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pH control on organic and organo-mineral colloids carrying major and trace elements in leachates of wetland sludge deposits.

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Abstract

Emission of colloids from treatment wetlands solid deposit (SD) may affect the speciation, toxicity and transfer of organic and inorganic pollutants, thereby controlling the associated environmental risks. This study investigated the nature of the colloids and their influence on the leaching of major and trace elements over a wide range of pH between 2 and 12. Results evidenced the mobilization of high quantity of organic carbon leached from the SD and Al-Fe colloidal minerals embedded by large organic molecules. Based on their varying affinity for the different colloidal phases, three groups of chemical species were established: (i) elements with low affinity for colloidal phases, mainly released in truly dissolved fraction (<3kDa) as inorganic species (Na, Rb, As, Sb, S, P, V); (ii) element strongly affected by the detachment of large colloids (> 30kDa), preferentially associated to organic colloids (Li, Ca, Mg, Sr, Ba, Mn, Zn) or to mineral colloids (Pb, Cr, Sc, Y); and (iii) element with high affinity for large and truly dissolved organic molecules (Cu, Co, Cd, Ni). Differences observed in the partitioning of elements can be attributed to variations in the pH/Eh of the solutions, the nature of the colloidal phases, and the ionic properties of the considered elements. Small pH variations were found to modify drastically the speciation of the elements solubilized with potential effect on their (bio)availability. Results obtained on this study can be used to enhance wastewater treatment through constructed wetland process and improve recovery technics applied on solid deposits (agriculture, compounds extraction...).

Abbreviation

TD: Truly Dissolved

SD: Solid Deposit

OC: Organic Carbon

SC: Small Colloids

LC: Large Colloids

tDOC: truly Dissolved Organic Carbon

1. Introduction

In natural soil systems, the mobility of non-soluble inorganic species is strongly controlled by the dynamics of soluble colloidal species [1–4]. Due to their high specific surface, colloids exhibit a high complexation capacity of various inorganic species, whose solubilization may thereby be strongly increased. Colloidal detachment is influenced by the nature of the colloids, the properties of the considered media but also by biological, chemical and hydrological factors [1,5,6]. Among the chemical factors, pH is probably the most important parameter controlling major and trace elements speciation in

soil system. By disturbing the organic supramolecular assemblies and organo-mineral association, pH change could induce the detachment of organic colloids in soil samples [5,7] and the release of associated elements. The mobilization of such organic molecules is known to trigger the detachment of colloidal metal-oxides and oxyhydroxides in various natural soil samples [6,8,9]. pH also controls the sorption capacity of the colloidal phases by affecting the dissociation of functional groups.

Vertical Flow Constructed/treatment Wetlands (VFCW) are a nature-based system (NBS) where domestic wastewaters are treated by percolation through successive stages of filters planted with reeds. In so-called “French systems”, the influent wastewater is not settled and a solid layer called surface solid deposit (SD) accumulates progressively at the surface of the first filter due to the retention of the mobile solid particles present in wastewater [10,11]. This layer is well oxygenated by contact with the atmosphere and percolation of water flows through the rhizosphere of the reeds. Intense aerobic microbial activities thereby occur and play a major role in the overall treatment performance [10–13].

SD is known to actively contribute to the performance of the treatment by favoring the retention of initially mobile pollutants transported with wastewaters' flow [10–12,14]. Contaminants, such as trace metals, that are not degraded can accumulate over time within the SD. The accumulation of contaminants in the SD poses a potential risk of mobilization. This risk can occur due to possible variations in treatment operating conditions (such as periods of flooding or pH fluctuations) or when the solid is extracted and used for its potential fertilizing and agronomic properties, which can lead to further spread of contaminants.

Banc et al., [15] investigated the mobilization of organic colloids and looked at their molecular size and their aromaticity. The nature of the organic molecules generated by the SD were highly dependent of the pH conditions. Under alkaline conditions, the destabilization of particulate organo-mineral complexes causes the detachment of aromatic and large organic molecules comprised between 0.45 μm and 30 kDa. Acidic conditions however were found to generate the mobilization of low molecular weight organic molecules (*i.e.* <3 kDa) with low aromatic content. The possible detachment of metal oxides with organic matter and the impact of such colloidal production on the release of trace elements were not investigated.

Questioning the mechanisms and roles of the detachment of colloids in the solubilization of trace metals retained in the solid fraction is of major interest for the entire constructed wetlands treatment process. Indeed, the colloidal detachment could promote the release of poorly soluble trace metals and reduce the treatment performance of these systems. Moreover, when reused in agricultural purposes, the mobilization of colloids and associated pollutants could disturb the geochemical cycle of the considered soil. Globally, the detachment of colloids could induce the release of pollutants retained in the SD with possible important environmental consequences. Despite the growing support of the European Union for the development of nature-based solutions and the significant environmental considerations, no research has been conducted on constructed wetlands.

The objectives of this work are to understand the mechanisms responsible for the detachment of colloidal particles, to determine the nature of such colloidal phases mobilized from the SD and their impact on element mobility initially stored in the SD. We hypothesize that colloids detached from SD are composed by organo-mineral colloids similarly to natural wetlands soil solutions but small change in pH conditions can lead to drastic change in colloidal properties and speciation of pollutants. To test these hypotheses, the molecular size of chemical species released from SD submitted to various pH conditions were monitored for the first time in order to unravel the links between the dynamics of organo and organo-mineral colloids and inorganic pollutants accumulated over years in the SD.

2. Materials and methods

2.1. Sampling and chemical analysis of solid deposits (SD)

Solid deposit samples investigated by Banc et al., [15] were used in this study. SD were sampled in winter time from the surface solid layer of the first-stage filter of the VFCW treatment plant of Vercia (France). The solid layer had been staying in place from the first day of operation of the treatment plant, i.e. for 14 years. Samples were collected and processed following the protocol reported by [16] and summarized below. Several kg of SD were collected over the whole depth (>15 cm) of the solid layer from 8 different spots at the surface of the first-stage filter. All samples were sorted manually on-site to remove reeds rhizomes and gravels, and subsequently mixed by shoveling. A representative sample of a few kg was then prepared by quartering, refrigerated and transported to the laboratory within a maximum of 4 hours. Then, representative sub-samples were prepared, crushed and sieved at 1 mm, freeze-dried and stored at 4 °C for further analytical assays.

The SD freeze-dried powders thus prepared were analyzed for their total contents in a series of elements. The powdered samples (200 mg) were suspended through alkaline fusion with LiBO_2 in a tunnel oven at 980 °C. After cooling, the sample was dissolved in a 0.5N HNO_3 solution. Major elements analysis was performed using ICP-OES iCap6500 ThermoFisher after 2-fold dilution in 2% HNO_3 aqueous solution. Trace elements were quantified with ICP-MS iCapQ ThermoFisher after 2-fold dilution in 2% HNO_3 aqueous solution. Results are given in Table S1 in supporting information.

2.2. Leaching protocol

A batch leaching protocol, based on the European standard method CENTS/TS 14429, was used to evaluate the effects of pH on the release of organic and inorganic compounds from the SD samples. The assays were performed in batch, using Nalgene® polypropylene centrifuge tubes in which SD were contacted with aqueous leaching solutions. Before the tests, all tubes were soaked in a 1M HCl aqueous solution overnight and then rinsed with deionized water.

Leaching assays were done at a solid-to-liquid ratio of 10 g of SD dry matter per liter of the leaching solution. The following leaching solutions were used: (i) ultrapure deionized water for natural pH conditions, (ii) nitric acid aqueous solutions for acidic conditions and (iii) potassium hydroxide aqueous solutions for alkaline conditions. Altogether, 5 acidic and 6 alkaline leaching solutions were used in addition to the use of ultrapure deionized water for the natural pH condition. All assays were stirred at room temperature in a rotary shaker set at 9 rpm until an apparent steady-state was reached, which was observed within 48 hours in preliminary experiments. All assays were duplicated.

2.3. Filtration and ultrafiltration of eluates

The suspensions obtained from the batch leaching assays were centrifuged at 10000 rpm for 10 min and the supernatants were filtered at 0.45 μm using Sartorius cellulose acetate filters to separate particulate organic matter (POM) in the filtrate (above 0.45 μm) from dissolved organic matter (below 0.45 μm). The 0.45 μm was further treated to separate the dissolved forms according to their molecular weight (MW) using a Jouan G4.12 centrifuge equipped with a swinging bucket rotor. Centrifugations were done at 3000 g and room temperature for 20 min in tubes equipped with Sartorius Vivaspin cellulose acetate ultrafiltration membranes of 30 kDa, 10 kDa and 3 kDa cutoff limits. Ultracentrifugation tubes were previously rinsed several times with a 0.1M NaOH solution followed by Milli-Q water to guarantee background concentrations of dissolved organic carbon (DOC) below 0.1 $\text{mg}\cdot\text{L}^{-1}$ in the ultrafiltrate. The

ultrafiltrates collected from the ultrafiltration of all the leachates obtained from the leaching assays were (i) analyzed for organic carbon concentration [15] and (ii) prepared for inorganic major and trace element concentrations analysis. For the latter, samples were evaporated and pre-digested with 14.6 mol.L⁻¹ distilled HNO₃ at 90°C overnight. After evaporation of HNO₃, the second step of digestion was performed using a mixture of 1 mL of 30% H₂O₂ and 2 mL of 14.6 mol.L⁻¹ distilled HNO₃ at 90°C overnight to eliminate the organic matter. After total evaporation, they were then dissolved in 0.37 mol.L⁻¹ HNO₃.

