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Abstract

Understanding the effect of soil redox conditions on contaminant dynamics is of significant importance for evaluating their lability, mobility and potential transfer to other environmental compartments. Under changing redox conditions, soil properties and constituents such as Fe and Mn (hydr)oxides and organic matter (OM) may influence the behaviour of associated metallic elements (ME). In this work, the redox-driven release and redistribution of Cu between different soil pools was studied in three soils having different contamination sources. This was achieved by subjecting soil columns to a series of alternating reducing and oxidizing cycles under non-limiting C conditions, and assessing their influence on soil pore water, leachate and solid phase composition. Results showed that, in all soils, alternating redox conditions led to an increase in the distribution of Cu in the more labile fractions, consequently enhancing is susceptibility to loss. This was generally linked to the redox-driven cycling of Fe, Mn and dissolved organic matter (DOM). In fact, results suggested that the reductive dissolution of Fe and Mn (hydr)oxides and subsequent reprecipitation as poorly-ordered phases under oxic conditions, contributed to the release and mobilization of Cu and/or Cu-containing organometallic complexes. However, the behaviour of Cu, as well as the mechanisms controlling Cu release and loss with redox cycling, were influenced by both soil properties (e.g. pH, contents of easily reducible Fe and Mn (hydr)oxides) and source of Cu contamination.

Keywords: metallic elements, copper leaching, iron oxides, dissolved organic matter, redox cycling

1. Introduction

The mechanisms governing metallic element (ME) release from soils subjected to changing water contents may be directly or indirectly related to variations in soil redox potentials. The release of ME may be linked to redox-driven processes such as the reductive dissolution of Fe and Mn (hydr)oxides (Du Laing et al., 2009; Frohne et al., 2011), or to the degradation of soil organic matter (SOM) with which they are often linked (Reddy and DeLaune, 2008).

Among the divalent transition metals, Cu is considered to be the one most tightly bound to organic matter (OM) and strongly associated with Fe and Mn (hydr)oxides and clay minerals (Phillips, 1999; Zhao et al., 2007). Apart from intrinsic soil and ME properties, the release of Cu from soils may depend on the mechanisms involved in the retention of Cu on soil constituents, and consequently on the source of Cu.

Copper is a contaminant diffused in the soil-water system by a range of anthropic activities and its release may pose a significant threat to environmental and human health. The use of Cu-containing pesticides in agriculture may result in the transfer of substantial amounts of Cu to arable soils. Vineyard topography and intense rainfalls may cause pesticide losses by surface runoff and leaching, potentially resulting in surface and groundwater contamination (Barrett and McBride 2006; Huguenot et al. 2010). In mining areas, soils may have high concentrations of ME either due to the mining activities, incorrect disposal of mine waste and flotation residue, or to the bedrock itself (Nimirciag, 2012). Since this mainly occurs in mountainous river valleys, the increasing possibility of flash floods may influence soil redox conditions (EEA, 2008; Popescu et al., 2013a). Urban soils may also present high contaminant concentrations, especially ME, exceeding threshold values (Ajmone-Marsan and Biasioli, 2010; Charlesworth et al., 2011) due to anthropic activities, such as traffic, industry and waste disposal. Rapid land use changes occurring in urban areas may often lead to soil compaction and extensive sealing (Biasioli and Ajmone-Marsan, 2007; Scalenghe and Ajmone-Marsan, 2009). Consequently, urban soils may be subject to water saturation for short periods of time following intense storms, therefore leading to changes in soil redox conditions.

Most research on Cu dynamics in soils has focused on the stability, release and mobility of Cu associated with Fe and/or Mn (hydr)oxides (Davranche and Bollinger, 2000; Loomer et al., 2011; Matocha et al., 2005), or OM (Amery et al., 2008; Businelli et al., 2009; Hernandez-Soriano and Jimenez-Lopez, 2012). Only few studies assessed the interdependence between these soil constituents in the attempt to identify the key processes controlling Cu release (Grybos et al., 2007; Parat et al., 2002). Moreover, most studies have thoroughly evaluated the behaviour of Cu under permanently oxic or anoxic environments, showing that Cu release may be either promoted or inhibited as a result of water saturation with respect to unsaturated conditions, as a function of soil mineral composition, quantity and quality of OM, and contamination source (Lindsay et al., 2011; Matocha et al., 2005; Wang and Staunton, 2006). However, our understanding of the effect of changing soil redox conditions on Cu behaviour and its potential environmental threat is still limited. Based on these considerations, we aimed at elucidating the influence of alternating reducing and oxidizing conditions on Cu release, mobilization and redistribution in soils with different sources of Cu contamination. We also evaluated the interactions between Cu dynamics and redox-driven Fe, Mn and dissolved organic matter (DOM) cycling.

2. Materials and methods

2.1. Soil characterisation

Three topsoils (0-20 cm) were sampled from areas exposed to different sources of Cu-containing contaminants: (i) a non-calcareous agricultural soil sampled from a vineyard (VIN) where Cu-containing phytochemicals, such as $CuSO_4$ in combination with glyphosate, were extensively applied for the control of mildew (Alessandria, Italy; 44.680601°N, 8.622292°E); (ii) a mine-impacted soil (MIN) located within pastures affected by Cu-containing mine tailings (Popescu et al., 2013b), and sampled in the vicinity of a flotation plant (Balan, Romania; 44.672789°N, 25.796523°E); and (iii) a compost-amended urban soil (IND) collected from an area affected by mass production automobile industry (Torino, Italy; 45.089939°N, 7.672155°E). Each soil sample

was composed of a series of subsamples (~1 kg each) and adequately homogenized. These 3 soils were selected for their similar Cu contents, which would provide a better understanding of the contamination source effect on the behaviour of Cu under redox conditions.

