Flooding by sea and brackish waters enhances mobility of Cd, Zn and Pb from airborne dusts in coastal soils

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HIGHLIGHTS

- Sea or brackish water flooding increases solubility of PTE from airborne dusts.
- Airborne PTE are much more mobilized than geogenic soil PTE.
- Contamination source has strong influence on the amount of PTE dissolved.
- Airborne PTE are made more soluble in arable than grassland soils.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Sea level rise and extreme weather conditions caused by climatic changes enhance the frequency and length of submersion events in coastal soils, causing deposited airborne dusts to get in contact with marine salts.

The behaviour of Cd, Zn and Pb from pedogenetic minerals and from dusts from mining and smelting activities, added to two soils under different agricultural management (arable and grassland) was examined after soil flooding for 1, 7 and 30 days with waters of increasing salinities (0, 4.37, 8.75, 17.25 and 34.5 g L^{-1}). A rain water event following 1 d flooding released an extra amount of metals. Concentration of potentially toxic elements (PTE), pH, dissolved inorganic and organic C were measured in solutions collected by gravity from soil columns. Speciation distribution of leached metals and oversaturation parameters were calculated by Visual Minteq 3.0 and showed that complexation by chloride ions for Cd and fulvic acids for Pb were the drivers of solubilisation, while Zn interacted with both.

Results showed that marine salts enhance up to 300 times leaching of Cd, and several times that of Zn and Pb from contaminated soils and that airborne toxic elements are much more mobilized than pedogenic ones. Smelter exhaust metals, particularly Pb, were made more mobile than those in mine tailings (up to 55 against 0.7 ng μg-1 Pb). Soil management strongly also influence mobilization by saline water: much lower amounts were leached from the grassland soil. Soil organic matter quality (DOC and humification) affects the extent of mobilization.

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The length of the flooding period did not result in coherent time trend patterns for the three metals, probably because of the multiple changes in solution parameters, but leached metals were always highly linearly correlated negatively with pH and positively with DOC.

1. Introduction

Atmospheric deposition of anthropogenic dusts represents a major pathway of potentially toxic elements (PTE) contamination at the soil surface, because silt-size and even larger particles can be transported over long distances and reach rural and even remote areas (Connan et al., 2013; Ghanavati et al., 2019). In the agricultural soils of Europe deposition rates were reported to reach 540 g of Zn and 101 g Pb ha^{-1} y^{-1}, but are lower for Ni and Cd (25 and 2.7 g ha^{-1} y^{-1}, respectively) and correspond to about 40 to 50 % of total Zn inputs, 55 to 70 % of total Ni and Pb and 50 % of total Cd (Nicholson et al., 2003). It has been estimated that from 50 to 93 % of the total input of PTE to agricultural soils in China derives from dry or wet deposition of airborne dusts (Peng et al., 2019).

Settable dust particles produced by mining activities, are mostly deposited within 10 to 70 km away from waste mineral deposits, but even coarse mineral particles, of the size of fine sand grains (up to 450 μm), can actually be carried several hundred kilometres away as a consequence of long range atmospheric transport mechanisms (van der Does et al., 2018). The large amounts of dust produced during mining and smelting activities are well known causes of long range contamination to both marine and terrestrial environments (Trifuoggi et al., 2017; Fernández-Caliani and Barba-Brioso, 2010; Concas et al., 2006). Airborne deposition induce impacts on crop growth by direct accumulation on leaves (Doğanlar and Atmaca, 2011) and by enriching the soil with contaminated clay- and silt-size fractions (Luo et al., 2019; Günthardt-Goerg et al., 2019; Shahid et al., 2017; Alahabadi et al., 2017; Popek, 2017; Schreck et al., 2013).

Compared to other causes of soil contamination by PTE, dust deposition is the most diffuse and makes the largest contribution to soil contamination by both dry and wet deposition. In the proximity of mining areas, annual dust deposition rates can reach 42 g m^{-2}, therefore surpassing, for some elements, the quantity that regulations allow to introduce by application of sewage sludge (Sánchez Bisquert et al., 2017). Following the general implementation of emissions regulations, in many countries the concentrations of several PTE in atmospheric aerosols has decreased in the last years and consequently their inputs to soil from the atmosphere were reduced (Luo et al., 2019; Bai et al., 2005), but the phenomenon is likely to exacerbate in the future because of climatic changes, as dust storms are foreseen to increase in frequency and intensity (Middleton, 2019).

In coastal areas, a rise in PTE contamination impacts could be enforced by another concomitant problem connected with the global climatic change: the sea level rise (SLR) (Kirezci et al., 2020). The fifth IPCC assessment report (AR5) predicts that the terrestrial sea level will continue to rise at higher rates than observed in the past four decades (IPCC, 2013). This will increase both the frequency and length of flooding by sea water in coastal soils. The effects of SRL on soil salinity can be exacerbated by reduced freshwater inputs from the mainland, caused by increasing water withdrawal for agriculture and longer drought spells. Upsurges of saltwater intrusion in soils (Weissman and Tully, 2020) will impact the biogeochemical cycles of most elements, microbiota diversity and emissions of greenhouse gases (GHG) in coastal areas (Mazhar et al., 2022). Additional negative effects may be expected if coastal soils are contaminated by PTE, as soil chemical and biological processes also concur to determine the mobility and redistribution of PTE (Hooda, 2010). Soil salinity intensifies the adverse effects of Cd pollution on plant growth and soil microbial biomass (Usman, 2015; Raiesi and Sadeghi, 2019), leading to the decline of soil microbial activity and its functions (Raiesi et al., 2018; Raiesi and Sadeghi, 2019;

Wang et al., 2019). It also increases the solubility of Pb and thus its mobility and bioavailability in soils because of the high ionic strength favouring the formation of Pb complexes with inorganic ligands (Usman, 2015; Abbaspour et al., 2008; Acosta et al., 2011; Almaroai et al., 2014; Smolders et al., 2015).

Salinization caused by flooding with marine waters of soils exposed to airborne contamination by PTE may therefore impose enhanced ecological risks (Bartkowiak et al., 2020), augmenting the mobility of Cd, Pb, and Zn (Chu et al., 2015). The level of mobilization depends not only on the nature of deposited dusts, such as chemical nature of PTE and particle size distribution, but also on soil characteristics such as dissolved organic carbon (DOC) and pH (Ponting et al., 2021; Correia et al., 2020; Acosta et al., 2011). The prediction of outcomes is complex, as length of the submergence periods is also likely to influence mobilization by affecting the composition of the soil solution and by the effect of reducing conditions that may modify manganese and iron oxides surfaces (Huang et al., 2013). Moreover, even soils with similar pedogenetic background may respond differently if kept under different management (e.g. arable vs. grassland), because of the difference in soil organic matter quality and biological activity. The combined effects of affecting factors such as pH, DOC and dissolved inorganic carbon (DIC), on mobilization of PTE, from different airborne sources and in differently managed soils, by flooding waters of increasing salinity, has never been investigated in a comprehensive experiment.

To shed light on the relative importance of factors affecting the consequences of increasing salinization and length of flooding events on the mobilization of PTE derived from airborne dusts, we therefore compared, in this work, the behaviour of Cd, Zn and Pb contaminants from two types of dusts, i.e. mine tailings and smelter exhaust dusts, added to two soils of similar physico-chemical properties but subjected to different agricultural management (arable and grassland), when exposed to flooding events of different length with fresh water, brackish water of increasing salinity and marine water.

