Chemical characteristics of wildfire ash across the globe and their environmental and socio-economic implications

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Abstract

The mobilisation of potentially harmful chemical constituents in wildfire ash can be a major consequence of wildfires, posing widespread societal risks. Knowledge of wildfire ash chemical composition is crucial to anticipate and mitigate these risks.

Here we present a comprehensive dataset on the chemical characteristics of a wide range of wildfire ashes (42 types and a total of 148 samples) from wildfires across the globe and examine their potential societal and environmental implications. An extensive review of studies analysing chemical composition in ash was also performed to complement and compare our ash dataset.

Most ashes in our dataset had an alkaline reaction (mean pH 8.8, ranging between 6 – 11.2). Important constituents of wildfire ash were organic carbon (mean: 204 g kg^{-1}), calcium, aluminium, and iron (mean: 47.9, 17.9 and 17.1 g kg^{-1}). Mean nitrogen and phosphorus ranged between 1 - 25 g

kg^{-1}, and between 0.2 to 9.9 g kg^{-1}, respectively. The largest concentrations of metals of concern for human and ecosystem health were observed for manganese (mean: 1488 mg kg^{-1}; three ecosystems > 1000 mg kg^{-1}), zinc (mean: 181 mg kg^{-1}; two ecosystems > 500 mg kg^{-1}) and lead (mean: 66.9 mg kg^{-1}; two ecosystems > 200 mg kg^{-1}). Burn severity and sampling timing were key factors influencing ash chemical characteristics like pH, carbon and nitrogen concentrations. The highest readily dissolvable fractions (as a % of ash dry weight) in water were observed for sodium (18%) and magnesium (11.4%). Although concentrations of elements of concern were very close to, or exceeded international contamination standards in some ashes, the actual effect of ash will depend on factors like ash loads and the dilution into environmental matrices such as water, soil and sediment. Our approach can serve as an initial methodological standardisation of wildfire ash sampling and chemical analysis protocols.

Keywords: water contamination and eutrophication; wildfire impacts; mobilization; water quality; ash redistribution; biogeochemical cycles

1. Introduction

Wildfires are a natural process fundamental to the functioning of many ecosystems (Pausas and Keeley, 2019). However, over the past decades, anthropogenic-driven changes in climate, land cover and fire use have substantially aggravated wildfire threats to human life, natural resources, and infrastructure in many regions worldwide (Doerr & Santín, 2016). Each year wildfires burn extensive vegetated areas both in fire-adapted and non-adapted regions, often altering vegetation structure and the topsoil. These perturbations can have substantial effects on key biogeochemical processes that affect the mobility and bioavailability of essential nutrients for plants and animals (e.g., nitrogen [N], phosphorus [P], potassium [K], magnesium [Mg]) and of potentially toxic elements or compounds (e.g., mercury [Hg], lead [Pb], polycyclic aromatic hydrocarbons [PAHs]) (Gustine et al., 2022; Harper et al., 2019; Santín et al., 2015a; van der Werf et al., 2017).

Although most research and public attention regarding contaminants and fire are focused on the mobilization of elements through smoke (Burke et al., 2020; Cascio, 2018; Chen et al., 2021; Xu et al., 2020), a large fraction of the chemical components mobilised during a fire are associated with the ash. Here we refer to wildfire ash as “the particulate residue remaining or deposited on the ground, from the burning of wildland fuels and consisting of mineral materials and charred organic components” (Bodí et al., 2014, p. 104). During burning of wildland fuels, many elements are not volatilized but concentrated in the ash (e.g., C, Ca, Al, Fe). Ash composition depends on the type of

elements and their concentrations in the ecosystem before the fire and on burning conditions (e.g., maximum temperature and duration), which can also determine the elements' geochemical form (Santín et al., 2015b). When deposited and incorporated into the soil, the typically alkaline and nutrient-rich ash can induce changes in soil pH and represents a nutrient flux to soils (the so-called 'fertilizing effect') (Bodí et al., 2014; Maass, 1995). However, ash is also susceptible to being transported by wind and water as part of sediment and debris during enhanced post-fire erosion (Nunes et al., 2018) (Fig. 1a, b). The transfer of ash-derived potentially toxic and eutrophying constituents to aquatic systems represents a major concern (e.g., Gomez-Isaza et al., 2022; Santín et al., 2015b; Smith et al., 2011) since it can damage aquatic ecosystems and severely disrupt drinking water supplies, carrying high environmental and socioeconomic costs (Hohner et al., 2019; Robinne et al., 2021). Adverse effects of both toxic compounds and nutrients in wildfire ash, which are highly dependent on dosage and duration of exposure, have been reported in aquatic ecosystems for macroinvertebrates (Brito et al., 2017; Harper et al., 2019), amphibians, fish and algae (e.g., Campos et al., 2012; Gonino et al., 2019; Oliveira-Filho et al., 2018; Pilliod et al., 2003). Wildfires often burn large watersheds that are key sources of drinking water for populated areas nearby (Hohner et al., 2019; Robinne et al., 2021). For example, the extreme fire season in south-east Australia in 2019-2020, which burned 5.8 million ha, threatened the drinking water of 5.5 million people, with several urban areas having to restrict water consumption (Neris et al., 2021).

The effects of wildfire ash are wide-ranging, and its mobilization can also pose a risk to human health. These include, for example, respiratory problems through ash inhalation by firefighters or post-fire restoration teams, and to the public nearby or downwind of active fires and recently burnt areas (e.g., Alexakis et al., 2020; Wan et al., 2021). Ash toxicity and the mobility of hazardous materials (including metals and metalloids like arsenic [As], chromium [Cr], and cadmium [Cd]) are specially elevated in fires in the wildland-urban interface that burn residential, commercial, and industrial infrastructure (Alshehri et al., 2022; Plumlee et al., 2014; Wan et al., 2021),

[Location of Figure 1]

For several decades, and despite its ubiquitous presence and potential importance, wildfire ash was largely overlooked as a topic of research. This is partly due to its high mobility, and hence rapid redistribution after fire, which makes wildfire ash more challenging to collect than other components of the post-fire environment, such as fire-affected soils or the eroded sediment (Bodí et al., 2014). Over the last few years, however, research interest in wildfire ash has gained traction, with studies assessing ash chemical characteristics in a diverse range of ecosystems such as tropical

and sub-tropical savannas (Brito et al., 2017; Brito et al., 2021; Caumo et al., 2022; Oliveira-Filho et al., 2018; Sánchez-García et al., 2021), tropical broadleaf forests (Audry et al., 2014), temperate eucalypt forests (Campos et al., 2015; Campos et al., 2016; Costa et al., 2014; Santín et al., 2012; 2015b; 2018; Silva et al., 2015; Wu et al. 2017), Mediterranean and temperate conifer forests (Balfour & Woods, 2013; Harper et al., 2019; Pereira et al., 2012; Simon et al., 2016; Tsai et al., 2015; Quigley et al., 2019; Wang et al., 2015), temperate heathlands (Marcos et al., 2008), boreal forests (Kohl et al., 2019), and wetlands (Liu et al., 2010). This previous research indicated that ash chemical composition is highly heterogeneous even for ash from the same or similar ecosystems (Table 1). For example, Balfour & Woods (2013) reported more than a threefold difference in Mg and Al (aluminum), and a difference of an order of magnitude for N and Mn (manganese) content in two ash types from high severity fires in temperate conifer forests in Yellowstone National Park (Wyoming, USA) and British Columbia (Canada). The differences in ash characteristics among ecosystems are also very notable when comparing values among studies (Table 1), however, the different sampling and laboratory techniques used across the studies makes a straightforward comparison difficult and highlights the need for standardized approaches.

With anthropogenically-driven changes in climate and land use increasing the frequency and severity of wildfires in many regions of the world (Jones et al., 2022), a more complete understanding of the chemical composition of wildfire ash and its driving factors is needed to facilitate assessment and prediction of its potential effects on the environment and human health. We address this knowledge gap here by analysing and evaluating the chemical characteristics of wildfire ash produced in a wide range of scenarios and following a standard analysis approach to facilitate comparison across study sites. To our knowledge this is the first study to present a comprehensive dataset of chemical characteristics of ash produced during vegetation fires of contrasting severity in different ecosystems across the globe. We report the following key chemical parameters for a wide range of wildfire ash types (42 types and a total of 148 samples) from different sampling locations, burn severities and ecosystems (Fig. 2): i) pH and electrical conductivity (EC); ii) the concentration of organic and inorganic carbon (OC and IC) and the total concentration of other major nutrients, including nitrogen (N), phosphorus (P), calcium (Ca), magnesium (Mg) and sodium (Na), and metals including aluminium (Al), iron (Fe), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb) and mercury (Hg); and iii) the dissolved concentrations of OC, ammonium (NH_4^+), fluorine (F^-), P, Ca, Mg, Na, Al, Fe and Mn. In addition, we also perform an extensive review of previous studies (16) assessing chemical composition in ash to complement and facilitate comparison with our field samples. The specific objectives of this study were to i) determine chemical characteristics of wildfire

ash produced across different ecosystems; ii) identify the main factors influencing ash chemical characteristics; and iii) evaluate the concentration levels of elements of concern found in ash and their potential socioeconomic, health, and environmental implications in relation to international contamination standards guidelines.

[Location of Figure 2]
[Location of Table 1]

2. Sampling and methods

2.1 Sampling and chemical characterisation of ash

Ash samples were collected from 29 sites directly affected by wildfires, or in some cases experimental wildfires, in 8 countries (Australia, Austria, Canada, South Africa, Spain, The Netherlands, United Kingdom and USA), spanning 11 ecosystems (Fig. 2). For some fires, ash from different soil burn severities was collected. Across sites, the number of samples ranged between one and 23, resulting in a total of 148 ash samples divided in 42 ash types according to sampling location, burn severity, ecosystems and the presence of rain before collection (Table 2 and Table S1). The general ash sampling procedure involved a series of sampling points along three parallel transects per soil burn severity (Parsons et al., 2010; Santín et al. 2015a). This sampling strategy is referred to as 'transect' in Table S1. In most cases, all samples within a transect were pooled together to form a composite sample. In a few cases, like in the AUSTRIA sample and the samples from Wales (UKSOWA, UKSWANG, UKSWANP), a composite sample made from samples taken at several similar points was used (sampling procedure referred to as 'composite' in Table S1). Complete details about the study sites, fire characteristics and sampling can be found in Table S1.
[Location of Table 2]

In this study we refer to the 'ash layer' as the powdery residue (mesh size: <1 mm) left on the ground after the burning of biomass and necromass. It is important to notice that this ash layer may also contain some burnt mineral soil in situations in which soil organic matter was completely or partially combusted and, thus, unaggregated mineral components became part of the ash layer (Parsons et al., 2010). This burnt soil residue is distinct from the underlying mineral soil layer (Fig. 1d) (Bodí et al., 2014; Santín et al., 2015b).

The ash samples were collected at various times after the respective fires had occurred or the fire had burned the sampling area. Fifteen of the ash types were collected within seven days (some

within hours) after the sampling area had burned; while the remaining 27 ash types were collected between one week and three months after the sampling area had burned (for specific sampling times see Table S1). A longer delay until sampling often arises from the remoteness of sites or the legal period until a site is deemed safe enough for sampling. Usually, the longer the time between the fire and the sampling, the higher the probability of some rain falling, which meant that 20 of the 42 ash types in this study received some rainfall before sampling (Table 2).

