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Influence of iron-rich water treatment residues and compost on the mobility of metal(loid)s in mine soils

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1 **INFLUENCE OF IRON-RICH WATER TREATMENT RESIDUES AND**

2 **COMPOST ON THE MOBILITY OF METAL(LOID)S IN MINE SOILS**

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19

20 **Abstract**

21

22 Two different amendments, an iron-rich water treatment residue (Fe-WTR), a municipal

23 solid waste compost (MSW-C) and their combination (Fe-WTR+MSW-C) were added

24 at different rates (from 2 to 4% w/w) to three mining soils (S1, S2, S3) mainly polluted

with As (from 371 to 22661 mg·kg^{-1}d.w.) and different co-occurring trace metals (i.e. Pb, Zn and Cu) to evaluate their effectiveness as metal(loid)s-immobilizing agents. After four months of soil-amendment contact, sequential extractions revealed that MSW-C and Fe-WTR induced an increase of the residual As (non extractable) fraction. Compost was the most effective amendment at increasing the residual As in treated soils (e.g. +16% in S1-MSW-C with respect to untreated S1), although its addition increased at the same time the exchangeable and water-soluble As fraction and the extractability of Pb, Zn and Cu, especially in S1-MSW-C. Leaching experiments highlighted a similar trend, with the highest cumulative fraction of As leached recorded in S1 and S2 soils amended with MSW-C (3.8 and 1.4-fold higher than respective controls), and the lowest recorded in S1 and S2 soils amended with Fe-WTR (1.2 and 1.8-fold lower than respective controls). On the other hand, Fe-WTR and Fe-WTR+MSW-C were the most effective at reducing the total cumulative concentration of metal (Pb, Zn and Cu) in soil leachate. The results of this study show that the amendments considered influenced with a different extent metal(loid)s mobility, and this was depending on soil and amendment characteristics, as well as the type and amount of contamination.

Keywords: arsenic; trace metals; polluted soils; amendments; sequential extraction; leaching tests

1.   Introduction

    Arsenic (As) and trace metals (TM) occur naturally in soils due to the weathering and oxidation of the underlying parent rock (Smedley and Kinniburgh, 2002). However,

due to anthropogenic activities, they can accumulate in soil to critical levels (Zhao et al., 2010). Mining activities, in particular, constitute one of the major source of As and TM (e.g. Pb, Cu and Zn), whose (combined) presence in primary sulphide ores is quite common. Sulphide oxidation in such minerals contributes to the release of TM and As in acidic mine effluents, spreading the contaminants in different environmental compartments (Dold, 2003).

The remediation strategies of soils affected by high levels of TM have generated a great deal of attention over the last decades (Mench et al., 2006). One such approach is based on the use of soil amendments that can immobilize the contaminants through sorption and/or precipitation reactions. However, reclamation of As and TM-co-contaminated soils using amendments is challenging as TM are mainly present in the soil solution as free or complexed cations, while As may be commonly found either as arsenate anion ($H_2AsO_4^-$, $HAsO_4^{2-}$) or as neutral arsenite (H_3AsO_3) in a wide pH range (i.e. 4.0 - 8.0) (Smedley and Kinniburgh, 2002).

In such As and TM-co-contaminated soils the addition of iron, aluminum, or manganese (hydr)oxide-based amendments may reveal effective, as they play a significant role in the retention and mobility of both metals and metalloids such as arsenic (Nagar et al. 2010; Nielsen et al., 2011; Castaldi et al., 2014). Accordingly, the drinking water treatment residuals (WTRs) resulting from the addition of iron, aluminium or calcium salts to raw water bodies, could be equally suitable for the "in-situ" fixation of As and TM co-contaminated soils (Makris et al., 2006; Nagar et al., 2010; Castaldi et al., 2014; Garau et al., 2014) as they are characterised by a significant content of amorphous Al and/or Fe oxides, a high surface area and a neutral pH (Wang et al., 2014).

1   The addition of sorbents containing organic matter, such as composts, to degraded

2   polluted soils, can in turn affect metal(loid)s mobility and restore soil biological and

3   physical properties (Alvarenga et al., 2009; Manzano et al., 2014). However, the

4   influence of compost amendment on metal(loid)s mobility, is controversial and not well

5   understood, being dependent on a number of variables comprising soil properties,

6   compost composition and nature of pollutant (Sharma et al., 2010; Udovic and

7   McBride, 2012; Sundman et al., 2015). For instance, soluble organic and inorganic (e.g.

8   phosphate and/or sulphate) compounds within composts can displace As from the soil

9   binding sites or form aqueous arsenic-organic matter complexes (Buschmann et al.,

10   2006; Wang and Mulligan, 2009). On the other hand, a decrease of soluble arsenic in

11   soils amended with organic matter has also been reported (Cao et al., 2003; Gadepalle et

12   al., 2008). The latter was explained by the fact that arsenate can be adsorbed onto

13   organic matter in acid soils, reaching a maximum adsorption around pH 5.

14   The organic matter of compost is expected to decrease the level of TM extractability

15   and their bioavailability in soil due its high content of functional groups (carboxyl,

16   phenolic, quinone, amino, sulfhydryl, and hydroxyl functional groups), the majority of

17   which are negatively charged at neutral pH and capable of forming strong complexes

18   with metal cations, as reported by several researchers (Wang and Mulligan, 2009;

19   Sundman et al., 2015). Nevertheless, it has been reported that the addition of compost

20   can increase the solubility of Pb or Cu, favouring their chelation by the dissolved

21   organic carbon (DOC) (Beesley and Dickinson, 2009) or increase the EDTA-extractable

22   fractions of Zn or Pb (Tandy et al., 2009; Pardo et al., 2011).

23   The complexity and heterogeneity of these aspects stress the importance of a more

24   clear and deep knowledge of the interactions between As, TM and organic or inorganic

amendments. Although some previous studies evaluated the potential use of similar amendments for the in situ remediation of metal(loid)-polluted soils, studies evaluating the effectiveness of WTR and MSW-compost, when simultaneously added to As- and TM-co-contaminated soils are lacking.

The aim of this work was therefore to evaluate the influence of Fe-WTR, municipal solid waste compost (MSW-C) and their combination on As and TM mobility in three different amended soils through sequential extraction procedures and leaching experiments.

2. Materials and Methods

2.1. Description of the sampling area

Soil samples were collected from an ancient mine located in the Sarrabus-Gerrei mining district, in the municipality of Salto di Quirra (SE Sardinia, Italy), where galena (PbS) and arsenopyrite (FeAsS) were the main minerals extracted. This mine is distributed along the banks of the homonymous stream and was running continuously from 1873 to its decadence in 1965. During the mining activity, residues containing great amount of As and trace metals were discharged from the flotation plant contaminating the area.

