



Remobilization of trace metals during laboratory resuspension of contaminated sediments from a dam reservoir

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Abstract

Purpose Dam reservoirs sometimes need to be fully drawn down, an operation that induces sediment resuspension. In the case of contaminated sediments, such resuspension may promote the remobilization of trace metals from the solid to the dissolved phase, threatening the water quality. The objective of this study is to evaluate the kinetic release and removal processes of trace metals during the resuspension of polluted sediments from a dam reservoir.

Materials and methods Total contents of trace elements were analyzed in the surface sediments collected in the dam. Ascorbate and sequential extractions were used to assess the trace metal fractionation. Aliquots of wet sediments were resuspended during a week using a 3-L glass reactor. Three solid/solution ratios (2.7, 5.0, and 9.4 g L⁻¹) were tested. The pH, Eh, dissolved oxygen, and temperature were continuously measured, and water samples were collected through a small pipe inserted into the reactor. Evolution of dissolved organic carbon, alkalinity, major ions, and trace element concentrations were measured in the water over the resuspension experiments. Another resuspension experiment was carried out to determine the quantity of elements that could be adsorbed onto the glass wall of the reactor.

Results and discussion High levels of As, Cd, Pb, and Zn were measured in the reservoir sediments, compared to the quality guidelines. The temporal evolutions of the dissolved elements were similar during the resuspension experiments, regardless of the mass of sediment used. Depending on the elements, different trends can be highlighted: (1) Cd, Cr, Cu, Ni, V, and Zn were not remobilized; (2) Al, Mo, As, Ba, and Sr continuously increased during the experiments; and (3) Mn, Co, Fe, and Pb increased at the beginning of the experiments and then were removed from the dissolved phase. Co was likely adsorbed onto Mn oxyhydroxides, whereas Pb appeared to be regulated by the Fe oxyhydroxides. The results from sequential extractions did not allow to relate these groups to specific distributions in the solid phase.

Conclusions The greater risk of water quality degradation for this reservoir would be posed by the remobilization of As, which showed the greatest and the most prolonged release during resuspension, because it could not be removed onto particles due to its speciation. Dissolved As reached a maximum of 30 µg L⁻¹ at the conclusion of the experiments, a concentration above the drinking water standard but well below the acute toxicity levels reported in the literature for fishes.

Keywords Dam reservoir · Metal remobilization · Sediment resuspension · Speciation

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1 Introduction

High levels of trace metals issued from a variety of sources (mining and ore treatment, industries, and runoff from urban watersheds) accumulate within sediments in many freshwater or marine environments (e.g., Cappuyns and Swennen 2005; Di Nanno et al. 2007; Ye et al. 2013). A major environmental risk in these areas is the remobilization of the contaminated particles and the increase in dissolved metal concentrations becoming more bioavailable for biota (Vink 2009; Hug Peter et al. 2014). Superville et al. (2014) and Kalnejais et al.

(2010), for example, underlined that sediment resuspension leads to an increase of dissolved pollutants, potentially threatening the quality of aquatic ecosystems even when measures have been taken to limit the historical sources of pollution. The quantity of dissolved metals that can be released during resuspension events is larger than the benthic flux that can be transferred continuously by diffusion from sediment pore water to the water column (Louriño-Cabana et al. 2011; Zheng et al. 2013; Superville et al. 2014). Indeed, sediment resuspension leads to a sharp change in the physico-chemical conditions surrounding solid particles (mainly solid/liquid ratio, pH, redox potential, and level of dissolved oxygen) when the water-sediment interface shows important redox gradients over short distances or if an anaerobic layer in sub-surface is resuspended. Resuspension may promote, especially in this case, the release of adsorbed or co-precipitated metals into the dissolved phase.

In the case of dam reservoirs, sediments are mainly resuspended during major dam releases (high flow pulses). The amount of resuspended sediment depends on the duration and on the type of technique used for reservoir sediment management. Reservoir flushing consists of increasing the flow velocity (by opening low-level outlets) to erode and transport the deposited sediments downstream of the dam. Sluicing operations allow the particles to pass through the reservoir without settling, for example by operating the reservoir at a lower level during floods (Palmieri et al. 2001). These techniques are necessary to maintain the capacity of the reservoirs and to promote the sediment continuity. In contrast, reservoirs sometimes need to be fully drawn down to allow for maintenance operations to be performed on the submerged parts of the dams. During these draining operations, the water level is slowly lowered to limit the sediment resuspension that may have adverse effect on the environment like O₂ depletion or clogging of spawning grounds. In general, the maximum suspended matter concentrations are usually maintained under 1 g L⁻¹ on average during the operations, but values above 10 g L⁻¹ have sometimes been measured for short periods of time corresponding to the highest sediment destabilizations (Poirel 2001; Jigorel and Morin 2003; Frémion et al. 2016).

During sediment resuspension, the distribution of trace metals between the solid and dissolved phases is affected by the chemical reactions of desorption-adsorption and dissolution-precipitation. In addition to the trace element concentration, these reactions are influenced by the concentrations of suspended particulate matter, the mineralogical phases, and the chemistry of the water column and pore water (pH, redox potential, dissolved oxygen content, organic matter content). These numerous parameters produce a large range of consequences. Cappuyns et al. (2006) considered the sediment as a chemical time bomb. Fetters et al. (2016) found that resuspension of three sediments contaminated by Zn, Cu, Ni, Cd, and Pb resulted in minimal releases from suspended particles,

likely because of scavenging onto organic matter and Fe oxides formed during sediment interaction with oxic water. This resulted in minimal or no toxicity for their model organisms (only *Hyalella Azteca* was affected by Zn). The kinetics of these reactions may also have a very important role for the trace element distributions in relation to the duration of resuspension. In the results of Saulnier and Mucci (2000) for example, the remobilized Fe was rapidly removed from the dissolved phase during the first hour of the anoxic sediment resuspension, whereas the removal processes of Mn and As became predominant after 1 week. In comparison, Gerringa (1990) had no data from the first hour of the resuspension and observed no Fe remobilization. Similarly, Caille et al. (2003) highlighted various readsorption rates depending on the elements.

The kinetics of these reactions is very difficult to evaluate in the field. Laboratory experiments are helpful to better understand the processes because the chemical distributions can be followed and because some major parameters can be controlled to mimic different resuspension events.

The objective of this study is to evaluate the risk of an increase in the concentration of dissolved metals during management operations of a polluted dam reservoir. Our approach is based on analyses and chemical modeling of the evolution of dissolved concentrations during laboratory experiments with water and polluted sediments from the site.

2 Materials and methods

All the materials were acid washed in 5% HNO₃ and rinsed with Milli-Q water before use. Reagents for total and sequential extractions were reagent grade.

2.1 Study site and sampling

The studied reservoir, located in the French Alps, is fed by two small rivers. The lithology of the watershed is a mix of crystalline and sedimentary rocks mainly constituted by limestones, dolostones, and gypsum, and alteration facies, such as *cargneules* or *rauhwakes* (altered carbonate rock indicating preferred dissolution of dolomite or evaporite clasts by sulfate-rich water; Lanteaume et al. 1990; Warren 2006). The reservoir has a surface of 9.5 ha and is operated to produce hydroelectricity. Sediment contamination by As, Cd, Pb, and Zn in the reservoir was due to the presence of two ancient mines of Cu and Pb-Zn in the watershed (<http://infoterre.brgm.fr>).

The reservoir was emptied in 1998 and 2008 to inspect the underwater parts of the dam. Nowadays, the safety inspections are preferably done using unmanned underwater vehicles, with the lake at the operational level. However, draining operations could be necessary to allow maintenance works.

Water and sediment were collected from the reservoir in June 2015. Water was pumped out from the shore and passed through a 0.4- μm ceramic filter. Sediment samples (0–10 cm surface layer) were collected at 11–12 m water depth with an interface UWITEC corer. The sediment was directly extracted to measure Eh and pH (with SenTix WTW electrodes inserted in the wet sediment) and placed into sealed glass jars to maintain its reduced state. It was manually homogenized in the laboratory in a N_2 filled glove-bag (O_2 residual < 1%) and divided into five sub-samples (sample 1 to 5) that were stored in individual glass jars at 4 °C in darkness. A new jar was opened for each resuspension experiment (sample 1 to 4), and Eh and pH were measured to check the adequate conservation of the sediments (Table 1).

2.2 Sediment characterization

The major mineralogical components were determined on the dry crushed sediments by X-Ray diffraction analysis (PANalytical X'Pert Pro MPD θ - θ diffractometer), using $\text{Co K}\alpha$ radiation (1.79 Å) and operating at 40 kV and 40 mA. The International Center of Diffraction Data PDF-2 database and the X'Pert Highscore plus software were used to interpret the X-ray diffraction patterns. The analysis was performed on sample 1, and it is assumed to be representative of the homogeneous original sediment.

Particles sizes were measured on the samples 1 to 4 using a laser diffraction particle size analyzer (Beckman Coulter LS13320 Multi Wave with an aqueous liquid module). The organic matter was removed from the wet sediments by H_2O_2 digestion, and the samples were dispersed into a deflocculating solution before their analyses.

The total organic carbon (TOC) was measured for samples 1 to 4. The inorganic carbon was removed from the dry crushed sediments by acid digestion (HCl 0.2 M for 1 day), and the remaining organic carbon was measured with a Thermo Scientific FLASH 2000 elemental analyzer.