For each sample, chemical parameters, including pH and EC, the total concentration (acid digest) of major nutrients (C, Ca, Mg, N, Na, P) and metals and metalloids (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn), and the readily dissolvable concentration (in water extracts) of Al, Ca, F, Fe, Mg, Mn, Na, NH_4^+, OC and P (chemical symbols thereafter preceded with a 'd') were analysed following established methods. As, Cd, Cr, carbonates ($CO_3^=$), and dissolved organic carbon (DOC) were analysed for some samples. In brief, pH and EC were determined in water, using an ash-to-water mass ratio of 1:20 after stirring for 5 min and waiting for 10 min (Buurman et al., 1996). Total N and C concentrations were determined using a Total Analyzer Leco TruSpec CHN (Leco Corp., St Joseph, MI, USA). The total concentrations of major nutrients, metals and metalloids were extracted from the ash samples (0.25 g) by microwave-assisted acid digestion (9 ml of 14.4 M $HNNO_3$, 3 ml of 12M HCl, 200 °C for 45 min) according to EPA Method 3051A and determined by ICP-OES spectrometry (Perkin Elmer, Optima 4300DV). Carbonates were analysed using a digital calcimeter (DB FOG-L Digital Calcimeter, BD Inventions, Thessaloniki, Greece). The IC was calculated from the concentration of $CO_3^=$, and this value was subtracted from total C to calculate total OC.
Readily dissolvable concentrations were analysed according to the leaching test described for wildfire ash by Hageman (2007) to determine the amount of these components that might be mobilised by water, thus influencing their bioavailability and toxicity. For this, 2 g of sample were weighed into 50 ml bottles. Then, 40 ml ultrapure water (sample:water ratio 1:20) was added and the bottles were shaken for 5 min. The supernatants were then filtered (0.45 µm pore-size) and analysed using colorimetry (dNH_4^+), inductively Coupled Plasma Mass Spectrometry and Atomic Absorption. Dissolved P (dPO_4) was analysed as PO_4 (see supplementary material for a detailed description of these methods).

We also performed mineralogical analyses in a select set of samples representative of different ecosystems, soil burn severity and rainfall before sampling (i.e., TAUS-H, TAUS-L, LECAN-H-, LECAN-L, SAMB, MUSA-H, MUSA-L, UKMA-H, UKSWANP, and NETHER). The analyses were performed by X-ray diffractometry (XRD) using an XRD Broker D8 advance in previously ground ash and were carried out

with a 40 kV and 40 mA current with CuKα radiation in continuous step mode with a coupled graphite crystal monochromate. The peaks were obtained in the angular range of $3<2\theta<70$ by step scanning at 2 s intervals per 0.02°. Additionally, ash samples were analysed using a Field Emission Scanning Electron Microscope (FE-SEM Zeiss Gemini 500 Ultra Plus with EDX-Image) at a resolution of 0.8 nm and an accelerating voltage of 30 kV.

2.2 Statistical analysis

First, we simplified soil burn severity field assessments by grouping ash types in two contrasting burn severity classes (i.e., low or high) according to the characteristics of the sampled area. These included chiefly ash colour (low severity when ash colour is dark and high severity when ash colour is light), and degree of vegetation combustion assessed by the diameter of surviving branches on live near-surface fuels (vegetation combustion is higher at high severity) (Keeley et al., 2009; Parsons et al., 2010; Santín et al., 2015b). This facilitates comparison between degrees of burn severity within and, to some degree, between study sites. A comparison of burn severities among ecosystems needs to be made with caution as the fire behaviour and combustion dynamics that result in a particular burn severity may differ (e.g., smouldering-dominated combustion in peatland fuels vs. flaming-dominated combustion in other fuels).

We grouped the 148 ash samples into the 42 ash types described above and used the median value for each ash type from the different sites and burn severity classes. The median was used as this value provides a better indication of the high inner-site variability observed amongst the chemical parameters than the mean. Subsequently, when calculating average values for the chemical parameters including all the ash types or when grouping the ash types by burn severity or ecosystems, we used the mean of the medians. The Spearman's rank correlation coefficient was used to test for correlations between the chemical parameters analysed (significance level set at $p < 0.05$). Relative intra-site variability in ash chemical parameters was quantified with the coefficient of variation (CV = (standard deviation/mean) x 100). The dissolved fraction was calculated as a percentage of dry ash weight with data given for both total and dissolved concentrations for Al, Ca, Fe, Mg, Mn, Na, and P.

To examine the main sources of variability in chemical properties among the 42 ash types, we identified groups (or clusters) of ashes with similar chemical characteristics by applying an unsupervised classification. For this, a hierarchical clustering analysis (Euclidean distance, Ward's method) was used to identify the optimal number of clusters (n = 3). This was followed by a non-

hierarchical clustering analysis (k-means) to classify the 42 ashes into the different clusters. To identify any significant predictor variables of the clusters, a supervised classification using logistic regression was applied. For this analysis, the third of the three clusters identified (cluster 3) was excluded due to its extreme values, which interfered with model fitting. B-Random K-Fold cross-validation estimated the accuracy of the model. A one-way analysis of variance (ANOVA) was used to test for overall statistical differences in chemical parameters between the clusters. If significant differences were observed, the Tukey's post-hoc test was applied to identify statistically significant clusters.

To examine the effect of burn severity on ash chemical properties, controlling for the effect of rain (presence vs. absence of rainfall) before sampling and ecosystems, linear-mixed effect models (one per chemical property) were fitted. Cluster 3 was excluded again from these analyses due to its extreme values. ANOVA Type III Wald F test with Kenward-Roger degrees of freedom was used to test for significant differences in the chemical characteristics between high and low burn severity classes, and between ecosystems. All variables were transformed (square root or log) to satisfy assumptions of normality, and all fitted models met the assumptions concerning normally distributed residuals, homoscedasticity, and linearity. All statistical analyses were done in R (R Core Team, 2014) and Microsoft Excel (2011).

3. Results and discussion

3.1. Ash chemical composition

3.1.1. Major nutrients

Of the chemical elements analysed, carbon was the main ash component, with a 96% of this C being in organic form (OC; mean: 204 g kg^{-1} ash; Table 3). The sum of OC and IC in our field samples (215 g kg^{-1} ash; Table 3) is within the overall ranges observed for total C in previous studies (50 – 460 g kg^{-1}; Table 1; e.g., Alshehri et al., 2002; Costa et al., 2014; Pereira et al., 2012; Ulery et al., 1993). In many cases, the concentration of C in the ash is higher than that of the pre- and post-burn mineral soil. For example, for the NAUS site (temperate eucalypt forest, Table 2), Santín et al. (2015b) reported 4 and 3.8% (40.0 and 38.1 g kg^{-1} of total C) for unburnt and burnt soil, respectively, while 24.7% (247 g kg^{-1} of total C) was observed in the ash from the same fire. Similarly, for the study sites from the sub-tropical savanna in South Africa (SAPB1, SAPB3 and SAMB), we observed total C contents in the ash an order of magnitude higher than in the pre- and post-burn soils (Sánchez-García et al., 2021). This

is because the main contributor to ash is usually vegetation and highlights the important role of ash in mobilizing and redistributing C in the landscape after fire (Bodí et al., 2014; Santín et al., 2012).

After C, Ca was the most abundant analysed component in the ash (average concentration 47.9 g kg^{-1} ash; ranging between 5.9 and 209 g kg^{-1} in ash from peatland and temperate mixed forest; Table 3 and 5). These ranges were similar in magnitude as the overall ranges observed in the literature (3.10 – 313 g kg^{-1}; e.g., Costa et al., 2014; Balfour & Woods, 2013; Ulery et al., 1993; Table 1), where the highest Ca concentration was also observed in ash from Mediterranean conifer forest (Ulery et al., 1993), and are likely related to the Ca concentration in the soil and vegetation before the fire, and to most ashes from this type of ecosystem being produced at higher burn severities (Table 2; see section 3.2.1).

Mean N content in the ash was 7.8 g kg^{-1} ash (0.78%), ranging from 3 g kg^{-1} (0.30%), in temperate shrubland, to 17.5 g kg^{-1} (1.75%) in upland grassland (Table 3 and 5). While the mean N content is similar to the ranges reported in the literature (0.10 – 19.8 g kg^{-1}; e.g., Alshehri et al., 2022; Balfour and Woods, 2013; Costa et al., 2014; Pereira et al., 2012; Table 1), N values of an order of magnitude lower than those found in our field samples were observed by Balfour and Woods (2013) in ash from temperate conifer forest (0.10 g kg^{-1}).

Mean Mg and P in the ash were 5.4 and 2.5 g kg^{-1} ash (Table 3), respectively, and were similar to those reported in the literature (e.g., Brito et al., 2017; Ulery et al., 1993; Table 1). Mean Na concentration (5 g kg^{-1}; Table 3) is slightly above the maximum value observed in previous studies where Na concentration ranges from 0.05 to 3.30 g kg^{-1} (e.g., Audry et al., 2014; Costa et al., 2014; Ferreira et al., 2005; Table 1)**.** Among ecosystems, the contents of these three elements were highly variable. For example, Mg concentrations differed by up to an order of magnitude between ash from peatland and Mediterranean shrubland (1.40 and 13.5 g kg^{-1}, respectively; Table 5). Similarly, differences of up to two orders of magnitude were reported for P between temperate eucalypt forest and sub-tropical savanna (0.3 and 5.90 g kg^{-1}; Table 5), and for Na between temperate shrubland and temperate conifer forest (0.20 and 10.5 g kg^{-1}; Table 5).

[Location of Table 3]
[Location of Table 4]
[Location of Table 5]

3.1.2. Metals and metalloids

Al and Fe were the third and fourth most abundant analysed elements in the ash, after C and Ca, with similar mean values (Al: 17.9 g kg^{-1} ash; Fe: 17.1 g kg^{-1} ash; Table 3), which were closer to the upper values of the overall ranges reported in previous studies (Al: 2.30 – 19.0 g kg^{-1}, Fe: 0.10 – 12.3 g kg^{-1}; e.g., Brito et al., 2017; Ulery et al., 1993; Table 1). Among ecosystems, differences of an order of magnitude were observed for both Al and Fe, with Mediterranean conifer forest showing the highest concentrations (34.2 and 29.7 g kg^{-1} for Al and Fe; Table 5) and boreal forest the lowest (1.20 g kg^{-1} for both, Al and Fe; Table 5) possibly as a result of differences in geology and vegetation among the sites and, also, due to the contribution of mineral soil to the ash (Cerrato et al., 2016).

Regarding Mn and Zn, the mean concentrations (1,488 and 181 mg kg^{-1} ash, respectively; Table 3) are within the overall ranges observed in the literature (Mn: 107 – 8,000 mg kg^{-1}; Zn: 29.90 – 36,058 mg kg^{-1}; Table 1). Lower concentrations (<100 mg kg^{-1}) were obtained for the remaining metals analysed (i.e., Pb, Cu, Hg, Ni, Cr, and Cd) similar to the concentrations reported in previous studies (e.g., Brito et al., 2017; Campos et al., 2016; Santos et al., 2023; Table 1). When looking at the concentrations among ecosystems, comparatively high Pb were observed in the peatland (Pb: 782 mg kg^{-1}; Table 5) and temperate mixed forest ash (Pb: 453 mg kg^{-1}; Table 5) possibly influenced by past industrial activity, the specific geogenic background of the areas and/or accumulation from atmospheric deposition from vehicle emissions (Paul et al., 2022; Stein et al., 2012). Regarding As, the mean concentration in our study (3,541 µg kg^{-1}; Table 3) was within the range reported in previous studies (1,040 – 42,000 µg kg^{-1} ash; e.g., Caumo et al., 2022; Silva et al., 2015; Table 1).

