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1 # Quantity, composition and water contamination potential of ash

2 # produced under different wildfire severities

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12

13 **ABSTRACT**

14 Wildfires frequently threaten water quality through the transfer of eroded ash and soil

15 into rivers and reservoirs. The ability to anticipate risks for water resources from wildfires

16 is fundamental for implementing effective fire preparedness plans and post-fire mitigation

17 measures. Here we present a new approach that allows quantifying the amount and

18 characteristics of ash generated under different wildfire severities and its respective

19 water contamination potential. This approach is applied to a wildfire in an Australian dry

20 sclerophyll eucalypt forest, but can be adapted for use in other environments.

21

22 The Balmoral fire of October 2013 affected 12,694 ha of Sydney's forested water supply

23 catchment. It produced substantial ash loads that increased with fire severity, with 6, 16

24 and 34 Mg ha^{-1} found in areas affected by low, high and extreme fire severity,

25 respectively. Ash bulk density was also positively related to fire severity. The increase

26 with fire severity in the total load and bulk density of the ash generated is mainly

27 attributed to a combination of associated increases in (i) total amount of fuel affected by

28 fire and (ii) contribution of charred mineral soil to the ash layer. Total concentrations of

29 pollutants and nutrients in ash were mostly unrelated to fire severity and relatively low

30 compared to values reported for wildfire ash in other environments (e.g. 4.0-7.3 mg As

31 kg^{-1}; 2.3-4.1 B mg kg^{-1}; 136-154 P mg kg^{-1}). Solubility of the elements analysed was also

32 low, less than 10% of the total concentration for all elements except for B (6-14%) and

33 Na (30-50%). This could be related to a partial loss of soluble components by leaching

34 and/or wind erosion before the ash sampling (10 weeks after the fire and before major

35 ash mobilization by water erosion).

Even with their relatively low concentrations of potential pollutants, the substantial total ash loads found here represent a water contamination threat if transported into the hydrological network during severe erosion events. For example, up to 4 Mg of ash-derived P could be delivered into a single water supply reservoir.

1. Introduction

Forest catchments are an important source of drinking water in many regions of the world and hence forest conservation is a fundamental part of the integrated management of water resources (Dudley and Stolton, 2003). Wildfires are one of the most important perturbations in forested regions that are subject to prolonged dry spells, with direct implications for water quality. In the dry temperate forests and woodlands of south-eastern Australia, wildfires are particularly frequent, with extensive wildfires having affected forested reservoir catchments since their establishment. Despite efforts of land and water managers to mitigate their effects, severe wildfires have impacted a range of forested water supply catchments in recent years (Sydney 2001 & 2013, Canberra 2003, Adelaide 2007 and Melbourne 2009; Smith et al., 2011). Moreover, future projections postulate a widespread increase of fire activity in this region, driven not only by climate but also by human factors and complex ecological interactions, with substantial financial and societal implications (Clarke et al., 2011; Doerr and Santín, 2013). The ability to anticipate the potential threats for water resources from wildfires is therefore of major importance to land and water supply managers not only in Australia, but also in many other fire-prone regions of the world. Identification and prediction of the main threats can help to implement not only effective fire response and preparedness plans, but also effective post-fire mitigation measures.

The main water contamination threat from wildfires is the post-fire enhancement of soil erosion and sediment transfer to surface water bodies due to the removal of vegetation and litter, the decrease in soil stability and increased runoff (Shakesby and Doerr, 2006; Malvar et al., 2011). However, enhanced post-fire soil erosion and runoff do not always lead to major erosion events, because *i)* impacts of fire on soil properties are not always consequential, *ii)* specific terrain conditions limit the erosion risk, and/or, *iii)* rainfall after fire is not intense/early enough to cause an erosive response (Moody et al., 2013). For example, in this context, previous research in the greater Sydney catchment region following severe and extensive wildfires in 2001, demonstrated that the sandstone terrain in this region is relatively resilient to fire-induced soil erosion compared to what has been reported from most other terrain types elsewhere. Annual soil erosion rates (and associated water contamination potential) in the post-fire period (0-2 yr) were modest (2-50 Mg ha^{-1}) when compared to fire-affected terrain in the USA or Spain (20-200 Mg ha^{-1}) due to the permeable geology and the abundance of preferential flowpathways in the soil, despite very high levels of soil water repellency (Shakesby et al., 2007).

In addition to post-fire soil erosion and its associated risks, there is an often-neglected component present in the burnt landscape with important implications for water contamination: ash. In the context of wildfire, 'ash' is defined as the 'particulate residue remaining, or deposited on the ground, from the burning of wildland fuels (i.e. biomass, necromass and soil organic matter) and consisting of mineral materials and charred organic components' (Bodi et al., 2014; p. 104). This highly erodible material can be rapidly mobilised both by wind and water erosion and transferred into water bodies. Ash quantity and composition is very variable, but overall, ash-derived nutrients and minor elements can have a major impact on water quality (Smith et al., 2011; Costa et al. 2014). Although wildfire ash is generally more erodible than soil due to its loose nature and lower bulk density, it is usually not examined as a distinct part of the sediment transported by wind and water erosion, and its associated water contamination potential has rarely been examined (Bodi et al., 2014).

To address this research gap we examined the properties and potential water quality implications of the ash layer deposited during a severe wildfire in a dry sclerophyll eucalypt forest south-west of Sydney, Australia. The Balmoral wildfire of October 2013 affected parts of greater Sydney's drinking water supply catchment area (Fig. 1) and raised concerns about the risk of water contamination from post-fire erosion (Murphy, 2014). Specific aims of the study were to examine the role of fire severity (i.e. degree of destruction of vegetation, and ground fuels) in determining (i) total ash loads (ii), ash chemical composition for constituents relevant to water quality, and (iii) the associated risks for water contamination.

2. Materials and methods

2.1 Study area and site selection

The climate of the study area (Fig. 1) is humid temperate with moist summers and cool winters and no marked dry season. Mean annual rainfall is 900-1000 mm, with extremes of 400 and 1600 mm. The bedrock comprises mainly quartzitic Hawkesbury Sandstone with shale outcrops and soils range in texture from sandy to sandy clay loams (Doerr et al., 2006). Deep canyons and gorges with intervening ridges and gently-sloping plateaus characterise the landscape, with the dominant vegetation cover being dry eucalypt forest with a dense shrubby understorey (Keith, 2004). The fire return interval in the area is in the order of 14-21 years (Enright et al., 2012). The study area had not burnt since a controlled fuel reduction burn in October 1996 (i.e. time since fire = 17 years).

114   The Balmoral wildfire burnt, between 17th and 30th of Oct. 2013, over 16,000 ha including

115   12,694 ha of dry, shrubby sclerophyll eucalypt forests in the water supply catchments

116   managed by Water New South Wales (Water NSW) (Murphy, 2014). It affected parts of

117   greater Sydney's drinking water supply catchment area including the Nepean and

118   adjacent catchments (Fig. 1). Sampling sites were selected along a ridge typical of the

119   region (Fig. 1) with a relatively homogeneous fuel load of 25-30 Mg ha^{-1} (fuel loads

120   comprising ground (litter, herbs and grasses), understory, bark and canopy fuels < 1 cm;

121   diameter estimated according to Chafer et al. (2004)). Dominant canopy vegetation

122   comprised scribbly gum (*Eucalyptus sclerophylla*), stringybarks (*E. eugenioides*, *E.*

123   *oblonga*) and ironbark (*E. fibrosa*) with a shrub layer up to 4 m high dominated by *Banksia*

124   sp, *Leptospernum* sp, *Acacia* sp and *Petrophile* sp. The proportion of the different fuel

125   components before the fire in the study area was: litter 40.2±2.9%, understory

126   36.1±2.6%, bark 10.2%±1.4, and canopy 13.6±0.6 (Chafer unpublished data). Despite

127   the terrain homogeneity, wind-driven differences in fire behaviour (winds greater than 45

128   km h^{-1} and blowing perpendicular to the orientation of the ridge) resulted in a range of

129   fire severities along the length of the ridge (Fig. 1). This provided an ideal context to

130   examine ash production in relatively homogenous areas impacted by different fire

131   severities. In the present study, fire severity is defined as the degree of destruction

132   (consumption) of aboveground and ground fuels (< 1 cm diameter), based on the

133   classification established for this region by Chafer et al. (2004) and Chafer (2008). It uses

134   remote sensing standard methods (differenced normalised burn ratio obtained from

135   Landsat imagery immediately before (~1 day) and after (~1 week) the fire) validated by

136   on site assessment of fuel consumption completeness. It has five fire severity classes

137   (Fig. 1):

138   i)   *Low fire severity:* ground and understory (< 0.5 m high) fuels burnt. Canopy

139   unaffected.

140   ii)   *Moderate fire severity:* ground and understory (< 4 m high) fuels burnt. Canopy

141   unaffected.

142   iii)   *High fire severity*: ground and understory (< 4 m high) fuels consumed. Canopy

143   scorched.

144   iv)   *Very high severity*: all available fuels consumed, including stems < 0.5 cm thick.

145   v)   *Extreme fire severity*: all available fuels consumed, including stems < 1 cm

146   thick.

147

148   Three fire severities were sampled, which allowed covering the full width of severity

149   classes: low, high and extreme (Fig. 1). In addition to the burnt sites, one unburnt site

150   was also sampled as a control (Fig. 1). All sampling sites were selected in flat areas

151   (slope angles 0-2.5º) to minimise any risk of redistribution of ash by water erosion having

152   occurred between the fire (late Oct. 2013) and sampling (early Jan. 2014).

153

154   Total rainfall between the wildfire and sampling was 148 mm, distributed over 18 rainy

155   days and with a maximum daily precipitation of 31 mm (data from Buxton Station

156   N.068166, ca. 8 km northwest of the study ridge). At the time of sampling no signs of

157   redistribution of ash by water erosion were evident at the study sites. However, the

158   lightest component of ash was not found (i.e. the white-grayish mineral-rich ash formed

159   by high combustion completeness and generally located on top of the darker and organic

160   richer ash; Bodi et al., 2014). It is therefore assumed that this light ash material had

161   suffered redistribution since the fire by wind erosion or had been partially lost by

162   dissolution and leaching.

163

164   *2.2 Sampling procedure*

165   Within each of the three fire severity classes studied (extreme, high and low), three

166   comparable sites were sampled as replicates (Fig. 1). At each replicate site, three

167   parallel transects (A, B, C) with a length of 18 m and 6 m apart were laid out in the

168   direction of the fire propagation (W-E) (Fig. 2a). At each transect (A, B and C), 10

169   sampling points (every 2 m) were established, resulting in a total of 30 sampling points

170   per sampling site (Fig. 2a,b). At each sampling point, a square (400 to 600 cm^2; size

171   depending on site conditions) was delimited and the 'non-cohesive' layer collected with

172   a brush (Fig. 2c). This material, referred to in this study as 'ash', is a mix of burnt residues

173   from litter, understory and overstorey, together with burnt surface mineral soil which has

174   lost its structure and became part of the ash (Bodi et al., 2014). This 'non-cohesive' ash

175   layer was consistently darker and more wettable than the underlying uncharred soil (Fig.

176   2d), which was brighter in color and water repellent at all sites and sampling points

177   irrespective of fire severity (i.e. resisted water drop infiltration > 5 s; Doerr, 1998). At the

178   time of ash sampling, materials > 1 cm were removed, including also any unburnt

179   material that had fallen to the ground after the fire (e.g. dead tree leaves and bark).

