Effects of wildfire on mercury mobilisation in eucalypt and pine forests

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Abstract

Wildfires and subsequent rainfall play an important role in the redistribution of major, minor and trace chemical elements, which could be mobilised from burnt soils and ashes. In particular, the fire-induced release of mercury (Hg) into the environment is relevant to study due to its volatilisation and toxicity. However, the impact of wildfire followed by rainfall on mercury redistribution is poorly documented. Hence, eucalypt- and pine-covered hillslopes (1-3) were surveyed in two burnt areas (Ermida and S. Pedro do Sul, Portugal), as well as in a non-burnt eucalypt slope (Ermida). Top-soils (0-2 cm) and ashes were sampled 4 and 14 weeks after the fire, the latter following an episode of heavy precipitation. In order to clarify the effect of temperature on Hg release from the soil, a heating experiment was also conducted. Results revealed that 30% of the Hg retained in eucalypt soils was released by the fire, corresponding to a loss of 1.0-1.1 g Hg ha⁻¹ of burnt soil. Levels in burnt eucalypt soils were twice the values registered in burnt pine soils for both fire severities. Mercury in ashes pointed to similar trend between the two types of vegetation. Results from the heating experiment with soil suggest that temperature reached in the wildfire was insufficient to destroy the most stable bonds of Hg-ligands. Mercury concentrations were not correlated with organic matter content, both in soils and ashes. It was estimated that rainfall caused a loss of 1.0 g Hg ha⁻¹ from ashes and an uptake of 0.5 g Hg ha⁻¹ of soil washed out. The difference between the previous estimations, 0.5 g Hg ha⁻¹, corresponds to the quantity of Hg transported to the surrounding area or eventually introduced into aquatic systems. Hence, the results obtained in the present study highlight the importance of wildfire and subsequent rainfall in the mobilisation of Hg in the environment.

Keywords: Wildfire; Mercury pathway; Runoff; Portugal

1. Introduction

Forest ecosystems undergo recurrent wildfires with serious impacts resulting from the destruction of vegetation coverage and severe changes in the properties of soil surface layers (e.g. Cerdà and Lasanta, 2005; Verma et al., 2012; Rubenacker et al., 2012). It is well known that the magnitude of these changes depends mainly on the nature of the soil, type and biomass of the vegetation coverage, fire severity, ash production, and post-fire climate conditions such as timing and intensity of precipitation events (e.g. Ulery et al., 1993, Neary et al., 1999; Certini, 2005; Maia et al., 2012; Verma et al., 2012). Wildfire can have profound effects on the functioning of the soil system (physical, chemical and biological elements), which can affect the sustained productivity and soil recovery of the burnt area (Certini, 2005; Doerr and Cerdà, 2005; Terefe et al., 2008; Robichaud, 2009; Verma et al., 2012, Guénon et al., 2013). Both the direct effects of fire and also the overall changes to the ecosystem encountered in post-fire situation can lead to short-, medium- and long-term changes in the soil. One of the most intuitive and important soil change, during burning is the alteration of organic matter content (Certini, 2005). Organic matter (LOI) is a key factor for forest soil since it has a direct and/or indirect influences on the physical, chemical and biological characteristics of the soil. Fire affects soil organic matter both quantitatively and qualitatively and its changes may range from its almost total destruction to increased contents in surface layers due to external inputs, as partly charred litter and leaves, forest necromass and residual ash (González-Pérez et al., 2004; Knicker et al., 2005; Certini, 2005; Mataix-Solera et al., 2011). Among the effects of wildfires, it is important to recognize and underline its impact on the chemical availability of trace elements and pathways (Navrátil et al., 2009; Jakubus et al., 2010; Aref et al., 2011). In fact, wildfires can release and deposited metals on soil surface, either directly by combustion of vegetation and soil organic matter mineralization and leaching from ashes-soil interactions (Ulery et al., 1993; Antilén et al., 2006; Jakubus et al., 2010; Pereira and Úbeda 2010). Although ash produced by forest fires is a very heterogeneous material

(depending strongly on plant species, type and part burnt, and combustion completeness), it primarily consists of oxides and hydroxides of base cations such as calcium, magnesium and potassium, but also includes trace metals (Ulery et al., 1993; Pereira et al., 2011a; Bodi et al., 2014). These compounds can be transported by overland flow and leached into the soil profile, and may have impacts on surface and groundwater chemical composition (Reneau et al., 2007; Cerdà and Doerr, 2008; Smith et al., 2011). Research studies on ash resulting from wildfires have been mainly focused on soil erosion, physical and hydrological properties of the ash (e.g. Doerr and Cerdà, 2005; Quintana et al., 2007; Cerdà and Doerr, 2008; Balfour and Woods, 2013; Gabet and Kookter, 2011; Pereira et al., 2015). The chemical composition of wildfire ash has received comparatively little research attention (Ulery et al., 1993; Pereira et al., 2011b, 2012; Santín et al., 2012), especially in what concerns its trace metals constituents (Engle et al., 2006; Pereira and Úbeda, 2010; Pereira et al., 2011a).

The toxic element mercury (Hg) is of particular concern due to its volatility, toxicity, persistence and the relevance of the atmospheric compartment in the global Hg cycle (Cheng and Schroeder, 2000; Huang et al., 2011), showing potentially harmful impact on the environment and on human health (Alloway, 1995; Cheng and Schroeder, 2000, Huang et al., 2011). Water, soil and vegetation take up Hg species following wet and dry deposition, being the uptake by vegetation an important pathway by which metals enters the food chain (Friedli et al., 2001; Roy and McDonald, 2013). Once deposited, Hg may undergo methylation by biological processes into the highly toxic methyl mercury, a potent neurotoxin with a strong tendency to bioaccumulated and then biomagnified within the food chain (Boening et al., 2000; Caldwell et al., 2000; Gnamus et al., 2000; Amirbahman et al., 2004). Various studies have quantified anthropogenic emissions of Hg (e.g. Pacyna et al., 2003; Pacyna and Pacyna, 2002). However, natural emissions, particularly associated with wildfires that have been accounted as one of the important Hg non-point sources, are less well documented (Sigler et al., 2003; Biswas et al., 2008; Navrátil et al., 2009; Wiedinmeyer and Friedli, 2007). Forest soils

accumulate Hg that is strongly sorbed to organic matter (Schwesig and Matzner, 2000; Biester et al., 2002; Grigal, 2003). The behaviour of Hg in soils is very complex and is mainly controlled by adsorption and desorption process, involving several chemical, physical and biological process (Reis et al., 2015). Its environmental and toxicological effects are however, highly dependent on Hg forms, as different species interact differently with soil constituents, exhibiting different behaviour, solubility, mobility and bioavailability (Biester et al., 2002; Bollen et al., 2008). Therefore, the identification of mercury species in soils contributes to understand the Hg behaviour and fate in the environment and its toxicity (Biester and Scholz, 1997; Rumayor et al., 2013). Methods based on species release from the matrix according to their desorption temperatures have been used to determine the speciation of Hg species in solid samples, including thermo-desorption (Biester et al., 2002; Rumayor et al., 2013, 2015; Reis et al., 2012, 2015).

During wildfires, Hg stored in vegetation, organic litter and soil tends to be associated with organic-rich ash and is released to the atmosphere predominantly in the form of gaseous elemental form (Hg^0), with up to 15% in the form of particulate mercury. Mercury released from fires can have local, regional and global impacts, since Hg^0 can be readily transported significant distances from the original source, whereas particulate Hg is likely to be deposited locally (Friedli et al., 2003a, 2003b; Sigler et al., 2003; Wiedinmeyer et al., 2007). The amount of Hg released during a wildfire is limited by Hg accumulation in the ecosystem, particularly in the soil, prior to burning (Biswas et al., 2007, 2008). Large Hg losses result from the low volatilization temperatures (100-300°C) of Hg species. For example, during some wildfires, elevated soil temperatures are sufficient to decompose Hg-humic acid bond (200-330°C; Biester and Scholz, 1997). Experimental burns performed on soils showed a 79% decrease in Hg content after burning (Mailman and Bodaly, 2005). Recent studies have reported Hg release from soils burned during both prescribe fires (Woodruff et al., 2001; Harden et al., 2004; Engle

et al., 2006) and wildfires (Biswas et al., 2007, 2008; Engle et al., 2006; Navrátil et al., 2009; Burke et al., 2010).

Fires, partitioning of Hg in soil and biomass, influence Hg pathways (Biswas et al., 2007, 2008; Witt et al., 2009). Additionally, runoff and wind can mobilise Hg bound to eroded soil, litter and ash particles, leading eventually to the transport of Hg to aquatic systems (Caldwell et al., 2000; Amirbahman et al., 2004). Engle et al. (2006) measured higher concentrations of Hg in surface ash one year following both wildfire and prescribed burns, and suggested that it was related to sorption of atmospheric Hg over the subsequent year, reflecting Hg's affinity for carbon in ash. However, very few studies have reported such effects on Hg pathways in burnt soils and ashes. Therefore, there is a need to better understand the terrestrial Hg cycle and, in particular, to investigate wildfires as a potential non-point source of Hg. Understanding this is important to predict the fate of atmospherically derived Hg in terrestrial ecosystems with important implications for the loading of Hg to water bodies (Obrist et al., 2009), which is reinforced by the knowledge about solute released due to the runoff and erosion, after wildfires (Lasanta and Cerdà, 2005).

