82134	2.96875	2.625

47.84097	3.197917	2.4375
47.8606	3.270833	2.708333
47.88022	3.96875	2.635417
47.89985	3.729167	2.770833
47.91948	3.395833	3.010417
47.9391	3.75	3.145833
47.95873	4.041667	3.364583
47.97836	3.958333	3.28125
47.99799	3.979167	3.552083
48.01761	3.552083	3.15625
48.03724	3.458333	3.625
48.05687	3.25	3.552083
48.07649	3.479167	3.1875
48.09612	3.708333	3.375
48.11575	3.395833	3.15625
48.13537	3.34375	3.197917
48.155	3.15625	2.833333
48.17463	3.052083	3.125
48.19426	3.072917	2.614583
48.21388	3.260417	2.885417
48.23351	3.40625	2.75
48.25314	3.53125	2.666667
48.27276	3.916667	3.15625
48.29239	4.072917	3.083333
48.31202	4.322917	3.041667
48.33164	5.041667	3.4375
48.35127	4.71875	3.552083
48.3709	5.53125	3.697917
48.39053	5.697917	3.864583
48.41015	5.395833	3.875
48.42978	5.635417	4.447917
48.44941	4.927083	4.614583
48.46903	4.84375	4.78125
48.48866	5.166667	4.583333
48.50829	4.604167	5.104167
48.52791	4.78125	4.291667
48.54754	4.541667	4.364583
48.56717	3.6875	4.135417
48.5868	4.104167	3.822917
48.60642	3.333333	3.875
48.62605	3.489583	3.46875
48.64568	3.28125	3.489583
48.6653	3.28125	3.3125
48.68493	3.354167	3.114583
48.70456	2.864583	3.104167

48.72418	2.947917	3.125
48.74381	2.791667	2.520833
48.76344	2.854167	2.770833
48.78307	2.770833	2.302083
48.80269	2.541667	2.541667
48.82232	2.333333	2.510417
48.84195	2.364583	2.375
48.86157	2.041667	2.229167
48.8812	2.34375	2.40625
48.90083	2.270833	2.489583
48.92045	2.447917	1.895833
48.94008	2.479167	2.15625
48.95971	2.3125	2.03125
48.97934	2.1875	2.114583
48.99896	2.46875	2.385417
49.01859	2.416667	2.40625
49.03822	2.635417	2.375
49.05784	2.572917	2.25
49.07747	2.458333	2.083333
49.0971	2.989583	2.416667
49.11672	2.9375	2.28125
49.13635	2.854167	2.447917
49.15598	3.375	2.552083
49.17561	2.791667	2.760417
49.19523	3.114583	2.677083
49.21486	3.447917	2.770833
49.23449	3.864583	2.625
49.25411	4.135417	2.90625
49.27374	4.1875	3.09375
49.29337	4.916667	2.875
49.31299	4.90625	3.166667
49.33262	5.864583	3.78125
49.35225	6.416667	3.854167
49.37188	6.791667	4.916667
49.3915	6.1875	5.354167
49.41113	5.885417	5.625
49.43076	5.072917	5.541667
49.45038	4.739583	6.0625
49.47001	4.5625	5.125
49.48964	4.802083	4.71875
49.50926	4.208333	4.208333
49.52889	3.75	4.489583
49.54852	3.5	4.625
49.56815	3.177083	4.479167
49.58777	2.947917	3.677083

49.6074	2.895833	3.4375
49.62703	2.5625	3.03125
49.64665	2.583333	3.020833
49.66628	2.802083	2.6875
49.68591	2.6875	2.5625
49.70553	2.520833	2.104167
49.72516	2.291667	2.260417
49.74479	2.135417	2.302083
49.76442	2.40625	2.489583
49.78404	2.270833	2.25
49.80367	2.416667	2.010417
49.8233	2.34375	2.395833
49.84292	2.28125	2.21875
49.86255	2.197917	2.135417
49.88218	2.458333	1.979167
49.9018	2.395833	2.34375
49.92143	2.145833	2.572917
49.94106	2.645833	2.166667
49.96069	2.510417	1.96875
49.98031	2.270833	2.25
49.99994	2.572917	2.239583
50.01957	3.145833	2.427083
50.03919	2.791667	2.5625
50.05882	3.21875	2.625
50.07845	2.84375	2.895833
50.09807	2.75	2.510417
50.1177	2.84375	2.53125
50.13733	3.322917	2.3125
50.15696	3.354167	2.78125
50.17658	3.291667	2.572917
50.19621	3.177083	2.729167
50.21584	3.260417	2.760417
50.23546	3.635417	2.833333
50.25509	3.364583	2.458333
50.27472	3.510417	2.927083
50.29434	3.322917	2.947917
50.31397	3.59375	3.385417
50.3336	3.927083	3.020833
50.35323	3.916667	3.447917
50.37285	3.708333	3.635417
50.39248	3.604167	3.197917
50.41211	3.989583	3.53125
50.43173	3.53125	3.28125
50.45136	3.229167	3.40625
50.47099	3.395833	3.625

50.49062	3.09375	2.895833
50.51024	3.447917	3.520833
50.52987	3.072917	3.416667
50.5495	3.041667	3.447917
50.56912	2.989583	3.083333
50.58875	3.052083	2.625
50.60838	2.552083	2.9375
50.628	2.583333	2.364583
50.64763	2.822917	2.552083
50.66726	2.510417	2.447917
50.68689	2.5625	2.583333
50.70651	2.3125	2.395833
50.72614	2.270833	2.0625
50.74577	2.395833	2.3125
50.76539	2.177083	2.34375
50.78502	2.364583	2.09375
50.80465	2.395833	1.947917
50.82427	2.302083	2.114583
50.8439	2.614583	2.041667
50.86353	2.5	2.552083
50.88316	2.625	2.479167
50.90278	2.447917	2.041667
50.92241	2.71875	2.1875
50.94204	2.395833	2.21875
50.96166	2.572917	2.40625
50.98129	2.760417	2.885417
51.00092	2.833333	2.53125
51.02054	2.916667	2.520833
51.04017	3.1875	2.989583
51.0598	3.229167	2.697917
51.07943	3.635417	2.927083
51.09905	3.645833	3.083333
51.11868	3.635417	3.145833
51.13831	3.385417	2.989583
51.15793	3.3125	2.895833
51.17756	3.34375	3.03125
51.19719	3.28125	3.333333
51.21681	3.052083	3.416667
51.23644	2.989583	3.333333
51.25607	2.864583	3.489583
51.2757	2.958333	2.989583
51.29532	2.8125	2.833333
51.31495	2.90625	3.052083
51.33458	2.59375	3.15625
51.3542	2.5	2.5625

51.37383	2.510417	2.635417
51.39346	2.770833	2.572917
51.41308	2.270833	2.354167
51.43271	2.375	2.5
51.45234	2.21875	2.375
51.47197	2.458333	2.1875
51.49159	2.28125	2.291667
51.51122	2.114583	1.854167
51.53085	2.125	1.947917
51.55047	2.322917	2.010417
51.5701	2.03125	2.229167
51.58973	2.40625	2.208333
51.60935	2.260417	2.072917
51.62898	2.34375	2.052083
51.64861	2.572917	2.291667
51.66824	2.541667	1.875
51.68786	2.229167	2.1875
51.70749	2.645833	2.322917
51.72712	2.583333	2.052083
51.74674	2.229167	2.072917
51.76637	2.729167	2.052083
51.786	2.96875	2.40625
51.80562	2.666667	2.71875
51.82525	2.760417	2.072917
51.84488	3.03125	2.375
51.86451	2.947917	2.552083
51.88413	3.364583	2.479167
51.90376	3.145833	2.75
51.92339	3.729167	2.739583
51.94301	3.489583	2.697917
51.96264	3.635417	2.802083
51.98227	3.552083	3.0625
52.00189	3.645833	3.177083
52.02152	3.364583	3.354167
52.04115	3.427083	3.239583
52.06078	3.15625	3.395833
52.0804	3.083333	3.302083
52.10003	3.25	3.15625
52.11966	2.90625	2.979167
52.13928	2.9375	2.666667
52.15891	2.65625	2.510417
52.17854	2.802083	2.78125
52.19816	2.375	2.604167
52.21779	2.260417	2.4375
52.23742	2.65625	2.333333

52.25705	2.40625	2.020833
52.27667	1.979167	2.447917
52.2963	2.208333	2.15625
52.31593	2.0625	2.15625
52.33555	2.114583	2.15625
52.35518	2.125	2.166667
52.37481	2.145833	1.979167
52.39443	2.041667	1.791667
52.41406	1.916667	2.0625
52.43369	1.875	1.875
52.45332	2	1.885417
52.47294	1.885417	1.958333
52.49257	2	1.84375
52.5122	2.072917	1.916667
52.53182	2.270833	2
52.55145	2.145833	1.958333
52.57108	1.979167	1.729167
52.5907	1.802083	1.885417
52.61033	1.854167	1.947917
52.62996	1.927083	1.739583
52.64959	1.979167	1.96875
52.66921	2.104167	2.03125
52.68884	1.989583	2
52.70847	1.895833	1.895833
52.72809	2.0625	1.697917
52.74772	2.260417	1.90625
52.76735	2.09375	1.90625
52.78697	2.5	2.21875
52.8066	2.020833	2.114583
52.82623	2.739583	2.229167
52.84586	2.510417	2.21875
52.86548	2.479167	1.989583
52.88511	2.739583	2.09375
52.90474	2.333333	2.083333
52.92436	2.614583	2.5
52.94399	2.78125	2.322917
52.96362	2.572917	2.229167
52.98324	2.375	2.197917
53.00287	2.989583	2.510417
53.0225	2.875	2.375
53.04213	3	2.864583
53.06175	2.84375	2.75
53.08138	3.552083	2.572917
53.10101	3.125	2.583333
53.12063	3.604167	3.041667

53.14026	3.229167	2.916667
53.15989	3.177083	3.229167
53.17951	3.0625	3.59375
53.19914	3.197917	3.333333
53.21877	3.041667	3.104167
53.2384	3.135417	2.6875
53.25802	3.333333	2.854167
53.27765	3.09375	2.927083
53.29728	2.927083	2.458333
53.3169	2.864583	3.010417
53.33653	2.770833	2.90625
53.35616	2.822917	2.791667
53.37578	2.489583	2.354167
53.39541	2.5	2.427083
53.41504	2.333333	2.427083
53.43467	2.5625	2.291667
53.45429	2.21875	2.510417
53.47392	2.21875	2.375
53.49355	2.072917	2.03125
53.51317	2.010417	2.270833
53.5328	2.135417	2.083333
53.55243	1.697917	2
53.57206	1.96875	2.25
53.59168	2.104167	1.8125
53.61131	2.083333	2.020833
53.63094	1.625	2.041667
53.65056	2	2.21875
53.67019	1.854167	1.822917
53.68982	1.84375	1.864583
53.70944	1.84375	1.96875
53.72907	2.052083	1.8125
53.7487	2.302083	1.739583
53.76833	1.96875	1.708333
53.78795	2.010417	1.875
53.80758	2.072917	1.677083
53.82721	1.90625	1.90625
53.84683	2.072917	1.864583
53.86646	1.9375	2.03125
53.88609	2.21875	1.90625
53.90571	2.166667	1.989583
53.92534	1.927083	1.979167
53.94497	1.885417	1.645833
53.9646	1.729167	1.864583
53.98422	2.229167	1.729167
54.00385	1.895833	2.291667

54.02348	1.96875	1.791667
54.0431	2.104167	1.760417
54.06273	1.822917	1.770833
54.08236	1.979167	1.822917
54.10198	1.677083	1.8125
54.12161	1.895833	1.645833
54.14124	1.90625	1.84375
54.16087	1.739583	1.65625
54.18049	1.8125	1.84375
54.20012	1.677083	1.885417
54.21975	1.979167	1.739583
54.23937	1.90625	1.8125
54.259	1.9375	1.5625
54.27863	1.916667	2
54.29825	1.822917	1.989583
54.31788	1.947917	1.96875
54.33751	2.0625	1.729167
54.35714	2.010417	2
54.37676	1.8125	1.833333
54.39639	1.90625	1.989583
54.41602	1.645833	1.697917
54.43564	2.0625	1.729167
54.45527	2.135417	1.979167
54.4749	1.927083	1.854167
54.49452	1.75	1.822917
54.51415	1.833333	1.645833
54.53378	1.833333	1.854167
54.55341	2.020833	2.0625
54.57303	1.84375	1.489583
54.59266	2.020833	2.135417
54.61229	1.84375	1.927083
54.63191	1.947917	1.791667
54.65154	1.802083	1.854167
54.67117	1.822917	1.75
54.69079	1.822917	1.979167
54.71042	1.854167	1.59375
54.73005	2.083333	2.114583
54.74968	2.010417	1.979167
54.7693	1.75	1.729167
54.78893	2.041667	1.864583
54.80856	2.072917	2.010417
54.82818	1.791667	1.8125
54.84781	1.770833	1.739583
54.86744	1.989583	1.6875
54.88706	1.78125	1.791667

54.90669	1.739583	1.520833
54.92632	1.729167	1.979167
54.94595	1.791667	1.822917
54.96557	1.708333	1.875
54.9852	1.489583	1.71875
55.00483	1.822917	1.666667
55.02445	1.822917	1.666667
55.04408	1.604167	1.71875
55.06371	2.09375	1.614583
55.08333	1.572917	1.947917
55.10296	2.052083	1.729167
55.12259	1.875	1.729167
55.14222	1.625	1.625
55.16184	1.583333	1.9375
55.18147	1.729167	1.760417
55.2011	2.1875	1.916667
55.22072	1.729167	1.802083
55.24035	1.71875	1.90625
55.25998	1.84375	1.875
55.2796	2.34375	1.572917
55.29923	1.96875	2.083333
55.31886	2.010417	2.21875
55.33849	1.989583	2.3125
55.35811	1.875	1.958333
55.37774	1.729167	2.135417
55.39737	1.947917	1.9375
55.41699	1.989583	2.114583
55.43662	1.90625	1.760417
55.45625	2.166667	1.979167
55.47587	1.9375	1.989583
55.4955	1.729167	1.760417
55.51513	1.989583	1.78125
55.53476	2.041667	1.875
55.55438	1.916667	1.864583
55.57401	1.84375	1.979167
55.59364	1.875	1.9375
55.61326	2.177083	1.947917
55.63289	2.104167	1.614583
55.65252	2.15625	1.958333
55.67214	2.197917	2.09375
55.69177	2.135417	1.927083
55.7114	2.21875	1.947917
55.73103	2.5	2.208333
55.75065	2.333333	2.052083
55.77028	2.229167	2.208333

55.78991	2.145833	2.291667
55.80953	2.041667	2.15625
55.82916	1.947917	2.21875
55.84879	2.052083	1.895833
55.86841	2.177083	2.197917
55.88804	2.479167	2.114583
55.90767	2.395833	1.96875
55.9273	2.260417	2.104167
55.94692	2.5	2.083333
55.96655	2.333333	2.239583
55.98618	1.96875	2.479167
56.0058	1.927083	2.0625
56.02543	1.927083	2.083333
56.04506	2.375	2.09375
56.06468	1.979167	2.03125
56.08431	2.166667	2.083333
56.10394	2.09375	1.8125
56.12357	1.989583	1.989583
56.14319	2.197917	2.083333
56.16282	2.239583	2.083333
56.18245	1.979167	1.729167
56.20207	1.96875	1.833333
56.2217	2.041667	1.708333
56.24133	2.041667	1.791667
56.26095	2.135417	1.708333
56.28058	2.041667	1.770833
56.30021	2.375	2.25
56.31984	2.458333	1.979167
56.33946	2.65625	2.104167
56.35909	3.416667	2.104167
56.37872	3.416667	2.03125
56.39834	3.114583	2.479167
56.41797	3.229167	2.40625
56.4376	2.864583	2.322917
56.45723	2.84375	2.479167
56.47685	2.333333	2.552083
56.49648	2.9375	2.083333
56.51611	2.864583	2.354167
56.53573	2.708333	2.510417
56.55536	2.791667	2.270833
56.57499	2.375	2.385417
56.59461	2.3125	2.083333
56.61424	2.15625	2.09375
56.63387	2.520833	2.052083
56.6535	2.177083	2.1875

56.67312	2.270833	1.833333
56.69275	1.927083	2.229167
56.71238	2.166667	2
56.732	2	1.927083
56.75163	2.322917	2.03125
56.77126	2.145833	2.03125
56.79088	2.385417	2.104167
56.81051	2.09375	2.135417
56.83014	2.020833	2.020833
56.84977	2.104167	2.010417
56.86939	2.166667	1.96875
56.88902	2.177083	1.916667
56.90865	2.270833	1.760417
56.92827	2.447917	1.895833
56.9479	2.427083	2.145833
56.96753	2.59375	2.239583
56.98715	2.510417	2.260417
57.00678	2.239583	2.229167
57.02641	2.447917	2.520833
57.04604	2.270833	2.4375
57.06566	2.322917	2.708333
57.08529	2.020833	2.322917
57.10492	2.364583	2.3125
57.12454	2.416667	2.3125
57.14417	2.166667	1.947917
57.1638	2.489583	2.40625
57.18342	2.21875	2.208333
57.20305	2.625	2.34375
57.22268	2.427083	2.458333
57.24231	2.614583	2.302083
57.26193	2.833333	2.666667
57.28156	2.8125	2.416667
57.30119	2.791667	2.552083
57.32081	2.8125	2.510417
57.34044	3.197917	2.447917
57.36007	2.84375	2.708333
57.37969	2.916667	2.541667
57.39932	2.916667	2.604167
57.41895	2.5625	3.020833
57.43858	2.416667	2.895833
57.4582	2.34375	2.510417
57.47783	2.46875	2.489583
57.49746	2.302083	2.5625
57.51708	2.4375	2.6875
57.53671	2.395833	2.177083

57.55634	2.40625	2.572917
57.57596	2.260417	2.354167
57.59559	2.104167	2.3125
57.61522	2.125	2.072917
57.63485	2.21875	1.927083
57.65447	2.447917	2.28125
57.6741	2.291667	2.041667
57.69373	1.947917	2.135417
57.71335	1.885417	1.90625
57.73298	1.875	2.041667
57.75261	2.135417	1.760417
57.77223	1.822917	1.96875
57.79186	2	1.916667
57.81149	2.03125	1.802083
57.83112	2.020833	1.6875
57.85074	2.291667	2.03125
57.87037	1.833333	2.270833
57.89	2.052083	2.083333
57.90962	2.135417	2.104167
57.92925	1.864583	1.916667
57.94888	1.916667	1.979167
57.9685	2.041667	1.854167
57.98813	1.708333	1.958333
58.00776	2.09375	1.875
58.02739	1.927083	2.041667
58.04701	2.041667	1.989583
58.06664	2.145833	2.072917
58.08627	2.1875	1.833333
58.10589	2.145833	1.96875
58.12552	1.895833	1.979167
58.14515	2.104167	2.072917
58.16477	2.239583	1.770833
58.1844	2.020833	1.979167
58.20403	2.010417	1.8125
58.22366	2.083333	1.78125
58.24328	1.979167	1.59375
58.26291	1.979167	1.666667
58.28254	1.854167	2.03125
58.30216	1.947917	1.75
58.32179	1.958333	1.8125
58.34142	1.75	1.552083
58.36104	1.90625	1.708333
58.38067	1.729167	1.59375
58.4003	1.84375	1.875
58.41993	1.822917	1.5625

58.43955	2.114583	1.46875
58.45918	1.458333	1.416667
58.47881	1.96875	1.65625
58.49843	1.65625	1.635417
58.51806	1.583333	1.8125
58.53769	1.8125	1.822917
58.55731	1.916667	1.5625
58.57694	1.78125	1.614583
58.59657	1.9375	1.791667
58.6162	1.875	1.78125
58.63582	1.791667	1.9375
58.65545	1.833333	1.791667
58.67508	1.9375	1.65625
58.6947	2.104167	1.75
58.71433	1.989583	1.604167
58.73396	1.833333	1.666667
58.75358	1.854167	1.8125
58.77321	1.739583	1.8125
58.79284	1.604167	1.895833
58.81247	1.708333	1.822917
58.83209	2	2.239583
58.85172	2.114583	1.875
58.87135	2.03125	1.78125
58.89097	1.90625	1.989583
58.9106	1.53125	1.833333
58.93023	1.895833	1.78125
58.94985	1.958333	1.947917
58.96948	1.822917	1.84375
58.98911	1.802083	1.666667
59.00874	1.489583	1.833333
59.02836	1.635417	1.604167
59.04799	1.989583	1.572917
59.06762	1.875	1.40625
59.08724	1.770833	1.739583
59.10687	1.71875	1.875
59.1265	1.614583	1.604167
59.14612	1.666667	1.739583
59.16575	1.75	1.729167
59.18538	1.541667	1.364583
59.20501	1.625	1.8125
59.22463	1.520833	1.770833
59.24426	1.708333	1.75
59.26389	1.604167	1.625
59.28351	1.75	1.791667
59.30314	1.9375	1.760417

59.32277	1.822917	1.447917
59.3424	1.75	1.583333
59.36202	1.552083	1.59375
59.38165	1.71875	1.635417
59.40128	1.677083	1.625
59.4209	1.677083	1.5625
59.44053	1.541667	1.583333
59.46016	1.885417	1.635417
59.47978	1.708333	1.552083
59.49941	1.697917	1.6875
59.51904	1.78125	1.770833
59.53867	1.854167	1.65625
59.55829	1.65625	1.645833
59.57792	1.75	1.635417
59.59755	1.770833	1.552083
59.61717	1.677083	1.697917
59.6368	2.03125	1.635417
59.65643	1.947917	1.75
59.67605	1.979167	1.71875
59.69568	1.947917	1.822917
59.71531	1.9375	1.416667
59.73494	2.010417	1.677083
59.75456	2.239583	2.041667
59.77419	2.177083	1.833333
59.79382	2.15625	1.958333
59.81344	2.572917	1.96875
59.83307	2.3125	2.40625
59.8527	2.364583	2.270833
59.87232	2.645833	2.28125
59.89195	2.28125	2.479167
59.91158	2.520833	2.520833
59.93121	2.5	2.635417
59.95083	2.833333	2.520833
59.97046	2.375	2.125
59.99009	2.416667	2.489583
60.00971	2.270833	2.40625
60.02934	2.083333	2.572917
60.04897	2.427083	2.6875
60.06859	2.34375	2.71875
60.08822	2.395833	2.1875
60.10785	2.072917	2.208333
60.12748	2.135417	2.229167
60.1471	2.3125	2.302083
60.16673	2.25	1.71875
60.18636	1.833333	2.25

60.20598	1.885417	2.104167
60.22561	2.28125	2.0625
60.24524	1.90625	2
60.26486	2.03125	1.8125
60.28449	2.177083	1.9375
60.30412	1.989583	1.802083
60.32375	2.020833	1.885417
60.34337	2.28125	1.927083
60.363	2.197917	2.041667
60.38263	1.802083	1.958333
60.40225	2.333333	1.916667
60.42188	2.09375	1.979167
60.44151	1.958333	1.677083
60.46113	2.260417	1.854167
60.48076	2.104167	1.854167
60.50039	2.03125	1.958333
60.52002	2.166667	2.104167
60.53964	2.25	1.989583
60.55927	2.354167	2.322917
60.5789	2.645833	2.15625
60.59852	2.333333	2.135417
60.61815	2.447917	2.177083
60.63778	2.145833	2.239583
60.6574	2.28125	2.510417
60.67703	2.0625	2.0625
60.69666	2.125	2.03125
60.71629	2.260417	2.1875
60.73591	2.25	1.979167
60.75554	2.322917	2.177083
60.77517	2.260417	2.21875
60.79479	2.229167	2.072917
60.81442	2.395833	2.15625
60.83405	2.083333	2.114583
60.85367	2.145833	2.104167
60.8733	2.322917	1.854167
60.89293	2.322917	2.15625
60.91256	2.166667	1.96875
60.93218	2.104167	2.125
60.95181	2.166667	2.020833
60.97144	1.9375	2
60.99106	1.895833	1.802083
61.01069	2.09375	2.145833
61.03032	1.90625	2.010417
61.04994	1.729167	1.854167
61.06957	2.104167	1.84375

61.0892	1.895833	2.15625
61.10883	2.239583	1.96875
61.12845	2.072917	1.96875
61.14808	2.21875	1.875
61.16771	2.197917	1.84375
61.18733	2.375	2.072917
61.20696	2.135417	1.979167
61.22659	1.9375	1.90625
61.24621	2.458333	1.770833
61.26584	2.1875	1.84375
61.28547	2.15625	1.989583
61.3051	2.354167	2.072917
61.32472	2.333333	2.229167
61.34435	2.145833	2.25
61.36398	2.416667	2
61.3836	2.020833	2.208333
61.40323	2.333333	1.958333
61.42286	2.510417	2.114583
61.44248	2.1875	1.979167
61.46211	2.28125	1.989583
61.48174	2.177083	2.114583
61.50137	2.197917	2.427083
61.52099	2.354167	2.09375
61.54062	2.34375	1.864583
61.56025	2.25	2.25
61.57987	2.135417	2.177083
61.5995	2.083333	2.25
61.61913	2.135417	1.895833
61.63875	2.208333	2.041667
61.65838	2.177083	2.208333
61.67801	1.8125	2.052083
61.69764	1.989583	1.854167
61.71726	1.802083	1.958333
61.73689	1.927083	2.010417
61.75652	1.895833	1.645833
61.77614	1.822917	2.145833
61.79577	1.864583	1.958333
61.8154	1.84375	1.96875
61.83502	1.895833	2.072917
61.85465	1.875	1.510417
61.87428	2.020833	1.697917
61.89391	1.75	1.53125
61.91353	1.583333	1.885417
61.93316	1.34375	1.697917
61.95279	1.645833	1.697917