2.2 Experimental set-up

Three different sites within the mining area were identified: site "S1" (39.548731, 9.520648 WGS84) located along the upper Baccu Locci stream next to several tailing ponds; site "S2" (39.529885, 9.572115 WGS84) located 5 km from the waste dumps (downstream the Baccu Locci river); site "S3" (39.547465, 9.533576 WGS84) located near an artificial lake. Surface soil (upper 20 cm) was randomly collected from the three sites and for each site a composite soil sample was prepared mixing different soil subsamples (Table 1). Such soil samples were named S1, S2 and S3 according to their site of origin. Particle size determined with the pipette method (Tan, 1996) allowed to classify S1, S2 and S3 soils as coarse sandy loam, loamy coarse sandy and sandy clay loam respectively (USDA classification). Soil mineralogy was determined on finely ground samples by X-ray diffraction (XRD) (PANalytical Empyrean X1-39). The XRD spectra were collected in the 2θ range from $4°$ to $70°$.

Differently amended contaminated soils were compared. Microcosms, each consisting of approx. 10 kg soil (10 cm depth), were separately treated with the following amendments: a) 2% (w/w) Fe-WTR [Fe-WTR]; b) 4% (w/w) municipal solid waste compost [MSW-C]; c) 1% (w/w) Fe-WTR + 2% (w/w) MSW-Compost [Fe-WTR+MSW-C]. All treatments were applied to triplicate microcosms and 3 additional microcosms were kept untreated (polluted-soil). Before addition to soil, the Fe-WTR (dried overnight at 105 °C) and MSW-C were finely ground and sieved to < 2 mm (Table 1). The Fe-WTR was provided by the Public limited company Abbanoa S.p.A. (Sardinia, Italy) and derived from the drinking-water treatment plant in Bidighinzu (Sassari, Italy) where the raw water was added with $Fe_2(SO_4)_3$ as coagulant. MSW-C, derived mainly from municipal and green waste composting, was provided by the Facility Plant Secit S.p.A. Consorzio Zir (Chilivani-Ozieri, Italy). Following

1   amendment incorporation, treated and untreated soils were mixed and moisture content

2   raised to 40% of their water holding capacity. Soils were then left in contact for 4

3   months at 20 °C, mixed twice a week and their water content maintained at a 40-50%

4   level.

5

6   *2.3 Soil characterisation and analytical determinations*

7

8   After 4 months of contact soils samples were air-dried and sieved to 2 mm for

9   analytical determinations. Soil pH, electric conductivity, total organic carbon and

10   nitrogen and total carbonate were determined for treated and untreated soils following

11   the national standard guidelines (Gazzetta Ufficiale, 1992) (Table 2).

12   Cation exchange capacity (CEC) was determined using the $BaCl_2$ and

13   triethanolamine method (Gazzetta Ufficiale, 1992). Dissolved organic carbon (DOC)

14   was determined on the soil leachates extracted after 24 h agitation of a 1:10 (w/v) soil to

15   deionised water suspension. Leachates were filtrated through a membrane filter of 0.20

16   μm pore size and their absorbance at 254 nm was determined (Brandstetter et al., 1993).

17   The determination of the point of zero charge has been performed by potentiometric

18   titration (Metrohm 902 Titrando).

19   The total concentration of Pb, As, Cd, Cu, and Zn in soils was determined after

20   digestion with an HNO_3 and HCl mixture (1:3 v/v ratio) using a Perkin Elmer Analyst

21   600 atomic absorption spectrometer (HGA-600 graphite furnace).

22   The mobility of arsenic in soil samples was determined by the sequential extraction

23   procedure of Wenzel et al. (2001). In particular, soil samples (1 g) were treated with 25

24   mL of a 0.05 M $(NH_4)_2SO_4$ solution and shaken for 4 h at 20 °C to extract the non-

specifically sorbed As (Fraction 1). The same samples were then treated with 25 mL of a 0.05 M $NH_4H_2PO_4$ solution and shaken for 16 h to extract the specifically sorbed As (Fraction 2). Soil samples were then treated with 25 mL of 0.2 M NH_4^+-oxalate buffer and shaken for 4 h to extract the As associated with amorphous and poorly crystalline hydrous oxides of Fe and Al (Fraction 3). Finally, samples were treated with 25 mL of 0.2 M NH_4^+-oxalate buffer+0.1 M ascorbic acid and shaken for 0.5 h in a water basin at 96 °C to extract the As associated with well-crystallized hydrous oxides of Fe and Al (Fraction 4). After each step of the extraction process the soil samples were centrifuged at 8000 rpm for 10 min and filtered to separate the liquid and solid phases.

The sequential extraction of metals was performed following the procedure of Basta and Gradwohl (2000). In particular, soil samples (1 g) were treated with 25 mL of a 0.5 M $Ca(NO_3)_2$ solution to extract the Me-exchangeable pool, and with 25 mL of a 1 M NaOAc solution at pH 5.0 to extract Me(II) forming weak surface complexes and finally with 25 mL of a 0.1 M Na_2EDTA solution to extract the surface complexed and precipitated metals. After each step of the extraction process, the samples were centrifuged at 8000 rpm for 10 min, filtered to completely separate the liquid and solid phases.

After the last wash, the residual fraction of As and TM in soil samples was determined by drying the solid phase overnight at 105 °C and digesting it with HNO_3 + HCl (1:3 ratio) in a Microwave Milestone MLS 1200. The metal(loid)s concentrations were determined as previously mentioned.

2.4 Leaching tests

1   Soil samples collected at the end of the contact time were also subjected to leaching

2   tests. Columns (100 mL-syringes) were filled with 70 g of untreated and treated soils

3   (NEN 7343, 1995). Three replicates per treatment were used.

4   Firstly, columns were fully saturated with deionised water according to the soil water

5   holding capacity (previously determined) and equilibrated for 24 h. Subsequently,

6   columns were continuously rinsed with deionised water at a rate of 0.2 mL·min^{-1}, so

7   that the total volume that passed through each column was 1050 mL. During the

8   experiment, samples of leachate were collected in 15 fractions of variable volume

9   (Table 3). Leachate pH and DOC were measured immediately after each sampling as

10   described for soils. Total arsenic and TM concentrations were determined in the

11   leachates as previously described.