Hence, this work aims to: (a) clarify the effect of a wildfire on mercury mobilisation from soils and ashes; (b) assess the influence of rainfall on the mercury pathway; and (c) evaluate the differences in Hg concentrations in soils and ashes between two vegetation types. For this purpose, soil and ashes were surveyed from eucalypt and pine forests burnt at different severities, as well as from a non-burnt eucalypt stand. Furthermore, in order to clarify the effect of temperature on Hg release a thermo-desorption assay of Hg from soils was performed in the laboratory.

2. Material and Methods

2.1. Characteristics of the study areas

Two recently burnt areas located in north-central Portugal: Ermida (E) (40° 43' 33" N, 8° 20' 60" W, 170 m a.s.l., Aveiro district); and S. Pedro do Sul (S) (40° 45' 35" N, 8° 10' 04" W, 370 m a.s.l., Viseu district) (Figure 1) were selected to conduct the present study. The wildfires destroyed 295 ha in Ermida (26th July 2010) and 5,066 ha in S. Pedro do Sul (6th August 2010) (DUDF, 2011). The burnt areas were predominantly covered by eucalypt (*Eucalyptus globulus* Labill.) and maritime pine (*Pinus pinaster* Ait.) plantations. The mean annual temperature varies within similar ranges, 12-19 °C and 13-15 °C, at E and S, respectively. Both areas are characterised by a humid meso-thermal climate, with wet winters and prolonged dry and warm summers (Köppen Csb; DRA, 2002). Over the past 30 years, the annual rainfall at E and S ranged from 960 to 2531 mm and 523 and 1757 mm, respectively (SNIRH, 2013). The soils of the two study areas are mapped as humic Cambisols and, to a lesser extent, Leptosols or Luvisols, developed over granite, mainly for S. Pedro do Sul, and schist, mainly for Ermida (Cardoso et al., 1971).

Fire severity was assessed according to the methodology described in Shakesby and Doerr (2006), Keizer et al. (2008) and Keeley (2009). Hence, fire severity assessment was based on the degree of consumption of the canopies of 10 randomly selected trees as well as of the litter layer (partial or total), and on ash colour (black, grey and/or white), which was classified by visual inspection. The ash samples were ranked by shade (from dark to light) by comparing the samples with each other, without using the standard of greyness for comparison (Stronach and McNaughton, 1989; Parsons et al., 2010). The fire severity at each slope was determined at 5 points along a transect (Figure 1). In Ermida, the fire consumed the tree canopies only partially but the litter layer entirely, and produced black ashes; in S. Pedro do Sul, the fire totally consumed both the tree canopies and, the litter layer, and produced grey-white ashes. On the basis of these observations, fire severity was classified as moderate in the case of Ermida and as moderate to high severity in the case of S. Pedro do Sul.

2.2. Sampling design

Three hillslopes were selected in Ermida (E), both in eucalypt (BE) and pine (BP) burnt stands: E-BE1, E-BE2, E-BE3; and E-BP1, E-BP2, E-BP3 (Figure 1). The distance between slopes was around 50-m. A non-burnt eucalypt slope (E-NBE) was also selected in an adjacent area. Three burnt pine slopes were sampled in S. Pedro do Sul (S) (S-BP1; S-BP2 and S-BP3) distancing around 50-m, as well as one burnt eucalypt slope (S-BE1). On each slope, one transect was laid out across the full length of the slope section. Five equidistant points were established from the top to the bottom of each slope to take into account ash and soil spatial heterogeneity (Figure 1). At each of the five points of the sampling transect, a grid was laid out and a plot of 50x60 cm was sampled for soil and ash. At each sampling plot the entire ash layer was collected with a brush and a spoon. Ash samples were carefully collected in order to avoid mixture with soil. After the removal of litter, gravel and stones, the upper 2-cm of soil was sampled. Upper soil layers were selected based on previous studies that documented the preferential retention of Hg associated with soil organic matter (Biswas et al., 2007; Navrátil et al., 2009). Ash and soil samples were stored in plastic bag without air retention and taken to the laboratory for analysis. In the laboratory, those samples were air-dried, homogenised and sieved (2-mm mesh). Samples were stored in plastic bags at -18 °C until further analysis.

Sampling at Ermida was performed at two occasions- 4 weeks after the fire (AF) and 14 weeks after the fire (ARF) - whereas sampling at S. Pedro do Sul was limited to a single occasion - 3 weeks after fire (AF). The AF samples in both areas did not reveal any signs of mobilization by overland flow. This agreed with the fact the first rainfall after the wildfires (as recorded by the network of rainfall gauges installed in the Ermida study area (Martins et al., 2013; Prats et al., 2014) between the first sampling in Ermida and in S. Pedro do Sul, and that it consisted of a small and low-intensity event (25 August 2010: $P = 4.3 \text{ mm}$; $I_{30} = 2.4 \text{ mm h}^{-1}$). By contrast, the second sampling in Ermida took place after a cumulative rainfall of 450 mm, with a maximum I_{30} of 30 mm h^{-1} . In total, 80 samples of ash and 90 samples of soils were analysed.

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210 **2.3. Heating experiment**

211 A heating experiment was performed in the laboratory to follow the thermo-desorption or
212 decomposition of Hg compounds (Biester et al., 2002; Lopez-Anton et al., 2010; Rumayor et al.,
213 2013, 2015; Reis et al., 2012, 2015) in non-burnt and burnt eucalypt soils from Ermida. Twelve
214 soil samples (approximately 10 g) of non-burnt and burnt eucalypt soils (Ermida) were placed
215 in a controlled-temperature muffle furnace and subjected to the following increasing
216 temperatures: 150 °C, 350 °C, 550 °C and 750 °C. These temperatures were chosen based on
217 previous studies mentioned above. Soil samples were maintained at each temperature for two
218 hours and thereafter three replicates were removed. Total Hg concentrations were
219 determined in all samples exposed to this sequence of temperatures.

220

221 **2.4. Analytical procedures**

222 Soil pH and electrical conductivity (EC) were measured in Milli-Q water suspension of soil (1:5
223 v/v for pH and 1:5 m/v for EC) according to the method described in ISO 10390 (2005) and ISO
224 11265 (1994), respectively. For pH determination, the suspension was mechanically shaken for
225 60 min, allowed to settle for 2 h and, after shaking the soil suspension again, the pH was
226 measured using a Metrohm 827 pH meter. For EC, the mixture was mechanically shaken for 30
227 min and filtered through a glass fiber filter (1.2 µm). Then, EC was measured in the filtrate with
228 a Chemtrix type 7 conductivity meter. The pH and EC of ash suspensions were determined by
229 mixing 6 g of ash with 36 ml of Milli-Q water, which was further mechanically shaken for 2 h
230 and finally filtered through a 0.45 µm microfiber filter (Pereira et al., 2011b). The pH and EC of
231 these suspensions were measured as previously described. Organic matter content (LOI) was
232 estimated by loss on ignition at 550 °C for 4 h (Botelho da Costa, 2004).

233 In order to assess aluminium (Al) concentrations in soils, approximately 500 mg of dry soil
234 samples (40 °C) were digested with HNO₃ (sp, 60% v/v) (95 °C for 2 h 45 min) in a DigiPrep

HotBlock – SCP Science, redissolved with H₂O₂ (sp, 30% v/v) and Milli-Q water and heated for 2 h at 95 °C. After cooling, the solution was diluted to 50 ml with Milli-Q water (USEPA 3050B, 1996) and Al was determined by atomic absorption spectrometry (AAS- Perkin Elmer, Analyst 600). Aluminum in soils and sediments is commonly used as a proxy of particles nature and size since it is a key factor of trace elements accumulation (Windom et al., 1989). Mercury analysis was performed using approximately 200 mg of dry soil and ashes (40 °C), which were thermally decomposed by controlled heating in an Hg analyser (AMA 254 LECO Instrument). The final decomposition products were passed through an Hg amalgamator heated to 700 °C and Hg⁰ was released and detected by absorption spectrometry at 254 nm (Costley et al., 2000). Quality control of the analytical procedure was ensured by the analysis of international certificate standards (MESS-3 and 277) and blanks that were prepared in a similar way to samples and run in parallel with them. Levels of Hg obtained in the reference materials were consistently within the ranges of certified values. Quantification limit was 22.7 ng g⁻¹.

2.5. Data analysis

Statistical analysis was performed with Sigmaplot 11.0. One-way analysis of variance was used to test whether non-burnt and burnt eucalypt soils were significantly different and a two-way analysis of variance was used to test statistical significance of the influence of the sampling periods (AF *versus* ARF), the vegetation type (eucalypt *versus* pine) and the sampling area (Ermida *versus* S. Pedro do Sul) on the pH, electrical conductivity, LOI, Al and Hg levels in soil and ashes. Specific differences between factors were detected *a posteriori* using the Tukey multicomparision test. Differences were considered significant at a $p < 0.05$. Normality of data was checked by using the Shapiro-Wilk test or Kolmogorov-Smirnov, whether distribution was until 50 samples or was more than 50 samples, respectively. The homogeneity of variances of data was checked by using the Levene median test. When normality and homogeneity of variances were not achieved, data were transformed as neperian logarithm (Ln) and square

root. Enrichment factors for soil and ashes were calculated as the quotient between Hg concentrations in samples collected following the rainfall episode (14 weeks after the fire) and 4 weeks after the fire at Ermida area. The Pearson or Spearman coefficients of correlation (whether variables were normally distributed or not, respectively) were used to determine any significant correlations between mercury concentrations in soil and ash and organic matter (LOI).

3. Results

3.1. Characteristics of soils and ashes

Table 1 presents the values of pH and electrical conductivity (EC) in soil and ash samples collected at Ermida and S. Pedro do Sul. On each slope of the selected areas, the variation coefficient of the means ($n=5$) of pH and EC were below 16 %. The soil collected in burnt eucalypt at Ermida showed values of pH and EC significantly ($p<0.05$) higher than the soil in non-burnt soil, with values 1.6 and 2.9 times greater, respectively.