Soil physical and chemical properties were determined in duplicate using standard methods (MIPAF, 2000) and reported in Table 1. Soil samples were air-dried, gently crushed and sieved to pass through a 2 mm sieve. Soil pH was measured potentiometrically in a 1:2.5 soil:KCl (1 M) suspension. Total C and N were measured by a dry combustion method (elemental analyser, NA2100, CE Instruments, Italy). Particle-size analysis was performed by the sieve-pipette method, using sodium hexametaphosphate as a dispersant (Gee and Bauder, 1986). Reducible and poorly crystalline Fe (hydr)oxides as well as associated Cu and Mn were extracted with dithionite-citrate-bicarbonate (DCB) and ammonium oxalate (AO), as described by Mehra and Jackson (1958) and Schwertmann and Cornell (1991), respectively. Although generally employed for Fe fractionation, DCB and AO extraction procedures could also be used to evaluate the dynamics of metals associated with Fe (hydr)oxides (Adamo et al., 2006). Metal distribution in progressively less labile metal pools was assessed in triplicate using the modified BCR sequential extraction described by Rauret et al. (2000). This procedure aims at extracting four ME fractions using: 0.11 M acetic acid (F1), 0.5 M hydroxylammonium chloride (F2), 8.8 M hydrogen peroxide and 1 M ammonium acetate at pH 2 (F3), and *aqua regia* (F4). Small aliquots of soil were further ground (<0.5 mm) to determine pseudo-total (PT) metal concentrations by microwave-assisted (Start D, MILESTONE, U.S.A.) *aqua regia* ($HCl:HNO_3$, 3:1) digestion. Total contents of Cu, Fe and Mn in all extracts were analyzed by flame atomic absorption spectrometry (FAAS, AAnalyst 400, Perkin Elmer, U.S.A.). Recoveries of the BCR procedure were calculated as the sum of metal concentrations extracted in each step normalized to the results of the PT metal digestion. In all soils, the BCR extraction yielded Fe, Mn and Cu recoveries ranging between 91-106, 96-116 and 88-108%, respectively.

2.2. Column mesocosm experiment

Soil columns (70 cm in height and 7 cm in diameter) were setup and subjected to alternating reducing and oxidizing conditions as previously described in Balint et al. (2013). Briefly, duplicate Plexiglass® columns were packed with 1.3 kg of each soil (<2 mm), subsequently saturated with a 10 mM $CaCl_2$ + 3 mM lactose solution and subjected to a series of redox cycles, each composed of 5 days anoxic and 2 days oxic conditions. Pore waters were extracted by Rhizon samplers (Rhizosphere Research Products, The Netherlands) installed at a depth of 20 cm from the soil surface, just before draining. Column leachates were collected from the bottom during drainage. After 4 successive redox cycles, columns were allowed to drain until the soils reached an average water content of approximately 70% field capacity (about 55 d), with a higher moisture content towards the bottom of the columns. The soils were subsequently re-saturated with fresh solution and the experiment continued with another series of 4 redox cycles as described above. This was carried out to simulate extensive soil drainage of previously submerged soils, in order to evaluate the effects of a longer oxic phase on Cu behaviour during subsequent redox cycling.

Soil pore waters and leachates were analysed spectrophotometrically for ferrous iron by the 1,10-phenanthroline method (Loeppert and Inskeep, 1996) and by FAAS for total Cu, Fe and Mn concentrations. Since total and reduced Fe concentrations in solution were similar, only the latter

were reported. Ultraviolet absorbance values at 254 nm were measured spectrophotometrically (HITACHI U-2000, U.S.A.) for all solutions after appropriate dilution (10 fold). Since, in contrast to the added lactose, soluble aromatic compounds absorb UV radiation at this wavelength, measured values were used to evaluate the release of soil-derived DOM in solution under reducing conditions.

After 8 redox cycles the soils were carefully removed from the columns and two 10 cm soil sections were extracted at depths corresponding to the uppermost (U) and lowest (L) layers of the soil. All soils were dried at 40°C and subjected to DCB, AO and modified BCR fractionation. Total Cu, Fe and Mn concentrations in the extracts of the 2 layers were compared with those of the initial, non-incubated soils.

3. Results and discussion

3.1. Influence of redox alternation on Fe, Mn, DOM and Cu dynamics in solution

For all soils redox cycling resulted in a general increase in measured pore water Fe and Mn concentrations (Fig. 1). These redox-sensitive elements are released into solution during soil submergence and their concentrations may be used as a proxy for reducing conditions. Observed trends may be attributed to the reductive dissolution of Fe and Mn (hydr)oxides under water saturated conditions, followed by rapid oxidation and reprecipitation during soil drainage. As observed in previous experiments (Balint et al., 2013; Biasioli et al., 2010), short-term oxidative reprecipitation favours the formation of Fe and Mn phases with a low degree of crystallinity which are more susceptible to reductive dissolution with successive redox cycles. On the other hand, the prolonged oxidative phase between the fourth and fifth redox cycle diminished the release of Fe and Mn into solution in the subsequent 4 cycles. This was particularly evident for Fe, probably due to an increase in crystallinity of reprecipitated (hydr)oxides that could have limited the subsequent dissolution during the following redox cycles. In fact, the rapid oxygenation of soluble Fe(II) generally leads to the formation of metastable ferrihydrite, which tends to transform into more stable goethite or hematite even under ambient conditions (Cornell and Schwertmann, 2003). Moreover, enhanced SOM ammonification and nitrification during this prolonged oxidative phase could have resulted in an increase in soil nitrate concentrations, that could have served as a preferential electron acceptor under subsequent anoxic conditions, partially inhibiting microbial reduction of Fe and Mn (hydr)oxides (Kirk, 2004).

Over the whole experimental period the release of Fe(II) into pore waters was more pronounced in MIN with respect to VIN and IND (Fig. 1), although Fe_{PT} and Fe_{DCB} concentrations were similar in all three soils (Table 1). This could be attributed to a higher content of Fe (hydr)oxides having a low degree of crystallinity in MIN with respect to VIN and IND, as suggested by their Fe_{AO} contents (Table 1). In fact, Fe (hydr)oxides present in MIN showed a higher susceptibility to reductive dissolution as evidenced by the higher Fe_{AO}/Fe_{DCB} ratio (0.40) with respect to the other soils (0.09 and 0.19 for VIN and IND, respectively). Another possible explanation for the different release of Fe from the three soils may be given by their pH values (Table 1). Although under reducing conditions soil pH generally converges towards circumneutral values (Ponnamperuma, 1972), the lower initial pH values of MIN probably allowed for a greater solubility of Fe(II) with respect to VIN and IND. Similarly, the greater release of Mn into soil pore waters during the reduction of VIN and

MIN with respect to IND was consistent with their initial Mn_{AO}/Mn_{DCB} ratios (0.84, 0.83 and 0.68 for VIN, MIN and IND respectively).