61.97241	1.760417	1.65625
61.99204	1.71875	1.625
62.01167	1.53125	1.729167
62.03129	1.53125	1.520833
62.05092	1.729167	1.479167
62.07055	1.71875	1.541667
62.09018	1.572917	1.729167
62.1098	1.46875	1.635417
62.12943	1.5	1.25
62.14906	1.4375	1.895833
62.16868	1.395833	1.489583
62.18831	1.635417	1.28125
62.20794	1.510417	1.354167
62.22757	1.427083	1.479167
62.24719	1.833333	1.291667
62.26682	1.677083	1.427083
62.28645	1.729167	1.541667
62.30607	1.552083	1.322917
62.3257	1.645833	1.5625
62.34533	1.802083	1.5625
62.36495	1.604167	1.4375
62.38458	1.666667	1.65625
62.40421	1.666667	1.447917
62.42384	1.4375	1.541667
62.44346	1.9375	1.541667
62.46309	1.666667	1.822917
62.48272	1.8125	1.84375
62.50234	1.604167	1.520833
62.52197	1.84375	1.677083
62.5416	1.84375	1.84375
62.56122	1.635417	1.625
62.58085	2.166667	1.583333
62.60048	1.604167	1.927083
62.62011	1.90625	1.927083
62.63973	1.84375	1.770833
62.65936	2.104167	1.822917
62.67899	1.958333	1.71875
62.69861	1.916667	1.885417
62.71824	2.15625	2.145833
62.73787	2.447917	2.114583
62.75749	2.145833	2.072917
62.77712	2.46875	1.916667
62.79675	2.239583	2.260417
62.81638	2.1875	2.177083
62.836	2.53125	2.572917

62.85563	2.09375	2.208333
62.87526	2.635417	1.979167
62.89488	2.21875	2.21875
62.91451	2.40625	2.385417
62.93414	2.458333	2.291667
62.95376	2.520833	2.166667
62.97339	2.59375	2.364583
62.99302	2.40625	2.479167
63.01265	2.28125	2.21875
63.03227	2.489583	2.208333
63.0519	2.260417	2.270833
63.07153	2.322917	2.260417
63.09115	2.166667	1.875
63.11078	2.09375	2.21875
63.13041	2.46875	1.822917
63.15003	1.90625	1.947917
63.16966	2.177083	2.21875
63.18929	1.989583	2.145833
63.20892	2.25	2.177083
63.22854	1.885417	2.083333
63.24817	1.833333	1.958333
63.2678	2.09375	1.864583
63.28742	1.885417	1.697917
63.30705	1.927083	1.770833
63.32668	1.979167	1.708333
63.3463	1.802083	1.791667
63.36593	2.072917	1.833333
63.38556	1.53125	1.822917
63.40519	1.65625	1.59375
63.42481	1.885417	1.625
63.44444	1.645833	1.708333
63.46407	1.770833	1.65625
63.48369	1.65625	1.864583
63.50332	1.9375	1.802083
63.52295	1.791667	1.583333
63.54257	1.677083	1.6875
63.5622	1.729167	1.635417
63.58183	1.78125	1.666667
63.60146	1.864583	1.8125
63.62108	1.84375	1.645833
63.64071	1.875	1.572917
63.66034	1.645833	1.791667
63.67996	2.020833	1.645833
63.69959	1.739583	1.760417
63.71922	1.875	1.770833

63.73884	2.197917	1.6875
63.75847	1.96875	1.9375
63.7781	2.177083	2.0625
63.79773	2.28125	1.75
63.81735	2.395833	1.947917
63.83698	2.791667	1.979167
63.85661	2.447917	2.104167
63.87623	3.083333	2.260417
63.89586	2.625	2.375
63.91549	2.979167	2.854167
63.93511	2.541667	2.427083
63.95474	2.229167	2.53125
63.97437	2.677083	2.416667
63.994	2.5625	2.53125
64.01362	2.666667	2.489583
64.03325	2.6875	2.46875
64.05288	2.895833	2.375
64.0725	2.395833	2.479167
64.09213	2.260417	2.5625
64.11176	2.385417	2.635417
64.13138	2.28125	2.520833
64.15101	2.21875	2.09375
64.17064	2.197917	2.166667
64.19027	2.125	2.072917
64.20989	1.854167	2.083333
64.22952	1.885417	2.125
64.24915	1.979167	1.958333
64.26877	1.96875	1.864583
64.2884	1.75	2.052083
64.30803	2.052083	1.78125
64.32765	2.072917	1.8125
64.34728	2.0625	1.947917
64.36691	1.9375	1.71875
64.38654	1.854167	1.760417
64.40616	1.59375	1.895833
64.42579	2.072917	1.875
64.44542	1.864583	1.71875
64.46504	2.302083	1.78125
64.48467	2.239583	1.833333
64.5043	2.197917	1.75
64.52392	2.489583	2.083333
64.54355	2.552083	1.96875
64.56318	2.510417	2.010417
64.58281	2.364583	2.177083
64.60243	2.479167	2.364583

64.62206	2.302083	2.260417
64.64169	2.239583	2.395833
64.66131	2.197917	2.135417
64.68094	2.541667	2.395833
64.70057	2.53125	2.260417
64.72019	2.364583	2.072917
64.73982	2.510417	2.177083
64.75945	2.4375	2.083333
64.77908	2.354167	2.333333
64.7987	2.447917	2.46875
64.81833	2.3125	2.1875
64.83796	2.645833	2.385417
64.85758	2.510417	2.364583
64.87721	2.458333	2.614583
64.89684	2.104167	2.427083
64.91646	2.291667	2.395833
64.93609	2.583333	2.197917
64.95572	2.552083	2.5
64.97535	2.479167	2.4375
64.99497	2.3125	2.208333
65.0146	2	2.229167
65.03423	2.302083	2.1875
65.05385	2.15625	2.229167
65.07348	1.96875	2.083333
65.09311	1.78125	2.072917
65.11274	2	1.90625
65.13236	1.708333	1.729167
65.15199	1.802083	1.854167
65.17162	1.979167	1.885417
65.19124	1.5625	2.09375
65.21087	1.729167	1.90625
65.2305	1.822917	1.854167
65.25012	1.71875	1.822917
65.26975	1.916667	1.4375
65.28938	1.791667	1.802083
65.30901	1.697917	1.625
65.32863	1.739583	1.927083
65.34826	1.78125	1.71875
65.36789	1.59375	1.572917
65.38751	1.770833	1.666667
65.40714	1.739583	1.875
65.42677	1.885417	1.71875
65.44639	1.78125	1.677083
65.46602	1.791667	1.96875
65.48565	1.770833	1.75

65.50528	1.708333	1.625
65.5249	1.979167	1.84375
65.54453	2.0625	1.729167
65.56416	1.864583	1.96875
65.58378	2.083333	2.104167
65.60341	2.041667	2.145833
65.62304	2	2.114583
65.64266	2.125	2.40625
65.66229	1.739583	2.104167
65.68192	1.614583	2.229167
65.70155	1.729167	1.833333
65.72117	1.572917	1.677083
65.7408	1.885417	1.666667
65.76043	1.6875	1.541667
65.78005	1.59375	1.6875
65.79968	1.729167	1.6875
65.81931	1.541667	1.84375
65.83893	1.635417	1.645833
65.85856	1.708333	1.604167
65.87819	1.645833	1.729167
65.89782	1.510417	1.614583
65.91744	1.625	1.541667
65.93707	1.229167	1.625
65.9567	1.604167	1.541667
65.97632	1.635417	1.59375
65.99595	1.53125	1.395833
66.01558	1.489583	1.395833
66.0352	1.65625	1.208333
66.05483	1.895833	1.479167
66.07446	1.822917	1.71875
66.09409	1.760417	1.552083
66.11371	1.729167	1.53125
66.13334	1.947917	1.84375
66.15297	2.041667	1.59375
66.17259	1.791667	1.739583
66.19222	1.770833	1.84375
66.21185	1.770833	1.59375
66.23147	1.645833	1.791667
66.2511	1.729167	1.395833
66.27073	1.916667	1.677083
66.29036	1.90625	1.729167
66.30998	1.9375	1.71875
66.32961	1.802083	1.739583
66.34924	1.96875	1.614583
66.36886	1.71875	1.666667

66.38849	1.791667	1.947917
66.40812	1.84375	1.760417
66.42774	1.8125	1.635417
66.44737	1.854167	1.875
66.467	1.520833	1.729167
66.48663	1.708333	1.697917
66.50625	1.625	1.510417
66.52588	1.604167	1.5
66.54551	1.479167	1.53125
66.56513	1.552083	1.854167
66.58476	1.5625	1.875
66.60439	1.427083	1.40625
66.62401	1.510417	1.46875
66.64364	1.729167	1.71875
66.66327	1.572917	1.333333
66.6829	1.416667	1.677083
66.70252	1.46875	1.447917
66.72215	1.34375	1.46875
66.74178	1.645833	1.447917
66.7614	1.427083	1.395833
66.78103	1.447917	1.510417
66.80066	1.520833	1.354167
66.82028	1.427083	1.427083
66.83991	1.3125	1.520833
66.85954	1.458333	1.375
66.87917	1.427083	1.59375
66.89879	1.510417	1.291667
66.91842	1.4375	1.46875
66.93805	1.541667	1.354167
66.95767	1.541667	1.40625
66.9773	1.46875	1.3125
66.99693	1.322917	1.53125
67.01655	1.583333	1.572917
67.03618	1.364583	1.395833
67.05581	1.541667	1.354167
67.07544	1.28125	1.395833
67.09506	1.541667	1.447917
67.11469	1.3125	1.46875
67.13432	1.520833	1.427083
67.15394	1.520833	1.46875
67.17357	1.354167	1.354167
67.1932	1.541667	1.3125
67.21282	1.489583	1.25
67.23245	1.322917	1.520833
67.25208	1.447917	1.385417

67.27171	1.489583	1.520833
67.29133	1.385417	1.260417
67.31096	1.385417	1.5
67.33059	1.53125	1.53125
67.35021	1.385417	1.395833
67.36984	1.208333	1.427083
67.38947	1.40625	1.291667
67.40909	1.291667	1.354167
67.42872	1.447917	1.458333
67.44835	1.572917	1.177083
67.46798	1.427083	1.34375
67.4876	1.208333	1.302083
67.50723	1.53125	1.427083
67.52686	1.395833	1.375
67.54648	1.5	1.395833
67.56611	1.270833	1.177083
67.58574	1.291667	1.15625
67.60536	1.333333	1.260417
67.62499	1.4375	1.354167
67.64462	1.552083	1.59375
67.66425	1.645833	1.510417
67.68387	1.604167	2
67.7035	1.447917	1.427083
67.72313	1.541667	1.90625
67.74275	1.541667	1.34375
67.76238	1.3125	1.458333
67.78201	1.5	1.604167
67.80163	1.46875	1.28125
67.82126	1.458333	1.40625
67.84089	1.458333	1.354167
67.86052	1.552083	1.34375
67.88014	1.40625	1.427083
67.89977	1.541667	1.364583
67.9194	1.59375	1.458333
67.93902	1.53125	1.53125
67.95865	1.697917	1.1875
67.97828	1.614583	1.552083
67.99791	1.666667	1.21875
68.01753	1.291667	1.583333
68.03716	1.739583	1.375
68.05679	1.635417	1.510417
68.07641	1.416667	1.395833
68.09604	1.416667	1.5625
68.11567	1.46875	1.604167
68.13529	1.395833	1.375

68.15492	1.28125	1.552083
68.17455	1.4375	1.427083
68.19418	1.59375	1.416667
68.2138	1.5	1.552083
68.23343	1.614583	1.375
68.25306	1.572917	1.395833
68.27268	1.395833	1.552083
68.29231	1.53125	1.53125
68.31194	1.291667	1.333333
68.33156	1.875	1.53125
68.35119	1.385417	1.625
68.37082	1.6875	1.6875
68.39045	1.635417	1.583333
68.41007	1.8125	1.635417
68.4297	1.729167	1.6875
68.44933	1.583333	1.614583
68.46895	1.5625	1.614583
68.48858	1.541667	1.46875
68.50821	1.541667	1.677083
68.52783	1.458333	1.510417
68.54746	1.291667	1.416667
68.56709	1.510417	1.354167
68.58672	1.5625	1.21875
68.60634	1.614583	1.572917
68.62597	1.4375	1.333333
68.6456	1.333333	1.479167
68.66522	1.302083	1.583333
68.68485	1.458333	1.385417
68.70448	1.145833	1.302083
68.7241	1.322917	1.375
68.74373	1.635417	1.291667
68.76336	1.364583	1.447917
68.78299	1.322917	1.53125
68.80261	1.385417	1.291667
68.82224	1.458333	1.708333
68.84187	1.104167	1.1875
68.86149	1.40625	1.333333
68.88112	1.364583	1.458333
68.90075	1.145833	1.666667
68.92037	1.34375	1.239583
68.94	1.4375	1.3125
68.95963	1.479167	1.395833
68.97926	1.354167	1.375
68.99888	1.427083	1.458333
69.01851	1.5	1.28125

69.03814	1.354167	1.302083
69.05776	1.427083	1.354167
69.07739	1.145833	1.395833
69.09702	1.239583	1.447917
69.11664	1.520833	1.40625
69.13627	1.489583	1.447917
69.1559	1.447917	1.447917
69.17553	1.59375	1.3125
69.19515	1.510417	1.583333
69.21478	1.21875	1.427083
69.23441	1.46875	1.208333
69.25403	1.4375	1.572917
69.27366	1.541667	1.270833
69.29329	1.489583	1.572917
69.31291	1.302083	1.510417
69.33254	1.510417	1.3125
69.35217	1.385417	1.510417
69.3718	1.375	1.34375
69.39142	1.645833	1.583333
69.41105	1.239583	1.458333
69.43068	1.28125	1.489583
69.4503	1.572917	1.333333
69.46993	1.3125	1.71875
69.48956	1.15625	1.5
69.50918	1.291667	1.40625
69.52881	1.520833	1.291667
69.54844	1.385417	1.458333
69.56807	1.479167	1.489583
69.58769	1.385417	1.447917
69.60732	1.395833	1.760417
69.62695	1.583333	1.635417
69.64657	1.59375	1.84375
69.6662	1.416667	1.46875
69.68583	1.635417	1.354167
69.70545	1.385417	1.375
69.72508	1.395833	1.21875
69.74471	1.3125	1.34375
69.76434	1.291667	1.229167
69.78396	1.291667	1.40625
69.80359	1.333333	1.520833
69.82322	1.40625	1.302083
69.84284	1.3125	1.458333
69.86247	1.302083	1.364583
69.8821	1.385417	1.427083
69.90172	1.5	1.5625

69.92135	1.583333	1.291667
69.94098	1.864583	1.4375
69.96061	1.53125	1.416667
69.98023	1.614583	1.614583
69.99986	1.427083	1.4375
70.01949	1.614583	1.614583
70.03911	1.65625	1.4375
70.05874	1.416667	1.322917
70.07837	1.5	1.46875
70.09799	1.770833	1.479167
70.11762	1.614583	1.333333
70.13725	1.59375	1.270833
70.15688	1.59375	1.447917
70.1765	1.458333	1.4375
70.19613	1.625	1.458333
70.21576	1.770833	1.6875
70.23538	1.552083	1.46875
70.25501	1.53125	1.322917
70.27464	1.572917	1.614583
70.29426	1.322917	1.489583
70.31389	1.260417	1.364583
70.33352	1.552083	1.447917
70.35315	1.489583	1.458333
70.37277	1.40625	1.28125
70.3924	1.385417	1.34375
70.41203	1.583333	1.322917
70.43165	1.4375	1.416667
70.45128	1.822917	1.510417
70.47091	1.270833	1.239583
70.49053	1.21875	1.052083
70.51016	1.395833	1.239583
70.52979	1.645833	1.3125
70.54942	1.322917	1.15625
70.56904	1.552083	1.375
70.58867	1.291667	1.1875
70.6083	1.21875	1.114583
70.62792	1.197917	1.458333
70.64755	1.177083	1.416667
70.66718	1.354167	1.416667
70.6868	1.364583	1.46875
70.70643	1.270833	1.385417
70.72606	1.447917	1.510417
70.74569	1.333333	1.34375
70.76531	1.3125	1.291667
70.78494	1.458333	1.625

70.80457	1.458333	1.28125
70.82419	1.479167	1.458333
70.84382	1.395833	1.447917
70.86345	1.239583	1.4375
70.88307	1.270833	1.541667
70.9027	1.5625	1.46875
70.92233	1.447917	1.416667
70.94196	1.40625	1.520833
70.96158	1.59375	1.447917
70.98121	1.364583	1.40625
71.00084	1.53125	1.375
71.02046	1.479167	1.291667
71.04009	1.583333	1.260417
71.05972	1.3125	1.354167
71.07935	1.46875	1.541667
71.09897	1.34375	1.40625
71.1186	1.239583	1.6875
71.13823	1.572917	1.53125
71.15785	1.385417	1.375
71.17748	1.677083	1.5625
71.19711	1.5	1.395833
71.21673	1.541667	1.385417
71.23636	1.458333	1.479167
71.25599	1.572917	1.552083
71.27562	1.802083	1.322917
71.29524	1.739583	1.479167
71.31487	1.458333	1.5
71.3345	1.385417	1.385417
71.35412	1.479167	1.364583
71.37375	1.552083	1.4375
71.39338	1.71875	1.458333
71.413	1.604167	1.541667
71.43263	1.5	1.395833
71.45226	1.645833	1.40625
71.47189	1.520833	1.5625
71.49151	1.760417	1.697917
71.51114	1.770833	1.541667
71.53077	1.677083	1.770833
71.55039	1.666667	1.833333
71.57002	1.739583	1.604167
71.58965	1.5	1.895833
71.60927	1.5	1.59375
71.6289	1.625	1.416667
71.64853	1.90625	1.583333
71.66816	1.65625	1.375

71.68778	1.53125	1.572917
71.70741	1.583333	1.635417
71.72704	1.625	1.510417
71.74666	1.53125	1.6875
71.76629	1.6875	1.5
71.78592	1.53125	1.541667
71.80554	1.552083	1.395833
71.82517	1.489583	1.520833
71.8448	1.34375	1.46875
71.86443	1.479167	1.333333
71.88405	1.614583	1.458333
71.90368	1.302083	1.364583
71.92331	1.541667	1.395833
71.94293	1.552083	1.65625
71.96256	1.552083	1.375
71.98219	1.59375	1.572917
72.00181	1.708333	1.614583
72.02144	1.385417	1.40625
72.04107	1.458333	1.520833
72.0607	1.520833	1.40625
72.08032	1.583333	1.59375
72.09995	1.645833	1.520833
72.11958	1.697917	1.385417
72.1392	1.416667	1.8125
72.15883	1.895833	1.59375
72.17846	1.552083	1.71875
72.19808	1.65625	1.541667
72.21771	1.552083	1.552083
72.23734	1.541667	1.458333
72.25697	1.34375	1.541667
72.27659	1.489583	1.4375
72.29622	1.395833	1.479167
72.31585	1.604167	1.5
72.33547	1.333333	1.40625
72.3551	1.333333	1.177083
72.37473	1.729167	1.53125
72.39435	1.53125	1.3125
72.41398	1.322917	1.270833
72.43361	1.25	1.354167
72.45324	1.5625	1.427083
72.47286	1.385417	1.5625
72.49249	1.427083	1.447917
72.51212	1.364583	1.416667
72.53174	1.166667	1.375
72.55137	1.364583	1.302083

72.571	1.395833	1.364583
72.59062	0.958333	1.145833
72.61025	1.354167	1.28125
72.62988	1.375	1.052083
72.64951	1.46875	1.427083
72.66913	1.458333	1.34375
72.68876	1.166667	1.489583
72.70839	1.458333	1.322917
72.72801	1.572917	1.479167
72.74764	1.416667	1.354167
72.76727	1.708333	1.46875
72.78689	1.59375	1.510417
72.80652	1.583333	1.479167
72.82615	1.3125	1.552083
72.84578	1.583333	1.59375
72.8654	1.229167	1.5
72.88503	1.65625	1.635417
72.90466	1.5	1.447917
72.92428	1.59375	1.375
72.94391	1.59375	1.302083
72.96354	1.4375	1.270833
72.98316	1.520833	1.53125
73.00279	1.541667	1.46875
73.02242	1.614583	1.385417
73.04205	1.364583	1.458333
73.06167	1.375	1.40625
73.0813	1.416667	1.447917
73.10093	1.510417	1.614583
73.12055	1.239583	1.21875
73.14018	1.5	1.114583
73.15981	1.302083	1.3125
73.17943	1.260417	1.375
73.19906	1.333333	1.354167
73.21869	1.479167	1.46875
73.23832	1.395833	1.322917
73.25794	1.427083	1.25
73.27757	1.28125	1.229167
73.2972	1.375	1.302083
73.31682	1.395833	1.520833
73.33645	1.583333	1.583333
73.35608	1.604167	1.302083
73.3757	1.510417	1.447917
73.39533	1.677083	1.614583
73.41496	1.90625	1.510417
73.43459	1.552083	1.458333

73.45421	1.270833	1.46875
73.47384	1.520833	1.354167
73.49347	1.40625	1.3125
73.51309	1.489583	1.583333
73.53272	1.791667	1.322917
73.55235	1.739583	1.489583
73.57197	1.520833	1.541667
73.5916	1.6875	1.354167
73.61123	1.708333	1.6875
73.63086	1.760417	1.6875
73.65048	1.916667	1.78125
73.67011	1.645833	1.677083
73.68974	1.8125	1.520833
73.70936	1.572917	1.760417
73.72899	1.604167	1.739583
73.74862	1.59375	1.5625
73.76824	1.833333	1.572917
73.78787	1.666667	1.677083
73.8075	1.770833	1.6875
73.82713	1.71875	1.802083
73.84675	2.083333	1.96875
73.86638	1.833333	1.802083
73.88601	1.875	1.6875
73.90563	2.010417	1.75
73.92526	1.96875	1.791667
73.94489	1.958333	1.822917
73.96452	1.760417	1.84375
73.98414	1.8125	1.75
74.00377	1.822917	1.604167
74.0234	1.65625	1.947917
74.04302	1.510417	1.84375
74.06265	1.666667	1.833333
74.08228	1.802083	1.479167
74.1019	1.895833	1.489583
74.12153	1.572917	1.875
74.14116	1.53125	1.333333
74.16079	1.677083	1.760417
74.18041	1.416667	1.46875
74.20004	1.489583	1.395833
74.21967	1.25	1.458333
74.23929	1.28125	1.354167
74.25892	1.385417	1.239583
74.27855	1.447917	1.40625
74.29817	1.145833	1.385417
74.3178	1.21875	1.427083

74.33743	1.3125	1.302083
74.35706	1.427083	1.5
74.37668	1.239583	1.072917
74.39631	1.135417	1.385417
74.41594	1.270833	1.447917
74.43556	1.354167	1.239583
74.45519	1.5	1.541667
74.47482	1.114583	1.375
74.49444	1.354167	1.4375
74.51407	1.416667	1.21875
74.5337	1.072917	1.09375
74.55333	1.3125	1.34375
74.57295	1.375	1.28125
74.59258	1.135417	1.385417
74.61221	1.25	1.375
74.63183	1.28125	1.447917
74.65146	1.541667	1.364583
74.67109	1.40625	1.375
74.69071	1.322917	1.46875
74.71034	1.239583	1.229167
74.72997	1.208333	1.395833
74.7496	1.625	1.354167
74.76922	1.416667	1.625
74.78885	1.666667	1.302083
74.80848	1.395833	1.677083
74.8281	1.40625	1.479167
74.84773	1.375	1.510417
74.86736	1.458333	1.302083
74.88698	1.572917	1.395833
74.90661	1.604167	1.375
74.92624	1.416667	1.53125
74.94587	1.59375	1.3125
74.96549	1.510417	1.614583
74.98512	1.239583	1.604167
75.00475	1.375	1.645833
75.02437	1.354167	1.635417
75.044	1.666667	1.385417
75.06363	1.614583	1.520833
75.08325	1.510417	1.583333
75.10288	1.46875	1.666667
75.12251	1.645833	1.552083
75.14214	1.833333	1.59375
75.16176	1.927083	1.8125
75.18139	2.25	1.708333
75.20102	2.270833	1.875

75.22064	2.333333	2.03125
75.24027	2.020833	2.239583
75.2599	1.791667	2.395833
75.27952	1.572917	2.166667
75.29915	1.791667	1.927083
75.31878	2.145833	1.989583
75.33841	1.822917	1.666667
75.35803	2.083333	1.59375
75.37766	1.885417	1.802083
75.39729	1.96875	1.604167
75.41691	1.916667	1.9375
75.43654	2.0625	2.083333
75.45617	1.822917	1.979167
75.47579	1.75	1.9375
75.49542	1.916667	1.65625
75.51505	1.927083	1.875
75.53468	1.833333	1.84375
75.5543	1.9375	1.916667
75.57393	1.875	1.479167
75.59356	1.770833	1.760417
75.61318	1.895833	1.40625
75.63281	1.6875	1.59375
75.65244	1.677083	1.541667
75.67206	1.739583	1.572917
75.69169	1.677083	1.583333
75.71132	1.572917	1.5
75.73095	1.520833	1.395833
75.75057	1.5625	1.46875
75.7702	1.604167	1.802083
75.78983	1.520833	1.916667
75.80945	1.40625	1.65625
75.82908	1.427083	1.625
75.84871	1.4375	1.385417
75.86833	1.489583	1.625
75.88796	1.5	1.739583
75.90759	1.802083	1.385417
75.92722	1.572917	1.4375
75.94684	1.447917	1.489583
75.96647	1.4375	1.572917
75.9861	1.614583	1.354167
76.00572	1.65625	1.354167
76.02535	1.427083	1.375
76.04498	1.4375	1.625
76.0646	1.677083	1.5625
76.08423	1.552083	1.635417

76.10386	1.364583	1.625
76.12349	1.520833	1.552083
76.14311	1.427083	1.770833
76.16274	1.46875	1.625
76.18237	1.416667	1.520833
76.20199	1.322917	1.447917
76.22162	1.354167	1.427083
76.24125	1.510417	1.5625
76.26087	1.395833	1.5
76.2805	1.666667	1.572917
76.30013	1.552083	1.3125
76.31976	1.40625	1.34375
76.33938	1.59375	1.5
76.35901	1.489583	1.291667
76.37864	1.416667	1.291667
76.39826	1.427083	1.541667
76.41789	1.479167	1.510417
76.43752	1.40625	1.677083
76.45714	1.427083	1.46875
76.47677	1.5	1.59375
76.4964	1.75	1.333333
76.51603	1.5	1.5625
76.53565	1.40625	1.364583
76.55528	1.552083	1.65625
76.57491	1.510417	1.510417
76.59453	1.635417	1.302083
76.61416	1.416667	1.53125
76.63379	1.4375	1.458333
76.65341	1.635417	1.729167
76.67304	1.520833	1.541667
76.69267	1.395833	1.489583
76.7123	1.541667	1.4375
76.73192	1.697917	1.53125
76.75155	1.666667	1.4375
76.77118	1.9375	1.614583
76.7908	1.697917	1.322917
76.81043	1.927083	1.729167
76.83006	1.6875	1.947917
76.84969	2.010417	1.46875
76.86931	1.979167	1.927083
76.88894	1.666667	1.5
76.90857	2.145833	1.9375
76.92819	1.854167	2.041667
76.94782	2.229167	1.697917
76.96745	1.864583	1.989583