As regard to pH values between sampling surveys (AF vs. ARF) in Ermida, the pH intervals in burnt soils AF (5.1-6.7) and ARF (4.6-6.5) and in ash 6.9-8.0 (AF) and 6.8-7.6 (ARF) were, in general, significantly ($p<0.05$) different either in soil or ash samples. Concerning the EC values, a similar pattern was observed in soil, 203-403 μScm^{-1} in AF and 125-368 μScm^{-1} in ARF, but pronouncedly significant differences were found in ash, 1050-1950 μScm^{-1} in AF and 125-360 μScm^{-1} in ARF. In general pH and EC in ash exceeded the values measured in soil.

Values of pH and EC of soil and ash from Ermida did not differ significantly ($p>0.05$) between the two vegetation coverages (eucalypt *versus* pine) (Table 1). A similar pattern was recorded for S. Pedro do Sul. Values of pH and EC of burnt soil and ash in Ermida were in general higher than in S. Pedro do Sul.

The AI content in non-burnt and burnt soils of the two areas, Ermida and S. Pedro do Sul, are depicted in Table 2. The AI values in Ermida varied between 2.0% and 2.9% for eucalypt soils

and between 3.0% and 3.6% for pines soils. Furthermore, no significant ($p>0.05$) differences were found between: (1) non-burnt and burnt sites (NBE *versus* BE1, BE2, BE3); (2) vegetation type (eucalypt *versus* pine) and (3) sampling periods (AF *versus* ARF). A similar pattern was followed for Al in S. Pedro do Sul, with a tendency to have higher concentrations in pine soils (2.9-3.2%) than in eucalypt soils (2.0%), but without statistical differences ($p<0.05$).

3.2. Mercury and loss on ignition in soil and ash after the fire

Figure 2 illustrate the values of Hg and loss on ignition (LOI) in the non-burnt soils from Ermida, as well as burnt soils and ashes from Ermida and S. Pedro do Sul collected 4 weeks after the fire (AF). The burnt eucalypt soils showed an increase of LOI in E-BE1 (34%) and E-BE2 (40%) in comparison to the non-burnt soils (E-NBE). Values of LOI in E-NBE and E-BE3 were not significantly different ($p>0.05$). An opposite pattern was observed for Hg concentrations in burnt eucalypt soils (mean values ranged between 61 and 62 ng g⁻¹), being significantly ($p<0.05$) lower than in non-burnt soils (88 ng g⁻¹). Additionally, no correlation ($r=0.326$, $p=0.157$) was observed between Hg levels and LOI. Mercury concentrations in burnt soils of eucalypt were significantly higher ($p<0.001$) than in soils from burnt pine slopes, both in Ermida and in S. Pedro do Sul. However, this pattern is not straightforward for the LOI values, as no significant differences ($p>0.05$) were found between E-BE1 and E-BP1 as well as between E-BE3 and E-BP2 in Ermida. The absence of significant differences ($p>0.05$) between types of vegetation (eucalypt *versus* pine) for LOI values was also observed in S. Pedro do Sul. Furthermore, a weak correlation was found for Hg concentrations and LOI levels ($r=0.318$, $p=0.02$).

The comparison of Hg and LOI values in ashes from Ermida and S. Pedro do Sul is also illustrated in Figure 2. Mercury concentrations differed among the slopes, either between the distinct eucalypt slopes or between the pine slopes. For example, Hg values in the eucalypt slope E-BE3 were significantly ($p<0.05$) higher than in E-BE1 and E-BE2. Additionally, Hg levels

in ashes from the pine slope E-BP1 were significantly ($p<0.05$) lower than from E-BP2 and E-BP3. Likewise to Hg levels in soils, also ashes derived from eucalypt biomass were significantly ($p<0.05$) enriched in Hg in comparison to ashes from burnt pines at both areas (Ermida and S. Pedro do Sul). As for LOI values in ashes, we were unable to statistically distinguish between the different vegetation types (eucalypt *versus* pine) in Ermida, since significant differences ($p<0.05$) were only found between E-BE2 and E-BP2. As for S. Pedro do Sul, LOI in ashes was significantly lower ($p<0.01$) in the eucalypt slope (S-BE1) than in the pine one's (S-BP1, S-BP2 and S-BP3). There were a poor correlation between Hg concentrations and LOI values ($r=0.314$, $p=0.03$). Ashes, as well as soils, from the moderate to high severity fire (HS) at S. Pedro do Sul showed lower levels of Hg compared to the moderate severity (MS) fire at Ermida (Figure 3). Despite this, significant differences ($p<0.05$) were only detected for samples collected in pine plots.

3.3. Mercury and loss on ignition in soil and ash after rainfall

Figure 4 shows Hg and LOI values in the non-burnt soils (E-NBE) and burnt soils and ashes of Ermida after the rainfall event (ARF). Burnt eucalypt soils contained significantly lower Hg concentrations ($62\text{--}67\text{ ng g}^{-1}$) than the corresponding non-burnt soils (86 ng g^{-1}). In opposition, burnt soils showed significantly higher LOI (23–26 %) than the non-burnt soils (16 %), with the exception of E-BE3. A lack of correlation ($r=-0.206$, $p=0.378$) was observed between Hg and LOI levels. The precipitation did not reduce the differences of Hg concentrations between eucalypt and pine areas that were observed immediately after fire (Figure 2 and 4). In fact, eucalypt soils exhibited significantly ($p<0.05$) higher levels of Hg than those in pine plantations. In general, these differences were also noticeable in ashes. Levels of LOI in soils differed among the slopes, either between the distinct eucalypt slopes or between the pine slopes. For example, LOI values in the eucalypt slopes (E-BE1, E-BE2 and E-BE3) were significantly ($p<0.05$) different between the three, while the pine slope E-BP2 were significantly ($p<0.05$) lower than

from E-BP1 and E-BP3. Poor correlation was observed between Hg and LOI values in soils and ashes ($r=0.434$, $p=0.02$) and a moderate correlation in ashes ($r=0.709$, $p=0.01$).

The effect of rainfall on Hg in burnt soils and ashes can be confirmed through the calculation of the enrichment factor (EF), as the ratio between Hg concentrations after and before the runoff period. Values of EF calculated for soils and ashes of eucalypt and pine stands from Ermida are presented in Figure 5. A contrasting situation was demonstrated by soils and ashes. Whereas EF_{soil} remained one or slight above (1.0-1.2), EF_{ash} were below one (0.3-0.6).

3.4. Mercury release during the Ermida fire

Values of the amount of Hg stored in soils for the four slopes in Ermida, under post-fire and post-rainfall conditions are given in Table 3. Taking into account the mass of 2-cm upper soils collected in a plot with 3000 cm² and the respective Hg concentration, we find that the amount of Hg stored in the eucalypt burnt slopes in Ermida ranged from 1.8 to 1.9 g Hg ha⁻¹, which was lower than the observed at non-burnt eucalypt area, 2.9 g Hg ha⁻¹ (Table 3). These quantities correspond to 34-38 % of the initial Hg in the soils. The average quantity of Hg release from the soil due to the wildfire (1.1 g Hg ha⁻¹) occurred at Ermida was calculated from the difference between the values in non-burnt soil (2.9 g Hg ha⁻¹) and burnt soils (1.8±0.05 g Hg ha⁻¹). It was also estimated the stored Hg in ashes AF and ARF, which ranged from 0.93-1.5 g Hg ha⁻¹ and 0.11-0.17 g Hg ha⁻¹, respectively (Table 3). After the rainfall event it was observed a loss of 1.0 g Hg ha⁻¹ from ashes and a slight enhancement of 0.5 g Hg ha⁻¹ in the soils.

3.5. Thermo-desorption of mercury from soil

Figure 6 illustrates the mercury concentrations in non-burnt and burnt eucalypt soils (collected 4 weeks after fire at Ermida) exposed to an increasing gradient of temperature. It was also plotted Hg levels in dry soil samples (40 °C) of Ermida that correspond to the initial reference values before the heating experiment. Mercury levels in all soil samples subjected to 40 and

150 °C were not significantly different. Moreover, burnt soils exhibited significantly lower (p<0.05) Hg levels at 40, 150 and 350 °C than non-burnt soils. The most pronounced loss of Hg was registered between 150 and 550 °C, through an apparent linear decrease with the temperature. However, previously burnt soils exhibited significantly lower Hg concentrations at 350 °C (18±5.3) than the non-burnt soils (34±3.3). Both non-burnt and burnt soils exposed to 550 °C showed residual values, corresponding to 3 and 4% of the initial Hg concentrations, respectively. After 750 °C, Hg levels in soils were below 1% of the initial Hg concentrations.

4. Discussion

4.1. Effects of fire and rainfall on physical and chemical properties of soils and ashes

The present study revealed an increment of EC and pH in burnt soils compared with non-burnt, which are in agreement with observations by several authors, who also reported that pH and EC values of burnt soils were greater than those of non-burnt soils (Hernández et al., 1998; Goforth et al., 2005; Quintana et al., 2007; Boerner et al., 2009; Granged et al., 2011a,b). Moreover, by comparing soil and ashes collected after fire (AF) and later after significant rainfall (ARF) a decrease was observed for both pH and EC values. In fact, soil pH and EC is generally increased after forest fires at least during a few months later, which can go up to 5 units after intense burning, in the case of soil pH and then return to similar levels to those of the corresponding unburnt soils (Cass et al., 1984; Ulery et al., 1993, 1995; Granged et al., 2011b). The higher values of pH and EC in soils and ashes collected after the wildfire (AF) can be explained by the release of ions from ash attributed to the mineralization of organic matter after fire, as well as by the mineralized nutrients contained in ash (Notario del Pino et al., 2008; Úbeda et al., 2009; Pereira et al., 2011b). Following the fire, substantial changes occurred in the soils of the burnt area. The vegetation, litter, and a portion of organic layer were at least oxidized by fire, which left behind the ash layer. As the ash was incorporated into

the soil it originates an increased in soil pH, as is supported by higher soil pH in burnt compared to the non-burnt soil (Amirbahman et al., 2004).