3.1.3. pH, EC and dissolved elements

For most samples ash pH was alkaline, with a mean value of 8.8, and overall values ranging from 6 to 11.2 (Table 4). Immediately after a fire, the ash pH shows a typical range from weak alkaline to caustic alkaline (Plumlee et al., 2014). The high typical pH of wildfire ash is attributed to high concentrations of compounds with alkali reactions such as oxocalcium (CaO) or potassium oxide (K_2O) (Bodí et al.,2014). Regarding EC, an average of 1,330 µS cm^{-1} in the deionized-water leachates was found, with values ranging from 32.5 to 13,700 µS cm^{-1} (Table 4). Among ecosystems, the lowest pH and EC values were observed in ash from peatland (pH: 7.1, EC: 237 µS cm^{-1}; Table 5) and the highest in sub-tropical savanna (pH:10.1, EC: 6,943 µS cm^{-1}; Table 5). This variability in EC and pH reflects the differences in environmental conditions of the sampling sites (e.g., soil and vegetation type, amount of precipitation and temperatures).

The most abundant dissolved elements analysed in our study are, in descending order, dCa, dNa, and dMg; which is in line with the presence of calcite ($CaCO_3$) in the ash, the high solubility of calcium sulphate ($CaSO_4 \cdot 2H_2O$) and mixed Ca sulphates, and syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) (Table 6). The least abundant dissolved elements are dF, dMn, and dFe, coinciding with rare elements in the composition of primary minerals (e.g., F) or elements with low solubility in environments with alkaline pH (e.g., Fe, Mn). Significant positive correlations were observed between pH and some of the nutrients (i.e., Ca, Mg, Na, and P) in line with the high solubility of oxide carbonates and Ca, Na and Mg oxides, whereas the increment in P might be explained by the increase in some calcium phosphates (e.g. $CaHPO_4$, $Ca_4H(PO_4)_3$) or Al or Fe phosphates ($AlPO_4$; $FePO_4$) because of the increase in pH (Stumm and Morgan, 1996).

Significant negative correlations were observed between pH and some metals like Al, Fe, Pb, and Hg (Fig. S1). This might be explained by the low solubility of oxyhydroxides of Fe and Al at neutral or alkaline pH, and by the loss of Pb and Hg through volatilization with the increase in fire temperature. This is also consistent with the trends when the dissolved elements in the deionized-water leachates are considered as a fraction of the total content, where Na and Mg were dissolved the most (18 and 11.4%, respectively), followed by Ca (4.6%) and P (1.7%). Mn, Al and Fe were dissolved the least with fractions ranging from 0.02 to 0.3% (Table 4).

To our knowledge, a limited number of studies have reported dissolved elements (deionized-water leachates) in wildfire ash (e.g., Brito et al., 2017; Burton et al., 2016; Hageman et al., 2008a and 2008b; Murphy et al., 2018; 2020; Pereira et al., 2012; Tsai et al., 2017; Wang et al., 2015; Wolf et al., 2011), but, in general, the ranges reported in the aforementioned studies are in the lower end of the ranges reported here. An exception is the study by Pereira et al. (2012) whose dissolved concentration values from Mediterranean conifer forest are closer to the upper ranges reported in this study. Besides differences between study sites (covering different ecosystems, burn severity, soil properties, geology and plant characteristics), these contrasting results might reflect the variety of methods used to estimate dissolved concentrations in those previous studies and our own. Given that no single standard procedure currently exists for the analysis of readily dissolvable elements in ash, differences in water:ash rates, stirring times and time in solution are likely to result in different estimations of dissolvable ash fractions. It is also worth noting that the dissolution values reported in this study are highly concentrated (water:sample ratio: 1:20) and the shaking time was relatively short (5 min), thus, our estimates of readily dissolvable fraction can be considered conservative, with the real effect from ash depending on its dilution factor into environmental matrices like soils,

sediments, water, or air. Standardizing the methodology to evaluate the dissolvable fraction of elements and potentially toxic substances in water bodies could be critically important, especially given the increase in the severity of wildfire impacts in many regions.

3.1.4. Mineralogy

The XRD results and FE-SEM images (Fig. S2) show an overall presence of primary minerals (i.e., quartz, muscovite, and microcline; Table 6), indicating that not only minerals in plants, but also some of the mineral fraction from soil becomes part of the ash layer, sometimes in substantial quantities. Quartz is present in all samples although in variable proportions (9-84%; Table 6). Microcline, muscovite and albite are also frequently observed, with hornblende, andesine or biotite being rare. In some of the samples, secondary minerals like hematite, and other minerals, like ilmenite ($FeTiO_3$), rutile (TiO_2), chromite ($FeCr_2O_4$), calcite ($CaCO_3$) or gypsum ($CaSO_4$) are also observed (Fig. S2).

[Location of Table 6]

3.2. Main sources of variability in chemical characteristics among ash types

3.2.1. Burn severity

Some differences were observed in the ash chemical characteristics when our data dataset was divided into ash form during high vs. low burn severity conditions. The pH of ash resulting from high severity wildfires tends to be higher than pH of low severity wildfires (i.e., 8.6 and 8.9 in low and high severity, respectively; Table 4). As mentioned earlier, this is linked to the more complete biomass combustion and larger quantities of oxides (CaO, KO_2) and carbonates produced at higher burn severities (Fig. 3) (Bodí et al., 2014; Pereira et al., 2012; Ulery et al., 1993). It is worth noting that changes in pH itself is a common stressor to aquatic life (Das et al., 2006). For example, Harper et al. (2019) assessed the toxicity of six ash types on the aquatic macroinvertebrate *Daphnia magna*, reporting a relationship between ash toxicity and higher ash pH. The only significant correlation observed by the authors among any of the analysed factors, both organic and inorganic contaminants, was with pH. In addition, high burn severity often leads to higher ash loads (e.g., Lewis et al., 2021; Santín et al., 2015b) and both, the chemical characteristics and the ash loads, need to be considered when determining ash environmental contamination potential (Santín et al. 2015b).

With regards to concentrations of OC and N, both were lower in the high severity ash, with average OC values of 362 and 119 g kg^{-1}, and average N values of 10.7 and 6.20 g kg^{-1} in ash from low and high burn severity, respectively (Table 3; Fig. 3). High burn severity is associated with a more complete combustion of the affected biomass and, therefore, a larger fraction of organic constituents is volatilized, rather than staying in the ash as pyrogenic organic components (Bodí et al., 2014; Paul et al., 2022). This trend has been reported previously for different ecosystems, like mixed conifer and oak forests in California (Alshehri et al., 2022; Goforth et al., 2005), a Mediterranean conifer forest in Portugal (Pereira et al., 2012) and temperate eucalypt forest in Australia (Santín et al., 2015b).

In contrast to OC and N, higher Ca and IC concentrations were observed in the ash from high burn severity (Ca: 37.5 and 53.6 g kg^{-1}; IC: 7.5 and 12.3 g kg^{-1} in low and high severity ash, respectively; Table 3), likely because of the larger quantities of carbonates typically produced at higher burn severities (Bodí et al., 2014). This agrees with the higher amount of calcite observed in high compared to low severity ash for samples collected before rain (i.e., LECAN-H, LECAN-L; Table 6). Al and Fe were also higher in the high severity ash (Al: from 9.90 to 22.3 g kg^{-1}, Fe: from 11.7 to 20.1 g kg^{-1} in low and high burn severity ash, respectively; Table 3). This relative enrichment is due to lower losses of these elements in comparison with others with lower volatilisation temperatures, such as C and N, which are the major components of the organic materials that comprise wildfire fuels (biomass, necromass and soil organic matter; Bodí et al., 2014). Al is often present in the mineral soil in much higher quantities than in biomass, so given that at higher burn severities the contribution of mineral surface soil to the ash layer is more probable, soil-derived Al might contribute more in ash from higher burn severity (Santín et al., 2015b). Burn severity has also been reported as a key parameter affecting ash toxicity in aquatic ecosystems. Mesquita et al. (2022) observed higher toxicity of ash formed at high severity from eucalypt and maritime pine forests in north-central Portugal to the aquatic organism *Lemma minor*. This toxicity was attributed to higher concentration of metals of concern in high than in low severity ash.

No significant differences were observed between ash from low and high burn severity for the remaining metals (Mn, Ni, Cu, Zn, Pb and Hg; Table 3), nor for most of the dissolved components (Table 4, S6).

3.2.2. Ash age and post-rainfall sampling

The cluster analysis, aimed at identifying the main sources of variability in ash chemical properties, classified the 42 ash types into three major clusters (or groups) according to overall similarities and differences in their chemical profiles (Fig. S3). Most ash types were classified in clusters 1 and 2 (a total number of 14 and 25, respectively), with chemical properties showing opposite trends between both clusters (Fig. S3). Cluster 2 exhibits significantly lower pH, EC and lower concentrations of P, Ca, Mg, Na, Zn, dPO_4, dMg, and dNa, and significantly higher concentrations of Al and Fe than cluster 1 (Fig. S4 and S5). From visual inspection of the clusters, sampling before rainfall seemed, *a priori*, a determining factor of whether the ash types were classified in cluster 1 or 2, with 12 out of 14 ash types in cluster 1 having been collected before any rainfall, and 17 out of 25 ash types in cluster 2 collected post-rainfall (Table 2). The supervised classification confirmed that sampling before or after rainfall was a significant predictor variable of the trends in chemical properties observed in clusters 1 and 2 (Table S2).

Acidification by rainwater, with its pH typically ranging from 4.5 - 5.6 (Charlson & Rodhe, 1982) and leaching of basic components, like HCO_3^-, could explain the lower pH in the group where most ashes were collected post-rainfall (cluster 2). Hence, it is possible that in cluster 2 leaching induced by rainfall could have removed some of the more abundant and, at the same time, more soluble elements in the ash (i.e., Ca, Mg, and Na), leaving the less water-soluble Al and Fe in higher relative proportions in the ash (Fig. S4). For instance, pH in ash from temperate eucalypt forest range from 6 to 11.1 (Table 5), with the lowest pH values having been collected after rainfall (Table S1). While surface runoff from hillslopes is the main transport mechanism of ash into streams and water bodies, *in-situ* leaching of major nutrients, metals and metalloids from ash into the soil, also during snow melt, might increase the risk of diffuse contamination via subsurface flow (Santín et al., 2015b; Smith et al., 2011), especially at sites where the hydrogeological conditions allow a high conductivity between the surface and shallow aquifers (e.g., karst or joint bedrocks). Nevertheless, current understanding of post-fire sub-surface processes remains very limited when compared with surface processes (Nunes et al., 2018).

In this study sampling before or after rainfall is also an indication of the age of the ash (i.e., the time elapsed since the fire to collection), with ash collected post-rainfall coinciding with the later post-fire sampling times (Table S1). Even without rainfall, if ash is not collected immediately after the fire, wind could mobilise the finest (and probably more reactive) fraction of the ash layer, which is a result of more complete combustion and tends to be more alkaline than the larger fractions (Bodí et

al., 2014). Therefore with "aging", ash pH may decrease as well as the concentration of some elements. This helps explain why some ash types from this study (e.g., ANUSA and SPAE) that were collected pre-rainfall, but already a few weeks after the sampled area had burned, were classified in the group where most ashes were collected after rainfall (i.e., cluster 2; Fig. S3). Our observations agree with Marcotte et al. (2022) who observed higher pH in ash analysed immediately after production (in a peat smouldering experiment) when compared with ash collected two months after a peatland wildfire in the Netherlands. Similarly, Campos et al. (2016) also reported reductions in elemental concentration (i.e., Cd, Co, Cu, Mn, Ni, Pb and V) four months after the fire compared with ash immediately after the fire from eucalypt and pine forest plantations (Portugal). These observations highlight the importance of considering both rainfall and sampling timing (i.e., time-since-fire) when examining chemical properties and the potential contamination risk in older ash. Failure to do so might lead to inaccurate estimations of the input of chemical component in soil and water and the potential toxicity of ash both airborne and in solution.