The pore water was extracted from one sample (sample 5) through sediment centrifugation at $3000\times g$ for 30 min. The filling of the centrifuge tube with the sediment sample and the pore water filtration (0.22 μm) were performed under nitrogen to avoid losses of trace elements due to Eh changes and oxyhydroxide precipitation.

The major ion concentrations were measured by a capillary electrophoresis system (Agilent 7100-A). The metal concentrations (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, Ti, U, V, Zn) were determined by inductively coupled plasma mass spectrometry (ICP-MS Perkin-Elmer NexION 300X). The quantification limits were 5 ng L^{-1} for As, Mo, and Cd; 0.2 $\mu\text{g L}^{-1}$ for Zn, Al, and Ti; and 10 ng L^{-1} for the other elements. ICP-MS measurements were quality checked by analyzing certified riverine water for trace metals (SLRS-5, National Research Council of Canada).

The total metal contents in the sediment were determined after a microwave acid digestion. Three mL of HCl (34%), 4 mL HNO_3 (67%), 20 drops of H_2O_2 , and 0.5 mL of HF (47–51%) were progressively added to 40 mg of dry sediment in Teflon tubes. The mixtures were digested at 170 °C (10 min) and then 250 °C (10 min; $P = 100$ bar) in an UltraWAVE Single Reaction Chamber (Milestone). The obtained solutions were diluted in Milli-Q water and measured by ICP-MS. The procedural blanks and reference sediment STSD-3 (Canadian Certified Reference Materials Project), a typical stream sediment, were analyzed repeatedly. Standard values are given for all the studied metals except Al, Ca, Cd, and Mg. The average difference ($n = 7$ extractions) between the measured and certified values is from 11 to 13% for As and Ni; 16 to 20% for Sr, Pb, and Mo; and less than 10% for the other elements.

Ascorbate and sequential extractions provide information on the element distribution between different solid phases in the sediment. The ascorbate extractions were carried out to more specifically quantify the trace metals bound to amorphous and easily reducible Fe and Mn oxides and hydroxides. Ferrihydrite and iron monosulfide (FeS) are considered soluble in the ascorbate solution, contrary to pyrite, hematite, or goethite (Ferdelman 1988; Kostka and Luther 1994; Anschutz et al. 1998). The reagent solution was made of a pH buffer of NaHCO_3 (pH 8; 50 g L^{-1}), ascorbic acid (20 g L^{-1}) to reduce reactive Mn and Fe oxides and hydroxides, and sodium citrate (50 g L^{-1}) which complexes with the dissolved metals. A total of 100 mg of dry crushed sediment was mixed with 10 mL of reagent solution, shaken for 24 h, and settled for 30 min. The supernatant was filtered through 0.22- μm filters and analyzed by ICP-MS.

The standardized BCR 3-step extraction scheme (Rauret 1998; Quevauviller 2007) was slightly modified to adapt the one of Tessier et al. (1979) to the first fraction, to separate the “exchangeable” and “carbonate” fractions. Sequential extractions were performed on the four samples with 1 g of dry crushed sediment. Between each step, the residues were washed for 15 min with Milli-Q and centrifuged to discard the supernatant. The sequential extraction includes the four following fractions:

- The exchangeable fraction (F1a) was extracted with 8 mL of 1 M MgCl_2 for 1 h at room temperature (adapted from Tessier et al. 1979).
- The carbonate-bound metals (F1b) were extracted with 40 mL of 0.11 M acetic acid for 16 h at room temperature. The F1b reagent and duration are the same as those of the first fraction in the standardized BCR three-step extraction scheme (Rauret 1998; Quevauviller 2007).
- The reducible fraction (F2 from BCR) was digested with 40 mL of a freshly prepared 0.5 M hydroxylamine hydrochloride solution for 16 h at room temperature.

Table 1 Main characteristics of the samples used in resuspension experiments and experimental settings. In situ values for sediment pore water Eh and pH were respectively +245 mV and 7.03

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Sediment					
Pore water (pH)	7.06	7.03	7.02	6.98	7.00
Pore water Eh (mV)	+188	+272	+80	+217	+125
Water content (g g ⁻¹) (n = 3)	0.469 ± 0.001	0.468 ± 0.006	0.463 ± 0.006	0.440 ± 0.010	0.417 ± 0.0019
Total organic carbon (%)	1.60 ± 0.09	1.72 ± 0.09	1.76 ± 0.04	1.76 ± 0.08	
Median size (μm)	11	10.5	9.5	12	
% of clay/silt/sand	28/67/5	30/68/2	31/63/6	28/67/5	
Resuspension experiment					
Resuspended mass (g L ⁻¹)	2.7	5.0	5.0	9.4	Adsorption experiment on the glass wall of the reactor (4.7 g L ⁻¹) + concentrations in the pore water
Resuspension duration (h)	120	3	120	160	

- The oxidizable fraction (F3 from BCR) was extracted with 10 mL of H₂O₂ (30%), carefully added in the tubes, and allowed to sit for 1 h at room temperature with occasional manual shaking. The uncovered tubes were then placed on a heating plate at 85 °C for 1 h. An additional 10 mL of H₂O₂ was added, and the tubes were heated at 85 °C until almost dry. A total of 50 mL of 1 M ammonium acetate was added to the cool residue and shaken at room temperature for 16 h.

Finally, the residual fraction is assumed to be equal to the total metal content minus the sum of the previous four fractions.

The procedural blanks were analyzed together with each series of sequential extractions. The sequential extraction procedure was performed four times on the reference material BCR-701 (Institute for Reference Materials and Measurements), which provided certified concentrations for six elements (Cd, Cr, Cu, Ni, Pb, and Zn) in the three fractions of the BCR extraction scheme. Good results were obtained for F2 (reducible) and F3 (oxidizable) as the mean contents of the elements obtained for these fractions differed less than 10% from the certified values, except for F2-Zn (+11%) and F2-Cd (-42%). The separation of F1 into two sub-fractions (F1a-exchangeable and F1b-carbonates) induced an overestimation of 12 to 40% above the certified value, except for Ni (6%).

2.3 Laboratory resuspension experiments

Aliquots of sediments were resuspended using an Applikon[®] bioreactor, a 3-L glass reactor in which the sediment is stirred by both a propeller assembly in the top and a magnetic stirrer on the bottom. The pH, Eh, dissolved oxygen, and

temperature were measured continuously with four probes (respectively AppliSens Gel 235 mm; Hamilton Polilyte Plus ORP Arc 225; AppliSens 235 mm and PT100 sensor) that passed through the head plate on the top of the reactor. The pH probe was calibrated before each experiment, and the redox potential probe was controlled with a reference solution. The Eh measurements are reported in mV relative to the standard hydrogen electrode. The measurements were recorded with 10 s to 1 min time steps.

Each resuspension experiment was performed on a new sample from a sealed jar (samples 1 to 4, Table 1). A mass of wet sediment was inserted into the 3-L reactor filled with filtered water collected from the sampling site. Ambient air was continuously bubbled into the reactor. A total of four experiments were conducted, with the sediment mass corresponding to 2.7, 5.0, and 9.4 dry sediment to water ratios (g L⁻¹). These values range between the regulation values and the highest values observed during dam management operations. The experiments were set for 120 or 160 h. The first test at 5.0 g L⁻¹ was stopped after only 3 h, due to a problem in data recording, and a second experiment was conducted with 5.0 g L⁻¹ for 120 h. Both experiments are discussed in the following text.

During each experiment, the water was sampled through a syringe connected to a small pipe inserted into the reactor. Water samples of 30 mL were collected successively at t0 (prior to sediment addition), 2, 5, 10, 20, and 30 min and 1, 1.5, 2, 5, 15, 24, 48, 72, 96, 120, and 160 h. The total volume collected represents a maximum of 18% of the initial water volume in the reactor. The concentrations measured in the dissolved phase are not corrected for this variation in the total volume. Each sample was separated into three aliquots: (a) 10 mL was filtered through 0.7-μm glass microfiber filters

and stored frozen in glass vials until the DOC analysis (Shimadzu TOC- V_{CSH} ; PROTEE laboratory); (b) 12 mL was filtered through 0.22- μm cellulose acetate membrane syringe filters for alkalinity and major ions (Metrohm microtitrator and capillary electrophoresis respectively); and (c) 8 mL was filtered through 0.22- μm cellulose acetate membrane syringe filters and acidified with ultrapure nitric acid for element determination (ICP-MS), including major and trace elements.

2.4 Adsorption onto the glass wall

A specific resuspension experiment was carried out with sample 5 to quantify the adsorption of the dissolved trace elements onto the glass wall of the tank (4.7 g L^{-1} for 160 h). The reactor was carefully washed before the resuspension of sediment, and the glass wall was rinsed with 25 mL of ultrapure HNO_3 2 M. At the end of the resuspension, the mixture was discarded, and the glass wall was rinsed several times with Milli-Q water to remove the solid particles and again with 25 mL of ultrapure HNO_3 2 M. The trace element concentrations were compared in these acidic rinsing solutions before and after the sediment resuspension.