The soil pH and EC changes with time is mainly due to the combustion of organic matter, the amount and chemical composition of ash produced during fire, which released large quantities of inorganic ions (cations), oxide, hydroxide and carbonates in soils, a decrease in organic acids produced during the biological oxidation of organic matter in the detritus (Ulery et al., 1993, 1995; Kutiel and Inbar, 1993; Hernández et al., 1998; Certini, 2005; Boerner et al., 2009; Verma and Jayakumar, 2012). Decreases of pH and EC in burnt soils and ashes with the time are usually attributed to the leaching of ash during rainfall, which diminish the ions concentration in ash, namely soluble hydroxides and carbonates (Ulery et al., 1993; Certini, 2005). Temporal variations of pH and EC were much more accentuated in ashes than in burnt soil suggesting that alterations in the former are associated with ash properties. Reductions in soil pH and EC during post-fire were also detected by other authors (Kutiel and Inbar, 1993; Hernandez et al., 1997; Kim et al., 2003; Granged et al., 2011b). Comparable ash pH values were observed in samples collected 2 and 3 days after the fire by Pereira et al., 2012 (pH = 6.89 - 6.98) and Pereira et al., 2014 (pH = 7.95) in a *Pinus pinaster* forest in Portugal, respectively. Similar values were also found by Kim et al. (2003) (pH = 7.24) and Goforth et al. 2005 (pH = 8.0) in samples collected 1 and 2 months after the fire, respectively. A temporal study with observations at 20 and 60 days post-fire revealed a decrease in ash pH from 12.0 to 9.3, respectively (Ulery et al., 1993). Electrical conductivity values found in ashes in the present study were also comparable to the findings of Pereira and co-authors (2011b; 2012) after a prescribed fire and those produced in laboratorial environments (Úbeda et al, 2009). In general, we found a tendency to have higher values in ashes than in soils, suggesting that ash deposition and heat associated with forest fire affect soil properties (Cass et al., 1984; Ulery et al., 1993; Kim et al., 2003; Goforth et al., 2005).

The low percentage of Al in the collected samples suggests that soils consisted mainly of a mixture of sand with a small proportion of fine particles.

4.2. Mercury retained in burnt soil

Total Hg in soils indicated that concentrations in burnt eucalypt soils were approximately 70% of the mercury contained in the corresponding non-burnt site. Current data are in line with other studies that have reported a decrease of Hg content in soils after wildfires due to its release as Hg(0) (gaseous) or particulate mercury (Engle et al., 2006; Biswas et al., 2007, 2008; Navrátil et al., 2009; Obrist et al., 2009; Burke et al., 2010). This pattern was consistent with other investigations conducted in soil samples that included litter, humus and organic soil (Amirbahman et al., 2004; Mailman and Bodaly, 2005). Comparisons between Hg concentration in non-burnt and burnt soils provides insight on the effect of wildfire on Hg distribution and cycling in forest (Engle et al., 2006). The higher Hg values found in non-burnt than burnt soils in the present study demonstrate that some of the Hg that was accumulated prior to burning was lost from soil to the surrounding environment when burnt, confirming the potential of wildfire to directly volatilize Hg, as a result of their low volatilization temperatures. Since, most of the Hg species are volatilized between 100-300 °C (Biester and Scholz, 1997) and during the wildfire in Ermida, the elevated soil temperatures sufficient (higher than 150°C) to mobilize the Hg compounds, which included conversion to gaseous forms and subsequent emission (Hg released from fire is predominantly as Hg⁰, with up to 15% in the form of particulate mercury; Friedli et al., 2001, 2003a, 2003b), vaporization of volatile compounds, and release as / on ash particles (our results showed higher levels of Hg in ashes than in soils). Another possibility is the conversion to more soluble forms that can be leached into the soil (Gimeno-García et al., 2001; Engle et al., 2006).

The loss of 1.0-1.1 g Hg ha⁻¹ due to the wildfire occurrence indicates that only a small portion of the Hg present in the upper 2- cm layer of soil was removed, where most of the Hg is likely to

be present. Due to volatilisation of Hg(0), most of the mercury forms present in top soils during wildfire tend to be sequentially released as temperature increase (Biester and Scholz, 1997; Reis, 2013). In fact, the progressive release of Hg from the soil was confirmed in the present study by the heating experiment. Above 150 °C the bonds of mercury-ligands are progressively destroyed up to 550 °C. The high proportion of Hg retained in burnt soils (70%) after the wildfire, suggests that temperature from the 2-cm upper layer of soils did not reach those elevated values (it should have been above 150 °C and below 350 °C). Furthermore, the Hg levels in non-burnt soils and burnt soils after being submitted to temperatures of 150 and 350°C were 83 and 34 ng g⁻¹ and 24 and 18°C, respectively, meaning that the temperature reached by the fire must have been above 150 °C and below 350 °C. Mercury concentration in the non-burnt and burnt soil (88 and 62 ng g⁻¹, respectively) was approximately the double and triple of the values found for the those samples, after being submitted to the temperature of 350 °C, respectively. According to this variation of Hg levels in non-burnt and burnt soils with temperature, one may speculate that the average temperature of the upper soil layer during fire reached values high enough to destroy the labile forms of Hg, which are released above 100 °C and below 200 °C, like Hg⁰ and HgCl₂, while most of Hg-humic acid bonds and HgS remained unbroken (Biester and Scholz, 1997). This hypothesis is probably valid to the other fire scenario (moderate to high fire severity occurred at S. Pedro do Sul), since Hg values in eucalypt and pine soils were comparable to levels recorded in the respective soils from Ermida.

4.3. Association of mercury with organic matter

In general, a similar pattern to pH and EC was followed by LOI (with the exception of ERM-BE3), where a steep increase approximately 35% was recorded for burnt eucalypt after the fire, in comparison with the non-burnt, that was maintained throughout the post-fire observation period. Our results confirms reports elsewhere in the literature, that suggested new inputs as partly charred litter and leaves, forest necromass and residual ash (Gimeno-

Garcia et al., 2000; Kim et al., 2003; Pardini et al., 2004; Knicker et al., 2005; Jovanovic et al., 2012). However, it is not unusual to find a decrease in LOI after fire due to the volatilization or oxidation of the organic matter, depending on the soil temperature reached during the fire (Terefe et al., 2008; Aref et al., 2011; Granged et al., 2011a). The extremely high values of LOI in ashes collect IAF, can be attributed to the incomplete vegetation combustion, as suggested by the ash dark color (Goforth et al., 2005).

Soil organic matter (SOM) has been considered a major factor to explain the retention of Hg in soil, mainly due to its high affinity with functional groups rich in sulphur and carboxyl present in soils (Engle et al., 2006; Biswas et al., 2007, 2008; Navrátil et al., 2009; Obrist et al., 2009). However, Obrist et al. (2012) also reported considerably higher soil carbon pools that were not associated with corresponding higher Hg stocks. The thermo-desorption assay performed in this study using non-burnt soils suggests that most of Hg was associated with ligands that were not destroyed during the wildfire (Biswas et al., 2007; Reis, 2013). Additionally, the absence of correlation ($r=0.326$, $p=0.157$) between Hg and LOI in burnt soils meaning that the organic matter content is insufficient to explain the Hg partitioning. It is likely the consumption of organic matter by the fire happens in parallel with input of LOI from the incomplete combustion of belowground biomass and litter. Consequently, Hg tends to be redistributed in the soil or released to the atmosphere. That tendency for a non-equilibrium situation is illustrated by burnt eucalypt soils in E-BE1 and E-BE2 that have 50% more LOI than the non-burnt eucalypt soils. Additionally, due to the ash content accumulated in the top of the burnt soils, the Hg may bind with ash and with the remaining charcoal, therefore explaining the low concentrations of Hg observed in the burnt site.

The mercury concentration in burnt soils of areas colonised by eucalypt were approximately twice the values measured in burnt pine soils. That difference occurs for both surveyed areas, Ermida and S. Pedro do Sul, despite the different fire severities in the two study areas (Figure 3). Those differences were not related to the enhancement of LOI ($r=0.318$, $p=0.02$).

Furthermore, they are unlikely related to the grain size distribution of the soil since aluminium, which is a proxy for particle size in soil (Windom et al., 1989), is not significantly different ($p>0.05$) in the two study areas. Additionally, the influence of different plant species on the soil characteristics is well documented (Mailman et al., 2005; Obrist et al., 2012). Nevertheless, further studies should confirm whether eucalypts, in comparison to pines, create conditions that favour Hg retention in soil.

Mercury concentrations in ashes were twice the values measured in soils. Furthermore, Hg in ashes collected in the eucalypt plots were significantly ($p<0.001$) higher than in the pine stands, both in Ermida and S. Pedro do Sul. These differences are in line with the values measured in soils. The quantity of organic matter in ashes did not explain those differences, since Hg is poorly correlated with LOI in ashes from the two burnt areas ($r=0.314$, $p=0.03$). Assuming that most of the collected ashes derived from the combustion of aboveground plant parts of eucalypt and pine, it seems that eucalypts accumulate more Hg than pines at Ermida. This difference is obvious from the box-plots of Hg levels for soils and ashes from the two plants coverage under both fire severities (Figure 3).