76.98707	1.9375	2.052083
77.0067	2.072917	2.0625
77.02633	1.8125	2.135417
77.04596	2.208333	2.03125
77.06558	1.979167	1.96875
77.08521	2.020833	2.041667
77.10484	2.239583	1.895833
77.12446	2.239583	1.90625
77.14409	1.90625	2.03125
77.16372	1.65625	2.052083
77.18334	1.65625	1.885417
77.20297	1.927083	1.916667
77.2226	1.59375	1.9375
77.24223	1.520833	1.854167
77.26185	1.770833	1.947917
77.28148	1.9375	1.708333
77.30111	1.666667	1.65625
77.32073	1.645833	1.75
77.34036	1.583333	1.5625
77.35999	1.260417	1.583333
77.37961	1.416667	1.635417
77.39924	1.583333	1.572917
77.41887	1.458333	1.708333
77.4385	1.354167	1.572917
77.45812	1.385417	1.260417
77.47775	1.5625	1.270833
77.49738	1.385417	1.375
77.517	1.427083	1.46875
77.53663	1.1875	1.291667
77.55626	1.322917	1.552083
77.57588	1.5	1.59375
77.59551	1.53125	1.4375
77.61514	1.427083	1.572917
77.63477	1.447917	1.291667
77.65439	1.447917	1.447917
77.67402	1.260417	1.614583
77.69365	1.28125	1.270833
77.71327	1.4375	1.541667
77.7329	1.333333	1.270833
77.75253	1.604167	1.697917
77.77215	1.614583	1.427083
77.79178	1.479167	1.520833
77.81141	1.34375	1.416667
77.83104	1.614583	1.302083
77.85066	1.395833	1.5

77.87029	1.59375	1.34375
77.88992	1.510417	1.583333
77.90954	1.458333	1.479167
77.92917	1.520833	1.5625
77.9488	1.729167	1.447917
77.96842	1.28125	1.510417
77.98805	1.770833	1.645833
78.00768	1.458333	1.583333
78.02731	1.510417	1.541667
78.04693	1.9375	1.635417
78.06656	1.625	1.40625
78.08619	1.697917	1.479167
78.10581	1.75	1.708333
78.12544	1.645833	1.583333
78.14507	1.739583	1.666667
78.16469	1.583333	1.4375
78.18432	1.541667	1.34375
78.20395	1.447917	1.697917
78.22358	1.729167	1.5625
78.2432	1.302083	1.6875
78.26283	1.385417	1.385417
78.28246	1.260417	1.645833
78.30208	1.541667	1.5
78.32171	1.229167	1.46875
78.34134	1.333333	1.458333
78.36096	1.302083	1.479167
78.38059	1.40625	1.59375
78.40022	1.395833	1.552083
78.41985	1.552083	1.614583
78.43947	1.21875	1.260417
78.4591	1.635417	1.447917
78.47873	1.104167	1.1875
78.49835	1.239583	1.229167
78.51798	1.333333	1.239583
78.53761	1.354167	1.375
78.55723	1.208333	1.239583
78.57686	1.145833	1.239583
78.59649	1.125	1.114583
78.61612	1.239583	1.260417
78.63574	1.364583	1.28125
78.65537	1.229167	1.177083
78.675	1.104167	1.09375
78.69462	1.28125	1.135417
78.71425	1.40625	1.395833
78.73388	1.291667	1.260417

78.7535	1.447917	1.34375
78.77313	1.25	1.177083
78.79276	1.385417	1.135417
78.81239	1.145833	1.260417
78.83201	1.354167	1.28125
78.85164	1.104167	1.291667
78.87127	1.34375	1.239583
78.89089	1.125	1.229167
78.91052	1.145833	1.104167
78.93015	0.979167	1.145833
78.94977	1.03125	1.197917
78.9694	1.09375	1.28125
78.98903	1.302083	1.302083
79.00866	1.1875	1.260417
79.02828	1.104167	1.260417
79.04791	1.104167	1.291667
79.06754	1.25	1.21875
79.08716	1.125	1.166667
79.10679	1.03125	1.104167
79.12642	1.3125	1.322917
79.14604	1.03125	1.166667
79.16567	1.260417	1.1875
79.1853	1.145833	1.0625
79.20493	1.458333	1.229167
79.22455	1.21875	1.333333
79.24418	1.479167	1.041667
79.26381	1.03125	1.3125
79.28343	1.208333	1.208333
79.30306	1.28125	1.072917
79.32269	1.072917	1.052083
79.34231	1.052083	1.416667
79.36194	1.270833	1.229167
79.38157	1.3125	1.125
79.4012	1.104167	1.21875
79.42082	1.010417	1.197917
79.44045	1.34375	1.34375
79.46008	0.989583	1.177083
79.4797	1.010417	1.03125
79.49933	1.072917	1.125
79.51896	1.1875	1.104167
79.53858	1.145833	1.114583
79.55821	1.104167	1.291667
79.57784	0.979167	1.385417
79.59747	1.25	1.15625
79.61709	1.302083	1.260417

79.63672	1.28125	1.177083
79.65635	1.322917	1.302083
79.67597	1.302083	1.40625
79.6956	1.1875	1.145833
79.71523	1.09375	1.21875
79.73486	1.291667	1.177083
79.75448	1.135417	0.927083
79.77411	1.09375	1.072917
79.79374	1.145833	1.104167
79.81336	1.4375	1.302083
79.83299	1.208333	1.114583
79.85262	1.197917	1.083333
79.87224	1.239583	1.177083
79.89187	1.1875	1.239583
79.9115	1.208333	1.229167
79.93113	1.59375	1.375
79.95075	1.208333	1.072917
79.97038	1.197917	1.1875
79.99001	1.15625	1.229167
80.00963	1.302083	1.40625
80.02926	1.0625	1.1875
80.04889	1.1875	1.270833
80.06851	1.364583	1.114583
80.08814	1.166667	1.072917
80.10777	1.25	1.260417
80.1274	1.260417	1.270833
80.14702	1.0625	1.104167
80.16665	1.260417	1.302083
80.18628	1.25	1.333333
80.2059	1.229167	1.125
80.22553	1.09375	1.239583
80.24516	0.958333	1.125
80.26478	1.166667	1.020833
80.28441	1.21875	1.229167
80.30404	0.989583	1.427083
80.32367	1.229167	1.354167
80.34329	1.1875	1.125
80.36292	1.135417	1.166667
80.38255	1.125	1.09375
80.40217	1.010417	1.145833
80.4218	1.09375	1.322917
80.44143	1.229167	1.166667
80.46105	1.28125	1.09375
80.48068	1.114583	1.1875
80.50031	1.010417	1.260417

80.51994	1.020833	1.21875
80.53956	1.09375	1.0625
80.55919	1.25	1.083333
80.57882	1.270833	1.041667
80.59844	1.166667	1.104167
80.61807	1.229167	1.177083
80.6377	1.1875	1.03125
80.65732	1.21875	1.34375
80.67695	1.09375	0.947917
80.69658	1.166667	1.197917
80.71621	1.270833	1.21875
80.73583	1.135417	1.322917
80.75546	0.989583	1.260417
80.77509	1.416667	1.09375
80.79471	1.28125	1.541667
80.81434	1.291667	1.291667
80.83397	1.302083	1.291667
80.85359	1.1875	1.0625
80.87322	0.989583	1.208333
80.89285	1.322917	1.114583
80.91248	1.354167	1.09375
80.9321	1.104167	1.177083
80.95173	1.114583	1.270833
80.97136	1.083333	1.15625
80.99098	1.125	1.395833
81.01061	1.333333	1.322917
81.03024	1.385417	1.21875
81.04986	1.145833	1.197917
81.06949	1.25	1.260417
81.08912	1.177083	1.239583
81.10875	1.291667	1.322917
81.12837	1.239583	1.427083
81.148	1.302083	1.3125
81.16763	1.166667	1.302083
81.18725	1.395833	1.447917
81.20688	1.416667	1.21875
81.22651	1.541667	1.208333
81.24613	1.333333	1.270833
81.26576	1.1875	1.4375
81.28539	1.46875	1.270833
81.30502	1.385417	1.364583
81.32464	1.125	1.333333
81.34427	1.291667	1.625
81.3639	1.385417	1.229167
81.38352	1.385417	1.427083

81.40315	1.6875	1.520833
81.42278	1.645833	1.583333
81.4424	1.583333	1.760417
81.46203	1.5	1.572917
81.48166	1.322917	1.5
81.50129	1.177083	1.427083
81.52091	1.4375	1.71875
81.54054	1.260417	1.5
81.56017	1.541667	1.479167
81.57979	1.40625	1.635417
81.59942	1.614583	1.34375
81.61905	1.333333	1.604167
81.63867	1.375	1.572917
81.6583	1.1875	1.15625
81.67793	1.447917	1.270833
81.69756	1.541667	1.447917
81.71718	1.604167	1.427083
81.73681	1.479167	1.40625
81.75644	1.416667	1.458333
81.77606	1.458333	1.104167
81.79569	1.510417	1.260417
81.81532	1.625	1.3125
81.83494	1.666667	1.583333
81.85457	1.458333	1.25
81.8742	1.375	1.479167
81.89383	1.40625	1.541667
81.91345	1.291667	1.3125
81.93308	1.1875	1.21875
81.95271	1.25	1.333333
81.97233	1.197917	1.333333
81.99196	1.302083	1.385417
82.01159	1.135417	1.395833
82.03121	1.3125	1.125
82.05084	1.260417	1.354167
82.07047	1.5625	1.145833
82.0901	1.354167	1.1875
82.10972	1.270833	1.15625
82.12935	1.53125	1.125
82.14898	1.302083	1.3125
82.1686	1.489583	1.1875
82.18823	1.25	1.416667
82.20786	1.3125	1.25
82.22748	1.104167	1.510417
82.24711	1.1875	1.34375
82.26674	1.34375	1.427083

82.28637	1.15625	1.40625
82.30599	1.260417	1.270833
82.32562	1.302083	1.09375
82.34525	1.302083	1.208333
82.36487	1.34375	1.322917
82.3845	0.96875	1.291667
82.40413	1.197917	1.302083
82.42375	1.083333	1
82.44338	1.239583	1.28125
82.46301	1.364583	1.197917
82.48264	0.96875	1.145833
82.50226	1.322917	1.072917
82.52189	1.135417	1.177083
82.54152	1.28125	1.3125
82.56114	1.385417	1.208333
82.58077	1.229167	1.114583
82.6004	1.145833	1.010417
82.62003	1.375	1.28125
82.63965	1.416667	1.34375
82.65928	1.427083	1.427083
82.67891	1.145833	1.3125
82.69853	1.229167	1.458333
82.71816	1.333333	1.385417
82.73779	1.197917	1.166667
82.75741	1.375	1.21875
82.77704	1.270833	1.125
82.79667	1.520833	1.28125
82.8163	1.385417	1.239583
82.83592	1.552083	1.197917
82.85555	1.291667	1.395833
82.87518	1.25	1.25
82.8948	1.447917	1.364583
82.91443	1.354167	1.270833
82.93406	1.322917	1.40625
82.95368	1.1875	1.239583
82.97331	1.291667	1.166667
82.99294	1.385417	1.28125
83.01257	1.385417	1.333333
83.03219	1.208333	1.291667
83.05182	1.395833	1.21875
83.07145	1.489583	1.229167
83.09107	1.375	1.260417
83.1107	1.395833	1.270833
83.13033	1.46875	1.458333
83.14995	1.322917	1.479167

83.16958	1.5	1.083333
83.18921	1.333333	1.364583
83.20884	1.677083	1.5625
83.22846	1.364583	1.354167
83.24809	1.34375	1.375
83.26772	1.322917	1.270833
83.28734	1.395833	1.208333
83.30697	1.229167	1.34375
83.3266	1.21875	1.458333
83.34622	1.583333	1.302083
83.36585	1.15625	1.322917
83.38548	1.333333	1.395833
83.40511	1.322917	1.197917
83.42473	1.239583	1.302083
83.44436	1.40625	1.364583
83.46399	1.270833	1.40625
83.48361	1.416667	1.395833
83.50324	1.416667	1.375
83.52287	1.5	1.677083
83.54249	1.395833	1.427083
83.56212	1.53125	1.364583
83.58175	1.635417	1.552083
83.60138	1.53125	1.354167
83.621	1.604167	1.666667
83.64063	1.416667	1.604167
83.66026	1.447917	1.229167
83.67988	1.729167	1.71875
83.69951	1.65625	1.541667
83.71914	1.489583	1.53125
83.73876	1.572917	1.59375
83.75839	1.572917	1.802083
83.77802	1.458333	1.604167
83.79765	1.677083	1.427083
83.81727	1.708333	1.65625
83.8369	1.614583	1.541667
83.85653	1.864583	1.46875
83.87615	1.895833	1.625
83.89578	1.989583	1.53125
83.91541	2.25	1.59375
83.93503	2.135417	1.802083
83.95466	2	1.833333
83.97429	1.59375	1.46875
83.99392	1.895833	1.4375
84.01354	1.885417	1.760417
84.03317	1.447917	1.739583

84.0528	1.447917	1.708333
84.07242	1.697917	1.53125
84.09205	1.677083	1.677083
84.11168	1.625	1.5625
84.1313	1.739583	1.572917
84.15093	2.020833	1.770833
84.17056	1.645833	1.645833
84.19019	1.739583	1.65625
84.20981	1.84375	1.520833
84.22944	1.479167	1.510417
84.24907	1.552083	1.53125
84.26869	1.354167	1.354167
84.28832	1.46875	1.385417
84.30795	1.479167	1.333333
84.32757	1.375	1.427083
84.3472	1.229167	1.416667
84.36683	1.125	1.447917
84.38646	1.166667	1.479167
84.40608	1.3125	1.46875
84.42571	1.375	1.34375
84.44534	1.489583	1.333333
84.46496	1.3125	1.40625
84.48459	1.114583	1.28125
84.50422	1.21875	1.1875
84.52384	1.020833	1.395833
84.54347	1.135417	1.177083
84.5631	1.291667	1.197917
84.58273	1.291667	1.5
84.60235	1.291667	1.34375
84.62198	1.302083	1.427083
84.64161	1.145833	1.25
84.66123	1.072917	1.489583
84.68086	1.291667	1.416667
84.70049	1.239583	1.15625
84.72011	1.364583	1.197917
84.73974	1.239583	1.375
84.75937	1.229167	1.322917
84.779	1.1875	1.375
84.79862	1.34375	1.239583
84.81825	1.302083	1.1875
84.83788	1.333333	1.28125
84.8575	1.052083	1.239583
84.87713	1.0625	1.385417
84.89676	1.302083	1.260417
84.91638	1.166667	1.15625

84.93601	1.114583	1.208333
84.95564	1.208333	1.270833
84.97527	1.135417	1.28125
84.99489	1.229167	1.177083
85.01452	1.1875	1.135417
85.03415	1.229167	1.197917
85.05377	1.166667	1.239583
85.0734	1.083333	1.34375
85.09303	1.135417	1.260417
85.11265	1.135417	1.177083
85.13228	1.15625	1.0625
85.15191	1.0625	1.15625
85.17154	1.166667	1.15625
85.19116	1.1875	1.1875
85.21079	1.1875	1.114583
85.23042	1.114583	1.229167
85.25004	1.1875	1.114583
85.26967	1.1875	1.354167
85.2893	1.177083	1.177083
85.30892	1.114583	1.270833
85.32855	1.489583	1.354167
85.34818	1.260417	1.1875
85.36781	1.302083	1.052083
85.38743	1.197917	1.15625
85.40706	1.28125	1.104167
85.42669	0.958333	1.28125
85.44631	1.375	1.21875
85.46594	1.229167	1.1875
85.48557	1.375	1.15625
85.5052	1.052083	1.270833
85.52482	1.03125	1.072917
85.54445	0.979167	1.1875
85.56408	1.291667	1.166667
85.5837	1.041667	1.15625
85.60333	1.291667	1.135417
85.62296	1.25	1.364583
85.64258	1.104167	1.25
85.66221	1.041667	1.09375
85.68184	0.989583	0.979167
85.70147	0.989583	1.135417
85.72109	1.177083	0.927083
85.74072	1.135417	1.177083
85.76035	1.125	1.104167
85.77997	0.864583	1.052083
85.7996	1.135417	1

85.81923	0.947917	1.125
85.83885	0.895833	1.15625
85.85848	1.104167	1.114583
85.87811	1.083333	0.96875
85.89774	0.916667	1.020833
85.91736	0.958333	1.135417
85.93699	1.03125	1.0625
85.95662	1.0625	1.1875
85.97624	1.09375	0.90625
85.99587	0.958333	1.166667
86.0155	1.15625	1.21875
86.03512	1.052083	1.104167
86.05475	1.020833	1.21875
86.07438	0.885417	1.125
86.09401	1.020833	1.166667
86.11363	1.125	1.114583
86.13326	1.125	1.15625
86.15289	0.9375	1
86.17251	1.125	1.114583
86.19214	0.854167	1.166667
86.21177	0.9375	1.09375
86.23139	1.03125	1.104167
86.25102	0.979167	1
86.27065	1.0625	1.125
86.29028	1	1.21875
86.3099	1.083333	1.0625
86.32953	1.145833	1.166667
86.34916	0.916667	1.291667
86.36878	1.1875	1.03125
86.38841	0.916667	1.041667
86.40804	1.208333	1.166667
86.42766	1.135417	1.083333
86.44729	0.9375	0.958333
86.46692	0.895833	1.208333
86.48655	1.177083	0.989583
86.50617	1.135417	1.3125
86.5258	1.21875	1.302083
86.54543	1.15625	1.197917
86.56505	1.385417	1.15625
86.58468	1.104167	1.166667
86.60431	1.145833	1.0625
86.62393	1.46875	1.229167
86.64356	1.145833	1.041667
86.66319	1.3125	1.041667
86.68282	1.135417	1.177083

86.70244	1.322917	1.34375
86.72207	1.46875	1.15625
86.7417	1.208333	1.135417
86.76132	0.9375	1.09375
86.78095	1.177083	1.114583
86.80058	1.052083	1.260417
86.8202	1.125	0.864583
86.83983	1.104167	1.260417
86.85946	1.260417	1.375
86.87909	1.3125	1.166667
86.89871	1.260417	0.989583
86.91834	1.229167	1.260417
86.93797	1.291667	1.21875
86.95759	1.385417	1.291667
86.97722	1.229167	1.416667
86.99685	1.427083	1.354167
87.01647	1.333333	1.0625
87.0361	1.40625	1.427083
87.05573	1.322917	1.28125
87.07536	1.3125	1.375
87.09498	1.4375	1.375
87.11461	1.375	1.1875
87.13424	1.375	1.479167
87.15386	1.322917	1.28125
87.17349	1.28125	1.333333
87.19312	1.395833	1.333333
87.21274	1.416667	1.291667
87.23237	1.604167	1.354167
87.252	1.46875	1.364583
87.27163	1.59375	1.583333
87.29125	1.375	1.3125
87.31088	1.510417	1.635417
87.33051	1.260417	1.3125
87.35013	1.260417	1.395833
87.36976	1.458333	1.072917
87.38939	1.65625	1.677083
87.40901	1.40625	1.4375
87.42864	1.427083	1.489583
87.44827	1.53125	1.4375
87.4679	1.28125	1.8125
87.48752	1.3125	1.447917
87.50715	1.166667	1.25
87.52678	1.458333	1.604167
87.5464	1.322917	1.489583
87.56603	1.4375	1.53125

87.58566	1.364583	1.25
87.60528	1.510417	1.239583
87.62491	1.416667	1.4375
87.64454	1.239583	1.1875
87.66417	1.4375	1.333333
87.68379	1.375	1.239583
87.70342	1.4375	1.145833
87.72305	1.375	1.239583
87.74267	1.25	1.072917
87.7623	1.59375	1.375
87.78193	1.333333	1.385417
87.80155	1.291667	1.322917
87.82118	1.21875	1.354167
87.84081	1.302083	1.260417
87.86044	1.583333	1.3125
87.88006	1.3125	1.291667
87.89969	1.270833	1.427083
87.91932	1.28125	1.541667
87.93894	1.53125	1.395833
87.95857	1.28125	1.270833
87.9782	1.25	1.333333
87.99782	1.21875	1.260417
88.01745	1.3125	1.34375
88.03708	1.239583	1.28125
88.05671	1.1875	1.28125
88.07633	1.385417	1.229167
88.09596	1.354167	1.322917
88.11559	1.40625	1.25
88.13521	1.4375	1.166667
88.15484	1.416667	1.208333
88.17447	1.302083	1.1875
88.19409	1.46875	1.447917
88.21372	1.604167	1.34375
88.23335	1.489583	1.34375
88.25298	1.541667	1.46875
88.2726	1.614583	1.552083
88.29223	1.479167	1.302083
88.31186	1.260417	1.510417
88.33148	1.458333	1.364583
88.35111	1.3125	1.46875
88.37074	1.510417	1.375
88.39036	1.354167	1.4375
88.40999	1.447917	1.270833
88.42962	1.614583	1.697917
88.44925	1.291667	1.375

88.46887	1.302083	1.604167
88.4885	1.270833	1.25
88.50813	1.125	1.447917
88.52775	1.260417	1.291667
88.54738	1.270833	1.229167
88.56701	1.197917	1.09375
88.58664	1.333333	1.28125
88.60626	1.260417	1.28125
88.62589	1.21875	1.208333
88.64552	1.114583	1.145833
88.66514	1.1875	1.333333
88.68477	1.041667	1.28125
88.7044	1.104167	1.4375
88.72402	1.229167	1.229167
88.74365	0.84375	1.395833
88.76328	1.375	1.25
88.78291	1.229167	1.166667
88.80253	1.166667	1.260417
88.82216	0.90625	1.1875
88.84179	1.104167	0.875
88.86141	1.072917	1.09375
88.88104	1.083333	1.104167
88.90067	0.8125	1.177083
88.92029	0.958333	1.229167
88.93992	0.864583	0.885417
88.95955	1.197917	1.0625
88.97918	1.020833	1.041667
88.9988	1	1.104167
89.01843	1.083333	1.135417
89.03806	0.9375	1.020833
89.05768	1.114583	1.010417
89.07731	0.875	1.135417
89.09694	1.020833	1.145833
89.11656	0.895833	1.0625
89.13619	1.0625	1.15625
89.15582	1.291667	1.177083
89.17545	1.135417	1.21875
89.19507	0.90625	1.09375
89.2147	1.052083	0.989583
89.23433	0.9375	0.947917
89.25395	0.958333	1.114583
89.27358	1.083333	0.885417
89.29321	0.979167	1.020833
89.31283	0.947917	1.020833
89.33246	1.21875	1.197917

89.35209	0.947917	1.010417
89.37172	0.96875	1.072917
89.39134	0.958333	1.145833
89.41097	1.03125	1
89.4306	0.958333	1.114583
89.45022	1.125	1.114583
89.46985	1.0625	0.90625
89.48948	1.125	1.28125
89.5091	1.15625	1.104167
89.52873	1.03125	1.21875
89.54836	1.041667	1.0625
89.56799	1.072917	1.177083
89.58761	0.947917	1.291667
89.60724	1.052083	1.145833
89.62687	1.21875	1.104167
89.64649	1.114583	1.09375
89.66612	1.072917	1.25
89.68575	1.0625	1.1875
89.70537	0.989583	1.104167
89.725	1.052083	1.072917
89.74463	1.041667	1.114583
89.76426	1.072917	1.104167
89.78388	1.166667	1.010417
89.80351	1.03125	1.072917
89.82314	0.96875	1.125
89.84276	1.0625	0.96875
89.86239	1	0.9375
89.88202	1.197917	0.989583
89.90164	1.15625	1.104167
89.92127	1.09375	1.010417
89.9409	0.864583	0.9375
89.96053	1.041667	1.177083
89.98015	1.010417	1.020833
89.99978	0.895833	1.104167

SI 4.4 A: XRD peaks and intensities

SI 4.4 A data were used to underpin the hydroxylapatite, calcite and kalcinite peaks seen in SI 4.4

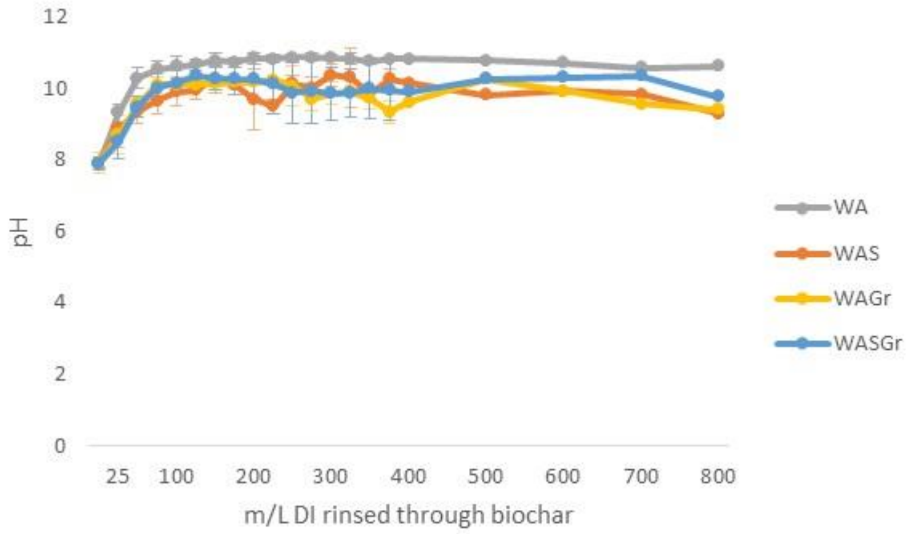
Eluate analysis

	PO_4^{3-} (mg/L)		SO_4^{2-} (mg/L)		NO_3^{-} (mg/L)	
mL DI	WASGr	SD	WASGr	SD	WASGr	SD
25	0.85	0.04	0.00	0.00	43.54	2.88
50	0.59	0.14	245.47	9.39	5.92	0.29
75	0.49	0.20	142.38	12.15	3.00	0.28
125	0.39	0.22	82.54	5.55	1.52	0.10
175	0.34	0.15	58.67	4.57	0.96	0.23
250	0.26	0.14	41.12	4.99	0.63	0.13
375	0.00	0.00	29.76	5.29	0.44	0.08
800	0.00	0.00	15.45	2.82	0.34	0.00
mL DI	WAGr	SD	WAGr	SD	WAGr	SD
25	0.72	0.16	0.00	0.00	45.99	14.58
50	0.37	0.31	213.24	91.49	5.45	3.16
75	0.31	0.14	139.34	15.16	2.96	0.19
125	0.00	0.00	60.07	30.10	1.07	0.44
175	0.00	0.00	58.40	8.72	3.61	4.41
250	0.00	0.00	38.13	3.01	0.60	0.17
375	0.00	0.00	18.30	8.98	1.69	1.89
800	0.00	0.00	31.93	20.68	0.69	0.54
mL DI	WA	SD	WA	SD	WA	SD
25	0.83	0.39	0.00	0.00	45.16	11.13
50	0.36	0.11	301.56	126.92	10.81	5.87
75	0.46	0.22	232.28	98.99	4.88	2.47
125	0.37	0.18	114.04	44.01	1.78	1.00
175	0.44	0.03	71.03	23.66	1.05	0.43
250	0.31	0.17	45.84	11.50	0.65	0.27
375	0.21	0.06	28.67	4.66	0.38	0.09
800	0.29	0.00	15.56	1.95	0.00	0.00
mL DI	WAS	SD	WAS	SD	WAS	SD
25	0.68	0.22	551.96	0.00	25.03	7.56
50	0.47	0.09	529.44	47.23	13.94	2.66
75	0.30	0.05	347.84	77.19	6.93	2.67
125	0.22	0.03	171.79	35.81	2.55	0.55
175	0.21	0.02	102.19	6.51	1.54	0.22
250	0.19	0.03	57.05	3.94	1.02	0.09
375	0.22	0.05	29.23	3.71	0.68	0.11
800	0.18	0.03	13.30	2.54	0.43	0.03

SI 4.5: Concentration of nutrients leached from wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash

sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) data

SI 4.5 data was used to populate figures 4.4, 4.5 and 4.6 (results and discussion section of chapter 4). These form the basis to understand the effect of rinsing biochar on the leaching of nutrients.