12   DOC, metal (Fe, Pb Cu and Zn) and arsenic concentrations in the leachates were

13   plotted in graphs that display their cumulative concentration (mg·kg^{-1} soil) (y-axis)

14   versus the cumulative water volume (x-axis) and adjusted to functions. Functions were

15   statistically analysed and they were selected according to the best adjustment indicated

16   by the significance of the model and their parameters. Such functions provide

17   information about the theoretical maximum concentration of As and TM leached from

18   the soil. These functions are sigmoidal or hyperbolic: $y = a/(1+\exp(-(x-b)/p))$ and

19   $y=(ax)/(b+x)$, where "a" is the maximum leached concentration of trace element

20   (mg·kg^{-1}), "b" is the volume of water required (mL) so that the element concentration is

21   half of the total leached (the x-value of the sigmoid's midpoint) and "p" is the steepness

22   of the curve. Graphs and fittings were performed using SigmaPlot 13.0.

23

24   *2.5 Statistical analysis of data*

1

2   Differences between means were tested using the statistical program SPSS 15.0.

3   Statistical tests performed include one-way analysis of variance (ANOVA) followed by

4   Duncan's test to determine whether there are any significant differences between the

5   means of each treatment, assuming a normal distribution of the dependent variable data

6   and homogeneity of variances.

7

8   **3. Results and Discussion**

9

10   *3.1 Effect of amendments on soil properties*

11

12   The S1, S2 and S3 soils showed different physico-chemical characteristics as well as

13   different concentrations of As and TM. XRD analysis showed the following crystalline

14   phases in S1 soil: quartz (38 wt %), illite-muscovite (38 wt %), clinoclhore (15 wt %),

15   sanidine (1 wt %) and beudantite 8 wt % [$PbFe_3(AsO_4)(SO_4)(OH)_6$], the latter resulting

16   from the process of weathering of galena (PbS) and arsenopyrite ($FeAsS_2$). The S2 soil

17   contained a mixture of 4 crystalline phases such as quartz (36 wt %), muscovite/illite

18   (40 wt %), sanidine (16 wt %) and clinochlore (8 wt %). The S3 soil contained the same

19   crystalline phases of S2 other than calcite (i.e. quartz 56 wt %; clinochlore 1 wt %;

20   sanidine 1 wt %; illite/muscovite 29 wt %, and calcite 13 wt %).

21   Soil pH in S1 was highly acidic while S2 and S3 soils were sub-alkaline. Total

22   organic carbon and DOC followed the order S1<S2<S3 (Table 1). Soil S3 had the

23   highest cation exchange capacity (CEC), which matched with the largest content of clay

24   (23%) and organic matter (4.15%), compared to the more sandy S1 and S2 soils. Total

1   As concentration was very high in S1 soil (22,661 mg·kg^{-1}) compared to S2 and S3 (371

2   and 749 mg·kg^{-1} respectively). However, even in these two latter soils the As

3   concentrations were largely exceeding the background-concentrations of EU soils

4   (Kabata-Pendias, 2000). Likewise, total Pb, Cu and Zn concentrations in S1 and Pb and

5   Zn in S2 soils were exceeding the background-concentrations of EU soils (Amlinger et

6   al., 2004) (Table 1).

7   After 4 months of contact the addition of Fe-WTR caused an increase of about one

8   unit of pH in soil S1 and triggered a slight pH decrease in the other two soils (Table 2).

9   The addition of MSW-C to S1 caused a strong increase of pH (~ 4 unit), in agreement

10   with previous studies, which showed that compost addition to highly acidic mine soil

11   resulted in alleviation of acidity (i.e. Tandy et al., 2009). The percentage of organic

12   carbon increased in all the treated samples, being higher in MSW-C soils. The addition

13   of compost caused an increase of DOC in S1 and S2 soils (+8.0, and +1.8 fold

14   respectively with respect to control) but not in S3. All the treatments induced an

15   increase of CEC in S1 and S2 soils, and this increase was always higher when compost

16   was present in the amended samples, either alone or in combination with Fe-WTR

17   (Table 2).

18

19   *3.2 Influence of amendments on As mobility*

20

21   To assess the amendments influence on the mobility and potential bioavailability of

22   As, the sequential extraction procedures of Wenzel et al. (2001) was used. The non-

23   specifically adsorbed As fraction (Fraction 1), was about 0.09, 0.54 and 0.92% of total

24   As in S1, S2 and S3 soil samples respectively (Fig. 1). This fraction, which accounts for

the easily exchangeable and water-soluble As, generally decreased in the soils amended

with Fe-WTR (~60 % lower whit respect to untreated soils), likely as consequence of

formation of insoluble complexes between As and Fe oxides and hydroxides, in

agreement with the results reported by several authors (e.g. Garau et al., 2014; Nagar et

al., 2015). By contrast, S1 and S2 soils treated with MSW-C showed an increase of

exchangeable and water-soluble As (>65 and 26% respectively, compared to control).

This increase could be mainly assigned: i) to the competition between humic substances

and dissolved organic carbon (significantly increased in S1- and S2-MSW-C) with As

for retention sites (Tandy et al., 2009); ii) to the potential of some ions in compost to

displace As from the Fe-oxide phases (e.g. arsenate by phosphate (Fitz and Wenzel,

2002)); iii) to the formation of As-(Me)-DOC soluble complexes (Wang and Mulligan,

2009). By contrast, the higher content of clay and organic matter in S3 soil (Tables 1-2)

likely buffered such effects driven by compost addition.

With the exception of S2 soil, all the amendments decreased significantly the As

amounts recovered in Fraction 2 (Fig. 1). In this step of the sequential extraction, the

arsenic species chemically bound to solid phase surfaces through inner-sphere

complexes (e.g. $H_2AsO_4^-$ and $HAsO_4^{2-}$ and/or $As(OH)_3$) are competitively exchanged by

phosphate anions (Wenzel et al., 2001). The decrease of this As fraction was

particularly evident in the S1 soil treated with MSW-C, where a 95% decrease was

observed (Fig. 1).

All the amendments reduced significantly the As extracted in both Fractions 3 and 4

from S1 soil. These fractions account for the As associated to amorphous and poorly

crystalline Fe and Al (hydr)oxides (Fraction 3) and for the As associated to well-

crystallized Fe and Al (hydr)oxides (Fraction 4). MSW-C added to S1 was the most

effective at decreasing the As in Fraction 3 (<89% compared to untreated S1); while all the amendments reduced As in Fraction 4 approximately by the same extent (i.e. ~25% compared to untreated S1). Arsenic in Fraction 3 was consistently reduced by all the amendments in S2 soil but not in S3 where only the MSW-C revealed effective. On the other hand, none of the treatments reduced As in Fraction 4 of S2 and S3 soils (Fig. 1).