The amount of Al recovered on the wall with the acid rinse solution represented 6 to 26% of the maximum amount of dissolved Al present in the reactor during the sediment resuspension, depending on the experiment. For the other elements, the amounts recovered on the glass only accounted for small percentages of the maximum dissolved concentrations measured during the resuspension experiments: 1 to 7% of Cr, 2 to 4% of Cd, 3% of Pb, and 1% of Fe and Zn. The percentages were below 1% for the other elements including As and Mn (0.1%). Except for Al, the underestimation of metal released due to the adsorption of elements onto the glass wall was thus very low. Furthermore, this fraction may have corresponded to colloidal or small particles attached to the glass wall and not to truly adsorbed ions.

2.5 Calculation of saturation index and speciation of dissolved components

The speciation of the dissolved elements and the saturation indexes for the minerals were calculated for each sample using the program Visual MINTEQ (version 3.0, Gustafsson, <http://vminteq.lwr.kth.se/>). Kinetics is not considered and it is assumed that the solution species are at equilibrium. The input data are the major and trace element concentrations, alkalinity, temperature, pH, and redox potential (pe) values at each sampling step. Because of the high Eh values in sediments, sulfides were assumed to be negligible. The adsorption and precipitation of the solid phases were not allowed in the simulations.

The NICA-Donnan model included in Visual MINTEQ was used to estimate the concentrations of organometallic complexes from DOC concentrations. The ratio of active dissolved organic matter (DOM) to DOC was set at 1.65 (e.g., Fathollahzadeh et al. 2015), which is the default value in Visual MINTEQ based on the results of Sjöstedt et al. (2010). This ratio indicates that 50% of DOM is C and that all the DOC may not be reactive towards the trace elements (approximately 83% of reactive DOC). Fulvic and humic acids were not measured because of the small amount of sample, and they were considered to constitute 90 and 10% of the active DOM, respectively (Malcolm 1985; Balistrieri and Blank 2008; Rigaud et al. 2013). By default in Visual MINTEQ, 100% of the active DOM is assumed to be fulvic acid.

The saturation index (SI) values are expressed as base-10 log: $\text{SI} = \log(\text{IAP}/\text{Ks})$, IAP is the ion activity product, and Ks is the solubility product. Thus, an SI value of approximately 0 ± 0.05 indicates that the mineral is in equilibrium with the solution (Monnin and Ramboz 1996). A positive or negative SI value specifies supersaturation or undersaturation respectively.

3 Results

3.1 Sediment characteristics

The main minerals observed with XRD in the total fraction of sediment were dolomite $\text{CaMg}(\text{CO}_3)_2$, calcite CaCO_3 , quartz SiO_2 , clinocllore $\text{Mg}_5\text{Al}(\text{AlSi}_3)\text{O}_{10}(\text{OH})_8$, muscovite $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, and albite $\text{NaAlSi}_3\text{O}_8$. These minerals are directly issued from the watershed.

The four samples were mainly composed of silt (4–63 μm , fractions ranging from 62 to 68%) and clay (28–31%). The sand fraction (mode approximately 95 μm) was weak and slightly lower in sample 2 compared to that in the others. The TOC and pH values were also very similar, attesting of the homogeneity of the samples (Table 1).

The samples were well protected in the sealed jars, but they encountered small evolutions in redox conditions. The redox potentials of the samples evolved during storage since the values measured before the experiments ranged from +80 to +272 mV (Table 1), compared to an in situ value of +245 mV. Except for sample 2 which showed a slightly higher Eh value, the decrease of Eh is due to the on-going degradation of the organic matter with the exclusion of oxygen.

3.1.1 Total concentrations of metals in the sediments

Total concentrations of the elements in the sediments are shown in Table 2, along with two sediment quality guidelines: (1) the probable effect concentrations (PEC) and threshold

Table 2 Total metal contents of sediment from the reservoir in mg kg⁻¹ dry weight (average of the four samples except for Al, Cd, and Zn). Threshold effect concentrations (TEC) and probable effect concentrations (PEC) from MacDonald et al. (2000) are reported together with the French regulatory threshold S1 (see text for details)

	Sediment total content (mg kg ⁻¹)	TEC/PEC (mg kg ⁻¹)	S1 (mg kg ⁻¹)
Al	19,237 ± 338 (sample 3 = 48,872 ± 6011)		
As	42.9 ± 0.7	9.79/33.0	30
Ba	343.7 ± 3.9		
Ca	85,727 ± 1126		
Cd	6.0 ± 0.3 (sample 4 = 11.2 ± 1.2)	0.99/4.98	2
Co	6.8 ± 0.2		
Cr	33.6 ± 0.9	43.4/111	150
Cu	10.1 ± 0.4	31.6/149	100
Fe	18,432 ± 266		
Mg		46,894 ± 403	
Mn		360.8 ± 5.7	
Mo		1.63 ± 0.02	
Ni	12.6 ± 0.4	22.7/48.6	50
Pb	212.7 ± 1.9	35.8/128	100
Sr	87.5 ± 1.2		
Ti	2068 ± 51		
V	46.2 ± 0.7		
Zn	686.5 ± 20.8 (sample 4 = 1141 ± 24)	121/459	300

effect concentrations (TEC) from MacDonald et al. (2000) and (2) the regulatory threshold S1 defined in the French legislation to help in assessing the environmental impacts of operations involving dredged or resuspended sediments from rivers or channels (NOR: DEVO0650505A, 2006).

The total concentrations of elements for the four samples were very homogeneous, except for Al (sample 3) or Zn and Cd (sample 4) exhibiting higher levels. The weighted means of the total contents and the associated errors are calculated according to Bevington and Robinson (2003, Chap. 4), taking into account the unequal uncertainties assigned to the four samples.

Four trace metals exhibited concentrations above the PEC values: As (42.9 ± 0.7 mg kg⁻¹), Cd (6.0 ± 0.3 and 11.2 ± 1.2 mg kg⁻¹), Pb (212.7 ± 1.9 mg kg⁻¹), and Zn (686.5 ± 20.8 and 1141 ± 24 mg kg⁻¹). Therefore, adverse effects on the benthic organisms are highly probable for these metals, and they also exceed the S1 level from the French legislation. Above these levels, the river sediments are assumed to be contaminated, which modifies the kind of management

operation that can be performed. The concentrations of Cu, Cr, and Ni were below the TEC and thus normally have no effect.

3.1.2 Metal distributions in the sediment

The results of the ascorbate and sequential extractions are presented in Fig. 1a, b as percentages of the total contents. Cd is not reported due to a problem in total recovery. The ascorbate extraction indicates that 52% of the total As was associated with the reactive fraction of Mn and Fe amorphous oxyhydroxides, followed by Pb (32%, Fig. 1a). The proportions of Cu, Zn, Co, Mn, Ba, Fe, Mo, and Ni ranged between 8 and 13% (Fig. 1a).

According to the sequential extractions (Fig. 1b), Fe, V, Cr, Al, and Ti were mainly in the residual fraction (> 92%). Mo, Ba, Co, Ni, and Pb ranged from 70 to 85% in the residual fraction and exhibited a wide range of values for the other

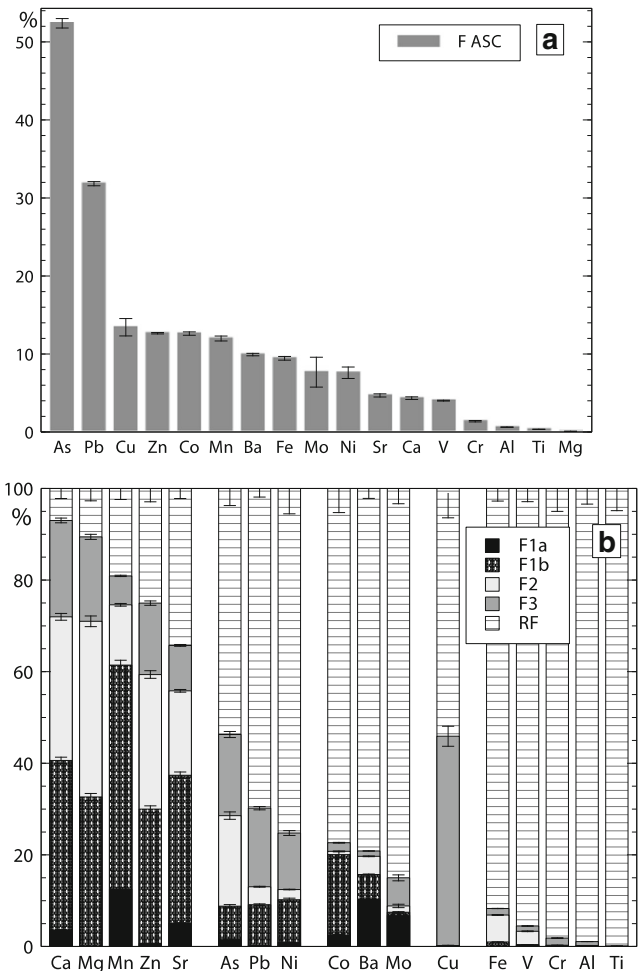


Fig. 1 Distribution of trace metals in **a** the ascorbate extraction fraction (F_{ASC}) and **b** the five sequential extraction fractions (F1a exchangeable, F1b carbonates, F2 reducible, F3 oxidizable, RF residual fraction) in % of total content, mean of the four samples

fractions, with Ba and Mo largely extracted in the exchangeable fraction F1a. Approximately half of the Cu and As were in the residual fraction. The rest of the Cu was in the oxidizable fraction (46%), whereas As was distributed in the first four fractions with the following decreasing order: F2 > F3 > F1b > F1a. Finally, Ca, Mg, Mn, Zn, and Sr showed very low proportions in the residual phase. Mn was largely associated with the first two fractions (F1a and F1b correspond to 13 and 49% of the total Mn), whereas Ca, Zn, and Sr were mainly in the carbonate and reducible fraction (F1b and F2). Mg cannot be measured in the first fraction F1a extracted with an MgCl_2 solution. Dolomite $\text{CaMg}(\text{CO}_3)_2$ was observed in the X-ray diffraction pattern, and 33% of Mg was extracted in the carbonate fraction. The reducible fraction (F2) accounted for 38% of the total Mg.