3.2.3. High concentration of metals in some ash

In the previous section we have discussed the major differences between the ash types classified in clusters 1 and 2. A small group of 3 ash types (NETHER, AUSTRIA, and UKSWANP) characterised by particularly high concentrations of metals were grouped into a third cluster (Fig. S3). In cluster 3, the average concentration of Ni and Cu was 2 - 3 times higher (51 and 81 mg kg^{-1}) than in clusters 1 and 2 (cluster 1: 23 and 30 mg kg^{-1}; cluster 2: 18 and 30 mg kg^{-1}); whereas the concentration of Zn in cluster 3 (690 mg kg^{-1}) was more than three times higher and over a sixfold higher than in clusters 1 and 2 (200 and 110 mg kg^{-1}, respectively). The concentration of Pb in cluster 3 was an order of the magnitude higher (444 mg kg^{-1}) compared with clusters 1 and 2 (21 and 48 mg kg^{-1}). These elements can accumulate in the soil and plant material over time and might be mobilised with the fire. In the case of UKSWANP (temperate conifer forest), the high concentration of metals is likely linked to contamination from past industrial activity in these areas (Bridges, 1969). Past industrial and farming activities along with lithology might also explain the high concentration of metals observed in the NETHER (peatland) ash (Joosten et al., 1987). The high concentration of Hg in the AUSTRIA ash (145 µg kg^{-1}) is most likely related with the geogenic background of the area. Follow-up analysis on the AUSTRIA ash showed an absence of dissolved Hg in the water (Sigmund, 2022, pers. comm.), indicating that the high concentration of total Hg observed in the ash does not pose an immediate risk for water supply in this area.

Finally, it is important to note that the FE-SEM images (Fig. S2) show that some toxic trace metals are associated with small-sized particles (<10 µm). This might facilitate their dispersal by wind and

their potential to entry the respiratory tract of exposed individuals if adequate measures, such as the use of masks during exposure, are not taken.

4. Health, environmental and socioeconomic implications of wildfire ash

Nutrient fluxes from ash, both transported in water and in smoke, are a key nutrient supplier to freshwater and some marine ecosystems and can cause adverse ecological effects like eutrophication, a major environmental concern (Bladon et al., 2014; Liu et al., 2010; Spencer et al., 2003). In freshwater ecosystems, nutrient inputs from ash might lead to eutrophication and increase in phytoplankton productivity, especially in oligotrophic waters (Ardyna et al., 2022; Tang et al., 2021). A range of negative effects related to the mobilization of wildfire ash has been reported for macroinvertebrates (Brito et al., 2017; Harper et al., 2019), amphibians, fish, and algae (e.g., Campos et al., 2012; Oliveira-Filho et al., 2018; Pilliod et al., 2003). For instance, Brito et al. (2017) assessed the ecotoxicology of three wildfire ash types from a Brazilian savanna (Table 1) on three aquatic species: a microcrustacean (*Ceriodaphnia dubia*), a fish (*Danio rerio*), and a mollusc (*Biomphalaria glabrata*). After 48 h of exposure, acute toxicity was observed on the microcrustacean (for all ash types) and the fish (for one of the ash types only), while no acute toxicity was reported on the mollusc for any of the ashes (Brito et al., 2017). The elemental concentrations analysed by Brito et al. (2017) were all within the overall ranges reported in this study (Table 1 and 3). In a similar study, Harper et al. (2019) assessed the toxicity to the macroinvertebrate *Daphnia magna* of a series of wildfire ash types, including FORCAN, TUSA, SPAU, SPAE, UKSOWA and WAUS from this study, and observed significant toxicity of three of these ashes to the macroinvertebrate (i.e., WAUS, TUSA and FORCAN). The toxicity was associated with the high pH and EC of these ashes.

Elevated concentrations of nutrients, toxic metals and metalloids from wildfire ash reaching water streams can also compromise drinking water quality, with major socioeconomic effects (Gustine et al., 2022; Smith et al., 2011). Threats to drinking water supplies following wildfires are a global concern, especially since forested catchments supply drinking water to one third of major cities globally (Abraham et al., 2017; Robinne et al., 2021). Water treatment following a wildfire can carry elevated costs. For instance, after the 2016 Horse River Fire affecting Fort McMurray (Canada), an estimated CA$9 M were allocated to water treatment (Pomeroy et al., 2019). In addition, consumption or exposure to elevated concentrations of metals in drinking water poses several risks to human health, mostly due to their persistence and tendency to bioaccumulate in biological tissues. For instance, consumption of Al, Hg, and Pb in high doses can be neurotoxic, elevated concentrations of solutes and metals (e.g., Na, Mg, and Fe) can affect drinking water aesthetics (i.e.,

turbidity, colour, and taste) and P can accelerate eutrophication and favour algae blooms (Smith et al., 2011).

Although water is the main transport medium of wildfire ash, ash can also be mobilised by smoke and wind, with further associated health and environmental risks that would be particularly relevant to *in-situ* workers or to the public near active fires or burnt areas. The wide array of components in wildfire ash have been related to a variety of health concerns. For instance, inhalation and ingestion of ash particles can cause various health problems because of exposure to potentially high concentrations of toxic metals and to particulate matter (PM_{10}) (Caumo et al., 2022; Wan et al., 2021). Negative effects on human skin cells have also been reported upon direct contact with wildfire ash extracts (Ré et al., 2021). When compared with our results, all the metals analysed by Ré et al. (2021) (i.e., Cr, Mn, Ni, Cu, Zn, As, Cd, Pb) were within the concentration ranges observed in our dataset (Table 3). Alkali compounds, especially in ash from high severity fires, and metals have been related to a range of health problems when in contact with body fluids from the gastrointestinal and respiratory systems or those present in the eyes (Plumlee et al., 2014). After the Thomas Fire in California (2018), Wan et al. (2021) assessed the inhalation risks of wildfire ash to farmworkers reporting a higher risk of human exposure to wildfire ash than to soil because of higher concentrations of elements of concern and a higher generation of dust in the ash than in the soil. In another study, Caumo et al. (2022), assessed ash exposure risks to human health after the Pantanal fires in Brazil (2020) indicating that vulnerable community groups, such as children and the elderly, might be particularly at risk from exposure to ash. The average concentrations of metals and metalloids analysed by Caumo et al. (2022) and Wan et al. (2021) were within the ranges of those reported here (Table 3), highlighting that most wildfire ash can actually pose a direct risk to human health. *Ex-situ* exposure to wildfire ash from atmospheric deposition of airborne particles might also represent a health risk (Avila et al., 2022; Lopez et al., 2022; Zhang et al., 2022).

In soil the deposition and incorporation of nutrients from wildfire ash can be associated with positive effects (i.e., the so-called fertilizing effect) and contribute to the post-fire restoration of the vegetation cover (Jensen et al., 2001; Maass, 1995; Marion et al., 1991). However, high concentrations of nutrients and metals from ash incorporation can also have a negative effect on soil quality, increase the risk of leaching to groundwater during heavy rainfall events, and negatively affect soil structure and aggregate stability, favouring its erosion (Fernández-Marcos, 2022).

4.1 Ash chemical composition in relation to international contamination guidelines

Since there are no existing guidelines for potentially hazardous ash, we use threshold and recommended values from a series of international guidelines addressing key nutrients and chemicals of environmental or health concern in fertilising products, sediments and soils. These can serve as reference points to contextualise the effects of the chemical concentrations we report in this study (Table 7). The EU regulation on fertilising products (Regulation 2019/1009) limits the content of key contaminants in products applied to land, including 'recovered wastes' such as biochar and ash-based products, and the Australian (Department of Environment and Conservation, 2010), Canadian (Fletcher, 2008; Pomeroy et al., 2019) and Dutch guidelines (MHSPE, 2000), establish maximum levels of potential contamination in soils and sediments from point and/or diffuse sources. Transport of contaminated sediment to water systems, not just in relation to wildfires but in other contexts such as agricultural systems, is a widely recognised concern; particularly in relation to drinking water supplies (Burton & Johnston, 2010; Wilkes et al., 2019). Ash concentrations above the levels established by these guidelines could therefore have detrimental effects on human and environmental health.

[Location of Table 7]

In general, the mean concentration of elements observed in the wildfire ash fall below the international maximum levels for fertilisers, soil and sediments presented in Table 7. Exceptions are P and Mn, with average concentrations slightly exceeding the Canadian's threshold levels for contaminated sediments. It is important to note that some of the parameters in specific ash types, however, were close or exceeded the international standards. For instance, the concentration of Pb in NETHER (peatland) ash (782 mg kg^{-1}) exceeded all international guidelines for fertilising products, soils, and sediments. Similarly, for SPAMA (Mediterranean conifer forest), and MUSA-H and UKSWANP ash (both temperate conifer forests) Ni concentrations (54.0, 64.0 and 61.3 mg kg^{-1}, respectively) were slightly above the European guidelines for organic fertilisers and the Australian's maximum sediment contamination levels (50.0 and 52.0 mg kg^{-1}, respectively). Copper in the NETHER ash (99.0 mg kg^{-1}) was close to the Canadian maximum level for sediments (110 mg kg^{-1}), and Zn in the same ash exceeded international guidelines (1,016 mg kg^{-1}), except for the EU regulation on inorganic fertilisers (1,500 mg kg^{-1}). Nevertheless, other factors beyond ash elemental concentration will also determine the actual effect of ash to humans and ecosystems, including the amount of ash, the bioavailability of the elements within it, their synergistic and antagonistic interactions, and ash dilution into environmental matrices.

4.2 Further research needs

The nutrients, metals, and metalloids analyzed in this study represent the most common but not the only constituents of wildfire ash. Other potentially hazardous compounds typically observed in ash, but not examined here, include polycyclic aromatic hydrocarbons (PAHs) (Campos et al., 2012; Harper et al., 2019), cyanide, and corrosive compounds like chloride (Cl^-) or sulphate (SO_4^-) (Smith et al., 2011). It has also been shown that the pyrogenic organic components (i.e., charcoal particles) present in the ash can contain high concentrations of environmentally persistent free radicals (EPFRs), that in contact with water, can form reactive oxygen species and pose a risk to ecosystem functions (Sigmund et al., 2021).

Wildfires may also burn areas where the geology is naturally high in metals or others with substantial atmospheric deposition of some elements (e.g., Hg from coal-fired power plants) (Burke et al., 2013; Stein et al., 2012). The ash layer is a mixture of mineral and charred organic materials, as shown by the mineralogical and chemical analyses of the ash. Therefore, lithology and geogenic concentrations, although not considered in this study, might be an important driver of ash composition and reactivity and contribute towards higher geochemical heterogeneity in ash.