180

181   For each sampling point 1-10 (Fig. 2a), the samples of the three transects with the same

182   number were pooled together to generate 10 composite samples per site (e.g. sample

183   number 1 = A_1+ B_1+ C_1). This resulted in 30 ash samples per fire severity class. The air-

184   dry weights of the different ash subsamples (i.e. A_n, B_n and C_n) were recorded separately

185   before pooling them so that variability within the sampling could be accounted for when

186   estimating ash loads (Mg ha^{-1}) (i.e. 30 ash weights per sampling site; 90 ash weights per

187   fire severity class).

188

189   After the sampling of the ash, samples of the soil layer not directly affected by the fire
190   were taken. For this, the soil surface that had been in contact with the ash layer was
191   carefully scraped to remove any charred residue and samples of 'subsurface soil', from
192   ~3 to ~8 cm soil depth from the mineral soil surface, were collected at the sampling points
193   A_5, B_5 and C_5 using a 5 x 5 cm sampling core. This resulted in 9 'subsurface soil' samples
194   per fire severity.

195

196   To provide control samples, an adjacent area not burnt by this fire was sampled (Fig. 1).
197   Three parallel transects were laid out in the same way as in the burnt sites (Fig. 2a).
198   First, the litter layer was taken from a square of 30 x 30 cm at each sampling point (10
199   per transect; i.e. n = 30). Secondly, the uppermost surface soil layer, organic rich and of
200   low cohesion, was sampled from the same 30 x 30 cm square (n = 30). Lastly, samples
201   of 'subsurface soil' (from ~3 to ~8 cm soil depth from the mineral soil surface) were taken
202   using the 5 x 5 cm sampling core at sampling points A_5, B_5 and C_5. Litter samples were
203   pooled together to generate a composite litter sample, and three replicates used for
204   further analyses.

205

206

207   *2.3 Laboratory analysis*

208   All samples were air-dried and their mass determined using a two-figure balance. In
209   order to estimate the bulk density of the ash layer, selected air-dried samples (12 per fire
210   severity) were placed into a 100 cm^3 cylinder and their net weights recorded. Soil
211   samples were sieved to remove any rock fragments and organic materials > 2 mm in
212   size, and a subsample was ground for analysis. For ash samples, sieving was not
213   necessary as all material < 1 cm is considered as ash, but a subsample was ground for
214   further analysis to reduce variability between subsamples. From the total sample set, a
215   representative subset was selected for further analysis: 27 ash samples (composite
216   sample numbers 1, 5 and 10 at each sampling site; i.e. 9 samples per fire severity); 12
217   samples of 'subsurface soil' (sampling point B_5 at each sampling site, i.e. 3 samples per
218   fire severity; and sampling points A_5, B_5 and C_5 at the unburnt control); 9 samples of the
219   organic-rich surface soil layer at the unburnt control ($A_{1,5,10}$, $B_{1,5,10}$, and $C_{1,5,10}$); and 3
220   samples of litter also from the unburnt control.

221

222   Total N and C concentrations (g or mg kg^{-1} ash/soil, dry weight) were determined in
223   ground samples using a Leco TruSpec CHN analyser.

224

225 Leaching tests were carried out according to the methodology of Hageman (2007). This
226 test is used to determine the amount of the water-leachable/water-soluble constituents
227 that may be mobilized by dissolution when the ash or soil comes in contact with rain. 3
228 g of sample (ground ash or < 2 mm unground soil) were weighed into 125 ml bottles.
229 Then 60 ml ultrapure water (sample:water ratio 1:20) was added and the bottles were
230 capped and shaken for 5 minutes. After shaking, the contents were allowed to settle for
231 10 minutes. After settling, pH and electric conductivity (EC) were measured in the
232 unfiltered leachate (sample:water ratio 1:20). The pH was measured with a Crison
233 micropH 2000 pH meter, with buffer solutions of pH 4, 7 and 9 and EC was measured
234 with a Crison GLP 31 apparatus, previously calibrated with a 0.1 M KCl solution.
235
236 The leachate was then filtered using a 0.45 μm pore-size nitrocellulose capsule filter. A
237 sub-sample of the filtrate was collected in plastic bottles and refrigerated. Another sub-
238 sample of the filtrate was acidified to pH < 1.5 with HNO_3 65% pure for atomic absorption
239 spectroscopy and inductively coupled plasma mass spectrometry analysis. Leaching
240 tests were not applied to the litter samples.
241
242 Phosphate (PO_4^{3-}) and ammonium (NH_4^+) concentrations (mg l^{-1}) were determined in
243 filtered leachate (sample:water ratio 1:20) using a Jasco V-630 spectrophotometer.
244 Fluoride (F^-) concentrations (mg l^{-1}) were also measured in filtered leachate using an ion-
245 selective fluoride electrode (Metrohm 692 pH/Ion Meter). Subsequently, the data
246 obtained (mg l^{-1}) were converted to mg kg^{-1} ash/soil (dry weight).
247
248 Concentration of major (Ca, K, Mg, Na, P) and minor (B, Cu, As, Cd, Hg and Pb)
249 elements were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-
250 MS) using a VARIAN 820-MS ICP-MS spectrometer. Concentrations of Fe, Al and Si
251 were determined by atomic absorption using a Perking Elmer Atomic Absorption
252 Spectrometer 1100B. Analysis was conducted on (i) acidified (pH < 1.5) filtered leachate
253 (sample:water ratio 1:20) and (ii) acid extracts of bulk samples obtained by total
254 digestion: 9 ml of HNO_3 65% pure and three ml of HCl 37% pure were added to 0.5 g of
255 ground sample and this subjected to microwave digestion (Ethos Plus Milestone
256 microwave) at 200 ºC during 50 minutes. Afterwards, the extracts were completed to 50
257 ml with ultrapure water (sample:solution ratio 1:100). The concentrations obtained (mg
258 or μg l^{-1}) were subsequently converted to g, mg or μg kg^{-1} ash/soil (dry weight).
259 Additionally, one ash sample from each fire severity (low, high and extreme) was
260 analyzed by scanning electron microscopy with energy dispersive x-ray spectroscopy
261 (SEM-EDS; ZEISS, model EVO515).

262

2.4 Statistical analyses

264 Statistical analyses were performed with the software IBM SPSS Statistics 19. The level
265 of significance used for all tests was 5% (i.e. $\alpha = 0.05$). To analyze the differences in ash
266 (or soil) properties between fire severities, one-factor ANOVAs were performed using fire
267 severity as the independent factor. Before the ANOVAs, the equality of variances for the
268 studied groups (i.e. fire severity classes – including 'unburnt control' for soil analyses)
269 was tested by the Levene's homoscedasticity test. In the cases where differences in
270 arithmetic means among classes were found to be statistically significant and variances
271 for the studied fire severity classes equal, the post-hoc Duncan's multiple range test was
272 performed to identify classes with significantly different means. In the cases of unequal
273 variances, the post-hoc Tamhane's T2 test was performed instead of Duncan's.

274

2.5 Water contamination potential calculations

276 The maximum water contamination potential from wildfire ash for the elements analysed
277 in this study, i.e. maximum ash inputs into the sub-catchments affected by fire, was
278 estimated using a 'worst-case' scenario. In this hypothetical scenario all the ash
279 generated is mobilized into the hydrological network. First, the ash loads (Mg ha^{-1}) were
280 modelled over the study area based on Landsat 8 satellite image analysis and the field
281 data collected here(Chafer et al. submitted). Afterwards, the total amounts of ash
282 produced at each fire severity class for the five burnt sub-catchments were calculated
283 and combined with the average concentration of each element in the ash characterized
284 for each fire severity class studied (Table 1). Given that ash produced in the two
285 intermediate fire severity classes (i.e. moderate and very high) was not available for
286 analysis, element concentrations in these classes had to be estimated. We therefore
287 used values from the class immediately below or above, applying the higher of the two
288 values for each element studied. This approximation for these two intermediate classes
289 was chosen because the aim was to derive the 'worst-case' scenario, and, therefore,
290 overestimation was preferable to underestimation. Using the same approach, the
291 maximum water contamination potential from water-soluble elements was also
292 estimated, by multiplying the total amounts of ash produced by the average
293 concentration of soluble elements in the ash generated in each fire severity class.

294

3. Results and Discussion

3.1 Ash loads and ash bulk density

297   Ash production, expressed as total ash loads (Mg ha⁻¹), increased significantly with fire
298   severity (Fig. 3). Extreme fire severity was associated with the highest ash production
299   (34.2±2.1 Mg ha⁻¹) whereas production at high fire severity sites was less than half
300   (15.9±0.9 Mg ha⁻¹). At low fire severity the ash production was the lowest, almost six
301   times less than at extreme fire severity sites (6.0±0.7 Mg ha⁻¹). Ash bulk density (g cm⁻³)
302   also increased notably with fire severity (Fig. 3), although the difference between fire
303   severity classes was only statistically significant between low severity (0.35±0.05 g cm⁻
304   ³) and high + extreme severities (0.54±0.04 and 0.59±0.03 g cm⁻³, respectively).

305   The ash loads and bulk density values determined for our study sites were similar to
306   those found for conifer forests in USA and Spain, where total ash loads ranged from 15
307   to 150 Mg ha⁻¹ and bulk density values ranged from 0.18 to 0.62 g cm⁻³ (Goforth et al.,
308   2005; Cerdá and Doerr, 2008; Woods and Balfour, 2008). The only relevant study in
309   Australian eucalypt forest known to the authors was carried out by Santín et al. (2012)
310   who investigated ash production in mature wet eucalypt forest near Melbourne affected
311   by extreme fire severity during the 2009 'Black Saturday' fires. They reported very similar
312   ash bulk densities (0.3-0.6 g cm⁻³), but much higher total ash loads (61-116 Mg ha⁻¹) to
313   those presented here. This is likely to be due to higher fuel loads and greater overall fire
314   severity for the 'Black Saturday' fires (Santín et al., 2012).

315   None of these previous studies have examined the role of variable fire severity in the
316   absolute amounts of ash generated. Pereira et al. (2013) reported thinner ash layers
317   generated under higher severities during a wildfire in a Mediterranean pine forest. They
318   found a significant relationship between ash colour and thickness of the ash layer present
319   immediately after the fire and suggested that brighter ash colours were associated with
320   a thinner ash layer because they indicate higher fuel combustion completeness (i.e.
321   higher fire severity). Along these same lines, Hudak et al. (2013) found a positive
322   correlation between surface fuel consumption and proportion of white ash covering the
323   ground after eight prescribed fires in four fuelbed types. Indeed, higher wildfire severities
324   are usually related to higher fuel combustion completeness (Chafer et al., 2004), which
325   reduces total mass of ash produced for a given fuel load and type. However, total ash
326   loads depend not only on combustion completeness, but also on total amount of fuel
327   affected. Under higher fire severities, more fuel (i.e. dead and live available biomass) is
328   affected by fire, which can lead to the overall positive relationship between fire severity
329   and total ash loads observed here. In addition to this, it is important to consider that not
330   only biomass from the vegetation and litter is available for burning. Soil organic matter is
331   also a potential fuel. When wildfire affects soil, the uppermost surface soil layer may loss
332   its structure and become part of the ash layer itself (Bodi et al., 2014). This mineral-

333 enriched soil-derived material can, therefore, be an important contributor to total ash
334 loads.

335 The contribution of burnt surface soil material is likely to increase with fire severity due
336 to associated greater depth of heat penetration and combustion of soil organic matter.
337 This link between fire severity and effects on the soil was already observed in the greater
338 Sydney region by Chafer (2008), who found, for two small wildfires, a positive correlation
339 between mean soil charring depth and fire severity. The increasing contribution of soil-
340 derived material to ash with increasing fire severity could, in part, explain not only the
341 higher ash loads but also the higher ash bulk density at higher fire severities found here
342 (Fig. 3).