4.4. The effect of rainfall after fire

Several studies have clearly pointed out that heavy rainfall and the subsequent surface runoff play an important role in soil erosion and therefore on transport of particles to downstream aquatic systems (Caldwell et al., 2000; Cannon et al., 2001; Robichaud et al., 2009; Malvar et al., 2011; Prats et al., 2014). These events are considered important inputs of contaminants from diffuse sources to rivers and estuaries (Schroeder and Munthe, 1998; Kelly et al., 2006; Obrist et al., 2009; Burke et al., 2010). Particularly, the first heavy rains after a wildfire caused an accentuated surface washing over the burnt areas of Ermida, which was attenuated over time (Martins et al., 2013; Prats et al., 2014). In general, this leads to a significant decrease of pH and EC in soils and ashes. The effect of rainfall showed a contrasting situation between soils

and ashes, since EF_{soil} remained one or slight above and EF_{ash} were below one. That Hg reduction in the ashes, which reached 30 to 60%, was accomplished with a decrease of LOI between 50 to 70%. Presumably, runoff promoted the removal of particulate Hg or solubilised the forms attached to the organic matter in ashes. That wash over showed to be effective in soils, since EF were near one. Values slightly above one may indicate the transference of Hg from ashes to soils. On the other hand, the atmospheric deposition of Hg on soil, with the rain (Lawson and Mason, 2001) is less plausible since ashes demonstrate a strong decrease in Hg concentrations.

Mercury concentrations in ash samples collected after the wildfire (AF) were much higher ($< 74 \text{ ng Hg g}^{-1}$; Fig. 3) compared to the one's reported by Friedli et al. (2001) ($< 7 \text{ ng Hg g}^{-1}$). These measurements of Hg concentrations were conducted on ash from controlled laboratory burnt experiments using vegetation and litter, which differs from ash produced following wildfire, due to the different combustion conditions, material and temperature reached during the experiment (Pereira et al., 2011a). High Hg levels still found in ash collected ARF (from 30 to 75 ng Hg g^{-1} ; Fig. 3) which are comparable but somewhat higher than the values found by Engle et al. (2006) in ashes collected 1 year after a forest prescribe fire and a wildfire (24.7 and 39.2 ng Hg g^{-1} , respectively). As mentioned before, Hg levels in ashes samples collected ARF were lower than in ashes collected AF. This temporal decrease of Hg in ashes can be attributed to their wash out by runoff and leaching into soils below after the first rainfalls. This hypothesis is reinforced by data of soil Hg concentrations where a slight increased ARF was observed.

4.5. Estimation of mercury budget

Burnt eucalypt slopes in Ermida were characterized by 1.1 g Hg ha^{-1} less than the control (non-burnt eucalypt slope) and this difference can be interpreted as Hg loss from the soil by fire. That quantity is in the same order of magnitude as values reported in literature for: a conifer wildfire ($2.2\text{-}4.9 \text{ g Hg ha}^{-1}$), a prescribed conifer fire ($2.2\text{-}5.1 \text{ g Hg ha}^{-1}$) (Engle et al., 2006), and a

Quebec boreal forest (1.5 g Hg ha^{-1}) (Sigler et al., 2003). Estimated values were higher than those reported for a desert sagebrush fire ($0.36 \text{ g Hg ha}^{-1}$) (Engle et al., 2006). In addition to 1.1 g of Hg released per ha to the atmosphere, Hg was also washed over following heavy rainfall. Rainfall caused a loss of 1.0 g Hg ha^{-1} from ashes and the slight enhancement of 0.5 g Hg ha^{-1} in the soils, meaning that it may have been a possible transference of Hg from ashes to soils. Therefore, the net value of 0.5 g Hg ha^{-1} could be lost to the adjacent terrestrial areas or eventually introduced into freshwater systems.

5. Conclusions

Results of this study provided the main findings:

- 30% of the Hg retained in eucalypt soils escaped during a wildfire, corresponding to a loss of $1.0\text{-}1.1 \text{ g Hg}$ per hectare. Temperature reached in the wildfire was insufficient to destroy the most stable bonds of Hg-ligands, as pointed by the thermo-desorption experiment.
- Soils and ashes from eucalypt hillslopes were consistently enriched in Hg relatively to pine areas. Ashes exhibited higher organic matter and Hg relatively to soils.
- The rainfall after the fire has a key role in the washed out of Hg from ashes deposited on the soil surface.
- This study points out the importance of merges the influence of wildfire with rainfall in the investigation of Hg cycling.

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6. References

Alloway B.J. Heavy metals in soils. Blackie Academic & Professional, Chapman and Hall, second edition.

Amirbahman A.R., Ruck P.L., Fernandez I.J., Kahl J.S., Haines T.A., 2004. The effect of fire on mercury cycling in the soils of forested watersheds: Acadia National Park, Maine, USA. *Water, Air and Soil Pollution*, 152, 313–331.

Antilén M., Araya N., Briceno M., Escudey M., 2006. Changes on chemical fractions of heavy metals in Chilean soils amended with sewage sludge affected by thermal impact. *Australian journal of Soil Research*, 44, 619-625.

Aref I.M., Atta H.A., Ghamade A.R., 2011. Effect of forest fires on tree diversity and some soil properties. *International Journal of Agriculture and Biology*, 13, 659-664.

Balfour V.N., Woods S.W., 2013. The hydrological properties and the effects of hydration on vegetation ash from the Northern Rockies, USA. *Catena*, 111, 9-24.

Biester H., Scholz C., 1997. Determination of mercury phases in contaminated soils – Hg-pyrolysis vs. sequential extractions. *Environmental Science and Technology*, 31, 233-239.

Biester H., Müller G., Schöler H.F., 2002. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. *The Science of the Total Environment*, 284, 191-203.

Biswas A., Blum J.D., Klaue B., Keeler G.J., 2007. Release of mercury from Rocky Mountain forest fires. *Global Biogeochemical Cycles*, 21, GB1002. doi:10.1029/ 2006GB002696.

595 Biswas A., Blum J.D., Keeler G.J., 2008. Mercury storage in surface soils in a central
 596 Washington forest and estimated released during the 2001 Rex Creek fire. *Science of the Total*
 597 *Environment*, 404, 129-138.

598 Bodi M.B., Mataix-Solera J., Doerr J., Cerdà A., 2011. The wettability of ash from burned
 599 vegetation and its relationship to Mediterranean plant species type, burn severity and total
 600 organic carbon content. *Geoderma*, 160, 599-607.

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

604 Boening D.W., 2000. Ecological effects, transport, and fate of mercury: a general review.
 605 *Chemosphere*, 40, 1335–1351.

606 Boerner, R.E., Hart, S., Huang, J., 2009. Impacts of fire and fire surrogate treatments.
 607 *Ecological Applications*, 19(2), 338-358.

608 Bollen A., Wenke A., Biester H., 2008. Mercury speciation analysis in HgCl₂-contaminated
 609 soils and groundwaters – implications for risk assessment and remediation strategies. *Water*
 610 *Resources*, 42, 91-100.

611 Botelho da Costa, J.V., 2004. Caracterização e constituição do solo. Fundação Calouste
 612 Gulbenkian, 7ª edição. Pp.123.

613 Burke M.P., Hogue T.S., Ferreira M., Mendez C.B., Navarro B., Lopez S., Jay J.A., 2010. The
 614 effect of wildfire on soil mercury concentrations in Southern California watersheds. *Water Air*
 615 *Soil Pollution*, 212, 369-385.

616 Caldwell C.A., Canavan C.M, Bloom N.S., 2000. Potential effects of forest fire and storm flow
 617 on total mercury and methylmercury in sediments of an arid-lands reservoir. *Science of the*
 618 *Total Environment*, 260, 125–133.

619 Cannon S.H., Bigio E.R., Mine E., 2001. A process for fire-related debris flow initiation, Cerro
 620 Grande fire, New Mexico. *Hydrological Processes*, 15, 3011-3023.

621 Cardoso J.C., Bessa M.T., Marado M.B., 1971. Carta dos solos de Portugal (1:1000000).
 622 Serviço de Reconhecimento e de Ordenamento Agrário, Secretaria de Estado da Agricultura,
 623 Lisboa, Portugal.

624 Cass A., Savage M.J., Wallis F.M., 1984. In: Kim E-J., Oh J.E., Chang Y.S., 2003. Effects of
 625 forest fire on the level and distribution of PCDD/Fs and PAHs in soil. Science of the Total
 626 Environment, 31, 177-189.

627 Cerdà A., Lasanta A., 2005. Long-term erosional responses after fire in the Central Spanish
 628 Pyrenees: 1. Water and sediment yield. Catena, 60, 256-263.

629 Certini G., 2005. Effects of fire on properties of forest soils: a review. Oecologia, 143, 1-10.

630 Cheng M.D., Schroeder W.H., 2000. Potential atmospheric transport pathways for mercury
 631 measured in the Canadian high artic. Journal of Atmospheric Chemistry, 35, 101-107.

632 Costley C.T., Mossop F., Dean J.R., Garden L.M., Marshall J., Carrol J., 2000. Determination
 633 of mercury in environmental and biological samples using pyrolysis atomic absorption
 634 spectrometry with gold amalgamation- Analytical Chimica Acta, 405, 179-183.