This protocol allowed to separate the soluble compounds into 3 fractions, namely large colloids LC above 30 kDa (with one sub-fractions between 0.45 μm and 30 kDa), small colloids SC between 30 kDa and 3 kDa (with 2 sub-fractions 30 to 10 kDa and 10 to 3 kDa), and truly dissolved TD constituents below 3 kDa. The proportions of the leached organic and inorganic compounds in each respective fraction were calculated at each pH tested as the ratio between the amounts leached in each fraction and the overall amount leached in the whole of the fractions. Results were expressed in mass %.

2.4. *Analysis of leached fractions*

After the completion of the leaching experiments, the suspensions were analyzed for pH, using a Consort C3020 meter equipped with Bioblock 11706358 pH probes calibrated with certified pH buffer solutions (pH 4.01, 7.00 and 10.00 at 25 °C).

Major and trace element concentrations previously identified in the solid matrix (see Table S1) were measured in all permeates obtained by filtration and ultrafiltration operations. Al, S and P concentration were determined by ICP-AES (Ultima2; Horiba Jobin Yvon SAS) with an uncertainty below 10%. Metal ion concentrations in solution were measured using a Quadrupole ICP-MS (Agilent Technologies 7700×). The concentrations were determined using a conventional external calibration procedure with multi-elemental solutions, acidified to 2% in nitric acid (HNO₃). Rhodium solution was used as an internal standard to correct the instrumental drift. The international geostandard SLRS-6 was used to check the validity and reproducibility of the results. Collision cell technology with helium (He) gas, was used to limit or eliminate potential interferences [17]. Typical uncertainties including all error sources were below ±5% for all the trace elements. The limit of detection and the isobaric interferences for all the groups of metal ions were calculated following the procedure at Rennes previously mentioned in [18].

2.5. *Thermodynamic modeling*

Predominance pH-Eh diagrams were obtained using PhreePlot [19], which contains an embedded version of the geochemical speciation program PHREEQC [20]. The “minteq.v4” database provided with this code was used. Saturation index calculation were performed using a coupled PHREEQC-ModelVII modeling approach [21]. ModelVII is a model dedicated to the calculation of protons and metals complexation to humic and fulvic acids [22]. In this study, saturation index calculations for Al

and Fe containing mineral phases were performed for each pH points individually. The inputs for the calculations included : (i) elements concentrations measured in solutions and (ii) dissolved organic carbon content > 3 kDa as humic acids and dissolved organic carbon content < 3 kDa as fulvic acids.

3. Results and discussion

3.1. Leaching of organic species

The mobilization of organic colloids induced by pH variations was measured (Fig. S1 of supporting information). A large investigation on the release of colloidal and dissolved organic matter from same samples have been already performed by Banc et al. [15]. The quantity and the molecular size of the leached organic molecules was strongly affected by the pH. Below pH 6, close to 60% of the dissolved OC leached was found in the TD fraction, whereas under alkaline conditions LC were predominantly mobilized, corresponding to up to 70% of the leached dissolved OC. Under alkaline conditions, the destabilization of organo-mineral aggregates due to electrostatic repulsion lead to the mobilization of large organic molecules. However, under acidic conditions, the release of TD molecules was attributed to the preferential mobilization of molecules with higher surface charge characterized by low molecular weight as observed by Pédrot et al. [6]. The proportion of small colloids SC was found relatively stable (around 10%) over the whole pH range.

3.2. Leaching of major trivalent metals (Fe, Al)

In addition to organic colloidal carriers, Fe- and Al-oxides and oxyhydroxides are known to control the solubility and mobility of numerous species [23]. It can be seen in Fig. 1 that the evolutions with pH of Al and Fe concentrations in the < 0.45 μm fraction were similar. Leached concentrations ranged between 0.08-250 mg/L for Al and 0.3-94 mg/L for Fe, respectively.

Only small proportions, less than 12% (Al) and 3% (Fe) of the total content in the solid deposits (see Table S1) were leached over the whole pH range tested. This observation revealed the stability of the Fe-Al phases of the SD. Increasing the pH of the solutions from ca. 5 up to pH 12 progressively increased the proportion of leached Al and Fe. An even more drastic increase was observed in the acidic range between pH 5 and pH 2, which was attributed to the dissolution of solid Al-Fe oxides under acidic conditions.

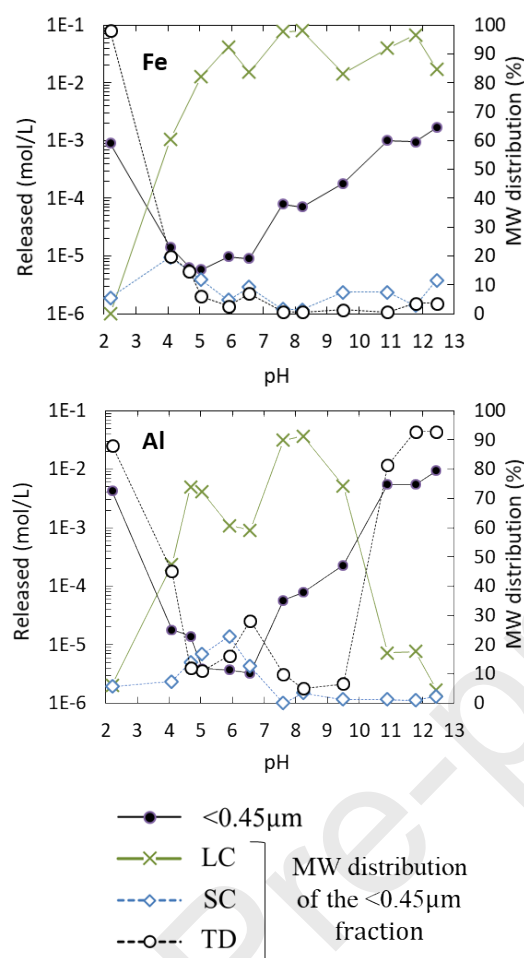


Fig. 1: Effect of pH on: (i) the overall release of Fe (a) and Al (b) expressed mol/L (●) ; (ii) the proportions of leached Fe (a) and Al (b) species in the forms of large colloids (x), small colloids (◇) and truly dissolved constituents (O).

For both Al and Fe, the increased leaching observed at acidic pH was predominantly observed in the TD fraction (< 3 kDa) where 90% of Fe and Al were analyzed. It was observed that when pH increased the proportion of TD species decreased while LC fraction increased up to 90 % and more at neutral to alkaline pH. By contrast with Fe, for pH >10, Al is mainly found in the TD fraction. Colloidal or TD forms of Al and Fe are thus highly pH-dependent. Calculated saturation index suggest the supersaturation of various Fe-oxyhydroxides species for pH>4 (Fig. 2a). In this pH range, Fe is largely mobilized in the LC fraction indicating a major control of Fe by leaching of oxyhydroxides. The presence of Fe in the TD fraction for acidic pH could be explained by two phenomenon. First, a possible dissolution of solid or colloidal Fe-oxyhydroxides detached from the SD as Fe-oxyhydroxides are known to be soluble under strong acidic conditions. Secondly, under strongly acidic conditions, pH-Eh diagram (plotted in the supporting information section) suggests that Fe was mainly released as Fe(II), while for the rest of the pH range, Fe(III) was probably predominant in solution. The presence of Fe(II) in acidic conditions despite oxic conditions was attributed to the capacity of highly protonated organic matter to reduce Fe(III) ions or minerals [24–27] and promote Fe(II) leaching in the TD fraction. The colloidal and TD forms of Al are mainly explained by the pH-dependent solubility of Al-oxyhydroxides. Indeed, calculated saturation index for Gibbsite and amorphous Al(OH)₃ (Fig. 2b) suggesting a major control of Al by inorganic mixed Fe/Al oxyhydroxides from pH 4 to 8. For the rest of the pH range, results suggest that Al is released in its ionic form in the TD fraction. These results are not specific to treatment wetlands solid deposits. Similar observations were reported during batch or leaching column experiments of natural wetlands soils at pH~6 [6,28,29]. The MW of Fe and Al species in LC fraction matched well with their oxyhydroxides forms [28,30]. Moreover studies showed that Fe/Al oxides were stabilized in

the aqueous phase by dissolved organic matter [31,32]. Various studies on wetlands soil solution highlighted the presence of mixed Fe/Al oxyhydroxides in the LC fraction [6,8,33].