The residual As, i.e. the fraction strongly retained and hardly (bio)available, was about 77, 44 and 36% of the total As in the untreated S1, S2 and S3 soils respectively. This fraction is not expected to be quickly released in soil, therefore providing useful information from an environmental point of view. This fraction increased significantly in all the soils after amendment addition (Fig. 1). The most effective amendment in this sense was MSW-C (>16, 50 and 54% in S1, S2 and S3 respectively compared to untreated soils).

The results of the sequential extraction highlighted a general suitability of all the treatments at fixing As in all the soils considered. Nonetheless, while the influence of Fe-WTR on the As immobilization could be (to some extent) anticipated given the significant content of Fe (hydr)oxides (Sarkar et al., 2007; Nielsen et al., 2011; Garau et al., 2014; Nagar et al. 2015), the results arising from MSW-C addition add a new contribution on the controversial and not well resolved role of the organic matter on arsenic mobility in soil (i.e. Cao et al. 2003; Tandy et al., 2009; Pardo et al., 2011; Udovic and McBride, 2012). The sequential extraction data indicated that As immobilization phenomena, induced by the amendments, were dominant with respect to As mobilization ones which occurred with a very limited extent (Fraction 1 increased in S1- and S2-MSW-C only by the 0.22 and 0.28% of total As respectively). Moreover, our results suggest that As immobilization in compost-amended soils occurs, similarly

1   to phosphate, via the formation of stable bonds such as arsenate mono- and di-esters

2   with the hydroxyl functional groups of compost (Wenzel et al., 2013). Additionally, the

3   formation of (insoluble) stable ternary complexes involving metal cations (e.g. Fe, Pb

4   and Cu, present at high concentration in the studied soils), the negatively charged

5   carboxylic groups of compost and As, could be an additional mechanism contributing to

6   As-fixation in the polluted amended soils (van Herwijnen et al., 2007; Sharma et al.,

7   2010).

8   On the other hand, the main mechanism governing the retention of As by WTRs

9   most likely involved the formation of inner-sphere complexes between the metalloid

10   and the surficial OH functional groups of Fe (hydr)oxides within Fe-WTR (Sarkar et al.,

11   2007; Castaldi et al., 2014; Nagar et al., 2015). Moreover, the formation of chemical

12   compounds of low-solubility (e.g. iron arsenates) could contribute to As immobilization

13   by Fe-WTR as previously suggested (Castaldi et al., 2014).

14

15   *3.3 Influence of amendments on TM mobility and potential bioavailability*

16

17   The water-soluble and readily exchangeable Pb fraction in S1 and S2 soils

18   (extraction with 0.5 M $Ca(NO_3)_2$) was 0.3 and 0.03 % of total Pb respectively, and the

19   amendment addition did not change significantly its concentration (Fig. 2). On the other

20   hand, all the treatments reduced significantly the water-soluble and exchangeable Cu

21   fraction in S1 (Fig. 2). Similarly, all the amendments reduced significantly the water-

22   soluble and readily exchangeable Zn with the exception of compost applied to soil S1.

23   In this case a 3-fold increase of the readily exchangeable Zn was detected as likely

24   consequence of the formation of soluble complexes between Zn and DOC (Martínez et

al., 2003). Besides, it cannot be excluded that the addition of compost containing several metal cations (such as Ca and Mg) could have affected the mobility of Zn due to ionic competition (Branzini and Zubillaga, 2012). Apart from this latter exception, all the amendments tested appeared effective at reducing the TM extracted with $Ca(NO_3)_2$ and this is relevant since this fraction represents the Me(II) pool most labile and potentially bio-available. This could be mainly explained with the capacity of the organic and inorganic components of the Fe-WTR and MSW-C employed to sorb the metals considered (i.e. Park et al., 2011; Garau et al., 2014). The TM fraction extracted with NaOAc represents metals bound to the weak acid-soluble phase as well as co(precipitated) with carbonate (Pickering, 1986). This fraction was 1.72, 3.35 and 2.22% of total Pb, Cu and Zn in S1 soil respectively. Such low percentages could be assigned to the low carbonate content in S1 soil. In S1-MSW-C, the increase of DOC probably favoured the enhancement of Pb, Zn and Cu within the acid-soluble fraction (+23, +248 and +14-fold respectively). In S2 soil the Zn extracted with NaOAc was ~10% of total Zn, highlighting the formation of weak surface complexes between this TM and soil colloids. The addition of all amendments caused a decrease of this fraction.

EDTA-extractable Pb, Zn and Cu increased in S1 soil after compost addition (+7.5, +255 and +23.5-fold for Pb, Zn and Cu respectively with respect to the untreated soil), highlighting the ability of these trace metals to form stable inner-sphere complexes with the functional groups of compost (Walker et al., 2003). The increase of TM extracted with EDTA could be also due to precipitation of metals as insoluble salts, e.g. as Me(II)- phosphates (phosphates are abundantly present in our compost) as suggested by Clemente et al. (2006). The fractions of Pb and Zn extracted with EDTA in the S2 soil

1   did not change following the addition of the sorbents, highlighting a higher stability of

2   TM in this soil.

3   The residual Pb, Zn and Cu fractions (i.e. the metal pools not readily bioavailable in

4   the short-term) did not change in the S1 and S2 soils treated with Fe-WTR and Fe-

5   WTR+MSW-C, while the addition of the sole compost caused a decrease of the residual

6   TM in S1 (<80, 81 and 49% for Pb, Zn and Cu respectively). This latter phenomenon

7   was the likely consequence of an increased metal chelation by the organic matter, and/or

8   the increased formation of insoluble salts (as supported by the increased amount of

9   metals extracted with NaOAc and EDTA; Fig. 2), in agreement with the results reported

10   by several authors (e.g. Clemente et al., 2006; Pardo et al., 2011).

11

12   *3.4 pH and DOC in soil leachates*

13

14   Figure 3 shows the pH values of soil leachates registered in each leachate fraction

15   collected from the three soils. In S1 soil, the control and Fe-WTR treatment registered

16   the lowest pH values while MSW-C and MSW-C+Fe-WTR provided the highest ones.

17   Leachate pH values in all the S2 and S3 soil samples were sub-alkaline. pH values had a

18   tendency to decrease in S1, being the difference between the beginning and the end of

19   leaching greater in S1-Fe-WTR.

