Effect of Redox Conditions on the Crystallinity of Fe Oxides in Soil

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The effects of four alternating redox cycles on the release of Fe and Mn ions from a mine-affected soil, their redistribution in operationally defined fractions, and their changes in oxide crystallinity were studied by column experiments, DCB (dithionite-citrate-bicarbonate) and AO (ammonium oxalate) extractions, and BCR (Bureau Communautaire de Référence) sequential extraction. The results showed an increase of the reductive dissolution of Fe and Mn oxides with each successive redox cycle, which lead to a relative decrease of the "free" ions concentration in the solid phase, especially in the amorphous one, which might have been lost by leaching. Compared to the non-incubated soils, a relative increase in the exchangeable fraction of the flooded soils was observed, which was more pronounced with depth, due to the higher moisture regimes maintained at the bottom of the column during draining. Therefore, alternate oxic-anoxic cycles may lead to the solubilisation and redistribution of Fe and Mn ions into more labile fraction which could increase the risk of release of heavy metals (HM) associated with them.

Keywords: redox, leaching, reductive dissolution, Fe and Mn oxides

The toxicity of heavy metals (HM) depends on their content and speciation in the liquid and solid phases of the soil. HM associated with Fe and Mn oxides might be released under redox conditions, therefore it is important to understand the mechanisms of reductive dissolution, changes in crystallinity and redistribution in operationally-defined fractions. An important issue arises when soils containing high amounts of HM are flooded, due to the possibility of contaminant diffusion from soil to other environmental compartments. In the context of climate change for which scenarios predict an increase of the frequency and intensity of extreme floods, as well as variations in rainfall patterns and intensities [1], soil moisture status may be significantly influenced. This may result in an increasing probability of submergence of contaminated soils that are not normally waterlogged, as in numerous metalliferous mining areas around the globe.

Anoxic conditions may cause the release of trace elements by reductive dissolution of oxide phases, i.e. Fe and Mn, to which they are associated [2] or through the oxidation of organic matter (OM) to which metals are complexed [3]. In addition, on the subsequent onset of oxic conditions they may be bound in a less stable form (i.e., on amorphous Fe (hydr)oxides). Some authors showed that soil redox oscillations may increase the crystallinity of Fe oxides in tropical area soils [4], thus increasing the stability of colloids which are potential carriers of HM, and the work of Contin et al. (2007) [5] concluded that redox cycles enhance fixation of some HM into Fe oxides.

However, few studies have dealt with the influence of alternating oxic and anoxic conditions on the solubilization and translocation of Fe and Mn ions in solution from mine-affected soils, and their redistribution among solid-phase components as a release mechanism of metal lability. This makes it highly necessary to assess changes in Fe and Mn chemical forms as their consequent dissolution may be particularly dangerous since it could trigger the release of HM, therefore shortening the pathways for human exposure.

The hypothesis of this study was that Fe and Mn released into solution from soil under reduction are mobilized and translocated during water drainage and are redistributed in the labile fractions of soil. Moreover, we believe that the effects of redox conditions are reflected also on the Fe and Mn ions partitioning at different depths in the soil, due to their varying moisture regimes. Column experiments are a useful method for assessing HM behaviour in soils under different moisture levels [6], although they were scarcely used in studying the effect of alternating drying and wetting cycles on metal mobility [7]. In order to assess the influence of alternating oxic-anoxic conditions on the release, mobility and transport of Fe and Mn, and the effect of intermittent submergence on their crystallinity and chemical fractionation in a mine-affected soil, column experiments, DCB and AO extractions, and BCR fractionation were performed.