343

344 *3.2 Ash and soil chemical characteristics*

345 3.2.1 Ash bulk composition

346 The concentrations of the analyzed elements in the ash generated under different fire
347 severities are shown in Table 1. Results are discussed by groups of elements: i) 'biogenic
348 elements' (B, C, Ca, Cu, K, Mg, N, Na, P), macro and micronutrients mainly derived from
349 biomass/necromass; ii) 'lithogenic elements' (Al, Fe, and Si), mainly derived from mineral
350 soil and thus present in much higher concentrations in soils than in vegetal material (see
351 Table 2); and iii) 'toxic elements' (As, Cd, Hg, Pb), derived from several sources but
352 particularly potent as water pollutants, (Bashkin, 2002, Kataba-Pendia 2010).

353

354 For biogenic elements, litter was richer than soils in B, Mg or Na (Table 2). Thus, it is
355 very probable that litter was a major source of these elements for the ash, provided that
356 the temperatures reached during the fire had not led to major losses (e.g. Mg is volatilized
357 at ~1100 °C and Na at ~900 °C; Bodi et al., 2014). Overall, the biogenic elements
358 analysed did not follow a single trend with fire severity. Concentrations of N, Mg and P
359 were similar irrespective of fire severity, but other elements displayed significant but
360 different trends (Table 1). B and K contents increased with fire severity (from 2.9±0.3 to
361 4.1±0.3 mg kg^{-1} for B and from 1.0±0.1 to 1.5±0.1 g kg^{-1} for K), whereas Ca content
362 decreased (from 3.6±0.4 to 2.3±0.1 g kg^{-1}). Na concentrations were similar for low and
363 high severity samples (119.4±7.9 and 118.6±8.2 mg kg^{-1}), but were significantly higher
364 in ash formed under extreme fire severity (141.9±6.0 mg kg^{-1}). C concentrations were
365 higher at low (247.3±39.5 g kg^{-1}) than at high and extreme fire severity (155.8±18.0 and
366 162.0±3.0 g kg^{-1}, Table 1). The higher C content in the low fire severity ash is very
367 probably related to a relatively higher proportion of pyrogenic organic components, i.e.

charcoal-type C enriched materials. Under higher fire severity more complete combustion of fuels is expected, and that leads to enrichment of mineral residues and less pyrogenic organic material remaining in ash (Bodi et al., 2011).

Regarding lithogenic elements (i.e. Al, Fe and Si), Al concentration significantly increased with fire severity (from 20.7 ± 1.7 to 39.5 ± 2.4 g kg^{-1}), whereas Fe and Si did not show clear trends (Table 1).

For toxic elements (As, Cd, Pb, Hg), the observed trends with fire severity were variable, as are their geochemical behaviours in general. Cd and Hg did not present significant differences between fire severities (Table 1). Hg concentrations were always low (< 5 µg kg^{-1}; Table 1) and below those found in litter and soil samples (Table 2), which points to a loss to the atmosphere during fire (volatilized ~ 300 °C; Bodi et al., 2014). As and Pb concentrations were significantly higher in ash formed under extreme fire severity (Table 1). This may indicate a relative enrichment of these elements at the greatest severity due to loss of other elements that still remained in ash at low and high fire severity.

Overall, the concentrations of most biogenic and toxic elements in the ash samples studied here (Table 1) were lower than those reported elsewhere in ash from wildfires, prescribed fires and laboratory burns, where, for instance, Ca, K, Mg and P are usually in the range of tens or several thousand mg kg^{-1} ash (Raison et al., 1985; Ferreira et al., 2005; Balfour and Woods, 2013; Audry et al., 2014; Bodi et al., 2014; Plumlee et al., 2014). It is important to note that concentrations of elements can vary substantially even when studying comparable types of ash. For example, Bodi et al. (2014) compared several studies reporting the composition of ash derived from the same fuel (*Pinus ponderosa*) and found variations of up to several orders of magnitude in the concentrations of some elements (e.g. Al, Ca, K, Mg, P). This high variability is attributed not only to different burning conditions and fuel properties, but also to the use of different methodologies for sampling and characterization of the ash (Bodi et al., 2014).

Other main reasons for the relatively low concentrations of biogenic elements in the ash analyzed here when compared to wildfire ash described elsewhere may be the combination of (i) the overall nutrient poor environment of the SE-Australian sandstone tablelands (Shakesby et al., 2007) and (ii) substantial contribution from the burnt surface mineral soil to the ash layer. The latter would lead to a 'dilution' of the burnt residues from vegetal fuels due to the incorporation of burnt surface soil material and, therefore, overall lowered concentrations of biogenic elements. The possibility of a substantial

contribution from burnt soil to the ash characterized in this study is also supported by the high concentrations of lithogenic elements (Al, Fe, and Si) in the sampled ash (Table 1) compared to previous studies (e.g. see Table 1 in Bodí et al., 2014). These are the main elements in the lithology of the study area (quartzitic sandstone and shale; Young, 1980), and they were found only in very low concentrations in litter (Table 2), which also supports the hypothesis of soil as being their main contributor to ash. Similarities in composition between ash (Table 1) and the the organic-rich surface soil layer at the unburnt control site (Table 2) further support the importance of burned soil material in contributing to the ash layer. Moreover, the SEM-EDS imagines of the studied ash (Fig. 4) showed the presence of high quantities of mineral material. These are mostly silica aggregates with morphologies and sizes (~200-1000 μm) indicating a soil origin.

3.2.2 Physicochemical characteristics of the water-soluble fraction of ash

Mean values of pH, EC, and concentration of water-extractable elements are reported in Table 3. The pH values for ash extract (6.1-6.4) were much higher than for the control unburnt organic-rich surface soil layer and subsurface soils (pH 5.2-5.5; Table 2). Similar differences have also been reported previously when comparing ash and litter (Ubeda et al., 2009; Pereira et al., 2011, 2014). In our case, ash pH did not significantly increase with fire severity (Table 3). This contrasts with the trend reported for wildfire ash in oak and pine forests in Portugal by Pereira et al. (2012), who estimated fire severity using ash colour and found an increase of pH from 7.3 in low severity (very dark brown) to 8.2 in high severity (light grey) ash.

All our ash pH values were lower than most values reported previously for wildfire ash, which typically range from weak alkaline (pH > 7) to caustic alkaline (pH > 10.5) (Plumlee et al., 2014). The high pH typical of wildfire ash is attributed to high concentrations of compounds with alkali reactions such as CaO or K_2O (Bodi et al., 2014). The lower pH values found here could be related to the fact that sampling was not carried out immediately after the fire. Costa et al. (2014) also recorded relatively low pH values of ~6 in ash collected five months after a wildfire in Portugal. Temporal evolution of wildfire ash can lead to hydration-carbonation reactions of oxides and formation of carbonates (Balfour et al., 2014), which are less reactive and soluble (Santos et al., 2009; Pan et al., 2012). However, this alone is probably not sufficient to explain the low pH values found here. The adsorption of rainwater by the ash layer could, by itself, have had an acidification effect. Rainwater has a pH of 4.5-5.6 (Charlson and Rodhe, 1982), and the majority of rainwater in Australia is mildly acidic (pH ~5) (GHD, 2008). The precipitation fallen between the fire and the sampling (148 mm) would translate into an input of ~1.5

442 mmol H^+ m^{-2}, which could indeed have led to acidification of the ash. In addition to this,

443 and given that there have been rainfall events prior to sampling, some soluble alkaline

444 components could have been lost by leaching. Leaching losses would also explain the

445 low concentrations of soluble elements in our ash samples (see below). The chemical

446 characterization of subsurface soil (~3-8 cm) does not indicate substantial leaching

447 transfer of soluble components from the ash into this soil layer (see section 3.2.3).

448 However, it is conceivable that some soluble components have bypassed this water

449 repellent soil layer during rainfall via preferential flow (cracks and biopores, Shakesby et

450 al. 2007) and entered the wettable subsoil.

451

452 Concentrations of soluble elements (e.g. Ca^{2+}, Mg^{2+}, K^+ and Na^+; Table 3) in the ash

453 samples investigated here were low compared to the typically more alkaline wildfire ash

454 reported from most other environments. For example, Plumlee et al. (2007) and

455 Hageman et al. (2008a,b) used the same 'leaching method' used here to characterize

456 ash generated in several wildfires in California. Californian wildfire ashes showed higher

457 EC (23-3200 µS cm^{-1}), and higher soluble contents for most of the elements examined

458 here: F^- (2-86 mg kg^{-1} ash), Ca (80-13580 mg kg^{-1} ash), Cu (64-1600 µg kg^{-1} ash), Mg

459 (2-86 mg kg^{-1} ash), As (20-270 µg kg^{-1} ash) or Hg (< 100-500 µg kg^{-1} ash). Only B (100-

460 1120 µg kg^{-1} ash), K (4-292 mg kg^{-1} ash), P (0.4-8 mg kg^{-1} ash) and Pb (4-8 µg kg^{-1} ash)

461 had concentrations within the same order of magnitude as in our samples (Table 3). It is

462 worth noting that the range of values recorded for Californian wildfire ashes is much

463 broader than for our sample set, indicating a higher variability in ash composition in the

464 former, where ash samples were taken from several burnt sites, with a greater diversity

465 in geology and vegetation than our study sites (Plumlee et al., 2007). Their highest

466 values correspond mainly to white ash (see Hageman et al., 2008b), a type of ash that

467 was not sampled in our investigation, as this is the lightest ash component and may had

468 already been lost at the time of sampling (see Section 2.1). Substantial redistribution of

469 light white ash by wind has, for example, been observed in the first few days after fire in

470 grassland environments (Pereira et al., 2015). Also, as explained above, some losses of

471 the most soluble ash components by leaching cannot be ruled out either.

472

473 As to the effect of fire severity on the solubility of elements in ash, it is important to

474 remember that solubility is conditioned by pH (Brookins, 1988). Given that differences in

475 ash pH between the fire severities studied here were not significant (Table 3), trends

476 may not be evident. That said, soluble B, Ca, Cu and Mg showed a significant decrease

477 with fire severity (Table 3). Soluble NH_4^+ and As concentrations were highest in extreme

478   fire severity ash whereas soluble PO_4^{3-} and Pb concentrations were the lowest there

479   (Table 3).

480

481   The solubility of the studied elements was generally low when compared to their total

482   concentrations in ash, with proportions < 1% for Al, As, Cd, Fe, Pb and Si; < 5% for Ca,

483   Cu, and P and < 10% for K and Mg. Solubility of B ranged widely, from ~6% for extreme

484   fire severity ash to 14% for low fire severity ash. Na was the most soluble component,

485   with values that ranged from 30% in extreme fire severity ash to 50% in the low fire

486   severity ash. Our results follow the general trend of Na > K > Mg > Ca > P, reported

487   previously for conifer forest ash by Grier (1975). They also agree with some of those

488   observed by Khanna et al. (1994) who studied the solubility of ash components derived

489   from laboratory combustion of eucalypt litter. Khanna et al. (1994) found the highest

490   solubility for K (68%), S (56%) and Mg (42%), intermediate solubilities for Ca (14%), Al

491   (17%) and P (11.3%) and the lowest for Fe (1%) and Mn (0.2%). It is important to note,

492   however, that they used a different methodology for water extraction, which involved a

493   much longer extraction period (15 days). Solubilisation of ash elements generally

494   increases (up to a point) with time and with the amount of water used in extraction

495   procedure (Khanna and Raison, 1986; Audry et al., 2014).