SI 4.6: Eluate pH measurements for wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) mg/L when rinsed by 0mL to 800mL of deionised water

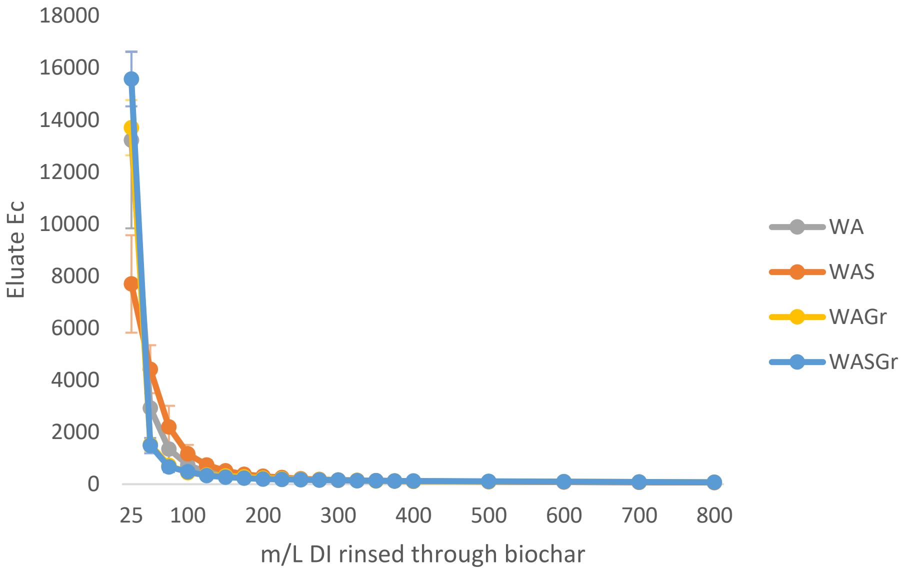
mL	WA pH	SD	delta pH	WAS pH	SD	delta pH	WAGr pH	SD	delta pH	WASGr pH	SD	delta pH
25	9.32	0.16	1.42	8.86	0.11	0.96	8.70	0.29	0.80	8.51	0.20	0.61
50	10.29	0.24	2.39	9.34	0.50	1.44	9.53	0.52	1.63	9.48	0.50	1.58
75	10.54	0.28	2.64	9.65	0.34	1.75	10.10	0.22	2.20	10.00	0.29	2.10
100	10.62	0.23	2.72	9.89	0.34	1.99	10.10	0.22	2.20	10.15	0.39	2.25
125	10.66	0.28	2.76	9.95	0.40	2.05	10.10	0.22	2.20	10.34	0.34	2.44
150	10.78	0.14	2.88	10.28	0.28	2.38	10.13	0.12	2.23	10.29	0.36	2.39
175	10.73	0.20	2.83	10.11	0.42	2.21	10.17	0.05	2.27	10.26	0.34	2.36
200	10.84	0.13	2.94	9.69	0.10	1.79	10.17	0.12	2.27	10.26	0.44	2.36
225	10.82	0.15	2.92	9.50	0.87	1.60	10.23	0.05	2.33	10.12	0.53	2.22
250	10.86	0.11	2.96	10.12	0.21	2.22	10.07	0.05	2.17	9.88	0.82	1.98
275	10.87	0.10	2.97	10.02	0.22	2.12	9.70	0.57	1.80	9.92	0.84	2.02
300	10.84	0.10	2.94	10.37	0.30	2.47	9.87	0.34	1.97	9.85	0.90	1.95
325	10.82	0.08	2.92	10.30	0.30	2.40	9.90	0.29	2.00	9.87	0.75	1.97
350	10.76	0.15	2.86	9.83	0.83	1.93	9.73	0.09	1.83	9.99	0.68	2.09
375	10.82	0.10	2.92	10.25	0.09	2.35	9.33	0.33	1.43	9.95	0.84	2.05
400	10.82	0.06	2.92	10.14	0.28	2.24	9.60	0.29	1.70	9.90	0.86	2.00
500	10.79	0.23	2.89	9.82	0.59	1.92	10.27	0.26	2.37	10.27	0.25	2.37
600	10.70	0.17	2.80	9.94	0.51	2.04	9.93	0.59	2.03	10.32	0.17	2.42
700	10.58	0.32	2.68	9.84	0.50	1.94	9.57	0.46	1.67	10.34	0.11	2.44
800	10.62	0.22	2.72	9.31	0.71	1.41	9.40	0.65	1.50	9.76	0.68	1.86

SI 4.6 A: Eluate pH measurements for wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) mg/L when rinsed by 0mL to 800mL of deionised water data

SI 4.6 A is the data that is used to populate the eluate pH figure for SI 4.4 forming part of the same discussion

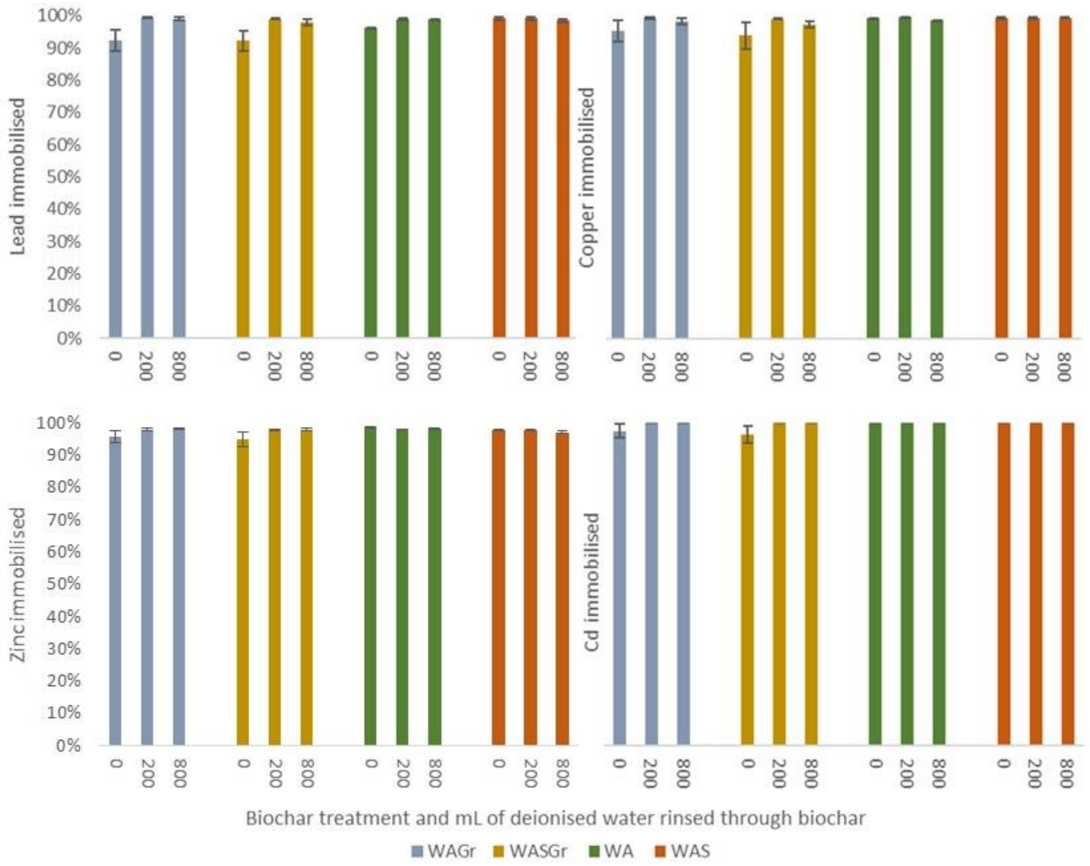
mL	WA EC (µS)	SD	WAS EC (µS)	SD	WAGr EC (µS)	SD	WASGr EC (µS)	SD
25	13223	3389	7697	1874	13700	1061	15577	1054
50	2923	1430	4420	922	1522	255	1482	295
75	1358	643	2207	806	726	97	658	194
100	737	297	1173	338	447	36	479	162
125	465	165	741	187	359	35	338	94
150	343	102	522	94	319	12	273	49
175	270	72	380	48	277	11	238	27
200	229	50	311	48	236	13	199	23
225	199	42	260	24	206	11	186	20
250	180	28	212	21	187	11	170	29
275	162	24	185	23	176	14	160	27
300	148	19	164	22	164	3	157	30
325	139	18	144	20	151	6	141	19
350	130	13	133	16	124	30	133	18
375	122	12	121	17	117	19	128	17
400	118	10	115	13	112	13	122	25
500	99	9	95	10	102	3	106	11
600	87	7	81	7	97	6	94	9
700	79	7	71	5	85	4	81	12
800	68	3	65	4	75	3	73	4

SI 4.7A: Eluate EC measurements for wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) mg/L when rinsed by 0mL to 800mL of deionised water data



SI 4.7B: Eluate EC measurements for wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) mg/L when rinsed by 0mL to 800mL of deionised water

4.3.3 Lead, copper, zinc and cadmium immobilisation



SI 4.8: Immobilisation by wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) mg/L when rinsed by 0mL, 200mL and 800mL of (A) lead, (B) copper, (C) zinc and (D) cadmium. The concentration of metals in solution was 10 mg/L.

SI 4.8 data are referred to in section 4.3.3 (results and discussion section of chapter 4) in reference to continued immobilisation of Pb, Cu, Zn and Cd for wood ash amended biochar that had been unrinsed and rinsed. Biochar that has been rinsed to mitigate nutrient leaching was still able to immobilise these metals.

	Cd % immobilised	Sd	Pb % immobilised	Sd	Zn % immobilised	Sd	Cu % immobilised	Sd
WAGr 0	98%	0.02	92%	0.03	96%	0.02	95%	0.03
WAGr 200	100%	0.00	99%	0.00	98%	0.00	99%	0.00
WAGr 800	100%	0.00	99%	0.00	98%	0.00	98%	0.01
WASGr 0	97%	0.03	92%	0.03	95%	0.02	94%	0.04
WASGr 200	100%	0.00	99%	0.00	98%	0.00	99%	0.00
WASGr 800	100%	0.00	98%	0.01	98%	0.00	97%	0.01
WA 0	100%	0.00	96%	0.00	99%	0.00	99%	0.00
WA 200	100%	0.00	99%	0.00	98%	0.00	99%	0.00
WA 800	100%	0.00	99%	0.00	98%	0.00	99%	0.00
WAS 0	100%	0.00	99%	0.00	98%	0.00	99%	0.00
WAS 200	100%	0.00	99%	0.00	98%	0.00	99%	0.00

WAS 800	100%	0.00	98%	0.00	97%	0.01	99%	0.00

SI 4.8A: Immobilisation by wood ash mixed cold with larch biochar (WA), wood ash mixed cold and granulated to <3mm (WAGr), wood ash sintered to larch biochar (WAS) and wood ash sintered to larch biochar and granulated to <3mm (WASGr) mg/L when rinsed by 0mL, 200mL and 800mL of (A) lead, (B) copper, (C) zinc and (D) cadmium data

SI 4.8A data are referred to in section 4.3.3 (results and discussion section of chapter 4) in reference to continued immobilisation of Pb, Cu, Zn and Cd for wood ash amended biochar that had been unrinsed and rinsed. Biochar that has been rinsed to mitigate nutrient leaching was still able to immobilise these metals.

iii) Supplementary material: Chapter 5

Contaminant removal time-scales

	Zn	Zn mg/L removed	% Zn removed	St Dev
1 min 1	0.25	10.27	98%	
1 min 2	0.28	10.24	97%	
1 min 3	0.37	10.15	96%	
1 min av	0.30	10.22	97%	0.5%
5 min 1	0.08	10.44	99%	
5 min 2	0.15	10.37	99%	
5 min 3	0.12	10.40	99%	
5 min av	0.12	10.40	99%	0.3%
15 min 1	0.18	10.34	98%	
15 min 2	0.01	10.51	100%	
15 min 3	0.06	10.46	99%	
15 min av	0.08	10.43	99%	0.7%
30 min 1	0.19	10.33	98%	
30 min 2	0.10	10.42	99%	
30 min 3	0.08	10.44	99%	
30 min av	0.12	10.40	99%	0.5%
1 hr 1	0.03	10.49	100%	
1 hr 2	0.00	10.52	100%	
1 hr 3	0.01	10.51	100%	
1 hr av	0.00	10.51	100%	0.1%
24 hr 1	0.00	10.52	100%	
24 hr 2	0.00	10.52	100%	
24 hr3	0.00	10.52	100%	
24 hr av	0.00	10.52	100%	0.0%
no bc 1	10.38	0.14	1%	
no bc 2	10.67	-0.15	-1%	
no bc 3	10.51	0.01	0%	
no bc av	10.52	0.00	0%	

SI 5.1A: immobilisation of Zn from Deep Boat Level mine water by larch biochar sintered with wood ash (WAS). SD (n=3).

SI 5.1A is the data to support figure 5.3A (results and discussion section of chapter 5)

	Zn	Zn mg/L removed	% Zn removed	St Dev
1 min 1	0.34	10.00	97%	
1 min 2	0.17	10.18	98%	
1 min 3	0.33	10.01	97%	
1 min av	0.28	10.06	97%	0.01
5 min 1	0.29	10.05	97%	
5 min 2	0.40	9.94	96%	
5 min 3	1.00	9.34	90%	
5 min av	0.56	9.78	95%	0.03
15 min 1	0.18	10.16	98%	
15 min 2	0.12	10.22	99%	
15 min 3	0.41	9.93	96%	
15 min av	0.24	10.10	98%	0.01
30 min 1	1.20	9.14	88%	
30 min 2	0.29	10.05	97%	
30 min 3	0.47	9.87	95%	
30 min av	0.65	9.69	94%	0.04
1 hr 1	0.73	9.61	93%	
1 hr 2	0.07	10.27	99%	
1 hr 3	0.08	10.26	99%	
1 hr av	0.29	10.05	97%	0.03
24 hr 1	0.07	10.27	99%	
24 hr 2	0.03	10.31	100%	
24 hr3	0.04	10.30	100%	
24 hr av	0.05	10.29	100%	0.00
no bc 1	11.01			
no bc 2	11.07			
no bc 3	8.94			
no bc av	10.34			

SI 5.1B: immobilisation of Zn from Tributary1 mine water by larch biochar sintered with wood ash (WAS). SD (n=3).

SI 5.1B is the data to support figure 5.3B (results and discussion section of chapter 5)

	Pb	Pb mg/L removed	% Pb removed	St Dev
1 min 1	0.26	1.32	83%	
1 min 2	0.15	1.43	90%	
1 min 3	0.23	1.34	85%	
1 min av	0.22	1.36	86%	0.03
5 min 1	0.22	1.36	86%	
5 min 2	0.26	1.32	83%	
5 min 3	0.55	1.03		
5 min av	0.34	1.23	85%	0.01
15 min 1	0.17	1.41	90%	
15 min 2	0.15	1.43	90%	
15 min 3	0.26	1.32	83%	
15 min av	0.19	1.38	88%	0.03
30 min 1	0.63	0.94		
30 min 2	0.23	1.34	85%	
30 min 3	0.30	1.27	81%	
30 min av	0.43	1.19	83%	0.02
1 hr 1	0.32	1.26	92%	
1 hr 2	0.12	1.45	92%	
1 hr 3	0.12	1.45	92%	
1 hr av	0.19	1.39	92%	0.00
24 hr 1	0.14	1.44	91%	
24 hr 2	0.10	1.48	94%	
24 hr3	0.11	1.47	93%	
24 hr av	0.11	1.46	93%	0.01
no bc 1	1.53			
no bc 2	1.44			
no bc 3	1.76			
no bc av	1.58			

SI 5.1C: immobilisation of Pb from Tributary1 mine water by larch biochar sintered with wood ash (WAS). SD (n=3).

SI 5.1C is the data to support figure 5.3B (results and discussion section of chapter 5)

Immobilization mechanisms

	Lower boat level pH	Trib 1 pH
no bc	**7.32**	**7.6**
1 min 1	8.12	8.7
1 min 2	8.24	9.0
1 min 3	8.15	8.9
1 min	**8.17**	**8.9**
5 min 1	8.67	9.1
5 min 2	8.57	9.1
5 min 3	8.58	9.1
5 min	**8.61**	**9.1**
15 min 1	8.85	9.2
15 min 2	8.95	9.2
15 min 3	8.97	9.3
15 min	**8.92**	**9.2**
30 min 1	9.1	9.4
30 min 2	9.11	9.5
30 min 3	9.15	10
30 min	**9.12**	**9.5**
1 hr 1	9.16	9.5
1 hr 2	9.25	9.3
1 hr 3	9.17	9.5
1 hr	**9.19**	**9.4**
24 hr 1	9.59	9.5
24 hr 2	9.68	9.5
24 hr3	9.77	9.6
24 hr	**9.68**	**9.5**
no bc 1	7.26	7.6
no bc 2	7.33	7.7
no bc 3	7.36	7.5
no bc	**7.32**	**7.6**

No mine water 1	10.71	10.0
No mine water 2	10.95	9.9
No mine water 3	10.84	9.9
No mine water	**10.83**	**9.9**

SI 5.2: Lower Boat Level and Tributary 1 pH values after contact for a known period of time with larch biochar sintered with wood ash (WAS). SD (n=3).

SI 5.2 is the data to support figure 5.4A (results and discussion section of chapter 5)

	Lower Boat Level pH change	St Dev	Tributary 1 pH change	St Dev
1 min 1	0.8		1.1	
1 min 2	0.9		1.4	
1 min 3	0.8		1.3	
1 min	**0.9**	**0.05**	**1.3**	**0.12**
5 min 1	1.4		1.5	
5 min 2	1.3		1.5	
5 min 3	1.3		1.5	
5 min	**1.3**	**0.045**	**1.5**	**0.00**
15 min 1	1.5		1.6	
15 min 2	1.6		1.6	
15 min 3	1.7		1.7	
15 min	**1.6**	**0.052**	**1.6**	**0.05**
30 min 1	1.8		1.8	
30 min 2	1.8		1.9	
30 min 3	1.8		1.9	
30 min	**1.8**	**0.022**	**1.9**	**0.05**
1 hr 1	1.8		1.9	
1 hr 2	1.9		1.7	
1 hr 3	1.9		1.9	
1 hr	**1.9**	**0.040**	**1.8**	**0.09**
24 hr 1	2.3		1.9	
24 hr 2	2.4		1.9	
24 hr3	2.5		2.0	

24 hr	**2.4**	**0.073**	**1.9**	**0.05**
No mine water 1	3.4		2.4	
No mine water 2	3.6		2.3	
No mine water 3	3.5		2.3	
No mine water	3.5	0.098	2.3	0.05

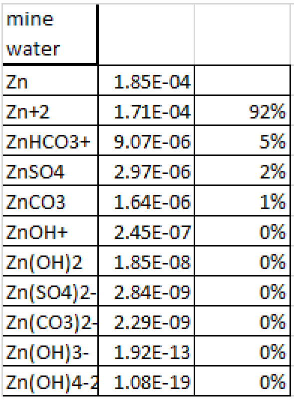
SI 5.3: Lower Boat Level and Tributary 1 changes to pH values after contact for a known period of time with larch biochar sintered with wood ash (WAS). SD (n=3).

SI 5.3 is the data to support figure 5.4A (results and discussion section of chapter 5)

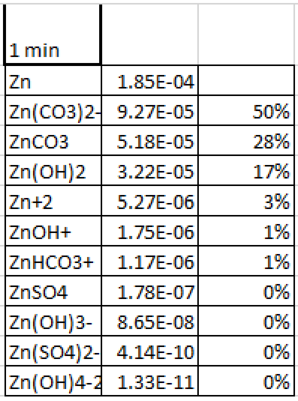
	units	pre WAS	1 min	5 min	15 min	30 min	1 hr	24 hr
temp	°C	15.2	15.2	15.2	15.2	15.2	15.2	15.2
pH		6.5	8.9	9.1	9.2	9.5	9.4	9.5
pe		7.4	7.4	7.4	7.4	7.4	7.4	7.4
Al	ppb	72.7	72.7	72.7	72.7	72.7	72.7	72.7
Alkalinity		26	155	160	170	190	190	190
Ca	ppm	2.9	6.2	5.6	7.3	16.0	11.3	5.5
Cd	ppb	42.9	42.9	42.9	42.9	42.9	42.9	42.9
Cu	ppb	16.4	16.4	16.4	16.4	16.4	16.4	16.4
K	ppm	0.9	35.6	27.9	36.2	38.3	42.8	39.0
Mg	ppm	2.5	5.4	6.0	5.4	7.0	6.6	5.78
N(3)	ppm		0.04	0.04	0.04	0.04	0.04	0.04
N(5)	ppm		0.3	0.3	0.3	0.3	0.3	0.3
P	ppm		0.3	0.3	0.3	0.3	0.3	0.3
Na	ppm	3.0	32.9	29.7	37.1	38	38.3	37.6
Pb	ppm	1.7	1.7	1.7	1.7	1.7	1.7	1.7
P	ppm		0.34	0.34	0.34	0.34	0.34	0.34
Zn	ppm	12.1	12.1	12.1	12.1	12.1	12.1	12.1
S(6)	ppm	11.0	26.5	26.5	26.5	26.5	26.5	26.5

SI 5.4A: PHREEQC inputs for contact time speciation analysis

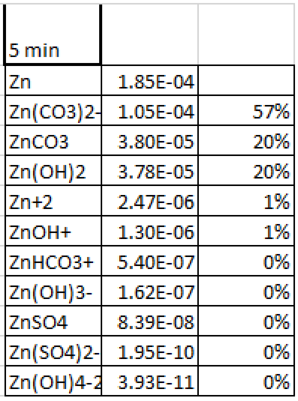
SI 5.4A is the data to support figure 5.4B and C (results and discussion section of chapter 5)



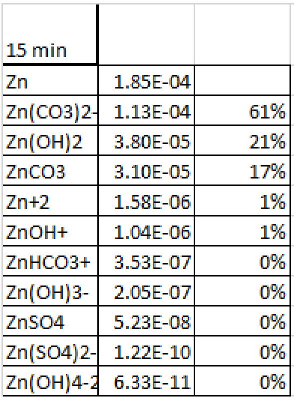
mine water		
Zn	1.85E-04	
Zn+2	1.71E-04	92%
ZnHCO3+	9.07E-06	5%
ZnSO4	2.97E-06	2%
ZnCO3	1.64E-06	1%
ZnOH+	2.45E-07	0%
Zn(OH)2	1.85E-08	0%
Zn(SO4)2-	2.84E-09	0%
Zn(CO3)2-	2.29E-09	0%
Zn(OH)3-	1.92E-13	0%
Zn(OH)4-2	1.08E-19	0%



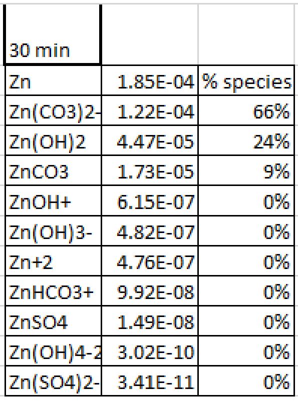
1 min		
Zn	1.85E-04	
Zn(CO3)2-	9.27E-05	50%
ZnCO3	5.18E-05	28%
Zn(OH)2	3.22E-05	17%
Zn+2	5.27E-06	3%
ZnOH+	1.75E-06	1%
ZnHCO3+	1.17E-06	1%
ZnSO4	1.78E-07	0%
Zn(OH)3-	8.65E-08	0%
Zn(SO4)2-	4.14E-10	0%
Zn(OH)4-2	1.33E-11	0%



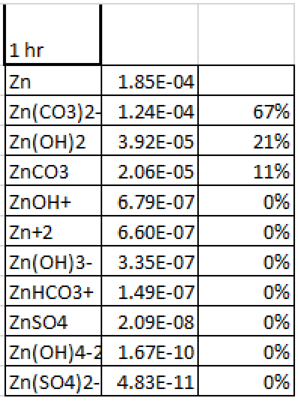
5 min		
Zn	1.85E-04	
Zn(CO3)2-	1.05E-04	57%
ZnCO3	3.80E-05	20%
Zn(OH)2	3.78E-05	20%
Zn+2	2.47E-06	1%
ZnOH+	1.30E-06	1%
ZnHCO3+	5.40E-07	0%
Zn(OH)3-	1.62E-07	0%
ZnSO4	8.39E-08	0%
Zn(SO4)2-	1.95E-10	0%
Zn(OH)4-2	3.93E-11	0%



