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Effects of post-fire soil stabilisation techniques on trace elements lost by erosion

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Abstract. The effect of two post-fire stabilisation techniques (Seeding and Mulching) on trace element (Al, B, Co, Cu, Fe, Mn, Mo and Zn) losses with eroded sediments was evaluated over a 13-month period following an experimental fire in a steep shrubland of a temperate-humid region (north-west Spain). With time, concentration of extractable Mn, Zn and Cu in sediments decreased, Fe tended to increase and Al, Co, B and Mo varied without a clear trend. Most sediments and trace element losses occurred during the first 3 months post-fire. Compared with the available elements in ash + burned topsoil, the fraction lost with sediments was highest for Mo (10–16%), intermediate for Mn (4%) and Zn (3%) and low for the rest (0.4–1.2%). Although minor effects of stabilisation techniques on element concentrations were found, accumulated mass losses of trace elements decreased 6–12 times in Mulching because of its 10-fold lower soil erosion rate; no significant changes were found in Seeding. Sediment nutrient losses are probably more important than those published for smoke, leaching or volatilisation. Our results suggest that the Zn and Cu enrichment in sediments from the first erosion events increase the risk of downslope water and soil contamination. In conclusion, soil stabilisation techniques are useful to prevent post-fire ecosystem damage.

Additional keywords: Burned Area Emergency Response, experimental fire, sediment, shrubland.

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Introduction

Increasing frequency and extent of anthropogenic wildfires are a global concern because of their ecological effects. The effects of fire on soils modify the soil's physical, chemical and biochemical properties. Soils characteristics are variably affected by fire depending on the burn severity. Burning can reduce organic matter, alter soil structure and porosity, trigger considerable losses of nutrients (through volatilisation, ash entrapment in smoke columns, leaching and erosion), and modify soil biological communities (Certini 2005). Most studies on the effects of fire on soil chemical quality have focussed on evaluating changes in organic matter (C, N) and available macro-nutrients (P, Ca, Mg, Na and K) (Khanna and Raison 1986; Carballas 1997; Couto-Vázquez and González-Prieto 2006; Úbeda *et al.* 2006).

Micro-nutrients, generally present in small quantities but essential for plant development, are of interest in the recovery of burned soils and vegetation. González Parra *et al.* (1996) found that both the total content and the easily reducible forms of Mn increased significantly after fire, because of the Mn supplied by the ash, whereas the exchangeable Mn did not show any variation. Presumably, Fe, Cu and Zn could behave similarly to Mn, although specific works were lacking until recently (Certini 2005). Knowledge of fire effects on micro-nutrients has increased substantially in recent years.

An increase of extractable Mn and Zn after prescribed fires was found by several authors (García-Marco and González-Prieto 2008; Pivello *et al.* 2010; Close *et al.* 2011), although Pereira *et al.* (2011) reported a significant decrease in water-soluble Mn and Zn in ashes compared with the original *Quercus robur* and *Q. suber* litter. For extractable Fe, the published results varied from decrease (García-Marco and González-Prieto 2008; Pereira *et al.* 2011) to no clear trend (Close *et al.* 2011) and even increase (Pivello *et al.* 2010). In the case of Cu, although García-Marco and González-Prieto (2008) did not find a significant change, Pivello *et al.* (2010) reported higher levels in burned soils, and for B it has been reported that its concentrations were higher in soil from burned forests than from unburned forests (Ponder *et al.* 2009). Despite these recent advances, Smith *et al.* (2011) and Stankov Jovanovic

et al. (2011) claimed that, until now, influence of fire on micro-nutrient behaviour and export in sediments is not completely known, primarily because of the lack of specific studies.

Erosion is widely recognised as a prevalent post-fire process (DeBano *et al.* 1998; Robichaud and Brown 1999; Martin and Moody 2001; Cerdà and Lasanta 2005), but whether or not it affects the long-term soil quality and site productivity is still under question (Helvey *et al.* 1985; Emmerich 1999; Thomas *et al.* 1999; Shakesby *et al.* 2002; Robichaud *et al.* 2006). Little is known about nutrient losses associated with the eroded material (de Koff *et al.* 2006; Gómez-Rey *et al.* 2013), especially in the case of micro-nutrients.

To reduce enhanced erosion rates, post-fire stabilisation techniques (e.g. seeding and mulching) of soils must be applied as soon as possible after the wildfire to accelerate development of ground and vegetation cover and to reduce surface runoff and prevent soil erosion (Pinaya *et al.* 2000; Robichaud *et al.* 2000; Vega *et al.* 2005; Wagenbrenner *et al.* 2006; Groen and Woods 2008; Robichaud 2009; Fernández *et al.* 2011, 2012). Despite its undoubted interest, few studies deal with the effects of fire on soil nutrient losses by erosion (DeBano *et al.* 1998; Gabet *et al.* 2005; Robichaud *et al.* 2006; Spigel and Robichaud 2007) and their reduction by post-fire stabilisation techniques (Thomas *et al.* 2000; Robichaud *et al.* 2006; Gómez-Rey *et al.* 2013).

Post-fire stabilisation techniques can potentially alter trace element concentration in the eroded sediments. Enhanced vegetation recovery by grass seeding can increase plant uptake of nutrients and thus reduce their availability in soils and sediments. If the tested techniques modify the runoff-infiltration ratio or reduce preferentially the erosion of some soil fractions, they can, consequently, alter the chemical composition of sediments. Therefore, we hypothesised that seeding and mulching might lead to changes in trace element concentrations in eroded sediments and that changes might depend on the effectiveness of such techniques. Accordingly, the objective of the present study was to evaluate, over 13 months, the effects of two post-fire stabilisation techniques (seeding and mulching) on the losses of eight trace elements (Al, B, Co, Cu, Fe, Mn, Mo and Zn) with the eroded sediments following an experimental fire of low intensity in a steep shrubland. The study site was in the temperate-humid region of north-west Spain, one of the areas with highest fire incidence in Europe (San Miguel and Camia 2009).