Besides ash chemical concentration, other factors, like ash loads (i.e., the amount of ash produced during a fire), the size of the fire-affected area, fuel type, structure and loads will also influence nutrient delivery and the potential contamination risk of ash. For instance, while higher concentrations of OC, N and P are typically found in ash from low burn severity, the higher ash loads produced in high severity fires might result in a larger nutrient delivery to aquatic ecosystems (Santín et al., 2015b). At the same time, the higher pH and larger amount of some toxic metals and metalloids typically observed in high severity ash might be associated with a higher contamination risk. Higher concentration of PAHs has also been reported in high severity compared to low severity ash (Chen et al., 2022). Therefore, we anticipate that burn severity, fuel type and ash loads, along with other factors controlling ash mobility like post-fire climatic conditions (i.e., size and intensity of rainfall events), hydrological surface processes (e.g., runoff and erosion) and the physical characteristics of ash (e.g., particle size, bulk density, and colour) will be determining factors of nutrient delivery to ecosystems and the final contamination potential of wildfire ash, but further research is needed to study these interactions. Finally, further studies looking at the effect of 'aging' on ash chemical properties and composition are needed to determine, for example, if change in chemical concentrations is primarily the effect of rainfall and time-since-fire.

It is important to highlight that no standard procedure currently exists for sampling wildfire ash. Besides climatic conditions and time post fire, other aspects like the ash collection method (e.g., brush vs. vacuum) will affect key determining factors of ash chemical composition such as the amount of mineral soil that is collected within the ash. Given the increased efforts over recent years to understand the widespread effects of wildfire ash, standardisation of sampling and chemical analysis protocols is necessary to facilitate comparison of wildfire ash chemical composition across studies. This will also aid the prediction and assessment of the social and environmental risks associated with wildfire ash. Considering the wide range of samples analysed in the current study, our approach, which includes the application of methods used in previous studies (e.g., Hageman, 2007; 2008; Murphy et al., 2018; Wan et al., 2021; Wolf et al., 2011), could be used as an initial standardisation of wildfire ash sampling and analysis protocols. However, we recommend an interlaboratory comparison study that evaluates the different set of methods used to help develop a firmer standard protocol for sampling and laboratory analysis of wildfire ash.

5. Conclusion

We have determined chemical characteristics for a wide range of wildfire ash types from contrasting burn severities in different ecosystems globally and examined their potential implications to society and the environment. Owing to the widespread potential effects of ash, we hope that the results presented here will be of interest to a diverse audience involving scientists in various disciplines (e.g., toxicology, aquatic ecology, soil science), decision makers in management and planning roles, drinking water managers, public health officials and policy makers who design prevention and mitigation strategies to address the risk of post-fire contamination. In addition, due to the potential risks to human health associated with ash exposure, this study will be of interest to firefighters and contractors working in fire-affected areas, as well as to the public located downwind of active fires or recently burned areas.

The main conclusions from this study are:

- Concentration of major nutrients, potentially toxic metals and readily dissolvable components in wildfire ash varied greatly among ecosystems. Important constituents of wildfire ash include OC (mean value 204 g kg^{-1}; ranging between 37 - 450 g kg^{-1}), Ca (47.9 g kg^{-1}; 1.3 – 215 g kg^{-1}), Al (17.9 g kg^{-1}; 0.6 – 69.3 g kg^{-1}), and Fe (17.1 g kg^{-1}; 0.6 – 77.2 g kg^{-1}). The largest concentrations of metals of concern for human and ecosystem health were

observed for Mn (1,488 mg kg^{-1}; 34.5 – 15,350 mg kg^{-1}); Zn (181 mg kg^{-1}; 25.5 – 1,016 mg kg^{-1}); Pb (66.9 mg kg^{-1}; 1 – 782 mg kg^{-1}).

- Burn severity significantly influenced key chemical parameters in wildfire ash, including pH and the concentration of major nutrients and metals like C, N, Ca, Al, Fe. pH, which controls the solubility of most elements, was higher in ash from high burn severity, and this could have a direct influence on the contamination potential of wildfire ash when in contact with water.
- Rainfall between the fire and the time of sampling has a significant influence on the concentrations of key chemical elements in ash. Not accounting for this factor or losses with wind might lead to inaccurate estimations of nutrient inputs to soil and water, and wildfire ash toxicity.
- Average concentrations of chemical species of concern for environmental and human health in wildfire ash were below international contamination standards for several environmental matrices and products, except in a few ash types (NETHER, AUSTRIA, and UKSWANP) in which the concentrations were very close or exceeded contamination thresholds. However, even where concentrations do not exceed international contamination standards in most ashes, the sudden pulse of nutrients, metals and metalloids can still have long-lasting effects in some ecosystems, with factors like the amount of ash, bioavailability of the elements within it, their synergistic and antagonistic interactions, and ash dilution into environmental matrices affecting the actual effect of ash to humans and ecosystems.
- Standardization of ash sampling methods and chemical analysis to facilitate future comparison across wildfire ash studies and ecosystems is needed. While the methods used in this study are a first approach at standardisation of sampling and chemical characterization analysis, a future interlaboratory comparison study could help evaluating the different methods used across studies and create consensus towards a standard protocol.

Author contributions

C. Sánchez-García: Conceptualization, Methodology, Leading of Writing – original draft, review & editing, Visualization. **C. Santín, J. Neris and S. Doerr:** Conceptualization, Methodology, Resources – laboratory samples, Writing – original draft, review & editing, Funding acquisition. **G. Sigmund:** Resources – laboratory samples; Writing – review & editing; **X. L. Otero**: Investigation – data collection; Writing – review & editing. **J. Manley:** Writing – component of an early draft, review &

editing. **G. González-Rodríguez:** Methodology, Resources – data analysis materials, Writing – review & editing. **C. Belcher, A. Cerdá, A. Marcotte, S. Murphy, C. Rhoades, G. Sheridan, T. Strydom, P. R. Robichaud**: Resources – laboratory samples, Writing – review & editing.

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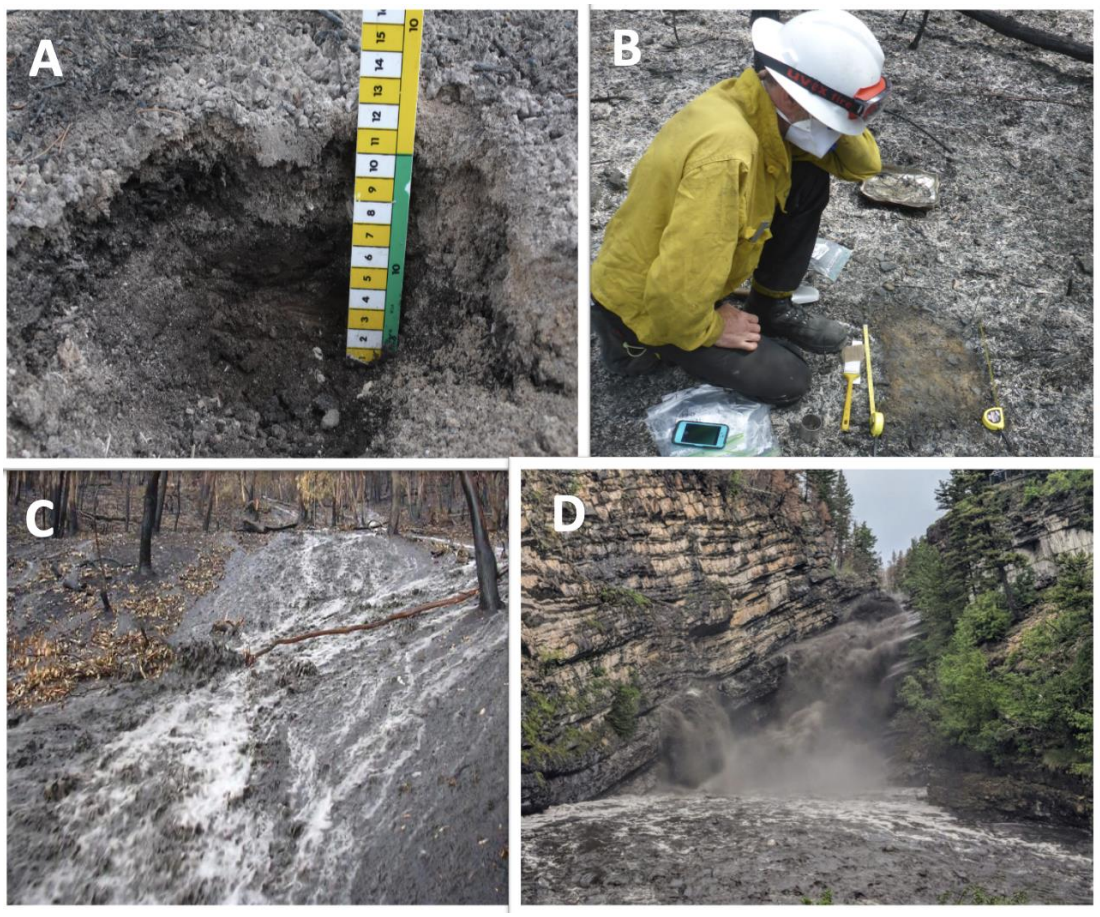

Figure 1. (A) Thick ash layer after a severe wildfire in conifer forest (Montana, USA; scale: cm; Image: S. Doerr). (B) Ash sampling following an experimental wildfire in eucalypt forest near Sydney, Australia (location WAUS in Table 2; Image: C. Santín). (C) Surface runoff entraining ash after a wildfire in SE Australian eucalypt forest (Image: R. Ferguson). (D) Ash transported by floodwater downstream of a wildfire in Alberta, Canada (Image: Parks Canada).

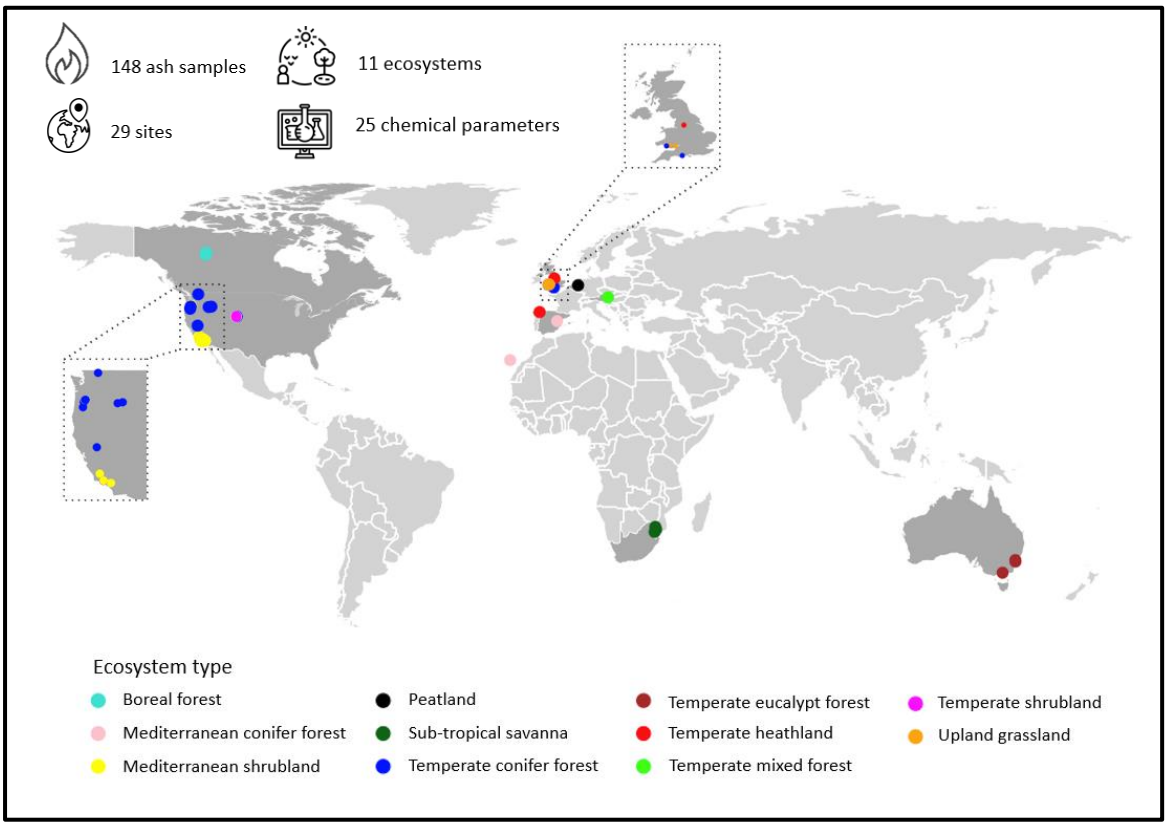

Figure 2. Ash sampling locations (dots) and ecosystems (colour of dots) included in this study. Darker grey shading indicates countries represented in the study.