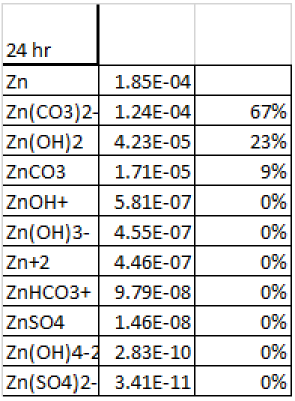
15 min		
Zn	1.85E-04	
Zn(CO3)2-	1.13E-04	61%
Zn(OH)2	3.80E-05	21%
ZnCO3	3.10E-05	17%
Zn+2	1.58E-06	1%
ZnOH+	1.04E-06	1%
ZnHCO3+	3.53E-07	0%
Zn(OH)3-	2.05E-07	0%
ZnSO4	5.23E-08	0%
Zn(SO4)2-	1.22E-10	0%
Zn(OH)4-2	6.33E-11	0%



30 min		
Zn	1.85E-04	% species
Zn(CO3)2-	1.22E-04	66%
Zn(OH)2	4.47E-05	24%
ZnCO3	1.73E-05	9%
ZnOH+	6.15E-07	0%
Zn(OH)3-	4.82E-07	0%
Zn+2	4.76E-07	0%
ZnHCO3+	9.92E-08	0%
ZnSO4	1.49E-08	0%
Zn(OH)4-2	3.02E-10	0%
Zn(SO4)2-	3.41E-11	0%



1 hr		
Zn	1.85E-04	
Zn(CO3)2-	1.24E-04	67%
Zn(OH)2	3.92E-05	21%
ZnCO3	2.06E-05	11%
ZnOH+	6.79E-07	0%
Zn+2	6.60E-07	0%
Zn(OH)3-	3.35E-07	0%
ZnHCO3+	1.49E-07	0%
ZnSO4	2.09E-08	0%
Zn(OH)4-2	1.67E-10	0%
Zn(SO4)2-	4.83E-11	0%



24 hr		
Zn	1.85E-04	
Zn(CO3)2-	1.24E-04	67%
Zn(OH)2	4.23E-05	23%
ZnCO3	1.71E-05	9%
ZnOH+	5.81E-07	0%
Zn(OH)3-	4.55E-07	0%
Zn+2	4.46E-07	0%
ZnHCO3+	9.79E-08	0%
ZnSO4	1.46E-08	0%
Zn(OH)4-2	2.83E-10	0%
Zn(SO4)2-	3.41E-11	0%

SI 5.4 B: PHREEQC outputs for contact time Zn speciation analysis

SI 5.4 B is the data to support figure 5.4B (results and discussion section of chapter 5)

mine water		
Pb	8.21E-06	% species
Pb+2	3.62E-06	44%
PbCO3	3.01E-06	37%
PbHCO3+	1.21E-06	15%
PbOH+	1.99E-07	2%
PbSO4	1.63E-07	2%
Pb(CO3)2-	4.95E-10	0%
Pb(OH)2	2.35E-10	0%
Pb(SO4)2-	9.31E-11	0%
Pb2OH+3	1.88E-11	0%
Pb(OH)3-	8.87E-15	0%
Pb3(OH)4	1.00E-15	0%
Pb(OH)4-2	7.23E-20	0%

1 min		
Pb	8.21E-06	% species
PbCO3	6.66E-06	81%
Pb(CO3)2-	1.40E-06	17%
PbOH+	9.91E-08	1%
Pb(OH)2	2.86E-08	0%
PbHCO3+	1.09E-08	0%
Pb+2	7.82E-09	0%
PbSO4	6.81E-10	0%
Pb(OH)3-	2.79E-10	0%
PbNO3+	1.64E-12	0%
Pb(SO4)2-	9.47E-13	0%
Pb(OH)4-2	6.21E-13	0%
Pb3(OH)4	3.22E-14	0%
Pb2OH+3	2.27E-14	0%

5 min		
Pb	8.21E-06	% species
PbCO3	6.08E-06	74%
Pb(CO3)2-	1.98E-06	24%
PbOH+	9.22E-08	1%
Pb(OH)2	4.22E-08	1%
PbHCO3+	6.30E-09	0%
Pb+2	4.58E-09	0%
Pb(OH)3-	6.53E-10	0%
PbSO4	4.02E-10	0%
Pb(OH)4-2	2.30E-12	0%
PbNO3+	9.65E-13	0%
Pb(SO4)2-	5.59E-13	0%
Pb3(OH)4	4.10E-14	0%
Pb2OH+3	1.23E-14	0%

15 min		
Pb	8.21E-06	% species
PbCO3	5.65E-06	69%
Pb(CO3)2-	2.42E-06	29%
PbOH+	8.35E-08	1%
Pb(OH)2	4.80E-08	1%
PbHCO3+	4.66E-09	0%
Pb+2	3.33E-09	0%
Pb(OH)3-	9.37E-10	0%
PbSO4	2.84E-10	0%
Pb(OH)4-2	4.19E-12	0%
PbNO3+	6.91E-13	0%
Pb(SO4)2-	3.95E-13	0%
Pb3(OH)4	3.85E-14	0%
Pb2OH+3	8.21E-15	0%

30 min		
Pb	8.21E-06	% species
PbCO3	4.41E-06	54%
Pb(CO3)2-	3.64E-06	44%
Pb(OH)2	7.88E-08	1%
PbOH+	6.91E-08	1%
Pb(OH)3-	3.09E-09	0%
PbHCO3+	1.83E-09	0%
Pb+2	1.40E-09	0%
PbSO4	1.13E-10	0%
Pb(OH)4-2	2.80E-11	0%
PbNO3+	2.85E-13	0%
Pb(SO4)2-	1.55E-13	0%
Pb3(OH)4	4.37E-14	0%
Pb2OH+3	2.92E-15	0%

1 hr		
Pb	8.21E-06	% species
PbCO3	4.73E-06	58%
Pb(CO3)2-	3.34E-06	41%
PbOH+	6.88E-08	1%
Pb(OH)2	6.24E-08	1%
PbHCO3+	2.48E-09	0%
Pb(OH)3-	1.94E-09	0%
Pb+2	1.75E-09	0%
PbSO4	1.43E-10	0%
Pb(OH)4-2	1.39E-11	0%
PbNO3+	3.58E-13	0%
Pb(SO4)2-	1.98E-13	0%
Pb3(OH)4	3.42E-14	0%
Pb2OH+3	3.62E-15	0%

24 hr		
Pb	8.21E-06	% species
PbCO3	4.35E-06	53%
Pb(CO3)2-	3.71E-06	45%
Pb(OH)2	7.45E-08	1%
PbOH+	6.52E-08	1%
Pb(OH)3-	2.91E-09	0%
PbHCO3+	1.80E-09	0%
Pb+2	1.31E-09	0%
PbSO4	1.10E-10	0%
Pb(OH)4-2	2.61E-11	0%
PbNO3+	2.70E-13	0%
Pb(SO4)2-	1.54E-13	0%
Pb3(OH)4	3.65E-14	0%
Pb2OH+3	2.54E-15	0%

SI 5.4C: PHREEQC outputs for contact time Pb speciation analysis

SI 5.4C is the data to support figure 5.4C (results and discussion section of chapter 5)

Solution Label	Pb	Zn	% Pb mobile	% Zn mobile
Trib 1 a	0.4	10.9		
Trib 1 b	0.5	11.2		
Trib 1 c	0.5	12.0		
Trib 1 Av	0.5	11.4	35%	95%
Acid trib 1 a	1.1	10.3		
Acid trib 1 b	1.4	11.0		
Acid trib 1 c	1.4	11.0		
Acid Trib 1 av	1.3	10.8		

SI 5.5: comparison of acidified and non-acidified Tributary 1 samples (n=3)

SI 5.5 is the data to support the PHREEQC speciation modelling of Pb and Zn in 5.3.3 (results and discussion section of chapter 5)

Name		Na 1s	Zn 2p ZnCO3	Zn 2p Zin-C-Hydrates	Zn 2p ZnCO3
Position		1073.78	1024.34	1026.61	1047.34
FWHM		2.57	2	2	2
Area		392.3	178.15	77.67	133.5
Lineshape	LA(1.3,230)	LA(1.3,230)	LA(1.3,230)	LA(1.3,230)	

B.E.	Cycle 0:24hrMW:Zn 2p + Na 1s:CPS	Zn 2p + Na 1s:Na 1s	Zn 2p + Na 1s:Zn 2p ZnCO3	Zn 2p + Na 1s:Zn 2p Zin-C-Hydrates	Zn 2p + Na 1s:Zn 2p ZnCO3	Background	Envelope
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03
1.09E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03

1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.54E+03	1.54E+03	1.54E+03	1.54E+03	1.54E+03	1.54E+03	1.54E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03

1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.09E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.09E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03	1.56E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.09E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.09E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03

1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.08E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.08E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.08E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03	1.57E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.57E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.61E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.58E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.58E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03

1.08E+03	1.58E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.58E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.57E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.57E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.59E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.58E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.63E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.60E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.62E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.60E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.60E+03
1.08E+03	1.61E+03	1.61E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.61E+03
1.08E+03	1.62E+03	1.61E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.61E+03
1.08E+03	1.61E+03	1.61E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.61E+03
1.08E+03	1.61E+03	1.61E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.61E+03
1.08E+03	1.62E+03	1.61E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.61E+03
1.08E+03	1.61E+03	1.62E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.62E+03
1.08E+03	1.63E+03	1.62E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.62E+03
1.08E+03	1.65E+03	1.62E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.62E+03
1.08E+03	1.64E+03	1.63E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.63E+03
1.08E+03	1.65E+03	1.63E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.63E+03
1.08E+03	1.63E+03	1.64E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.64E+03
1.08E+03	1.64E+03	1.64E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.64E+03
1.08E+03	1.64E+03	1.65E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.65E+03
1.08E+03	1.65E+03	1.65E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.65E+03
1.08E+03	1.67E+03	1.66E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.66E+03
1.07E+03	1.66E+03	1.67E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.67E+03

1.07E+03	1.68E+03	1.67E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.67E+03
1.07E+03	1.68E+03	1.68E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.68E+03
1.07E+03	1.68E+03	1.69E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.69E+03
1.07E+03	1.71E+03	1.70E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.70E+03
1.07E+03	1.69E+03	1.70E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.70E+03
1.07E+03	1.70E+03	1.71E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.71E+03
1.07E+03	1.71E+03	1.72E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.72E+03
1.07E+03	1.70E+03	1.72E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.72E+03
1.07E+03	1.72E+03	1.72E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.72E+03
1.07E+03	1.73E+03	1.73E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.73E+03
1.07E+03	1.72E+03	1.73E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.73E+03
1.07E+03	1.74E+03	1.73E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.73E+03
1.07E+03	1.73E+03	1.73E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.73E+03
1.07E+03	1.74E+03	1.73E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.73E+03
1.07E+03	1.71E+03	1.73E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.73E+03
1.07E+03	1.72E+03	1.72E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.72E+03
1.07E+03	1.73E+03	1.72E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.72E+03
1.07E+03	1.74E+03	1.71E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.71E+03
1.07E+03	1.72E+03	1.71E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.71E+03
1.07E+03	1.71E+03	1.70E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.70E+03
1.07E+03	1.70E+03	1.69E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.69E+03
1.07E+03	1.70E+03	1.69E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.69E+03
1.07E+03	1.69E+03	1.68E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.68E+03
1.07E+03	1.67E+03	1.67E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.67E+03
1.07E+03	1.68E+03	1.67E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.67E+03
1.07E+03	1.67E+03	1.66E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.66E+03
1.07E+03	1.65E+03	1.65E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.65E+03
1.07E+03	1.64E+03	1.65E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.65E+03
1.07E+03	1.64E+03	1.64E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.64E+03
1.07E+03	1.64E+03	1.64E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.64E+03
1.07E+03	1.60E+03	1.63E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.63E+03
1.07E+03	1.61E+03	1.63E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.63E+03
1.07E+03	1.61E+03	1.63E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.63E+03
1.07E+03	1.59E+03	1.62E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.62E+03
1.07E+03	1.60E+03	1.62E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.62E+03
1.07E+03	1.62E+03	1.62E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.62E+03
1.07E+03	1.62E+03	1.62E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.62E+03
1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.62E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.60E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.59E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.57E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.58E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03

1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.60E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.62E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.59E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.61E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.57E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.59E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.07E+03	1.58E+03	1.59E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.59E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.07E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.07E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03	1.58E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03

1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.07E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.07E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.07E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03

1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03	1.55E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03	1.59E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03

1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03	1.60E+03
1.06E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03	1.61E+03
1.06E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.06E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.06E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.06E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03	1.62E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.06E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.60E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.62E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.65E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.66E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.64E+03
1.05E+03	1.64E+03	1.63E+03	1.63E+03	1.63E+03	1.64E+03	1.63E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03

1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.65E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.68E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.68E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.65E+03	1.64E+03	1.65E+03
1.05E+03	1.69E+03	1.64E+03	1.64E+03	1.64E+03	1.65E+03	1.64E+03	1.65E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.65E+03	1.64E+03	1.65E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.65E+03	1.64E+03	1.65E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.65E+03	1.64E+03	1.65E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.65E+03	1.64E+03	1.65E+03
1.05E+03	1.66E+03	1.64E+03	1.64E+03	1.64E+03	1.66E+03	1.64E+03	1.66E+03
1.05E+03	1.68E+03	1.64E+03	1.64E+03	1.64E+03	1.66E+03	1.64E+03	1.66E+03
1.05E+03	1.70E+03	1.64E+03	1.64E+03	1.64E+03	1.66E+03	1.64E+03	1.66E+03
1.05E+03	1.69E+03	1.64E+03	1.64E+03	1.64E+03	1.66E+03	1.64E+03	1.66E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.67E+03	1.64E+03	1.67E+03
1.05E+03	1.67E+03	1.64E+03	1.64E+03	1.64E+03	1.67E+03	1.64E+03	1.67E+03
1.05E+03	1.68E+03	1.65E+03	1.65E+03	1.65E+03	1.68E+03	1.65E+03	1.68E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.68E+03	1.65E+03	1.68E+03
1.05E+03	1.71E+03	1.65E+03	1.65E+03	1.65E+03	1.69E+03	1.65E+03	1.69E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.69E+03	1.65E+03	1.69E+03

1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.69E+03	1.65E+03	1.69E+03
1.05E+03	1.68E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.71E+03	1.65E+03	1.65E+03	1.65E+03	1.71E+03	1.65E+03	1.71E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.71E+03	1.65E+03	1.71E+03
1.05E+03	1.68E+03	1.65E+03	1.65E+03	1.65E+03	1.71E+03	1.65E+03	1.71E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.71E+03	1.65E+03	1.71E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.71E+03	1.65E+03	1.71E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.67E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.70E+03	1.65E+03	1.70E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.69E+03	1.65E+03	1.69E+03
1.05E+03	1.70E+03	1.65E+03	1.65E+03	1.65E+03	1.69E+03	1.65E+03	1.69E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.68E+03	1.65E+03	1.68E+03
1.05E+03	1.69E+03	1.65E+03	1.65E+03	1.65E+03	1.68E+03	1.65E+03	1.68E+03
1.05E+03	1.69E+03	1.66E+03	1.66E+03	1.66E+03	1.68E+03	1.66E+03	1.68E+03
1.05E+03	1.68E+03	1.66E+03	1.66E+03	1.66E+03	1.68E+03	1.66E+03	1.68E+03
1.05E+03	1.69E+03	1.66E+03	1.66E+03	1.66E+03	1.67E+03	1.66E+03	1.67E+03
1.05E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.67E+03	1.66E+03	1.67E+03
1.05E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.67E+03	1.66E+03	1.67E+03
1.05E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.67E+03	1.66E+03	1.67E+03
1.05E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.05E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.05E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.05E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.05E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.05E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.68E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.63E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.68E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03

1.04E+03	1.68E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.68E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.68E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.67E+03
1.04E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03

1.04E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03	1.63E+03
1.04E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.04E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.04E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03

1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.03E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03	1.64E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.66E+03	1.65E+03	1.65E+03	1.66E+03
1.03E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03	1.65E+03
1.03E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03	1.66E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.69E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.68E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.68E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.68E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.69E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.69E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03
1.03E+03	1.68E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.67E+03	1.68E+03
1.03E+03	1.67E+03	1.67E+03	1.68E+03	1.68E+03	1.67E+03	1.67E+03	1.68E+03
1.03E+03	1.67E+03	1.67E+03	1.68E+03	1.68E+03	1.67E+03	1.67E+03	1.68E+03
1.03E+03	1.66E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.67E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.67E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03

1.03E+03	1.71E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.70E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.69E+03
1.03E+03	1.70E+03	1.68E+03	1.68E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03
1.03E+03	1.71E+03	1.68E+03	1.68E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03
1.03E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03
1.03E+03	1.70E+03	1.68E+03	1.68E+03	1.69E+03	1.68E+03	1.68E+03	1.69E+03
1.03E+03	1.71E+03	1.68E+03	1.68E+03	1.69E+03	1.68E+03	1.68E+03	1.70E+03
1.03E+03	1.70E+03	1.68E+03	1.69E+03	1.70E+03	1.68E+03	1.68E+03	1.70E+03
1.03E+03	1.71E+03	1.68E+03	1.69E+03	1.70E+03	1.68E+03	1.68E+03	1.70E+03
1.03E+03	1.72E+03	1.69E+03	1.69E+03	1.70E+03	1.69E+03	1.69E+03	1.70E+03
1.03E+03	1.70E+03	1.69E+03	1.69E+03	1.71E+03	1.69E+03	1.69E+03	1.71E+03
1.03E+03	1.70E+03	1.69E+03	1.69E+03	1.71E+03	1.69E+03	1.69E+03	1.71E+03
1.03E+03	1.72E+03	1.69E+03	1.69E+03	1.71E+03	1.69E+03	1.69E+03	1.71E+03
1.03E+03	1.71E+03	1.69E+03	1.69E+03	1.71E+03	1.69E+03	1.69E+03	1.72E+03
1.03E+03	1.74E+03	1.69E+03	1.69E+03	1.72E+03	1.69E+03	1.69E+03	1.72E+03
1.03E+03	1.70E+03	1.69E+03	1.69E+03	1.72E+03	1.69E+03	1.69E+03	1.72E+03
1.03E+03	1.70E+03	1.69E+03	1.69E+03	1.72E+03	1.69E+03	1.69E+03	1.73E+03
1.03E+03	1.71E+03	1.69E+03	1.69E+03	1.72E+03	1.69E+03	1.69E+03	1.73E+03
1.03E+03	1.72E+03	1.69E+03	1.70E+03	1.72E+03	1.69E+03	1.69E+03	1.73E+03
1.03E+03	1.72E+03	1.69E+03	1.70E+03	1.73E+03	1.69E+03	1.69E+03	1.73E+03
1.03E+03	1.74E+03	1.69E+03	1.70E+03	1.73E+03	1.69E+03	1.69E+03	1.73E+03
1.03E+03	1.75E+03	1.69E+03	1.70E+03	1.73E+03	1.69E+03	1.69E+03	1.73E+03
1.03E+03	1.73E+03	1.70E+03	1.70E+03	1.73E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.72E+03	1.70E+03	1.71E+03	1.73E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.76E+03	1.70E+03	1.71E+03	1.73E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.76E+03	1.70E+03	1.71E+03	1.72E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.76E+03	1.70E+03	1.72E+03	1.72E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.75E+03	1.70E+03	1.72E+03	1.72E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.73E+03	1.70E+03	1.73E+03	1.72E+03	1.70E+03	1.70E+03	1.74E+03
1.03E+03	1.75E+03	1.70E+03	1.73E+03	1.72E+03	1.70E+03	1.70E+03	1.75E+03
1.03E+03	1.76E+03	1.71E+03	1.74E+03	1.72E+03	1.71E+03	1.71E+03	1.75E+03

1.03E+03	1.76E+03	1.71E+03	1.74E+03	1.72E+03	1.71E+03	1.71E+03	1.76E+03
1.03E+03	1.76E+03	1.71E+03	1.75E+03	1.72E+03	1.71E+03	1.71E+03	1.76E+03
1.03E+03	1.75E+03	1.71E+03	1.76E+03	1.72E+03	1.71E+03	1.71E+03	1.77E+03
1.03E+03	1.76E+03	1.71E+03	1.76E+03	1.72E+03	1.71E+03	1.71E+03	1.77E+03
1.02E+03	1.77E+03	1.71E+03	1.77E+03	1.72E+03	1.71E+03	1.71E+03	1.78E+03
1.02E+03	1.77E+03	1.71E+03	1.78E+03	1.72E+03	1.71E+03	1.71E+03	1.78E+03
1.02E+03	1.78E+03	1.72E+03	1.78E+03	1.72E+03	1.72E+03	1.72E+03	1.79E+03
1.02E+03	1.78E+03	1.72E+03	1.79E+03	1.72E+03	1.72E+03	1.72E+03	1.79E+03
1.02E+03	1.77E+03	1.72E+03	1.79E+03	1.72E+03	1.72E+03	1.72E+03	1.80E+03
1.02E+03	1.80E+03	1.72E+03	1.80E+03	1.72E+03	1.72E+03	1.72E+03	1.80E+03
1.02E+03	1.80E+03	1.72E+03	1.80E+03	1.73E+03	1.72E+03	1.72E+03	1.80E+03
1.02E+03	1.80E+03	1.72E+03	1.80E+03	1.73E+03	1.72E+03	1.72E+03	1.80E+03
1.02E+03	1.80E+03	1.73E+03	1.80E+03	1.73E+03	1.73E+03	1.73E+03	1.80E+03
1.02E+03	1.81E+03	1.73E+03	1.80E+03	1.73E+03	1.73E+03	1.73E+03	1.80E+03
1.02E+03	1.82E+03	1.73E+03	1.80E+03	1.73E+03	1.73E+03	1.73E+03	1.80E+03
1.02E+03	1.81E+03	1.73E+03	1.80E+03	1.73E+03	1.73E+03	1.73E+03	1.80E+03
1.02E+03	1.80E+03	1.74E+03	1.80E+03	1.74E+03	1.74E+03	1.74E+03	1.80E+03
1.02E+03	1.81E+03	1.74E+03	1.79E+03	1.74E+03	1.74E+03	1.74E+03	1.79E+03
1.02E+03	1.81E+03	1.74E+03	1.79E+03	1.74E+03	1.74E+03	1.74E+03	1.79E+03
1.02E+03	1.78E+03	1.74E+03	1.79E+03	1.74E+03	1.74E+03	1.74E+03	1.79E+03
1.02E+03	1.80E+03	1.74E+03	1.78E+03	1.74E+03	1.74E+03	1.74E+03	1.78E+03
1.02E+03	1.78E+03	1.74E+03	1.78E+03	1.74E+03	1.74E+03	1.74E+03	1.78E+03
1.02E+03	1.79E+03	1.74E+03	1.77E+03	1.74E+03	1.74E+03	1.74E+03	1.78E+03
1.02E+03	1.78E+03	1.74E+03	1.77E+03	1.75E+03	1.74E+03	1.74E+03	1.77E+03
1.02E+03	1.77E+03	1.75E+03	1.77E+03	1.75E+03	1.75E+03	1.75E+03	1.77E+03
1.02E+03	1.77E+03	1.75E+03	1.77E+03	1.75E+03	1.75E+03	1.75E+03	1.77E+03
1.02E+03	1.75E+03	1.75E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.76E+03
1.02E+03	1.77E+03	1.75E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.76E+03
1.02E+03	1.74E+03	1.75E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.76E+03
1.02E+03	1.76E+03	1.75E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.76E+03
1.02E+03	1.75E+03	1.75E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.76E+03
1.02E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.73E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.74E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.73E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.72E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.74E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03

1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.74E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.73E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.73E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.73E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.77E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.78E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03
1.02E+03	1.81E+03	1.81E+03	1.81E+03	1.81E+03	1.81E+03	1.81E+03	1.81E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03
1.02E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03	1.79E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03

1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03	1.77E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03	1.78E+03
1.02E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03	1.76E+03
1.02E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03
1.01E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.01E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03
1.01E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.01E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03	1.75E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03	1.73E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03
1.01E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03

1.01E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03	1.74E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03
1.01E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03	1.68E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03
1.01E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03	1.70E+03
1.01E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03	1.69E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03
1.01E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03	1.71E+03
1.01E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03	1.72E+03

SI 5.6: XPS Zn peaks

SI 5.6 is the data to support figure 5.5A and B in section 5.3.3 (results and discussion section of chapter 5)

Lower Boat Level	Ca mg/L	St dev	K mg/L	St dev	Mg mg/L	St dev	Na mg/L	St dev
DD no mine 1	9.8		39.5		1.2		37.7	
DD no min 2	17.2		38.8		1.3		35.8	
DD no mine 3	11.6		43.3		1.2		37.9	
AV no mine	12.8	3.1	40.6	2.0	1.2	0.1	37.1	1.0
1min1	22.3		36.4		8.6		45.5	
1min2	20.2		31.9		8.5		31.7	
1min3					9.8		36.1	
av 1min	30.2	1.0	34.2	2.3	9.0	0.6	37.8	5.7
1hr1	21.0		38.9		8.4		39.4	
1hr2	19.9		42.1		8.3		41.8	
1hr3	24.5		39.7		8.8		38.8	
av 1hr	21.8	2.0	40.2	1.4	8.5	0.2	40.0	1.3

SI 5.7: Lower Boat Level base cation concentrations

Trib 1	Ca mg/L	St dev	K mg/L	St dev	Mg mg/L	St dev	Na mg/L	St dev
DD no mine 1	4.0		40.0		3.5		37.1	
DD no min 2	9.9		39.1		0.0		40.1	
DD no mine 3	8.5		36.6		4.6		36.8	
AV no mine	7.5	2.5	38.6	1.4	2.7	2.0	38.0	1.5
DD 1 min 1	8.1		38.2		5.1		34.1	
DD 1 min 2	5.4		41.3		5.8		37.7	
DD 1 min 3	4.9		27.6		5.3		27.0	
Av 1 min	6.1	1.4	35.7	5.9	5.4	0.3	32.9	4.4
DD 1 hr 1	16.7		43.4		7.9		39.4	
DD 1 hr 2	11.0		41.8		6.3		36.1	
DD 1 hr 3	6.4		43.2		5.8		39.7	
Av 1 hr	11.4	4.2	42.8	0.7	6.7	0.9	38.4	1.7

SI 5.8: Tributary 1 base cation concentrations

SI 5.8 and SI 14 are the data to support figures 5.6A, B, C and D in section 5.3.3 (results and discussion section of chapter 5) which chart the changes in eluate base cations with and without contaminant.