Material and methods

Site description and experimental design

The experimental field was located in the Monte Cabalar (42°38′58″N; 8°29′31″W, 660 m above sea level) at A Estrada (Galicia, north-west Spain). The area has a temperate and rainy climate. During the study period (October 2009–December 2010), accumulated precipitation monitored *in situ* was 3036 mm, ~25% higher than those of 2437 and 2256 mm respectively recorded for the same period in the nearest automatic meteorological stations located at Rebordelo-Cotobade (367 m above sea level, 20 km to the south) and Pereira-Forcarei (717 m above sea level, 14 km to the east) (MeteoGalicia, see http://www2.meteogalicia.es/galego/observacion/estacions/estacions.asp, accessed 22 April 2013). The soil, developed over granite and with a slope of 38–54%, is acidic, with sandy loam texture, relatively high organic-matter content and low C : N ratio. Vegetation cover is dominated by gorse *Ulex europaeus* L. with some *Pteridium aquilinum* (L.) Kuhn., *Ulex gallii* Planch., *Daboecia cantabrica* (Huds.) K. Koch and *Pseudoarrenhaterum longifolium* Rouy, with an average height of 123 cm and 100% of ground cover.

After selecting an area of homogeneous slope, orientation, soil type and vegetation cover, 12 experimental plots (30 × 10 m each) were established with the longest dimension parallel to the maximum slope. On June 2009, the shrub was cut and laid down directly on the ground to favour litter and duff combustion, and 3 months later (14–15 October) plots were burned with the backfire technique to favour soil organic cover consumption and soil heating. The rate of fire spread was slow (0.30–0.33 m min^{-1}). The soil temperature reached during fires was monitored with 10 thermocouples (K type) per plot; it was moderate at the mineral soil surface (153°C) and low at 2-cm soil depth (34°C). The fire reduced by 3.5 ± 0.4 kg m^{-2} the initial fuel loading of 3.8 ± 0.2 kg m^{-2}.

To monitor post-fire erosion, the plots were delimited by a geotextile fabric fixed to posts. Sediment fences, made from a geotextile fabric similar to that described by Robichaud and Brown (2002) and located at the downhill portion of the plots, were used for periodic collection of sediments. After the experimental fire, three treatments were arranged in a fully randomised design with four replications. The treatments were: (i) Control, burned plots without any soil stabilisation; (ii) Mulching, burned plots with 230 g m^{-2} of straw mulch and (iii) Seeding, burned plots with a mixture of seeds sown at a rate of 45 g m^{-2} (*Lolium multiflorum*, 35%; *Trifolium repens*, 25%; *Dactylis glomerata*, 20%; *Festuca arundinacea*, 10%; *Festuca rubra*, 5%; *Agrostis tenuis*, 5%). The soil stabilisation treatments were applied on 6 November 2009 manually in order to minimise soil perturbation.

Sampling and chemical analysis of soil, ashes and sediments

Soil samples were taken from the top soil layer (0–5-cm depth) immediately before ('unburned soil', US) and after burning ('burned soil', BS). Immediately after the fire, but before the application of soil stabilisation treatments, 'ash samples' (ashes and charred plant and litter debris) were randomly taken in 10 squares (15 × 15 cm) of each plot, weighed, thoroughly homogenised and combined to give a composite ash sample per plot; then, soil samples were taken from the top soil layer (BS), weighed and combined to give a composite soil sample per plot. The same was done for unburned soil (US) after removing the plant litter. Composite soil samples were sieved (2 mm) and homogenised, then sub-samples were air-dried for chemical analyses. The average concentrations of extractable elements found in these samples (ash, US and BS) are shown in Table 1.

After each sediment-producing rain event, eroded sediments were collected and transported to the laboratory, where they were dried, thoroughly homogenised and weighed. A sub-sample was taken for chemical analysis.

For extractable trace element analyses, soil, ash or sediments (10 g; two replicates per sample) were shaken for 2 h with a mixture of 1 M NH_4Ac and 0.005 M DTPA (soil, ashes or sediments to solution ratio of 1 : 5); the extracts were

Table 1. Concentration of extractable nutrients (mg kg^{-1} DW) in unburned soil (US), burned soil (BS) and ash at the beginning of the study

Values are mean ± standard deviation ($n = 12$)

	US	BS	Ash
Extractable Al	370 ± 65	385 ± 95	208 ± 102
Extractable Fe	747 ± 194	470 ± 148	314 ± 84
Extractable Mn	1.4 ± 0.8	1.8 ± 1.6	153.5 ± 45.8
Extractable Zn	0.92 ± 0.58	1.50 ± 0.45	17.18 ± 5.61
Extractable Cu	0.09 ± 0.17	0.03 ± 0.03	7.52 ± 3.13
Extractable Co	0.09 ± 0.02	0.07 ± 0.02	0.14 ± 0.03
Extractable B	0.11 ± 0.05	0.11 ± 0.03	2.48 ± 0.74
Extractable Mo	0.00 ± 0.00	0.00 ± 0.01	0.04 ± 0.04

filtered through cellulose filter paper and then analysed for trace elements (Al, B, Co, Cu, Fe, Mn, Mo and Zn) by simultaneous ICP-OES (Varian Vista Pro, Mulgrave, Australia). Available B and Mo levels were below analytical equipment detection limits in more than 60% of soil samples analysed.

Statistical analysis

Data on concentrations and mass of trace elements in the sediments from each erosion event were statistically analysed by repeated-measures ANOVA (RM-ANOVA), with time as within-subjects factor and treatment as between-subjects factor, using Greenhouse-Geisser corrections if assumption of sphericity was not met according to Mauchly's sphericity test. The effects of soil stabilisation treatments on the accumulated mass of eroded sediments and trace elements were statistically analysed by one-way ANOVA. The Levene's test was used for verifying the equality of variances among groups. In the case of homoscedasticity, significant differences among the mean groups were established at $P < 0.05$ using the Bonferroni's test for multiple comparisons (RM-ANOVA) or the Tukey's test (one-way ANOVA). In the case of unequal variances, the original data were subjected to the Tukey's ladder of power or to Cox-Box transformations to obtain equality of variances and then significant differences among the mean groups were established as previously explained.