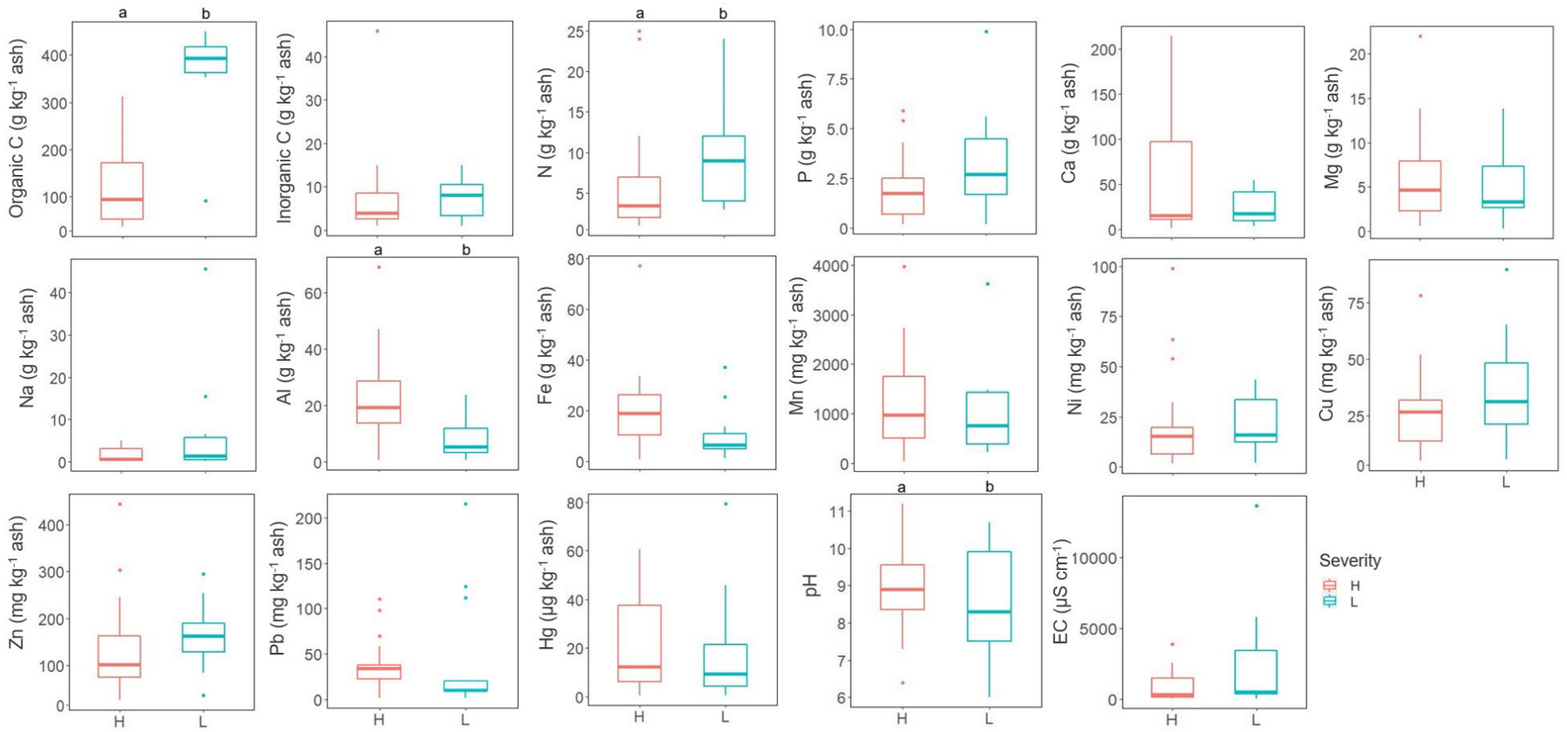

Figure 3. Total element content, pH and EC for the ash types grouped by burn severity (H: high severity, L: low severity). Central line, bottom and top edges of the boxes are the median, 25th and 75th percentiles. Lines extending above and below the boxes represent maximum and minimum values. Dots are the outliers. Different letters above each boxplot (a – b) indicate significant differences between high and low severity (controlling for the effect of rain and ecosystem) at $p < 0.05$ (Table S4). Absence of letters above the boxplots indicates non-significant differences.

Table 1. Chemical characteristics of wildfire ash reported in previous studies (pH, electrical conductivity [EC], major nutrients, metals, and metalloids). Where more than one value exists for a given study, ecosystem type, and fire characteristics, the ranges (i.e., minimum, and maximum values) are given.

Ecosystem	Dominant vegetation	Burn severity	Rain between fire and sampling	pH	EC	IC	OC	C	N	P	Ca	Mg	Na	Al	Fe	Mn	Ni	Cu	Zn	Pb	Cr	As	Cd	Hg	Publication
					($\mu S\ cm^{-1}$)	($g\ kg^{-1}$ ash)										($mg\ kg^{-1}$ ash)						($\mu g\ kg^{-1}$ ash)			
Mediterranean conifer forest	*Pinus pinaster* Aiton and *Quercus suber* L.	Low	No	7.4	-	20	-	460	17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Pereira et al. (2012)*
		High	No	8.3	-	34	-	180	9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Pinus ponderosa Douglas	High	ns	7.8 - 9.3	-	-	20.8	-	-	2	94 - 313	1-7	0.1	5 - 19	1 - 6	1000 - 6000	-	-	-	-	-	-	-	-	Ulery et al. (1993)
	Pinus pinaster Aiton	High	ns	-	-	-	-	-	-	8.9	22.2	15.5	3.3	-	1.5	2570	-	57	201	-	-	-	-	-	Ferreira et al. (2005)
Mediterranean mixed oak woodland	*Quercus douglasii* Hook. & Arn., *Quercus virginiana* Mill	High	No	-	-	-	-	-	-	-	280 - 302	-	-	-	-	-	-	-	-	-	-	-	-	0.01 - 0.02	Ku et al. (2018)*
		Low	No	-	-	-	-	-	-	-	37.3 - 80.2	-	-	-	-	-	-	-	-	-	-	-	-	0.01 - 0.04	
	Quercus velutina Lam, *Quercus agrifolia* Née, *Arbutus menziesii* Pursh, *Pinus ponderosa* Douglas	High	No	-	-	-	-	-	50	0.5	-	64.8	-	-	-	-	-	-	-	1442	19	-	-	-	-	Alshehri et al. (2022)*
		Low	No	-	-	-	-	-	144	3.4	-	16.9	-	-	-	-	-	-	-	36058	180	-	-	-	-	
Tropical savanna	Cerrado stricto	High	No	7.8	-		-	-	-	-	0.7	38.4	5.2	-	11	1.2	139	5.7	-	29.9	3.5	15.2	-	100	-	Brito et al. (2017)
	Pasture	High	No	7.9	-		-	-	-	-	7.7	19.8	6.2	-	13.7	12.3	250	3	-	85.5	3.4	12.8	-	200	-	
	Transition area between vereda and campo cerrado	High	No	7.9	-		-	-	-	-	0.9	11.9	1.9	-	17.8	3.0	317	1.3	-	47.8	6.6	20	-	300	-	

Tropical savanna and semi-deciduous forest (Pantanal)	ns	ns	ns	-	-	-	-	-		-	-	-		-	-	-	4.8 - 13	9.0 - 187	-	3.3 - 224	7.8 - 49.1	1040 - 6340	40 - 13120	-	Caumo et al. (2022)**
Temperate conifer forest	*Pinus menziesii* Pursh, *Pinus contorta* Douglas ex Loudon and *Thuja plicata* Donn ex D. Don,	High	ns	8.8	-	38.4	24.1	-	0.1	6.1	151	9.5	0.6	8.1	8.7	8000	-	-	500	-	-	-	-	-	Balfour and Woods (2013)
	Pinus ponderosa Douglas and *Pinus contorta* Douglas ex Loudon	High	ns	10.3	-	56.6	15.5	-	1.5	3.8	276	2.9	0.7	2.3	3.8	300	-	-	500	-	-	-	-	-	
	Pinus pinaster Aiton	Moderate	Negligible	7.1 - 7.3	1350 - 1600	-	-	-	-	-	-	-	-	-	-	281 - 656	21 - 32	33 - 54	-	62 - 106	-	-	250 - 301	-	Campos et al. (2016)*
		ns	ns	6 - 6.1	-	-	-	17 - 354	15.7 - 19.8	-	3.1 - 8.6	0.8 - 1.4	0.0 - 5.1	-	0.1 - 0.2	107 - 190		3.1 - 4.3	32 - 68	-	-	-	-	-	Costa et al. (2014)
		Low	No	-	-	-	-	-	-	-	-	-	-	-	-	373	20	83	244	52	19	28000	170	-	Santos et al. (2023)
Tropical broadleaf forest	*Anogeissus latifolia* (Roxb. Ex DC.), *Terminalia crenulata* Roth and *Tectona grandis* L. f.	ns	ns	-	-	-	-	-	-	-	22.5	6.7	0.5	-	4.9	1270	-	-	150	-	-	-	-	-	Audry et al. (2014)*
Temperate eucalypt forest	*Eucalyptus globulus* Labill.	Moderate	Negligible	6.9 - 8	1050 - 1950	-	-	-	-	-	-	-	-	-	-	262 - 600	21 - 27	36 - 52	-	57 - 117	-	-	343 - 495	-	Campos et al. (2016)*
		Moderate to High	No	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6 - 23	-	-	-	-	Wu et al. (2017)
		Low	No	-	-	-	-	-	-	-	-	-	-	-	-	413	20	84	270	50	22	24000	620	-	Santos et al. (2023)
		Moderate to High	No	-	-	-	-	-	-	-	-	-	-	-	-	190	30	80	180	94	82	42000	600	-	Silva et al. (2015)
	Mixed species	High	Yes	-	-	1 - 2	63 - 79	65 - 80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Santín et al. (2012)

	Eucalyptus regnans F. Muell.	Moderate to High	Yes	-	-	2	163	163	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Santín et al. (2012)
Orchard	Avocado, orange, and lemon trees	Low to High	Yes	-	-	-	-	-	-	-	-	-	-	-	-	-	33	74	225	18.7	64	8040	800	13.2	Wan et al. (2021)
Overall ranges (minimum and maximum values)				6 - 10.3	1050 - 1950	1 - 56.6	15.5 - 163	50 - 460	0.1 - 19.8	0.7 - 8.9	3.1 - 313	0.8 - 15.5	0.05 - 3.3	2.3 - 19	0.1 - 12.3	107 - 8000	1.3 - 33	3.1 - 187	29.9 - 36058	3.3 - 224	7.8 - 82	1040 - 42000	40 - 1312 0	0.01 - 13.2	

ns: not stated.