Maximum measured Zn and Pb removal and late stage immobilisation mechanisms

Sample	Zn	Pb	L of mine water	kg of WAS	mg removed Zn	mg removed Pb	mg/g removed Zn	mg/g removed Pb
Trib1 1	11.7	1.8						
Trib1 2	12.3	1.8						
Trib1 3	12.4	1.6						
Trib1 Av	12.1	1.7						
0.1g 1	0.1	0.0	0.04	0.0001	12.0	1.7	4.8	0.7
0.1g 2	0.2	0.1	0.04	0.0001	12.0	1.7	4.8	0.7
0.1g 3	0.1	0.0	0.04	0.0001	12.0	1.7	4.8	0.7

av					12.0	1.7	4.8	0.7
0.05g 1	0.5	0.0	0.04	0.00005	11.6	1.7	9.3	1.3
0.05g 2	0.3	0.0	0.04	0.00005	11.9	1.7	9.5	1.4
0.05g 3	0.4	0.0	0.04	0.00005	11.7	1.7	9.3	1.3
av					11.7	1.7	9.4	1.4
0.03g 1	2.4	0.1	0.04	0.00003	9.7	1.7	13.0	2.2
0.03g 2	3.2	0.1	0.04	0.00003	8.9	1.7	11.9	2.2
0.03g 3	2.4	0.1	0.04	0.00003	9.7	1.7	13.0	2.2
av					9.4	1.7	12.6	2.2
0.02g 1	4.5	0.1	0.04	0.00002	7.7	1.7	15.3	3.3
0.02g 2	5.2	0.1	0.04	0.00002	6.9	1.6	13.8	3.3
0.02g 3	4.5	0.1	0.04	0.00002	7.7	1.7	15.3	3.3
av					7.4	1.7	14.8	3.3
0.01g 1	9.7	0.1	0.04	0.00001	2.5	1.6	9.8	6.5
0.01g 2	8.7	0.1	0.04	0.00001	3.4	1.7	13.6	6.6
0.01g 3	8.3	0.1	0.04	0.00001	3.9	1.7	15.5	6.6
av					3.2	1.7	13.0	6.6
0.006g 1	11.1	0.3	0.04	0.000006	1.0	1.4	6.7	9.5
0.006g 2	11.0	0.1	0.04	0.000006	1.1	1.6	7.2	10.7
0.006g 3	10.6	0.1	0.04	0.000006	1.5	1.6	10.0	10.7
av					1.2	1.7	8.0	10.3
0.003g 1	11.8	0.3	0.04	0.000003	0.3	1.4	4.4	19.3
0.003g 2	12.1	0.3	0.04	0.000003	0.0	1.4	0.4	18.5
0.003g 3	12.3	0.4	0.04	0.000003	-0.1	1.3	-2.0	17.6
av					0.1	1.7	0.9	18.5
0.002g 1		0.5	0.04	0.000002		1.2		24.2
0.002g 2		0.6	0.04	0.000002		1.2		23.4
0.002g 3		0.6	0.04	0.000002		1.2		23.4
av						1.7		23.7
0.002g 1		0.8	0.047	0.000002		0.9		22.3
0.002g 2		0.8	0.047	0.000002		0.9		21.8
0.002g 3		0.8	0.047	0.000002		0.9		22.1
av								22.1

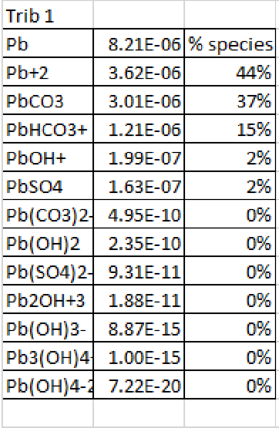
SI 5.9: immobilisation and maximum measured removal of Zn and Pb from Tributary1 mine water by larch biochar sintered with wood ash (WAS)

SI 5.9 are the data to highlight the maximum measured removal of Zn and Pb which are discussed in section 5.3.4 (results and discussion section of chapter 5)

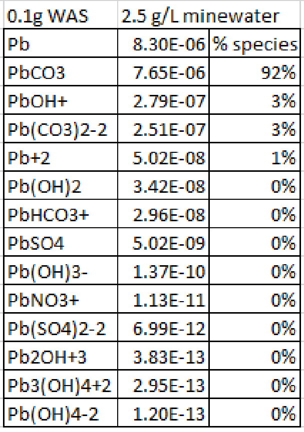
Trib 1	unit	mine water	0.1g	0.05g	0.03g	0.02g	0.01g	0.006g	0.003g
temp	°C	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2
pH		6.5	8.52	8.34	7.97	7.92	7.64	7.63	7.61
pe		7.4	4.0	4.0	4.0	4.0	7.4	4.0	4.0
Al	ppb	72.7	72.7	72.7	72.7	72.7	72.7	72.7	72.7
Alkalinity		26	65	55	42	42	40	30	28
Ca	ppm	2.89	7.20	7.48	4.64	4.88	4.16	3.64	3.16
Cd	ppb	42.9	42.9	42.9	42.9	42.9	42.9	42.9	42.9
Cu	ppm	16.4	16.4	16.4	16.4	16.4	16.4	16.4	16.4
K	ppm	0.92	7.88	5.08	3.56	5.76	3.24	2.32	1.76
Mg	ppm	2.50	2.96	2.92	2.76	2.80	2.68	2.72	2.60
N(3)	ppm	0.00	0.04	0.04	0.04	0.04	0.04	0.04	0.04
N(5)	ppm	0.00	0.26	0.26	0.26	0.26	0.26	0.26	0.26
Na	ppm	2.95	11.04	7.96	5.96	7.76	6.2	5.08	4.24
P	ppm	0.00	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Pb	ppm	1.72	1.72	1.72	1.72	1.72	1.72	1.72	1.72
S(6)	ppm	11.00	26.45	26.45	26.45	26.45	26.45	26.45	26.45
Zn	ppm	12.12	12.12	12.12	12.12	12.12	12.12	12.12	12.12

SI 5.10 A: PHREEQC inputs for exhaustion speciation analysis

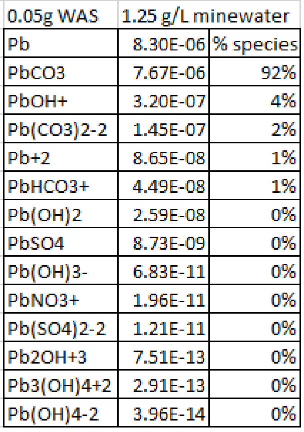
SI 5.10 A are the PHREEQC input data to support the discussion around mobile and immobile metal species in section 5.3.4 (results and discussion section of chapter 5)



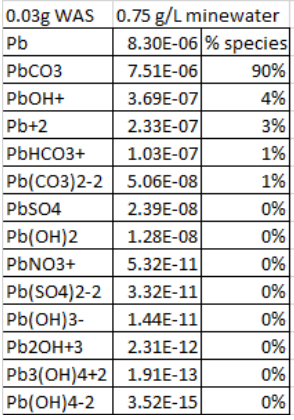
Trib 1		
Pb	8.21E-06	% species
Pb+2	3.62E-06	44%
PbCO3	3.01E-06	37%
PbHCO3+	1.21E-06	15%
PbOH+	1.99E-07	2%
PbSO4	1.63E-07	2%
Pb(CO3)2-	4.95E-10	0%
Pb(OH)2	2.35E-10	0%
Pb(SO4)2-	9.31E-11	0%
Pb2OH+3	1.88E-11	0%
Pb(OH)3-	8.87E-15	0%
Pb3(OH)4	1.00E-15	0%
Pb(OH)4-	7.22E-20	0%



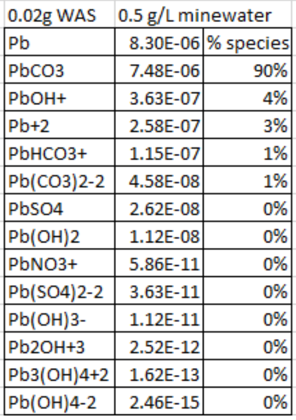
0.1g WAS	2.5 g/L minewater	
Pb	8.30E-06	% species
PbCO3	7.65E-06	92%
PbOH+	2.79E-07	3%
Pb(CO3)2-2	2.51E-07	3%
Pb+2	5.02E-08	1%
Pb(OH)2	3.42E-08	0%
PbHCO3+	2.96E-08	0%
PbSO4	5.02E-09	0%
Pb(OH)3-	1.37E-10	0%
PbNO3+	1.13E-11	0%
Pb(SO4)2-2	6.99E-12	0%
Pb2OH+3	3.83E-13	0%
Pb3(OH)4+2	2.95E-13	0%
Pb(OH)4-2	1.20E-13	0%



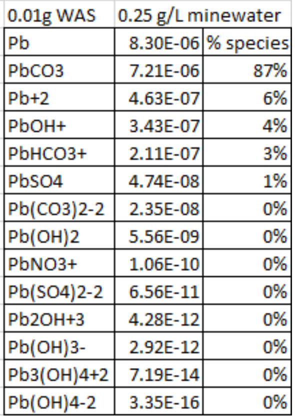
0.05g WAS	1.25 g/L minewater	
Pb	8.30E-06	% species
PbCO3	7.67E-06	92%
PbOH+	3.20E-07	4%
Pb(CO3)2-2	1.45E-07	2%
Pb+2	8.65E-08	1%
PbHCO3+	4.49E-08	1%
Pb(OH)2	2.59E-08	0%
PbSO4	8.73E-09	0%
Pb(OH)3-	6.83E-11	0%
PbNO3+	1.96E-11	0%
Pb(SO4)2-2	1.21E-11	0%
Pb2OH+3	7.51E-13	0%
Pb3(OH)4+2	2.91E-13	0%
Pb(OH)4-2	3.96E-14	0%



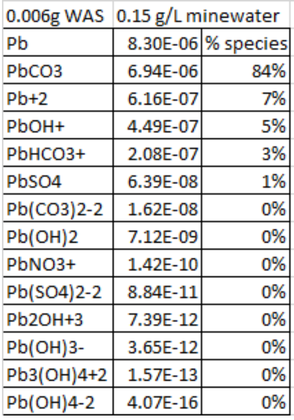
0.03g WAS	0.75 g/L minewater	
Pb	8.30E-06	% species
PbCO3	7.51E-06	90%
PbOH+	3.69E-07	4%
Pb+2	2.33E-07	3%
PbHCO3+	1.03E-07	1%
Pb(CO3)2-2	5.06E-08	1%
PbSO4	2.39E-08	0%
Pb(OH)2	1.28E-08	0%
PbNO3+	5.32E-11	0%
Pb(SO4)2-2	3.32E-11	0%
Pb(OH)3-	1.44E-11	0%
Pb2OH+3	2.31E-12	0%
Pb3(OH)4+2	1.91E-13	0%
Pb(OH)4-2	3.52E-15	0%



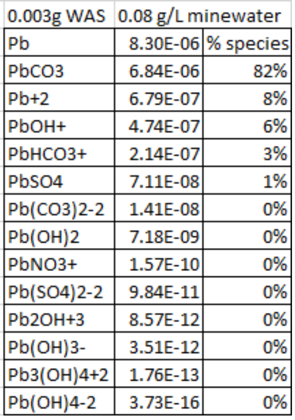
0.02g WAS	0.5 g/L minewater	
Pb	8.30E-06	% species
PbCO3	7.48E-06	90%
PbOH+	3.63E-07	4%
Pb+2	2.58E-07	3%
PbHCO3+	1.15E-07	1%
Pb(CO3)2-2	4.58E-08	1%
PbSO4	2.62E-08	0%
Pb(OH)2	1.12E-08	0%
PbNO3+	5.86E-11	0%
Pb(SO4)2-2	3.63E-11	0%
Pb(OH)3-	1.12E-11	0%
Pb2OH+3	2.52E-12	0%
Pb3(OH)4+2	1.62E-13	0%
Pb(OH)4-2	2.46E-15	0%



0.01g WAS	0.25 g/L minewater	
Pb	8.30E-06	% species
PbCO3	7.21E-06	87%
Pb+2	4.63E-07	6%
PbOH+	3.43E-07	4%
PbHCO3+	2.11E-07	3%
PbSO4	4.74E-08	1%
Pb(CO3)2-2	2.35E-08	0%
Pb(OH)2	5.56E-09	0%
PbNO3+	1.06E-10	0%
Pb(SO4)2-2	6.56E-11	0%
Pb2OH+3	4.28E-12	0%
Pb(OH)3-	2.92E-12	0%
Pb3(OH)4+2	7.19E-14	0%
Pb(OH)4-2	3.35E-16	0%



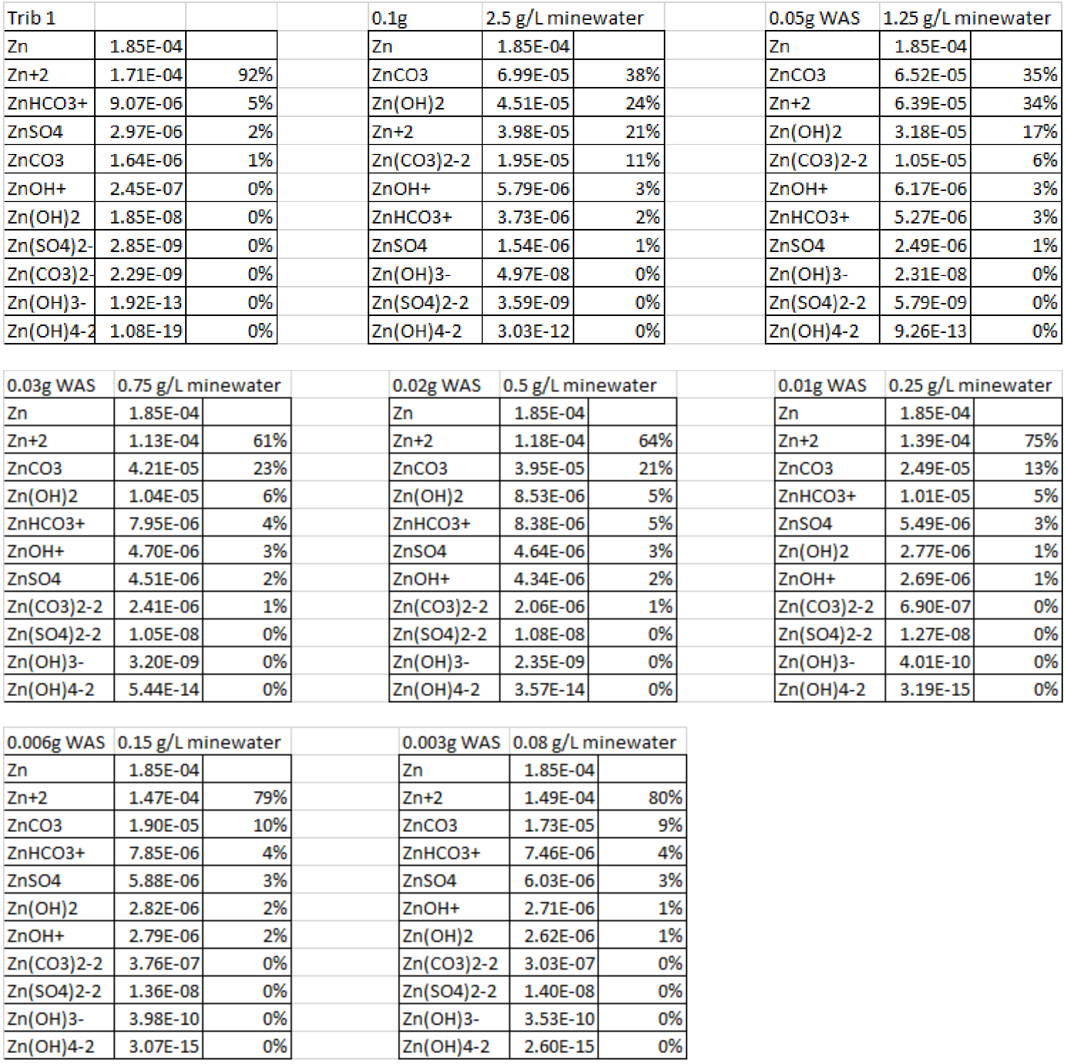
0.006g WAS	0.15 g/L minewater	
Pb	8.30E-06	% species
PbCO3	6.94E-06	84%
Pb+2	6.16E-07	7%
PbOH+	4.49E-07	5%
PbHCO3+	2.08E-07	3%
PbSO4	6.39E-08	1%
Pb(CO3)2-2	1.62E-08	0%
Pb(OH)2	7.12E-09	0%
PbNO3+	1.42E-10	0%
Pb(SO4)2-2	8.84E-11	0%
Pb2OH+3	7.39E-12	0%
Pb(OH)3-	3.65E-12	0%
Pb3(OH)4+2	1.57E-13	0%
Pb(OH)4-2	4.07E-16	0%



0.003g WAS	0.08 g/L minewater	
Pb	8.30E-06	% species
PbCO3	6.84E-06	82%
Pb+2	6.79E-07	8%
PbOH+	4.74E-07	6%
PbHCO3+	2.14E-07	3%
PbSO4	7.11E-08	1%
Pb(CO3)2-2	1.41E-08	0%
Pb(OH)2	7.18E-09	0%
PbNO3+	1.57E-10	0%
Pb(SO4)2-2	9.84E-11	0%
Pb2OH+3	8.57E-12	0%
Pb(OH)3-	3.51E-12	0%
Pb3(OH)4+2	1.76E-13	0%
Pb(OH)4-2	3.73E-16	0%

SI 5.10 B: PHREEQC outputs for exhaustion Zn speciation analysis

SI 5.10 B are the PHREEQC output data to support the discussion around mobile and immobile metal species in section 5.3.4 (results and discussion section of chapter 5)



Trib 1		
Zn	1.85E-04	
Zn+2	1.71E-04	92%
ZnHCO3+	9.07E-06	5%
ZnSO4	2.97E-06	2%
ZnCO3	1.64E-06	1%
ZnOH+	2.45E-07	0%
Zn(OH)2	1.85E-08	0%
Zn(SO4)2-	2.85E-09	0%
Zn(CO3)2-	2.29E-09	0%
Zn(OH)3-	1.92E-13	0%
Zn(OH)4-2	1.08E-19	0%

0.1g	2.5 g/L minewater	
Zn	1.85E-04	
ZnCO3	6.99E-05	38%
Zn(OH)2	4.51E-05	24%
Zn+2	3.98E-05	21%
Zn(CO3)2-2	1.95E-05	11%
ZnOH+	5.79E-06	3%
ZnHCO3+	3.73E-06	2%
ZnSO4	1.54E-06	1%
Zn(OH)3-	4.97E-08	0%
Zn(SO4)2-2	3.59E-09	0%
Zn(OH)4-2	3.03E-12	0%

0.05g WAS	1.25 g/L minewater	
Zn	1.85E-04	
ZnCO3	6.52E-05	35%
Zn+2	6.39E-05	34%
Zn(OH)2	3.18E-05	17%
Zn(CO3)2-2	1.05E-05	6%
ZnOH+	6.17E-06	3%
ZnHCO3+	5.27E-06	3%
ZnSO4	2.49E-06	1%
Zn(OH)3-	2.31E-08	0%
Zn(SO4)2-2	5.79E-09	0%
Zn(OH)4-2	9.26E-13	0%

0.03g WAS	0.75 g/L minewater	
Zn	1.85E-04	
Zn+2	1.13E-04	61%
ZnCO3	4.21E-05	23%
Zn(OH)2	1.04E-05	6%
ZnHCO3+	7.95E-06	4%
ZnOH+	4.70E-06	3%
ZnSO4	4.51E-06	2%
Zn(CO3)2-2	2.41E-06	1%
Zn(SO4)2-2	1.05E-08	0%
Zn(OH)3-	3.20E-09	0%
Zn(OH)4-2	5.44E-14	0%

0.02g WAS	0.5 g/L minewater	
Zn	1.85E-04	
Zn+2	1.18E-04	64%
ZnCO3	3.95E-05	21%
Zn(OH)2	8.53E-06	5%
ZnHCO3+	8.38E-06	5%
ZnSO4	4.64E-06	3%
ZnOH+	4.34E-06	2%
Zn(CO3)2-2	2.06E-06	1%
Zn(SO4)2-2	1.08E-08	0%
Zn(OH)3-	2.35E-09	0%
Zn(OH)4-2	3.57E-14	0%

0.01g WAS	0.25 g/L minewater	
Zn	1.85E-04	
Zn+2	1.39E-04	75%
ZnCO3	2.49E-05	13%
ZnHCO3+	1.01E-05	5%
ZnSO4	5.49E-06	3%
Zn(OH)2	2.77E-06	1%
ZnOH+	2.69E-06	1%
Zn(CO3)2-2	6.90E-07	0%
Zn(SO4)2-2	1.27E-08	0%
Zn(OH)3-	4.01E-10	0%
Zn(OH)4-2	3.19E-15	0%

0.006g WAS	0.15 g/L minewater	
Zn	1.85E-04	
Zn+2	1.47E-04	79%
ZnCO3	1.90E-05	10%
ZnHCO3+	7.85E-06	4%
ZnSO4	5.88E-06	3%
Zn(OH)2	2.82E-06	2%
ZnOH+	2.79E-06	2%
Zn(CO3)2-2	3.76E-07	0%
Zn(SO4)2-2	1.36E-08	0%
Zn(OH)3-	3.98E-10	0%
Zn(OH)4-2	3.07E-15	0%

0.003g WAS	0.08 g/L minewater	
Zn	1.85E-04	
Zn+2	1.49E-04	80%
ZnCO3	1.73E-05	9%
ZnHCO3+	7.46E-06	4%
ZnSO4	6.03E-06	3%
ZnOH+	2.71E-06	1%
Zn(OH)2	2.62E-06	1%
Zn(CO3)2-2	3.03E-07	0%
Zn(SO4)2-2	1.40E-08	0%
Zn(OH)3-	3.53E-10	0%
Zn(OH)4-2	2.60E-15	0%

SI 5.10 C: PHRREQC outputs for exhaustion Pb analysis

SI 5.10 C are the PHREEQC output data to support the discussion around mobile and immobile metal species in section 5.3.4 (results and discussion section of chapter 5)

mg WAS per L of minewater	% Pb removal	% Zn removal	% immobile Pb species	% immobile Zn species
2.50	97%	99%	99%	79%
2.50	97%	99%	99%	79%
2.50	97%	99%	99%	79%
1.25	98%	96%	99%	66%
1.25	99%	98%	99%	66%
1.25	98%	96%	99%	66%
0.75	97%	80%	97%	39%
0.75	97%	73%	97%	39%
0.75	97%	80%	97%	39%
0.50	97%	63%	94%	36%
0.50	96%	57%	94%	36%
0.50	97%	63%	94%	36%
0.25	95%	20%	97%	25%
0.25	96%	28%	97%	25%
0.25	96%	32%	97%	25%
0.15	83%	8%	93%	21%
0.15	93%	9%	93%	21%
0.15	94%	12%	93%	21%
0.08	84%	3%	92%	20%
0.08	81%	0%	92%	20%
0.08	85%	4%	92%	20%

n =	21	21
corr =	0.79	0.91
t stat=	5.645555179	9.552181016
p value =	9.60105E-06	5.476E-09
	r = 0.79	r = 0.91
	p<0.01	p<0.01

SI 5.11: Zn and Pb removal correlations with Zn and Pb immobile species

SI 5.11 are the correlation data to support the discussion around the correlation between mobile and immobile metal species and metal immobilisation in section 5.3.4 (results and discussion section of chapter 5)

change in base cation	g WAS per L of minewater	Ca mg/L	SD mg/L	Mg mg/L	SD mg/L
Av 0.1g 40mL	2.50	0.00	0.61	0.00	0.11
Av 0.05g 40mL	1.25	0.28	0.06	-0.04	0.06
Av 0.03g 40mL	0.75	-2.56	0.15	-0.20	0.00
Av 0.02g 40mL	0.50	-2.32	0.49	-0.16	0.11
Av 0.01g 40mL	0.25	-3.04	0.34	-0.28	0.06
Av 0.006g 40mL	0.15	-3.56	0.15	-0.24	0.06
Av 0.003g 40mL	0.08	-4.04	0.15	-0.36	0.06

SI 5.12: Change in base cation concentrations post contact with known quantities of larch biochar sintered with wood ash (WAS). SD N=3.