496

497   3.2.3 Soil chemical characteristics

498   The soils analysed exhibited acid pH (~5.2-5.5) and low EC values (< 50 μS cm^{-1}) (Table

499   2), what is typical of soils developed under nutrient-poor lithologies such as the quartzitic

500   sandstone and shale of the study area (Young, 1980). Importantly, no statistically

501   significant differences were found between the characteristics of the subsurface soils (3-

502   8 cm depth) from the different fire severity sites or between these and the unburnt control

503   (Table 2). This supports the visual observation that, irrespective of fire severity, the fire

504   had not directly affected the near-surface soil layer. The organic-rich surface soil layer

505   in the unburnt control site exhibited very similar characteristics to the subsurface soils,

506   except for higher C and N concentrations, which is expected due to its organic-rich

507   nature.

508

509   *3.3 Water contamination potential of wildfire ash*

510   3.3.1 Contamination potential from eroded ash

511   Ash is usually highly water absorbent due to its high porosity (Cerda and Doerr, 2008;

512   Bodi et al., 2014). Therefore, despite it being more erodible than soil due to its loose

513   nature and lower bulk density, wildfire ash can have a protective effect on the soil in post-

514   fire landscapes, which have lost the interception capacity of the canopy and litter layer

515   (Bodi et al., 2014). This 'protective' role of ash may be particularly relevant in areas where

516   soils show high levels of water repellency, as is the case for the study region (Doerr et

517   al., 2006). In these soils, the water repellent surface soil layer does not readily absorb

518   water (Fig. 2d). In the absence of litter, rainfall can thus be rapidly transported via

519   overland flow, leading to accelerated soil erosion or, where macropores facilitate

520   infiltration, via subsurface flow, leading to the transport of potential contaminants to

521   groundwater (Lasanta and Cerdà, 2005; Shakesby and Doerr, 2006). This 'protective'

522   effect of the ash layer by water absorption is time-limited as ash does become

523   compacted, and part of can be lost by wind erosion and by dilution during rainfall events,

524   leading to a decline in its water storage capacity over time (León et al. 2013; Balfour et

525   al., 2014).

526   When storm events exceed the water storage capacity threshold of the ash layer, this

527   layer may be entrained very effectively in surface runoff, and eventually be transported

528   into surface water bodies. The maximum inputs (Mg) of the studied elements that could

529   potentially reach the sub-catchments affected by the Balmoral fire are presented in Table

530   4. These values are based on a 'worst-case' ash-erosion scenario (see Section 2.5 for

531   more details) and it is important to consider that (i) it is highly unlikely that all ash

532   produced is transported off the hillslopes, but also that (ii) some of the water repellent

533   soil and sediment stored in drainage channels may be also mobilized and could add to

534   the total sediment flux and thus pollution risk.

535   As an example, Fig. 5 illustrates the distribution of P present in ash (kg ha^{-1}) for the whole

536   area burnt in the Balmoral wildfire. Water contamination due to P has been the subject

537   of concern for Sydney Catchment Authority (now Water New South Wales) following

538   previous wildfires (Sydney Catchment Authority, Personal Communication). P is a key

539   biogenic element from the water pollution perspective, because it is a limiting factor for

540   primary productivity, and, if present in its bioavailable form, it can thus enhance

541   eutrophication when ash is transported into the hydrological network (Smith et al., 2011).

542   Our approach used here gives the maximum inputs of this element that could reach the

543   rivers and reservoirs affected by the fire (Table 4). For example, up to 3.7 Mg of P derived

544   from wildfire ash could potentially be delivered into the 'West lake Nepean' reservoir

545   (Table 4). These figures are unlikely to be reached, but can be useful to catchment

546   managers as 'maximum potential risk values', in order to inform decisions about the

547   location and nature of post-fire mitigation measures and strategies at high-risk areas.

548   Furthermore, the information on ash quantity and characteristics provided by the

549 approach introduced here also enables its incorporation into post-fire erosion and risk
550 analysis models.

551 Whilst the concentrations of elements in wildfire ash analyzed here are relatively low
552 compared to those reported from ash examined elsewhere (see Bodi et al., 2014), the
553 total ash loads are substantial and could pose an important contamination potential
554 during a major storm event. If a major storm occurs following a prolonged dry period and
555 hence low river flow or water supply reservoir levels, this would exacerbate the pollution
556 potential. Such a scenario is not unlikely as the most severe fires often occur following
557 prolonged droughts (Smith et al., 2011). In addition to the threat from its specific chemical
558 constituents (Table 4), ash may also affect water quality by causing increases in turbidity
559 from suspended solids. This was indeed the case in the study area after torrential rains
560 in March 2014, when a water supply treatment plant had to be temporarily closed
561 because turbidity values were too high for the water to be treated (Water NSW,
562 unpublished data).

563

564 Finally, when evaluating the water contamination potential from ash, it is also important
565 to take into account the chemical partitioning of a specific element in the ash (e.g.
566 associated to iron oxides/hydroxides or to organic pyrogenic compounds) as it can
567 determine its pollutant potential. Geochemical forms of different elements may change
568 when ash is mobilized from the production sites (i.e. oxic surface soils) into
569 suboxic/anoxic sediments in rivers and reservoirs. For example, changes in the redox
570 conditions canrelease P and toxic metals to the water by reduction of adsorptive Fe(III)
571 oxides/hydroxides into non–sorptive Fe (II) carbonate or sulphide (Salomons and
572 Förstner, 1984; Jensen et al., 1992; Howarth et al., 2011). Another important point to
573 consider is that the pollution potential from wildfire ash can be enhanced by the
574 accumulative effect of recurrent wildfires, when, for example, the concentration of a
575 eutrophication nutrient, such as P, exceeds the critical load of the aquatic system after
576 several inputs from consequent fire-erosion cycles (Salomons and Förstner, 1984;
577 Wetzel, 2001).

578

579 3.3.3 Contamination potential from leaching

580 When rainfall events exceed the water storage capacity threshold of the ash layer, but
581 are of insufficient intensity to lead to ash erosion (i.e. prolonged periods of moderate
582 rainfall), water contamination may still occur by leaching, when water percolates through
583 the ash. Water-soluble contaminants may then enter the rivers and reservoirs via
584 subsurface flow. A maximum water contamination potential assuming all water-soluble

585 components are transported to the reservoir is estimated in Table 5. These values,
586 however, are 'worst-case scenario' as not all soluble elements leached from ash would
587 be expected to end up in the hydrological network. A proportion is likely to precipitate,
588 over time and space, due to changes in water chemistry, with some also being retained
589 in the soil system (e.g. in organo-mineral complexes) or taken up by microorganisms and
590 plants (Bodi et al., 2014).

591 It is important to note, that, as highlighted in section 3.2.2, some leaching from the ash
592 layer may have occurred prior to sampling. Therefore, the 'worst-case' figures calculated
593 for this 'aged' ash at the time of investigation (Table 5) may be lower than immediately
594 after fire. In addition to this, soluble organic compounds, which have not been the focus
595 of this study, are also potentially important pollutants. For example polycyclic aromatic
596 hydrocarbons (PAHs), which are generated during wildfires (Vergnoux et al., 2011), are
597 of great concern for water supply managers due to their carcinogenic potential. However,
598 a previous study identifying potential acute effects from PAHs in surface waters after
599 severe wildfires in Australian eucalyptus forests (2009 'Black Saturday Fires', Victoria)
600 suggests that they are unlikely to be a common main cause for fire-related ecological
601 impacts in this region (Schäfer et al., 2010).

602 3.3.4 Implications for post-fire land and water management decisions

603 Research by the scientific community is continuously improving our understanding of
604 both post-fire environmental threats (e.g. Moody et al., 2014; Wagenbrenner et al., 2015)
605 and potential strategies to mitigate these (Robichaud et al. 2014). However, scientific
606 investigations are often carried out in isolation and knowledge transfer between
607 researchers and the land-management community is not always effective. The current
608 study involves direct collaboration and knowledge transfer. Wildfire research undertaken
609 within Sydney's Drinking Water Catchments is actively incorporated in wildfire
610 management policies and fire management practices by the two principal organisations
611 responsible for managing these ecologically important forested catchments: Water NSW
612 (formerly Sydney Catchment Authority) and the Office of Environment and Heritage.
613 Water NSW actively incorporate published research into their fire management policies
614 and procedures, and also report continuously on research that is being undertaken in
615 the forested catchments (www.sca.nsw.gov.au/science-and-
616 education/science/catchment/wildfires). The Office of Environment and Heritage
617 actively engages in wildfire research and management practices that intern continuously
618 influence and update the fire management policies and procedures within their

619   organisation as new information is published (http://www.environment.nsw.gov.au/fire/)
620   (Anon 2013).

621   This study is the first step in incorporating the water contamination risk derived from
622   wildfire ash into fire responses and mitigation plans in Sydney's Drinking Water
623   Catchments. Further steps will include validation of the methodology for other
624   environments within the catchments, and development of ash erosion "probability
625   scenarios" by accounting for factors such as topography, vegetation cover and rainfall
626   patterns in determining ash erosion and associated water pollution risk.

627

4. Conclusions

629   The new approach presented here for estimating the water contamination potential from
630   wildfire ash delivers spatially distributed scenarios (e.g. Fig. 5, Tables 4 and 5) that can
631   be used to guide land and water supply managers with regard to fire response,
632   preparedness plans and post-fire mitigation measures. This approach can be adapted
633   and applied to other environments, and its outputs incorporated into post-fire erosion and
634   risk analysis models. Furthermore, the relationship found here between ash loads and
635   fire severity, as well as the composition of the ash generated under different fire
636   severities, can be used to predict ash loads and their contamination potential for future
637   wildfires and management burns not only in other areas of the studied catchment, but
638   also elsewhere in the region under comparable vegetation and soil characteristics.

639   Specific conclusions from this study are:

640   *i)* The Balmoral wildfire (Sydney, October 2013) produced substantial ash loads of up to
641   34 Mg ha^{-1}. The ash loads were positively related to fire severity (i.e. degree of vegetation
642   and ground fuel destruction). This is mainly attributed to a combination of increasing (a)
643   total fuel affected by fire and (b) contribution of ´burnt mineral soil´ to the ash layer, with
644   increasing fire severity.

645   *ii)* The contribution of soil material to the ash layer can be substantial, both in terms of
646   overall ash loads and ash composition. Soil inputs, therefore, need to be considered in
647   wildfire ash investigations as they can greatly influence ash characteristics and,
648   therefore, the potential of wildfire ash as a water contamination threat.

649   *iii)* Concentrations of most of the elements analyzed were relatively low when compared
650   to wildfire ash examined elsewhere. However, given the overall total ash loads, there is

651 potential for substantial water quality impacts. Beyond chemical pollutant effects, this
652 includes also increases in turbidity when ash reaches the reservoir as suspended solids.

653

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661

662 **References**

663 Audry, S., Akerman, A., Riotte, J., Oliva, P., Maréchal, J-C., Fraysse, F., Pokrovsky,
664   O.S., Braun, J-J., 2014. Contribution of forest fire ash and plant litter decay on
665   stream dissolved composition in a sub-humid tropical watershed (Mule Hole,
666   Southern India) *Chemical Geology,* 372, 144-161.

667 Balfour, V.N., Doerr, S.H., Robichaud, P.R., 2014. The temporal evolution of wildfire ash
668   and implications for post-fire hillslope hydrology. *International Journal of Wildland*
669   *Fire*, 23, 733-745.