Experimental part

Soil sampling

Mine-affected soil samples were collected from the river valley of the town of Bălan, Harghita county, Romania. Pyrite and mixed Cu-Pb-Zn deposits have been mined in this area for centuries and copper ore had been extracted and processed by flotation until 2004. For this study, 8 soil samples were collected from pastures at different distances from the main contamination source, which was the preparation plant where Cu flotation had been performed. To ensure their representativeness, each sample consisted of 5 subsamples taken from an area of 400 m^2. Following preliminary analysis, the physico-chemical properties and the concentration of total Fe and Mn were similar. Consequently, all samples used for this experiment were mixed and homogenized and the resulting sample was denominated "BAL".

Determination of soil properties

The physical and chemical characterization of the soil was performed according to the regulations of the Italian

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Ministry of Agricultural and Forestry Policies [8]. The sample was air-dried, gently crushed and sieved to pass through a 2 mm sieve. A small portion was further ground for microwave-assisted (Start D, MILESTONE, U.S.A.) *aqua regia* (HCl:HNO_3, 3:1 solution) digestion and pseudototal (PT) metal concentrations (Fe, Mn) were determined by flame atomic absorption spectrometry (FAAS, AAnalyst 400, Perkin Elmer, U.S.A.). All analyses were carried out in duplicate and the results were accepted if the coefficient of variation was within 5%.

Soil *p*H was determined potentiometrically in a KCl solution (1 M), 1:2.5 soil/solution ratio. Particle-size analysis of the soil material (<2 mm) was conducted by the sieve-pipette method after dispersion of the sample with sodium hexametaphosphate [9], without destruction of oxides and organic matter. Total carbon and total nitrogen contents were measured in duplicate by dry combustion with an elemental analyser (NA2100, CE Instruments, Italy).

Column experiment

The column experiment involved mixing 1.850 g of each soil (<2 mm) with perlite (20% v/v), which is an inert volcanic glass, and packing into Plexiglass® columns (70 cm in height and 7 cm in diameter), over 100 g of glass beads (fig. 1). The glass beads and addition of perlite to the soils were adopted to facilitate percolation through the soils. Rhizon samplers (Rhizosphere Research Products, The Netherlands) were inserted into the soils at a depth of 10 and 30 cm (Upper and Lower Rhizon, respectively) from the surface, and allowed for non-destructive sampling of the soil solution during the experiment. Four columns were set up to insure reproducibility of the experiment. Data reported are the average of the results.

Soils were initially flooded to about 4 cm above the surface with a 10 mM $CaCl_2$ + 3 mM lactose solution added from the bottom of the columns in order to expel air from the soil pores. Calcium chloride was used to substitute for the soil solution while lactose was added as a labile organic C source to favour the onset of anoxic conditions. After flooding, headspaces were flushed with N_2 and columns sealed tighly. All soils were subsequently subject to oxic-anoxic cycles by draining the columns on 2, 9, 16 and 23 d from the beginning of the experiment, and re-flooding with fresh solution after 2 d of oxic conditions. Each redox cycle was therefore composed of 2 d oxic followed by 5 d anoxic conditions.

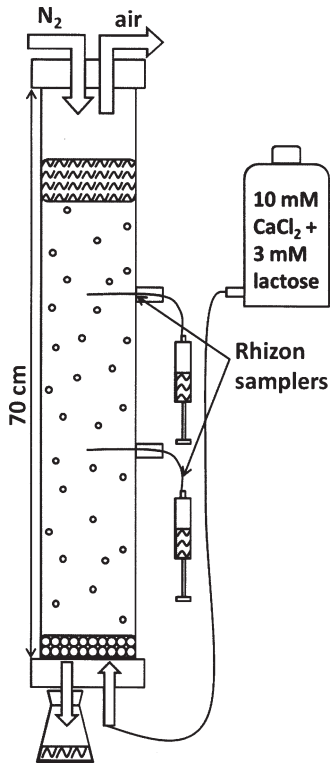

Fig. 1. Sketch of the column experimental setup

Percolation waters were collected during column draining, while soil solutions were sampled from the Rhizon samplers just before draining. All solutions were analysed for total metal (Fe and Mn) contents by FAAS, while ferrous Fe was determined spectrophotometrically by the 1,10-phenanthroline method [10].