SI 5.12 are the data to support figure 5.7A illustrating the change in base cation concentration which is viewed in conjunction with Zn removal percentages in section 5.3.4 (results and discussion section of chapter 5)

cm-1	**2.5g WAS / L minewater**	**0.5g WAS / L minewater**	**0.08g WAS / L minewater**
2000	0.0167	0.0224	0.0055
1999	0.0168	0.0226	0.0057
1998	0.0169	0.0227	0.0057
1997	0.0170	0.0228	0.0057
1996	0.0169	0.0228	0.0057
1995	0.0169	0.0228	0.0056
1994	0.0168	0.0228	0.0056
1993	0.0169	0.0228	0.0056
1992	0.0171	0.0228	0.0057
1991	0.0171	0.0228	0.0057
1990	0.0172	0.0228	0.0057
1989	0.0171	0.0229	0.0057
1988	0.0171	0.0229	0.0057
1987	0.0171	0.023	0.0058
1986	0.0171	0.023	0.0058
1985	0.0172	0.0231	0.0059
1984	0.0173	0.0232	0.006
1983	0.0175	0.0234	0.0061
1982	0.0178	0.0236	0.0062
1981	0.018	0.0237	0.0062
1980	0.0179	0.0235	0.0061
1979	0.0176	0.023	0.0058
1978	0.017	0.0224	0.0054

1977	0.0166	0.0219	0.0052
1976	0.0163	0.0217	0.0051
1975	0.0162	0.0216	0.005
1974	0.0161	0.0216	0.005
1973	0.0161	0.0216	0.0049
1972	0.0161	0.0217	0.0048
1971	0.0162	0.0218	0.0049
1970	0.0163	0.0219	0.005
1969	0.0163	0.0219	0.0052
1968	0.0163	0.0218	0.0052
1967	0.0162	0.0218	0.0052
1966	0.0162	0.0218	0.0052
1965	0.0163	0.022	0.0052
1964	0.0164	0.0221	0.0053
1963	0.0165	0.0222	0.0054
1962	0.0165	0.0222	0.0054
1961	0.0164	0.0221	0.0053
1960	0.0163	0.022	0.0052
1959	0.0162	0.0219	0.0051
1958	0.0162	0.0219	0.0051
1957	0.0162	0.022	0.0051
1956	0.0164	0.0221	0.0052
1955	0.0165	0.0222	0.0052
1954	0.0166	0.0222	0.0052
1953	0.0166	0.0223	0.0052
1952	0.0167	0.0224	0.0053
1951	0.0168	0.0225	0.0054
1950	0.0168	0.0225	0.0054
1949	0.0167	0.0224	0.0054
1948	0.0168	0.0224	0.0054
1947	0.0168	0.0224	0.0055
1946	0.0168	0.0225	0.0055
1945	0.0168	0.0225	0.0054
1944	0.0168	0.0226	0.0054
1943	0.0168	0.0226	0.0054
1942	0.0169	0.0226	0.0054
1941	0.0169	0.0226	0.0055
1940	0.017	0.0226	0.0055
1939	0.017	0.0225	0.0055
1938	0.0169	0.0225	0.0055
1937	0.0169	0.0225	0.0055
1936	0.0169	0.0225	0.0055
1935	0.0169	0.0226	0.0055
1934	0.017	0.0227	0.0056
1933	0.017	0.0227	0.0056

1932	0.017	0.0228	0.0056
1931	0.0171	0.0229	0.0057
1930	0.0171	0.0229	0.0057
1929	0.0172	0.0228	0.0056
1928	0.0171	0.0228	0.0056
1927	0.0171	0.0228	0.0056
1926	0.0171	0.0228	0.0055
1925	0.0171	0.0228	0.0055
1924	0.0171	0.0228	0.0055
1923	0.0172	0.0229	0.0055
1922	0.0173	0.0229	0.0056
1921	0.0174	0.023	0.0057
1920	0.0174	0.023	0.0057
1919	0.0174	0.0231	0.0058
1918	0.0174	0.0231	0.0057
1917	0.0173	0.0231	0.0057
1916	0.0173	0.0231	0.0057
1915	0.0174	0.0232	0.0057
1914	0.0174	0.0232	0.0057
1913	0.0174	0.0231	0.0057
1912	0.0174	0.0231	0.0057
1911	0.0174	0.0231	0.0057
1910	0.0174	0.0231	0.0056
1909	0.0174	0.0231	0.0056
1908	0.0174	0.0231	0.0057
1907	0.0174	0.0231	0.0057
1906	0.0174	0.0231	0.0057
1905	0.0175	0.0232	0.0057
1904	0.0175	0.0232	0.0057
1903	0.0175	0.0232	0.0057
1902	0.0174	0.0232	0.0057
1901	0.0174	0.0232	0.0057
1900	0.0175	0.0232	0.0058
1899	0.0175	0.0232	0.0058
1898	0.0175	0.0232	0.0058
1897	0.0175	0.0233	0.0058
1896	0.0175	0.0233	0.0058
1895	0.0175	0.0233	0.0058
1894	0.0175	0.0232	0.0058
1893	0.0175	0.0232	0.0058
1892	0.0175	0.0232	0.0058
1891	0.0174	0.0232	0.0058
1890	0.0174	0.0232	0.0058
1889	0.0174	0.0232	0.0058
1888	0.0174	0.0232	0.0058

1887	0.0174	0.0232	0.0058
1886	0.0175	0.0232	0.0058
1885	0.0175	0.0233	0.0058
1884	0.0176	0.0233	0.0059
1883	0.0176	0.0233	0.0059
1882	0.0176	0.0233	0.0059
1881	0.0176	0.0233	0.0059
1880	0.0176	0.0233	0.0059
1879	0.0175	0.0233	0.0058
1878	0.0175	0.0233	0.0058
1877	0.0175	0.0233	0.0058
1876	0.0175	0.0233	0.0058
1875	0.0176	0.0233	0.0059
1874	0.0176	0.0233	0.0059
1873	0.0176	0.0233	0.0059
1872	0.0176	0.0233	0.0059
1871	0.0176	0.0234	0.0059
1870	0.0176	0.0233	0.0059
1869	0.0176	0.0233	0.0059
1868	0.0176	0.0233	0.0058
1867	0.0176	0.0233	0.0058
1866	0.0176	0.0233	0.0058
1865	0.0176	0.0234	0.0058
1864	0.0176	0.0234	0.0058
1863	0.0176	0.0234	0.0058
1862	0.0176	0.0233	0.0058
1861	0.0176	0.0233	0.0059
1860	0.0176	0.0233	0.0059
1859	0.0176	0.0233	0.0059
1858	0.0177	0.0233	0.0059
1857	0.0177	0.0233	0.0059
1856	0.0177	0.0234	0.0059
1855	0.0177	0.0234	0.0059
1854	0.0176	0.0234	0.0059
1853	0.0177	0.0235	0.0059
1852	0.0177	0.0235	0.0059
1851	0.0177	0.0235	0.0059
1850	0.0177	0.0234	0.0059
1849	0.0177	0.0235	0.0059
1848	0.0177	0.0235	0.0059
1847	0.0177	0.0235	0.0059
1846	0.0176	0.0234	0.0059
1845	0.0176	0.0234	0.0059
1844	0.0177	0.0234	0.0059
1843	0.0177	0.0234	0.0059

1842	0.0177	0.0234	0.0059
1841	0.0177	0.0234	0.0059
1840	0.0177	0.0235	0.0059
1839	0.0177	0.0235	0.0059
1838	0.0177	0.0235	0.0059
1837	0.0177	0.0235	0.0059
1836	0.0177	0.0235	0.0059
1835	0.0177	0.0235	0.0059
1834	0.0177	0.0235	0.0059
1833	0.0177	0.0235	0.0059
1832	0.0176	0.0235	0.0058
1831	0.0176	0.0235	0.0058
1830	0.0176	0.0234	0.0058
1829	0.0176	0.0234	0.0057
1828	0.0177	0.0234	0.0058
1827	0.0177	0.0235	0.0058
1826	0.0177	0.0235	0.0058
1825	0.0177	0.0235	0.0058
1824	0.0177	0.0236	0.0058
1823	0.0177	0.0236	0.0058
1822	0.0177	0.0236	0.0058
1821	0.0177	0.0236	0.0058
1820	0.0177	0.0236	0.0058
1819	0.0176	0.0235	0.0058
1818	0.0176	0.0235	0.0058
1817	0.0176	0.0234	0.0057
1816	0.0176	0.0235	0.0057
1815	0.0177	0.0235	0.0058
1814	0.0178	0.0236	0.0059
1813	0.0178	0.0236	0.0059
1812	0.0179	0.0237	0.0059
1811	0.0178	0.0237	0.0059
1810	0.0178	0.0237	0.0059
1809	0.0179	0.0237	0.0059
1808	0.0179	0.0237	0.0059
1807	0.0179	0.0237	0.0059
1806	0.018	0.0238	0.0059
1805	0.018	0.0238	0.0059
1804	0.0181	0.0238	0.0059
1803	0.0181	0.0239	0.0059
1802	0.0182	0.0239	0.0059
1801	0.0183	0.0239	0.006
1800	0.0183	0.024	0.006
1799	0.0184	0.024	0.006
1798	0.0184	0.0241	0.0061

1797	0.0184	0.0241	0.006
1796	0.0184	0.0241	0.006
1795	0.0184	0.0241	0.006
1794	0.0184	0.0241	0.006
1793	0.0184	0.0241	0.006
1792	0.0184	0.024	0.006
1791	0.0184	0.024	0.006
1790	0.0183	0.024	0.006
1789	0.0183	0.024	0.006
1788	0.0182	0.024	0.006
1787	0.0182	0.024	0.006
1786	0.0181	0.0239	0.006
1785	0.0181	0.0239	0.006
1784	0.0181	0.0239	0.006
1783	0.0181	0.0239	0.0059
1782	0.0181	0.0239	0.0059
1781	0.0181	0.0239	0.0059
1780	0.0181	0.0239	0.006
1779	0.018	0.0239	0.006
1778	0.018	0.024	0.006
1777	0.018	0.024	0.006
1776	0.0181	0.024	0.006
1775	0.0181	0.024	0.006
1774	0.0181	0.024	0.006
1773	0.0181	0.024	0.006
1772	0.0181	0.024	0.006
1771	0.0181	0.024	0.006
1770	0.0181	0.024	0.006
1769	0.0181	0.024	0.006
1768	0.0181	0.024	0.006
1767	0.0181	0.024	0.006
1766	0.0181	0.024	0.006
1765	0.018	0.024	0.006
1764	0.018	0.024	0.006
1763	0.018	0.024	0.0059
1762	0.018	0.024	0.0059
1761	0.0181	0.024	0.0059
1760	0.0181	0.024	0.006
1759	0.0181	0.024	0.006
1758	0.0181	0.024	0.006
1757	0.0181	0.024	0.006
1756	0.0181	0.024	0.006
1755	0.0181	0.024	0.0061
1754	0.0181	0.0241	0.0061
1753	0.0181	0.0241	0.0061

1752	0.0181	0.0241	0.0061
1751	0.0181	0.0241	0.0061
1750	0.0181	0.0241	0.0061
1749	0.0182	0.0241	0.0061
1748	0.0182	0.0241	0.006
1747	0.0182	0.0241	0.006
1746	0.0182	0.0241	0.006
1745	0.0182	0.0241	0.0061
1744	0.0182	0.0242	0.0061
1743	0.0182	0.0242	0.0061
1742	0.0182	0.0242	0.0061
1741	0.0182	0.0242	0.0061
1740	0.0182	0.0242	0.0061
1739	0.0182	0.0242	0.0061
1738	0.0182	0.0242	0.0061
1737	0.0183	0.0243	0.0062
1736	0.0183	0.0243	0.0062
1735	0.0184	0.0244	0.0063
1734	0.0184	0.0244	0.0063
1733	0.0184	0.0244	0.0062
1732	0.0184	0.0243	0.0062
1731	0.0184	0.0243	0.0062
1730	0.0184	0.0243	0.0061
1729	0.0184	0.0243	0.0062
1728	0.0184	0.0244	0.0062
1727	0.0184	0.0244	0.0062
1726	0.0184	0.0244	0.0062
1725	0.0184	0.0245	0.0062
1724	0.0184	0.0245	0.0062
1723	0.0184	0.0245	0.0063
1722	0.0185	0.0246	0.0063
1721	0.0185	0.0246	0.0063
1720	0.0185	0.0246	0.0062
1719	0.0185	0.0246	0.0062
1718	0.0186	0.0246	0.0063
1717	0.0186	0.0247	0.0063
1716	0.0187	0.0247	0.0063
1715	0.0187	0.0247	0.0063
1714	0.0187	0.0248	0.0064
1713	0.0187	0.0249	0.0064
1712	0.0187	0.0249	0.0064
1711	0.0188	0.025	0.0064
1710	0.0188	0.025	0.0064
1709	0.0188	0.025	0.0065
1708	0.0189	0.0251	0.0065

1707	0.0189	0.0251	0.0065
1706	0.019	0.0251	0.0065
1705	0.019	0.0251	0.0065
1704	0.0191	0.0252	0.0065
1703	0.0191	0.0252	0.0065
1702	0.0191	0.0253	0.0065
1701	0.0192	0.0253	0.0066
1700	0.0192	0.0254	0.0066
1699	0.0193	0.0254	0.0066
1698	0.0193	0.0254	0.0066
1697	0.0193	0.0255	0.0067
1696	0.0194	0.0255	0.0067
1695	0.0194	0.0255	0.0067
1694	0.0194	0.0255	0.0067
1693	0.0195	0.0255	0.0067
1692	0.0195	0.0256	0.0067
1691	0.0195	0.0256	0.0067
1690	0.0196	0.0256	0.0067
1689	0.0196	0.0256	0.0067
1688	0.0197	0.0256	0.0067
1687	0.0197	0.0256	0.0067
1686	0.0197	0.0256	0.0068
1685	0.0197	0.0257	0.0068
1684	0.0197	0.0256	0.0067
1683	0.0198	0.0256	0.0067
1682	0.0198	0.0256	0.0067
1681	0.0198	0.0256	0.0067
1680	0.0198	0.0256	0.0067
1679	0.0198	0.0256	0.0067
1678	0.0199	0.0256	0.0067
1677	0.0199	0.0256	0.0067
1676	0.02	0.0257	0.0068
1675	0.02	0.0257	0.0068
1674	0.0201	0.0257	0.0068
1673	0.0201	0.0257	0.0068
1672	0.0201	0.0257	0.0068
1671	0.0201	0.0257	0.0068
1670	0.0202	0.0258	0.0069
1669	0.0202	0.0258	0.0069
1668	0.0203	0.0258	0.0069
1667	0.0203	0.0259	0.0069
1666	0.0203	0.0259	0.0069
1665	0.0203	0.0259	0.0069
1664	0.0204	0.026	0.0069
1663	0.0204	0.026	0.0069

1662	0.0205	0.0261	0.0069
1661	0.0205	0.0261	0.007
1660	0.0206	0.0261	0.007
1659	0.0206	0.0262	0.007
1658	0.0207	0.0262	0.0071
1657	0.0207	0.0262	0.0071
1656	0.0208	0.0263	0.0071
1655	0.0209	0.0263	0.0071
1654	0.021	0.0264	0.0071
1653	0.021	0.0265	0.0072
1652	0.0211	0.0265	0.0072
1651	0.0211	0.0266	0.0072
1650	0.0211	0.0266	0.0072
1649	0.0212	0.0266	0.0072
1648	0.0213	0.0267	0.0073
1647	0.0214	0.0268	0.0074
1646	0.0214	0.0268	0.0074
1645	0.0214	0.0269	0.0074
1644	0.0215	0.0269	0.0075
1643	0.0215	0.027	0.0075
1642	0.0215	0.027	0.0075
1641	0.0216	0.0271	0.0075
1640	0.0216	0.0272	0.0075
1639	0.0217	0.0272	0.0076
1638	0.0218	0.0273	0.0076
1637	0.0218	0.0274	0.0077
1636	0.0219	0.0275	0.0077
1635	0.022	0.0276	0.0078
1634	0.022	0.0276	0.0079
1633	0.022	0.0277	0.0079
1632	0.0221	0.0278	0.0079
1631	0.0221	0.0278	0.0079
1630	0.0221	0.0279	0.0079
1629	0.0222	0.0279	0.0079
1628	0.0222	0.028	0.0079
1627	0.0222	0.0281	0.008
1626	0.0223	0.0281	0.008
1625	0.0223	0.0282	0.0081
1624	0.0224	0.0283	0.0081
1623	0.0224	0.0284	0.0082
1622	0.0224	0.0284	0.0082
1621	0.0224	0.0285	0.0082
1620	0.0225	0.0286	0.0083
1619	0.0225	0.0286	0.0083
1618	0.0226	0.0287	0.0084

1617	0.0226	0.0288	0.0084
1616	0.0226	0.0288	0.0084
1615	0.0226	0.0289	0.0085
1614	0.0225	0.0289	0.0085
1613	0.0225	0.0289	0.0085
1612	0.0226	0.029	0.0085
1611	0.0226	0.029	0.0085
1610	0.0226	0.0291	0.0085
1609	0.0226	0.0291	0.0086
1608	0.0226	0.0292	0.0086
1607	0.0227	0.0292	0.0086
1606	0.0227	0.0293	0.0086
1605	0.0227	0.0293	0.0087
1604	0.0227	0.0294	0.0087
1603	0.0227	0.0294	0.0087
1602	0.0228	0.0295	0.0087
1601	0.0228	0.0295	0.0087
1600	0.0228	0.0296	0.0088
1599	0.0228	0.0296	0.0088
1598	0.0229	0.0297	0.0088
1597	0.0229	0.0297	0.0089
1596	0.0229	0.0298	0.0089
1595	0.0229	0.0298	0.0089
1594	0.0229	0.0299	0.0089
1593	0.023	0.0299	0.0089
1592	0.023	0.0299	0.0089
1591	0.023	0.03	0.0089
1590	0.023	0.03	0.009
1589	0.0231	0.03	0.009
1588	0.0231	0.0301	0.009
1587	0.0231	0.0301	0.009
1586	0.0231	0.0302	0.009
1585	0.0231	0.0302	0.009
1584	0.0232	0.0302	0.009
1583	0.0232	0.0303	0.009
1582	0.0232	0.0303	0.009
1581	0.0233	0.0304	0.0091
1580	0.0233	0.0304	0.0091
1579	0.0233	0.0305	0.0091
1578	0.0233	0.0305	0.0091
1577	0.0233	0.0306	0.0091
1576	0.0233	0.0306	0.0091
1575	0.0233	0.0306	0.0091
1574	0.0234	0.0306	0.0091
1573	0.0234	0.0306	0.0092

1572	0.0235	0.0307	0.0092
1571	0.0235	0.0307	0.0092
1570	0.0235	0.0307	0.0091
1569	0.0236	0.0307	0.0091
1568	0.0236	0.0307	0.0091
1567	0.0236	0.0307	0.0091
1566	0.0236	0.0307	0.0092
1565	0.0236	0.0307	0.0092
1564	0.0236	0.0307	0.0092
1563	0.0236	0.0307	0.0092
1562	0.0237	0.0307	0.0092
1561	0.0238	0.0307	0.0092
1560	0.0239	0.0308	0.0093
1559	0.0239	0.0309	0.0093
1558	0.024	0.0309	0.0092
1557	0.024	0.0309	0.0092
1556	0.0241	0.0309	0.0092
1555	0.0241	0.0309	0.0092
1554	0.0242	0.031	0.0093
1553	0.0243	0.031	0.0093
1552	0.0245	0.031	0.0093
1551	0.0246	0.0311	0.0093
1550	0.0247	0.0311	0.0093
1549	0.0248	0.0312	0.0093
1548	0.025	0.0312	0.0093
1547	0.0251	0.0313	0.0093
1546	0.0253	0.0314	0.0093
1545	0.0255	0.0314	0.0094
1544	0.0257	0.0315	0.0094
1543	0.0258	0.0316	0.0094
1542	0.026	0.0317	0.0095
1541	0.0262	0.0318	0.0095
1540	0.0264	0.032	0.0095
1539	0.0265	0.0321	0.0095
1538	0.0267	0.0321	0.0095
1537	0.0269	0.0322	0.0095
1536	0.027	0.0322	0.0095
1535	0.0272	0.0322	0.0096
1534	0.0274	0.0323	0.0096
1533	0.0276	0.0324	0.0096
1532	0.0278	0.0325	0.0096
1531	0.028	0.0326	0.0097
1530	0.0282	0.0327	0.0097
1529	0.0284	0.0328	0.0098
1528	0.0286	0.0329	0.0098

1527	0.0289	0.033	0.0099
1526	0.0291	0.0331	0.0099
1525	0.0293	0.0332	0.0099
1524	0.0295	0.0333	0.01
1523	0.0297	0.0334	0.01
1522	0.03	0.0336	0.0101
1521	0.0302	0.0337	0.0101
1520	0.0304	0.0338	0.0101
1519	0.0306	0.0339	0.0101
1518	0.0307	0.034	0.0102
1517	0.031	0.0341	0.0102
1516	0.0312	0.0343	0.0103
1515	0.0315	0.0344	0.0104
1514	0.0317	0.0345	0.0105
1513	0.0319	0.0346	0.0105
1512	0.0322	0.0348	0.0105
1511	0.0324	0.0348	0.0105
1510	0.0326	0.0349	0.0106
1509	0.0328	0.035	0.0106
1508	0.0331	0.0351	0.0107
1507	0.0333	0.0354	0.0108
1506	0.0335	0.0356	0.0108
1505	0.0337	0.0358	0.0109
1504	0.0339	0.0358	0.0109
1503	0.034	0.0359	0.0109
1502	0.0342	0.0359	0.011
1501	0.0345	0.036	0.011
1500	0.0347	0.0361	0.0111
1499	0.0349	0.0362	0.0111
1498	0.0351	0.0364	0.0112
1497	0.0353	0.0366	0.0113
1496	0.0356	0.0367	0.0114
1495	0.0358	0.0369	0.0114
1494	0.036	0.0369	0.0115
1493	0.0362	0.037	0.0115
1492	0.0364	0.0371	0.0115
1491	0.0367	0.0372	0.0115
1490	0.0368	0.0374	0.0115
1489	0.037	0.0375	0.0116
1488	0.0372	0.0377	0.0116
1487	0.0374	0.0378	0.0117
1486	0.0376	0.0379	0.0117
1485	0.0377	0.038	0.0118
1484	0.038	0.0381	0.0118
1483	0.0382	0.0382	0.0119

1482	0.0384	0.0383	0.0119
1481	0.0386	0.0384	0.012
1480	0.0388	0.0385	0.012
1479	0.039	0.0386	0.0121
1478	0.0392	0.0387	0.0121
1477	0.0394	0.0388	0.0122
1476	0.0396	0.0389	0.0122
1475	0.0399	0.0391	0.0123
1474	0.0401	0.0392	0.0124
1473	0.0403	0.0394	0.0125
1472	0.0404	0.0396	0.0125
1471	0.0406	0.0397	0.0125
1470	0.0407	0.0398	0.0125
1469	0.0409	0.0399	0.0126
1468	0.0411	0.04	0.0126
1467	0.0413	0.04	0.0127
1466	0.0415	0.0402	0.0127
1465	0.0417	0.0403	0.0128
1464	0.0418	0.0405	0.0129
1463	0.042	0.0406	0.0129
1462	0.0422	0.0406	0.0129
1461	0.0424	0.0406	0.0129
1460	0.0426	0.0407	0.0129
1459	0.0429	0.0407	0.013
1458	0.043	0.0409	0.013
1457	0.0431	0.0412	0.0131
1456	0.0432	0.0414	0.0131
1455	0.0433	0.0414	0.0131
1454	0.0434	0.0414	0.0131
1453	0.0436	0.0415	0.0131
1452	0.0438	0.0415	0.0131
1451	0.0439	0.0416	0.0132
1450	0.0441	0.0417	0.0132
1449	0.0442	0.0418	0.0132
1448	0.0444	0.0419	0.0132
1447	0.0445	0.042	0.0132
1446	0.0446	0.0421	0.0132
1445	0.0447	0.0421	0.0132
1444	0.0448	0.0422	0.0132
1443	0.045	0.0423	0.0132
1442	0.0451	0.0423	0.0132
1441	0.0452	0.0424	0.0132
1440	0.0454	0.0425	0.0133
1439	0.0456	0.0425	0.0133
1438	0.0458	0.0426	0.0133

1437	0.0459	0.0428	0.0133
1436	0.046	0.043	0.0134
1435	0.0461	0.0431	0.0134
1434	0.0463	0.0431	0.0134
1433	0.0465	0.0432	0.0134
1432	0.0468	0.0433	0.0135
1431	0.047	0.0434	0.0135
1430	0.0472	0.0435	0.0135
1429	0.0473	0.0436	0.0135
1428	0.0475	0.0437	0.0136
1427	0.0477	0.0438	0.0136
1426	0.0479	0.0439	0.0136
1425	0.0481	0.044	0.0137
1424	0.0483	0.0441	0.0137
1423	0.0485	0.0442	0.0137
1422	0.0487	0.0442	0.0137
1421	0.0489	0.0442	0.0137
1420	0.0491	0.0444	0.0138
1419	0.0492	0.0446	0.0138
1418	0.0492	0.0447	0.0138
1417	0.0493	0.0447	0.0138
1416	0.0494	0.0447	0.0138
1415	0.0494	0.0447	0.0138
1414	0.0495	0.0447	0.0138
1413	0.0496	0.0447	0.0138
1412	0.0497	0.0447	0.0138
1411	0.0497	0.0446	0.0138
1410	0.0497	0.0446	0.0137
1409	0.0496	0.0445	0.0137
1408	0.0495	0.0444	0.0137
1407	0.0494	0.0443	0.0136
1406	0.0492	0.0442	0.0135
1405	0.049	0.0441	0.0135
1404	0.0488	0.044	0.0135
1403	0.0486	0.044	0.0135
1402	0.0485	0.0438	0.0134
1401	0.0484	0.0438	0.0134
1400	0.0482	0.0437	0.0134
1399	0.048	0.0436	0.0133
1398	0.0477	0.0435	0.0133
1397	0.0476	0.0434	0.0132
1396	0.0473	0.0433	0.0132
1395	0.047	0.0431	0.0131
1394	0.0466	0.043	0.0131
1393	0.0462	0.0428	0.013

1392	0.0459	0.0426	0.013
1391	0.0456	0.0424	0.0129
1390	0.0452	0.0422	0.0128
1389	0.0449	0.042	0.0127
1388	0.0444	0.0418	0.0126
1387	0.0439	0.0416	0.0126
1386	0.0434	0.0414	0.0125
1385	0.0429	0.0412	0.0124
1384	0.0425	0.041	0.0124
1383	0.0421	0.0408	0.0123
1382	0.0417	0.0406	0.0123
1381	0.0413	0.0404	0.0122
1380	0.0409	0.0403	0.0122
1379	0.0405	0.0401	0.0121
1378	0.0402	0.0399	0.012
1377	0.0398	0.0397	0.012
1376	0.0395	0.0396	0.0119
1375	0.0391	0.0394	0.0119
1374	0.0387	0.0393	0.0118
1373	0.0383	0.0392	0.0117
1372	0.038	0.039	0.0117
1371	0.0377	0.0389	0.0117
1370	0.0375	0.0387	0.0117
1369	0.0372	0.0386	0.0116
1368	0.0369	0.0385	0.0116
1367	0.0366	0.0383	0.0115
1366	0.0364	0.0382	0.0115
1365	0.0361	0.0381	0.0114
1364	0.0359	0.0379	0.0113
1363	0.0356	0.0378	0.0113
1362	0.0353	0.0377	0.0113
1361	0.035	0.0375	0.0112
1360	0.0347	0.0374	0.0112
1359	0.0345	0.0373	0.0112
1358	0.0342	0.0372	0.0112
1357	0.034	0.037	0.0112
1356	0.0338	0.0369	0.0111
1355	0.0336	0.0368	0.0111
1354	0.0334	0.0367	0.0111
1353	0.0331	0.0366	0.011
1352	0.0329	0.0365	0.011
1351	0.0328	0.0364	0.011
1350	0.0326	0.0364	0.011
1349	0.0324	0.0363	0.011
1348	0.0323	0.0362	0.011