3.2 Results of the resuspension experiments

3.2.1 Evolution of physico-chemical conditions in water

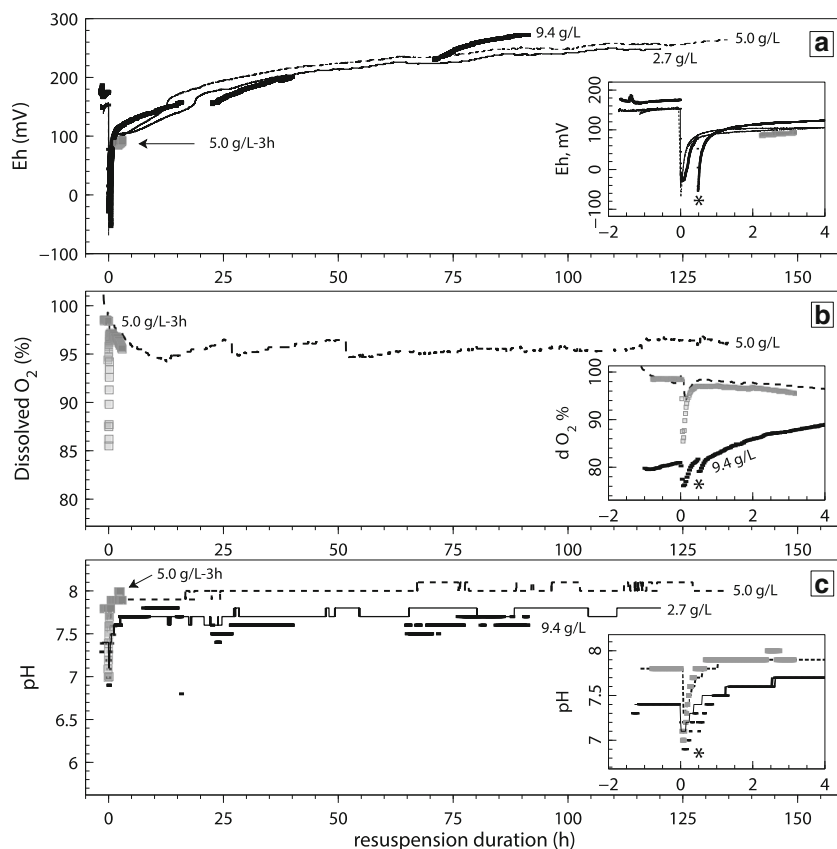
The evolution of Eh, dissolved O_2 , and pH during the four resuspension experiments (made at room temperature, 24 to 30 °C) is shown in Fig. 2, where t_0 corresponds to the time of the water sampled just before the addition of sediment into the bioreactor. The pH values originated at approximately 7.2–7.8, decreased immediately by 0.4–0.5 units with the sediment

addition and then increased and stabilized up to 7.5 and 8.0 after 1 h (Fig. 2c). The Eh values followed the same pattern with an instantaneous decrease of 200 mV with the sediment addition, a rapid increase for 1 h and a continuous but slow increase up to the end of experiment (Fig. 2a). Rapid oxidation reactions of reduced species occurring at the beginning of the experiments are evidenced by the sharp drop of Eh when sediments were added into the reactor, a portion of which were due to reactions with the pore water elements (see the enlargement in Fig. 2a). The dissolved O_2 concentration showed the same pattern with a small but immediate decrease that did not exceed 1 mg L^{-1} when the sediment was added into the reactor (Fig. 2b). The saturation level of the dissolved O_2 remained above 85% for the duration of the resuspension experiments. These observations are consistent with the lowering of Eh, pH, and dissolved oxygen measured by Frémion et al. (2016) downstream a reservoir during a sluicing operation.

It must be noted that the magnetic stirrer stopped unexpectedly between 0 and 30 min for the 9.4 g L^{-1} experiment. It was restarted at 30 min, inducing changes similar to those occurring at t_0 with a rapid decrease and then an increase of pH, Eh, and dissolved oxygen (see “*” in the insets Fig. 2a–c).

Finally, the DOC concentrations ranged between 1 and 5.6 mg L^{-1} depending on the experiments (Electronic Supplementary Material, Fig. A1). This range partly results

Fig. 2 Measurements in water. **a** Redox potential (Eh, mV), **b** dissolved O_2 (dO_2 , %), and **c** pH, during the entire resuspension experiments. These values are zoomed on the first 4 h in the three insets. t_0 corresponds to the time of the water sampled just before the addition of sediment into the reactor. Oxygen saturation values are not displayed for the 2.7- and 9.4 g L^{-1} experiments due to calibration problems of the probe



from an evolution of the water during the storage before the experiments. The DOC concentrations remained relatively stable and did not show any clear trend over the resuspension experiments.

3.2.2 Trends of dissolved elements during sediment resuspension

The variations in Ca^{2+} , alkalinity (expressed as HCO_3^-), Mg, and SO_4^{2-} are reported in Fig. 3. Ca^{2+} , Mg, and alkalinity remained relatively constant during the first hour, and then, they increased continuously up to the end of the experiments (or to 72 h for the experiment 5.0 g L⁻¹ for 120 h, Fig. 3a–c). SO_4^{2-} increased after 5 h of experiment (Fig. 3d). Na^+ and NO_3^- (not shown) remained relatively constant over the duration of the resuspension, except for a slight decrease between t_0 and 2 min for some of the experiments.

Cl^- and K^+ (not shown) continuously increased during the experiments up to 0.5 mmol L⁻¹ at 120 or 160 h. This increase is due to the continuous leakage of electrolyte from the redox probe, because their molar ratio is constantly near 1. This had no influence on the experiment because speciation calculations indicate that 99.8% of the Cl was on the free ion form Cl^- , and thus the complexes of Cl with trace metals were negligible.

The other dissolved element concentrations are reported in Figs 4, 5, and 6. In a general way, the decreasing or increasing trends of the dissolved concentrations, as well as their kinetics,

were similar for each element between the four experiments. However, different trends in temporal variations can be highlighted and separated into three groups described below.

The dissolved concentrations of Al, Mo, As, and Ba increased from the beginning of the experiment up to their maximum values at the end of experiment, but their trends were slightly different (Fig. 4). Whereas Mo increased continuously (Fig. 4c), Ba and Sr showed decreasing or stable concentrations during the first hour (Fig. 4d, e). Al tended to reach a plateau after 15–24 h, except for the 2.7-g L⁻¹ experiment where it increased continuously (Fig. 4b). The trends for As were also variable (continuous increase or plateau, Fig. 4a), but the concentrations were above the drinking water standard of 10 $\mu\text{g L}^{-1}$ after 2 or 30 min only ($= 1.33 \cdot 10^{-4}$ mmol L⁻¹; World Health Organization 2011; directive 98/83/CE-03/11/98), and they reached a maximum of 30 $\mu\text{g L}^{-1}$ ($4.0 \cdot 10^{-4}$ mmol L⁻¹).

The Fe, Mn, Co, and Pb concentrations increased immediately at the start of experiment (Fig. 5). Then, the Co and Mn decreased very rapidly after 2 min of resuspension (Fig. 5a, b), whereas the Fe remained relatively constant at its high level for up to 1 or 2 h before decreasing (Fig. 5c). Pb continuously increased from 0 to 5 h and then continuously decreased (Fig. 5d). Its maximum values were always below the environmental quality guideline of 14 $\mu\text{g L}^{-1}$ ($6.8 \cdot 10^{-5}$ mmol L⁻¹, directive 2013/39/UE-12/08/2013). At the conclusion of the experiment, the Fe, Mn, Co, and Pb have dissolved concentrations below or equal to the initial values.