670 Bashkin, V.N., 2002. Modern biogeochemistry. Kluwer Academic Publisher. Dordrecht,
671   The Netherlands.561pp.

672 Bodí, M.B., Mataix-Solera, J., Doerr, S.H., Cerdà, A., 2011. The wettability of ash from
673   burned vegetation and its relationship to Mediterranean plant species type, burn
674   severity and total organic carbon content. *Geoderma,* 160, 599–607.

675 Bodí, M.B., Martin, D.A., Balfour, V.N., Santín, C., Doerr, S.H., Pereira, P., Mataix-
676   Solera, J., Cerdà, A., 2014. Wildland fire ash: production, composition and eco-
677   hydro-geomorphic effects. *Earth-Science Reviews,* 130, 103-127.

678 Brookins, D.G., 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlang, New York,
679   176pp.

680 Cerdà, A., Doerr, S.H., 2008. The effect of ash and needle cover on surface runoff and
681   erosion in the immediate post-fire period. *Catena,* 74, 256–263.

682 Chafer, C.J., 2008. A comparison of fire severity measures: An Australian example and
683   implications for predicting major areas of soil erosion. *Catena,* 74, 235-245.

684 Chafer, C.J., Noonan, M., Macnaught, E., 2004. The post-fire measurement of fire
685   severity and intensity in the Christmas 2001 Sydney wildfires. *International*
686   *Journal of Wildland Fire,* 13, 227–240.

687 Chafer, C.J., Santín, C., Doerr, S.H. Modelling and quantifying the spatial distribution of
688   post-wildfire ash loads. *International Journal of Wildland Fire*, (submitted)

689 Charlson, R.J., Rodhe, H., 1982 Factors controlling the acidity of natural rainwater.
690   *Nature*, 295, 683- 685.

691 Clarke, P.J., Knox, K.J.E., Campbell, M.L., Copeland, L.M., 2009. Post-fire recovery of
692   woody plants in the New England Tableland Bioregion. *Cunninghamia,* 11, 221-
693   239.

694 Clarke, H., Smith, P., Pitman, A.P, 2011. Regional signatures of future fire weather over
695   eastern Australia from global climate models. *International Journal of Wildland*
696   *Fire*, 20, 550-562.

697 Costa, M.R., Calvao, A.R., Aranha, J. 2014. Linking wildfire effects on soil and water
698   chemistry of the Marão River watershed, Portugal, and biomass changes
699   detected from Landsat imagery. *Applied Geochemistry,* 44, 93–102.

700 Doerr, S.H., 1998. On standardizing the 'Water drop penetration time' and the 'molarity
701   of an ethanol droplet' Techniques to classify soil hydrophobicity: a case study
702   using medium textured soils. *Earth Surfaces Processes and Landforms* 23, 663-
703   668.

704 Doerr, S.H., Santín, C., 2013. Wildfire: A Burning Issue for Insurers. Lloyd's of London,
705   36pp.

706 Doerr, S.H., Shakesby, R.A., Blake, W.H., Humphreys, G.S., Chafer, C., Wallbrink, P.J,
707   2006. Effects of differing wildfire severity on soil wettability in Australian eucalypt
708   catchments. *Journal of Hydrology*, 319, 295-311.

709 Dudley, N., Stolton, S., 2003. Running Pure: The Importance of Forest Protected Areas
710   to Drinking Water. Research Report for the World Bank and WWF Alliance for
711   Forest Conservation and Sustainable Use. ISBN 2-88085-262-5.

712 Enright, N.J., Keith, D.A., Clarke, M.F., Miller, B.P., 2012. Fire regimes in Australian
713   sclerophyllous shrubby ecosystems: heathlands, heathy woodland and mallee
714   woodland. In: Bradstock, RA Gill, AM Williams J (eds) Flammable Australia: fire
715   regimes, biodiversity and ecosystems in a changing world. CSIRO, Collingwood,
716   Victoria, pp. 215-234.

717 Ferreira, A.J.D., Coelho, C.O.A., Boulet, A.K., Lopes, F.P., 2005. Temporal patterns of
718   solute loss following wildfires in Central Portugal. *International Journal of*
719   *Wildland Fire,* 14, 401-412.

720 GHD (2008) NSW Sport and Recreation. Southern Highlands Regional Shooting
721   Complex: Environmental   Assessment.   202p.
722   www.planning.nsw.gov.au/asp/pdf/06_0232_hilltop_ea_report.pdf   (accessed
723   18/12/2014)

724 Gill, A.M., 2012. Bushfires and Biodiversity in southern Australian Forests. pp 235-252
725   in: *Flammable Australia*. Eds Bradstock, R.A., Gill, M, Williams R.J. CSIRO
726   publishing, Collingwood, Victoria

727 Goforth, B.R., Graham, R.C., Hubbert, K.R., Zanner, C.W., Minnich, R.A, 2005. Spatial
728   distribution and properties of ash and thermally altered soils after high-severity
729   forest fire, southern California. *International Journal of Wildland Fire,* 14, 343–
730   354.

731 Grier, C.C., 1975. Wildfire effects on nutrient distribution and leaching in a coniferous
732   ecosystem. *Canadian Journal of Forest Research,* 5, 599–607.

733 Hageman, P.L., 2007. U.S. Geological Survey field leach test for assessing water
734   reactivity and leaching potential of mine wastes, soils, and other geologic and
735   environmental materials: U.S. Geological Survey Techniques and Methods
736   Report   5-D3,   http://pubs.usgs.gov/tm/2007/05D03/pdf/TM5-D3_508.pdf
737   (accessed 18/12/2014).

738 Hageman, P.L., Plumlee, G.S., Martin, D.A., et al., 2008a. Leachate geochemical results
739   for ash samples from the June 2007 Angora wildfire near Lake Tahoe in Northern
740   California, 2008. US Geological Survey Open-File Report 2008-1170. Reston,
741   VA: US Geological Survey.

742 Hageman, P.L., Plumlee, G.S., Martin, D.A., et al., 2008b. Leachate geochemical results
743   for ash and burned soil samples from the October 2007 Southern California
744   wildfires. US Geological Survey Open-File Report 2008-1139. Reston, VA: US
745   Geological Survey.

746 Howarth, R., Chan, F., Conley, D.J., Garnier, J., Doney, S.C., Marino, R., Billen G., 2011.
747   Coupled biogeochemical cycles: eutrophication and hypoxia in temperate
748   estuaries and coastal marine ecosystems. *Frontiers in Ecology and the*
749   *Environment*, 9, 18-26.

750 Hudak, A.T., Ottmar, R.D., Vihnanek, R.E., Brewer, N.W., Smith, A.M.S., Morgan, P.,
751   2013. The relationship of post-fire white ash cover to surface fuel consumption.
752   *International Journal of Wildland Fire*, 22, 780–785.

753 Jensen, H. S., Kristensen, P., Jeppesen, E., Skytthe, A., 1992. Iron:phosphorus ratio in
754   surface sediment as an indicator of phosphate release from aerobic sediments in
755   shallow lakes. *Hydrobiologia,* 235/236, 731–743.

756 Kataba-Pendias, A., 2010. Trace metals in soils and plants. CRS press, Baton Rouge.
757   432 pp.

758 Keane, R.E., 2012. Describing wildland surface fuel loading for fire management: a
759   review of approaches, methods and systems. *International Journal of Wildland*
760   *Fire,* 22, 51-62.

761 Keith, D.A., 2004. Ocean Shores to Desert Dunes: the native vegetation of New South
762   Wales and the ACT. Hurstville, N.S.W.: Dept. of Environment and Conservation,
763   Australia. 353pp.

764 Khanna, P.K., Raison, R.J., 1986. Effect of fire intensity on solution chemistry of surface
765   soil under a *Eucalyptus pauciflora* forest. *Australian Journal of Soil Research,* 24,
766   426–434.

767 Khanna, P.K., Raison, R.J., Falkiner, R.A., 1994. Chemical properties of ash derived
768   from Eucalyptus litter and its effects on forests soils. *Forest Ecology and*
769   *Management,* 66, 107–125.

770 Khanna, P.K., Ludwin, B., Raison, R.J., 1996. Comparing modelled and observed effects
771   of ash additions on chemistry of a highly acid soil. *Australian Journal of Soil*
772   *Research,* 34, 999–1013.

773 Lasanta, A., Cerdà, A., 2005. Long-term erosional responses after fire in the Central
774   Spanish Pyrenees: 2. Solute release. *Catena*, 60, 80-101.

775 León, J., Bodí, M.B., Cerdà, A., Badía, C., 2013. The contrasted response of ash to
776   wetting. The effects of ash type, thickness and rainfall events. *Geoderma,* 209–
777   210, 143–152.

778 Malvar, M.C., Prats, S.A., Nunes, J.P., Keizer, J.J., 2011. Post-fire overland flow
779   generation and inter-rill erosion under simulated rainfall in two eucalypt stands in
780   north-central Portugal. *Environmental Research,* 111, 222–236.

781 Moody, J.A., Shakesby, R.A., Robichaud, P.R., Cannon, S.H., Martin, D.A., 2013.
782   Current research issues related to post-wildfire runoff and erosion processes.
783   *Earth-Science Reviews,* 122, 10–37.

784   Murphy, J. 2014. Hall Road Fire *Bushfire Bulletin* 30, 27-29.

785   Pan,S-Y,   Chang,E.E.,   Chiang, P.C., 2012. CO_2 Capture by accelerated carbonation
786   of alkaline wastes: A review on its principles and applications. *Aerosol and Air*
787   *Quality Research*, 12, 770–791.

788   Pereira, P., Úbeda, X., Martin, D., Mataix-Solera, J., Guerrero, C., 2011. Effects of a low
789   severity prescribed fire on water-soluble elements in ash from a cork oak
790   (*Quercus suber*) forest located in the northeast of the Iberian Peninsula.
791   *Environmental Research,* 111, 237–247.

792   Pereira, P., Úbeda, X., Martin, D.A., 2012. Fire severity effects on ash chemical
793   composition and water-extractable elements. *Geoderma,* 191, 105–114.

794   Pereira, P., Cerdá, A., Úbeda, X., Mataix-Solera, J., Martin, D., Jordan, A., Burguet, M.
795   2013. Spatial models for monitoring the spatio-temporal evolution of ashes after
796   fire – a case study of a burnt grassland in Lithuania. *Solid Earth*, 4, 153–
797   165.Pereira, P., Úbeda, X., Martin, D.A., Mataix-Solera, J., Cerdà, A., Burguet,
798   M., 2014. Wildfire effects on extractable elements in ash from a Pinus pinaster
799   forest in Portugal. *Hydrological Processes,* 28, 3681–3690.

800   Pereira, P., Cerdà, A., Úbeda, X.,Mataix-Solera, J., Arcenegui, V., Zavala, L.M., 2015.
801   Modelling the impacts of wildfire on ash thickness in a short-term period. *Land*
802   *Degradation and Development*, 26, 180-192.

803   Plumlee, G.S., Martin, D.A., Hoefen, T., et al., 2007. Preliminary analytical results for ash
804   and burned soils from the October 2007 Southern California Wildfires. US
805   Geological Survey Open-File Report 2007-1407. Reston, VA: US Geological
806   Survey. http://pubs.usgs.gov/of/2007/1407 (accessed 01/05/2014).

807   Plumlee, G.S., Morman, S.A., Hoefen, T.M., Meeker, G.P., Wolf, R.E., Hageman, P.L.,
808   2014. The environmental and medical geochemistry of potentially hazardous
809   materials produced by disasters: *Treatise on Geochemistry*, 9, 257-304.