Simple regression models between soil properties as dependent variables and the inverse of the accumulated precipitation as independent variable were explored after checking the fulfilment of the assumptions of linear regressions (independence, homoscedasticity and normality), and the best models were selected maximising the adjusted R^2 and minimising the standard error of the estimated residues. Statistical procedures were performed with SPSS 15.0 for Windows.

Results

Extractable nutrient concentration in sediments

The extractable Al concentration of the sediments varied without a clear trend during the study period (Fig. 1*a*), with values close to that of ashes in the first sediments collected and similar to or higher than those of burned and unburned soil in the other samples (Table 1); in most cases, Al levels in Control and Seeding sediments were even higher than that of burned topsoil and two-fold that in ashes. No significant treatment or treatment × date interaction was shown by the RM-ANOVA.

Through the study period, the concentration of extractable Fe in sediments (Fig. 1*b*) tended to increase but the fitting to either linear or curvilinear regression models was middling (<30% of variance explained, data not shown). Although the sampling date explained 65% of the variance (Table 2), neither treatment nor interaction effect on sediment-Fe concentration was found with the RM-ANOVA. Comparing the sediments collected in the first 5 and last 8 months, the Fe concentration in the former tended to be lower (most values between those of ash and burned soil), whereas in the latter Fe concentration was almost always between those of unburned and burned topsoil, largely doubling that in ash (Table 1).

The initial extractable Mn concentration in sediments was 2/3 that in ashes but 20 and 70 times higher than those in burned and unburned topsoils respectively and, despite a steady decline with time, at the end of the study it was still 4–6 times higher than in the surface layer of burned soil (Table 1, Fig. 1*c*). Extractable Mn concentration was neither affected by the emergency stabilisation treatment considered nor by the treatment × date interaction, but it was strongly influenced by the sampling date (78% of variance explained; Table 2). In all cases with the accumulated precipitation as independent variable, linear and curvilinear (inverse and logarithmic) regression models, explaining 50–60% of the variance, were found for extractable Mn in the sediments (Table 3).

Very high extractable Zn concentrations were found in the first sediments collected: 5–6 times the concentrations in ash and 60–100 times those in burned and unburned topsoils (Table 1, Fig. 1*d*). Zinc concentrations decreased steadily, their values being above those of ash during the first 2–3 months. The RM-ANOVA showed a small, but significant, effect of treatment × date interaction and a strong effect of sampling date on sediment-Zn concentration (36 and 94% of variance explained respectively; Table 2), with highest values in Mulching and lowest in Control plots for the sediments collected 42 ($P < 0.05$), 48 ($P < 0.01$) and 340 ($P = 0.07$) days after fire (Fig. 1*d*). The evolution of extractable Zn concentration in the sediments fits very well to a curvilinear inverse regression model with the accumulated precipitation as independent variable that explained 84% of the variance (Table 3).

In the first sediments collected, extractable Cu concentration was from slightly higher (Mulching) to more than 3-fold higher (Control, Seeding) than in ashes and 100–270 times higher than in the topsoils (Table 1, Fig. 2*a*). These very high initial concentrations decreased by 2 orders of magnitude in the second sampling of sediments, varying then without a clear trend around values 2–6 times higher than in topsoils. As with extractable Mn, extractable Cu was influenced by the sampling date (63% of variance explained; Table 2), but not by treatments or treatment × date interaction. The evolution of extractable Cu concentration in the sediments fits to a curvilinear inverse regression model with the accumulated precipitation as independent variable that explained 46% of the variance (Table 3).

Extractable Co concentration in sediments varied, without any trend during the study, from values above to below the range