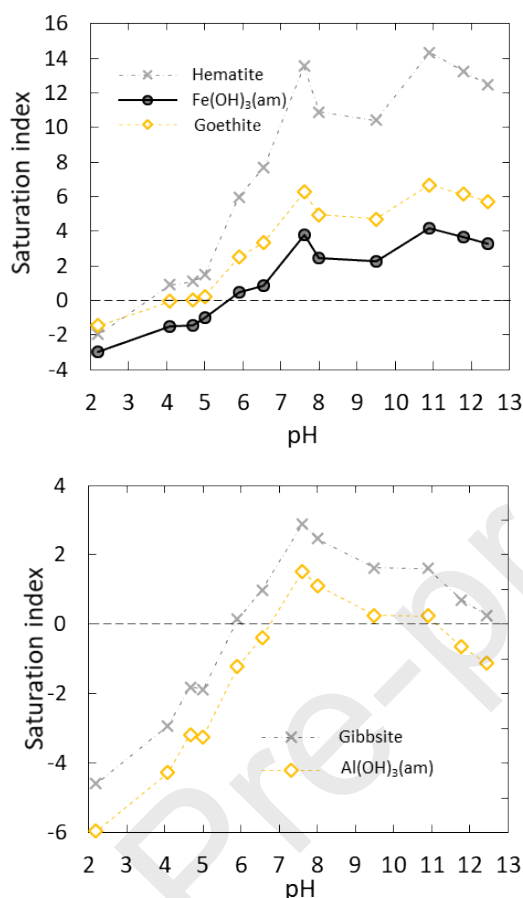


Fig. 2: Calculated saturation index of Fe (a) and Al-oxyhydroxides (b) phases of the solutions released from the SD performed using a coupled PHREEQC-ModelVII modeling.

3.3 Leaching of trace elements

3.3.1 Leaching of alkali and alkaline earth metals (Li, Na, Rb, Mg, Ca, Sr, Ba)

The concentrations of alkali and alkaline earth metals in the different MW fractions of the leachates collected over the tested pH range are shown in Fig. 3. The alkaline metals analyzed (Li, Na and Rb) showed different solubility patterns. While Rb was rather leached under alkaline conditions, up to a maximum of $\sim 5.5 \mu\text{mol/L}$ at pH 12, Li was preferentially leached under acidic conditions with a maximal concentration of $\sim 5.2 \mu\text{mol/L}$ at pH 2. Na leaching was only slightly affected by pH with concentrations comprised between 2 mmol/L at pH 8.2 and 3 mmol/L at pH 2.2. Na and Rb were mostly present in the TD fraction. Although proportions of large and small colloidal increased with pH, LC and SC fractions remained below 25% of overall leached quantities. On the contrary, the MW of leached Li species was much more affected by the pH. Below pH 7.5, more than 80% of leached Li was measured in the TD fraction while above pH >8 more than 90%, of leached Li was in the LC fraction although the overall leaching of Li was relatively stable. The distribution of the MW of leached Li species was like that observed with the alkaline-earth metals discussed above. This observation was attributed to the

similar ionic properties of Li and alkaline-earth metals species [34]. The molecular weight distribution of Na, Rb and Li leached species was consistent with observations reported by other in acidic wetlands soil solution [8,9,28,35]. However, Pédrot et al. [6], working on natural wetland soils, reported that at pH 7.2 leached Rb species exhibited sizes above 30kDa (corresponding to the LC fraction in the present study). The authors suggested associations of Rb with Fe-Al oxides. The high OC content of the SD solutions however could reduce the availability of Al-Fe-oxides sites as organic matter is a competitor for soil mineral surface sites [36,37].

All alkaline-earth metals followed in this study (Ca, Mg, Sr, Ba) exhibited similar pH-dependent leaching patterns with similar MW distribution of the leached species (Fig. 3). These elements were globally more sensitive to acidic conditions. Leaching of Ca, Mg and Sr were found minimal at slightly alkaline pH (pH~8). A minor different pattern was observed however for Ba which exhibited a V-shaped profile of leached concentration vs. pH with a minimal leaching observed under natural pH conditions (pH 6.5). For these four elements, the pH of minimal leaching was also the pH of transition of the leached species MW from TD species to the LC fraction. If Ca, Mg and Sr showed similar MW distributions of the leached species according to pH, the situation was slightly different with Ba. Whereas leached species of Ca, Mg and Sr were increasingly observed in the large colloids LC fraction with increasing pH (up to more than 90% at pH 12), Ba species were in the large colloidal fraction at pH 7.6. The MW distribution of these alkaline earth elements was consistent with results obtained on slightly acidic wetlands [28] and peat [8] soil solution. However, Raudina et al. [9], measured more than 50% of these elements in the LC fraction in peat soil solution despite very acidic conditions with a pH of 3.3. In the latter study, Mg, Ca, Sr and Ba measured in the colloidal fraction (> 3kDa) were suspected to be electrostatically bond to organic molecules. In our study, the high concentration in background electrolytes measured in acidic conditions, responsible for the shrinkage of the electric double layer of the organic molecules [38], could explain the very low sorption of alkaline and alkaline earth metals to organic molecules measured under acidic conditions. Moreover, the important competition with other metals for organic and/or oxides surface binding sites could also explain these results.

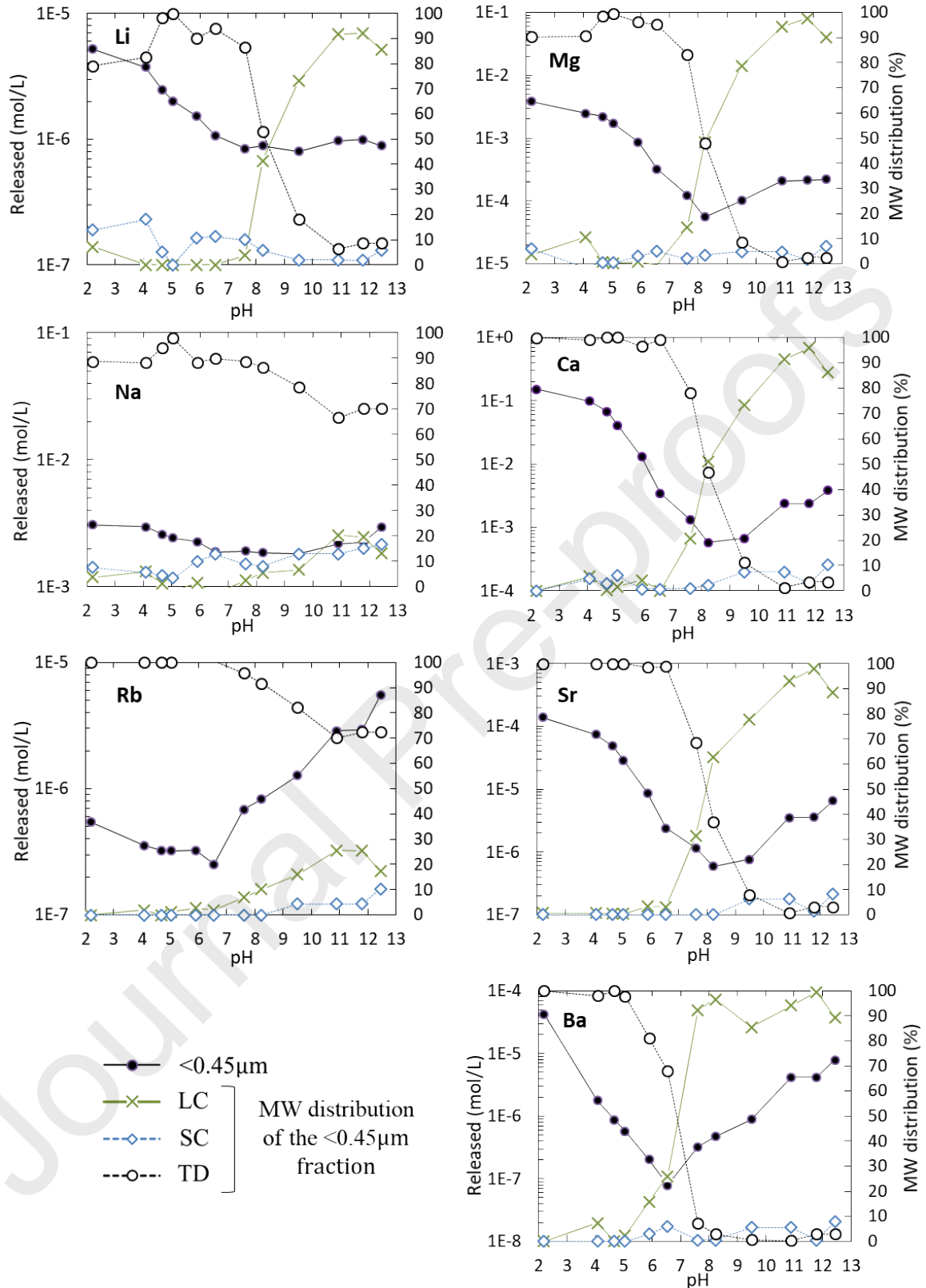


Fig. 3: Effect of pH on: (i) the overall release of alkaline and alkaline-earth metals expressed in $\mu\text{g/L}$ (\bullet); (ii) the proportions of leached alkaline and alkaline-earth metals in the forms of large colloids (\times), small colloids (\diamond) and truly dissolved constituents (\circ).