635 Doerr S.H., Shakesby R.A., Walsh R.P.D., 2000. Soil water repellency: its causes,
 636 characteristics and hydro-geomorphological significance. Earth-Science Reviews, 51, 33-65.

637 Doerr S.H., Cerdà A., 2005. Fire effects on soil system functioning: new insights and future
 638 challenges. International Journal of Wildland Fire, 14, 339-342.

639 DRA (Direção Regional do Ambiente do Centro), 2002. Plano de Bacia Hidrográfica do Rio
 640 Vouga, 1ª fase, Análise e diagnóstico da situação de referência. Análise biofísica, Anexos.
 641 Lisboa, Portugal.

642 <http://www.arhcentro.pt/website/LinkClick.aspx?fileticket=86UOh6WtK%2bY%3d&tabid=284>.

643 DUDF (Direção de Unidade de Defesa da Floresta), 2011. Relatório anual de áreas ardidas e
 644 ocorrências 2010 (in Portuguese). Autoridade Florestal Nacional (AFN), Lisboa, Portugal.

645 Engle M.A., Gustin M.S., Johnson D.W., Murphy J.F., Miller W.W., Walker R.F., Wright J.,
 646 Markee M., 2006. Mercury distribution in two Sierran forest and one desert sagebrush steppe
 647 ecosystems and the effects of fire. *Science of the Total Environment*, 367, 222-233.

648 Friedli H.R., Radke L.F., Lu J.Y., 2001. Mercury in smoke from biomass fires. *Geophysical*
 649 *Research Letters*, 28, 3223–3226.

650 Friedli HR, Radke LF, Lu JY, Banic CM, Leaitch WR, MacPherson JI, 2003a. Mercury emissions
 651 from burning of biomass from temperate North American forests: laboratory and airborne
 652 measurements. *Atmospheric Environment*, 37, 253–267.

653 Friedli HR, Radke LF, Prescott R, 2003b. Mercury emissions from the August 2001 wildfires
 654 in Washington State and an agricultural waste fire in Oregon and atmospheric mercury budget
 655 estimates. *Global Biogeochemical Cycles*, 17 (2), 1–8.

656 Gabet E.J., Bookter A., 2011. Physical chemical and hydrological properties of Ponserosa
 657 pine ash. *International Journal of Wildland Fire*, 20, 443-452.

658 Gimeno-Garcia E., Andreu V., Rubi J.L., 2007. Changes in organic matter, nitrogen,
 659 phosphorus and cations in soil as a result of fire and water erosion in a Mediterranean
 660 landscape. *European Journal of soil Science*, 51, 201-210.

661 Ginzburg O., Steinberger, Y., 2012. Effects of forest wildfire on soil microbial-community
 662 activity and chemical components on temporal-seasonal scale. *Plant Soil*, 360 (1-2), 243-257.

663 Gnamus A., Byrne A.R., Horvat M., 2000. Mercury in the Soil-plant-deer-predator food
 664 chain of a temperate forest in Slovenia. *Environmental Science Technology*, 34, 3337-3345.

665 Goforth B.R., Graham R.C., Hubbert K.R., Zanner C.W., Minnich R.A., 2005. Spatial
 666 distribution and properties of ash and thermally altered soils after high-severity forest fires,
 667 southern California. *International Journal of Wildland Fire*, 14, 343-354.

668 Granged A.J.P., Jordán A., Zavala L.M., Muñoz-Rojas M., Mataix-Solera J., 2011a. Short-term
 669 effects of experimental fire for a soil under eucalyptus forest (SE Australia). *Geoderma*, 167-
 670 168, 125-134.

671 Granged A.J.P., Zavala L.M., Jordán A., Bárcenas-Moreno G., 2011b. Post-fire evolution of
672 soil properties and vegetation cover in a Mediterranean heathland after experimental burning:
673 a 3-year study. *Geoderma*, 164, 85-94.

674 Grigal D.F., 2003. Mercury sequestration in forest and peatlands: A review. *Journal of*
675 *Environmental Quality*, 32, 393-405.

676 Guénou R., Vennetier M., Dupuy N., Roussos N., Pailler R., Gros R., 2013. Trends in recovery
677 of mediterranean soil chemical properties and microbial activities after infrequent and
678 frequent wildfires. *Land Degradation & Development*, 24, 115-128.

679 Harden J.W., Neff J.C., Sandberg D.V., Turetsky M.R., Ottmar R., Gleixner G., Fries T.L.,
680 Manies K.L., 2004. Chemistry of burning the forest floor during the FROSTFIRE experimental
681 burn, interior Alaska, 1999. *Global Biogeochemical Cycles*, 18, GB3014, 1–13.

682 Hernández T., Garcia C., Reinhardt I., 1997. Short-term effect of wildfire on the chemical,
683 Biochemical and microbiological properties of Mediterranean pine forest soils. *Biology and*
684 *Fertility of Soils* 25, 109-116.

685 Huang X., Li M., Friedli H.R., Song Y., Chang D., Zhu L., 2011. Mercury emissions from
686 biomass burning in China. *Environmental Science and Technology*, 45, 9442-9448.

687 ISO (International Standard Organization), 2005. ISO 10390: Soil Quality – Determination of
688 pH. Geneve, Switzerland.

689 ISO (International Standard Organization), 1994. ISO 11265: Soil Quality – Determination of
690 the specific electrical conductivity. Geneve, Switzerland.

691 Jakubus M., Kaczmarek Z., Michalik J., Grzelak, M., 2010. The effect of different tree
692 plantings and soil preparation methods on contents of selected heavy metals in post-fire soils.
693 *Fresenius Environmental Bulletin*, 19 (2a), 312-317.

694 Jovanovic V.P.S., Illic M.D., Markovic M.S., Mitic V.D., Mandic S.D.N., Stojanovic G.S., 2011.
695 Wild fire impact on copper, zinc, lead and cadmium distribution in soil and relation with

696 abundance in selected plants of *Lamiaceae* family from Vidlic Mountain (Serbia).
 697 Chemosphere, 84, 1584-1591.

698 Keeley J.E., 2009. Fire intensity, fire severity and burnt severity: a brief review and
 699 suggested usage. International Journal of Wildland fire 18, 116-126.

700 Kelly E.N., Schindler D.W., St. Louis V.L., Donald D.B., Vladicka K.E., 2006. Forest fire
 701 increases mercury accumulation by fishes via food web restructuring and increased mercury
 702 inputs. Proceedings of National Academy of Sciences, 103, 19380-19385.

703 Keizer J.J., Doerr S.H., Malvar M.C., Prats S.A., Ferreira R.S.V., Onãte M.G., Coelho C.O.A.,
 704 Ferreira A.J.D., 2008. Temporal variation in topsoil water repellency in two recently burnt
 705 eucalypt stands in north-central Portugal. Catena 74(3), 192–204.

706 Kim E-J., Oh J.E., Chang Y.S., 2003. Effects of forest fire on the level and distribution of
 707 PCDD/Fs and PAHs in soil. Science of the Total Environment 31, 177-189.

708 Kutiel P., Inbar M., 1993. Fire impacts on soil nutrients and soil erosion in a Mediterranean
 709 pine forest plantation. Catena, 20, 129-139.

710 Lasanta A., Cerdà A., 2005. Long-term erosional responses after fire in the Central Spanish
 711 Pyrenees: 2. Solute release. Catena, 60, 81-100.

712 Lawson N.M. and Mason R.P., 2001. Concentration of mercury, methylmercury, cadmium,
 713 lead, arsenic, and selenium in the rain and stream water of two contrasting watersheds in
 714 western Maryland. Water Research, 35(17), 4039–4052.

715 Lopez-Anton M.A., Yuan Y., Perry R., M.R., Maroto-Valer M.M, 2010. Analysis of mercury
 716 species present during coal combustion by thermal desorption. Fuel, 89, 629-634.

717 Maia P., Pausas J., Arcenegui V., Guerrero C., Pérez-Bejarano A. Mataix-Solera J., Varela
 718 M.E.T., Fernandes I., Pedrosa E.T., Keizer J.J., 2012. Wildfire effects on the soil seed bank of a
 719 maritime pine stand – the importance of fire severity. Geoderma, 191, 80-88.

720 Mailman M., Bodaly R.A., 2005. Total mercury, methylmercury, and carbon in fresh and
 721 burned plants and soil in Northwestern Ontario. Environmental Pollution, 138, 161-166.

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

725 Martins M.A.S., Machado A. I., Serpa D., Prats S.A., Faria S.R., Varela M.E.T., Gonzalez-
 726 Pelayo O., Keizer J.J., 2013. Runoff and inter-rill erosion in a Maritime Pine and a eucalypt
 727 plantation following wildfire and terracing in north-central Portugal. Journal of Hydrology and
 728 Hydromechanics 61, 4, 261-269.

729 Mataix-Solera J., Cerdà A., Arcenegui V., Jordán A., Zavala L.M., 2011. Fire effects on soil
 730 aggregation: a review. Earth-Science Reviews, 109, 44-60.

731 Navrátil T., Hojdová M., Rohovec J., Penížek V., Vařilová, Z., 2009. Effect of fire on pools of
 732 Mercury in forest soil, Central Europe. Bull Environ Contam Toxicol, 83, 269-274.

733 Neary D.G., Klopatek C.C., DeBano L.F., Fgollott P.F., 1999. Fire effects on belowground
 734 sustainability: a review and synthesis. Forest Ecological Management. 122, 51-71.

735 Notario del Pino J., Dorta A.I., Rodriguez R.A., Arbelo R.C., Navarro R.F.J., Mora H.J.L., Amas
 736 H.C.M., Guerra G.J.A., 2008. Analysis of the 1:5 soil water extract in burnt soils to evaluate fire
 737 severity. Catena, 74, 246-255.