810   Raison, R.J., Khanna, P.K., Woods, P.V., 1985. Mechanisms of element transfer to the
811   atmosphere during vegetation fires. *Canadian Journal of Forest Research,* 15,
812   132-139.

813   Robichaud, P.R, Hakjun, R., Lewis, S.A., 2014. A synthesis of post-fire Burned Area
814   Reports from 1972 to 2009 for western US Forest Service lands: trends in wildfire
815   characteristics and post-fire stabilisation treatments and expenditures.
816   *International Journal of Wildland Fire*, 23, 929-944.

817   Salomons, W., Förstner, U., 1984. *Metals in the Hydrocycle*. Springer-Verlag. 349 pp.

818   Santín, C., Doerr, S.H., Shakesby, R.A., Bryant, R., Sheridan, G.J., Lane, P.N.J., Smith,
819   H.G., Bell, T.L., 2012. Carbon forms and sequestration potential within ash
820   deposits from forest fires: new insights from the 2009 'Black Saturday' fires,
821   Australia. *European Journal of Forest Research*, 131(4), 1245-1253.

822   Santos, A., Ajbary, M., Morales-Florez, V., Kherbeche, A., Piñero M., Esquivias, L., 2009.
823   Larnite powders and larnite/silica aerogel composites as effective agents for CO_2
824   sequestration by carbonation. *Journal of Hazardous Materials,* 168, 1397–1403.

825   Schäfer, R.F., Hearn, L., Kefford, B.J., Mueller, J.F., Nugegoda, D., 2010. Using silicone
826   passive samplers to detect polycyclic aromatic hydrocarbons from wildfires in
827   streams and potential acute effects for invertebrate communities. *Water*
828   *Research*, 44, 4590-4600.

829   Shakesby, R.A., Doerr, S.H., 2006. Wildfire as a hydrological and geomorphological
830   agent. *Earth-Science Reviews*, 74, 269-307.

831   Shakesby, R.A., Wallbrink, P.J., Doerr, S.H., English, P.M., Chafer, C., Humphreys,
832   G.S., Blake, W.H., Tomkins K.M., 2007. Distinctiveness of wildfire effects on soil
833   erosion in south-east Australian eucalypt forests assessed in a global context.
834   *Forest Ecology and Management*, 238, 347–364.

835   Smith, H.G., Sheridan G.J., Lane, P.N.J, Nyman, P., Haydon, S., 2011. Wildfire effects
836   on water quality in forest catchments: a review with implications for water supply.
837   *Journal of Hydrology,* 396, 170-192.

838   Spencer, C.N., Gabel, K.O., Hauer, F.R., 2003. Wildfire effects on stream food webs and
839   nutrient dynamics in Glacier National Park, USA. *Forest Ecology and*
840   *Management,* 178, 141–153.

841   Úbeda, X., Pereira, P., Outeiro, L., Martin, D.A., 2009. Effects of fire temperature on the
842   physical and chemical characteristics of the ash from two plots of cork oak
843   (*Quercus suber*). *Land Degradation and Development,* 20, 589–608.

844   Vergnoux, A., Malleret, L., Asia, L., Doumenq, P., Theraulaz, F., 2011. Impact of forest
845   fires on PAH level and distribution in soils. *Environmental Research,* 111, 193–
846   198.

847   Wagenbrenner, J.W., MacDonald, L.H., Coats, R.N., Robichaud, P.R., Brown, R.E.
848   (2015) Effects of post-fire salvage logging and a skid trail treatment on ground
849   cover, soils, and sediment production in the interior western United States. *Forest*
850   *Ecology and Management*, 335, 176-193.

851   Wetzel, R.G., 2001. Limnology. Lake and river ecosystems. Academic Press. 3th edition.

852   1006 pp.

853   Woods, S.W., Balfour, V., 2008. The effect of ash on runoff and erosion after a forest

854   wildfire, Montana, U.S.A. *International Journal of Wildland Fire,* 17, 535–548.

855   Young, R.W., 1980. Soils of the Illawarra region, Wollongong Studies in Geography

856   No.10, Department of Geography, University of Wollongong, 4pp.

857

859   Table 1. Mean concentrations (± standard error of mean) of main elements in ash.

860   Number of samples = 9 for each fire severity class. Note different units for different

861   elements.

	Fire Severity Class					
	Low		High		Extreme	
B (mg kg^{-1})	2.9 ±	0.3 ^{a}	3.4 ±	0.2 ^{ab}	4.1 ±	0.3 ^{b}
C (g kg^{-1})	247.3 ±	39.5 ^{a}	155.8 ±	18.0 ^{b}	162.0 ±	3.0 ^{b}
Ca (mg kg^{-1})	3621.4 ±	372.8 ^{a}	2775.6 ±	288.2 ^{ab}	2294.9 ±	113.1 ^{b}
Cu (mg kg^{-1})	6.3 ±	0.4 ^{a}	5.1 ±	0.3 ^{b}	5.3 ±	0.2 ^{b}
K (mg kg^{-1})	1063.8 ±	73.2 ^{a}	1243.9 ±	72.4 ^{a}	1532.6 ±	83.9 ^{b}
Mg (mg kg^{-1})	896.0 ±	81.1 ^{a}	809.3 ±	69.2 ^{a}	905.3 ±	35.6 ^{a}
N (g kg^{-1})	3.9 ±	0.5 ^{a}	3.2 ±	0.3 ^{a}	3.0 ±	0.3 ^{a}
Na (mg kg^{-1})	119.4 ±	7.9 ^{a}	118.6 ±	8.2 ^{a}	141.9 ±	6.0 ^{b}
P (mg kg^{-1})	140.0 ±	9.5 ^{a}	136.5 ±	7.1 ^{a}	153.7 ±	4.5 ^{a}
Al (g kg^{-1})	20.7 ±	1.7 ^{a}	32.1 ±	2.3 ^{b}	39.5 ±	2.4 ^{c}
Fe (g kg^{-1})	24.7 ±	4.0 ^{ab}	18.0 ±	2.1 ^{a}	39.5 ±	8.0 ^{b}
Si (g kg^{-1})	2.1 ±	0.0 ^{a}	2.1 ±	0.0 ^{a}	2.3 ±	0.0 ^{b}
As (mg kg^{-1})	5.1 ±	0.7 ^{ab}	4.0 ±	0.3 ^{a}	7.3 ±	0.8 ^{b}
Cd (ug kg^{-1})	88.3 ±	5.7 ^{a}	79.6 ±	6.6 ^{a}	82.5 ±	7.0 ^{a}
Hg (ug kg^{-1})	1.7 ±	0.9 ^{a}	1.8 ±	0.8 ^{a}	4.2 ±	1.1 ^{a}
Pb (mg kg^{-1})	10.7 ±	1.0 ^{a}	12.6 ±	0.7 ^{a}	21.4 ±	2.2 ^{b}

Different superscript letters indicate groups with significantly different means for each
element (more details Section 2.4); n.d. not determined.

862

863 Table 2. Mean values (± standard error of mean) of pH, EC and concentrations of water-extractable elements
864 each fire severity class. Note different units for different elements.

	Unburnt control site		Burnt sites			
			Subsurface soils			
	Litter layer	Surface soil organic layer	Unburnt	Low fire severity	High fire severity	Extreme fire severity
pH	n.d	5.3 ±0.2	5.5± 0.1[a]	5.3± 0.1[a]	5.2± 0.2 [a]	5.2± 0.2[a]
E.C. (μS cm^{-1})	n.d	29.1 ±3.6	14.4± 2.8[a]	17.2± 1.7[a]	22.1± 8.1 [a]	28.6± 11.3[a]
B (mg kg^{-1})	6.0 ±0.3	1.0 ±0.2	0.8± 0.1[a]	0.6± 0.4[a]	1.0± 0.2 [a]	1.3± 0.1[a]
C (g kg^{-1})	n.d	102.3 ±7.8	40.2± 2.0[a]	38.1± 4.4[a]	38.6± 2.4 [a]	50.0± 4.6[a]
Ca (mg kg^{-1})	4.8 ±0.3	913.3 ±102.1	324.3± 11.4[a]	470.6± 235.9[a]	371.6± 67.4 [a]	421.7± 103.2[a]
Cu (mg kg^{-1})	4.3 ±0.3	2.6 ±0.2	1.9± 0.2[a]	2.4± 1.0[a]	1.7± 0.3 [a]	1.2± 0.1[a]
K (mg kg^{-1})	489.9 ±13.5	688.1 ±81.0	590.6± 59.6[a]	640.1± 199.7[a]	541.4± 30.6 [a]	631.9± 68.7[a]
Mg (mg kg^{-1})	931.8 ±17.3	452.0 ±22.1	358.9± 35.1[a]	365.2± 92.3[a]	388.9± 54.1 [a]	444.8± 29.5[a]
N (g kg^{-1})	n.d	1.5 ±0.2	0.7± 0.1[a]	0.6± 0.1[a]	0.6± 0.0 [a]	0.6± 0.1[a]
Na (mg kg^{-1})	209.7 ±6.4	58.3 ±4.1	50.2± 12.8[a]	35.3± 10.2[a]	39.6± 5.9 [a]	39.3± 3.2[a]
P (mg kg^{-1})	0.1 ±0.0	65.6 ±3.4	46.2± 3.1[a]	47.1± 12.7[a]	48.4± 8.2 [a]	66.0± 16.5[a]
Al (g kg^{-1})	0.6 ±0.1	26.1 ±1.0	29.9± 4.7[ab]	25.3± 5.3[a]	45.4± 4.7 [c]	40.0± 4.2[bc]
Fe (g kg^{-1})	0.3 ±0.1	49.9 ±8.4	29.8± 3.6[a]	19.8± 1.1[b]	14.8± 2.6 [b]	17.8± 2.3[b]
Si (g kg^{-1})	0.9 ±0.0	2.1 ±0.0	1.7± 0.2[a]	1.8± 0.2[a]	1.9± 0.2 [a]	2.1± 0.3[b]
As (mg kg^{-1})	0.1 ±0.0	5.3 ±0.8	5.1± 0.7[a]	3.9± 0.3[a]	3.8± 0.2 [a]	4.2± 1.4[a]
Cd (ug kg^{-1})	102.1 ±4.3	55.5 ±6.1	31.0± 3.2[a]	23.2± 4.4[a]	32.5± 2.6 [a]	25.1± 4.2[a]
Hg (ug kg^{-1})	72.6 ±5.6	7.9 ±1.4	5.4± 2.1[a]	5.8± 2.4[a]	6.7± 1.4 [a]	6.9± 1.8[a]
Pb (mg kg^{-1})	0.6 ±0.1	13.1 ±1.0	12.9± 1.9[a]	10.5± 2.1[a]	14.2± 3.6 [a]	13.5± 2.6[a]

For subsurface soils significantly different means are indicated by different superscirpt letters (more details Section 2.4). Note the litter and the surface soil organic layer from the unburnt site are not included in this statistical analysis.

865

866 Table 3. Mean values (± standard error of mean) of pH, EC and main elements

867 concentrations in subsurface soils (3-8 cm depth). Number of samples = 9 for each fire

868 severity class and = 3 for the unburnt control. For the unburnt control site, values for

869 the litter layer (n = 3) and the organic-rich surface soil layer (n =9) are also reported.