3.3.2 Leaching of divalent metals (Mn, Co, Ni, Cu, Zn, Cd, Pb)

It can be seen in Fig. 4 that these elements exhibited similar profiles with respect to the effect of pH on their solubilization. The lowest leaching was globally observed at pHs around neutrality (6.5 to 8.2). Only very small fractions of the total contents of the considered elements in the SD were leached under these conditions (below 1 % regardless on the element). A very sharp increase was observed in the leaching of all the considered elements when the medium was acidified. At pH 2, the leached concentrations were 2 to 3 orders of magnitude higher than observed close to neutrality, corresponding to the solubilization of 20 to 80% of the total contents depending on the considered element. Increasing pH also enhanced leaching but in proportions which were not the same for all elements. In most cases, the pH increased from close to neutrality up to 12 enhanced leaching to a similar extent as observed by acidification at pH 2 (same order of magnitude for Ni and Cd, slightly smaller for Co and Zn, slightly higher for Cu and Pb). In contrast, in the case of Mn, increasing pH enhanced leaching only in a marginal proportion.

Fig. 4 also shows that all the considered elements were leached predominantly in the TD fraction under acidic conditions. Under neutral to alkaline conditions however, the distribution was not the same for all elements. Mn and Zn were leached mostly in the form of LC. Co, Ni, Cu and Cd were found in similar proportions in all the size fractions. Enrichment of the TD fraction in these trace metals has been also observed in organic-rich wetlands [28] and peat pore waters [8]. Finally, in the case of Pb, the large colloids were predominant over almost the entire pH range (4 to 12). Truly dissolved species were found predominant only at pH below 4. The affinity of Pb for large colloids has been already reported in rich organic soils [1,6,8].

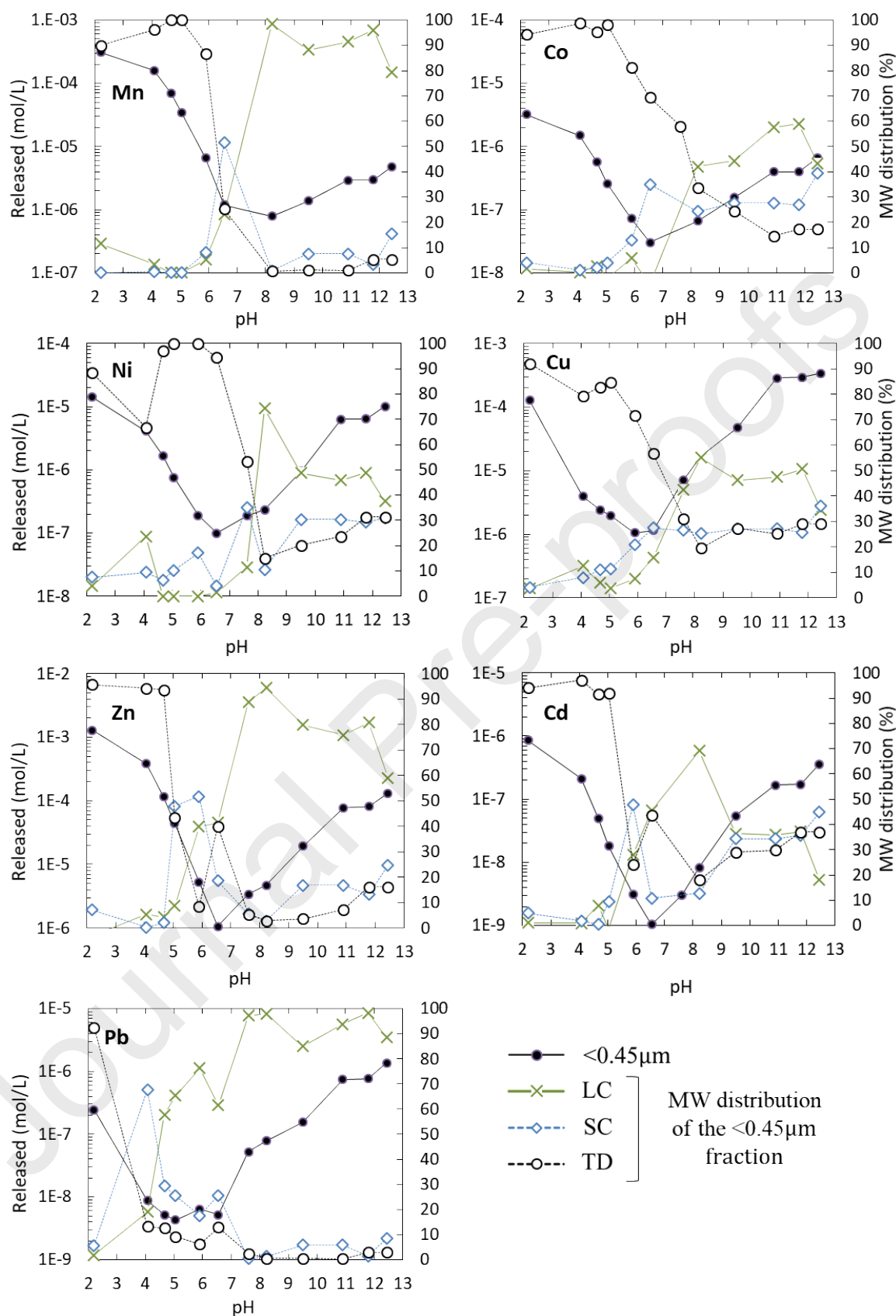


Fig. 4: Effect of pH on: (i) the overall release of divalent metals expressed in mol/L (●); (ii) the proportions of leached trace metals in the forms of large colloids (x), small colloids (◇) and truly dissolved constituents (O).

3.3.3 Leaching of trivalent elements (Cr, Sc, Y)

Three of the elements monitored in this study are trivalent (Sc(III) and Y(III)) or likely to occur in a trivalent form in the conditions of the study (Cr(III)). The pH-dependent leaching profiles of these elements were found similar as shown in Fig. 5. The lowest leaching was recorded under close to neutral pH conditions (pH 6.5) with leached concentrations of 20, 1 and 2 nmol/L for Cr, Sc and Y, respectively. Solubilization was enhanced in similar proportions by decreasing or increasing pH. However, less than 5% of the total contents in Cr, Sc and Y were leached, even under extreme acidic (pH 2) or alkaline (pH 12) conditions, revealing the high stability of the bearing phases in the solid deposits.

The MW distributions of the leached species were also very similar for the 3 elements. Large colloids were largely predominant (50% to more than 90%) at pH above 5-6 and truly dissolved species below pH 5. Small colloids were present in significant proportions (30-60%) only between pH 5 and 7 or so.

While Sc and Y may only occur under a trivalent form, Cr may be commonly observed under hexavalent or trivalent forms. The hexavalent form Cr(VI) is described as much more soluble and toxic than the trivalent form Cr(III) [39,40]. It occurs mostly under the form of the oxyanion CrO_4^{2-} . Results obtained here suggested that Cr was released in its trivalent form since the pH dependent MW distribution of leached Cr species was the same as to those observed for cationic species and more precisely to trivalent species Y(III) and Sc(III). Moreover, the pH-Eh diagram (see supporting information) suggest that the present experimental conditions, Cr is mainly released as Cr(III). This observation was consistent with other published studies on natural peat soil solution where the presence of trivalent elements in the colloidal fraction (>3kDa) was also reported [8,9].