2. Materials and methods

2.1. Soils

The two soils (Chromic Endoskelectric Cambisols) selected for this study are located (46° 08′ 00″ N, 13° 13′ 40″ E) in the upper plain of Friuli-Venezia Giulia (Italy) and belong to two contiguous fields under different land use: arable and grassland. Soils samples were taken with an auger from the surface layer (5–20 cm), sieved (2 mm) and stored moist at 4 °C to preserve biological activity. Part of sample for chemical analyses has been air-dried. Their physico-chemical properties and contents of PTE are reported in Table 1. Soil pH was measured at a 1:2.5 soil to water ratio. Total inorganic carbon, total organic carbon (C$_{org}$) and total nitrogen (TN) contents were assessed with a CHNS Elemental Analyzer (Vario Microcube, Elementar, Langenselbold, Germany). Carbonates were calculated by difference, subtracting the organic carbon (HCl treated soil) from the total carbon content. Soil texture was measured in a Bouyoucos' cylinder with an ASTM 152H hydrometer.

Cation exchange capacity (CEC) was measured with BaCl$_2$ buffered at pH 8.2 with triethanolamine (TEA) (Mehlich, 1953). Non-humic (non-phenolic) and humic organic C were extracted by a single extraction with 0.1 M Na$_4$P$_2$O$_7$ plus 0.1 M NaOH and separated by solid phase extraction (SPE) on cross-linked polyvinylpirrolidone (PVP) (De Nobili et al., 2008). Soluble organic carbon (DOC), was extracted following Yin et al. (2002) and measured by a Shimadzu TOC analyzer.

Table 1

Physico-chemical properties of the arable and grassland soils. PTE concentrations are reported as mean $\pm$ standard deviation.

Soil type	Arable soil	Grassland soil
Clay (%)	17	9
Silt (%)	38	40
Sand (%)	45	51
WHC[a] (mL/100 g)	63	71
Carbonates (g Kg^{-1})	1	2
pH	5.7	6.0
CEC (cmol Kg^{-1})	21.5	20.5
Corg (g Kg^{-1})	14.2	16.8
TN (g Kg^{-1})	1.4	1.8
Non-humic to humic extractable C ratio	0.7	0.5
Total Fe (μg g^{-1})	32,309 $\pm$ 1,852	29,867 $\pm$ 1,687
Total Mn (μg g^{-1})	1,297 $\pm$ 112	1,663 $\pm$ 72
Total Cd (μg g^{-1})	1.91 $\pm$ 0.02	1.80 $\pm$ 0.23
Total Pb (μg g^{-1})	34.4 $\pm$ 2.2	43.2 $\pm$ 4.5
Total Zn (μg g^{-1})	72.2 $\pm$ 4.3	70.7 $\pm$ 5.4

[a] WHC: Water Holding Capacity.

2.2. PTE sources

Fine mine tailing dust (MT) was collected from abandoned flotation ponds deposits at the site of a blenda and galena mine (Cave del Predil, Friuli Venezia Giulia, Italy - 46° 26′ 36″ N, 13° 34′ 10″ E). The dust contained Cd 22 $\pm$ 2 μg g^{-1}, Pb 5194 $\pm$ 75 μg g^{-1} and Zn 11,512 $\pm$ 270 μg g^{-1}. Smelter exhaust dust (SE) was collected from the stack of a Pb smelter in Žerjav (Meza Valley, Slovenia - 46° 28′ 55″ N, 14° 52′ 05″). The major PTEs were Cd 0.8 μg g^{-1}, Pb 40,754 $\pm$ 6903 μg g^{-1} and Zn 17 $\pm$ 6 μg g^{-1}.

The crystallographic compositions and particle size distributions of the two dusts are reported in the Figs. S1 and S2 of the supplementary materials.

2.3. Artificial seawater and synthetic rain

Artificial seawater (SW) was prepared according to the standard ISO 10253:2006 and contained all the main salts present in natural seawater: NaCl$_2$ (26.7 g L^{-1}), MgCl$_2$ (2.2 g L^{-1}), MgSO$_4$ (3.2 g L^{-1}), CaCl$_2$ (1.2 g L^{-1}), KCl (0.7 g L^{-1}), NaHCO$_3$ (0.2 g L^{-1}), H$_3$BO$_3$ (0.05 g L^{-1}).

Synthetic rainwater (RW) was prepared dissolving 1.11 g L^{-1} CaSO$_4$, 1.50 g L^{-1} NH$_4$Cl, 1.92 g L^{-1} NaNO$_3$ and 0.32 g L^{-1} sodium acetate (C$_2$H$_3$NaO$_2$) in distilled water (Letardi et al., 2017).

2.4. Experimental plan

Contaminated surface soils were prepared by mixing uncontaminated 2 mm-sieved moist soils (equivalent dry weight 300 g) with either mine tailings (7 g) or smelter exhaust dusts (0.95 g). These levels of contamination were chosen in order to achieve with both dusts a comparable contamination level for at least one element (i.e. Pb) and are representative of a high-medium deposition level. Soils were then preincubated moist at 25 °C for one week.

Two leaching experiments were conducted on artificially contaminated soils and non-contaminated control soils, simulating: a) a short-term inundation (1d) by sea or brackish waters followed by a rain event, or b) a medium (7d) and long-term (30d) inundation.

The flooding treatments (1d, 7d and 30d) were imposed using distilled water (SW0) brackish water and SW at four levels of salinity, i. e. 4.37 g L^{-1}, 8.75 g L^{-1}, 17.5 g L^{-1} and 34.5 g L^{-1} (SW1), which corresponded to serial dilutions of SW from 1, to 1/2, 1/4, and 1/8 of sea water concentration.

Short-term flooding (first experiment) was imposed in 50 mL plastic syringes equipped with a valve, on moist soil aliquots, corresponding to 20 g dry weight, by slowly pouring 25 mL of distilled water (control) or SW from the top of the syringe. After 24 h of equilibration, the valve was opened and the solution leached from the nozzles by gravitational pull was collected. Mobilization by rain was simulated on soils that had been exposed to 1d flooding and draining. Soils were left to equilibrate for one more day at room temperature (about 23 °C) and 25 mL of RW were then added and collected immediately after leaching.

Prolonged flooding (second experiment) was imposed on aliquots of moist soil corresponding to 20 g of dry soil, that were kept submerged under 25 mL of SW in 50 mL test tubes. The test tubes were incubated at 25 °C for 7 or 30 days maintaining a constant layer between 3 and 4 cm of water above the soil by replacing eventual weight losses. At the end of the incubation period, tubes were swirled to suspend soil and centrifuged (4000 rpm) for 20 min to separate the supernatant solution for analyses.

All solutions were analysed for dissolved organic and dissolved inorganic C (DOC and DIC), electrical conductivity (EC), pH and PTE concentrations.

2.5. Analysis of potentially toxic elements

The concentrations of Cd, Pb, and Zn were measured in soils, MT dust, SE dust and solutions collected after the described experiments.

Digestion was carried out according to the USEPA 3052 method (USEPA 3052, 1995). Samples of mine tailings and smelter dust (0.3 g) and soils (0.5 g) were placed in Teflon tubes and treated with 10 mL of 67 % HNO$_3$. Digestion was carried out at 180 °C for 10 min by placing tubes in a microwave irradiation oven. After digestion, all extracts were quantitatively transferred to 20-mL certified flasks, brought to volume with ultrapure water (Millipore Direct-Q System) and then filtered with 0.2 μm Whatman polytetrafluoroethylene (PTFE) membrane filters. Similarly, solutions collected during the experiments were filtered with 0.2 μm Whatman filters. Filtered solutions were diluted with reagent grade water and scandium was added as internal standard (1 mg L^{-1}).

Metals were detected and quantified by plasma optical emission spectrometry (ICP-OES 5800 Agilent technologies). The calibration was performed using 0.2 to 20 μg mL^{-1} standard solutions prepared in 0.67 % ultrapure nitric acid from a 1000 ppm multielement certified solution (Merck solution IV). The method detection limit (MDL) was calculated for each element as 3 times the standard deviation of a blank solution.