After the flooding/draining experiment the soils were carefully removed, and two 10 cm soil sections sampled from each column at depths corresponding to the upper (U) and lower (L) layer of the column. These sections were dried at 40°C and, together with the initial, non-incubated soil (I), were subjected to the DCB and AO extraction, and BCR fractionation [11].

Extraction with DCB and AO

The fractionation of Fe was performed by extraction with dithionite-citrate-bicarbonate (DCB) and with ammonium oxalate (AO), in duplicate [12]. DCB is expected to extract "free Fe", i.e. all the soil Fe which is not included in silicates, while AO at *p*H 3 complexes organic-bound Fe and Al and their amorphous or poorly-crystallized oxides. The concentration of Fe and Mn in the extracts were analyzed by FAAS.

BCR fractionation

The fractionation of metals in the soil sampled at the two different heights of the column (U and L) was studied in order to assess the redistribution of released and translocated Fe and Mn ions and effect of different moisture regimes on their partitioning. The BCR procedure aims at fractionating metals into the phases where the metal resides, in a sequence which extracts metals with a progressively reduced lability. Step 1 (F1) of the BCR includes metals that can be released by ion exchange and/or are co-precipitated with carbonates and are extracted with a weak acid (acetic acid, 0.11 M); step 2 (F2) represents the fraction of metals bound to Fe and Mn oxyhydroxides and are releasable under reducing conditions (using hydroxylammonium chloride, 0.5 M); step 3 (F3) of the BCR contains metals bound to organic matter and sulfides (extracted with hydrogen peroxide, 8.8 M and ammonium acetate, 1.0 M, pH 2); the residual phase (F4) represents the remaining metals which are not bound to silicates and is digested with *aqua regia*.

The influence of redox cycles on the redistribution of Fe and Mn among the four operationally defined fractions was investigated by comparing the results obtained for the intermittently submerged soils with those of the initial soil (I), which had not been waterlogged. *Aqua regia* digestion was also performed directly on the bulk soils to determine metal recovery with the BCR procedure. All determinations were carried out in triplicate and metal concentrations (Fe and Mn) quantified by FAAS.

All reagents were analytical grade provided by Fluka, Sigma-Aldrich and J.T.Baker and the standard solutions used were provided by CertiPUR by MERCK. All plastic and glassware were washed, acid-soaked overnight in 10% HNO_3 and rinsed with deionised water prior to use.

Results and discussions

Soil properties

The main physico-chemical properties of the soil sample used in the study are presented in table 1. The low *p*H of the soil could be attributed to the acidic bedrock, but

possibly also partly due to the oxidation of the copper-bearing sulphide deposits that causes the formation of acid mine drainage and subsequent acidification of soils. Likewise, due to the exploration and exploitation of metal ores, elements from various minerals can be released into the environment [13]. It is therefore essential to assess their potential mobilization under redox conditions, in relation with the reductive dissolution of Fe and Mn oxides. In the studied area, the main sources of iron, copper, lead and zinc are pyrite (FeS_2), chalcopyrite ($CuFeS_2$), galena (PbS), and sphalerite ((Zn,Fe)S), respectively [14].

pH_{KCl}	5.0
C_{tot} (g kg^{-1})	38
N_{tot} (g kg^{-1})	4
Fe (g kg^{-1})	39
Mn (mg kg^{-1})	97
Clay (g kg^{-1})	36
Silt (g kg^{-1})	316
Texture (ISSS)	loam