Fig. 3 Evolution during the resuspension experiments (h, log scale) of **a** Ca^{2+} , **b** the alkalinity (expressed as HCO_3^-), **c** Mg, and **d** SO_4^{2-} in the dissolved phase (mmol L⁻¹). t_0 points are the concentrations in water prior to the addition of sediment. The curves correspond to the various masses of dry sediment used

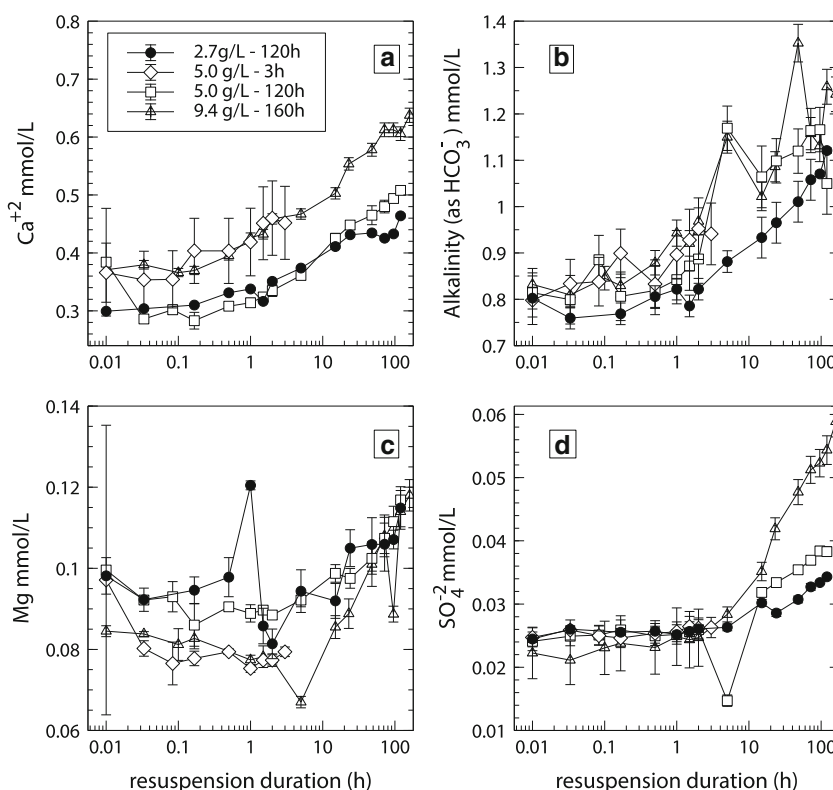
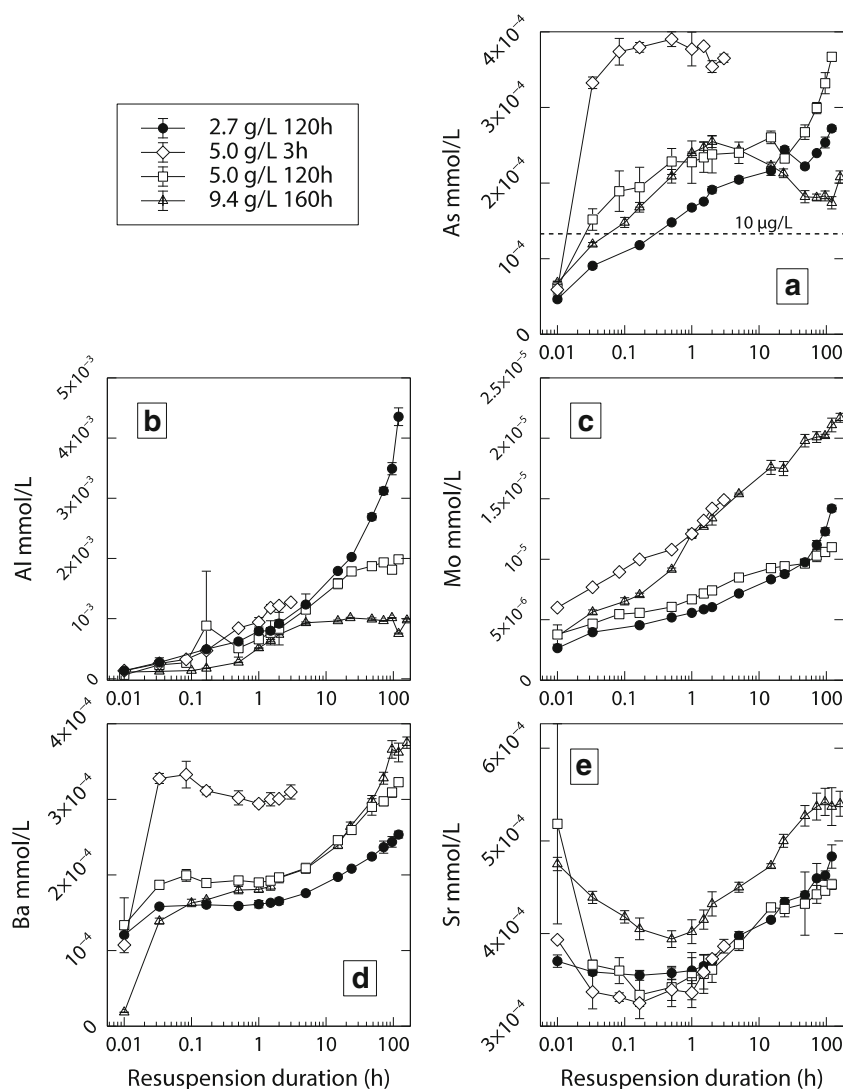


Fig. 4 Evolution of **a** As, **b** Al, **c** Mo, **d** Ba, and **e** Sr concentrations in the dissolved phase (mmol L^{-1}) during the experiments of sediment resuspension (h, log scale). t_0 points are the concentrations in water prior to the addition of sediment. The curves correspond to the various masses of dry sediment used. The line “ $10 \mu\text{g L}^{-1}$ ” for As corresponds to the WHO drinking water standard



Finally, Ni, Cu, Cd, and Zn (and Cr and V, not shown) belong to a third group of elements which exhibited a very fast decrease since the beginning of the experiments and had more or less constant values after a few minutes up to 1 h (Fig. 6).

The concentrations measured at t_0 were sometimes different between the experiments (e.g., Cd, Ni, or Ba), and we have no explanation for that. However, these differences did not influence the temporal trend during the experiment, except in the case of Cd.

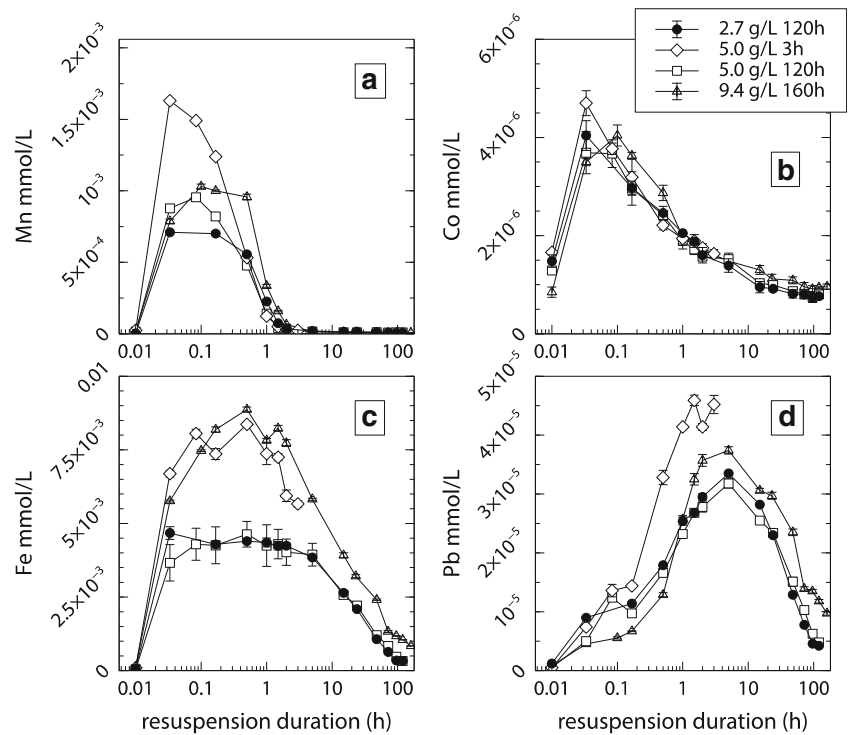
3.2.3 Contribution from pore water

The inputs of dissolved metals due to pore water dilution occurred immediately when the sediments are added into the reactor. These inputs were calculated for the elements between t_0 and 2 min using the pore water concentrations determined in sample 5, the different volumes of pore water (7.2 mL for the 2.7-g L^{-1} experiment, 13 mL for 5.0 g L^{-1} , and 22 mL for

9.4 g L^{-1}), and the total volume of the mixtures (3 L). For these three experiments in which the amount of pore water increased, the pore water inputs accounted for 33, 76, and 83% of the dissolved Fe, respectively, measured after 2 min of sediment resuspension. These inputs constituted 15, 21, and 40% of the dissolved Mn at 2 min. For Zn, they constituted 7, 30, and 162%, showing that during the $9.4\text{-g L}^{-1}\text{-160-h}$ experiment, a portion of the dissolved Zn that was released in the solution because of the pore water dilution had already been adsorbed in the suspended sediment solid phase between t_0 and 2 min. For the $9.4\text{-g L}^{-1}\text{-160-h}$ experiment, involving the highest pore water volume, this input represented 18 to 24% of the 2-min concentrations for As, Ba, and Co. The inputs were below 13% for the other elements and experiments.

The pore water dilution induced fast reactions, especially linked to the behavior of Fe and Mn, and their oxidation contributed to the fast decrease in oxygen content, which would be the case in any field experiment.