738 Obrist D., Johnson D.W., Lindberg S.E., 2009. Mercury concentrations and pools in four
 739 Sierra Nevada forest sites, and relationships to organic and nitrogen. Biogeosciences, 6, 765-
 740 777.

741 Obrist D., Johnson D.W., Edmonds R.L., 2012. Effects of vegetation type on mercury
 742 concentrations and pools in two adjacent coniferous and deciduous forest. Journal of Plant
 743 Nutrition and Soil Science, 175, 68-77.

744 Pacyna J.M., Pacyna E., 2002. Global emissions of mercury from anthropogenic sources in
 745 1995. Water, Air, and Soil Pollution, 137, 149-165.

746 Pacyna J.M., Pacyna E.G., Steenhuisen F, Wilson S, 2003. Mapping 1995 global
 747 anthropogenic emissions of mercury. Atmospheric Environment, 37(S1), S109–S117.

748 Parson A., Robichaud P. R., Lewis S.A., Napper C., Clark J.T., 2010. Field guide for mapping
 749 post-fire soil burn severity. General Technical Report RMRS-GTR-243. U.S. Department of
 750 Agriculture, Forest Services, Fort Collins, Colorado.

751 Pereira P., Úbeda X., 2010. Spatial distribution of heavy metals released from ashes after a
 752 wildfire. *Journal of Environmental Engineering and Landscape Management*, 18(1), 13-22.

753 Pereira P., Úbeda X., Martin D., 2011a. Heavy metals released from leaf litter exposed to
 754 different fire temperatures. A laboratory experiment. *Darnaus Vystymosi Strategia ir Pratica*
 755 (Sustainable Development Strategy and Practice), 1, 137-154.

756 Pereira P., Úbeda X., Martin D., Mataix-Solera J., Guerrero, C., 2011b. Effects of a low
 757 severity prescribed fire on water-soluble elements in ash from a cork oak (*Quercus suber*)
 758 forest located in the northeast of the Iberian Peninsula. *Environmental Research*, 111, 237-
 759 247.

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

762 Pereira P., Úbeda X., Martin D.A., Mataix-Solera J., Cerdà A., Burguet M., 2014. Wildfire
 763 effects on extractable elements in ash from a *Pinus pinaster* forest in Portugal. *Hydrological*
 764 *Processes*, 28, 3681-3690.

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

768 Prats S.A., Martins, M.A.S., Malvar, M.C., Ben-Hur, M., Keizer, J.J., 2014. Polyacrylamide
 769 application versus forest residue mulching for reducing post-fire runoff and soil erosion.
 770 *Science of the Total Environment* 468-469, 464-474.

771 Quintana J.R., Cala V., Moreno A.M., Parra J.G., 2007. Effect of heating on mineral
 772 components of the soil organic horizon from a Spanish juniper (*Juniperus thurifera* L.)
 773 woodland. *Journal of Arid Environments*, 71, 45-56.

774 Reis A., 2013. Challenges in mercury speciation and fractionation in soil and sediment. PhD
 775 Thesis. University of Aveiro.

776 Reis A.T., Coelho A.P., Rodrigues S.M., Rocha R., Davidson C.M., Duarte A.C., Pereira E.,
 777 2012. Development and validation of a simple thermo-desorption technique for mercury
 778 speciation in soils and sediments. *Talanta*, 99, 363-368.

779 Reis A.T., Coelho A.P., Rucandio I., Davidson C.M., Duarte A.C., Pereira E., 2015. Thermo-
 780 desorption: A valid tool for mercury speciation in soils and sediments? *Geoderma*, 237-238,
 781 98-104.

782 Reneau S.I., Katzman D., Kuyumjian G.A., Lavine A., Malmon D.V., 2007. Sediment delivery
 783 after a wildfire. *Geology*, 35(2), 151-154.

784 Robichaud P.R., 2009. Post-fire stabilization and rehabilitation. In: Granged AJP, Zavala LM,
 785 Jordán A, Bárcenas-Moreno G, 2011a. Post-fire evolution of soil properties and vegetation
 786 cover in a Mediterranean heathland after experimental burning: a 3-year study. *Geoderma*,
 787 164, 85-94.

788 Roy M., McDonald L.M., 2013. Metal uptake in plants and heath risk assessments in metal-
 789 contaminated smelter soils. *Land Degradation & Development*. DOI:10.1002/ldr.2237.

790 Rubenacker A., Campitelli P., Velasco M., Ceppi S., 2012. Fire impact on several chemical
 791 and physicochemical parameters in a forest soil. *Soil health and land use management*. Dr.
 792 Maria C. Hernandez Soriano (Ed.), in Tech. [http://www.interchopen.com/books/soil-health-](http://www.interchopen.com/books/soil-health-and-land-use-management/fire-impact-on-several-chemical-and-physicochemical-parameters-in-a-forest-soil)
 793 [and-land-use-management/fire-impact-on-several-chemical-and-physicochemical-parameters-](http://www.interchopen.com/books/soil-health-and-land-use-management/fire-impact-on-several-chemical-and-physicochemical-parameters-in-a-forest-soil)
 794 [in-a-forest-soil](http://www.interchopen.com/books/soil-health-and-land-use-management/fire-impact-on-several-chemical-and-physicochemical-parameters-in-a-forest-soil).

795 Rumayor M., Diaz-Somoano M., Lopez-Anton M.A., Martinez-Tarazona M.R., 2013. Mercury
 796 compounds characterization by thermal desorption. *Talanta*, 114, 318-322.

797 Rumayor M., Diaz-Somoano M., Lopez-Anton M.A., Martinez-Tarazona M.R., 2015.
 798 Application of thermal desorption for the identification of mercury species in solids derived
 799 from coal utilization. *Chemosphere*, 119, 459-465.

800 Santín C., Doerr S.H., Shakesby R.A., Bryant R. Sheridan G.J., Lane P.N.J., Smith H.G., Bell
801 T.L., 2012. Carbon loads, forms and sequestration potential within ash deposit produced by
802 wildfires: new insights from the 2009 'Black Saturday' fires, Australia. *European Journal of*
803 *Forest Research*, 131, 1245-1253.

804 Schroeder W.H., Munthe J., 1998. Atmospheric mercury – an overview. *Atmospheric*
805 *Environment*, 32, 809-822.

806 Schwesig D, Matzner E, 2000. Pools and fluxes of mercury and methylmercury in two
807 forested catchments in Germany. *The Science of the Total Environment*, 260, 213–223.

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

810 Sigler J.M., Lee X., Munger W., 2003. Emission and long-range transport of gaseous mercury
811 from a large-scale Canadian boreal forest fire. *Environmental Science Technology*, 37, 4343-
812 4347.

813 Smith H.G., Sheridan G.J., Lane P.N.J., Nyman P. Haydon S., 2011. Wildfires effects on water
814 quality in forest catchments: A review with implications for water supply. *Journal of Hydrology*,
815 396, 170-192.

816 SNIRH, 2013. Sistema Nacional de Informação de Recursos Hídricos. <http://www.snirh.pt>.

817 Stronach N.R.H., McNaughton S.J., 1989. Grassland fire dynamics in the Serengeti
818 ecosystem, and a potential method of retrospectively estimating fire energy. *Journal of applied*
819 *Ecology*, 26, 1025-1033.

820 Terefe T., Mariscal-Sancho I., Peregrina F., Espejo R., 2008. Influence of heating on various
821 properties of six Mediterranean soils. A laboratory study. *Geoderma*, 143, 273-280.

822 Úbeda X., Pereira P., Outeiro L., Martin D., 2009. Effects of fire temperatures on the
823 physical and chemical characteristics of the ash from two plots of cork oak (*Quercus Suber*).
824 *Land Degradation and Development*, 20, 589-608.

825 Ulerý A.L., Graham R.C., Amrhein A., 1993. Wood-ash composition and soil pH following
826 intense burning. *Soil Science*, 156, 358-364.

827 Ulerý A.L., Graham R.C., Chadwick O.A., 1995. Decadescale changes of soil carbon, nitrogen
828 and exchangeable cations under chaparral and pine. *Geoderma*, 65, 121-134.

829 USEPA (United states Environmental Protection Agency), 1996. USEPA 3050B: Acid
830 digestion of sediments, sludges and soils. Washington, DC.

831 Varela M.E., Benito E., Keizer J.J., 2010. Wildfire effects on soil erodibility of woodlands in
832 NW Spain. *Land Degradation & Development* 21, 75-82.

833 Verma S., Jayakumar S., 2012. Impact of forest fire on physical, chemical and biological
834 properties of soil: A review. *Proceedings of International Academy of Ecology and*
835 *Environmental Sciences*, 2, 168-176.

836 Wang L., Dibdiakova J., 2014. Characterization of ashes from different woods parts of
837 Norway spruce tree. *Chemical Engineering Transactions*, 37, 37-42.

838 Wiedinmeyer C., Friedli H., 2007. Mercury emission estimates from fires: an initial inventory
839 for the United States. *Environmental Science Technology*, 41, 8092-8098.

840 Windom H.L., Schropp S.J., Calder F.D., Ryan J.D., Smith R.G., Burney L.C., Lewis F.G.,
841 Rawlinson C.H., 1989. Natural trace metal concentrations in estuarine and coastal marine
842 sediments of Southeastern United States. *Environmental Science and Technology*, 23, 314-320.

843 Witt E.L., Kolka R.K., Nater E.A., Wickman T.R., 2009. Forest fires effects on mercury
844 deposition in the Boreal Forest, *Environmental Science Technology*, 43, 1776-1782.