2.6. Speciation modelling

In order to rationalize the speciation of metals in the analysed solutions at equilibrium with the expected solid phases and CO$_2$ dissolved at atmospheric pressure, data was computed with Visual Minteq 3.1 (Gustafsson, 2011), using measured PTE concentrations, pH, DOC and DIC values. Interactions with DOC were computed by the Nica-Donnan model (Kinniburgh et al., 1996) according to parameters included in the program.

3. Results

After only 1 day of contact with artificial brackish waters of increasing salinity, the mobility of all the examined PTE, increased for both soil management types in the uncontaminated control soils (Fig. 1) and even more so in the contaminated soils for both soil managements and dust types (Figs. 2 and 3).

Even the amounts released from the soil columns by synthetic rain water (RW) increased, if the rain event followed 1d flooding by saline waters. From these soils, the simulated rain event displaced much larger amounts of PTE than expected from dilution calculations based on the amount of solution retained by soil columns (Fig. S3 in supplementary materials). On the contrary, in the case of soils that had been flooded with water that contained no dissolved salts, the amounts released by the simulated subsequent rain event were always lower than those that
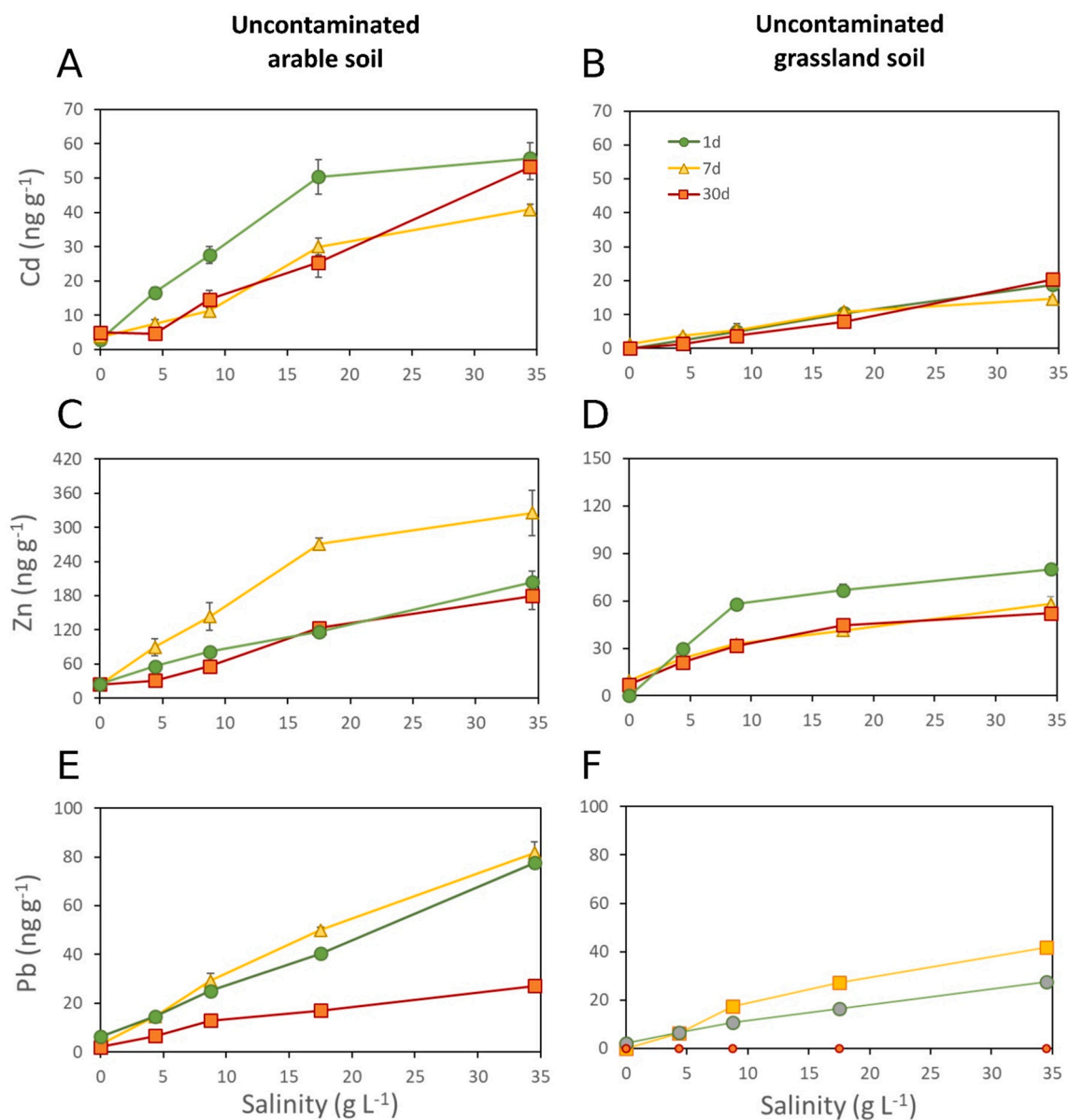
Fig. 1. Amounts of Cd, Zn and Pb mobilized (ng g^{-1} dry soil) from the uncontaminated arable (left) and grassland (right) control soils after 1, 7 and 30 days of flooding with waters of increasing salinity. Data points are averages of replicates (n = 3) and bars represent standard deviation.

could result from the displacement of the solution volume retained by the soil columns. This suggested the possibility that equilibrium might have not been reached during 1d of flooding, so that further dissolution occurred in the retained water. Soils were therefore also subjected to medium (7d) and long (30d) flooding periods.

In control soils (Fig. 1), the slower dissolution of pedogenically inherited minerals containing PTE was also suggested by the fact that the amounts of leached PTE all displayed highly significant linear dependence with salinity after 30d, but deviate from linearity when soils had been flooded for shorter periods.

3.1. Effect of soil management

The DOC of the solutions directly extracted from soils that were not exposed to flooding increases in waters of increasing salinity and, although the two soils are very close in composition and, in particular, have a similar organic C content, the grassland soil releases significantly more C than the arable soil at all levels of salinity (Fig. S4 in supplementary materials). The DOC measured in the leached solutions,

however, also varied with flooding time and dust source (Tables S1 and S2 in supplementary materials). Also the pH and dissolved inorganic C (DIC) of solutions leached from the two soils differed in all treatments.

Significantly larger amounts of Cd, Pb and particularly Zn were leached from the non-contaminated arable, compared to the non-contaminated grassland soils (Fig. 1), in spite of the fact that the two soils had about the same PTE content (Table 1). Also from the contaminated soils, saline waters released larger amounts of PTE from the arable than from the grassland soil, irrespectively of the source of contamination (Figs. 2 and 3). However, considering the normalized amounts (ng mobilized per total mg of metal) of PTE leached at the largest salt concentrations, this remains always true for the SE contaminated soils, whereas differences are actually not always significant for Zn and Pb after 1d in the case of MT contaminated soils (Figs. 4 and 5).