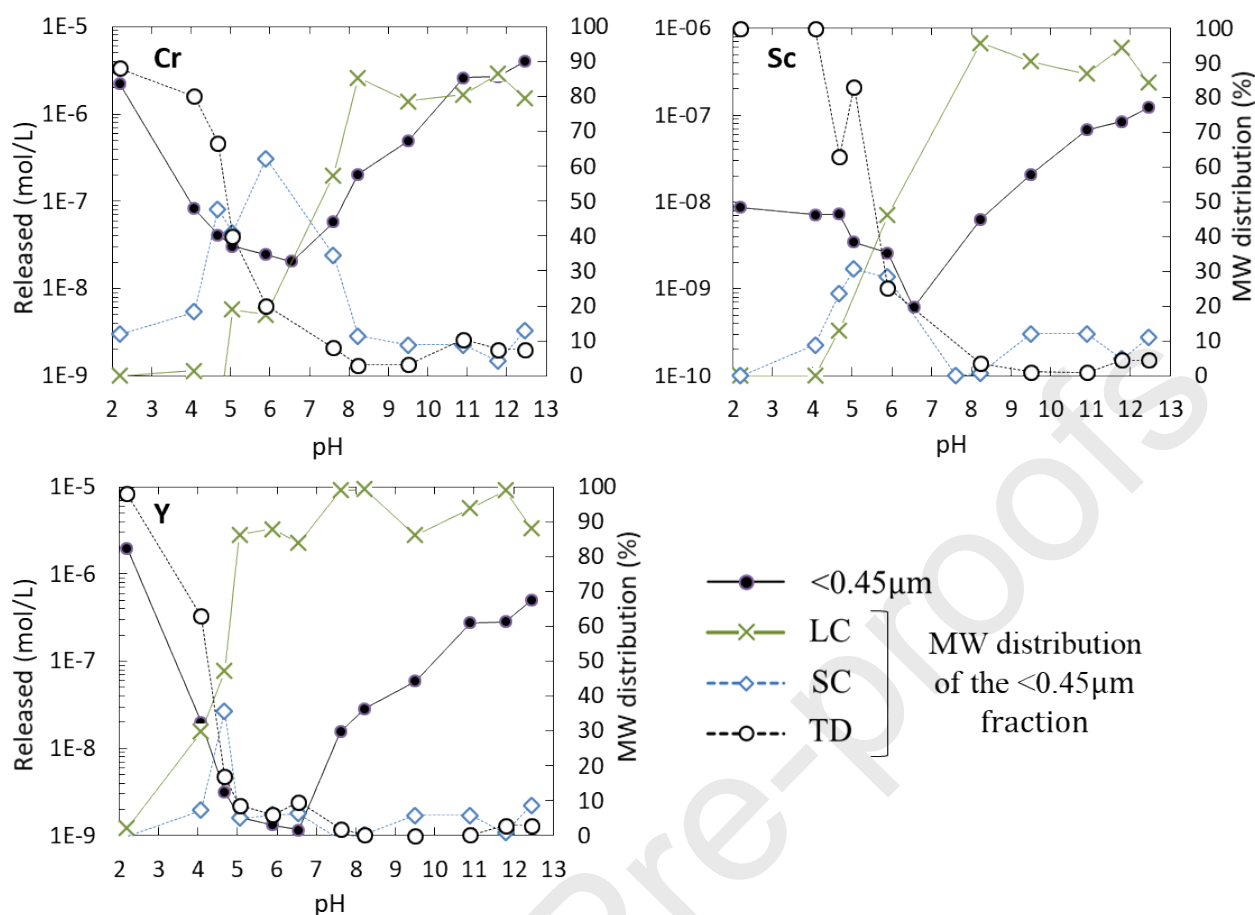


Fig. 5: Effect of pH on: (i) the overall release of trivalent species expressed in mol/L (●); (ii) the proportions of leached trace metals in the forms of large colloids (x), small colloids (◇) and truly dissolved constituents (O).

3.4 Leaching of anionic species (*V, As, Sb, S, P*)

Several elements are known to occur in the form of (oxy)anions in aqueous solutions. This is the case for V, As, Sb, S, P in the present study. Cr may also occur in the form of oxyanions in its hexavalent state, but it was not the case here as discussed above.

Results of V, As, Sb, S and P leaching gathered in Fig. 6 showed that these elements were quite soluble since 20 to 80 % of their total contents in the solid matrix were leached depending on the pH. Their lowest solubilization was recorded at pH close to neutrality as it was also observed for the other elements discussed in the sections above. The effect of pH on leaching was however relatively specific to the considered elements. As and P showed a classical profile, observed for most elements, where decreasing or increasing pH induced a similar increase of their leaching. For S, Sb and V however, acidification had a low (Sb) to very low effect, (S and V except at pH 2 where leaching of V was strongly increased), whereas increasing pH from 6-7 to 12 increased leaching in a regular manner. The leaching of V was particularly affected by pH, with an increase by more than 2 orders of magnitude between pH 4-5 and pH 12-13. The dynamics of As and Sb depend on their oxidation states [41,42]. In our pH and Eh conditions, As is expected to be mainly released as As(V) and Sb as Sb(V), pentavalent forms being less toxic compare to trivalent ones [42].

Fig. 6 also showed that the pH-dependent distribution among different MW fractions of leached species were very similar for all these elements, which is not surprising because these elements are known to exhibit similar chemical behavior and compete for the same binding sites [43]. Over the entire pH range, all the elements considered here were predominantly released in the form of truly dissolved species. The proportion of large colloids increased however at alkaline pH but decreased in most cases at extreme alkaline pH. The proportion of small colloids was in all cases marginal, except for P species at pH 6-9. These results emphasize the necessity to consider the role of organic and/or mineral colloidal carrier phases emission to assess the S, P, As, Sb and V mobility in SD porous media. In other natural systems, such as in agricultural soil solutions [2] or solutions extracted from forest soil samples [44], the presence of colloidal P species has also been demonstrated and their mobility was reported as a major source of P losses.

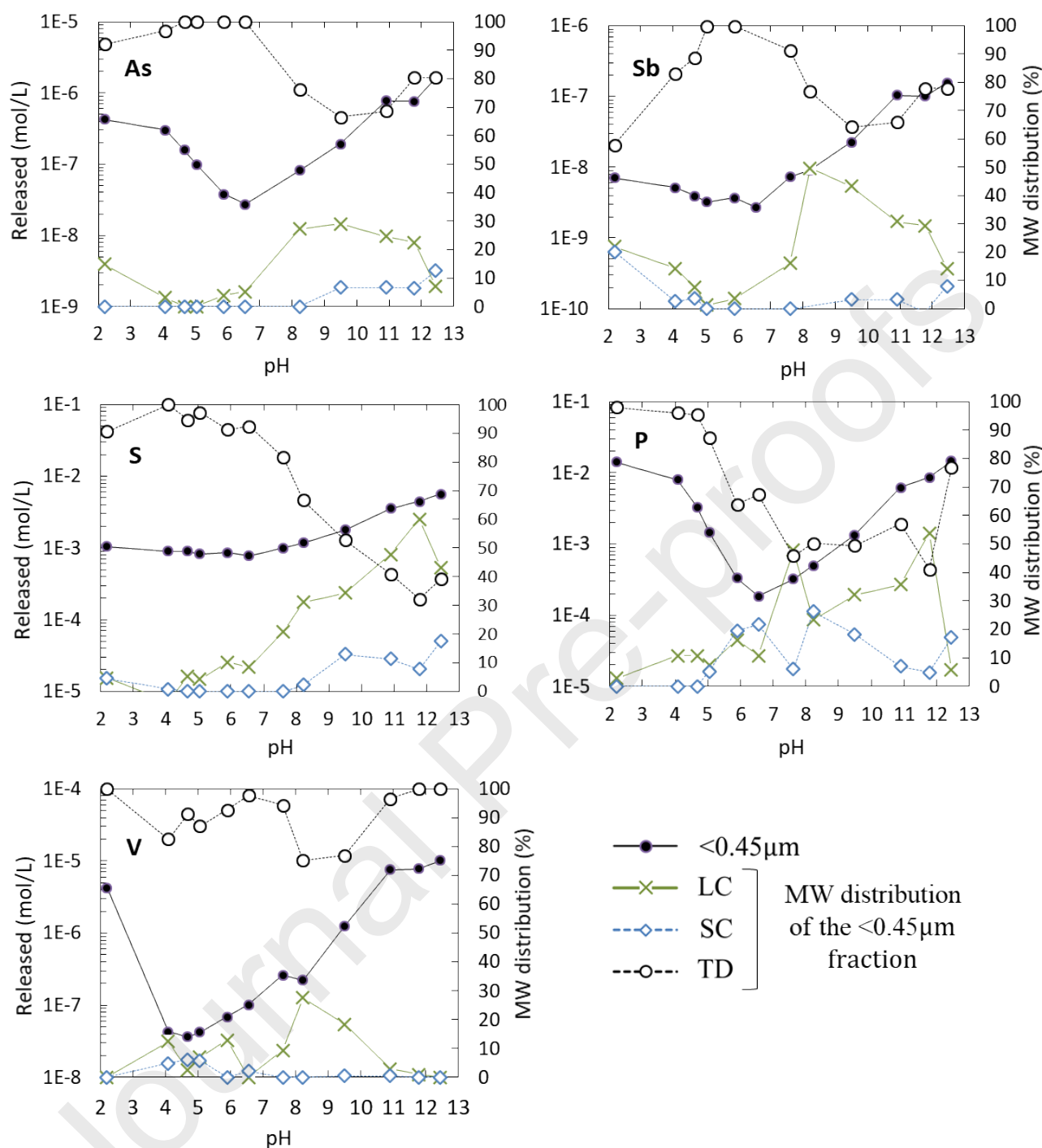


Fig. 6: Effect of pH on the leaching behavior of As, Sb, S, P, V expressed in $\mu\text{g/L}$ (\bullet) and their proportions of leached species in the forms of large colloids (x), small colloids (\diamond) and truly dissolved constituents (O).