* Estimated values from information in the publication.

** Contains a substantial soil fraction.

Table 2. Abbreviated names of the 42 ash types examined in this study and descriptors of the ecosystems and fires where they were collected. For a more complete description of ash sampling locations, collection protocols and number of samples see Table S1.

Ecosystem	Ash name	Country	Site name and fire year	Fire type	Burn severity	Rain before ash sampling
Boreal forest	LECAN-H, LECAN-L	Canada	Lady Evelyn Falls, 2014	Wildfire	High and Low	No rain
	FORCAN, FORCANC	Canada	Fort Providence, 2012-16	Experimental forest fire	High	No rain
Mediterranean conifer	SPAE	Spain	East Pine Forest, 2009	Wildfire	High	No rain
	SPAMA	Spain	Madre del Agua, 2018	Wildfire	Low	14 mm
Mediterranean shrubland	OLDUSA	United States (USA)	Old Fire, 2003	Wildfire	High	No rain
	PIUSA	United States (USA)	Piru-1 Fire, 2003	Wildfire	High	20 mm
	TUSA	United States (USA)	Thomas Fire, 2018	Wildfire	High	No rain
Peatland (raised bog)	NETHER	The Netherlands	De Peel, 2020	Wildfire	High	~75 mm*
Sub-tropical savanna	SAMB	South Africa	Mopani, 2018	Experimental grassland fire	Low	No rain
	SAPB1, SAPB3	South Africa	Pretoriuskop, 2018	Experimental grassland fire	Low	No rain
	SASB	South Africa	Satara, 2018	Experimental grassland fire	Low	No rain
Temperate conifer forest	ANUSA	United States (USA)	Angora Fire, 2007	Wildfire	High	No rain
	BUCKUSA	United States (USA)	Buck Fire, 2020	Wildfire	High	33 mm
	BUSA	United States (USA)	Beachie Creek Fire, 2020	Wildfire	High	13 mm
	CUSA	United States (USA)	Cold Springs Fire, 2020	Wildfire	High	14 mm
	HUSA	United States (USA)	Holiday Farm Fire, 2020	Wildfire	High	34 mm
	MUSA-H, MUSA-L	United States (USA)	Mesa Fire, 2018	Wildfire	High and low	5 mm
	RIVERUSA	United States (USA)	Riverside Fire, 2020	Wildfire	High	34 mm
	RUSA1C, RUSA1U, RUSA2C, RUSA2U	United States (USA)	Ryan Fire, 2019	Wildfire	High	107 mm
	UKSWANP	United Kingdom	Swansea Kilvey Hill, 2020	Wildfire	Low	No rain
	UKWARE, UKWAREBA	United Kingdom	Wareham Forest, 2020	Wildfire	Low	No rain
Temperate eucalypt forest (dry)	NAUS-H, NAUS-L	Australia	Nepean, 2014	Wildfire	High and low	148 mm
	TAUS-H, TAUS-L	Australia	Thomson, 2019	Wildfire	High and low	60 mm
	WAUS, WAUSC	Australia	Warragamba, 2014	Experimental forest fire	High	No rain
Temperate heathland	SPAU	Spain	Uria, 2017	Wildfire	High	No rain
	UKMA-H, UKMA-L	United Kingdom	Saddleworth, 2018	Wildfire	High and low	No rain

Temperate mixed forest	AUSTRIA	Austria	Hirschwang Fire, 2021	Wildfire	Low	No rain
Temperate shrubland	OVUSA	United States (USA)	Overland Fire, 2003	Wildfire	High	22 mm
Upland grassland	UKSOWA	United Kingdom	South Wales, 2018	Wildfire	Low	No rain
	UKSWANG	United Kingdom	Swansea Kilvey Hill, 2020	Wildfire	Low	No rain

Table 3. Arithmetic mean and median (in brackets next to the mean) and coefficient of variation (CV) for all ash types (n = 20 for IC and n = 42 for the rest of parameters), and also, values grouped by low- and high burn severity for all chemical parameters analysed (low severity: n = 7 for IC, and n = 15 for other parameters; high severity: n = 13 for IC, and n = 27 for the other parameters). The ranges of values (i.e., minimum and maximum) are given in brackets below the mean and median.

Chemical parameters	Units	All ash types	CV (%)	Low burn severity	CV (%)	High burn severity	CV (%)
IC	(g kg^{-1} ash)	10.6 (6.5) (1 - 59)	125	7.5 (7.3) (1 - 15)	66	12.3 (4.1) (1 - 59)	147
OC	(g kg^{-1} ash)	204 (143) (37 - 450)	75	362 (397) (92 - 450)	34	119 (99.4) (37 - 312)	70
N	(g kg^{-1} ash)	7.8 (5.5) (1 - 25)	88	10.7 (9.0) (3 - 24)	68	6.2 (4.4) (1 - 25)	99
P	(g kg^{-1} ash)	2.5 (2.3) (0.2 - 9.9)	83	3.4 (2.7) (0.2 - 9.9)	77	2.0 (2.0) (0.2 - 5.9)	77
Ca	(g kg^{-1} ash)	47.9 (17) (1.3 - 215)	127	37.5 (32.0) (3.4 - 208.6)	134	53.6 (14.4) (1.3 - 215)	123
Mg	(g kg^{-1} ash)	5.4 (4.3) (0.3 - 22)	85	4.9 (3.3) (0.3 - 13.8)	76	5.6 (4.3) (0.6 - 22)	90
Na	(g kg^{-1} ash)	5 (0.8) (0.1 - 88.6)	301	11.3 (1.4) (0.1 - 88.6)	215	1.5 (0.6) (0.1 - 5.0)	106
Al	(g kg^{-1} ash)	17.9 (15.8) (0.6 - 69.3)	80	9.9 (9.5) (0.6 - 23.7)	84	22.3 (20.0) (0.6 - 69.3)	68
Fe	(g kg^{-1} ash)	17.1 (16.4) (0.6 - 77.2)	82	11.7 (7.1) (1.1 - 27.0)	92	20.1 (19.1) (0.7 - 77.2)	74
Mn	(mg kg^{-1} ash)	1488 (921) (34.5 - 15350)	160	1964 (762) (218 - 15350)	193	1223 (938) (34.5 - 3979)	82
Ni	(mg kg^{-1} ash)	22.1 (15.8) (1.7 - 99)	91	24.6 (17.6) (2.2 - 61.3)	71	20.7 (15.5) (1.7 - 99)	105
Cu	(mg kg^{-1} ash)	33.2 (29.2) (5.2 - 98.7)	70	40.1 (31.5) (5.7 - 94)	67	29.4 (27.3) (5.2 - 98.7)	71
Zn	(mg kg^{-1} ash)	181 (137) (25.5 - 1016)	98	209 (164) (36 - 538)	69	166 (102) (25.5 - 1016)	117
Pb	(mg kg^{-1} ash)	66.9 (28.2) (1 - 782)	202	73.6 (10.0) (1 - 435)	161	63.2 (34.3) (1.1 - 782)	231
Cr	(mg kg^{-1} ash)	34.0 (31.8) (10 - 71.6)	54	38.7 (48.7) (10 - 57.7)	49	30.4 (27.4) (10 - 71.6)	56
Hg	(µg kg^{-1} ash)	24.4 (13.7) (0.5 - 145)	115	27.6 (16.5) (0.5 - 145)	140	22.6 (12.7) (0.5 - 82.9)	94
As	(µg kg^{-1} ash)	3541 (3248) (463 - 9666)	79	3331 (4352) (629.6 - 5011)	71	3604 (2807) (463 - 9666)	84
Cd	(µg kg^{-1} ash)	292 (181) (78 - 1133)	100	467 (180) (89 - 1133)	124	239 (195) (78 - 552)	67

Table 4. Mean and median (in brackets next to the mean), readily dissolvable fraction (as a % of the total element content) and coefficient of variation (CV) for all ash types (n = 33 for DOC, and n = 42 for the rest of parameters), and also, values grouped by low- and high burn severity for pH, electrical conductivity (EC), dissolved organic carbon (DOC) and the dissolved concentrations (low severity: n = 12 for DOC, and n = 15 for other parameters; high severity:, n = 21 for DOC, and n = 27 for the other parameters). The ranges of values (i.e., minimum, and maximum) are given in brackets below the mean and median.

Chemical parameters	Units	All ash types	Dissolved fraction (%)	CV (%)	Low burn severity	CV (%)	High burn severity	CV (%)
pH		8.8 (8.8) (6 - 11.2)	-	14.4	8.6 (8.3) (6 - 10.7)	16	8.9 (8.9) (6.4 - 11.2)	13
EC	($\mu S\ cm^{-1}$)	1330 (510) (32.5 - 13700)	-	178	2275 (657) (32.5 - 13700)	160	804 (315) (37.5 - 3880)	123
DOC	(mg kg^{-1} ash)	1103 (913) (93.2 - 3622)	-	83.0	1651 (1714) (198 - 3622)	62	790 (447) (93.2 - 2406)	88
dNH_4^+	(mg kg^{-1} ash)	29.9 (12.2) (0.5 - 474)	-	241	22.0 (19.6) (0.5 - 64.6)	82	34.2 (11.9) (0.5 - 474)	161
dF	(mg kg^{-1} ash)	4.4 (2.3) (0.5 - 32.7)	-	152	3.3 (2.1) (0.5 - 9.9)	94	4.9 (2.3) (0.5 - 32.7)	161
dPO_4	(mg kg^{-1} ash)	55.4 (5.6) (0.3 - 973)	1.7	295	145 (44.5) (0.3 - 973)	175	5.3 (4.8) (0.3 - 20.6)	86
dCa	(mg kg^{-1} ash)	1081 (505) (28.2 - 5864)	4.6	127	883 (307) (32.7 - 2813)	109	1190 (552) (28.2 - 5864)	132
dMg	(mg kg^{-1} ash)	390 (234) (16.9 - 3067)	11.4	147	344 (292) (19.6 - 1242)	86	416 (159) (16.9 - 3067)	166
dNa	(mg kg^{-1} ash)	456 (68.1) (2.5 - 4681)	18.0	215	687 (221) (16.4 - 4681)	161	328 (38.7) (2.5 - 3893)	247
dAl	(mg kg^{-1} ash)	18.9 (5.0) (0.5 - 318)	0.2	296	18.8 (5.0) (0.5 - 197)	262	18.9 (5.0) (0.5 - 318)	218
dFe	(mg kg^{-1} ash)	1.3 (1.0) (0.5 - 4.4)	0.02	61.7	1.4 (1.0) (1 - 4.4)	68	1.2 (1.0) (0.5 - 3.7)	57
dMn	(mg kg^{-1} ash)	1.9 (1.0) (0.4 - 10.2)	0.3	121	2.0 (1.4) (0.5 - 9.3)	115	1.9 (1.0) (0.4 - 10.2)	128

Table 5. Means of the ash types grouped by ecosystems for all chemical parameters analysed. The ranges of values are given in brackets, i.e., minimum and maximum, except where data is available for only one ash type for a given ecosystem (each ash type is comprised by several ash samples). See Table S1 for sample numbers.