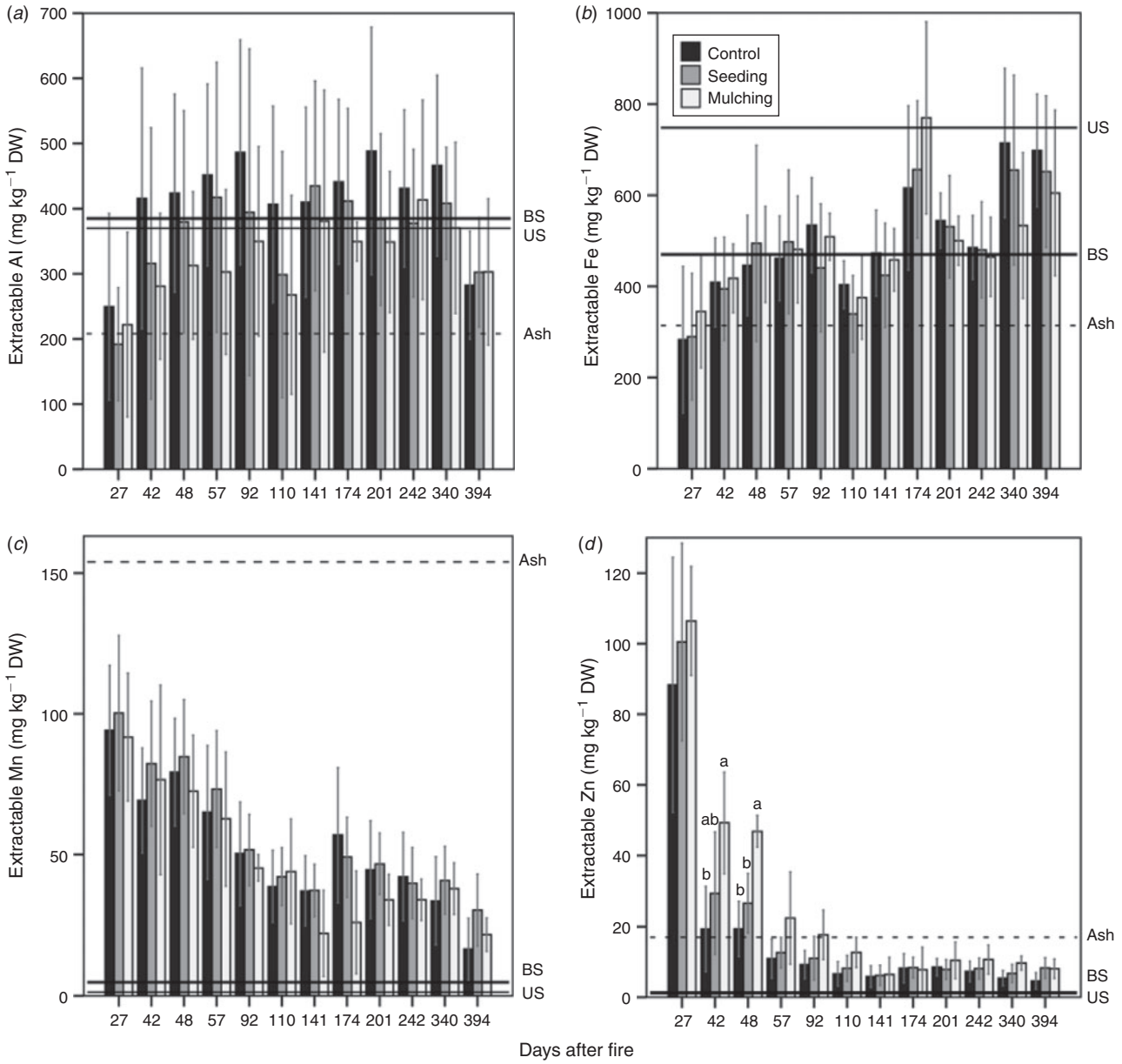

Fig. 1. Evolution of extractable (*a*) Al, (*b*) Fe, (*c*) Mn and (*d*) Zn concentrations in the sediments eroded during the first 13 months after the experimental fire in the Control, Seeding and Mulching treatments. Horizontal lines show the mean values in ash, unburned soil (US) and burned soil (BS) at the beginning of the study. Error bars refer to s.d. and for a given sampling date, different letters (a, b) indicate statistically significant differences ($P < 0.05$) among treatments.

found for ashes and topsoils (Table 1, Fig. 2*b*). As with extractable Mn and Cu, the extractable Co was influenced by the sampling date (87% of variance explained; Table 2), but not by treatment or treatment × date interaction.

On seven of the sampling dates, the levels of extractable B in the sediments were below the detection limits and on the other five sampling dates their concentrations were much closer to those in topsoils than to those in ashes (Table 1, Fig. 2*c*). As a result, the RM-ANOVA showed that most of the variance (98%) was explained by the date of sediment collection (Table 2).

Data on Mo concentration in sediments showed continuous oscillations during the study, ranging from values below the detection limit to over 4- and 40-fold those of ashes and topsoils respectively (Table 1, Fig. 2*d*). The date of sediment collection explained 81% of the variance according to the RM-ANOVA.

Mass of nutrients lost with sediments

The RM-ANOVA showed that the mass of eroded sediments was strongly influenced by the treatment and sampling date (91 and 95% of variance explained), but their interaction explained

Table 2. Results of the repeated-measures ANOVA for trace element contents in sediment (mg kg^{-1}) with treatment (T) as between-subjects and date (D) as within-subjects factor

*, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$; n.s., not significant

	Treatment		Date		Treatment × Date	
	Partial η^2	P	Partial η^2	P	Partial η^2	P
Extractable Al	0.096	n.s.	0.445	***	0.150	n.s.
Extractable Fe	0.010	n.s.	0.645	***	0.165	n.s.
Extractable Mn	0.143	n.s.	0.782	***	0.124	n.s.
Extractable Zn	0.162	n.s.	0.943	***	0.357	*
Extractable Cu	0.364	n.s.	0.634	***	0.204	n.s.
Extractable Co	0.011	n.s.	0.873	***	0.190	n.s.
Extractable B	0.293	n.s.	0.975	***	0.223	n.s.
Extractable Mo	0.353	n.s.	0.808	***	0.225	n.s.

Table 3. Significant regression models ($P < 0.0005$) between trace element contents in sediment (mg kg^{-1}) and the accumulated precipitation (mm) as the independent variable

	Regression model	R^2	Equation
Extractable Mn	Linear	0.549	$y = 88.61 - (0.024\,x)$
	Inverse	0.494	$y = 33.16 + (17\,039\,x^{-1})$
	Logarithmic	0.598	$y = 251.8 - (28.06 \log x)$
Extractable Zn	Inverse	0.836	$y = -4.958 + (22\,638\,x^{-1})$
Extractable Cu	Inverse	0.461	$y = -3.239 + (4855\,x^{-1})$

83% of the variance, showing a stronger effect for sediments in Control and Seeding than for those in Mulching, with more stable values during the study period. The accumulated mass of sediments at the end of the study decreased ($P < 0.05$) in the following order: Control (3897 kg ha^{-1}); Seeding (3117 kg ha^{-1}); Mulching (381 kg ha^{-1}). Very similar results were found for the extractable trace element losses with the sediments; a strong influence of treatment (76–97% of the variance explained, $P < 0.001$), date (81–93% of the variance explained, $P < 0.001$) and treatment × date interaction (64–73% of the variance explained, $P < 0.001$) was observed. However, the effect was somewhat less important for Cu (71, 58 and 34% of the variance explained for treatment, date and treatment × date interaction), and the interaction between factors was weaker for Co (53% of the variance explained, $P < 0.001$).

