

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

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

17

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

20

21 **1. Introduction**

22

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

1 due to anthropogenic activities, they can accumulate in soil to critical levels (Zhao et al.,
2 2010). Mining activities, in particular, constitute one of the major source of As and TM
3 (e.g. Pb, Cu and Zn), whose (combined) presence in primary sulphide ores is quite
4 common. Sulphide oxidation in such minerals contributes to the release of TM and As
5 in acidic mine effluents, spreading the contaminants in different environmental
6 compartments (Dold, 2003).

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

15 In such As and TM-co-contaminated soils the addition of iron, aluminum, or
16 manganese (hydr)oxide-based amendments may reveal effective, as they play a
17 significant role in the retention and mobility of both metals and metalloids such as
18 arsenic (Nagar et al. 2010; Nielsen et al., 2011; Castaldi et al., 2014). Accordingly, the
19 drinking water treatment residuals (WTRs) resulting from the addition of iron,
20 aluminium or calcium salts to raw water bodies, could be equally suitable for the “in-
21 situ” fixation of As and TM co-contaminated soils (Makris et al., 2006; Nagar et al.,
22 2010; Castaldi et al., 2014; Garau et al., 2014) as they are characterised by a significant
23 content of amorphous Al and/or Fe oxides, a high surface area and a neutral pH (Wang
24 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

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

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

9

10 **2. Materials and Methods**

11

12 *2.1. Description of the sampling area*

13

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

21

22 *2.2 Experimental set-up*

23

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

13 Differently amended contaminated soils were compared. Microcosms, each
14 consisting of approx. 10 kg soil (10 cm depth), were separately treated with the
15 following amendments: a) 2% (w/w) Fe-WTR [Fe-WTR]; b) 4% (w/w) municipal solid
16 waste compost [MSW-C]; c) 1% (w/w) Fe-WTR + 2% (w/w) MSW-Compost [Fe-
17 WTR+MSW-C]. All treatments were applied to triplicate microcosms and 3 additional
18 microcosms were kept untreated (polluted-soil). Before addition to soil, the Fe-WTR
19 (dried overnight at 105°C) and MSW-C were finely ground and sieved to < 2 mm
20 (Table 1). The Fe-WTR was provided by the Public limited company Abbanoa S.p.A.
21 (Sardinia, Italy) and derived from the drinking-water treatment plant in Bidighinzu
22 (Sassari, Italy) where the raw water was added with $\text{Fe}_2(\text{SO}_4)_3$ as coagulant. MSW-C,
23 derived mainly from municipal and green waste composting, was provided by the
24 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 BaCl₂ 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 HNO₃ 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 (NH₄)₂SO₄ solution and shaken for 4 h at 20 °C to extract the non-

1 specifically sorbed As (Fraction 1). The same samples were then treated with 25 mL of
2 a 0.05 M $\text{NH}_4\text{H}_2\text{PO}_4$ solution and shaken for 16 h to extract the specifically sorbed As
3 (Fraction 2). Soil samples were then treated with 25 mL of 0.2 M NH_4^+ -oxalate buffer
4 and shaken for 4 h to extract the As associated with amorphous and poorly crystalline
5 hydrous oxides of Fe and Al (Fraction 3). Finally, samples were treated with 25 mL of
6 0.2 M NH_4^+ -oxalate buffer+0.1 M ascorbic acid and shaken for 0.5 h in a water basin at
7 96 °C to extract the As associated with well-crystallized hydrous oxides of Fe and Al
8 (Fraction 4). After each step of the extraction process the soil samples were centrifuged
9 at 8000 rpm for 10 min and filtered to separate the liquid and solid phases.

10 The sequential extraction of metals was performed following the procedure of Basta
11 and Gradwohl (2000). In particular, soil samples (1 g) were treated with 25 mL of a 0.5
12 M $\text{Ca}(\text{NO}_3)_2$ solution to extract the Me-exchangeable pool, and with 25 mL of a 1 M
13 NaOAc solution at pH 5.0 to extract Me(II) forming weak surface complexes and finally
14 with 25 mL of a 0.1 M Na_2EDTA solution to extract the surface complexed and
15 precipitated metals. After each step of the extraction process, the samples were
16 centrifuged at 8000 rpm for 10 min, filtered to completely separate the liquid and solid
17 phases.