870 Note different units for different elements.

	Fire Severity Class					
	Low		High		Extreme	
pH	6.4 ±	0.2 [a]	6.1 ±	0.1 [a]	6.2 ±	0.2 [a]
E.C. (µS cm^{-1})	56.4 ±	5.5 [a]	51.9 ±	6.4 [a]	43.3 ±	4.1 [a]
F^{-} (mg kg^{-1})	0.9 ±	0.0 [a]	0.8 ±	0.0 [a]	0.8 ±	0.0 [a]
PO$_4^{3-}$ (mg kg^{-1})	17.8 ±	3.4 [a]	7.0 ±	1.7 [b]	2.0 ±	0.1 [b]
NH4+(mg kg^{-1})	<LoD		<LoD		9.9 ±	1.9
B (ug kg^{-1})	357.7 ±	28.8 [a]	315.6 ±	52.0 [ab]	221.0 ±	23.2 [b]
Ca (mg kg^{-1})	65.7 ±	14.3 [a]	44.5 ±	7.8 [ab]	27.2 ±	3.8 [b]
Cu (ug kg^{-1})	72.2 ±	11.3 [a]	43.1 ±	5.9 [b]	20.2 ±	2.9 [c]
K (mg kg^{-1})	93.9 ±	7.2 [a]	115.2 ±	18.6 [ab]	68.4 ±	3.8 [b]
Mg (mg kg^{-1})	49.8 ±	6.1 [a]	35.3 ±	5.1 [b]	19.5 ±	2.0 [c]
Na (mg kg^{-1})	58.9 ±	4.3 [a]	48.1 ±	4.1 [b]	41.3 ±	2.1 [b]
Al (mg kg^{-1})	<LoD		<LoD		<LoD	
Fe (mg kg^{-1})	2.3 ±	0.7 [a]	5.8 ±	1.0 [a]	1.6 ±	0.4 [a]
Si (mg kg^{-1})	<LoD		<LoD		<LoD	
As (ug kg^{-1})	13.7 ±	1.0 [a]	14.5 ±	0.8 [a]	18.2 ±	1.1 [b]
Cd (ug kg^{-1})	0.0 ±	0.0 [a]	0.0 ±	0.0 [a]	0.0 ±	0.0 [a]
Hg (ug kg^{-1})	0.5 ±	0.0 [a]	0.6 ±	0.0 [a]	0.6 ±	0.0 [a]
Pb (ug kg^{-1})	8.9 ±	0.8 [a]	13.7 ±	1.8 [a]	3.3 ±	0.4 [b]

Different superscript letters indicate groups with significantly different means for
each parameter/element (more details Section 2.4); <LoD below limit of
detection (2 mg kg^{-1} for NH^{4+} and Fe; 10 mg kg^{-1} for Al; 20 mg kg^{-1} for Si)

871

872   Table 4. Maximum water contamination potential (total amounts, in Mg) from elements

873   contained in wildfire ash for the five sub-catchments affected by the Balmoral wildfire

874   (October 2013).

|	West lake Nepean	Nepean River	Avon River	Cordeaux River	Wollondoola Creek
B	0.1	0.1	0.1	0.2	0.2
C	4686.6	3843.3	7101.3	11356.6	8683.0
Ca	75.2	62.0	114.0	182.5	143.9
Cu	0.1	0.1	0.2	0.3	0.3
K	35.0	29.3	53.7	76.6	61.7
Mg	22.4	18.7	34.4	51.2	40.8
N	86.1	71.1	131.1	205.0	162.1
Na	3.3	2.8	5.1	7.4	5.9
P	3.7	3.1	5.7	8.4	6.8
Al	902.2	748.9	1371.1	1939.9	1573.7
Fe	734.9	634.0	1135.5	1486.1	1128.7
Si	56.2	47.0	86.3	127.3	102.7
As	0.1	0.1	0.2	0.3	0.2
Cd	0.0	0.0	0.0	0.0	0.0
Hg	0.0	0.0	0.0	0.0	0.0
Pb	0.4	0.4	0.6	0.8	0.7

875

876 Table 5. Maximum water contamination potential (in kg) from wildfire ash leaching for

877 the five sub-catchments affected by the Balmoral wildfire (October 2013).

	West lake Nepean	Nepean River	Avon River	Cordeaux River	Wollondoola Creek
F^-	21.5	17.8	32.9	50.1	39.9
PO_4^{3-}	231.9	185.7	339.7	640.7	468.2
NH_4^+	n.d	n.d	n.d	n.d	n.d
B	8.0	6.7	12.2	19.5	15.7
Ca	1219.8	1000.7	1831.1	3074.3	2401.9
Cu	1.2	1.0	1.8	3.2	2.4
K	2778.3	2292.2	4177.5	6624.8	5470.8
Mg	942.8	774.8	1414.5	2378.9	1873.0
Na	1283.1	1060.1	1950.1	3079.0	2444.1
Al	n.d	n.d	n.d	n.d	n.d
Fe	132.1	106.7	192.6	316.4	268.3
Si	n.d	n.d	n.d	n.d	n.d
As	0.4	0.3	0.6	0.9	0.7
Cd	0.0	0.0	0.0	0.0	0.0
Hg	0.0	0.0	0.0	0.0	0.0
Pb	0.3	0.2	0.4	0.7	0.6

n.d. not determined (concentrations of these elements in the analyzed samples were below limit of detection, see Table 3).

878

Figures

880

881
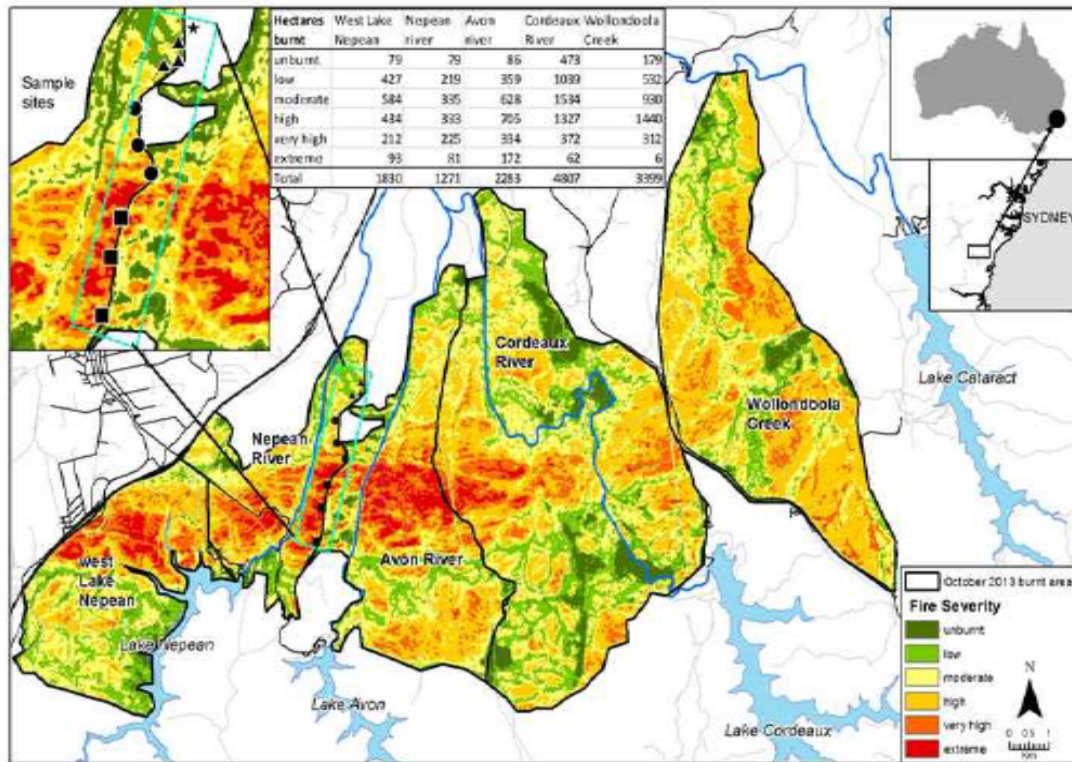
Fig.1. Location map of the study area burnt by the Balmoral wildfire (October 2013,

Sydney, Australia) with the fire severity classification according to Chafer (2008). Left

top: Close up of the sampling area and location of the sampling sites at extreme

(squares), high (circles) and low (triangles) fire severities, and the unburnt control

(star). Note the limits and names of the five sub-catchments within the burnt area, and

the table with the number of hectares burnt in each sub-catchment.