845 Woodruff L.G., Harden J.W., Cannon W.F., Gough L.P., 2001. Mercury loss from the forest
846 floor during Wildland fire. *EOS Transactions of American Geophysical Union*, 82 (47), Fall
847 Meeting, Supplement, Abstract B32B-0117.

Table 1- pH and electrical conductivity (EC, μScm^{-1}) in soil and ashes of non-burnt (NBE) and burnt eucalypt (BE1, BE2, BE3) and maritime pine (BP1, BP2, BP3) slopes at Ermida (E) and S. Pedro Sul (S). Samples were collected 4 weeks after fire (AF) at E and S and 14 weeks later after a rainfall period (ARF) at E. Mean values $\pm$ standard errors are given. Asterisks indicate significant differences between non-burnt and burnt eucalypt samples. Different letters denote statistically significant differences ($p < 0.05$) between sites (for the same survey). Different symbols denote statistically significant differences ($p < 0.05$) between surveys (for each site).

Sampling Area	Type of sample	Site	Survey	pH	EC (μScm^{-1})
ERMIDA (E)	SOIL	NBE	AF	$4.0 \pm 0.01 \nabla$	$120 \pm 5.0 \nabla$
			ARF	$3.9 \pm 0.09 \nabla$	$125 \pm 5.0 \nabla$
		BE1	AF	$6.4 \pm 0.10 *a\nabla$	$363 \pm 7.5 *ad\nabla$
			ARF	$6.0 \pm 0.02 *a\Diamond$	$220 \pm 10.0 *a\Diamond$
		BE2	AF	$6.0 \pm 0.08 *b\nabla$	$290 \pm 10.0 *b\nabla$
			ARF	$4.8 \pm 0.04 *b\Diamond$	$173 \pm 2.5 *b\Diamond$
		BE3	AF	$6.7 \pm 0.07 *a\nabla$	$403 \pm 2.5 *c\nabla$
			ARF	$6.5 \pm 0.03 *c\Diamond$	$368 \pm 7.5 *c\Diamond$
		BP1	AF	$5.8 \pm 0.02 b\nabla$	$335 \pm 15.0 a\nabla$
			ARF	$5.5 \pm 0.04 d\Diamond$	$125 \pm 10.0 d\Diamond$
		BP2	AF	$5.9 \pm 0.06 b\nabla$	$393 \pm 7.5 cd\nabla$
			ARF	$5.7 \pm 0.04 d\Diamond$	$310 \pm 5.0 b\Diamond$
		BP3	AF	$5.1 \pm 0.07 d\nabla$	$203 \pm 2.5 b\nabla$
			ARF	$4.6 \pm 0.04 b\Diamond$	$125 \pm 5.0 d\Diamond$
	ASH	BE1	AF	$7.2 \pm 0.15 a\nabla$	$1950 \pm 50 a\nabla$
			ARF	$6.8 \pm 0.03 a\Diamond$	$275 \pm 25 a\Diamond$
		BE2	AF	$6.9 \pm 0.01 a\nabla$	$1050 \pm 50 b\nabla$
			ARF	$6.8 \pm 0.11 a\nabla$	$360 \pm 10 a\Diamond$
		BE3	AF	$8.0 \pm 0.13 b\nabla$	$1550 \pm 150 c\nabla$
			ARF	$7.6 \pm 0.05 b\Diamond$	$188 \pm 3 a\Diamond$
		BP1	AF	$7.3 \pm 0.08 a\nabla$	$1375 \pm 125 bc\nabla$
			ARF	$6.9 \pm 0.11 ac\Diamond$	$235 \pm 5 a\Diamond$
		BP2	AF	$7.9 \pm 0.05 b\nabla$	$1600 \pm 150 ac\nabla$
			ARF	$7.0 \pm 0.10 ac\Diamond$	$140 \pm 10 a\Diamond$
		BP3	AF	$7.1 \pm 0.18 a\nabla$	$1350 \pm 100 bc\nabla$
			ARF	$7.3 \pm 0.13 bc\nabla$	$325 \pm 35 a\Diamond$
S. PEDRO SUL (S)	SOIL	BE1	AF	$5.6 \pm 0.02 a$	$200 \pm 0 a$
		BP1	AF	$5.0 \pm 0.24 a$	$200 \pm 5 a$
		BP2	AF	$5.0 \pm 0.13 a$	$193 \pm 3 a$
		BP3	AF	$5.4 \pm 0.23 a$	$163 \pm 8 a$
	ASH	BE1	AF	$6.8 \pm 0.03 a$	$900 \pm 100 a$
		BP1	AF	$6.7 \pm 0.02 a$	$550 \pm 50 a$
		BP2	AF	$6.7 \pm 0.20 a$	$600 \pm 50 a$
		BP3	AF	$6.4 \pm 0.20 a$	$675 \pm 25 a$

Table 2- Aluminum concentrations (%) in soil of non-burnt (NBE) and burnt eucalypt (BE1, BE2, BE3) and maritime pine (BP1, BP2, BP3) slopes at Ermida (E) and S. Pedro Sul (S). Samples were collected 4 weeks after fire (AF) at E and S and 14 weeks later after a rainfall period (ARF) at E. Mean values $\pm$ standard errors are given. Different letters denote statistically significant differences ($p < 0.05$) between sites (for the same survey). Different symbols denote statistically significant differences ($p < 0.05$) between surveys (for each site).

Sampling Area	Type of sample	Site	Survey	Al (%)
ERMIDA (E)	SOIL	NBE	AF	$2.0 \pm 0.03 \nabla$
			ARF	$2.1 \pm 0.14 \nabla$
		BE1	AF	$2.5 \pm 0.11 \text{ a}\nabla$
			ARF	$2.6 \pm 0.22 \text{ a}\nabla$
		BE2	AF	$2.5 \pm 0.21 \text{ a}\nabla$
			ARF	$2.9 \pm 0.09 \text{ a}\nabla$
		BE3	AF	$2.8 \pm 0.04 \text{ a}\nabla$
			ARF	$2.7 \pm 0.25 \text{ a}\nabla$
		BP1	AF	$3.2 \pm 0.07 \text{ a}\nabla$
			ARF	$3.0 \pm 0.06 \text{ a}\nabla$
		BP2	AF	$3.6 \pm 0.11 \text{ a}\nabla$
			ARF	$3.4 \pm 0.18 \text{ a}\nabla$
		BP3	AF	$3.1 \pm 0.13 \text{ a}\nabla$
			ARF	$3.2 \pm 0.02 \text{ a}\nabla$
S. PEDRO DO SUL (S)	SOIL	BE1	AF	$2.0 \pm 0.09 \text{ a}$
		BP1	AF	$2.9 \pm 0.15 \text{ a}$
		BP2	AF	$3.1 \pm 0.06 \text{ a}$
		BP3	AF	$3.2 \pm 0.08 \text{ a}$

Table 3- Mercury budget (g Hg ha^{-1}) in non-burnt (NBE) and burnt eucalypt soils and ashes (BE1, BE2, BE3) collected at Ermida 4 weeks after fire (Post-fire) and 14 weeks later after a rainfall period (Post-rainfall). Mean values $\pm$ standard deviation (SD) are given.

Sampling area	Site	Post-Fire		Post-Rainfall	
		Soil	Ash	Soil	Ash
Ermida (E)	NBE	2.9	-	2.9	-
	BE1	1.9	0.93	2.3	0.17
	BE2	1.9	0.99	2.3	0.11
	BE3	1.8	1.5	2.2	0.14
	E-BE (Mean $\pm$ SD)	1.8 $\pm$ 0.05	1.1 $\pm$ 0.31	2.3 $\pm$ 0.08	0.14 $\pm$ 0.03

Figure 1

Figure 2

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Figure 4

Figure 5

Figure 6

Figure captions

Figure 1- Location of sampling sites (Ermida and S. Pedro do Sul) and design for soil and ash sampling.

Figure 2- Mercury concentrations (ng g^{-1}) and LOI (%) in soils and ashes collected at Ermida (E) and S. Pedro do Sul (S) 4 weeks after fire (AF). Mean and associated standard errors are given. *Asterisks* indicate significant differences for Hg levels and LOI between non-burnt and burnt eucalypt areas at Ermida (BE1, BE2, BE3). Different lowercase and uppercase letters denote statistically significant differences ($p < 0.05$) between areas for Hg levels and LOI, respectively.

Figure 3- Mercury concentrations in soils and ashes collected at Ermida (moderate severity – MS) and S. Pedro do Sul (moderate/high severity – HS). Samples were collected 4 weeks after the fire. Median, 25 and 75 percentiles, maximum, minimum and extreme values (o) are presented. *Asterisks* indicate significant differences between fire severities for both vegetation coverage.

Figure 4- Mercury concentrations (ng g^{-1}) and LOI (%) in soils and ashes collected at Ermida (E) 14 weeks after fire and after a rainfall episode (ARF). Mean and associated standard errors are given. *Asterisks* indicate significant differences for Hg levels and LOI between non-burnt and burnt eucalypt areas in Ermida (BE1, BE2, BE3). Different lowercase and uppercase letters denote statistically significant differences ($p < 0.05$) between areas for Hg levels and LOI, respectively.

Figure 5- Enrichment factors (EF) calculated by the quotient between Hg levels in the soils and ashes collected after rainfall (14 weeks after the fire) and 4 weeks after the fire at Ermida (eucalypt and pine areas).

Figure 6- Variation of Hg levels (ng g^{-1}) with exposure temperature ($^{\circ}\text{C}$) of non-burnt and burnt eucalypt soils from Ermida.