The observed increase in pore water Fe and Mn concentrations with successive redox cycles inevitably led to an increase in their loss in column leachates during drainage (Fig. 1). However, although concentrations of both Fe and Mn in leachates and pore waters were positively correlated (r=0.673 and 0.910 for Fe and Mn, respectively; P<0.001), Fe contents in the leachates were greater than those observed in the pore waters, particularly for the last four redox cycles. This was probably due to an increasing gradient in the release of Fe with soil depth as a direct result of successive redox cycles. In fact, in a similar experiment, Balint et al. (2013) observed an increasing difference in the Fe content of pore waters sampled from the top and bottom of a soil column with redox cycling. The incomplete soil aeration at the bottom of the column during both the short-term and prolonged oxidative phases could have possibly contributed to enhancing the differences in Fe concentrations between pore waters and column leachates.

With successive redox cycles UV absorbance (254 nm) of soil pore waters tended to increase for all soils under study (Fig. 2), suggesting a release of aromatic OM from soil constituents. Aromaticity was shown to be an good indicator of DOM reactivity towards inorganic species such as Fe, Mn and Cu (Amery et al., 2008; Weishaar et al., 2003). In fact, the soil pore water UV absorbance values were significantly correlated to Fe (r=0.844; P<0.001) and Mn concentrations (r=0.730; P<0.001). The release of DOM under reducing conditions generally decreased in the order MIN>VIN>IND, in line with the decreasing contents of total organic C (Table 1), and Fe_{AO}/Fe_{DCB} and Mn_{AO}/Mn_{DCB} ratios as reported above. This was supported by the widely held notion that metal (hydr)oxides are remarkable sorbents for DOM in soils (Kalbitz et al., 2000; Shaheen et al., 2014). The reductive dissolution of Fe and Mn (hydr)oxides, as well as the increase in pH under anoxic conditions could have resulted in the mobilization of OM, including aromatic moieties, previously stabilized on soil minerals. All soils, but particularly VIN and MIN showed a strong decrease in absorbance values of soil pore waters between the fourth and fifth redox cycles. This could be attributed to (i) enhanced mineralization of previously stabilized SOM during the prolonged oxidative phase, and/or (ii) the stabilization of aromatic moieties within coprecipitates or on new surfaces resulting from the reprecipitation and aging of Fe and Mn (hydr)oxides. Nonetheless, the smaller increase in absorbance values observed during the last with respect to the first series of redox cycles suggested that prolonged soil oxidation could have limited but did not inhibit the successive release of DOM. Absorbance values of soil leachates showed similar trends to those observed for pore waters throughout the experiment. This suggested that under alternating redox conditions some of the DOM released during soil flooding could be lost during drainage.

For all soils, submersion initially led to a release of Cu into pore waters and subsequent loss in the leachates. This was generally followed by a steady decrease in Cu pore water concentrations, reaching values below detection limits by the second (for IND) and fourth (for VIN and MIN) reductive phases (Fig. 3). In contrast to VIN and MIN, IND generally showed undetectable pore water and leachate Cu concentrations throughout the experiment, suggesting that the subalkaline pH of this soil strongly limited Cu release and mobilization. In fact, Cu solubility decreases at pH values close to neutrality and redox potentials below +340 mV typically encountered in saturated soils (Frohne et al., 2011). However, the presence of Cu in solution during the first redox cycle in

IND was probably due to the release and loss of Cu-OM complexes that could have been soluble even at these pH values. The high affinity of Cu for OM has been previously shown to strongly determine Cu speciation and dynamics in soil-water systems (Wang and Staunton, 2006). Nonetheless, the apparent absence of Cu mobility in the alkaline soil with subsequent alternating redox conditions does not exclude metal redistribution due to the redox-driven release of Fe/Mn (hydr)oxide-associated Cu, and its immediate reprecipitation.

The lower soil pH values of VIN and MIN generally resulted in a greater release and consequent loss of Cu with respect to IND throughout the experiment. The increase in pH values with successive redox cycles could have nonetheless limited Cu solubility under reducing conditions, particularly in VIN that already had an initial pH value close to neutrality. The high amounts of Cu in the AO-extractable fraction in these soils (Table 1) suggest that redox cycling may have resulted in the release of Cu associated with OM and/or Fe/Mn (hydr)oxides having a low degree of crystallinity due to their reductive dissolution. However, the absence of significant positive correlations between soil solution Cu concentrations and the release of Fe, Mn and DOM with successive redox cycles could be a result of their different Cu sources. Vineyard soils like VIN generally receive significant amounts of Cu-containing phytochemicals, such as $CuSO_4$ in combination with glyphosate having amine, carboxylate and phosphate functional groups, capable of forming strong coordination complexes with metals. The presence of glyphosate in VIN and its potential to strongly chelate and mobilize Cu could have been responsible for the relatively high metal concentrations observed in the soil leachates. As reported by Barrett and McBride (2006), these effects may subside as the herbicide is gradually removed from solution either by leaching or by adsorption on mineral surfaces and OM. After the prolonged oxidative phase between the fourth and the fifth redox cycles, higher Cu concentrations were released in both pore waters and leachates, probably as a result of the degradation of OM involved in the complexation and/or bridging of Cu. During this phase, glyphosate which, according to Wang et al. (2009), could also be involved in the formation of bridging mechanisms between Cu(II) and other soil constituents, such as Fe/Mn (hydr)oxides, might also have been decomposed. In mine-impacted soils like MIN, Balint et al. (2014) have shown that the dissolution of Cu-containing minerals (e.g. $CuFeS_2$, Cu_2S, CuS, $CuSO_4$ and Cu_2O) rather than the release of Cu associated with Fe and Mn (hydr)oxides may primarily drive Cu dynamics under alternating redox conditions, and possibly be responsible for the relatively high Cu concentrations in pore waters and leachates observed in this study. The prolonged oxidative phase between the fourth and the fifth redox cycle led to higher pore water Cu concentrations possibly resulting from the exposure of Cu sulfides and subsequent Cu release in solution during the successive onset of reducing conditions (Fig. 3). This was in contrast with the enhanced fixation of Cu into Fe oxides with redox cycling reported by Contin et al. (2007), further confirming that the source of Cu may play an important role in determining Cu dynamics.