20   Figure 3 also shows DOC concentration vs the cumulative real volume of leachate.

21   Points were fitted to hyperbolic functions in which "a" ($mg \cdot kg^{-1}$) represents the

22   maximum DOC concentration leached and "b" (mL) the volume of water required to

23   leachate half concentration of maximum DOC (Table 4). In S1 and S2, DOC was higher

24   in the treatments with compost, in line with the characteristics of MSW-C soils, and in

1 agreement with the results reported by other researchers (Beesley and Marmiroli, 2011;

2 Karami et al., 2011). This is of concern, since previous studies found that DOC can be

3 responsible for the increase of trace metal concentration in the soil solution, due to the

4 formation of soluble complexes between metals and organic molecules (Moreno-

5 Jiménez et al., 2013).

6 In S3 soil, where the initial content of DOC was not modified by the amendments

7 addition (Tables 1 and 2), the estimation of DOC maximum concentration was similar

8 in all the treatments, and it was higher and more rapidly leached than in S1 and S2 soils,

9 as indicated by the combination of a higher "a" and a lower "b" coefficients.

10

11 *3.5 Arsenic and trace metal concentration in soil leachates*

12

13 Figure 4 shows As and metal leaching curves displaying the cumulative trace

14 element concentration versus the cumulative real volume of leachate.

15 Arsenic leaching patterns, which represent the contribution of the most soluble

16 fractions of arsenic in soil and the As replenishment from other less soluble fractions

17 (Wennrich et al., 2012), were different among the different amended soils. In S1 soil,

18 points were fitted to hyperbolic curves, while S2 and S3 to sigmoidal functions. The

19 sigmoidal fitting suggests that arsenic leaching in S2 and S3 soils could have occurred

20 more slowly than in S1 during the first fractions within all the treatments (until reaching

21 the midpoint "b"), showing a greater availability of arsenic in S1 soil. Fe-WTR was the

22 treatment which strongly reduced the estimation of total cumulative As leached in S1

23 and S2 (<11 and 45% respectively), according with the results reported by several

24 researchers that used iron oxi(hydroxi)des or iron-rich WTR as sorbents in polluted

soils (Hartley et al., 2004; Alvarez-Ayuso et al., 2013; Nagar et al., 2015). S1 and S2

soil samples treated with MSW-C showed the highest of maximum As concentration

leached on soil basis (up to 69 and 5.5 mg·kg^{-1} respectively, ~0.3 and 1.3% of total As)

(Table 4). Equally, As maximum concentration in S1-Fe-WTR+MSW-C was 2.7-fold

time higher than in control, pointing out that MSW-C added singly impaired the

scenario provided by the combined treatment. The increase of As leached in the S1 and

S2 amended with compost could be related to the increase of DOC, which can compete

with As for retention sites as well as favour the formation of As-(Me)-DOC soluble

complexes (Wang and Mulligan, 2009). In S3 soil, according to the sigmoidal model, all

the treatments favoured a decrease of As leached. In this soil Fe-WTR added singly was

not as efficient as the combined treatment. Further, although the highest estimated As

concentration was similar for Fe-WTR and MSW-C, this latter promoted a higher

leaching of As, as pointed out by a lower "b" coefficient (a lower "b" value means a

lower volume of water required to leachate the same metal(loid) concentration). In any

case, compost treatment in S3 soil was effective to limit total cumulative concentration

of As leached, as consequence of the strong buffering capacity of this soil, which

mitigated the detrimental effects of compost DOC on the arsenic solubility (Warren et

al., 2003). These results, which provided important information about As leaching in the

different treated soils, seem in line with those of the sequential extraction.

Fe-WTR and Fe-WTR+MSW-C in S2 and S3 soils, as observed within the graphs

and the model equations, did not contribute to the Fe release, despite the incorporation

of the iron-bearing materials (Figure 4). The high leachate pH in these treatments could

have limited Fe release from soils, while MSW-C singly added promoted the highest

increases of Fe leaching in S2 and S3. In the other hand, the low leachate pH in S1 Fe-

WTR promoted an estimation of Fe maximum concentration leached 5 fold-higher than in the control (Figure 4, Table 4).

It was only possible to display Pb, Cu and Zn leaching on S1 soil, as in the other two soils their concentrations were under the detection limit. Points were better fitted to a hyperbolic model than to a sigmoidal, and hence, the leaching curves with greater slopes estimated a more rapid leaching (Figure 4). Pb was the less mobile element compared to Cu and Zn in the S1 control sample, denoting a low leaching. Fe-WTR and Fe-WTR+MSW-C were the treatments that highly reduced the total cumulative Me(II) concentration at the end of leaching, while the highest Me(II) leaching was detected in S1-MSW-C (+9.25, +1.50, and +1.46-fold for Pb, Cu and Zn respectively with respect to control). The model equations showed that Fe-WTR+MSW-C was the best treatment for the reduction of maximum Pb and Zn concentration according to the parameters "a" and "b". For Cu, this treatment obtained the same results of Fe-WTR. The reduction of leached Pb, Cu and Zn in the soils treated with iron-rich residues, can be assigned to the formation of strong inner-sphere complexes between metals and the oxyhydroxide surfaces of Fe-WTR or to co-precipitation processes, in line with other leaching studies employing amorphous Al or Fe-oxide (Houben et al., 2012; Alvarez-Ayuso et al., 2013).

The MSW-C singly added favoured the highest metal leaching, as likely consequence of the DOC increase, according with the results reported by other authors (Wang and Mulligan, 2009). Besides, as mentioned above, the increase of As leached by MSW-C treatments in S1 and S2, suggests the formation of soluble complexes As-Me-DOC, with Me acting as bridge (Wang and Mulligan, 2009). However, other researches showed that the addition of organic matter to contaminated soils can reduce TM

leaching by complexation with the functional groups of OM or by the diffusion of TM into organic matter pores (Tsang et al., 2013; Beesley and Marmiroli, 2011). So, according with van Herwijnen et al. (2007), it can be concluded, that the organic matter role on TM leaching processes is mainly affected by the soil characteristics.

The combined Fe-WTR+MSW-C treatment favored a strong reduction of trace metal leaching in S1 soil. In the literature good synergisms between organic matter and iron-rich amendments can be found. For example, Mench et al. (2006) and Ruttens et al. (2006) found a decrease of Pb and Zn leaching in a contaminated soil amended with compost and/or inorganic metal immobilizing soil amendments.

4. Conclusions

Fe-WTR and MSW-C showed a different ability to immobilize metal(loid)s in the polluted soils examined, so highlighting that the efficacy of any amendment is a complex function which is depending on the type and amount of contamination, as well as on the amendments and soil characteristics (i.e. pH, content of clay and organic matter).

Overall, the addition of Fe-WTR, MSW-C and their combination revealed a valuable strategy to increase the non extractable fraction of As in the three different mining soils. This is certainly useful since the As residual fraction is not expected to be released in the medium-long term. However, if the compost addition caused an increase of DOC (as well as in S1 and S2 soils), an increase of water-soluble and non-specifically adsorbed As was detected.