1347	0.0321	0.0361	0.0109
1346	0.0319	0.0361	0.0109
1345	0.0318	0.036	0.0109
1344	0.0316	0.0359	0.0109
1343	0.0315	0.0358	0.0109
1342	0.0314	0.0358	0.0108
1341	0.0312	0.0357	0.0108
1340	0.0311	0.0356	0.0108
1339	0.031	0.0356	0.0108
1338	0.0309	0.0356	0.0108
1337	0.0308	0.0355	0.0107
1336	0.0306	0.0355	0.0107
1335	0.0305	0.0354	0.0107
1334	0.0304	0.0353	0.0107
1333	0.0303	0.0353	0.0107
1332	0.0302	0.0352	0.0107
1331	0.0301	0.0352	0.0107
1330	0.03	0.0352	0.0107
1329	0.03	0.0351	0.0107
1328	0.0299	0.0351	0.0107
1327	0.0298	0.0351	0.0107
1326	0.0297	0.035	0.0107
1325	0.0296	0.035	0.0107
1324	0.0296	0.035	0.0107
1323	0.0295	0.035	0.0107
1322	0.0295	0.0349	0.0107
1321	0.0294	0.0349	0.0106
1320	0.0294	0.0349	0.0106
1319	0.0293	0.0349	0.0106
1318	0.0292	0.0349	0.0106
1317	0.0292	0.0348	0.0106
1316	0.0291	0.0348	0.0106
1315	0.029	0.0348	0.0106
1314	0.029	0.0348	0.0106
1313	0.0289	0.0348	0.0106
1312	0.0289	0.0347	0.0106
1311	0.0288	0.0347	0.0106
1310	0.0288	0.0347	0.0106
1309	0.0288	0.0347	0.0106
1308	0.0287	0.0347	0.0106
1307	0.0287	0.0347	0.0107
1306	0.0286	0.0347	0.0107
1305	0.0286	0.0347	0.0107
1304	0.0285	0.0347	0.0107
1303	0.0285	0.0347	0.0107

1302	0.0285	0.0347	0.0107
1301	0.0284	0.0347	0.0107
1300	0.0284	0.0347	0.0107
1299	0.0284	0.0347	0.0107
1298	0.0283	0.0347	0.0107
1297	0.0283	0.0347	0.0107
1296	0.0283	0.0347	0.0107
1295	0.0283	0.0347	0.0107
1294	0.0282	0.0347	0.0107
1293	0.0282	0.0348	0.0107
1292	0.0282	0.0348	0.0107
1291	0.0282	0.0348	0.0107
1290	0.0282	0.0348	0.0107
1289	0.0281	0.0348	0.0107
1288	0.0281	0.0348	0.0107
1287	0.0281	0.0348	0.0108
1286	0.0281	0.0348	0.0108
1285	0.0281	0.0349	0.0108
1284	0.0281	0.0349	0.0108
1283	0.0281	0.0349	0.0109
1282	0.0281	0.035	0.0109
1281	0.0281	0.035	0.0109
1280	0.0281	0.035	0.0109
1279	0.0281	0.035	0.0109
1278	0.0281	0.035	0.011
1277	0.0281	0.0351	0.011
1276	0.0281	0.0351	0.011
1275	0.028	0.0351	0.011
1274	0.028	0.0352	0.011
1273	0.028	0.0352	0.0111
1272	0.028	0.0352	0.0111
1271	0.028	0.0352	0.0111
1270	0.028	0.0352	0.0112
1269	0.028	0.0353	0.0112
1268	0.028	0.0353	0.0112
1267	0.028	0.0353	0.0112
1266	0.028	0.0354	0.0112
1265	0.028	0.0354	0.0112
1264	0.028	0.0354	0.0112
1263	0.028	0.0355	0.0113
1262	0.0281	0.0355	0.0113
1261	0.0281	0.0355	0.0113
1260	0.028	0.0355	0.0113
1259	0.028	0.0356	0.0113
1258	0.0281	0.0356	0.0113

1257	0.0281	0.0356	0.0114
1256	0.0281	0.0356	0.0114
1255	0.0281	0.0357	0.0114
1254	0.0281	0.0357	0.0115
1253	0.028	0.0357	0.0115
1252	0.028	0.0357	0.0115
1251	0.028	0.0357	0.0115
1250	0.028	0.0358	0.0115
1249	0.028	0.0358	0.0115
1248	0.028	0.0358	0.0115
1247	0.028	0.0358	0.0115
1246	0.028	0.0359	0.0116
1245	0.0281	0.0359	0.0116
1244	0.0281	0.0359	0.0116
1243	0.028	0.036	0.0116
1242	0.028	0.036	0.0116
1241	0.028	0.036	0.0116
1240	0.0281	0.036	0.0116
1239	0.0281	0.0361	0.0116
1238	0.0281	0.0361	0.0117
1237	0.0281	0.0362	0.0117
1236	0.0281	0.0362	0.0117
1235	0.0281	0.0362	0.0117
1234	0.0281	0.0362	0.0117
1233	0.0281	0.0362	0.0117
1232	0.0282	0.0363	0.0118
1231	0.0282	0.0363	0.0118
1230	0.0282	0.0364	0.0118
1229	0.0283	0.0364	0.0119
1228	0.0283	0.0365	0.0119
1227	0.0283	0.0365	0.0119
1226	0.0283	0.0365	0.012
1225	0.0284	0.0366	0.012
1224	0.0284	0.0366	0.012
1223	0.0285	0.0367	0.0121
1222	0.0285	0.0367	0.0121
1221	0.0285	0.0368	0.0121
1220	0.0286	0.0368	0.0122
1219	0.0286	0.0369	0.0123
1218	0.0287	0.0369	0.0123
1217	0.0288	0.037	0.0124
1216	0.0288	0.0371	0.0124
1215	0.0289	0.0371	0.0125
1214	0.0289	0.0372	0.0125
1213	0.029	0.0373	0.0126

1212	0.0291	0.0374	0.0127
1211	0.0291	0.0374	0.0128
1210	0.0292	0.0375	0.0128
1209	0.0293	0.0375	0.0129
1208	0.0293	0.0376	0.0129
1207	0.0294	0.0377	0.013
1206	0.0295	0.0378	0.013
1205	0.0296	0.0379	0.0131
1204	0.0296	0.038	0.0132
1203	0.0297	0.038	0.0132
1202	0.0298	0.0381	0.0133
1201	0.0299	0.0382	0.0133
1200	0.03	0.0383	0.0134
1199	0.0301	0.0384	0.0134
1198	0.0301	0.0384	0.0135
1197	0.0302	0.0385	0.0135
1196	0.0303	0.0386	0.0136
1195	0.0304	0.0387	0.0136
1194	0.0305	0.0388	0.0137
1193	0.0307	0.0389	0.0137
1192	0.0308	0.039	0.0138
1191	0.0309	0.0391	0.0139
1190	0.031	0.0392	0.014
1189	0.0312	0.0393	0.014
1188	0.0313	0.0394	0.0141
1187	0.0315	0.0396	0.0142
1186	0.0316	0.0397	0.0142
1185	0.0317	0.0398	0.0143
1184	0.0318	0.0399	0.0143
1183	0.032	0.04	0.0144
1182	0.0321	0.04	0.0144
1181	0.0322	0.0401	0.0145
1180	0.0324	0.0403	0.0145
1179	0.0325	0.0404	0.0146
1178	0.0326	0.0405	0.0147
1177	0.0328	0.0406	0.0147
1176	0.0329	0.0407	0.0148
1175	0.0331	0.0408	0.0149
1174	0.0332	0.0409	0.015
1173	0.0334	0.0411	0.0151
1172	0.0336	0.0412	0.0152
1171	0.0337	0.0413	0.0153
1170	0.0339	0.0414	0.0153
1169	0.034	0.0415	0.0154
1168	0.0342	0.0417	0.0155

1167	0.0344	0.0418	0.0156
1166	0.0346	0.0419	0.0157
1165	0.0348	0.0421	0.0157
1164	0.035	0.0422	0.0158
1163	0.0353	0.0424	0.0159
1162	0.0355	0.0425	0.0159
1161	0.0357	0.0427	0.0159
1160	0.0359	0.0428	0.016
1159	0.0361	0.043	0.0161
1158	0.0363	0.0432	0.0161
1157	0.0365	0.0433	0.0162
1156	0.0367	0.0434	0.0162
1155	0.0369	0.0436	0.0163
1154	0.037	0.0437	0.0163
1153	0.0372	0.0437	0.0164
1152	0.0373	0.0438	0.0165
1151	0.0374	0.0439	0.0165
1150	0.0375	0.044	0.0166
1149	0.0376	0.0441	0.0167
1148	0.0377	0.0442	0.0167
1147	0.0377	0.0442	0.0168
1146	0.0378	0.0443	0.0168
1145	0.0379	0.0444	0.0169
1144	0.038	0.0445	0.0169
1143	0.0381	0.0446	0.017
1142	0.0383	0.0447	0.0171
1141	0.0385	0.0448	0.0172
1140	0.0387	0.045	0.0174
1139	0.0389	0.0451	0.0175
1138	0.0391	0.0453	0.0176
1137	0.0394	0.0455	0.0177
1136	0.0396	0.0457	0.0178
1135	0.0399	0.0458	0.0179
1134	0.0401	0.046	0.018
1133	0.0404	0.0462	0.0182
1132	0.0407	0.0464	0.0184
1131	0.041	0.0466	0.0186
1130	0.0413	0.0469	0.0187
1129	0.0416	0.0471	0.0189
1128	0.042	0.0474	0.019
1127	0.0423	0.0476	0.0192
1126	0.0427	0.0479	0.0194
1125	0.0431	0.0482	0.0197
1124	0.0435	0.0486	0.0199
1123	0.044	0.0489	0.0201

1122	0.0444	0.0493	0.0203
1121	0.0448	0.0496	0.0206
1120	0.0453	0.05	0.0208
1119	0.0457	0.0504	0.021
1118	0.0461	0.0507	0.0213
1117	0.0466	0.0511	0.0215
1116	0.047	0.0515	0.0218
1115	0.0474	0.0518	0.0221
1114	0.0478	0.0522	0.0223
1113	0.0483	0.0526	0.0226
1112	0.0487	0.053	0.0229
1111	0.0491	0.0534	0.0231
1110	0.0496	0.0539	0.0234
1109	0.05	0.0543	0.0237
1108	0.0505	0.0547	0.024
1107	0.0509	0.0551	0.0243
1106	0.0513	0.0555	0.0246
1105	0.0518	0.0559	0.0249
1104	0.0522	0.0563	0.0252
1103	0.0526	0.0567	0.0255
1102	0.0531	0.0571	0.0258
1101	0.0536	0.0576	0.0261
1100	0.0541	0.058	0.0264
1099	0.0546	0.0585	0.0268
1098	0.055	0.059	0.0271
1097	0.0555	0.0594	0.0275
1096	0.056	0.0599	0.0278
1095	0.0564	0.0603	0.0282
1094	0.0568	0.0607	0.0285
1093	0.0572	0.0611	0.0288
1092	0.0576	0.0615	0.0292
1091	0.058	0.0618	0.0295
1090	0.0584	0.0621	0.0298
1089	0.0587	0.0624	0.0301
1088	0.0589	0.0626	0.0302
1087	0.0591	0.0628	0.0303
1086	0.0591	0.0628	0.0303
1085	0.0591	0.0628	0.0302
1084	0.0591	0.0628	0.03
1083	0.0591	0.0628	0.0298
1082	0.0591	0.0628	0.0297
1081	0.0592	0.0628	0.0295
1080	0.0592	0.0629	0.0295
1079	0.0594	0.0631	0.0296
1078	0.0596	0.0633	0.0297

1077	0.0599	0.0636	0.0299
1076	0.0603	0.0639	0.03
1075	0.0607	0.0642	0.0303
1074	0.0611	0.0646	0.0305
1073	0.0616	0.0651	0.0308
1072	0.0621	0.0656	0.0311
1071	0.0626	0.066	0.0313
1070	0.0631	0.0665	0.0316
1069	0.0636	0.067	0.0319
1068	0.0642	0.0674	0.0322
1067	0.0647	0.0679	0.0326
1066	0.0653	0.0684	0.0329
1065	0.0658	0.0689	0.0332
1064	0.0664	0.0693	0.0336
1063	0.067	0.0697	0.0339
1062	0.0675	0.0702	0.0341
1061	0.0681	0.0706	0.0344
1060	0.0687	0.0711	0.0346
1059	0.0693	0.0716	0.0348
1058	0.0698	0.072	0.0351
1057	0.0704	0.0725	0.0353
1056	0.071	0.0729	0.0355
1055	0.0716	0.0734	0.0357
1054	0.0722	0.0738	0.036
1053	0.0728	0.0743	0.0363
1052	0.0734	0.0748	0.0366
1051	0.0741	0.0754	0.0369
1050	0.0747	0.0758	0.0372
1049	0.0753	0.0763	0.0375
1048	0.0759	0.0768	0.0378
1047	0.0765	0.0773	0.0381
1046	0.077	0.0777	0.0384
1045	0.0775	0.0782	0.0386
1044	0.078	0.0786	0.0389
1043	0.0784	0.0789	0.0391
1042	0.0789	0.0792	0.0393
1041	0.0793	0.0796	0.0395
1040	0.0798	0.0799	0.0397
1039	0.0803	0.0803	0.0398
1038	0.0807	0.0806	0.04
1037	0.0812	0.081	0.0402
1036	0.0817	0.0813	0.0404
1035	0.0821	0.0817	0.0407
1034	0.0825	0.082	0.0409
1033	0.0828	0.0822	0.0411

1032	0.0831	0.0825	0.0412
1031	0.0834	0.0827	0.0413
1030	0.0837	0.0828	0.0414
1029	0.0839	0.0829	0.0414
1028	0.084	0.083	0.0415
1027	0.084	0.0831	0.0415
1026	0.084	0.0831	0.0414
1025	0.084	0.083	0.0414
1024	0.084	0.083	0.0413
1023	0.084	0.083	0.0412
1022	0.0839	0.0829	0.0411
1021	0.0839	0.0828	0.041
1020	0.0838	0.0827	0.0408
1019	0.0838	0.0826	0.0407
1018	0.0837	0.0825	0.0405
1017	0.0836	0.0825	0.0403
1016	0.0836	0.0824	0.0402
1015	0.0835	0.0823	0.04
1014	0.0834	0.0821	0.0398
1013	0.0832	0.082	0.0396
1012	0.083	0.0818	0.0393
1011	0.0828	0.0816	0.039
1010	0.0825	0.0813	0.0387
1009	0.0822	0.081	0.0384
1008	0.082	0.0808	0.0381
1007	0.0818	0.0807	0.0378
1006	0.0815	0.0805	0.0374
1005	0.0812	0.0803	0.0371
1004	0.0809	0.0801	0.0367
1003	0.0806	0.0798	0.0363
1002	0.0803	0.0796	0.0359
1001	0.08	0.0793	0.0355
1000	0.0797	0.0791	0.0352
999	0.0794	0.0789	0.0348
998	0.0791	0.0787	0.0344
997	0.0788	0.0785	0.0341
996	0.0785	0.0783	0.0337
995	0.0782	0.0781	0.0334
994	0.0779	0.0779	0.033
993	0.0776	0.0777	0.0326
992	0.0773	0.0775	0.0323
991	0.0771	0.0773	0.032
990	0.0769	0.077	0.0317
989	0.0766	0.0768	0.0314
988	0.0765	0.0766	0.0311

987	0.0764	0.0765	0.0308
986	0.0763	0.0763	0.0306
985	0.0762	0.0762	0.0304
984	0.0761	0.0761	0.0302
983	0.0759	0.076	0.03
982	0.0757	0.0758	0.0298
981	0.0755	0.0756	0.0296
980	0.0753	0.0754	0.0293
979	0.075	0.0752	0.0291
978	0.0747	0.0749	0.0288
977	0.0743	0.0747	0.0286
976	0.074	0.0744	0.0283
975	0.0736	0.0741	0.028
974	0.0732	0.0738	0.0278
973	0.0729	0.0735	0.0275
972	0.0725	0.0733	0.0273
971	0.0722	0.073	0.0271
970	0.0719	0.0727	0.0269
969	0.0716	0.0725	0.0268
968	0.0714	0.0723	0.0268
967	0.0712	0.0722	0.0268
966	0.0712	0.0722	0.027
965	0.0712	0.0722	0.0273
964	0.0713	0.0723	0.0277
963	0.0713	0.0724	0.028
962	0.0713	0.0724	0.0281
961	0.071	0.0722	0.028
960	0.0707	0.072	0.0277
959	0.0703	0.0718	0.0273
958	0.0699	0.0714	0.027
957	0.0694	0.0711	0.0266
956	0.0688	0.0707	0.0262
955	0.0682	0.0702	0.0259
954	0.0676	0.0698	0.0255
953	0.067	0.0693	0.0251
952	0.0664	0.0689	0.0248
951	0.0657	0.0684	0.0245
950	0.0651	0.0679	0.0242
949	0.0645	0.0674	0.024
948	0.0639	0.067	0.0238
947	0.0633	0.0666	0.0235
946	0.0628	0.0661	0.0233
945	0.0622	0.0657	0.0231
944	0.0616	0.0653	0.0228
943	0.0609	0.0648	0.0225

942	0.0603	0.0644	0.0223
941	0.0596	0.0639	0.0221
940	0.059	0.0634	0.0219
939	0.0585	0.063	0.0217
938	0.0579	0.0625	0.0214
937	0.0573	0.0621	0.0212
936	0.0568	0.0617	0.021
935	0.0562	0.0613	0.0207
934	0.0558	0.061	0.0206
933	0.0553	0.0607	0.0204
932	0.0549	0.0603	0.0203
931	0.0545	0.06	0.0201
930	0.0541	0.0596	0.0199
929	0.0536	0.0593	0.0198
928	0.0532	0.059	0.0197
927	0.0528	0.0587	0.0195
926	0.0525	0.0584	0.0194
925	0.0521	0.0582	0.0193
924	0.0518	0.058	0.0192
923	0.0515	0.0578	0.019
922	0.0511	0.0575	0.0189
921	0.0509	0.0573	0.0189
920	0.0506	0.0571	0.0188
919	0.0503	0.0569	0.0187
918	0.05	0.0567	0.0186
917	0.0496	0.0565	0.0185
916	0.0493	0.0562	0.0183
915	0.049	0.056	0.0182
914	0.0488	0.0557	0.0181
913	0.0485	0.0555	0.0181
912	0.0483	0.0553	0.018
911	0.0481	0.0552	0.018
910	0.0479	0.055	0.018
909	0.0476	0.0549	0.0179
908	0.0474	0.0547	0.0179
907	0.0472	0.0545	0.0178
906	0.0469	0.0543	0.0177
905	0.0467	0.0541	0.0177
904	0.0465	0.054	0.0176
903	0.0463	0.0538	0.0175
902	0.0461	0.0536	0.0174
901	0.0459	0.0535	0.0174
900	0.0457	0.0534	0.0173
899	0.0456	0.0532	0.0173
898	0.0454	0.0531	0.0172

897	0.0452	0.0529	0.0171
896	0.0451	0.0528	0.0171
895	0.0449	0.0526	0.0171
894	0.0448	0.0525	0.017
893	0.0447	0.0524	0.017
892	0.0446	0.0523	0.017
891	0.0445	0.0522	0.0169
890	0.0443	0.0521	0.0169
889	0.0443	0.052	0.0168
888	0.0443	0.0519	0.0168
887	0.0445	0.052	0.0169
886	0.0449	0.0522	0.0169
885	0.0456	0.0525	0.0171
884	0.0465	0.053	0.0172
883	0.0476	0.0535	0.0174
882	0.049	0.0542	0.0176
881	0.0507	0.055	0.0179
880	0.0526	0.056	0.0183
879	0.0548	0.0571	0.0187
878	0.057	0.0582	0.0191
877	0.0593	0.0592	0.0195
876	0.0614	0.0601	0.0198
875	0.0632	0.0609	0.02
874	0.0646	0.0614	0.0201
873	0.0652	0.0614	0.02
872	0.0647	0.061	0.0197
871	0.063	0.0601	0.0192
870	0.0605	0.0589	0.0186
869	0.0576	0.0576	0.0181
868	0.0549	0.0563	0.0177
867	0.0527	0.0552	0.0173
866	0.051	0.0544	0.0171
865	0.0497	0.0537	0.0169
864	0.0487	0.0531	0.0167
863	0.0479	0.0526	0.0166
862	0.0472	0.0521	0.0164
861	0.0466	0.0517	0.0163
860	0.0461	0.0514	0.0161
859	0.0457	0.0511	0.016
858	0.0453	0.0509	0.0159
857	0.045	0.0507	0.0158
856	0.0447	0.0504	0.0158
855	0.0445	0.0502	0.0157
854	0.0443	0.05	0.0157
853	0.0441	0.0499	0.0157

852	0.0439	0.0498	0.0157
851	0.0438	0.0497	0.0157
850	0.0438	0.0495	0.0157
849	0.0438	0.0494	0.0156
848	0.0438	0.0493	0.0156
847	0.0436	0.0491	0.0155
846	0.0434	0.049	0.0155
845	0.0431	0.0489	0.0154
844	0.0429	0.0488	0.0153
843	0.0428	0.0487	0.0153
842	0.0427	0.0486	0.0153
841	0.0426	0.0485	0.0153
840	0.0425	0.0485	0.0153
839	0.0425	0.0485	0.0152
838	0.0424	0.0484	0.0152
837	0.0423	0.0483	0.0153
836	0.0423	0.0483	0.0153
835	0.0423	0.0482	0.0153
834	0.0423	0.0482	0.0153
833	0.0423	0.0482	0.0153
832	0.0422	0.0483	0.0153
831	0.0422	0.0482	0.0153
830	0.0422	0.0482	0.0152
829	0.0421	0.0481	0.0152
828	0.0421	0.0481	0.0153
827	0.0421	0.0481	0.0153
826	0.0421	0.0481	0.0153
825	0.0421	0.0481	0.0154
824	0.0421	0.0481	0.0154
823	0.0421	0.0482	0.0154
822	0.0421	0.0482	0.0153
821	0.042	0.0482	0.0153
820	0.0419	0.0481	0.0153
819	0.0418	0.048	0.0153
818	0.0417	0.048	0.0153
817	0.0418	0.048	0.0154
816	0.0418	0.048	0.0154
815	0.0419	0.048	0.0155
814	0.0419	0.048	0.0155
813	0.0419	0.048	0.0155
812	0.0418	0.048	0.0156
811	0.0418	0.048	0.0156
810	0.0418	0.0479	0.0157
809	0.0418	0.0479	0.0158
808	0.0418	0.0478	0.016

807	0.0418	0.0478	0.0161
806	0.0417	0.0477	0.0163
805	0.0417	0.0477	0.0165
804	0.0417	0.0477	0.0166
803	0.0418	0.0477	0.0167
802	0.0418	0.0477	0.0169
801	0.0418	0.0477	0.017
800	0.0418	0.0477	0.0171
799	0.0418	0.0477	0.0171
798	0.0418	0.0476	0.0172
797	0.0418	0.0476	0.0171
796	0.0419	0.0475	0.0171
795	0.0419	0.0475	0.017
794	0.0419	0.0474	0.0169
793	0.0419	0.0474	0.0169
792	0.0419	0.0473	0.0168
791	0.0419	0.0473	0.0167
790	0.0419	0.0472	0.0166
789	0.0419	0.0471	0.0166
788	0.0419	0.0471	0.0165
787	0.0419	0.047	0.0165
786	0.042	0.047	0.0166
785	0.042	0.047	0.0166
784	0.042	0.047	0.0168
783	0.0421	0.047	0.0169
782	0.0421	0.047	0.017
781	0.0421	0.0469	0.017
780	0.0422	0.0469	0.0171
779	0.0422	0.0469	0.0171
778	0.0422	0.0469	0.0171
777	0.0423	0.0469	0.0171
776	0.0424	0.0469	0.017
775	0.0424	0.0469	0.0169
774	0.0424	0.047	0.0168
773	0.0425	0.047	0.0168
772	0.0426	0.047	0.0167
771	0.0427	0.0471	0.0166
770	0.0427	0.0471	0.0166
769	0.0428	0.0471	0.0165
768	0.0428	0.0472	0.0164
767	0.043	0.0472	0.0164
766	0.0431	0.0473	0.0163
765	0.0432	0.0474	0.0163
764	0.0434	0.0475	0.0163
763	0.0435	0.0475	0.0164

762	0.0436	0.0476	0.0164
761	0.0437	0.0477	0.0163
760	0.0438	0.0477	0.0163
759	0.044	0.0478	0.0163
758	0.0441	0.0478	0.0163
757	0.0442	0.0479	0.0164
756	0.0443	0.048	0.0164
755	0.0443	0.048	0.0164
754	0.0444	0.0481	0.0164
753	0.0444	0.0481	0.0164
752	0.0444	0.0482	0.0163
751	0.0445	0.0483	0.0163
750	0.0446	0.0483	0.0163
749	0.0447	0.0484	0.0164
748	0.0448	0.0484	0.0164
747	0.0448	0.0484	0.0164
746	0.0449	0.0484	0.0164
745	0.045	0.0484	0.0163
744	0.0451	0.0484	0.0163
743	0.0452	0.0485	0.0163
742	0.0453	0.0485	0.0163
741	0.0453	0.0486	0.0163
740	0.0453	0.0486	0.0162
739	0.0454	0.0486	0.0162
738	0.0454	0.0486	0.0162
737	0.0455	0.0487	0.0162
736	0.0456	0.0487	0.0162
735	0.0457	0.0488	0.0162
734	0.0458	0.0488	0.0162
733	0.0459	0.0488	0.0162
732	0.046	0.0489	0.0163
731	0.0461	0.0489	0.0163
730	0.0462	0.0489	0.0163
729	0.0463	0.049	0.0163
728	0.0464	0.0492	0.0164
727	0.0465	0.0493	0.0164
726	0.0466	0.0495	0.0164
725	0.0467	0.0496	0.0163
724	0.0469	0.0497	0.0164
723	0.0471	0.0499	0.0164
722	0.0473	0.05	0.0165
721	0.0475	0.0502	0.0165
720	0.0478	0.0504	0.0166
719	0.0481	0.0507	0.0167
718	0.0485	0.051	0.0168

717	0.0491	0.0513	0.0168
716	0.0499	0.0518	0.0169
715	0.0508	0.0523	0.017
714	0.0517	0.0528	0.0171
713	0.0522	0.053	0.0171
712	0.0523	0.0531	0.0171
711	0.0521	0.0529	0.0171
710	0.0516	0.0527	0.0171
709	0.0511	0.0525	0.017
708	0.0506	0.0523	0.017
707	0.0503	0.0522	0.017
706	0.0501	0.0521	0.0169
705	0.05	0.0521	0.0169
704	0.0499	0.0521	0.0169
703	0.0499	0.0521	0.017
702	0.0499	0.0521	0.017
701	0.05	0.0521	0.0171
700	0.05	0.0521	0.0172

SI 5.13: FTIR spectra of know quantities of larch biochar sintered with wood ash (WAS) after 24 hours of contact with Tributary 1

SI 5.13 are the FTIR data to underpin Figure 4.7B in section 5.3.4 (results ands discussion section chapter 5)