Relative to Control, the accumulated mass of trace elements lost with sediments at the end of the study period was 59–98% in Seeding but only 7–18% in Mulching (Table 4); differences of Mulching with Control and Seeding were statistically significant ($P < 0.05$–0.01).

The trace elements lost by erosion accounted for 1.4–67.6% and 1.0–44.3% of the amounts supplied by ash in Control and Seeding treatments. These figures were significantly higher than the 0.25–7.5% found in Mulching (Table 4). In all treatments, the percentages were higher for Mo, Al, Fe and Co, intermediate for Mn and Zn, and lower for Cu and B. Taking as reference the extractable nutrients in ash + burned topsoil, losses by erosion were low in Mulching for all elements (0.08–1.7%); the same was true in Seeding and Control for Al, Fe, Cu, Co and B (0.37–1.2%), but not for Zn and Mn (3–4%) and, especially, Mo (10–16%).

Discussion

The lower extractable Al concentration in ashes than in the unburned soil ($P < 0.001$) reflects the low solubility of Al reported for wood ashes (Demeyer *et al.* 2001), but contrasts with the increase in water-soluble Al from ash collected after a prescribed fire in *Quercus* forests (Pereira *et al.* 2011). The similar levels in burned and unburned soil disagree with the reduction in exchangeable Al in surface soils after repeated prescribed fires in a Brazilian cerrado (Pivello *et al.* 2010). These contrasting results are likely related to differences in vegetation cover, fire intensity and extractant used. During the study period, the variations of extractable Al in sediments did not follow any identifiable trend. Besides a significant but weak correlation with sediment pH_{KCl} ($r = -0.405$; $P < 0.05$), related to the predominance of Al in negative charges of exchangeable complex, no relationships with soil characteristics were found; consequently, the factors involved in sediment-Al evolution remained largely unknown.

Significant post-fire decrease of exchangeable (Groeschl *et al.* 1993), water-soluble (Pereira *et al.* 2011) and available Fe (García-Marco and González-Prieto 2008; Ponder *et al.* 2009; Pivello *et al.* 2010; Close *et al.* 2011) has been usually reported. In the same way, compared with the unburned soil, the extractable Fe decreased slightly in the burned soil and significantly in ashes ($P < 0.05$) after our experimental fire. In the sediments, the negative correlation between extractable Fe concentration and pH_{KCl} ($r = -0.538$; $P < 0.001$) agree with the results of Pivello *et al.* (2010) for burned soils and explain partially the increase of sediment-Fe concentration throughout the study. Emergency stabilisation treatments had no effect on sediment Fe concentration. Except for Mulching plots, with values six-fold lower, the amount of extractable Fe lost with the eroded sediments (Table 4) was similar or higher than that of 1.2 kg ha^{-1} year^{-1} reported for a tropical dry savannah forest catchment (Townsend and Douglas 2004). In Seeding and Control plots, the Fe eroded with sediments during the first post-fire year was less than 1% of the ash + burned topsoil Fe pool, but it might represent 30–47% of the extractable Fe in ashes. This could explain the depletion of soil-available Fe in these plots (Gómez-Rey *et al.* 2013) and in surface soils affected by recurrent prescribed fires (Pivello *et al.* 2010; Close *et al.* 2011). Post-fire reduction of available Fe could constitute a fertility problem in soils with low levels of plant-available Fe (García-Marco and González-Prieto 2008).

In agreement with most studies about fire effects on soil total and chemically extractable Mn (Chambers and Attiwill 1994; González Parra *et al.* 1996; De Marco *et al.* 2005; García-Marco and González-Prieto 2008; Close *et al.* 2011; Smith *et al.* 2011), we found higher extractable Mn concentrations in the burned soil ($P < 0.005$) and especially in sediments and ashes, than in the unburned soil. All these authors pointed out that such a post-fire increase was a result of the contribution of ash from burned vegetation and the physiochemical breakdown of Mn complexed with organic matter. This is also likely in our