3.2. Effect of contamination source

A further insight can be obtained by considering amounts of PTE
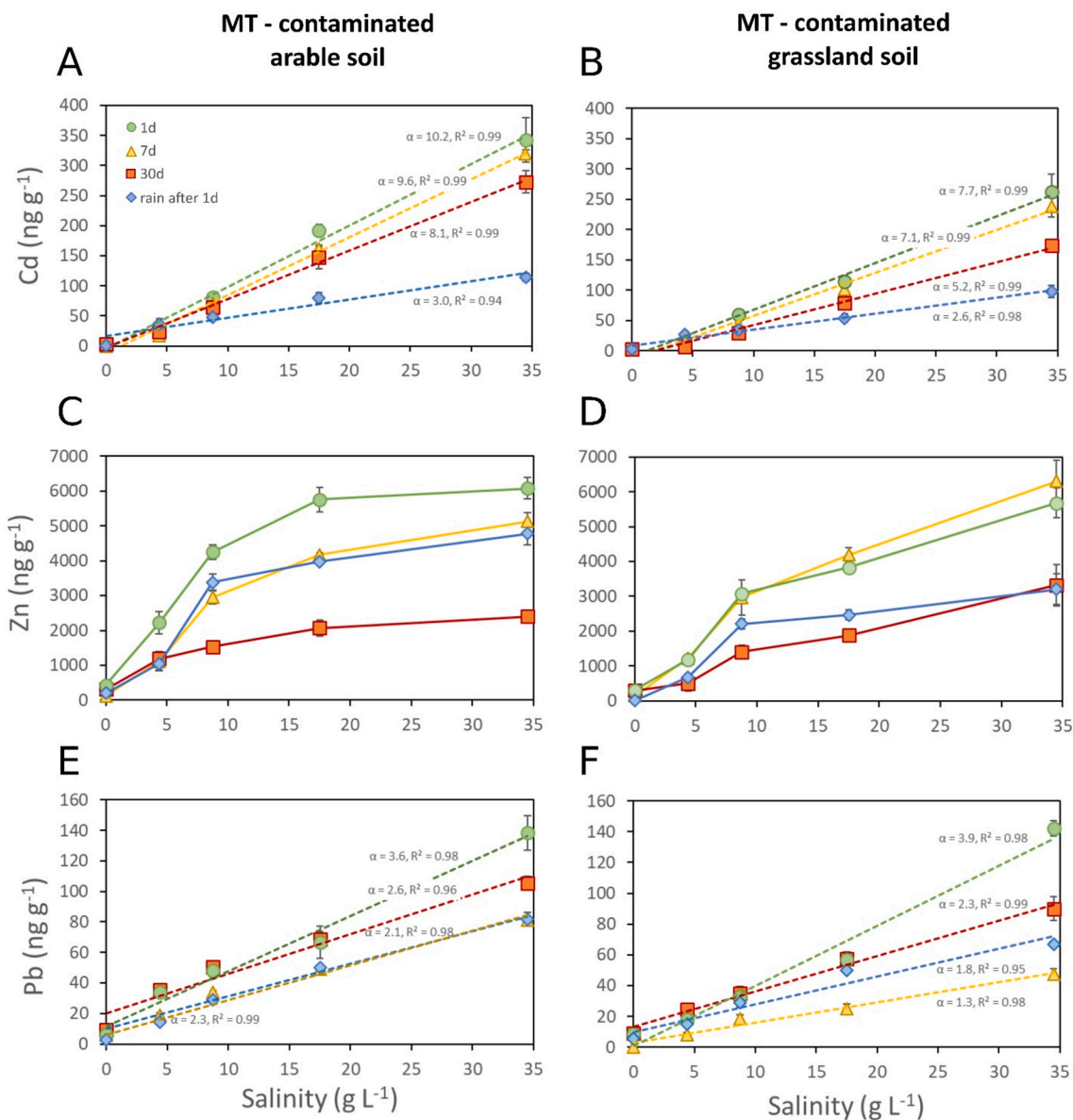
Fig. 2. Amounts of Cd, Zn and Pb mobilized (ng g^{-1} dry soil) from the mine tailings (MT) contaminated arable (left) and grassland (right) soils by waters of increasing salinity and by a simulated rain event that followed 1d flooding. Data points represent averages of replicates (n = 3) and bars represent standard deviation. Data points are interpolated by linear regression (dotted lines), when r^2 > 0.90.

normalized to the total soil content: at the highest salinity level (34.5 g L^{-1}), much larger normalized amounts of PTE were dissolved by marine water from the SE than from the MT contaminated soils (Figs. 4 and 5).

The two dust sources had different mineralogical composition and particle size distributions: the MT dust, being derived from processing of a blenda ore embedded in carbonatic rocks contained mostly mineral sulphides and sulphates, whereas the SE dust contained oxides (Figs. S1 and S2 in supplementary materials).

The two dusts also differed in their particle size distribution: the MT dust was mostly composed of medium to very fine sand particles (500–60 μm) (54.6 %) with only 13 % by weight in the range of silt (2–60 μm), whereas the SE dust contained 38.1 % of silt particles and was mostly composed (42.4 %) of clay-size particles (< 2 μm) (Fig. S2 in supplementary materials). Size distribution apparently affected dissolution at higher salt concentrations, as could be suggested by the levelling off of the concentration trends of Zn in MT contaminated soils (Fig. 2C and D). In fact, the leachates from soil flooded for 30d displayed a linearly increasing trend, but this was not the only affecting factor.

However, Cd (Fig. 2A and B), showed a nearly perfect linear increase in mobility with increasing salinity in both soils after all flooding periods. Conversely, in leachates collected after 1d, in spite of the lower level of contamination reached for this metal with the addition of SE (1.95 versus 11.96 μg Cd g^{-1} soil) and of the smaller size of contaminating particles, Cd displayed, especially in the arable soil, a tendency to level off at the two highest salt concentrations (Fig. 3A).

When flooding with saline water at the maximum salt concentration was prolonged for 7 and 30 days of flooding, the amount of Cd leached per gram of soil from the MT contaminated arable and grassland soils decreased slightly (Fig. 2A and B), while the amount of Cd mobilized from SE contaminated soils after 7 and 30 days was significantly larger (Fig. 3A and B). This remains true (Figs. 4 and 5) considering the normalized amounts leached (ng mobilized μg^{-1} metal in soil).