Table 1
MAIN PHYSICO-CHEMICAL PROPERTIES OF THE STUDIED SOILS

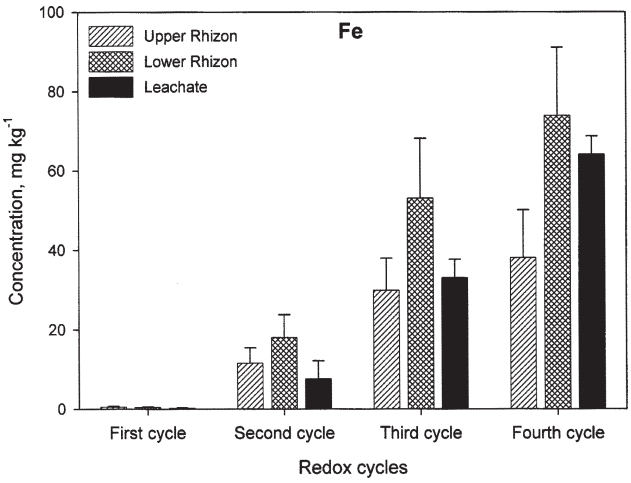

Fig. 2. Amount of Fe_{TOT} relased in solution, as extracted by Rhizon samplers and leached through the column in the four redox cycles

Reductive dissolution of Fe and Mn

Soil solution sampling and analysis during the column experiment served to monitor the mobility and transport of Fe and Mn ions in submerged soils as a function of redox cycles. For all soils, Fe and Mn were released in solution with the establishment of anoxic conditions and their concentrations tended to increase with each successive redox cycle (figs. 2 and 3). This could be due to the fact

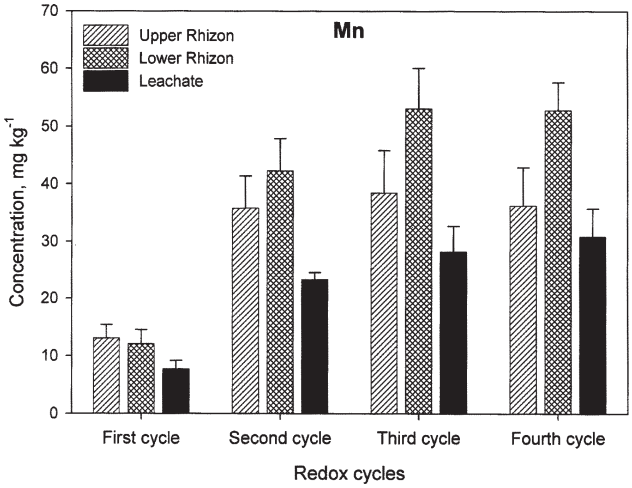

Fig.3. Amount of Mn relased in solution, as extracted by Rhizon samplers and leached through the column in the four redox cycles

that the oxidation of the soil leads to the reprecipitation of Fe and Mn (hydr)oxides with a low degree of crystallinity and, therefore, more prone to reductive dissolution during the subsequent anoxic period. Under anaerobic conditions Fe and Mn oxides are solubilized due to the reduction of Fe (III) to Fe (II), and of Mn (IV) to Mn (III) and Mn (II) mainly caused by Eh decrease [15]. Although the amount of Fe (II) in solution is generally used as a reliable indicator of the establishment of anoxic conditions [16], higher concentrations of Fe (III) measured in solution suggested that some of the reduced Fe could have been re-oxidized during soil solution sampling. This could have been due to the relatively long time needed for extraction of the solution with the Rhizon samplers, and thus justified the use of total Fe to follow redox cycling of this element instead of Fe (II) concentrations alone. Manganese reduction and the related increasing concentrations in solution occurred earlier than Fe (III), in line with its higher reduction potential. In fact, whereas significant reductive dissolution of Mn was already observed in the first cycle, Fe concentrations in solution during this cycle were relatively low and only increased after the second cycle. Accordingly, the amount of dissolved Fe and Mn leached from the columns during the oxic phase followed the same trend. As for the soil solutions, the amount of Fe lost from the column in the first cycle was negligible. Moreover, Fe and Mn concentrations in soil solutions sampled from LR and UR were initially similar, but with subsequent redox cycles higher concentrations were observed in LR with respect to UR. This suggests that the successive submergence and draining of soils did not only cause a change in the susceptibility of these metals to reductive dissolution, but also resulted in a vertical displacement of metal oxides with each redox cycle. Their diminished concentration found in the leachates could be due to the rapid precipitation of amorphous Fe and Mn