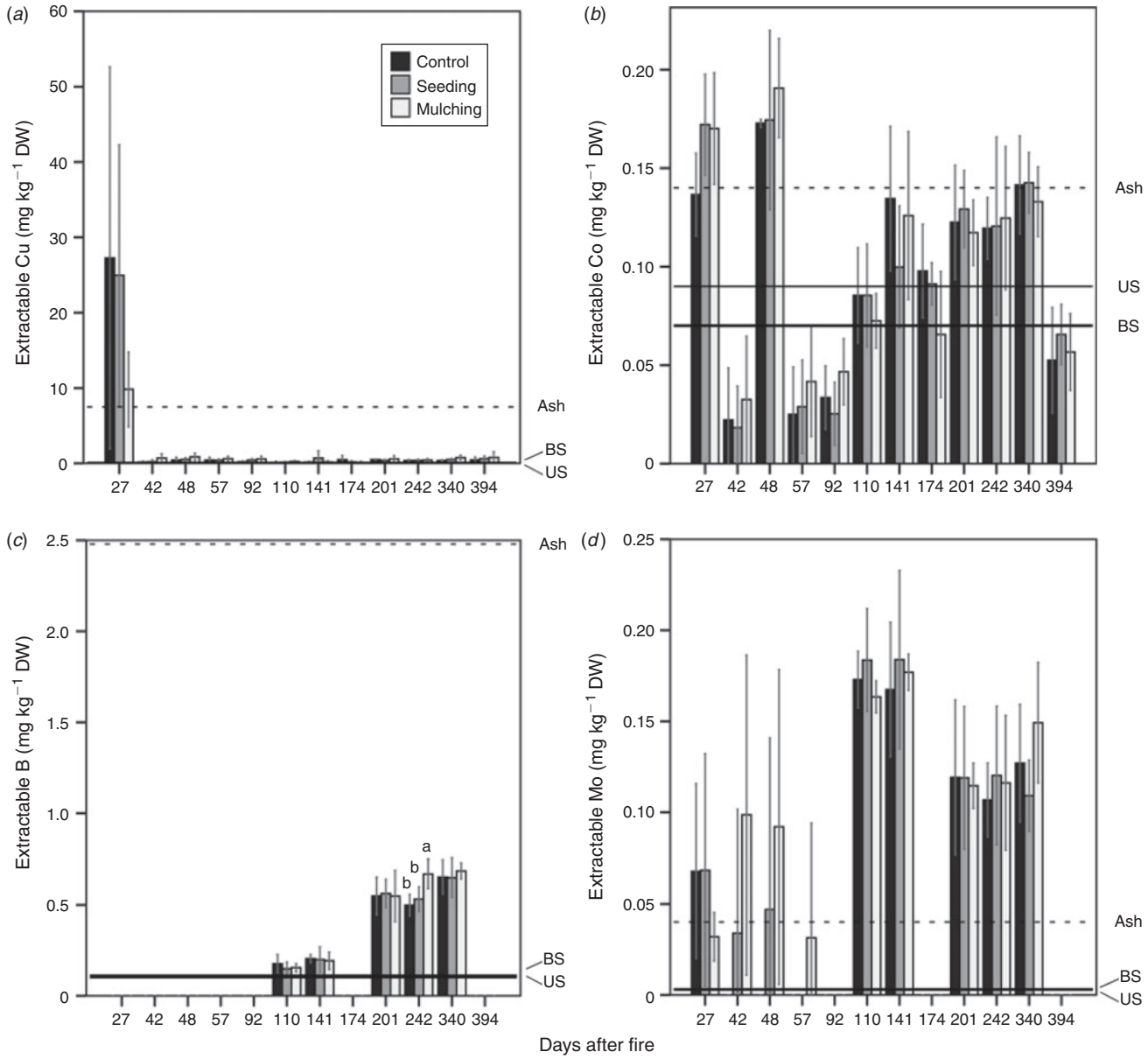

Fig. 2. Evolution of extractable (*a*) Cu, (*b*) Co, (*c*) B and (*d*) Mo concentrations in the sediments eroded during the first 13 months after the experimental fire in the Control, Seeding and Mulching treatments. Horizontal lines show the mean values in ash, unburned soil (US) and burned soil (BS) at the beginning of the study. Error bars refer to s.d. and for a given sampling date, different letters (a, b) indicate statistically significant differences ($P < 0.05$) among treatments.

case, because Gómez-Rey *et al.* (2013) found that sediments of the present study were mainly constituted by charred plant and litter material. Although Pivello *et al.* (2010) found a negative correlation between pH and Mn in burned soils, we found a positive correlation ($r = 0.633$; $P < 0.001$) between pH_{KCl} and extractable Mn. It has been reported that 1 year after a prescribed fire there is no difference in extractable Mn between unburned and burned soils (García-Marco and González-Prieto 2008; Ponder *et al.* 2009). In the same way, we found that the extractable Mn concentration in sediments, unaffected by the emergency stabilisation treatments, decreased steadily with time, indicating that Mn is easily lost; however, 1 year after the fire, the sediments were still notably enriched in Mn compared with the burned topsoil. Consequently, at the end of the study, the amount of extractable Mn lost by erosion (182 g ha^{-1} in Control; Table 4) was 9-fold that in suspended sediments reported by Townsend and Douglas (2004) and accounted for 9–10% of the Mn supplied by ashes and around 4% of ash + burned topsoil Mn reserves in Control and Seeding, with much lower percentages (0.7 and 0.3%) in Mulching.

Fire increases the availability of Zn in soils (García-Marco and González-Prieto 2008; Close *et al.* 2011; Stankov Jovanovic *et al.* 2011) and the same was true in the present study for ashes and sediments ($P < 0.005$), the effects lasting for at least 1 year

Table 4. Accumulated mass of trace elements (g ha^{-1}) lost by erosion in the plots under each treatment (C, Control; S, Seeding; M, Mulching), and percentage of elements in ash and ash + burned topsoil they accounted for

Within each row, different superscript letters show statistically significant differences between treatments for each variable: mass of trace elements; percentage of ash trace elements lost by erosion; percentage of ash + burned topsoil trace elements lost by erosion. $P < 0.05$ for Cu, Co, B, Mo; $P < 0.01$ for Al, Fe, Mn and Zn

	Mass of trace elements			Percentage of ash trace elements lost by erosion			Percentage of ash + burned topsoil trace elements lost by erosion		
	C	S	M	C	S	M	C	S	M
Extractable Al	1783^{a}	1094^{a}	152^{b}	66.34^{a}	40.71^{a}	5.66^{b}	0.91^{a}	0.56^{a}	0.08^{b}
Extractable Fe	1900^{a}	1232^{a}	208^{b}	46.81^{a}	30.35^{a}	5.12^{b}	0.80^{a}	0.52^{a}	0.09^{b}
Extractable Mn	182^{a}	171^{a}	12.7^{b}	9.74^{a}	9.15^{a}	0.68^{b}	4.26^{a}	4.00^{a}	0.30^{b}
Extractable Zn	30.2^{a}	28.2^{a}	5.34^{b}	13.62^{a}	12.71^{a}	2.41^{b}	3.10^{a}	2.90^{a}	0.55^{b}
Extractable Cu	1.35^{a}	1.29^{a}	0.25^{b}	1.39^{a}	1.33^{a}	0.26^{b}	1.23^{a}	1.18^{a}	0.23^{b}
Extractable Co	0.42^{a}	0.41^{a}	0.04^{b}	24.60^{a}	24.01^{a}	2.34^{b}	1.18^{a}	1.15^{a}	0.11^{b}
Extractable B	0.56^{a}	0.33^{a}	0.08^{b}	1.75^{a}	1.03^{a}	0.25^{b}	0.62^{a}	0.37^{a}	0.09^{b}
Extractable Mo	0.36^{a}	0.24^{a}	0.04^{b}	67.64^{a}	44.32^{a}	7.46^{b}	15.59^{a}	10.21^{a}	1.72^{b}