Airborne dust source effects are immediately evident in the case of Pb, considering that the contaminated soils were added about the same amount of this element (1852 and 1970 μg g^{-1} with MT and SE, respectively), because much more Pb was mobilized from SE than from
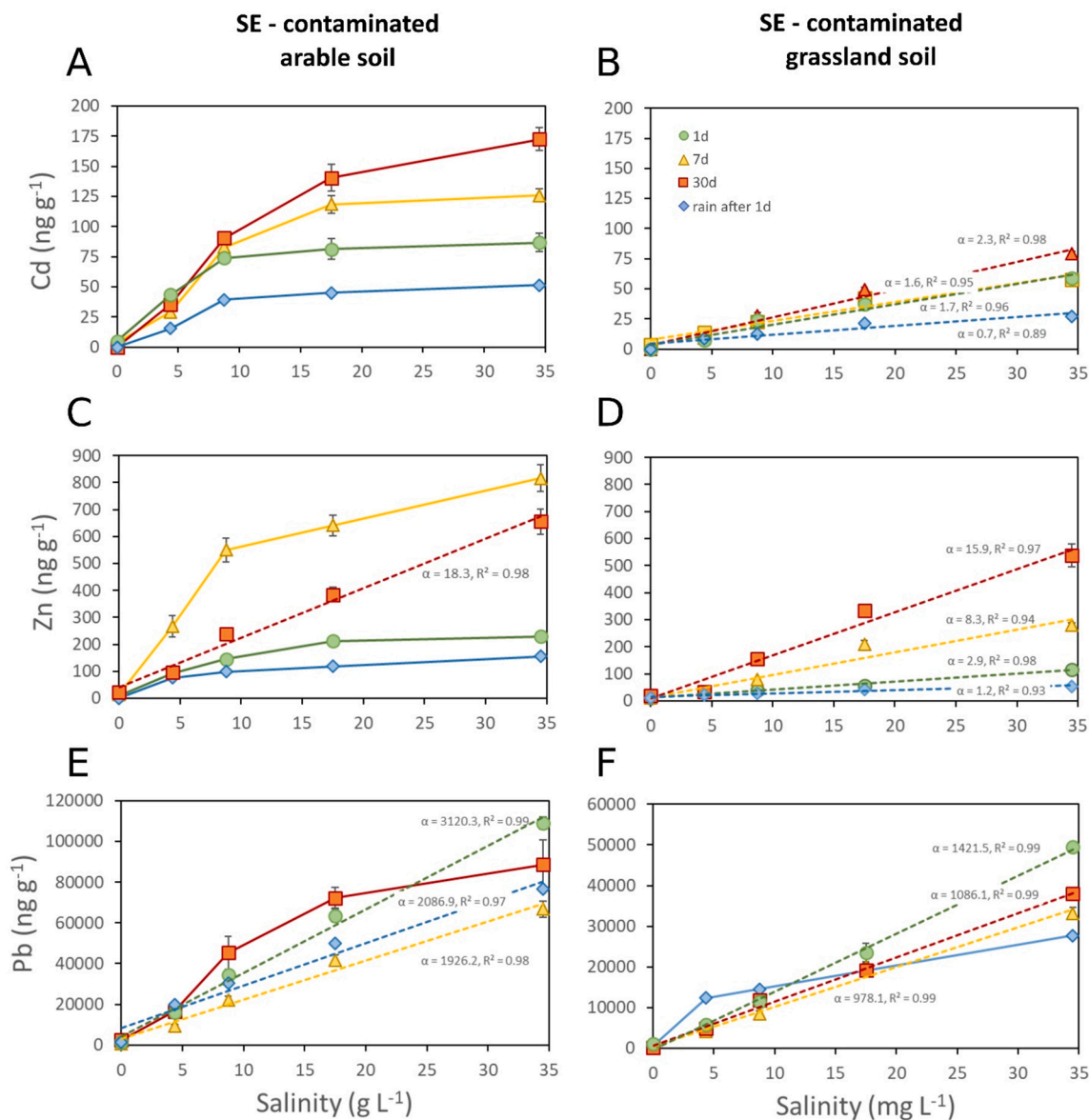
Fig. 3. Amounts of Cd, Zn and Pb mobilized (ng g^{-1} dry soil) from the smelter exhaust (SE) contaminated arable (left) and grassland (right) soils by waters of increasing salinity and by a simulated rain event that followed 1d flooding. Data points represent averages of replicates (n = 3) and bars represent standard deviation. Data points are interpolated by linear regression (dotted lines), when r^2 > 0.90.

MT contaminated soils. In particular, in soils flooded for 7 or 30 days, with water of increasing salinity, Pb mobilization trends from both sources were well described by linear models, but these displayed significantly different slopes (Figs. 2E, F, 3E, and F), as much more Pb was solubilized from the SE dust.

Zinc mobility displayed, in all cases, a tendency to level off at higher salinity (Fig. 2C and D), notwithstanding the fact that in the SE contaminated soils the amount of added Zn was much lower, resulting in lower concentrations of the element in the leached solutions. The type of source contamination also influenced the effect of longer submergence periods: larger amounts of Zn were mobilized from SE in both arable and grassland soils after 7 and 30 days than after 1d (Fig. 3C and D).

3.3. Effect of flooding time

Increasing the length of the flooding period did not result in coherent time trend patterns, probably because of the multiple changes registered in the many parameters involved. Flooding had a significant effect on the composition of the leached solutions. In fact, it affected the DOC, the pH and DIC of the water phase (Tables S1 and S2 in supplementary materials), among these, pH and DOC where significantly correlated with the amount of mobilized PTE. Application of linear regression models between dissolved PTE concentrations and solution parameters affected by flooding time showed significant correlation with pH and DOC (Figs. 6 and 7), but not with DIC (data not shown).

In both arable and grassland soil the amounts of Cd mobilized at the highest salinity level from MT dust decreased with flooding time. The same happened for Zn, whereas Pb displayed a minimum in mobility after 7d. In the case of SE contaminated soils, the amount of Cd mobilized increased with time, whereas that of Zn decreased from 7 to 30 days of flooding in the arable soil, but increased in the grassland soil.

3.4. Speciation modelling

The combined effects of salinity, pH, DOC and DIC on the speciation and solubility of potentially formed species were modelled with Visual

MT - contaminated soils
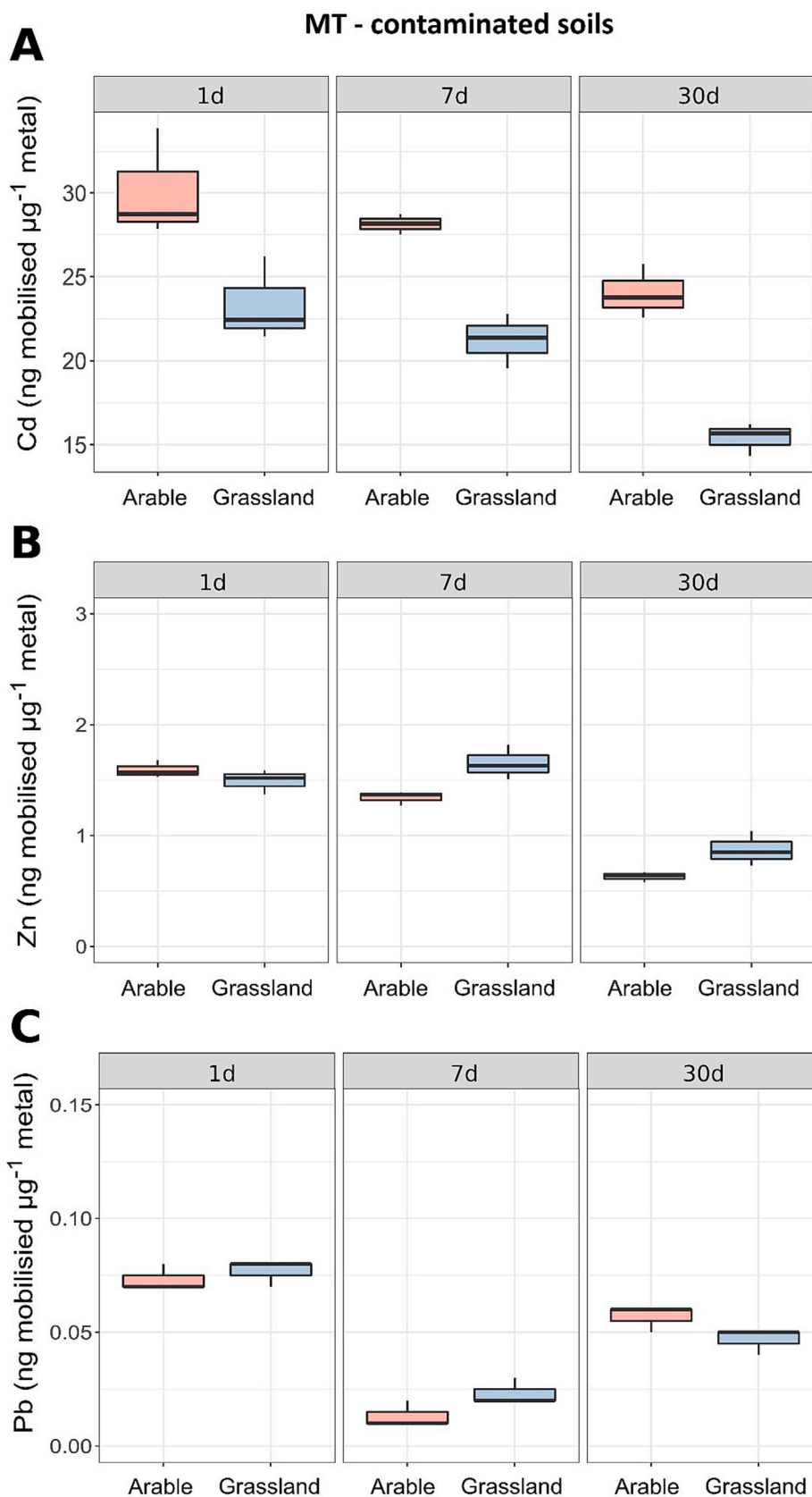
Fig. 4. Normalized amounts of Cd, Zn and Pb (ng per μg^{-1} of metal in soil) mobilized from the mine tailing dust (MT) contaminated arable (left) and grassland (right) soils by artificial seawater (34.5 g L^{-1}).