	Initial		Upper Layer		Lower Layer	
	DCB	AO	DCB	AO	DCB	AO
Fe (g kg^{-1})	12.8 ± 0.0	5.2 ± 0.0	12.4 ± 0.1	4.9 ± 0.2	11.0 ± 0.5	4.6 ± 0.1
% of PT	33	13	32	13	28	12
Mn (mg kg^{-1})	623 ± 10	517 ± 10	608 ± 12	441 ± 8	513 ± 44	378 ± 18
% of PT	64	53	62	45	52	39

Table 2
METAL CONCENTRATIONS IN DITHIONITE-CITRATE-BICARBONATE (DCB) AND AMMONIUM OXALATE (AO) SOIL EXTRACTS

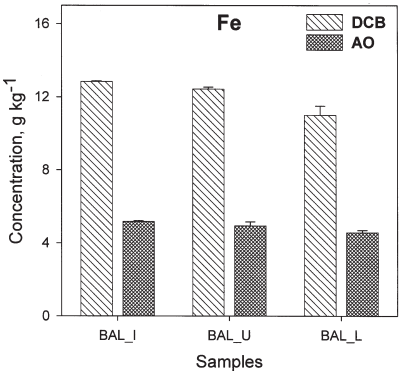

Fig. 4. DCB and AO extractions of Fe performed on initial (I) and column - incubated soil (U, L - upper and lower layers, respectively) after 4 redox cycles

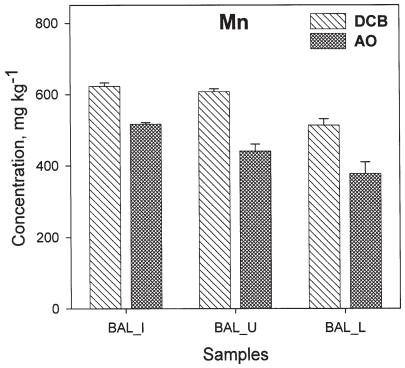

Fig. 5. DCB and AO extractions of Mn performed on initial (I) and column - incubated soil (U, L - upper and lower layers, respectively) after 4 redox cycles

(hydr)oxides during drainage or to Fe and Mn ions adsorption on the newly exposed sites of soil particles.

Our hypothesis is that these effects of alternating soil redox conditions on Fe and Mn (hydr)oxides could determine the release into the soil solution of associated HM. However, other processes such as changes in *p*H under anoxic conditions and OM degradation could influence the release of HM [17]. These mechanisms could have important implications when dealing with contaminated soils.

Crystallinity of Fe and Mn oxides

Results of the extraction with dithionite-citrate-bicarbonate (DCB) and ammonium oxalate (AO) are reported in table 2. The former reduces all the Fe which is not in the silicates, the so-called "free" Fe, while the latter dissolves only the less crystalline, amorphous phase. Although these extractions are specific for Fe oxides, they can nevertheless give a preliminary assessment of metal contents associated with oxides and organic matter (e.g. adsorbed, co-precipitated, complexed) and their potential release from soils under anoxic conditions. Therefore, Mn was also determined in the DCB and AO extracts.

On average, 31 and 13% of PT Fe concentrations in soil were extracted in DCB and AO, respectively indicating that nearly half of the "free" Fe is amorphous or bound to organic matter. On the other hand, between 52-64% of PT Mn was DCB-extractable primarily in a low crystallinity degree form or bound to organic matter.