Fe-WTR revealed the most effective amendment at reducing the total cumulative concentration of As leached in S1 and S2, while in the same soils the addition of MSW-C caused the leaching of the highest As fractions, as a likely consequence of the competition between compost dissolved organic carbon and As for the same retention sites and of the formation of As-(Me)-DOC soluble complexes, in line with the results of the sequential extractions. Trace metals water-solubility detected by the leaching curves showed a positive relationship with TM mobility estimated in batch tests.

Notwithstanding the static character of the sequential extractions, the information obtained were in good agreement with those gained from the leaching test. However, while sequential extractions can provide a snapshot of the amendment influence on metal(loid)s mobility and their potential bioavailability, leaching models offer valuable complementary information regarding the long term effectiveness of the amendment at fixing As and TM. In this sense, the combined use of sequential extractions and leaching tests can be of help in the selection of amendments for *in-situ* remediation of polluted soils as well as a valuable tool for risk assessment in metal(loid)s contaminated areas.

References

Alvarenga, P., Gonçalves, A.P., Fernandes, R.M., de Varennes, A., Vallini, G., Duarte, E., Cunha-Queda, A.C., 2009. Organic residues as immobilizing agents in aided phytostabilization: (I) effects on soil chemical characteristics. Chemosphere 74, 1292–1300.

Alvarez-Ayuso, E., Otones, V., Murciego, A., Garcia-Sanchez, A., 2013. Evaluation of different amendments to stabilize antimony in mining polluted soils. Chemosphere 90, 2233–2239.

Amlinger, F., Pollack, M., Favoino, E., 2004. Heavy metals and organic compounds from wastes used as organic fertilisers. Final report for ENV. A. 2./ETU/2001/0024., Final report for ENV. A. 2./ETU/2001/0024.

Basta, N., Gradwohl, R., 2000. Estimation of Cd, Pb, and Zn Bioavailability in Smelter-Contaminated Soils by a Sequential Extraction Procedure. J. Soil Contam. 9, 149–164.

Beesley, L., Dickinson, N., 2009. Carbon and trace element mobility in an urban soil amended with green waste compost. J. Soils Sediments 10, 215–222.

Beesley, L., Marmiroli, M., 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. Environ. Pollut. 159, 474–480.

Brandstetter, A., Sletten, R.S., Mentler, A., Wenzel, W.W., 1993. Estimating dissolved organic carbonin natural waterby UV absorbance (254nm). Z. Pflanzenernaehr. Bodenkd 159, 605–607.

Branzini, A., Zubillaga, M.S., Comparative use of soil organic and inorganic amendments in heavy metals stabilization. Appl. Environ. Soil Sci. 2012, 721032.

Buschmann, J., Kappeler, A., Lindauer, U., Kistler, D., Berg, M., Sigg, L., 2006. Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum. Environ. Sci. Technol. 40, 6015–6020.

Cao, X., Ma, L., Shiralipour, A., 2003. Effects of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyperaccumulator, *Pteris vittata* L. Environ. Pollut. 126, 157–167.

Castaldi, P., Mele, E., Silvetti, M., Garau, G., Deiana, S., 2014. Water treatment residues as accumulators of oxoanions in soil . Sorption of arsenate and phosphate anions from an aqueous solution. J. Hazard. Mater. 264, 144–152.

Clemente, R., Escolar, A., Bernal, M.P., 2006. Heavy metals fractionation and organic matter mineralisation in contaminated calcareous soil amended with organic materials. Bioresour. Technol. 97, 1894–1901.

Dold, B., 2003. Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. J. Geochemical Explor. 80, 55–68.

Fitz, W.J., Wenzel, W.W., 2002. Arsenic transformations in the soil-rhizosphere-plant system: Fundamentals and potential application to phytoremediation. J. Biotechnol. 99, 259–278.

Gadepalle, V.P., Ouki, S.K., Van Herwijnen, R., Hutchings, T., 2008. Effects of amended compost on mobility and uptake of arsenic by rye grass in contaminated soil. Chemosphere 72, 1056–1061.

Garau, G., Silvetti, M., Castaldi, P., Mele, E., Deiana, P., Deiana, S., 2014. Stabilising metal(loid)s in soil with iron and aluminium-based products: microbial, biochemical and plant growth impact. J. Environ. Manage. 139, 146–153.

Gazzetta Ufficiale, 1992. Metodi ufficiali di analisi chimica dei suoli. DM 11 maggio 1992, suppl. G.U. 121, 25 maggio 1992. [Official Gazette of the Italian Republic. Official methods for chemical analysis of soils. Ministerial Decree 05-25-1992].

Hartley, W., Edwards, R., Lepp, N.W., 2004. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. Environ. Pollut. 131, 495–504.

Houben, D., Pircar, J., Sonnet, P., 2012. Heavy metal immobilization by cost-effective amendments in a contaminated soil: Effects on metal leaching and phytoavailability. J. Geochemical Explor. 123, 87–94.

Kabata-Pendias, A., 2000. Trace elements in soils and plants, Third Edition: Soils and Soil Processes. CRC Press, Boca Raton, pp. 27–48.

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N.W., Beesley, L., 2011. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. J. Hazard. Mater. 191, 41–48.

Makris, K.C., Sarkar, D., Datta, R., 2006. Evaluating a drinking-water waste by-product as a novel sorbent for arsenic. Chemosphere 64, 730–741.

Manzano, R., Esteban, E., Peñalosa, J.M., Alvarenga, P., 2014. Amendment application in a multi-contaminated mine soil: effects on soil enzymatic activities and ecotoxicological characteristics. Environ. Sci. Pollut. Res. 21, 4539–4550.

Martínez, C.E., Jacobson, A.R., McBride, M.B., 2003. Aging and temperature effects on DOC and elemental release from a metal contaminated soil. Environ. Pollut. 122, 135–143.

Mench, M., Vangronsveld, J., Lepp, N., Bleeker, P., Ruttens, A., Geebelen, W., 2006. Phytoremediation of Metal-Contaminated Soils. In: J.-L. Morel et al. (Ed.), Phytoremediation of Metal-Contaminated Soils. Springer Netherlands, pp. 109–190.

Moreno-Jiménez, E., Clemente, R., Mestrot, A., Meharg, A.A., 2013. Arsenic and selenium mobilisation from organic matter treated mine spoil with and without inorganic fertilisation. Environ. Pollut. 173, 238–244.