SE - contaminated soils
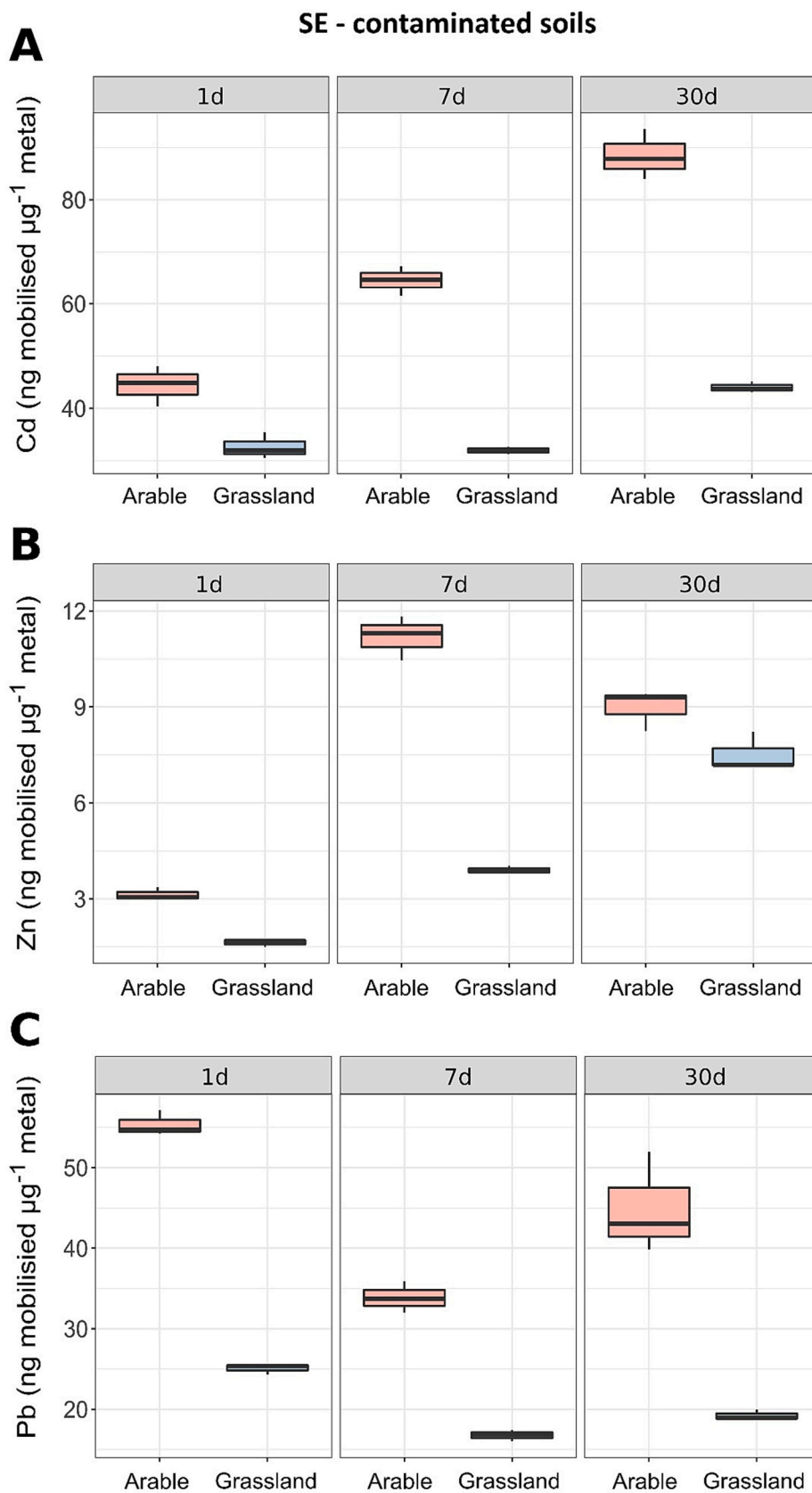
Fig. 5. Normalized amounts of Cd, Zn and Pb (ng per μg^{-1} of metal in soil) mobilized from the smelter exhaust dust (SE) contaminated arable (left) and grassland (right) soils by artificial seawater (34.5 g L^{-1}).