Other mechanisms that could be responsible for the contrasting decrease in Cu concentrations (Fig. 3) with increasing release of Fe/Mn (Fig. 1) and DOM (Fig. 2) with successive redox cycles could include: (i) the increase in the retention of Cu and/or Cu-OM complexes on new binding sites exposed during the reductive dissolution of Fe/Mn (hydr)oxides (Charlatchka and Cambier, 2000; Zheng and Zhang, 2011); and (ii) the lower dissolution kinetics of coprecipitated Cu (Davranche and Bollinger, 2000).

3.2. Influence of redox cycling on Fe, Mn and Cu extracted by DCB and AO

In the studied soils, Fe_{DCB} and Fe_{AO} accounted for 32-34% and 3-13% of Fe_{PT} contents, respectively (Table 1), suggesting the presence of notable amounts of reducible Fe. Similarly, 55-71% and 43-60% of Mn_{PT} contents were extracted in DCB and AO, respectively (Table 1). In fact, alternating redox conditions caused the reductive dissolution of Fe and Mn (hydr)oxides, and the consequent release and leaching of Fe and Mn from all studied soils (Fig. 1). Nevertheless, the solubilised concentrations represented only a small fraction of the reducible Fe and Mn (less than 1 and 10%, respectively).

Iron fractionation of the soils before and after redox cycling evidenced a relative increase in Fe_{AO} for VIN and IND, but not for MIN (Fig. 4). Considering that both preferential dissolution and loss of easily reducible Fe oxides, as well as transformation of more ordered into less crystalline oxides as a result of redox cycling may influence Fe_{AO} contents, the ratio of Fe_{AO}/Fe_{DCB} better described the observed changes. An increase in this ratio (1.8 to 2.1-fold) was evidenced in VIN and IND as a result of redox cycling, suggesting that the reductive dissolution of more crystalline phases followed by reprecipitation as less ordered Fe oxides was probably more important than the preferential loss of easily reducible Fe from the soil columns. This is in line with the results obtained by Zheng and Zhang (2011), who observed a 1.8-fold increase in amorphous Fe oxide concentrations in soil under a wetting-drying regime, while total reducible Fe oxide contents remained relatively unchanged. This was not the case for MIN, in which the lack of change in the Fe_{AO}/Fe_{DCB} ratio before and after incubation, together with the relatively high concentrations of Fe in column leachates (Fig. 1) indicated that the loss of easily reducible Fe (hydr)oxides was probably the dominating process. The differences in Fe_{AO}/Fe_{DCB} ratios between the uppermost and lowest soil layers observed for VIN and IND further support the hypothesis that repeated water saturation and drainage resulted in the dissolution of Fe (hydr)oxides, transport of dissolved Fe along the soil column, and subsequent reprecipitation as poorly crystalline phases with their accumulation in the deeper soil layers. This increase in easily reducible Fe (hydr)oxides in the lower soil layers could also explain the increasing difference between Fe concentrations in column leachates and soil pore waters with successive redox cycles (Fig. 1).

Both AO and DCB-extractable Mn tended to decrease in all soils after column incubation, with the greatest decrease generally observed for the deepest soil layer (Fig. 4). Moreover, the substantial decrease in the Mn_{AO}/Mn_{DCB} ratio observed for MIN and IND as a result of redox cycling suggests that preferential dissolution of easily reducible Mn (hydr)oxides under saturated conditions with limited reprecipitation during drainage dominated Mn dynamics in these soils. This was supported by the relatively high amounts of Mn leached during the column experiment, which accounted for 4 to 10% of the DCB-extractable Mn.

In all studied soils, we observed higher Cu_{AO} with respect to Cu_{DCB} contents both before and after redox cycling (Fig. 4). The lower Cu_{DCB} concentrations were previously interpreted as a poor association of Cu with both crystalline and poorly ordered oxides (Flores-Vélez et al., 1996), or attributed to Cu-containing mineral phases not solubilized by reductive dissolution (Balint et al., 2014). However, we cannot exclude that Fe (hydr)oxide-associated Cu could have precipitated at the pH of the DCB extraction (pH 7.2). On the other hand, the relatively high Cu_{AO} contents

obtained may be attributed to the strong complexing action of AO (Flores-Vélez et al., 1996) or to the presence of Cu minerals readily mobilized at the pH of AO extraction (pH 3) (Balint et al., 2014). Ammonium oxalate Cu contents extracted before and after redox cycling did not show any differences for VIN and MIN, suggesting that redox alternations did not influence the fraction of Cu associated with Fe (hydr)oxides having a low degree of crystallinity. In IND, redox cycling led to contrasting results, with an increase in Cu_{AO} contents in the uppermost soil layer and a decrease in the bottom of the column. The transformation of more ordered into less crystalline oxides, as evidenced by the notable increase in Fe_{AO}/Fe_{DCB} ratio observed for this soil, may suggest that these changes could have influenced the distribution of (hydr)oxide-associated Cu in favour of the poorly crystalline phases. However, considering that the subalkaline soil pH limited Cu mobility during the incubation, we have no reasonable explanation for the lower Cu_{AO} contents observed in the lowest soil layer.