The amount of free Fe seemed to decrease during the four redox cycles, being partly removed from the lower layer of the column (fig. 4). This could be due, on one hand, to the possibility that Fe entered in more stabile structures that are not soluble in DCB (e.g., silicates) or, on the other hand, to its removal through leaching. However, the maximum amount of Fe released in the column solution was 100 times lower than the potentially reducible Fe, as obtained by DCB fractionation. Moreover, it is more plausible that Fe was solubilised by the reductive dissolution of Fe (hydr)oxides with a low degree of crystallinity, as suggested by the 1% decrease in AO-extractable Fe.

A decrease in AO concentration after redox alternations was more pronouncedly observed for Mn (fig. 5). As in the case of Fe, the same hypothesis can be made regarding the decrease in the amount of Mn extracted with DCB and AO after incubation, as compared to the initial soil. If we consider as amorphous the Mn oxides dissolved by AO, we can assume that leached Mn ions were mainly removed from the system through draining. This is supported by the fact that the concentration of solubilised Mn in the soil solution represented around 9% of the DCB-extractable Mn. This suggests that, in our case, Mn oxides could play a more important role in the release of HM than Fe oxides.

BCR sequential extraction

The data of the release of metals in solution account for a relatively small proportion of the total metals present in the soils. Previous experiments [16,18] have shown that the most serious consequence of alternating redox conditions is the progressive transformation of Fe oxides from crystalline to amorphous phases, the latter being more readily dissolved during the subsequent anaerobiosis.

The BCR procedure aims at fractionating metals into the phases where the metal resides. The four fractions obtained are progressively less labile and therefore more resistant to the reductive dissolution. F1 contains the metals that can be released to the environment through ion exchange. F2 includes the metals that are associated with Fe and Mn oxides. The F3 fraction is relevant to metals associated with organic matter and sulfide minerals while F4 comprises the metals fixed in crystalline phase, with low mobility and only available after weathering. The fractions of the metals in the upper (U) and lower (L) parts of the column were compared to those of the original, untreated soil (I).

As expected, the fractions of Fe and Mn shift, in general, towards more labile forms as the exchangeable fraction increases in all soils after the four reduction-oxidation cycles (fig. 6). F1 increased towards the bottom of the column at the expense of F2 and the reducible Fe fraction was higher in the initial soil with respect to those subject to redox cycles (fig. 6). This was due to the reductive dissolution of Fe and Mn (hydr)oxides and their

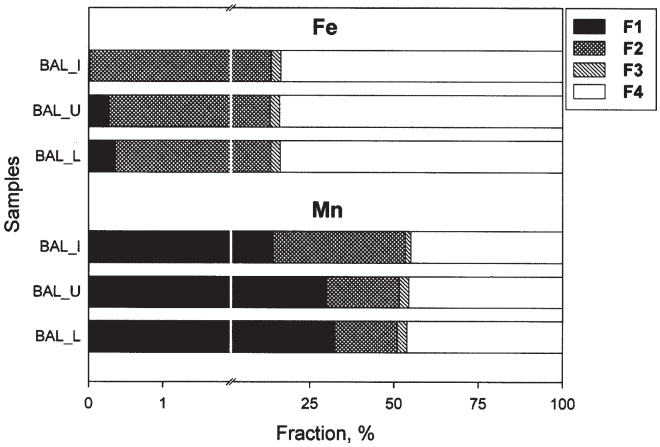

Fig. 6. BCR metal fractionation performed on initial (I) and column-incubated soil (U, L - upper and lower layers, respectively) after 4 redox cycles. Note the break in the fraction scale

	Sample	F1	F2	F3	F4	Sum	Initial	Recovery, %
Fe ($g\ kg^{-1}$)	BAL_I	0.0±0,0	5.4±0.0	1.2±0.0	33.6±0.5	40.2±0.5	38.2±1.5	105
	BAL_U	0.1±0.0	5.3±0.1	1.2±0.0	34.1±0.7	40.6±0.8	39.2±0.7	104
	BAL_L	0.1±0.1	5.3±0.1	1.1±0.0	33.7±0.6	40.2±0.8	38.5±2.0	105
Mn ($mg\ kg^{-1}$)	BAL_I	156±2	440±2	20±0	503±13	1119±16	1008±10	111
	BAL_U	332±8	240±41	32±0	505±19	1108±69	993±12	112
	BAL_L	350±18	202±16	32±1	499±24	1083±60	937±44	116