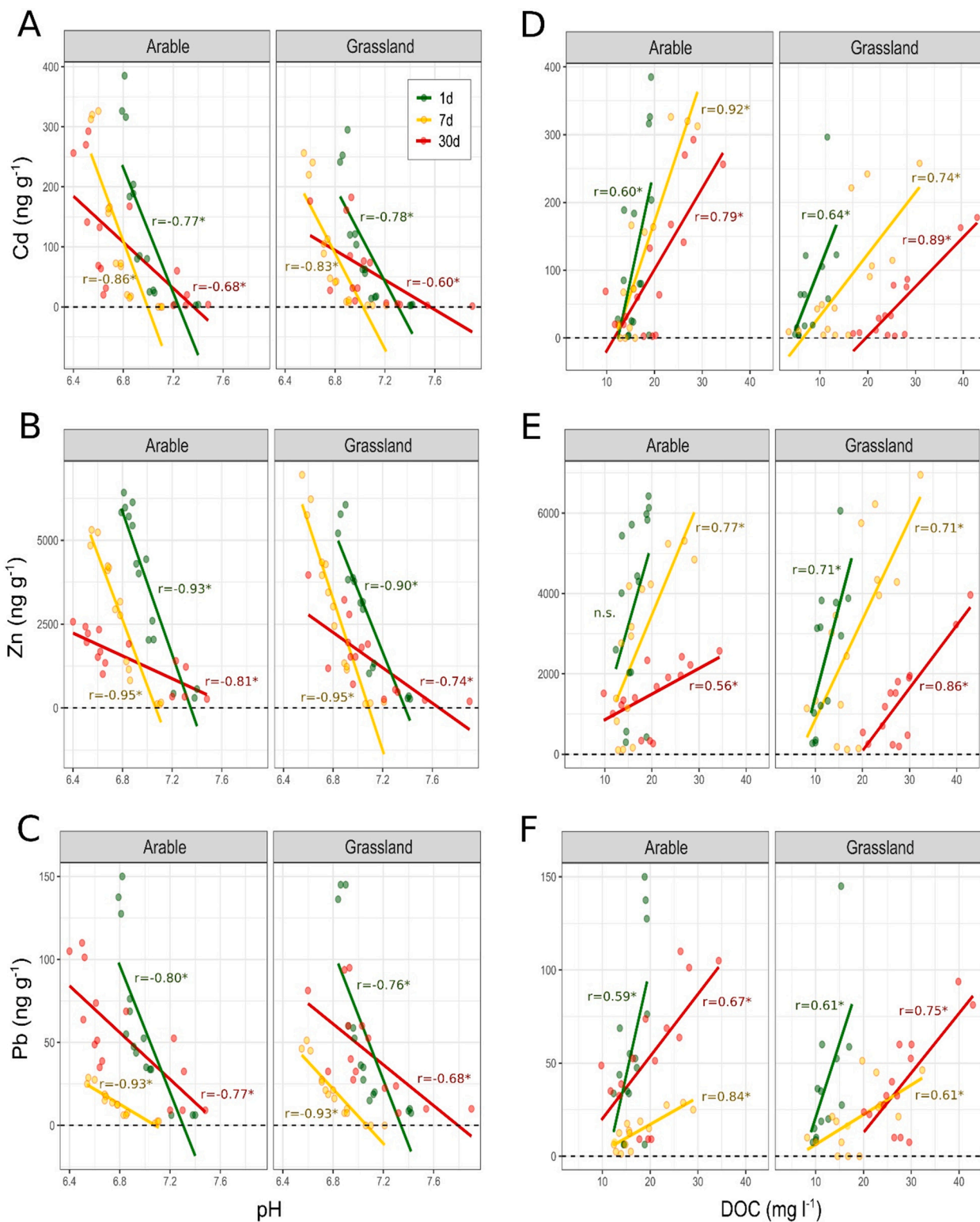# MT - contaminated soils

Fig. 6. Linear correlations between PTE mobilized from mine tailing (MT) contaminated arable and grassland soils and pH and DOC of leached solutions, after 1, 7 and 30 days of flooding. Asterisk of r-values indicate statistically significant linear regressions ($p < 0.05$).
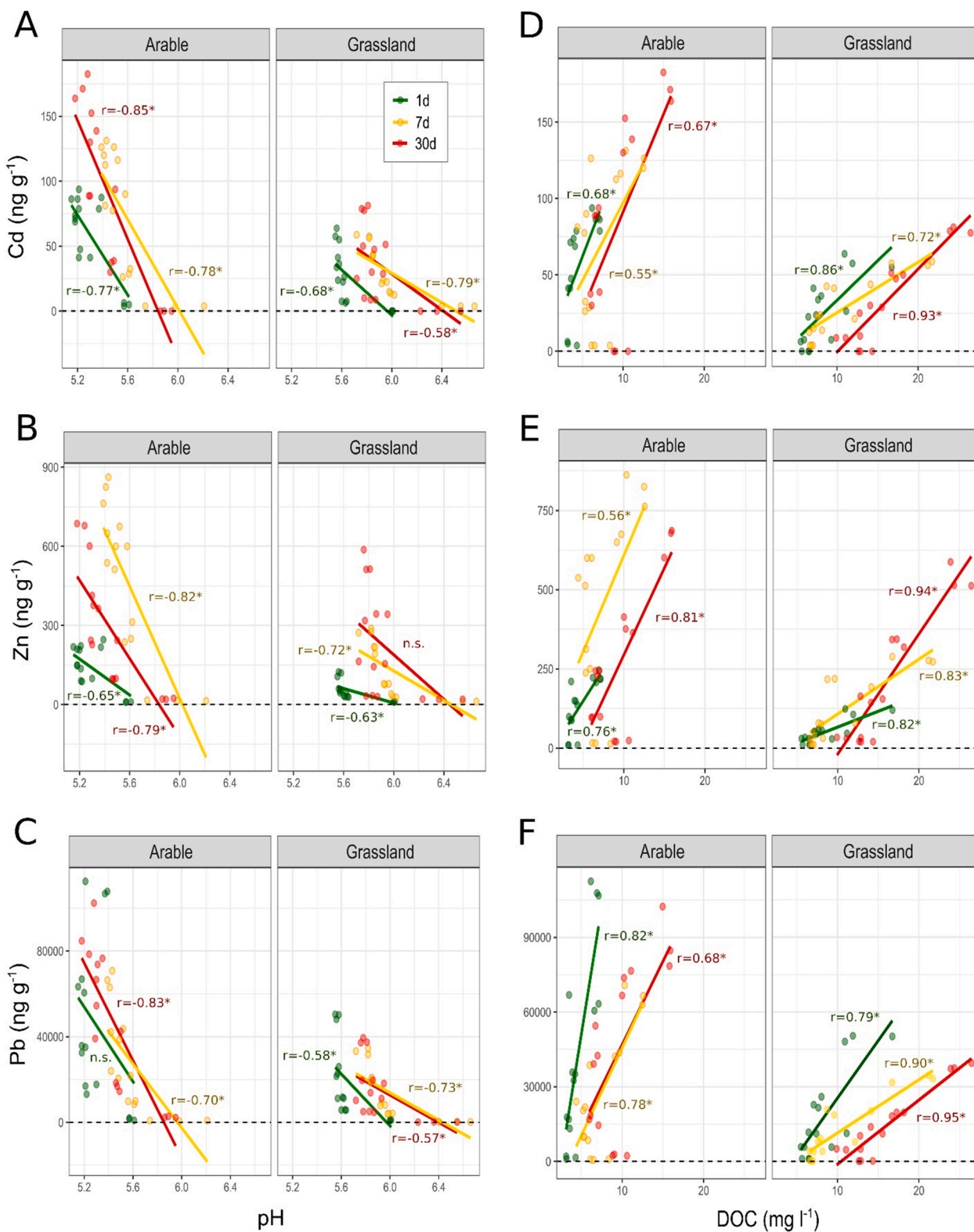
SE - contaminated soils

Fig. 7. Linear correlations between PTE mobilized from smelter exhaust (SE) contaminated arable and grassland soils and pH and DOC of leached solutions, after 1, 7 and 30 days of flooding. Asterisk of r-values indicate statistically significant linear regressions (p < 0.05).

MinteQ 3.1.

3.4.1. Speciation of Cd, Pb and Zn leached from contaminated soils by non-saline water

Modelling shows that the small amount of Cd (4 µg L^{-1}) mobilized from the SE contaminated arable soil by non-saline water (Table S3) after 1d was mostly leached in association with DOC: either as an electrostatically held cation within the Donnan layer (48 %), or as fulvic acids (FA) complexed metal (26 %). There were virtually no changes in its speciation distribution with flooding time from 1 to 7 days. The Cd concentration in the solution leached after 30 days was below detection limit, so modelling results cannot be considered.

Similarly, Zn was mostly (60 to 77 %) associated to DOC, but only as electrostatically held ion and from 23 to 40 % of it was mobilized as free Zn^{2+} ion. The proportion of free ion decreased with prolonged flooding, reaching a minimum after 30 days (Table S3).

Lead, the most abundant PTE in the solutions leached from SE contaminated soils, was also mostly associated to DOC (>70 %), but the amount complexed by FA greatly increased after 7 and 30 days reaching respectively 76 and 68 % of the total.

In non-saline solutions leached from the MT (Table S3) contaminated arable soil Cd (3 µg L^{-1}) was mostly leached as complexed by FA, but the concentration of the element in the solution leached after 30 days was below detection limit. Zn in this case was in large part leached as free Zn^{2+} ion and practically all Pb (>90 %) was complexed by FA.

All solutions were undersaturated with respect to all possible species considered by the model. In non-saline solutions leached from the MT contaminated arable soil, after 1d Cd mostly complexed by FA, this portion reaches >80 % after 30d, Zn was mostly leached as free Zn^{2+} ion (>60 %) and this species proportionally increased with time. >70 % Pb was complexed by FA after 1d and it reached >90 % after 30d.

In the grassland soil contaminated by SE Cd was mostly complexed by FA, this proportion reaches >80 % after 30d. Zn was mostly leached as free Zn^{2+} ion (>60 % and increasing with time) and >70 % Pb complexed by FA after 1d reached >90 % after 30d.