3.3. Influence of redox cycling on the distribution of Fe, Mn and Cu

Sequential chemical extractions are widely used to estimate the distribution of ME between more or less labile pools in the solid phase, as well as their susceptibility to mobilization. The modified BCR procedure (Rauret et al., 2000) extracted operationally-defined fractions of ME which may be released from soil by ion exchange and carbonate dissolution (F1), reduction of Fe-Mn oxides (F2), oxidation of OM and sulfide minerals (F3) and extreme weathering of the crystalline phase (F4). The four fractions obtained are progressively more resistant to reductive dissolution, and commonly referred to as exchangeable, reducible, oxidizable and residual metal pools. In general, redox cycling resulted in an increase in the labile pools of Fe, Mn and Cu (Fig. 5). An increase in easily mobilizable Fe and Mn fractions was previously attributed to alternating reducing and oxidizing conditions (Balint et al., 2013) and soil flooding (Kashem and Singh, 2004), particularly under non-limiting C conditions. We observed an increase in exchangeable and easily reducible Fe contents (F1 and F2) and a general decrease in the less labile, oxidizable fraction (F3), particularly in VIN and IND (Fig. 5). Similarly, MIN showed an increase in the exchangeable and a decrease in the oxidizable fraction, although no changes in the reducible Fe pool were observed. These results are consistent with the successive reductive dissolution and reprecipitation as less ordered Fe (hydr)oxides during redox cycling, that led to a change in the distribution of Fe in favour of more labile phases. Moreover, differences in the proportion of easily reducible Fe in the upper and lower soil layers were in line with the AO-extractable Fe contents reported previously, confirming the mobilization and reprecipitation of Fe towards the bottom of the soil column.

Redox cycling also resulted in a relative decrease in reducible Mn (1.3, 2.2 and 3.6-fold for VIN, MIN and IND, respectively), and a corresponding increase in the exchangeable fraction (1.2, 2.2 and 1.7-fold for VIN, MIN and IND, respectively) for all soils, particularly at the deeper soil layer (Fig. 5). This was in line with the substantial release of Mn in solution under anoxic conditions (Fig. 1) due to the reductive dissolution of Mn (hydr)oxides, which resulted in a consequent increase in Mn retention on cation exchange sites (Fig. 5), and loss with column leachates (Fig. 1). Moreover, in subalkaline soils like IND, Mn released under anoxic conditions may subsequently precipitate as carbonates, which could explain the limited loss of Mn in soil leachates (Fig. 1), even though BCR

fractionation evidenced a remarkable change in the distribution of Mn in favour of the most labile fraction as a result of redox cycling.

Similarly to the changes in the distribution of Fe and Mn, redox cycling also resulted in a relative increase in Cu in the more labile fractions with respect to the initial soils (Fig. 5). However, changes in the distribution of Cu between the different fractions suggest that the underlying mechanisms differed in the three soils studied. In fact, the decrease in Cu associated with the oxidizable fraction and increase in reducible and exchangeable forms observed for VIN suggest that redox cycling (i) could enhance the decomposition of Cu-containing organo-metallic complexes, and (ii) result in a redistribution of oxide-associated Cu in favour of the more easily reducible forms. In contrast, MIN showed a relative increase in the exchangeable fraction, while both reducible and oxidizable pools remained relatively unchanged, suggesting that the redox-driven release and mobilization of Cu (Fig. 3) was not necessarily linked to Fe and Mn cycling. These results are in line with our previous findings which indicated that Cu mobility in mine-affected soils may be a result of the dissolution of Cu-containing minerals, such as chalcopyrite, enhanced by alternating redox conditions (Balint et al., 2014). Changes in the distribution of Cu for IND confirmed that, although subalkaline soil pH limited the loss of Cu from the soil column (Fig. 3), redox cycling nonetheless resulted in an increase in the proportion of Cu in the more labile fractions (Fig. 5), probably through precipitation as carbonates or association with newly formed reducible Fe oxides.

4. Conclusions

In contrast to studies on the behaviour of Cu and other ME in permanently saturated soils that generally showed a relative increase in ME stability due to adsorption on freshly-exposed Fe and Mn (hydr)oxides (Kashem and Singh, 2004) or complexation with OM (Zheng and Zhang, 2011), our results showed that alternating redox conditions may actually increase the lability of Cu and consequently its susceptibility to loss. Soil properties and source of Cu contamination were both shown to play an important role in determining Cu behaviour under redox cycling. The alternating reductive dissolution of Fe and Mn (hydr)oxides and reprecipitation as poorly crystalline phases brought about by changes in soil redox conditions, contributed to the release and mobilization of Cu and/or Cu-containing organometallic complexes, as well as an increase in the amount of Cu associated with these easily reducible oxides. Although subalkaline soil pH values strongly limited Cu loss through leaching, we nonetheless observed a redistribution of Cu to more labile forms linked to the redox-driven cycling of Fe/Mn (hydr)oxides. In contrast, in mine-impacted soils, Cu behaviour was predominantly controlled by the effects of alternating redox conditions on the Cu-containing minerals present rather than on Fe and Mn cycling. This study therefore emphasized the importance of understanding the behaviour of redox-sensitive soil constituents for a better assessment of the potential risk posed by Cu leaching and transport from contaminated soils to other environmental compartments.

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Highlights

- Alternating redox conditions favoured Cu distribution in the more labile pools
- Cu dynamics were linked to the redox-driven cycling of Fe, Mn and DOM
- Cu behaviour was shown to be affected by soil properties and contamination source
- Alkaline pH limited Cu loss, but did not exclude redox-driven metal redistribution
- Redox cycling also promoted Cu release from Cu-containing minerals

Table 1. Main physico-chemical properties of the studied soils.

	VIN	MIN	IND
pH_{KCl}	6.7	5.1	8.5
C_{tot} (g kg^{-1})	26.3	38.4	34.1
C_{org} (g kg^{-1})	26.3	38.4	16.8
N_{tot} (g kg^{-1})	2.2	3.7	0.6
Fe_{PT} (g kg^{-1})[a]	39.8	38.2	37.8
Fe_{DCB} (g kg^{-1})[b]	12.8	12.8	11.6
Fe_{AO} (g kg^{-1})[c]	1.1	5.2	2.2
Mn_{PT} (mg kg^{-1})	963	1140	1029
Mn_{DCB} (mg kg^{-1})	685	623	657
Mn_{AO} (mg kg^{-1})	578	517	446
Cu_{PT} (mg kg^{-1})	90	101	100
Cu_{DCB} (mg kg^{-1})	14	16	1
Cu_{AO} (mg kg^{-1})	45	56	34
Clay (g kg^{-1})	298	40	70
Silt (g kg^{-1})	381	320	280
Texture (ISSS)	light clay	loam	sandy loam/loam