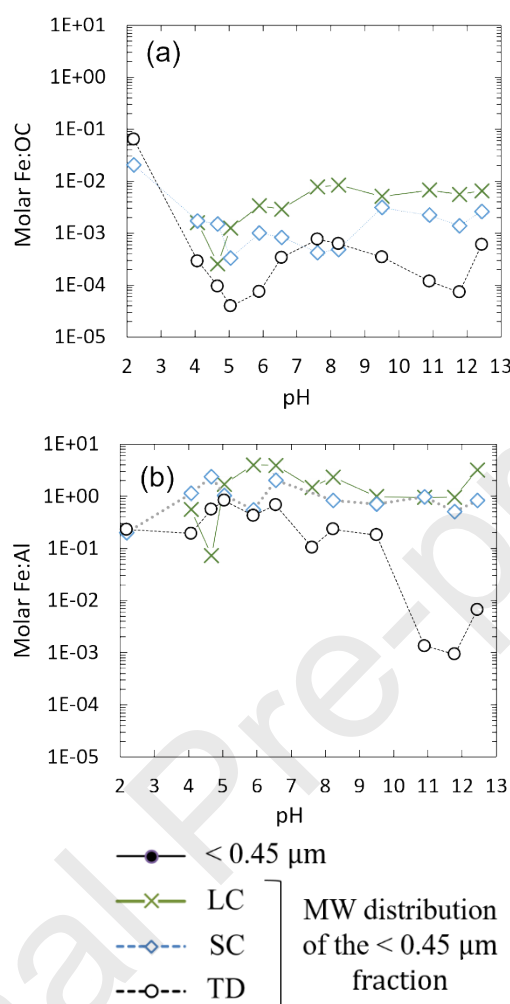
In natural soil system Vanadium mainly occurs as V(III), V(IV) and V(V) [45]. According to the pH-Eh diagram of equilibrium (Fig. S1), V was probably released mainly as V(V) in the experimental conditions of the present study. This form is the most mobile and toxic [46]. This speciation was confirmed by the fact that more than 80% of leached V was solubilized in the form of truly dissolved species (Fig. 6) as observed for anionic species. V(V) has been reported to have a strong affinity for

complexation with mineral surfaces [46]. Published studies conducted on natural soil solution reported that V was solubilized by organic and/or inorganic colloids to a higher extent than observed here [8,9,28]. This could be attributed to a lower availability of binding sites in our study due to competition with organic molecules or inorganic elements such as phosphorus.

3.5 Determination of the colloidal carrier phases and elements association

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In all the MW fractions obtained by filtration or ultrafiltration of the leachates at different tested pHs, predominant measured elements were mainly organic carbon, followed by Fe and Al. The molar ratios of these elements were therefore calculated to assess, in a first approach, the possible nature of the phases constituting the colloids in LC and SC fractions. Results are shown in Fig. 7. It was observed that Fe/OC



and Fe/Al ratios fluctuated with pH in each respective MW fraction. However, excluding some of the results obtained at extreme pH values, the fluctuations within each MW fraction followed horizontal lines, suggesting that pH in the range of 4 to 13 and 2 to 10 for Fe/OC, respectively Fe/Al did not profoundly modify the nature of the phases. As already discussed before, the enrichment of the LC fraction in Fe and Al could be explained by the mobilization of Fe and Al oxides from the SD. However, the concomitant released of OC, Fe and Al suggest that organic molecules and Fe/Al oxides are closely related, thus forming possible large organo-mineral colloids as reported in many published studies [31,33,47,48]. These results, therefore, require a more precise investigation of the specific role of organic and/or inorganic colloidal phases in the mobilization of the elements studied here. Moreover, numerous elements are only weakly (P, As, Sb, S, Na, Rb, V) or partly (Cu, Co, Ni, Cd) associated with released colloids and need further consideration to understand if the measured elements in the TD fraction is mainly composed by aqueous species (comprising free ionic forms and inorganic complex) or composed by element-TD organic molecules associations. Classically, a plot of the element concentration as a function of OC, Fe and Al is used to distinguish between the main carrier for trace elements [8,28,49]. The percentage of each element leached, versus OC and Fe percentage remaining in each ultrafiltrate and for each pH are shown in Fig. 8 to 10.

Fig. 7: Evolution of the molar ratios of (a) Fe:OC and (b) Al:Fe over the pH range in the large colloidal fraction (x), small colloidal fraction (◇) and truly dissolved fraction (O).

Co, Ni, Cu and Cd concentrations significantly change with the ultrafiltration cut-off but, as shown previously, even at neutral to alkaline pH, more than 20% of these elements were released in the TD fraction. Fig. 7a. shows that the variations of OC and Cu concentrations with pH in the ultrafiltrates were positively correlated to each other from near neutral to alkaline pH conditions. The same behavior was observed for Co, Ni, and Cd (results not shown here). For pH values above 5-6, the release of these elements is strongly controlled by the mobilization of colloidal but also TD organic molecules. Co, Ni, Cu and Cd are classically classified as “borderline” cations which means that they can form strong covalent binding with all organic ligands [50] and thus, small organic ligands mobilized from the solid deposit layer. The high affinity of these divalent metals for low MW organic compounds from natural origins has been previously documented [8,33]. However, the correlation between Cu and OC was degraded under acidic conditions which could be explained by the increased protonic competition for organic binding sites. Affinity of these elements for LC sorption sites decreases to a greater extent with acidification. A higher site density and a more important fraction in weak acid groups, still deprotonated in acidic conditions, is generally found in small organic molecules (fulvic acids with MW = 1.5 kDa) compare to large organics molecules (humic acids with MW > 15kDa) [22,38]. These properties give TD organic molecules mobilized from SD the ability to increase the solubilization of these divalent transition metals even under relatively acidic conditions. Thus, part of the TD divalent metals should be associated with organic molecules under acidic conditions. As observed previously, the MW distribution of Co, Ni, Cu and Cd slightly contrasts with those of divalent (Zn, Mn, Pb) and trivalent (Y, Cr, Sc) metals, which are strongly associated with large colloidal fraction.

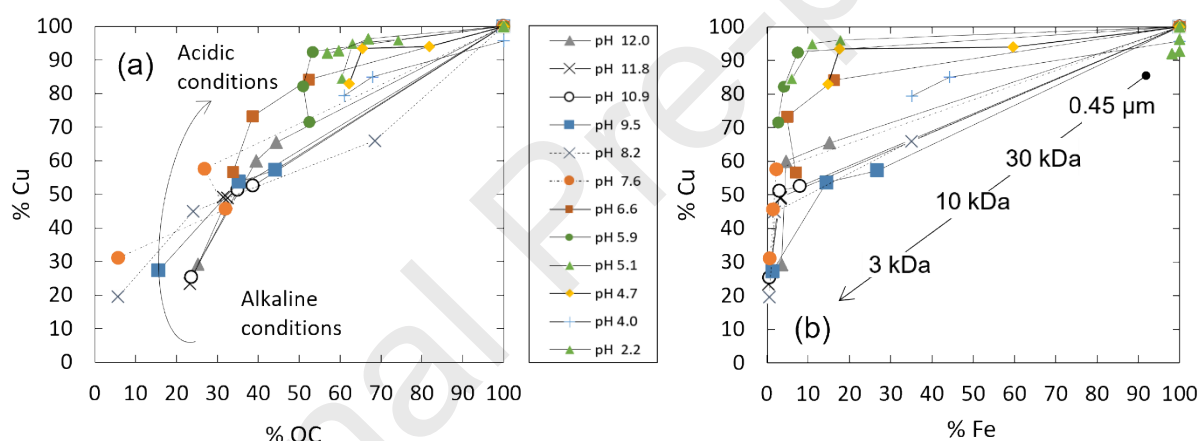


Fig. 8: Percentage of Cu leached in the different (ultra)filtrates (30, 10 and 3 kDa) over the pH range as a function of (a) OC and (b) Fe concentrations remaining in solution. Concentrations measured in the 0.45 μm solutions represent 100% of the considered element.