Fig. 5 Evolution of **a** Mn, **b** Co, **c** Fe, and **d** Pb concentrations in the dissolved phase (mmol L^{-1}) during the experiments of sediment resuspension (h, log scale). t_0 points are the concentrations in water prior to the addition of sediment. The curves correspond to the various masses of dry sediment used



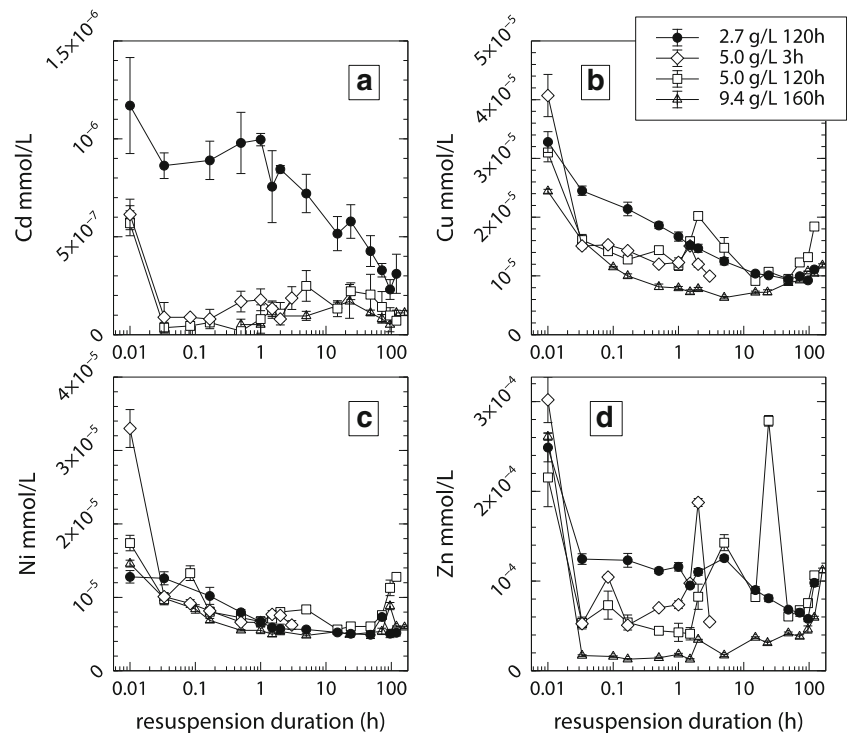
4 Discussion

4.1 Particle concentration effect

The trace element concentrations show very similar trends during the resuspension experiments, regardless of the mass

of sediment used. However, there are no proportional relations between these masses and the dissolved concentrations. The maximum values of dissolved Al or As, for example, are obtained for 2.7 and 5.0 g L^{-1} of suspended sediment (Fig. 4a, b), and the highest Ba and Mn concentrations are obtained for the 5.0- g L^{-1} -3-h experiment (using sample 2, Fig. 4d and Fig.

Fig. 6 Evolution of **a** Cd, **b** Cu, **c** Ni, and **d** Zn in the dissolved phase (mmol L^{-1}) during the experiments of sediment resuspension (h, log scale). t_0 points are the concentrations in water prior to the addition of sediment. The curves correspond to the various masses of dry sediment used



5a). The dissolved concentrations of the other elements are almost identical for all experiments. These similar trends indicate that the amount of suspended matter does not play a major role in the remobilization of trace elements in our studied range of sediment concentrations. The characteristics of the sediments were almost identical, except for the redox potentials measured at the opening of the sealed jars, and the variability in this parameter may explain the slight differences observed, for example between the two experiments with 5.0 g L^{-1} of resuspended sediments (samples 2 and 3).

The so-called particle concentration effect (i.e., the effect of the particle concentration on the trace metal partition between the water and particles) is a key factor in predicting the fate of trace metals during resuspension events, and it was extensively discussed in the literature. The “particle concentration effect” was indeed evidenced in several studies, reflecting a decline in partition coefficients (K_d) as the quantity of suspended particulate matter (SPM) increases (e.g., Schell et al. 1980; O’Connor and Connolly 1980; Balls 1989; Benes and Poliak 1990; Turner et al. 1993; Bird and Schwartz 1996). This observation has been attributed to a variety of causes that were listed by Benoit and Rozan (1999), including particle-particle interactions, the co-existence of rapidly exchanging and irreversible bounding sites on the particles and filtration artifacts, or the contribution of trace elements bound to colloids included in the filtrate fraction. Conversely, no clear trends between the dissolved concentrations and the amount of sediment used were observed in many other studies based on resuspension experiments of natural sediments (Gerringa 1990; Brassard et al. 1994; Petersen et al. 1997; Simpson et al. 2000; Caetano et al. 2003; Caille et al. 2003; Di Nanno et al. 2007; Ho et al. 2012; Huang et al. 2012), and our results agree with these previous works. Kalnejais et al. (2010) was the only one to find a positive relationship between the amount of resuspended sediment and the dissolved concentrations of trace elements, but their samplings were done after only 20 min, so the chemical equilibrium was surely not reached. The “particle concentration effect” remains controversial and seems to be highly dependent on the experimental design, in particular the range of SPM that is investigated and the separation techniques that lead or not to the inclusion of colloids in the dissolved phase (McKinley and Jenne 1991). In our case, the range of sediment concentration studied is rather limited compared to other studies where a particle concentration effect was observed and is probably too narrow to evidence such an effect. The lack of trend between dissolved concentrations and the amount of sediment used tend to confirm the conclusion of Cantwell et al. (2002), who argued that the sediment characteristics are more determinant than the amount of suspended particulate matter.

4.2 Kinetic trends

As previously described, the trends observed during resuspension allow for the distinguishing of three groups of elements

that are likely controlled by similar adsorption/desorption and precipitation/dissolution processes, as follows: (i) increase in dissolved concentrations from the beginning of the experiment up to a maximum value at the end of experiment (Al, Mo, As, Ba, Sr), (ii) increase in dissolved concentrations during the first minutes/hours of the experiment followed by a continuous decrease (Fe, Mn, Co, Pb), and (iii) very fast decrease at the beginning of the experiments and relatively constant values after a few minutes (Ni, Cu, Cd, Zn).

Numerous studies have shown that the sorption of radioactive or metallic trace elements on natural particles resulted from several kinetic processes, involving rapid but also slow processes such as oxidation processes, inner sphere complexation, and migration of cations in clay structures (e.g., Dzombak and Morel 1985; Benes et al. 1992; Comber et al. 1996; Millward and Liu 2003). The kinetic trends that we observed agree with the presence of multiple sorption sites presenting different affinities and exchange velocities. In particular, trace metals belonging to the second group (Fe, Mn, Co, Pb) show a desorption stage followed by readsorption. Such two-stage kinetic behaviors were also observed for Co and Mn by Ciffroy et al. (2001, 2003) and Garnier et al. (2006), and they were successfully modeled by these authors by taking into consideration two sorption sites on the particles. In these kinds of resuspension experiments, the contact time between the resuspended sediments and water and the sampling time are crucial parameters. Our 1-week experiments clearly illustrate that variations exist over this time scale, and thus, the resuspension duration must be considered in the design of the experiments, which must be as close as possible to the field conditions.

4.3 Release and removal processes

The main processes responsible for trace element exchanges between water and particles are described below in relation to the speciation of the dissolved trace elements and their distribution between the chemical fractions of the solid phase.

4.3.1 Behavior of carbonates

Calcite and dolomite, observed by diffraction and present in the watershed, are the major mineral phases of this sediment. The saturation indexes ($\log SI$) of calcite and ordered and disordered dolomite were always negative in our experiments (Electronic Supplementary Material, Fig. A2), and the increases in Mg^{2+} , Ca^{2+} , and HCO_3^- concentrations occurring after 1 or 2 h are related to the dissolution of these carbonate minerals. The saturation indexes for calcite and dolomite moved towards zero, but the equilibrium was not reached after 120 or 160 h (Electronic Supplementary Material, Fig. A2). The ratio of Ca/Mg increased from 3–4.5 to 4–6 within the first 24 h, attesting to the dissolution of a mix of calcite

(CaCO₃), dolomite (CaMg(CO₃)₂), and possibly magnesian calcite. This ratio became more stable after 24 h. Therefore, the increase of Ca, Mg, and HCO₃⁻ may thus be due to the dissolution of dolomite.

The SO₄²⁻ increased with a kinetics similar to that of alkalinity, Mg²⁺, and Ca²⁺ (Fig. 3) and may be associated with the dissolution of a sulfate mineral. Such a mineral has not been evidenced by XRD, but gypsum has been reported in the watershed, as well as rocks altered by sulfate-rich water (*cargneules*).

Like calcite and dolomite, all the metal-carbonate minerals (BaCO₃, SrCO₃, FeCO₃, ZnCO₃, PbCO₃, CuCO₃, MnCO₃, or NiCO₃) were undersaturated during the experiments according to Visual MINTEQ (data not shown). Therefore, precipitation cannot remove these metals from the solution, whereas the dissolution of carbonates can release metals previously adsorbed or co-precipitated. This is particularly the case for Sr and Ba, which exhibited kinetics similar to that of Ca, Mg, and HCO₃⁻, in agreement with the very similar dissolution rates of these carbonate species (Pokrovsky and Schott 2002). The similarity of the Sr and Ba behavior was also highlighted by Curti (1999), due to their similar ionic radius and selectivity constants on calcite. The sequential extraction was in agreement with this for Sr and Mg, which showed an important involvement in the fraction F1b associated with the carbonates (32 and 33%, respectively), but not for Ba (low F1b fraction).