in the latter as found by Stankov Jovanovic *et al.* (2011). The increased Zn concentration in sediments from mulching plots could be associated with changes in pH ($r = 0.70$ and 0.77, $P < 0.01$, for pH_{H_2O} and pH_{KCl} respectively) or to the inputs with the added straw (wheat straw contains 15–70 mg Zn kg^{-1} DW; Plank 1989; Johnson *et al.* 2000). Most of the variance of Zn concentration in sediments was explained by a curvilinear inverse regression model with the accumulated precipitation (Table 3). This result could be due either to (i) fast leaching from burned soil and ashes if Zn is highly soluble, as found by Zhan *et al.* (1996) in wood ash for a similar pH; or (ii) the preferential erosion of Zn-rich particles if Zn is slowly leached from ash, as reported by Menzies and Gillman (2003) and Gafur *et al.* (2004). In the present study, the extractable Zn lost by erosion (30 g ha^{-1} in Control) accounted for 13.6 and 3.1% of extractable Zn in ashes and ash + burned topsoil; these important losses were only significantly reduced (by a factor of six) in the Mulching treatment.

Post-fire Cu dynamics were similar to that of Zn: its availability increased (García-Marco and González-Prieto 2008; Close *et al.* 2011; Stankov Jovanovic *et al.* 2011) and sediments remained enriched in Cu compared with the burned topsoil for at least 1 year. However, the fast and sudden changes of Cu availability in the initial sediments collected (from higher than in ashes in the first erosion event to 2 orders of magnitude lower in the second erosion event) were only observed for this element and are likely related to the evolution of pH ($r = 0.609$; $P < 0.001$) and also to the accumulated precipitation, although Zhan *et al.* (1996), Menzies and Gillman (2003) and Gafur *et al.* (2004) reported that Cu is leached slowly from ash. The strong losses of Cu that occurred during the first erosion event could be due to a flush of organic matter, clay or silt in the runoff following the fire, as suggested by Quinton and Catt (2007) for peaks in Cu concentration observed in some erosion events from agricultural soils. Despite the low absolute amount of Cu lost by erosion (1.3 g ha^{-1} in Control), it accounted for 1.4 and 1.2% of the extractable Cu in ashes and ash + burned topsoil, agreeing with the opinion that erosion of ash could cause relevant losses of Cu from the burned system (Menzies and Gillman 2003; Gafur *et al.* 2004).

No clear trend could be identified for Co concentration in sediments during the study, meanwhile fire effects on Co availability (ash > unburned soil ≥ burned soil) are compatible with those (burned soil ≥ unburned soil) reported by García-Marco and González-Prieto (2008) considering that these authors jointly sampled ashes and burned soil. One year after forest fires, Aref *et al.* (2011) found no effects on Co availability in two of three soils and a significant increase in the third. Although quantitatively small (0.42 g ha^{-1} in Control, Table 4), the amount of Co lost with the eroded sediments was qualitatively important because it accounted for 25% of the extractable Co supplied by ashes and around 1.2% of the extractable Co in ash + burned topsoil. As for most studied elements, Co losses decreased by 1 order of magnitude in Mulching because of the reduction in the amount of eroded sediments.

Boron concentration did not differ between unburned and burned soil and was 20-fold higher in ashes, but the only published reference we found reported higher levels of extractable B in burned forest soils than in unburned ones (Ponder *et al.* 2009). The wide difference between extractable B concentration in ashes and sediments from the first erosion event could be due either to high losses in soluble form, as this element is quickly leached from ashes (Khanna *et al.* 1994) or to a preferential erosion of ash or soil particles impoverished in B. The evolution of extractable B in sediments cannot be discussed because in half of sampling dates it was below the detection limits of the method employed.

The analytical constraints do not allow a sound discussion of Mo results; however, it seemed that, although experimental fire increases only slightly the extractable Mo in soils, ashes were 12–15 times enriched in Mo compared with the burned and the unburned soil. Aref *et al.* (2011) found an enhanced Mo availability in one of three studied soils, and no changes in the other two, 1 year after the wildfires. Our results also suggested that Mo losses with the eroded sediments were quantitatively small (≤0.36 g ha^{-1}, Table 4), but they could be qualitatively important: up to 68 and 15.6% of Mo in ash and ash + burned topsoil in Control, values being approximately 1/3 and 9-fold lower in Seeding and Mulching.

Moreover, soil-available Mo in these plots was below the detection limit (Gómez-Rey *et al.* 2013), highlighting the

Table 5. Range of estimated concentration (mg kg^{-1} DW) and accumulated mass (g ha^{-1}) of trace elements in eroded sediments of the present study compared with reference levels (mg kg^{-1} DW)

A Estrada values estimated considering that 5% of total soil nutrient was removed by DTPA and EDTA extractants (Chen *et al.* 1996; Fernández-Calviño *et al.* 2012); DEC, European Union limit for concentrations of heavy metals in soil receiving sewage sludge application (CEC 1986); Galicia, generic reference levels for protection of ecosystems established for soils in Galicia (Macías-Vázquez and Calvo de Anta 2009); USA, ecological soil screening levels for cobalt (US EPA 2005), copper (US EPA 2006), manganese(US EPA 2007*a*) and zinc (US EPA 2007*b*); Australia, reference levels for ecological investigation established for soils in Australia (DEC 2010)

	A Estrada		Reference levels (mg kg^{-1} soil DW)			
	(mg kg^{-1})	(g ha^{-1})	DEC	Galicia	USA	Australia
Total Al	1337–15 330	3040–35 660				
Total Fe	1946–19 263	4160–38 000				
Total Mn	75–2720	254–3640		850	220–4300	500
Total Zn	0.30–1013	107–604	150–300	200	46–160	200
Total Cu	19–2787	5–27	50–140	50	28–80	100
Total Co	0.1–4.8	0.8–8.4		40	30–120	50
Total B	2.1–15.7	1.6–11.2				
Total Mo	0.2–4.7	0.8–7.2		5		40

importance of the losses of Mo-enriched sediments. Molybdenum is essential for atmospheric N_2 fixation by legumes (Rosolem and Caires 1998), which play an important role in the recovery of N cycling in burnt ecosystems (Hendricks and Boring 1999). Consequently, if erosion leads to a significant depletion of available Mo it could affect the N cycle.