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

22

23 *2.4 Leaching tests*

24

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 $0.2 \text{ mL}\cdot\text{min}^{-1}$, 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 ($\text{mg}\cdot\text{kg}^{-1}$ 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 ($\text{mg}\cdot\text{kg}^{-1}$), “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 %), clinocllore (15 wt %),
15 sanidine (1 wt %) and beudantite 8 wt % [$\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$], 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 $\text{S1} < \text{S2} < \text{S3}$ (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

1 the easily exchangeable and water-soluble As, generally decreased in the soils amended
2 with Fe-WTR (~60 % lower with respect to untreated soils), likely as consequence of
3 formation of insoluble complexes between As and Fe oxides and hydroxides, in
4 agreement with the results reported by several authors (e.g. Garau et al., 2014; Nagar et
5 al., 2015). By contrast, S1 and S2 soils treated with MSW-C showed an increase of
6 exchangeable and water-soluble As (>65 and 26% respectively, compared to control).
7 This increase could be mainly assigned: i) to the competition between humic substances
8 and dissolved organic carbon (significantly increased in S1- and S2-MSW-C) with As
9 for retention sites (Tandy et al., 2009); ii) to the potential of some ions in compost to
10 displace As from the Fe-oxide phases (e.g. arsenate by phosphate (Fitz and Wenzel,
11 2002)); iii) to the formation of As-(Me)-DOC soluble complexes (Wang and Mulligan,
12 2009). By contrast, the higher content of clay and organic matter in S3 soil (Tables 1-2)
13 likely buffered such effects driven by compost addition.

14 With the exception of S2 soil, all the amendments decreased significantly the As
15 amounts recovered in Fraction 2 (Fig. 1). In this step of the sequential extraction, the
16 arsenic species chemically bound to solid phase surfaces through inner-sphere
17 complexes (e.g. H_2AsO_4^- and HAsO_4^{2-} and/or $\text{As}(\text{OH})_3$) are competitively exchanged by
18 phosphate anions (Wenzel et al., 2001). The decrease of this As fraction was
19 particularly evident in the S1 soil treated with MSW-C, where a 95% decrease was
20 observed (Fig. 1).

21 All the amendments reduced significantly the As extracted in both Fractions 3 and 4
22 from S1 soil. These fractions account for the As associated to amorphous and poorly
23 crystalline Fe and Al (hydr)oxides (Fraction 3) and for the As associated to well-
24 crystallized Fe and Al (hydr)oxides (Fraction 4). MSW-C added to S1 was the most

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

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

13 The results of the sequential extraction highlighted a general suitability of all the
14 treatments at fixing As in all the soils considered. Nonetheless, while the influence of
15 Fe-WTR on the As immobilization could be (to some extent) anticipated given the
16 significant content of Fe (hydr)oxides (Sarkar et al., 2007; Nielsen et al., 2011; Garau et
17 al., 2014; Nagar et al. 2015), the results arising from MSW-C addition add a new
18 contribution on the controversial and not well resolved role of the organic matter on
19 arsenic mobility in soil (i.e. Cao et al. 2003; Tandy et al., 2009; Pardo et al., 2011;
20 Udovic and McBride, 2012). The sequential extraction data indicated that As
21 immobilization phenomena, induced by the amendments, were dominant with respect to
22 As mobilization ones which occurred with a very limited extent (Fraction 1 increased in
23 S1- and S2-MSW-C only by the 0.22 and 0.28% of total As respectively). Moreover,
24 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 $\text{Ca}(\text{NO}_3)_2$) 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

1 al., 2003). Besides, it cannot be excluded that the addition of compost containing
2 several metal cations (such as Ca and Mg) could have affected the mobility of Zn due to
3 ionic competition (Branzini and Zubillaga, 2012). Apart from this latter exception, all
4 the amendments tested appeared effective at reducing the TM extracted with $\text{Ca}(\text{NO}_3)_2$
5 and this is relevant since this fraction represents the Me(II) pool most labile and
6 potentially bio-available. This could be mainly explained with the capacity of the
7 organic and inorganic components of the Fe-WTR and MSW-C employed to sorb the
8 metals considered (i.e. Park et al., 2011; Garau et al., 2014). The TM fraction extracted
9 with NaOAc represents metals bound to the weak acid-soluble phase as well as
10 co(precipitated) with carbonate (Pickering, 1986). This fraction was 1.72, 3.35 and
11 2.22% of total Pb, Cu and Zn in S1 soil respectively. Such low percentages could be
12 assigned to the low carbonate content in S1 soil. In S1-MSW-C, the increase of DOC
13 probably favoured the enhancement of Pb, Zn and Cu within the acid-soluble fraction
14 (+23, +248 and +14-fold respectively). In S2 soil the Zn extracted with NaOAc was
15 ~10% of total Zn, highlighting the formation of weak surface complexes between this
16 TM and soil colloids. The addition of all amendments caused a decrease of this fraction.