4.3.2 Role of oxyhydroxides

Fe and Mn oxides and hydroxides have a key role in the distribution of trace metals in sediment and can remove significant amounts of trace elements from the dissolved phase through co-precipitation or adsorption (Hem 1977; Morin et al. 1999; Simpson and Batley 2003). In the study by Atkinson et al. (2007), for example, the release of dissolved Pb is lower when the sediments are resuspended in water with a higher dissolved oxygen content, because the good oxygenation of the slurry promotes a faster precipitation of Fe and Mn oxides and hydroxides, which act to sink the Pb.

The redox potential in sediments is a crucial parameter for the metal speciation. During sediment resuspension, particles experience major changes in the chemical conditions, including a large variation in the redox potential from the suboxic or anoxic conditions prevailing in the sediments to the strong oxidizing conditions of the surface waters.

When performed with oxidized sediments, the resuspension experiments show a low and slow release of trace metals, or even none (Saulnier and Mucci 2000; Hwang et al. 2011; Ho et al. 2012). In contrast, studies of the resuspension of anoxic sediments show a rapid release of Fe and Mn to the solution associated with the oxidation reactions of AVS, followed by a removal in the solid phase (Hirst and Aston

1983; Saulnier and Mucci 2000; Caetano et al. 2003; Caille et al. 2003; Hwang et al. 2011; Ye et al. 2013). Depending on the study, other trace elements (e.g., As, Cd, Cu, Pb) are sometimes found to follow the trend of Fe and Mn. Finally, Vink et al. (2017) showed that the readily reducible fraction of iron, identified by 1 M CaCl₂ extraction, may be an important parameter to improve the predictions of As release from aerobic soils stored under water.

In our experiments, the dissolved concentrations of Fe, Mn, Co, and Pb showed this trend exactly: a release in the dissolved phase followed by removal due to precipitation and/or adsorption onto the oxides and hydroxides. In our case, the AVS content of the resuspended sediment is probably low because the sediment is slightly organic (1.6–1.8% of TOC) and not strongly reduced. The fact that SO₄²⁻ did not increase at the beginning also confirms that AVS, which could be oxidized, were negligible or absent. In contrast, the addition of pore water had a large impact, as illustrated by our calculations for Fe and Mn. This pore water input cannot be removed from the system, except by drying the sediment, which is not recommended. Such an input will occur during real operations, but with pore water that is probably more dilute.

After a maximum of 1 h of resuspension in well-oxygenated water, the Fe and Mn concentrations began to decrease. The time during which we observed maximum dissolved concentrations was longer for Fe (up to 2 h) than that for Mn, and it also decreased more gradually, in contrast to the results of Hirst and Aston (1983), Saulnier and Mucci (2000), and Caetano et al. (2003), who found a faster decrease of Fe compared to Mn. The saturation indexes (SI) calculated with Visual MINTEQ indicate supersaturation of several Fe oxides and (oxy)hydroxides (e.g., ferrihydrite and goethite, Fig. 7), but the Fe concentration remained elevated up to 24 h. These SI values indicate that the formation of Fe oxyhydroxides is possible but do not take into account the kinetics of the precipitation reactions. For Mn, the SI were calculated for pyrolusite (MnO₂) and manganite (MnOOH), which remain undersaturated in all cases, even if Mn was trapped in the solid phase since 2 min of resuspension. Mn may precipitate in a different, less soluble form, than the ones considered in Visual MINTEQ. The difference of trends between our experimental data and the calculation of SI may be due to the existence of Fe and Mn colloidal phases.

Co and Pb are likely removed from the dissolved phase by adsorption or co-precipitation with the newly formed oxyhydroxides. According to the kinetic evolution of their concentrations, Co is likely associated with Mn, as it is usually observed in the literature (Fig. 5a, b; Rigaud et al. 2013), whereas Pb seems to be regulated by the Fe oxyhydroxides (Fig. 5b, c). Adsorption onto oxide surfaces is known to control the As mobility in the environment. In our case, the slight stabilization or decrease in the As concentrations observed during the 5-g L⁻¹ and 9.4-g L⁻¹ experiments might reflect

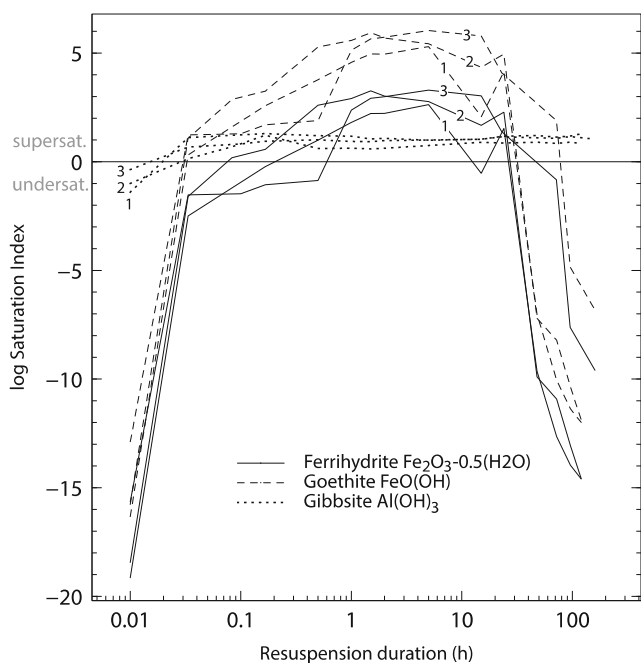


Fig. 7 Saturation indexes (logSI) of two iron oxyhydroxides (goethite and ferrihydrite) and one aluminum hydroxide (gibbsite), calculated with Visual MINTEQ for each sample of the resuspension experiments: (1) 2.7 g L⁻¹ for 120 h, (2) 5.0 g L⁻¹ for 120 h, and (3) 9.4 g L⁻¹ for 160 h. LogSI value around 0 ± 0.05 indicates that the mineral is in equilibrium with the solution, and a positive or negative logSI value specifies supersaturation or undersaturation, respectively

the adsorption of a small amount of As onto the Fe oxyhydroxides, but the release processes remained greater than the adsorption since the dissolved concentrations continued to increase later on.

4.3.3 Complexation with organic ligands

The speciation of the dissolved Fe, Pb, and As, calculated with Visual MINTEQ, is shown in Fig. 8. For these calculations, the proportion of fulvic and humic acids was considered to be 90 and 10% of the total active DOM, respectively.

Vink et al. (2017) demonstrated that DOM concentration shifts and compositional changes (HA/FA) must be taken into account to obtain a better model simulation of metal behaviors during the storage of aerobic soils under water and the reduction of organic matter. However, the small changes in redox conditions and the constant values of DOC during our experiments were not comparable with those of their study (Eh and DOC ranging from +200 to -200 mV and from 10 to 200 mg L⁻¹, respectively), and this effects were probably very limited here.

The Mn and Zn, as well as Sr, Co, and major elements, Ca, Na, Cl, K, and Mg (not shown), were relatively insensitive to DOM and remained in the free ionic forms (Mn²⁺, Zn²⁺, Sr²⁺,

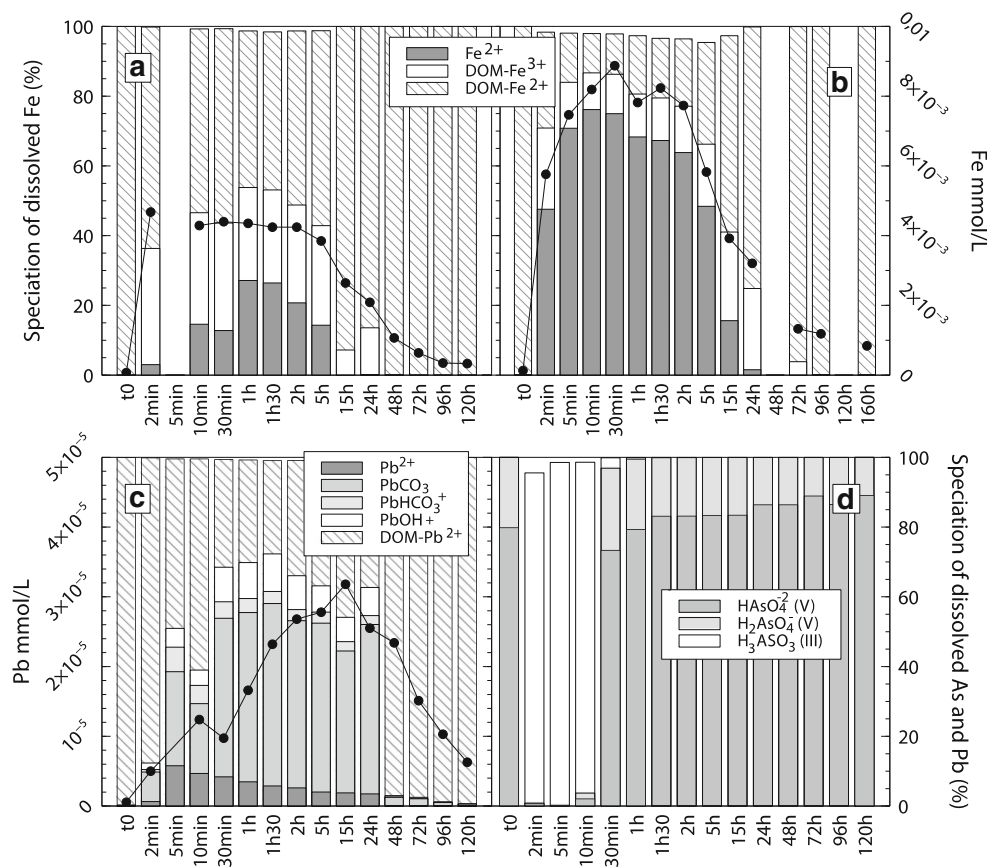
etc.). A major portion of the Al was also present as the inorganic complex Al(OH)₄⁻ (not shown).