Compared to other divalent transition metals, Zn and Mn are mostly associated to the large colloidal fraction (Fig. 4). Fig. 9 evidenced a clear positive correlation between OC and Fe and these elements suggesting their sorption to large Fe/Al-organic colloids. Differences with other divalent transition metals could be explained reasonably well by the Irving-Williams series which describe the complex stability among the first transition metals: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. In this series, ionic contribution in the Zn and Mn bonding to ligands is more important [51]. This property relates them to the so-called “hard” cations. Hard cations are highly charged containing highly electronegative atoms having the properties to transfer electronic charges to the outer sphere with “hard” organic ligands [50,52]. Alkaline and alkaline earth metals, considered as “hard” cations, are also mainly associated to large organic molecules in this study. The molecular weight and polyelectrolyte properties [38] give to the large organic molecules mobilized from solid deposit an important ability to electrostatically sorb and solubilized Mn, Zn, Ca, Mg, Sr and Ba.

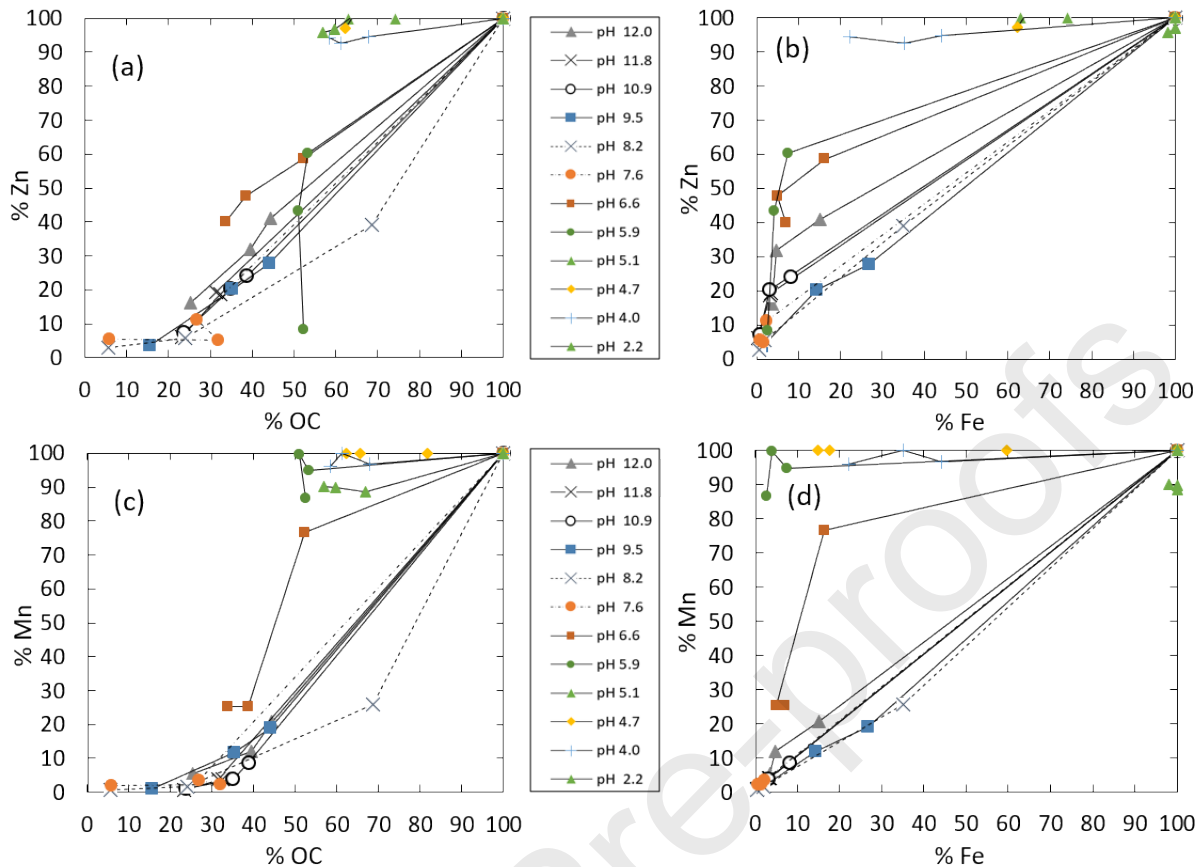


Fig. 9: Evolution of leached Zn (a,b) and Mn (c,d) percentage versus (a,c) OC and (b,d) Fe remaining in solution after each ultrafiltration (30, 10, 3 kDa) of the various solutions. Concentrations measured in the 0.45 μm solutions represent 100% of the considered element.

Pb, Y, Sc, and to a lesser extent Cr, are largely associated with LC fractions for a large pH range (Fig. 4 and 5). This leaching pattern is similar to that observed for Fe and differs from that of OC suggesting their preferential bounding with large oxides colloids. Pb (Fig. 10. a and b) but also Cr, Y (Fig10. c and d) and Sc concentrations is positively correlated to OC and Fe concentrations. Finally, iron oxides and iron oxides-organic particles could be Cr, Pb, Y and Sc carriers and remobilizing phases in the SD. This result is supported by studies having demonstrated their affinity for iron oxides and organo-mineral colloids [53,54].

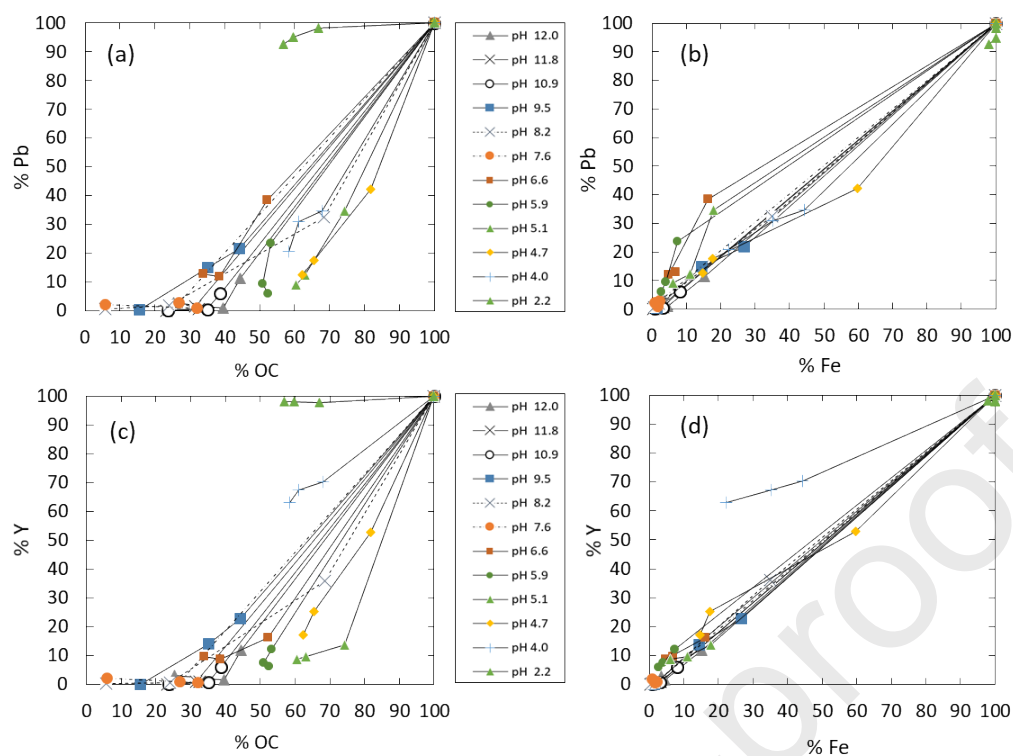


Fig. 10: Percentage of Pb and Y leached in the different (ultra)filtrates (30, 10 and 3 kDa) over the pH range as a function of (a,c) OC and (b,d) Fe concentrations remaining in solution. Concentration measured in the 0.45 μ m solutions containing 100% of the considered element.

Surprisingly, phosphorus, whose important affinity for Fe-oxides is often used to quantify the amount of available sites on these surfaces [55], as well as Sb(V) and As(V) who tend to behave similarly to P [56], are preferentially released in the TD fraction (Fig. 5). The low sorption rates of these elements to the Fe/Al-oxides could be due to the important adsorption competition with organic molecules for the oxides binding sites [36,37]. P, As and Sb measured in the LC could be associated with Fe-oxides but large organic molecules could also influence their lixiviation through ternary complexes involving either Fe/Al oxides-OM complex or cationic bridging [57]. The proportion of P, As and Sb located in the TD fraction could be considered as inorganic complex or complexed by Fe-oxides organized as primary beads with a MW < 3 kDa [31].