NEN 7343, 1995. Leaching Characteristics of Solid Earthy and Waste Materials. Leaching Tests. Determination of the Leaching of Inorganic Components from Granular Materials with the Column Test, Netherlands Standardisation Institute

Nagar, R., Sarkar, D., Makris, K.C., Datta, R., 2010. Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals. Chemosphere 78, 1028–1035.

Nagar, R., Sarkar, D., Punamiya, P., Datta, R. 2015. Drinking water treatment residual

amendment lowers inorganic arsenic bioaccessibility in contaminated soils: a long-term study. Water Air Soil Pollut. 226, 366.

Nielsen, S.S., Petersen, L.R., Kjeldsen, P., Jakobsen, R., 2011. Amendment of arsenic and chromium polluted soil from wood preservation by iron residues from water treatment. Chemosphere 84, 383–389.

Pardo, T., Clemente, R., Bernal, M.P., 2011. Effects of compost, pig slurry and lime on trace element solubility and toxicity in two soils differently affected by mining activities. Chemosphere 84, 642–650.

Park, J.H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., Chung, J.W., 2011. Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. J. Hazard. Mater. 185, 549–574.

Pickering, W.F., 1986. Metal ion speciation - soils and sediments (a review). Ore Geol. Rev. 1, 83–146.

Ruttens, A., Colpaert, J. V, Mench, M., Boisson, J., Carleer, R., Vangronsveld, J., 2006. Phytostabilization of a metal contaminated sandy soil. II: Influence of compost and/or inorganic metal immobilizing soil amendments on metal leaching. Environ. Pollut. 144, 533–539.

Sarkar, D., Makris, K.C., Vandanapu, V., Datta, R., 2007. Arsenic immobilization in soils amended with drinking-water treatment residuals. Environ. Pollut. 146, 414–419.

Sharma, P., Ofner, J., Kappler, A., 2010. Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. Environ. Sci. Technol. 44, 4479–4485.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Sundman, A., Karlsson, T., Persson, P., 2015. Reactivity of Fe from a natural stream water towards As(V). Appl. Geochem. 61, 185–191.

Tan, K.M., 1996. Soil Sampling. Preparation and Analysis, Marcel Dek. ed. NY.

Tandy, S., Healey, J.R., Nason, M.A., Williamson, J.C., Jones, D.L., 2009. Remediation of metal polluted mine soil with compost: co-composting versus incorporation. Environ. Pollut. 157, 690–697.

Tsang, D.C.W., Olds, W.E., Weber, P.A., Yip, A.C.K., 2013. Soil stabilisation using AMD sludge, compost and lignite: TCLP leachability and continuous acid leaching. Chemosphere 93, 2839–2847.

Udovic, M., McBride, M.B., 2012. Influence of compost addition on lead and arsenic bioavailability in reclaimed orchard soil assessed using *Porcellio scaber* bioaccumulation test. J. Hazard. Mater. 205-206, 144–149.

van Herwijnen, R., Hutchings, T.R., Al-Tabbaa, A., Moffat, A.J., Johns, M.L., Ouki, S.K., 2007. Remediation of metal contaminated soil with mineral-amended composts. Environ. Pollut. 150, 347–354.

Walker, D.J., Clemente, R., Roig, A., Bernal, M.P., 2003. The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean

soils. Environ. Pollut. 122, 303–312.

Wang, S., Mulligan, C.N., 2009. Enhanced mobilization of arsenic and heavy metals from mine tailings by humic acid. Chemosphere 74, 274–279.

Wang, C., Yuan, N., Pei, Y., 2014. Effect of pH on metal lability in drinking water treatment residuals. J. Environ. Qual. 43, 389–397.

Warren, G.P., Alloway, B.J., Lepp, N.W., Singh, B., Bochereau, F.J.M., Penny, C., 2003. Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Sci. Total Environ. 311, 19–33.

Wennrich, R., Daus, B., Müller, K., Stärk, H.-J., Brüggemann, L., Morgenstern, P., 2012. Behaviour of metalloids and metals from highly polluted soil samples when mobilized by water - Evaluation of static versus dynamic leaching. Environ. Pollut. 165, 59–66.

Wenzel, W.W., Kirchbaumera, N., Prohaskab, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta 436, 309–323.

Wenzel, W.W, 2013. Arsenic, in: Alloway, B.J. (Ed.), Heavy Metals in soils: trace metals and metalloids in soils and their bioavailability. Third Edition. Springer Netherlands, pp. 241–282.

Zhao, F.-J., McGrath, S.P., Meharg, A.A., 2010. Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu. Rev. Plant Biol. 61, 535–559.

1 **Figure captions**

2

3 **Fig. 1.** Arsenic released after sequential extraction. For each soil samples and for each

4 fraction of the sequential extraction, mean values followed by different letters denote

5 statistically significant differences according to the Duncan's test ($P < 0.05$). For each

6 soil samples of the residual fraction, mean values followed by different letters denote

7 statistically significant differences according to the Duncan's test ($P < 0.05$).

8

9 **Fig. 2.** Trace metals released after sequential extraction. For each soil samples and for

10 each step of the sequential extractions, mean values followed by different letters denote

11 statistically significant differences according to the Duncan's test test ($P < 0.05$). For

12 each soil samples of the residual fraction, mean values followed by different letters

13 denote statistically significant differences according to the Duncan's test ($P < 0.05$).

14

15 **Fig. 3.** pH and DOC in soil leachates

16

17 **Fig. 4.** Arsenic and trace metal concentration in soil leachates

18
19

Table 1

Characterization of S1, S2 and S3 soils, iron-rich water treatment residue (Fe-WTR) and municipal solid waste compost (MSW-C). Mean ± SE

	S1 soil	S2 soil	S3 soil	Fe-WTR	MSW-C
pH_{H2O}	3.77±0.01	7.58±0.03	8.10±0.03	7.15±0.06	7.93±0.10
pH_{KCl}	3.31±0.03	7.52±0.01	8.60±0.12	7.36±0.08	7.22±0.07
EC ($mS·cm^{-1}$)	0.44±0.04	0.33±0.01	0.26±0.00	1.24±0.03	3.26±0.09
Ash (%)	93.5±1.15	92.3±1.07	85.7±1.01	56.67±0.29	42.05±0.73
Total organic C (%)	1.04±0.13	2.50±0.16	4.15±0.08	8.42±0.13	27.34
Total N (%)	0.03±0.005	0.16±0.00	0.08±0.00	0.61±0.64	2.18±0.18
Total carbonate (%)	0.29±0.08	0.26±0.05	21.17±0.59	0.07±0.00	0.03±0.00
CEC ($cmol_{(+)}·kg^{-1}$ d.w.)	10.07±0.91	12.34±1.59	21.47±1.64	75.02±1.78	93.30±1.96
pH_{PCZ}	4.60	7.90	6.60	6.60±0.11	-
DOC ($mg·kg^{-1}$ d.w.)	30.12±0.12	190.3±1.15	432.4±2.21	103.3±2.02	573.5±4.82
$mg·kg^{-1}$ d.w.					
Total As	22,661±144	371.3±0.4	749.0±266.3	n.d.	n.d.
Total Cd	9.34±1·10-5	9.28±0.00	9.79±0.00	0.24±0.00	n.d.
Total Cu	411.6±44.9	46.01±1.65	18.97±0.93	51.48±1.12	19.24±1.74
Total Fe (%)	3.91±0.27	2.24±0.06	0.44±0.03	13.42±0.44	0.56±0.08
Total Mn	646.5±19.9	838.5±36.5	455.0±34.2	231.3±37.4	140.5±5.7
Total Pb	2161.8±273.5	123.87±10.89	74.19±12.46	25.69±0.77	3.72±0.15
Total Zn	1534.6±841.3	279.09±51.28	56.64±5.41	235.33±14.39	30.52±3.20