[a] pseudo-total

[b] dithionite-citrate-bicarbonate

[c] ammonium oxalate

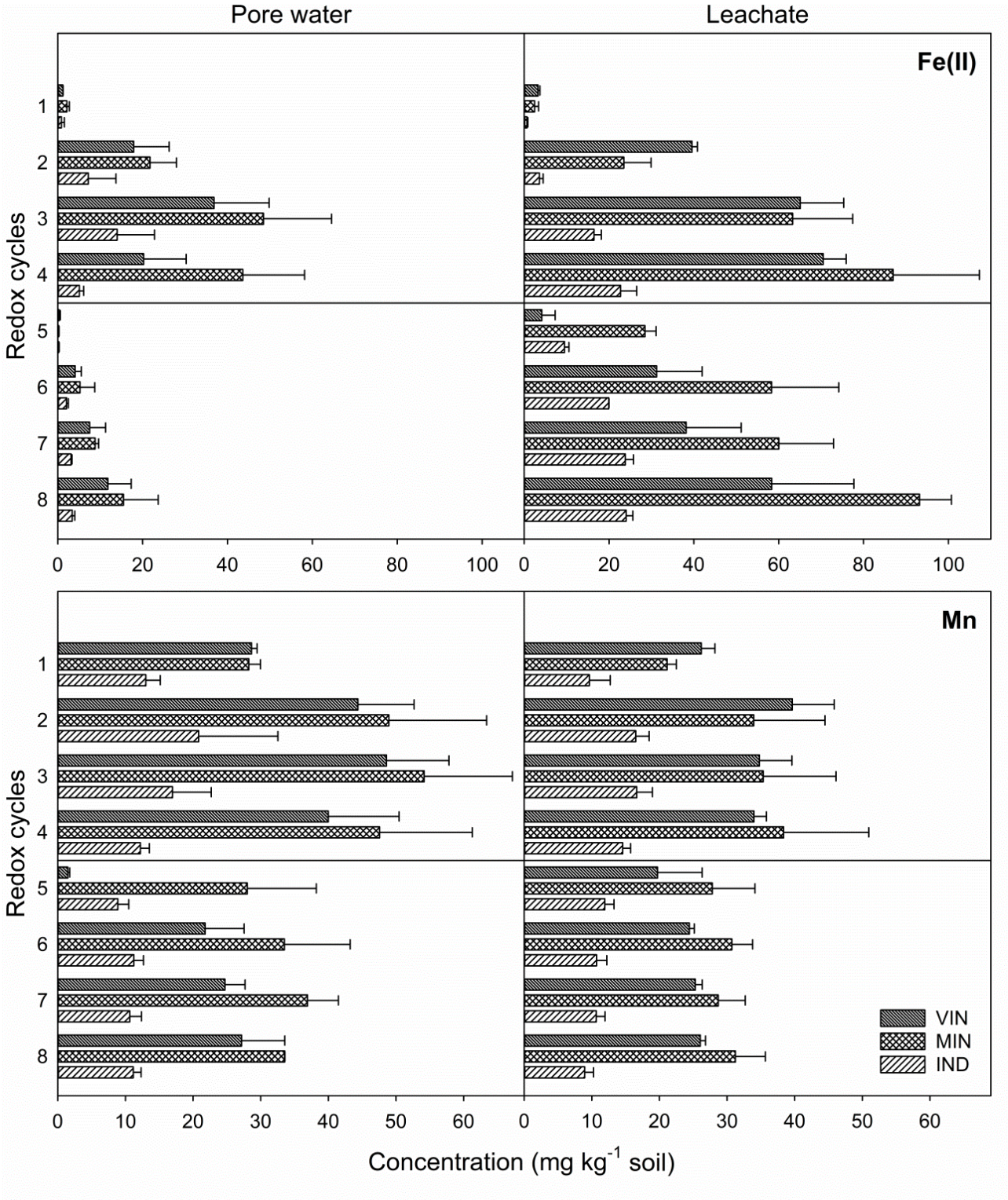

Fig. 1. Variations in the concentrations of ferrous iron and Mn in soil pore waters and column leachates with successive redox cycles. Error bars represent standard deviations. Line between 4th and 5th cycle represents prolonged oxidative phase (VIN, vineyard soil; MIN, mine-affected soil; IND, industrial soil).