3.6 Environmental implication

During their life cycle, VFCW solid deposits may be exposed to variable geochemical, biological and hydrological factors that may affect the release of organic and inorganic colloids and associated trace elements. pH is one of the key factors of influence. The experimental results obtained from this study showed the necessity to limit the mobilization of organic and/or inorganic colloids as these carrier phases promote the mobilization of inorganic pollutants. The release of such colloidal carrier phases would be minimal at pH values around neutrality, while mobilization of organo-mineral colloids increases with alkalization. The installation of acidic conditions should be avoided as they would enhance the release of most trace metals in the form of small inorganic complexes (Fig. 11) known to be more toxic and bioavailable than the organic complexes [58].

The reuse of treated wastewaters is a highly promising approach for addressing water scarcity challenges and supporting sustainable agricultural practices but face the challenging necessity to limit pollutants accumulation in soils through irrigation [59]. Ultrafiltration can serve as a method for the removal of

pollutants from treated wastewater [60]. Data obtained during this study could be used to adapt the size of the filtering process depending on the pH on the wastewaters arriving to the treatment plant and thus increase the performance of the procedure and limit membrane fouling.

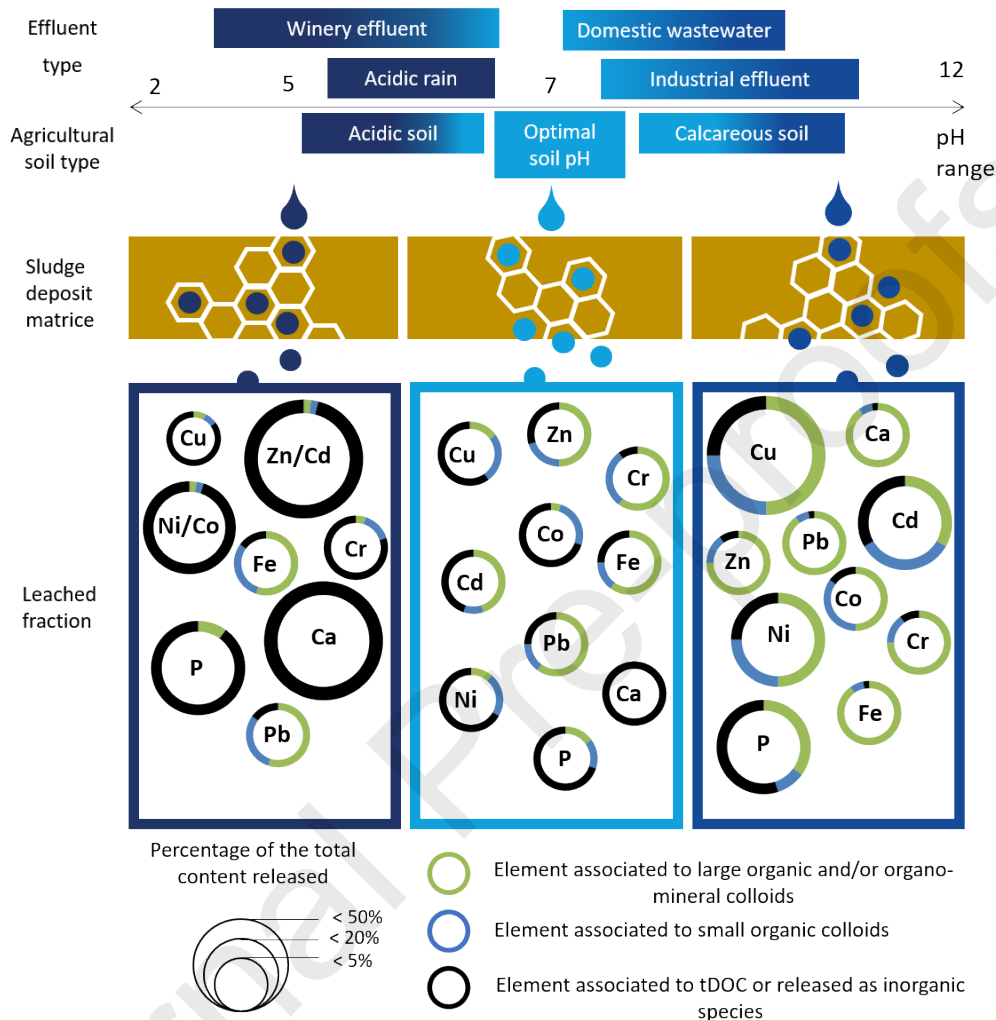


Fig. 11. Schematic representation of the possible effects of pH on the release of major and trace elements from VFW solid deposits either *in situ* at the surface of the CW filter or *ex situ* at the surface of soils receiving applications of dredged solid.

Organic solid from extensive domestic wastewater treatment plants may be used as organic amendment by spreading them onto agricultural soil [61]. Currently, only trace metals total content is regulated (Directive 1986/278/EEC). The solid-solution distribution and the speciation of the pollutants contained in the released fraction, will govern the bioavailability and possible toxicity of the solid micropollutants [58,62]. This study revealed that instead of focusing solely on the total content of micropollutants, it is crucial to evaluate and monitor the solid's capacity to generate colloidal carrier phases.

4 Conclusion

The nature of the colloidal phases detached from solid deposit submitted to varying pH conditions were investigated using ultrafiltration technics. In addition to the expected release of an important amount of organic matter, this study evidenced the important control exerted by organo-mineral colloids on various inorganic contaminants from the solid deposit. Organic molecules have a stronger influence on the geochemical fate of inorganic constituents within the solid deposit layer compared to natural wetland soils. This is mainly attributed to their capacity to complex trace contaminants, stabilize Fe-Al oxides, and compete for inorganic binding sites.

Depending on their affinity for colloids and their sensibility to pH variations, the element released from the SD could be assigned to three different leaching patterns. The first leaching pattern involves the significant influence of large Fe/Al-organic colloids on the leaching behavior of divalent metals (Mg, Ca, Sr, Ba, Mn, Zn, Pb) and trivalent elements (Sc, Y, Cr). The second leaching pattern is composed of divalent metals (Co, Ni, Cu, Cd) with a high affinity for colloidal organic matter but also for small organics leached in the TD fraction. For these two first groups, the pH drastically influences the distribution of these elements as small acidifications of the solution could considerably increase the proportion of elements released as “truly” dissolved species. Finally, the third leaching pattern is composed of elements mainly released in the “truly” dissolved fraction regardless of pH conditions. This group is composed of metalloids (As, Sb), non-metals (P, S), alkaline (Na, Rb) and transition metals (V).

Given the potential fluctuations between oxic and anoxic conditions resulting from significant periods of flooding, it is imperative to conduct further investigations to assess the precise influence of redox conditions on the mobilization of colloids from solid deposits.

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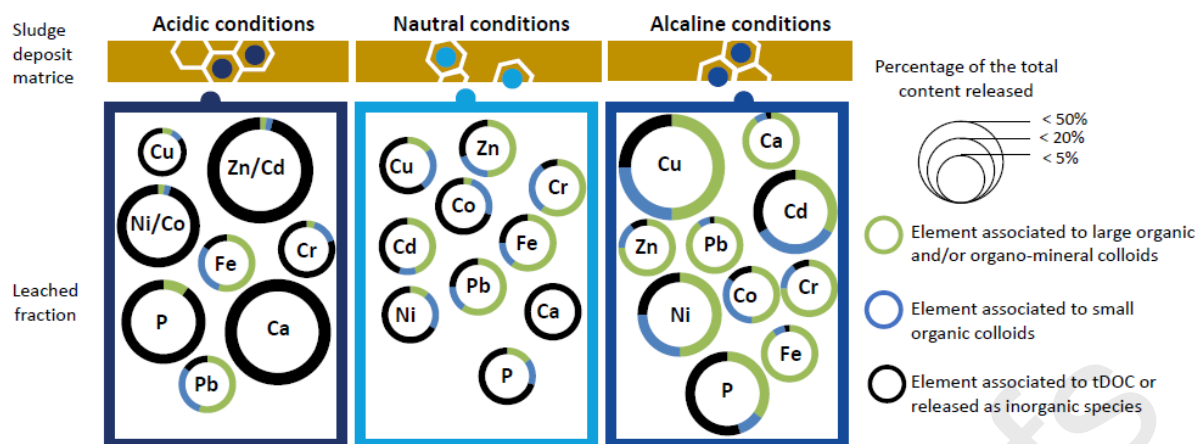
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Declaration of interests

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Organic and organo-mineral colloids control of major and trace elements leached from treatment wetland sludge deposits. Influence of pH conditions.

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Highlights

- Study of colloid-mediated elements released from treatment wetland sludge deposit.
- pH and nature of colloids are major factors controlling elements speciation.
- Large colloidal fraction is composed by organic and organo-mineral colloids.
- Small organic molecules (< 3kDa) induce the leaching of Cu, Cd, Co and Ni.
- Mineral colloids have low impact on anionic species compared to natural soils.