		Ecosystem										
Chemical parameters	Units	Boreal forest	Mediterranean conifer forest	Mediterranean shrubland	Peatland	Sub-tropical savanna	Temperate conifer forest	Temperate eucalypt forest	Temperate heathland	Temperate mixed forest	Temperate shrubland	Upland grassland
IC	(g kg^{-1} ash)	ns*	15	2.0	2.0	ns	11 (1 - 46)	2 (1 - 2)	7.0	ns	4.0	2.0
OC	(g kg^{-1} ash)	ns	121 (115 - 127)	54	99	ns	206 (37 - 450)	280 (208 - 353)	424	ns	47	397
N	(g kg^{-1} ash)	7.3 (2.0 - 11.0)	4.7 (4.4 - 5)	3.3 (1.0 - 8.0)	9.0	4.3 (3.0 - 6.0)	10.3 (1.0 - 25.0)	4.3 (2.0 - 7.0)	9.7 (2.0 - 16.0)	5.0	3.0	17.5 (12.0 - 23.0)
P	(g kg^{-1} ash)	3.0 (1.3 - 5.9)	2.2 (0.2 - 2.5)	4.1 (2.6 - 5.5)	2.3	5.9 (3.8 - 9.9)	2.1 (0.5 - 7.2)	0.3 (0.2 - 0.5)	2.2 (1.6 - 2.6)	1.8	1.4	3.7 (2.7 - 4.7)
Ca	(g kg^{-1} ash)	107 (42.0 - 167)	105 (76.1 - 133)	122 (13.5 - 215)	5.9	33.0 (17.2 - 45.5)	25.5 (4.1 - 105)	32.4 (1.3 - 177)	18.5 (9.5 - 29.4)	209	10.2	9.9 (8.0 - 11.8)
Mg	(g kg^{-1} ash)	7.1 (3.3 - 12)	9.7 (5.5 - 13.8)	13.5 (5.7 - 22.0)	1.4	9.3 (6.7 - 13.8)	3.7 (0.6 - 8.1)	3.3 (0.9 - 9.9)	3.5 (1.2 - 6.4)	6.2	4.2	1.5 (0.3 - 2.7)
Na	(g kg^{-1} ash)	1.0 (0.1 - 3.1)	1.4 (1.4 - 1.7)	1.9 (0.3 - 4.6)	0.4	5.2 (1.4 - 15.4)	10.5 (0.2 - 88.7)	1.0 (0.1 - 5.0)	1.7 (0.7 - 3.6)	0.4	0.2	3.2 (0.7 - 5.7)
Al	(g kg^{-1} ash)	1.2 (0.6 - 2.4)	34.2 (32.8 - 35.6)	16.6 (13.6 - 226)	29	6.7 (3.7 - 9.8)	23.9 (1.9 - 69.3)	21.3 (7.0 - 36.3)	8.9 (5.2 - 11.6)	22.9	21.3	7.4 (2.8 - 11.9)
Fe	(g kg^{-1} ash)	1.2 (0.6 - 2.2)	29.7 (28.9 - 30.6)	17.9 (15.8 - 19.1)	29	6.4 (4.9 - 8.7)	24.5 (1.2 - 77.2)	16.5 (4.3 - 33.3)	7.7 (5.9 - 8.6)	18.1	17.1	10.4 (7.1 - 13.7)
Mn	(mg kg^{-1} ash)	1161 (497 - 2558)	954 (320 - 1589)	435 (199 - 710)	248	850 (244 - 1436)	2628 (218 - 15350)	585 (180 - 1001)	487 (34.5 - 1000)	755	787	2527 (1430 - 3624)
Ni	(mg kg^{-1} ash)	5.3 (1.7 - 15)	42.9 (32 - 53.8)	40 (5.5 - 99)	45.4	20.7 (9 - 43.3)	20.3 (2.5 - 63.6)	14.9 (3.9 - 21)	24.2 (17 - 33.5)	46.6	7.3	26.7 (16 - 37.4)
Cu	(mg kg^{-1} ash)	14.4 (5.7 - 29)	31.1 (30 - 32.2)	31.8 (12.5 - 52)	98.7	26.5 (21.3 - 31.5)	37.5 (7.6 - 94)	15.5 (5.2 - 31.5)	47.5 (12.5 - 89.9)	48.8	30.9	49.2 (48.3 - 50)
Zn	(mg kg^{-1} ash)	160 (62 - 303)	238 (172 - 304)	144 (74 - 250)	1016	161 (129 - 189)	172 (59.8 - 516)	68.7 (25.5 - 144)	117 (40 - 210)	538	99.9	217 (181 - 254)
Pb	(mg kg^{-1} ash)	7.5 (1 - 24)	34.5 (10 - 59)	35.6 (10 - 58.7)	782	10	44.1 (10 - 115)	17 (10 - 35)	92.8 (27.5 - 216)	435	69.6	118 (112 - 125)
Hg	(µg kg^{-1} ash)	7.5 (3.3 - 12.7)	12.8 (10.9 - 14.6)	34.6 (16.9 - 48.2)	82.9	4.6 (2.5 - 7.6)	26.5 (4 - 60.7)	6.9 (0.5 - 22.4)	32.6 (8.2 - 79.5)	145	43.4	19 (16.5 - 21.5)
pH		9.4 (8.3 - 10.3)	9.3 (9.1 - 9.4)	9.8 (7.4 - 11.2)	7.1	10.1 (9.9 - 10.7)	8.8 (7.5 - 9.7)	7.6 (6 - 11.1)	8.8 (7.2 - 10.3)	8.8	8.7	8.1 (7.9 - 8.3)
EC	(µS cm^{-1})	1704 (901 - 2500)	400 (233 - 566)	1688 (767 - 2570)	237	6943 (3430 - 13700)	387 (57.7 - 1429)	727 (32.5 - 3880)	1086 (364 - 1505)	657	259	408 (293 - 523)
dNH_4^+	(mg kg^{-1} ash)	13.4 (0.5 - 22)	10.3 (4.5 - 16)	161 (0.5 - 474)	12.3	7.7 (4.8 - 10.7)	26.8 (6 - 66.1)	6.3 (0.5 - 10.5)	36.5 (12 - 64.6)	23.6	28.6	26.4 (19.6 - 33.1)
dF	(mg kg^{-1} ash)	0.5 (0.5 - 0.5)	6.3 (3.2 - 9.3)	1.4 (0.5 - 3.3)	2.2	4.2 (0.5 - 8.6)	8.4 (2.1 - 32.7)	0.8 (0.5 - 1.4)	3.1 (2 - 5.1)	0.5	0.5	2.5 (0.5 - 4.5)
dPO_4	(mg kg^{-1} ash)	18.8 (0.3 - 69.3)	5 (4.4 - 5.6)	6.4 (3.1 - 13)	0.3	312 (35.5 - 973)	9 (0.3 - 48.1)	4.2 (0.6 - 6.1)	81 (0.3 - 233)	0.3	5.9	281 (191 - 370)
dCa	(mg kg^{-1} ash)	3744 (1364 - 5864)	1088 (1075 - 1101)	845 (136 - 2000)	568	200 (121 - 307)	931 (156 - 2813)	158 (28.2 - 578)	1995 (543 - 4862)	2264	795	181 (114 - 248)
dMg	(mg kg^{-1} ash)	1684 (407 - 3067)	476 (232 - 720)	295 (26.3 - 624)	77.2	217 (137 - 274)	236 (23.8 - 1242)	188 (16.9 - 645)	371 (328 - 442)	378.0	159	279 (172 - 386)
dNa	(mg kg^{-1} ash)	337 (51 - 860)	71.9 (16.8 - 127)	336 (30.4 - 831)	38.7	1388 (221 - 4681)	282 (2.5 - 1917)	692 (23.6 - 3893)	741 (185 - 1766)	44.6	14.1	205 (148 - 262)
dAl	(mg kg^{-1} ash)	0.6 (0.5 - 1)	9.7 (5 - 14.4)	5 (5 - 5)	5.0	5 (5 - 5)	21.4 (5 - 197)	5.7 (1 - 17)	114 (5 - 318)	19.1	5.0	5 (5 - 5)
dFe	(mg kg^{-1} ash)	0.9 (0.5 - 1.4)	1 (1 - 1)	1 (1 - 1)	1.0	1 (1 - 1)	1.3 (1 - 3.7)	1.6 (1 - 2.9)	1.4 (1 - 2.2)	1.0	1.0	3.2 (2 - 4.4)
dMn	(mg kg^{-1} ash)	1.7 (0.4 - 3.2)	1 (1 - 1)	1.3 (0.5 - 2.3)	0.5	1.2 (0.5 - 2)	2 (0.5 - 7.7)	2.8 (1 - 10.2)	2.3 (1 - 4.8)	0.5	0.5	4.9 (0.5 - 9.3)

* Not studied

Table 6. Semiquantitative estimation (%) of minerals in the ash

Sample	Quartz	Muscovite	Microcline	Albite	Biotite	Calcite	Syngenite	Gypsum	Hornblende	Andesine	Hematite
TAUS-H	80	16	1	3	nd	nd	nd	nd	nd	nd	nd
TAUS-L	76	14	7	3	nd	nd	nd	nd	nd	nd	nd
LECAN-H	11	nd	9	3	3	62	8	4	nd	nd	nd
LECAN-L	45	nd	11	9	nd	35	nd	2	nd	nd	nd
SAMB	58	nd	nd	nd	nd	42	nd	nd	nd	nd	nd
MUSA-H	20	14	12	36	nd	10	nd	2	6	nd	nd
MUSA-L	9	12	13	nd	nd	9	nd	3	5	49	nd
UKMA-H	84	3	7	1	nd	2	nd	3	nd	nd	nd
UKSWANP	51	14	nd	nd	nd	11	nd	nd	nd	nd	18
NETHER	69	6	11	11	nd	nd	nd	2	nd	nd	2

*nd: not detected

Table 7. International guidelines and thresholds for total nutrients, and toxic metals and metalloids for a range of environmental matrices and products. Average concentrations observed in this study for wildfire ash are included for comparison.

	Mean concentration observed in this study with ranges in brackets	EU regulation on fertilising products (EU 2019/1009 of 5 June 2019). Maximum levels		Ecological investigation levels. Government of Western Australia	Sediment quality guidelines. Ontario Government, Canada. Severe effect levels	Dutch intervention values for soil remediation and indicative levels for serious contamination	US EPA Soil screening levels. Carcinogenic target risk
Element	Wildfire ash	Organic fertilisers	Inorganic fertilisers	Sediment	Sediment	Soil/sediment	Residential soil
Units	(mg kg^{-1})	(mg kg^{-1})		(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})
As	3.5 (0.5 - 9.7)	40	40	70	33	55	0.7
Cd	0.3 (0.08 - 1.1)	1.5	3 - 60	10	10	12	2100
Cr	34 (10 - 71.6)	ns	ns	370	110	380	ns
Cu	33.2 (5.2 - 98.7)	300	600	270	110	190	ns
Hg	0.02 (0.0005 - 0.2)	1	1	1	2	10	ns
Mn	1488 (34.5 - 15350)	ns	ns	ns	1100	ns	ns
Ni	22.1 (1.7 - 99)	50	100	52	75	210	15000
P	2500 (200 - 9900)	ns	ns	ns	2000	ns	ns
Pb	66.9 (1 - 782)	120	120	220	250	530	82/2.6**
Zn	181 (25.5 - 1016)	800	1500	410	820	720	ns

*ns: not specified

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