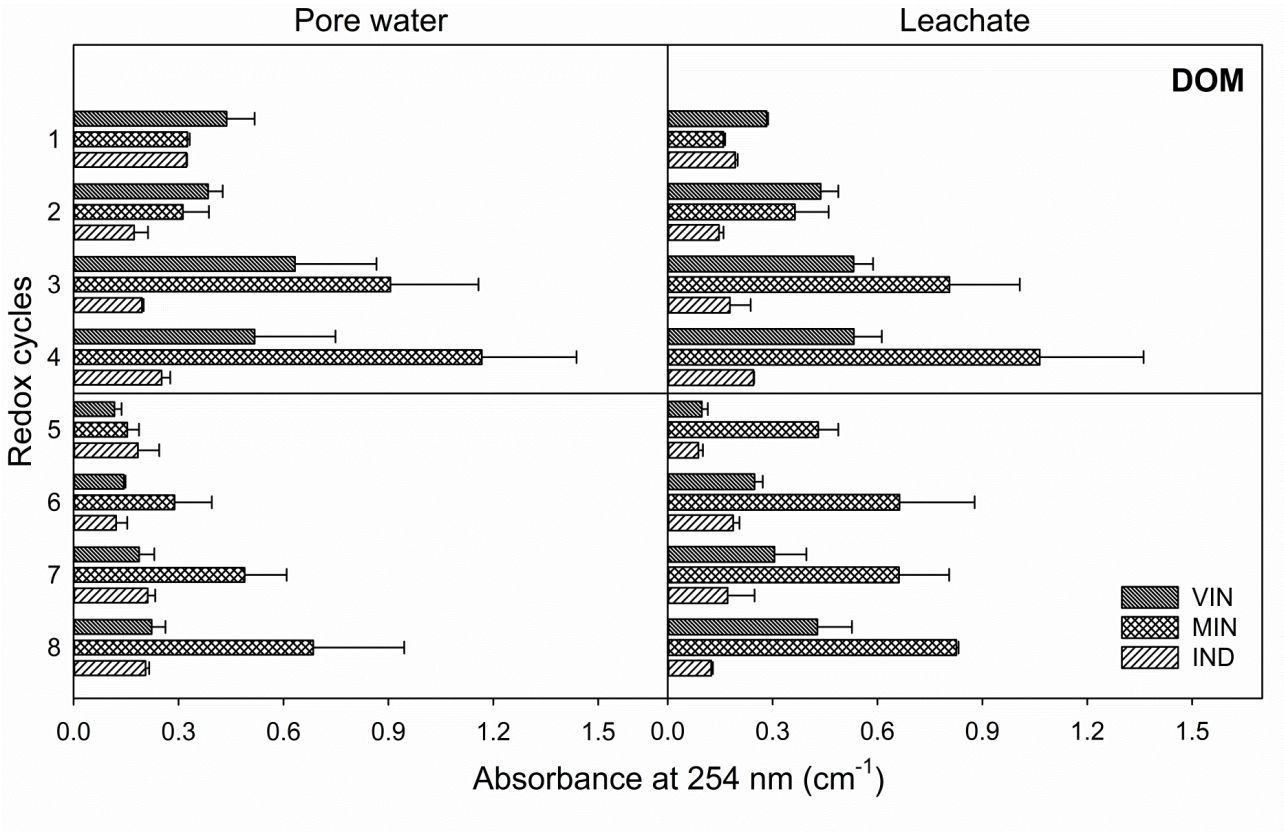

Fig. 2. Variations in absorbance values (at 254 nm) of soil pore waters and column leachates with successive redox cycles. Error bars represent standard deviations. Line between 4th and 5th cycle represents prolonged oxidative phase (VIN, vineyard soil; MIN, mine-affected soil; IND, industrial soil).

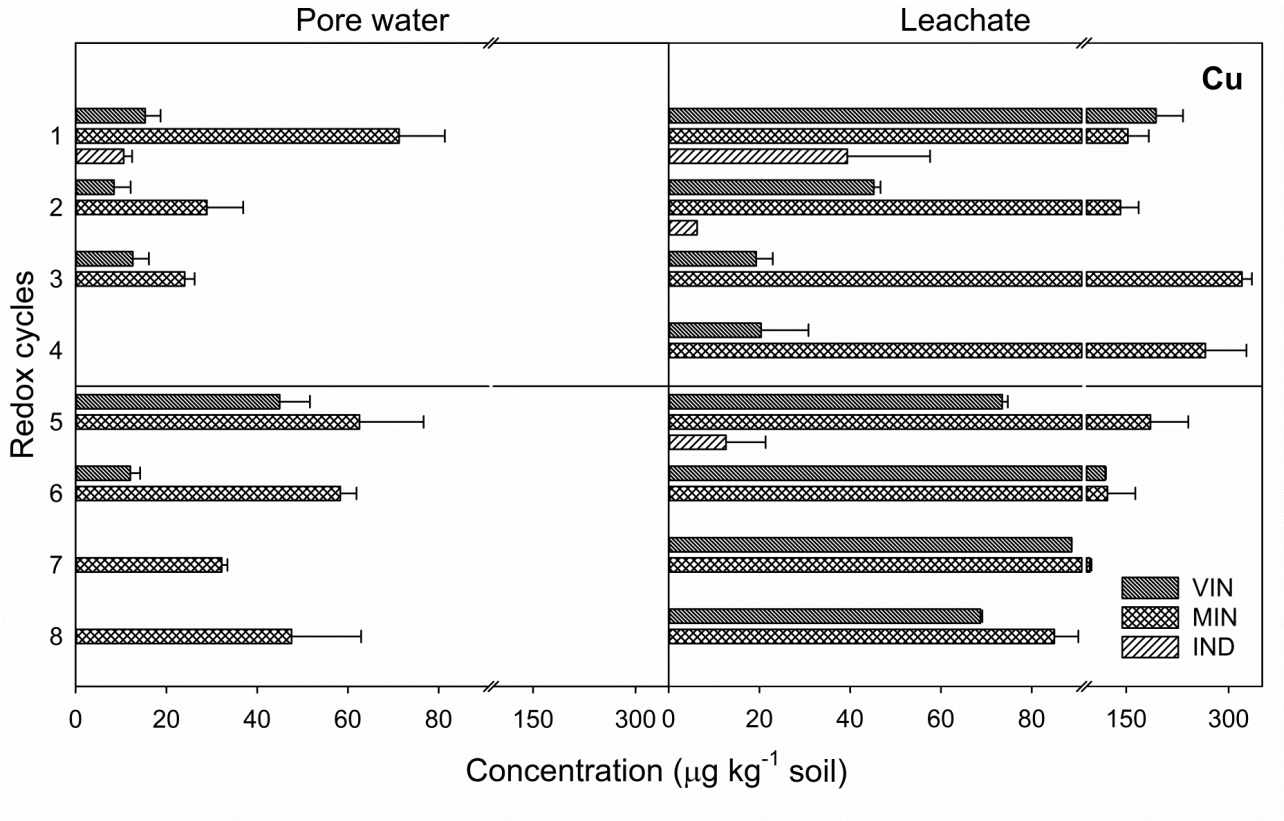

Fig. 3. Variations in the concentrations of Cu in soil pore waters and column leachates with successive redox cycles. Error bars represent standard deviations. Line between 4th and 5th cycle represents prolonged oxidative phase (VIN, vineyard soil; MIN, mine-affected soil; IND, industrial soil).