Table 3
DISTRIBUTION OF Fe AND Mn AMONG FRACTIONS OBTAINED BY BCR SEQUENTIAL EXTRACTION BEFORE (I) AND AFTER (U, L – UPPER AND LOWER LAYERS, RESPECTIVELY) REDOX CYCLES

transformation into less crystalline forms which are more prone to solubilization. The increase in more labile Fe fractions in the samples taken from the bottom of the soil columns, as compared to the top, showed that 2 days of aerobic conditions were not sufficient to uniformly oxidize the soils. This led to a more pronounced drying of the upper layer of the soils, as opposed to the increasingly moist conditions toward the bottom of the columns. The consequent Eh and *p*H gradients might have been responsible for the changes in Fe and Mn fractionation. The different vertical gradients present in the drained soil columns were assumed to be similar to field situations where during the drainage of floodwater through the soil, oxic conditions would prevail at the surface even though deeper soil horizons could still be affected by anaerobic conditions.

Flooding and draining leads to soil weathering which, in turn, influences the aging of the soil. Our results that showed an increase in the lability of Fe, particularly in F2, with time were in line with those obtained by Pueyo et al. (2008) [19] for the aging of an acidic, sandy loam soil contaminated by sludge particles and acidic wastewater. The authors explained that this phenomena might have been caused by the oxidation of pyrite, which would lead to a decrease in pH and solubilization of Fe compounds. In the case of flooded soils treated with organic matter, Kashem and Singh (2004) [17] observed that Fe in the most labile fractions (equivalent of F1) increased drastically with respect to the non-flooded ones while F2 decreased.

The speciation of Mn changes significantly in the submerged soil in view of the changes in solubility this element undergoes on reduction. While in all initial soils the exchangeable fraction was less than 20%, the oxido-reductive cycles caused an increase in F1 of up to more than 30%. Moreover, F1 showed an increase towards the bottom of the column confirming that Mn fractionation, just like Fe is also dependent on the different oxido-reductive conditions in the soil column. While F2 decreased in all samples the oxidative and residual fractions remained relatively unchanged. The concentrations of each fraction of both Fe and Mn are presented in table 3. The recovery of the BCR procedure was calculated as a percentual of the four fractions sum from the PT concentration. The overestimation of the values obtained in the four fraction could be due to the relative excess caused by the addition of perlite to the soil, to the complex sequential extraction procedure, and to the removal of Fe and Mn from the soil by draining.

Kashem and Singh (2004) [17] also found that under flooded conditions Fe and Mn concentrations in the mobile fraction increased at the expense of the less labile ones. Aging of contaminated soil had a similar effect, as reported by Pueyo et al. (2008) [19] who found that over a period of 18 months exchangeable and oxidizable fractions increased while reducible and residual fractions decreased.

Conclusions

The assessment of alternating oxic-anoxic conditions effect on the release, crystallinity and redistribution of Fe and Mn in mine-affected soils revealed the possible prevailing mechanisms controlling their mobility in intermittently submerged soils. The solubilisation of Fe and Mn oxide coatings and their reprecipitation as poorly crystalline (hydr)oxides, combined with the solubilisation of the amorphous phase and redistribution in more labile phases might pose an important environmental issue in this type of area. The results showed that alternating redox conditions causes increased reductive-dissolution of Fe and Mn (hydr)oxides which may affect the release of HM associated with them. They might enhance HM release from their surface followed by HM immobilization by adsorption on the newly-formed binding sites or by coprecipitation or occlusion in the fresh oxides.

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