888
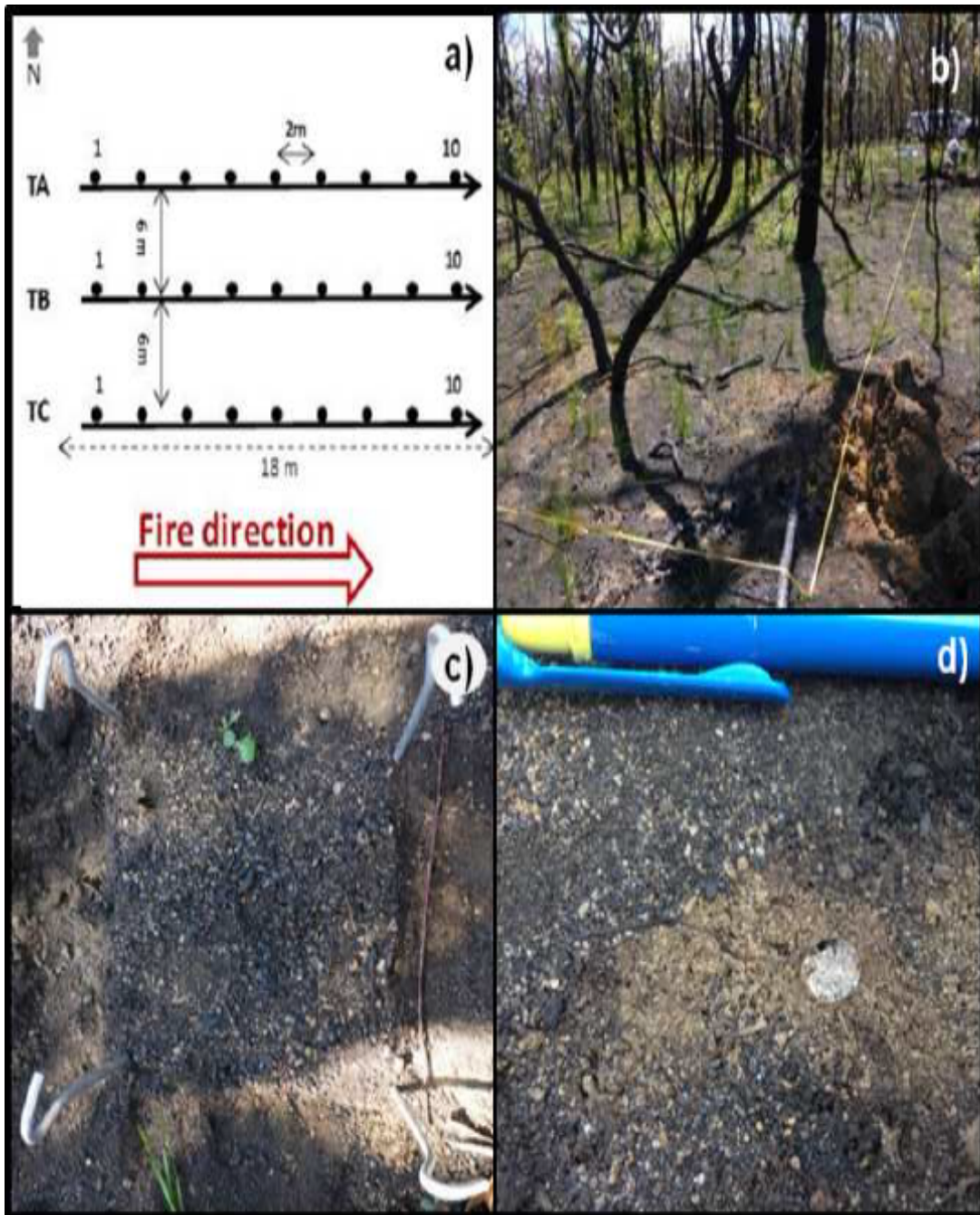
Fig. 2. Sampling design: a) schematic of the sampling grid with sampling points at each burnt site; b) sampling at Extreme Severity Site 1; c) exposed ash sample prior to collection at a sampling point; d) a water droplet resisting infiltration into the water repellent soil below the ash layer.
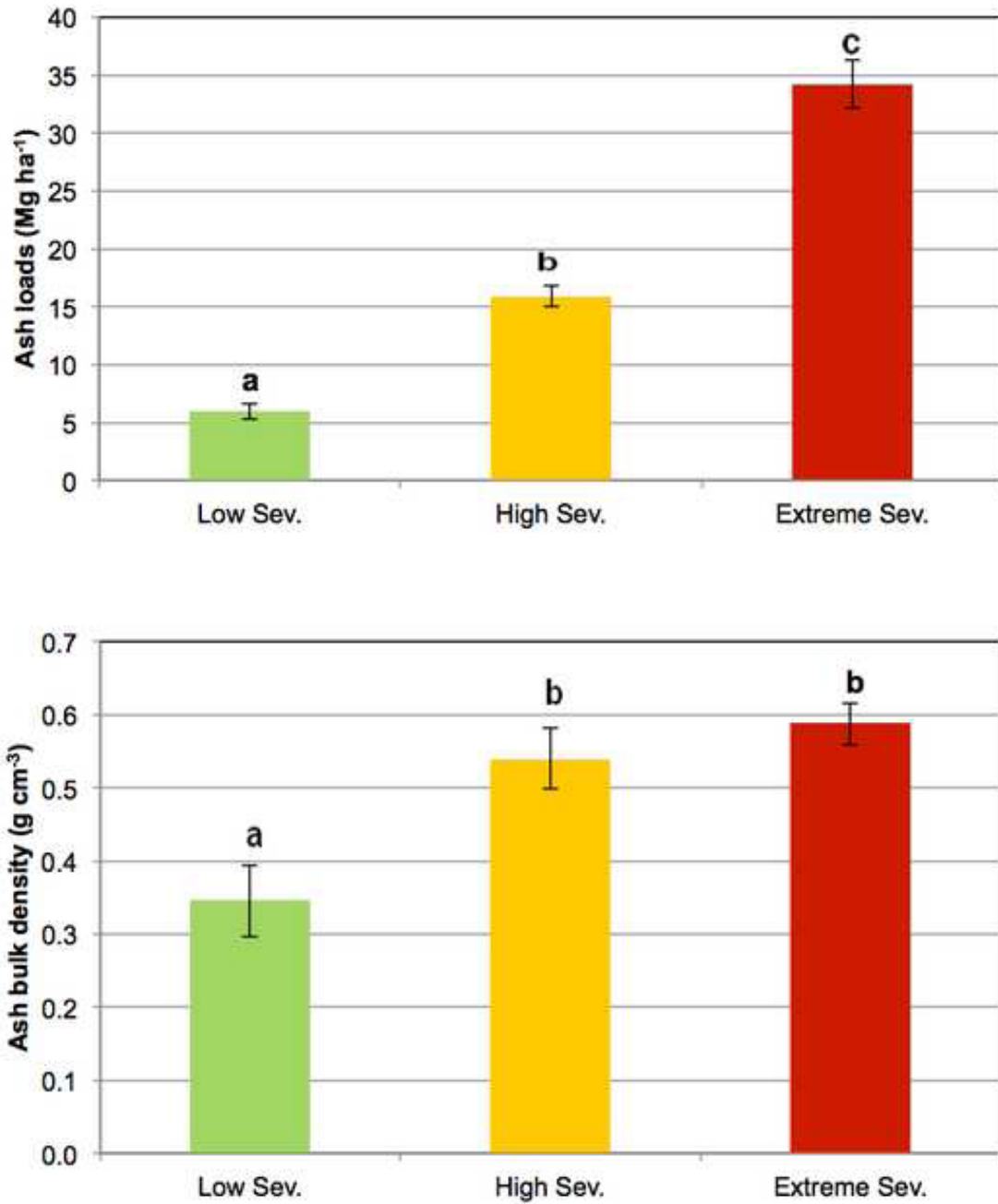
896

897   Fig. 3. Average ash loads (top; Mg ha^{-1}) and ash bulk density (bottom; g cm^{-3}) for the

898   three fire severity classes studied. Error bars represent standard error of the mean.

899   Letters indicate classes with means significantly different ((more details Section 2.4).

900   For each fire severity class n = 90 for ash loads, and n = 12 for ash bulk density.
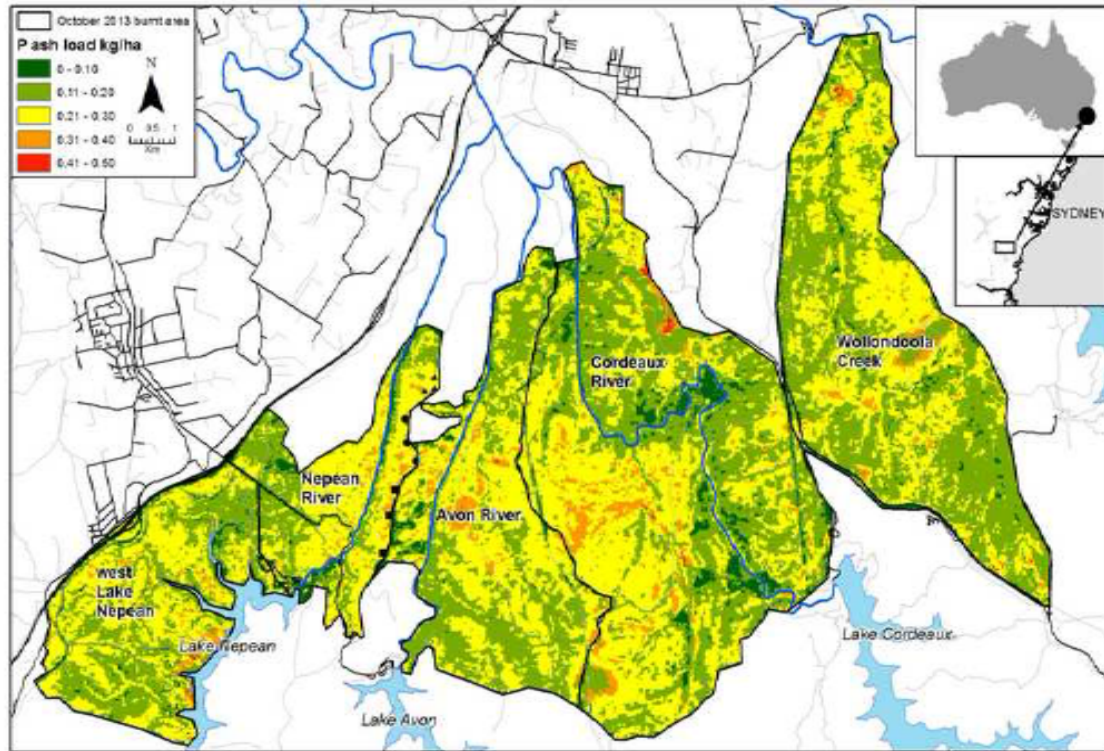
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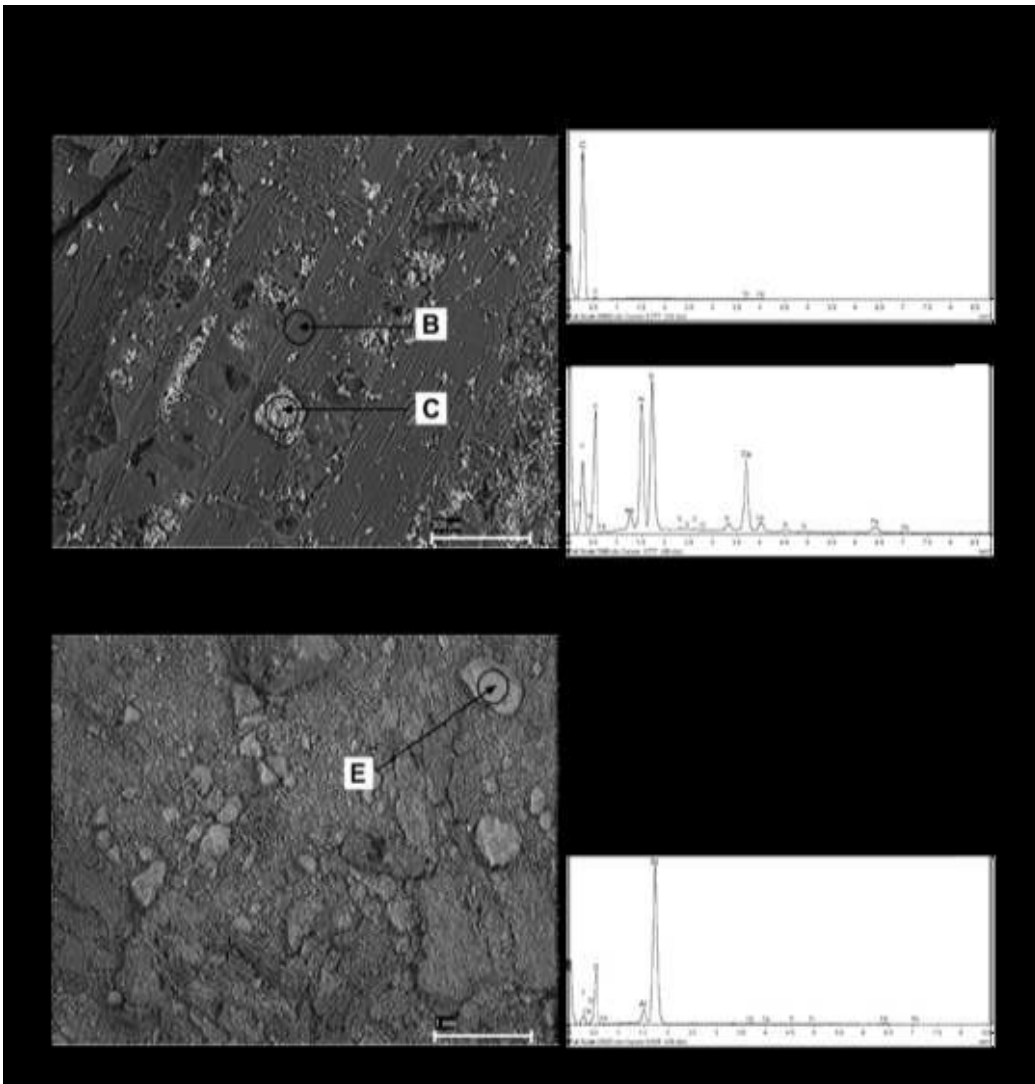
Fig. 4. SEM-EDS imagery of wildfire ash: A) Ash sample with both organic (B) and
inorganic (C) components. D) Ash sample with notable contribution of inorganic (silica)
complexes (E). (B), (C) and (E) Energy dispersive spectra showing the element
distribution in several ash components.

910

911

912   Fig. 5. Estimated loads (kg ha^{-1}) of total phosphorous (P) in ash generated by the

913   Balmoral wildfire for the whole area burnt by the fire (Note the limits and names of the

914   five sub-catchments within the burnt area).