17 EDTA-extractable Pb, Zn and Cu increased in S1 soil after compost addition (+7.5,
18 +255 and +23.5-fold for Pb, Zn and Cu respectively with respect to the untreated soil),
19 highlighting the ability of these trace metals to form stable inner-sphere complexes with
20 the functional groups of compost (Walker et al., 2003). The increase of TM extracted
21 with EDTA could be also due to precipitation of metals as insoluble salts, e.g. as
22 Me(II)- phosphates (phosphates are abundantly present in our compost) as suggested by
23 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” ($\text{mg}\cdot\text{kg}^{-1}$) 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 oxo(hydroxi)des or iron-rich WTR as sorbents in polluted

1 soils (Hartley et al., 2004; Alvarez-Ayuso et al., 2013; Nagar et al., 2015). S1 and S2
2 soil samples treated with MSW-C showed the highest of maximum As concentration
3 leached on soil basis (up to 69 and 5.5 mg·kg⁻¹ respectively, ~0.3 and 1.3% of total As)
4 (Table 4). Equally, As maximum concentration in S1-Fe-WTR+MSW-C was 2.7-fold
5 time higher than in control, pointing out that MSW-C added singly impaired the
6 scenario provided by the combined treatment. The increase of As leached in the S1 and
7 S2 amended with compost could be related to the increase of DOC, which can compete
8 with As for retention sites as well as favour the formation of As-(Me)-DOC soluble
9 complexes (Wang and Mulligan, 2009). In S3 soil, according to the sigmoidal model, all
10 the treatments favoured a decrease of As leached. In this soil Fe-WTR added singly was
11 not as efficient as the combined treatment. Further, although the highest estimated As
12 concentration was similar for Fe-WTR and MSW-C, this latter promoted a higher
13 leaching of As, as pointed out by a lower “b” coefficient (a lower “b” value means a
14 lower volume of water required to leachate the same metal(loid) concentration). In any
15 case, compost treatment in S3 soil was effective to limit total cumulative concentration
16 of As leached, as consequence of the strong buffering capacity of this soil, which
17 mitigated the detrimental effects of compost DOC on the arsenic solubility (Warren et
18 al., 2003). These results, which provided important information about As leaching in the
19 different treated soils, seem in line with those of the sequential extraction.

20 Fe-WTR and Fe-WTR+MSW-C in S2 and S3 soils, as observed within the graphs
21 and the model equations, did not contribute to the Fe release, despite the incorporation
22 of the iron-bearing materials (Figure 4). The high leachate pH in these treatments could
23 have limited Fe release from soils, while MSW-C singly added promoted the highest
24 increases of Fe leaching in S2 and S3. In the other hand, the low leachate pH in S1 Fe-

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

3 It was only possible to display Pb, Cu and Zn leaching on S1 soil, as in the other two
4 soils their concentrations were under the detection limit. Points were better fitted to a
5 hyperbolic model than to a sigmoidal, and hence, the leaching curves with greater
6 slopes estimated a more rapid leaching (Figure 4). Pb was the less mobile element
7 compared to Cu and Zn in the S1 control sample, denoting a low leaching. Fe-WTR and
8 Fe-WTR+MSW-C were the treatments that highly reduced the total cumulative Me(II)
9 concentration at the end of leaching, while the highest Me(II) leaching was detected in
10 S1-MSW-C (+9.25, +1.50, and +1.46-fold for Pb, Cu and Zn respectively with respect
11 to control). The model equations showed that Fe-WTR+MSW-C was the best treatment
12 for the reduction of maximum Pb and Zn concentration according to the parameters “a”
13 and “b”. For Cu, this treatment obtained the same results of Fe-WTR. The reduction of
14 leached Pb, Cu and Zn in the soils treated with iron-rich residues, can be assigned to the
15 formation of strong inner-sphere complexes between metals and the oxyhydroxide
16 surfaces of Fe-WTR or to co-precipitation processes, in line with other leaching studies
17 employing amorphous Al or Fe-oxide (Houben et al., 2012; Alvarez-Ayuso et al.,
18 2013).