Sediments in the present study were enriched in some trace elements (Zn, Cu, Co and Mo) compared with ashes, a feature not observed for macro-nutrients (Gómez-Rey *et al.* 2013). This enrichment might be related to the preferential transport of fine particles, such as clay or silt, and of organic matter with which these metals could be associated, as has been suggested for Zn and Cu enrichment in sediments from agricultural soils (Quinton and Catt 2007; Fernández-Calviño *et al.* 2008, 2012); moreover, this result is consistent with the enrichment in clay and silt reported for sediments from burned soils (Thomas *et al.* 1999). The increase in these trace elements in sediments was mainly observed during the first months after the fire (but during a year for Mo). It could have several important environmental repercussions because it can adversely affect: (i) the re-vegetation of burned areas, because essential nutrients for plant growth are removed from the soil; (ii) water quality if sediments with toxic concentrations of trace elements reach the surrounding aquatic systems and (iii) soil quality where sediments are deposited if soil contamination thresholds are surpassed. With regard to the last point, during the first months after the fire, concentration of total Mn, Zn and Cu in sediments might exceed the maximum metal concentrations allowed by the EU in soils treated with sewage sludge (CEC 1986) and the reference levels for ecosystems protection established in Galicia (Macías-Vázquez and Calvo de Anta 2009), Australia (DEC 2010) and the USA (US EPA 2005, 2006, 2007*a*, 2007*b*; see Table 5).

Nutrient losses by erosion are significant compared with those by volatilisation or ash entrapment in smoke columns during the fire, as well as with post-fire losses by leaching. On the basis of the data supplied by Alves *et al.* (2010), we estimated that total particulate losses of trace elements with the smoke from the experimental fire they performed in a Portuguese Mediterranean shrubland with a fuel load of 15.6 Mg ha^{-1} amounted to 382, 50, 13 and 0.8 g ha^{-1} for Fe, Zn and Mo and Co. Such values were lower than the estimated total amounts of these trace elements lost by erosion in Control and Seeding treatments (Table 5), although the higher fuel loading consumed in our plots (35 Mg ha^{-1}) should be taken into account. The losses we found from erosion were also higher than those of total particulate Cu (~15 g ha^{-1}) and Zn (~70 g ha^{-1}) by stormwater runoff reported by Stein *et al.* (2012) 1–2 years following wildfires in California. Nutrient losses by erosion we measured also exceeded the particulate losses with runoff from the Cerro Grande Fire area (New Mexico), calculated on the basis of the Gallaher and Koch (2004) data assuming that, relative to pre-fire values, the additional mass of metals transported in runoff during the first year come from the burned area. Boron was an exception to the above with calculated losses (Zn, 23 g ha^{-1}; Mo, 0.34 g ha^{-1}; Mn, 805 g ha^{-1}; Al, 3282 g ha^{-1}; B, 11 g ha^{-1}; Co, 2.4 g ha^{-1}; Cu, 4.8 g ha^{-1}; Fe, 2070 g ha^{-1}) below those we observed in Control and Seeding treatments (see Table 5). For most of the studied nutrients, substantial losses by volatilisation are not expected because their volatilisation temperatures are higher than the flaming temperatures of woody fuels (1100°C), except in the case of Zn (407–907°C).

Except for minor effects on Zn concentration, the stabilisation techniques used in this study did not change trace element concentration in sediments, but Mulching greatly reduced nutrient mass losses by decreasing the amount of eroded sediments. Therefore, it seems that the effectiveness of stabilisation techniques for reducing nutrient losses rely almost completely on their efficacy in controlling erosion. Although the available information on the effectiveness of post-fire stabilisation treatments for erosion reduction is scarce and contradictory, it is well known that at least 60% of ground cover is needed to mitigate erosion rates (Robichaud *et al.* 2000). Seeding has limited ability to reduce erosion, especially in the first post-fire year, because of the time it needs to provide a sufficient ground cover (Groen and Woods 2008), whereas mulching provides immediate ground cover and protection from raindrop impact and overland flow. Under similar climatic conditions to the present

study (Díaz-Raviña *et al.* 2012), the reduction of erosion rates with straw mulching (73–94%) was twice that with herbaceous seeding (34–42%) during the first 4 months after application. However, mulch effectiveness depends on strand length, ground cover amount, thickness of application and longevity (Bautista *et al.* 1996; Wagenbrenner *et al.* 2006; Groen and Woods 2008; Robichaud *et al.* 2010; Fernández *et al.* 2011; Robichaud *et al.* 2013*a*, 2013*b*).

Conclusions

No effects of post-fire soil stabilisation techniques on trace element concentration in sediments were found, except minor effects on Zn. During the study period, the concentration of Fe in sediments tended to increase whereas those of Mn, Zn and Cu decreased. No clear trend was identified for Co, B and Mo. Expressed as percentages of these trace element supplied by ashes, losses by erosion in Control and Seeding were high for Mo, Al and Fe, intermediate for Co, Zn and Mn, and low for Cu and B. Compared with the available elements in ash + burned topsoil, the fraction lost with sediments was highest for Mo, intermediate for Mn and Zn and low for the rest. Our results suggest that sediment losses are probably more important than those reported in the literature for smoke, leaching or volatilisation. Unless effective post-fire soil stabilisation techniques (Mulching) are applied for reducing trace element losses with sediments, fires can affect medium-term soil quality *in situ* (burned soil) and *ex situ* (sediment deposition areas).

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