The speciation of PTE was similar in leacheates from the MT contaminated grassland soil, except that Zn, although it was mostly leached as free Zn^{2+} ion, was increasingly associated with carbonate and bicarbonate ions, this fraction accounted for >30 % of the leached element after 30 days, so that oversaturation of smithsonite occurred.

3.4.2. Speciation of PTE leached from contaminated soils by sea water

When soil flooding was carried out with water containing salts at the largest concentration tested (34.5 g L^{-1}), the presence of chloride ions strongly modified the speciation of solubilized PTE (see Supplementary material, Tables S4 and S5). Associations with chloride, either as CdCl$^+$ or CdCl$_2$(aq) represented in all cases >90 % of the mobilized Cd. The amount of free Zn^{2+} decreased, but 30 % of this element was associated with chloride under different forms (ZnCl$^+$, ZnCl$_2$(aq), ZnCl$_3^-$ and ZnCl$_4^{2-}$) and about 10 % of the solubilized element was predicted to form an ionic couple with sulphate. Also Pb was, for the most part, associated with chloride. The model indicated that leached solutions were oversaturated with Zn and Pb carbonates such as cerrusite (PbCO$_3$) and fosgenite (a chlorocarbonate of Pb), both as amorphous and crystalline forms. Oversaturation indexes decrease with time, probably because of the occurrence of precipitation) this would explain the lower concentration of the elements observed in some solutions leached after 30d of flooding.

4. Discussion

The soils used in this experiment are located within a scarcely polluted area, and PTE are in great part inherited from the parent material. Metals inherited from rocks alteration may be occluded in sparingly soluble, highly crystalline, with large size mineral particles, or have undergone some type of aging process (Siegel, 2002). Albeit more PTE were leached from all soil treatments at increasing salinities, much lower fractions of PTE were proportionally leached from the control soils than from the soils contaminated with the two dusts. This demonstrates that salinity mobilizes airborne PTE much more than the corresponding elements inherited trough rock weathering.

Flooding with marine or brackish water rapidly modifies the composition of the soil solution and of the exchange complex, shifting the existing chemical equilibria and affecting the solubility of toxic metals (Du Laing et al., 2009). The mobilization observed for Cd, Zn and Pb is partly driven by cation exchange: the strong increase in ionic strength weakens, in fact electrostatic attractions with solid surfaces, but even more so by changes in their speciation, because the complexation of the divalent cations by chloride lowers and even reverses the charge of the metals in solution. The speciation distributions of trace metals in SW were calculated by Turner et al. (1981) and showed that solubility is principally governed by hydrolysis and complexation with chloride and carbonate ions. Our modelling results confirmed this and showed that even after a relatively short contact time speciation changes strongly enhances the mobility of PTE in soils.

However, other factors contribute to the observed mobilization: the interaction with some DOC components such as solubilized fulvic acids (FA) further reduces attraction by negatively charged surfaces, decreasing the possibility that these elements might compete with the much more abundant cations in seawater for sorption on solid surfaces (Welikala et al., 2018).

Complexation and electrostatic attraction by FA are driven by the electronic configuration of the element, the dissolution of its solid forms and by pH, therefore significant changes may occur with the length of flooding, depending on the source of contamination, as confirmed by our experiments. In fact, in our leaching experiments, amounts of PTE leached and leaching trends strongly depended on the source of contamination. Dissolution rates were certainly influenced by the nature and size distribution of PTE bearing minerals in the dusts, but also by the presence of carbonates contained in MT dust, as shown by differences in pH and DIC (see supplementary materials).

Our experiments mimic the situation experienced under field conditions by airborne contaminants accumulated at the soil surface. Under the experimental conditions chosen, the low thickness of the overlaying water layer did not allow soils to become fully anaerobic during incubation, so the pH changed only slightly with time. These conditions were selected to reflect those expected to occur in the upper part (0–2 cm) of the surface layer of coastal flooded soils, unless the overlaying waters become anaerobic. For this reason, extensive reduction of Fe and Mn oxides did not occur in our experiment. Stronger reduction may be eventually possible in the field, favoured by the presence of easily decomposable organic matter or poorly oxygenated (euterophic) waters.

The pH of leacheates decreased with salinity, but was more strongly affected by the source of contamination. In the case of MT, which contained a large amount of carbonates, pH significantly increased already after 1d and remained higher even after much longer flooding periods. Amounts of PTE mobilized from MT dust were negatively correlated to soil pH. Differences between amounts of Cd, Zn and Pb leached from MT and SE contaminated soil were not large, but a much smaller pH change was observed in solution leached from the arable soil. The SE also differed in that the amount of mobilized metals increased with time from 1 to 7 days of contact with saline waters, albeit less significantly for the grassland soil. Although, within the different treatments, the pH of all leached solutions varied only less than one unit, pH changes affected the mobilization of PTE. Highly significant negative linear correlations were found with this parameter for solutions leached after all flooding periods (Figs. 6 and 7).

Mobilization, on the contrary, linearly increased with DOC at all flooding times (Figs. 6 and 7). Significant correlations were displayed for all metals and across the displayed range of DOC concentrations and lengths of submergence for both MT and SE contaminated soils.

The combination of chemo-physical modifications induced by the salts dissolved in marine or brackish waters become evident comparing

trends of short and long submergence periods. This added time dimension enhances the complexity of the system (Liu et al., 2019). The significant difference in the amount of DOC solubilized by marine and brackish waters from the two uncontaminated soils at all salinity levels may have affected the behaviour of Pb, but only marginally that of Cd and Zn. In fact, speciation modelling indicated that a substantial fraction of the solubilized Pb was associated with FA in solution. However, this did not result in larger amounts of this element being mobilized from the grassland soil. It is possible that some of the potentially mobilized Pb could have been retained by interactions (e.g. complexation) with the solid fractions of humified C (Welikala et al., 2018), which was larger in the grassland soil compared to the arable (Table 1). Qualitative differences, generated by soil cultivation, may have therefore overcome the small quantitative difference in SOM between the two soils.

5. Conclusions

Our work shows that, by increasing the salinity of soils in coastal areas, the predicted SLR and the increased frequency of extreme storm events driven by global climate changes will enhance the impact of PTE contamination by favouring the dissolution and mobility in soil of PTE contained in airborne dusts originated from mining and smelting activities. Very small airborne dust particles offer a large interface with the liquid phase: air deposited PTE are known to be potentially more mobile in rain water than those contained in soil mineral particles, but our results show they become up to 300 times more mobile when soil is flooded or infiltrated with marine and brackish waters.

We demonstrated that the extent of mobilization which varies from element to element depends on the dust source and the salinity of flooding waters, but their effects are modulated by even small variations in soil characteristics, such as DOC and pH that depend also on soil management. Significantly lower amounts of PTE were leached from the grassland than from the arable soil, showing that modifications of soil organic matter quality, may significantly affect the extent of PTE mobilization by salinity.

Soil flooding may trigger biochemical redox processes, that are not the simple result of the blockage of gaseous exchange with the atmosphere, but the direct consequences of microbial activity. These often result in the modification of both the water phase and of the solid surfaces of minerals in soil. In our experiment, flooded soils were kept aerobic, as is expected to happen at the surface of soils flooded with oxygenated waters. Anaerobic conditions, although more likely to occur in subsurface layers, may eventually occur in the field and may modify the observed effect of flooding time, by inducing the reduction of Fe and Mn oxides. This aspect will need to be investigated with further experiments.

CRediT authorship contribution statement

Elisa Pellegrini: Data curation, Formal analysis, Investigation. **Marco Contin:** Investigation, Methodology, Writing – review & editing. **Sadat Mazhar:** Investigation, Methodology, Writing – original draft. **Carlo Bravo:** Data curation, Formal analysis. **Maria De Nobili:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.171038.

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