n.d.: under detection limit.

Table 2

Characterization of S1, S2 and S3 soils amended with Fe-WTR, MSW-C and Fe-WTR+MSW-C. Mean ± SE

	S1 soil			S2 soil			S3 soil		
	Fe-WTR	*MSW-C*	*Fe-WTR+MSW-C*	*Fe-WTR*	*MSW-C*	*Fe-WTR+MSW-C*	*Fe-WTR*	*MSW-C*	*Fe-WTR+MSW-C*
pH_{H2O}	4.47±.0.04	7.87±0.01	4.98±0.02	7.46±0.03	7.82±0.02	7.81±0.02	7.94±0.02	8.22±0.01	8.15±0.01
pH_{KCl}	4.07±0.04	7.35±0.02	4.26±0.02	7.37±0.02	8.08±0.05	7.87±0.05	8.24±0.05	8.66±0.15	8.54±0.07
pH_{PCZ}	4.00±0.02	4.90±0.05	3.90±0.01	3.10±0.02	8.10±0.04	7.90±0.05	7.10±0.04	6.60±0.06	7.30±0.07
EC (dS·m^{-1})	0.68±0.01	0.45±0.02	0.99±0.03	0.32±0.00	0.55±0.01	0.49±0.01	0.33±0.00	0.40±0.00	0.27±0.00
Ash (%)	92.1±1.37	83.9±1.65	91.2±1.84	92.8±1.97	92.2±1.93	92.8±1.84	85.3±1.64	85.4±1.32	86.0±1.67
Total organic C (%)	1.51±0.24	1.93±0.02	1.73±0.11	2.66±0.03	2.95±0.06	2.72±0.07	4.54±0.10	4.90±0.09	4.71±0.13
Total N (%)	0.08±0.015	0.07±0.003	0.11±0.002	0.14±0.006	0.18±0.001	0.14±0.003	0.13±0.00	0.09±0.00	0.11±0.00
CEC (cmol$_{(+)}$·kg^{-1} d.w.)	12.15±0.55	16.44±0.89	16.47±1.97	16.52±0.41	17.44±0.09	17.04±0.86	21.03±0.17	24.67±1.22	20.98±0.23
DOC (mg·kg^{-1} d.m.)	30.36±0.15	240.3±3.01	36.23±0.21	157.2±1.31	340.6±2.32	204.3±1.87	432.6±2.01	438.4±2.17	434.6±2.388

Table 3

Number of fractions collected, volume that passed through the columns and cumulative volume.

Fraction	Volume (mL)	Cumulative volume (mL)
1	30	30
2	30	60
3	30	90
4	30	120
5	30	150
6	50	200
7	50	250
8	50	300
9	50	350
10	70	420
11	70	490
12	90	580
13	120	700
14	150	850
15	200	1050

Table 4

Leaching equations. Coefficients "a" in mg·kg^{-1} and "b" in mL.

	Treatment	S1 soil Model	a	b	R^2	S2 soil Model	a	b	p	R^2	S3 soil Model	a	b	p	R^2
DOC	Control		95.4	216.8	0.955		542.7	442.0		0.986		745.6	171.7		0.97
	Fe-WTR	y=(ax)/(b+x)	189.5	336.7	0.997	y=(ax)/(b+x)	705.0	711.2		0.991	y=(ax)/(b+x)	797.3	114.7		0.98
	MSW-C	)	479.6	336.0	0.983	)	744.9	332.6		0.985	)	725.1	167.2		0.98
	Fe-WTR+MSW-		650.5	974.7	0.988		570.8	332.0		0.970		784.8	156.8		0.94
As	Control		18.4	43.6	0.925		4.03	556	21	0.991		14.9	530.2	20	0.99
	Fe-WTR	y=(ax)/(b+x)	16.3	3867	0.998	y=a/(1+exp(-(x-b)/p))	2.24	452	19	0.988	y=a/(1+exp(-(x-b)/p))	9.93	524.3	20	0.98
	MSW-C	)	69.1	888.2	0.984		5.55	607	25	0.985		9.75	346.1	20	0.96
	Fe-WTR+MSW-		49.1	973.3	0.990		3.52	589	24	0.987		6.84	532.0	22	0.97
Fe	Control		45.2	79.9	0.823		6.91	365.0		0.992		0.94	140.2		0.93
	Fe-WTR	y=(ax)/(b+x)	208.5	1308	0.957	y=(ax)/(b+x)	4.50	201.3		0.990	y=(ax)/(b+x)	1.17	205.8		0.87
	MSW-C	)	44.1	146.5	0.977	)	7.70	271.9		0.985	)	1.56	210.8		0.99
	Fe-WTR+MSW-		40.7	350.3	0.981		4.78	309.3		0.979		1.49	93.6		0.94
Pb	Control		1.77	8.73	0.776										
	Fe-WTR	y=(ax)/(b+x)	0.89	35.3	0.792	-					-				
	MSW-C	)	16.3	89.2	0.937										
	Fe-WTR+MSW-		0.58	43.7	0.655										
Cu	Control		3.65	99.4	0.893										
	Fe-WTR	y=(ax)/(b+x)	0.10	9.5·10$^-$	0.999	-					-				
	MSW-C	)	5.48	143.4	0.985										
	Fe-WTR+MSW-		0.12	24.9	0.758										
Zn	Control		14.3	63.8	0.878										
	Fe-WTR	y=(ax)/(b+x)	1.95	242.9	0.972	-					-				
	MSW-C	)	20.8	142.2	0.946										
	Fe-WTR+MSW-		0.81	98.2	0.951										