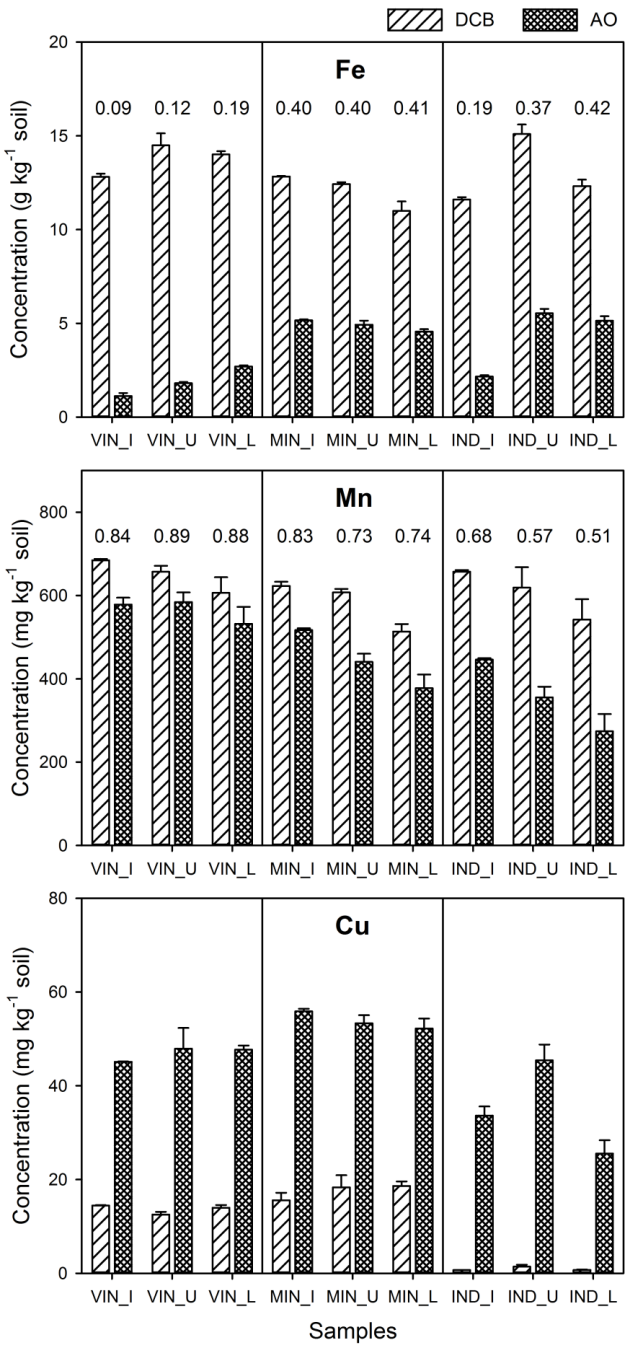

Fig. 4. DCB and AO-extractable Fe, Mn, and Cu contents in initial (I) and column-incubated soils (U, L – upper and lower layers), respectively. Numbers above the columns represent the AO/DCB ratios for Fe and Mn. Error bars represent standard deviations (VIN, vineyard soil; MIN, mine-affected soil; IND, industrial soil).

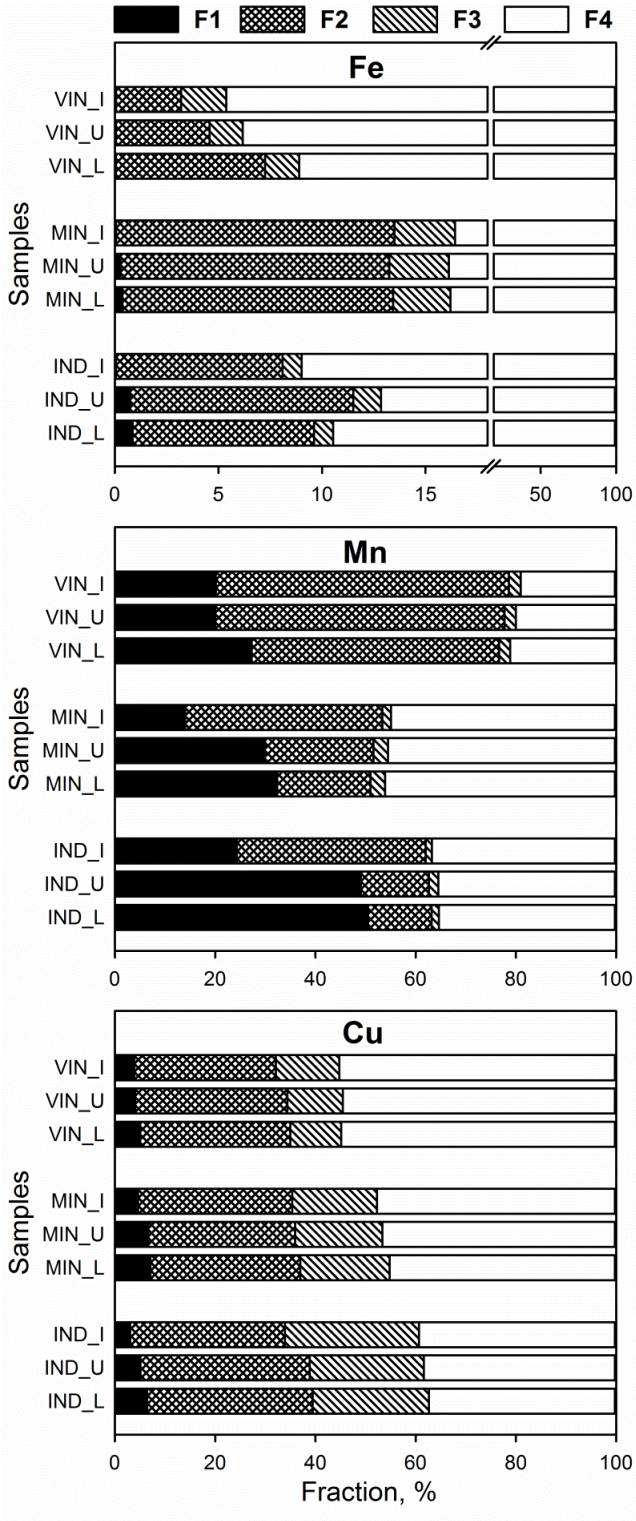

Fig. 5. Distribution of Fe, Mn and Cu between BCR fractions in initial (I) and column-incubated soils (U, L – upper and lower layers), respectively. Note the brake in the fraction scale of Fe (VIN, vineyard soil; MIN, mine-affected soil; IND, industrial soil).