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

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

5 The combined Fe-WTR+MSW-C treatment favored a strong reduction of trace metal
6 leaching in S1 soil. In the literature good synergisms between organic matter and iron-
7 rich amendments can be found. For example, Mench et al. (2006) and Ruttens et al.
8 (2006) found a decrease of Pb and Zn leaching in a contaminated soil amended with
9 compost and/or inorganic metal immobilizing soil amendments.

10

11 **4. Conclusions**

12

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

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

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

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

17

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21

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- 22

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 1Characterization of S1, S2 and S3 soils, iron-rich water treatment residue (Fe-WTR) and municipal solid waste compost (MSW-C). Mean \pm SE

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

n.d.: under detection limit.

Table 2Characterization of S1, S2 and S3 soils amended with Fe-WTR, MSW-C and Fe-WTR+MSW-C. Mean \pm SE

	S1 soil			S2 soil			S3 soil		
	<i>Fe-WTR</i>	<i>MSW-C</i>	<i>Fe-WTR+MSW-C</i>	<i>Fe-WTR</i>	<i>MSW-C</i>	<i>Fe-WTR+MSW-C</i>	<i>Fe-WTR</i>	<i>MSW-C</i>	<i>Fe-WTR+MSW-C</i>
pH _{H2O}	4.47 \pm 0.04	7.87 \pm 0.01	4.98 \pm 0.02	7.46 \pm 0.03	7.82 \pm 0.02	7.81 \pm 0.02	7.94 \pm 0.02	8.22 \pm 0.01	8.15 \pm 0.01
pH _{KCl}	4.07 \pm 0.04	7.35 \pm 0.02	4.26 \pm 0.02	7.37 \pm 0.02	8.08 \pm 0.05	7.87 \pm 0.05	8.24 \pm 0.05	8.66 \pm 0.15	8.54 \pm 0.07
pH _{PCZ}	4.00 \pm 0.02	4.90 \pm 0.05	3.90 \pm 0.01	3.10 \pm 0.02	8.10 \pm 0.04	7.90 \pm 0.05	7.10 \pm 0.04	6.60 \pm 0.06	7.30 \pm 0.07
EC (dS·m ⁻¹)	0.68 \pm 0.01	0.45 \pm 0.02	0.99 \pm 0.03	0.32 \pm 0.00	0.55 \pm 0.01	0.49 \pm 0.01	0.33 \pm 0.00	0.40 \pm 0.00	0.27 \pm 0.00
Ash (%)	92.1 \pm 1.37	83.9 \pm 1.65	91.2 \pm 1.84	92.8 \pm 1.97	92.2 \pm 1.93	92.8 \pm 1.84	85.3 \pm 1.64	85.4 \pm 1.32	86.0 \pm 1.67
Total organic C (%)	1.51 \pm 0.24	1.93 \pm 0.02	1.73 \pm 0.11	2.66 \pm 0.03	2.95 \pm 0.06	2.72 \pm 0.07	4.54 \pm 0.10	4.90 \pm 0.09	4.71 \pm 0.13
Total N (%)	0.08 \pm 0.015	0.07 \pm 0.003	0.11 \pm 0.002	0.14 \pm 0.006	0.18 \pm 0.001	0.14 \pm 0.003	0.13 \pm 0.00	0.09 \pm 0.00	0.11 \pm 0.00
CEC (cmol ₍₊₎ ·kg ⁻¹ d.w.)	12.15 \pm 0.55	16.44 \pm 0.89	16.47 \pm 1.97	16.52 \pm 0.41	17.44 \pm 0.09	17.04 \pm 0.86	21.03 \pm 0.17	24.67 \pm 1.22	20.98 \pm 0.23
DOC (mg·kg ⁻¹ d.m.)	30.36 \pm 0.15	240.3 \pm 3.01	36.23 \pm 0.21	157.2 \pm 1.31	340.6 \pm 2.32	204.3 \pm 1.87	432.6 \pm 2.01	438.4 \pm 2.17	434.6 \pm 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	Model	<i>S1 soil</i>			<i>S2 soil</i>				<i>S3 soil</i>					
			a	b	R ²	Model	a	b	p	R ²	Model	a	b	p	R ²
DO C	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=	2.24	452	19	0.988	y=	9.93	524.3	20	0.98
	MSW-C)	69.1	888.2	0.984	a/(1+exp(-	5.55	607	25	0.985	a/(1+exp(-	9.75	346.1	20	0.96
	Fe-WTR+MSW-		49.1	973.3	0.990	(x-b)/p))	3.52	589	24	0.987	(x-b)/p))	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										