In contrast, the dissolved Fe, Pb (Fig. 8a–c), Cd, Cu, and Ni (not shown) were complexed with the DOM, sometimes up to 100%. Their speciation was also assessed with two other DOM compositions: 100% FA (by default in Visual MINTEQ) and 70% FA + 30% HA. Not surprisingly, the percentage of metal complexed to DOM depends on their affinity for the humic acids (Electronic Supplementary Material, Fig. A3). For most of them, it increased with the proportion of HA in relation with their complexation constants. The difference in the FA and HA constants also has an influence on the theoretical proportion of the organic complex (e.g., Pb vs Fe, Electronic Supplementary Material, Fig. A3).

For Pb and Fe, the ratio of inorganic versus organic species widely varies over the resuspension period (Fig. 8a–c): when the total concentrations of dissolved Fe and Pb were high, the percentages of organic complexes decreased, and the proportions of Fe²⁺ and inorganic complexes of Pb increased. The higher complexation of Fe with dissolved organic matter compared to that of Mn may have promoted its unusual longer stabilization in the dissolved phase compared to previous results (Hirst and Aston 1983; Saulnier and Mucci 2000; Caetano et al. 2003).

Several studies have shown that DOM plays a role in As behavior, by increasing its mobility in both reducing and oxidizing environments through complexation (Redman et al. 2002; McArthur et al. 2004; Liu et al. 2013; Dang et al. 2014) or competition for adsorption on iron oxide surfaces (Mehmood et al. 2009; Du et al. 2014). Very few studies reported apparent binding stability constants (K_s) between dissolved As and DOM species. Dang et al. (2014) reported K_s values ranging between 2.0 and 4.7 for As-DOM complexes from anoxic marine sediments. Lin et al. (2017) measured K_s values of 5.1, 4.9, 4.0, and 5.5 for As(III) with four different types of DOM. Finally, Fakour and Lin (2014) employed a two-site (strong and weak) ligand binding model to describe the results of complexation experiments with As(III) and As(V) and various HA and FA concentrations. For the strong sites, they obtained K_s values ranging from 1.5 to 2.6 and 2.5 to 4 respectively for As(III) and As(V). The apparent K_s from the literature could be added into Visual MINTEQ; however, these values greatly vary between studies because of the specific DOM characteristics and solution chemistry. As an example, the speciation of As(III) calculated for the solution at 2 min of the 2.7-g L⁻¹ experiment gave 0.5 and 70% of DOM-H₃AsO₃ complexes when using a K_s of 2.0 and 4.7 from Dang et al. (2014). For As(V), such a calculation cannot be done due to a limitation of the NICA-Donnan model in Visual MINTEQ. Indeed, AsO₄³⁻ is the only species that can react with DOM in the model, but it represents only to 0.01% of total As, HAsO₄²⁻ being the main species of As(V).

Fig. 8 Dissolved speciation calculated with Visual MINTEQ (DOM/DOC = 1.65, DOM = 90% FA and 10% HA). (a) Fe for the 2.7-g L⁻¹-120-h experiment and (b) 9.4-g L⁻¹-160-h experiment. (c) Zn for the 5.0-g L⁻¹-120-h experiment. (d) As for the 5.0-g L⁻¹-120-h experiment. Total concentrations of Fe and Pb are shown in mmol L⁻¹ in insets (a), (b), and (d)



Whereas the organic complexation likely plays an important role in maintaining As in the dissolved phase, it cannot be calculated with Visual MINTEQ from the available data. The major changes in the form of As according to the model are thus related to Eh variations. As(III) was predominant at a low Eh, globally between 2 and 10–30 min depending on the experiment (Fig. 8d). Its main form is H₃AsO₃ (81–93% of total As). For a higher Eh (at t₀ or after 30 min, Fig. 8d), the oxidized As(V) was present as HAsO₄²⁻ (64–89%) and H₂AsO₄⁻ (11–36%).

4.4 Chemical extractions

Ascorbate or sequential extractions provide information on the initial distribution of the elements in the solid phase (Tessier et al. 1979; Tessier and Campbell 1987; Stone and Marsalek 1996), which may help to estimate the capacity of trace elements to be mobilized during changes in the physico-chemical conditions.

In our case, the ascorbate extractions revealed that As and Pb are mainly associated with the amorphous phases of Mn or Fe. These phases can be rapidly remobilized, but they only represent approximately 10% of the total Mn and Fe. This distribution may explain their progressive increase in the

solution and the difference in the behavior observed for Zn, Cu, and Ni.

The sequential extractions do not provide the same information. Indeed, the groups of trace elements that exhibit similar release trends during the resuspension do not correspond to their distribution between the fractions of sequential extractions. As and Pb show the same fractionation (Fig. 1b); few As and Pb are associated with the exchangeable F1a fraction; in contrast, large proportions of As and Pb are measured in the ascorbate extracts (Fig. 1a). Large proportions of Mn (49%), Sr (32%), Zn (29%), Ca, and Mg are extracted in the F1b fraction (carbonate-bound), but their temporal trends are clearly different (Fig. 5a, Fig. 4e, and Fig. 6d). Indeed, even if they are released during the carbonate dissolution, Mn (and possibly Zn) will tend to precipitate whereas Ca, Mg, and Sr do not.

Frémion et al. (2016) found that the chemical fractions obtained from their sequential extraction were consistent with their observations during in situ monitoring of a sluicing operation. Their most easily mobilized elements (As, Cd, Mn, Zn) exhibited the highest concentrations in the dissolved phase, compared to other elements, such as Cr and Pb, that were mainly in the residual fraction. In contrast, Di Nanno et al. (2007) did not find any correlation between such fractions and the metal concentrations during resuspension experiments. Finally, the sequential extractions that were

separately carried out by Ho et al. (2012) on a wet suboxic and an oxidized sediment showed that the changes in the trace element distributions due to oxidation explained well the various leaching behaviors of the trace elements at pH 2 to 8, but not their lower leachability at pH levels from 9 to 11 after oxidation. In conclusion, the information provided by these extractions may be useful to compare various sediments but is not sufficient to predict the behavior of the trace elements during resuspension. This is partly due to the adsorption or precipitation reactions that can occur in the first hours of sediment resuspension and remove trace elements from the solution (Caetano et al. 2003). Furthermore, many studies questioned the relevance of these “operationally defined fractions” compared to the nature of real solid phases, because of the lack of selectivity of the reagents and the influences of experimental setting (e.g., Miller et al. 1986; Kim and Fergusson 1991; Gómez Ariza et al. 2000; Gleyzes et al. 2002; Quevauviller 2007; Cappuyns et al. 2007).

4.5 Pollutants of concern

The metals above the threshold values in our sediment are As, Cd, Pb, and Zn. Among them, only As will be of great concern in case of resuspension. In our results, the other elements (Cd, Zn) do not show important release, or they may be adsorbed onto Fe or Mn oxyhydroxides (Pb), whereas As showed the strongest release in the dissolved phase, and its concentration was still increasing at the end of the experiments. The concentrations were always above the drinking water standard of $10 \mu\text{g L}^{-1}$ ($= 1.33 \cdot 10^{-4} \text{ mmol L}^{-1}$; World Health Organization 2011; directive 98/83/CE-03/11/98), but they remained below the toxicity levels for fish. According to the data reported by Kumari et al. (2017) on acute toxicity of inorganic As measured on fish after 48 to 96 h of exposure, the LC50 values ($7.3 \cdot 10^{-2}$ to $1.2 \text{ mmol As L}^{-1}$) exceeded by at least a factor two the maximal concentrations of dissolved As measured during our resuspension experiments. This important release is obviously associated with the greater availability from the solid phase. The maximum quantities of dissolved As represent 4 to 18% of the total amount of As in the resuspended sediments, whereas they reach only 1% for Cd, Pb, and Zn (Table 3). Such availability is clearly evidenced from the ascorbate extraction, from which 52% of the As can be extracted. Paul et al. (2009) demonstrated that ascorbate extraction is efficient in differentiating arsenic associated with poorly crystalline iron (hydr)oxides, and in our case, As must be associated with Fe and Mn oxyhydroxides quickly dissolved during the first minutes of resuspension. Dissolved As was not removed by adsorption later, because of its anionic form (or its possibility of being complexed with DOM).

5 Conclusions

A resuspension experiment was set up to simulate a draining operation of a dam reservoir. Three different solid/liquid ratios were tested to examine the possible range of variations occurring during a real operation, but they did not induce significant changes in the concentrations of trace metals released, nor their kinetic variations. Consequently, the elements can be grouped together according to the trends in their concentrations over the resuspension duration: (1) decreasing or stable (e.g., Cd and Zn), (2) temporary increase followed by a decrease (Fe, Mn, Co, and Pb), and (3) continuous increase until the end of experiment (e.g., Al, As). The trace elements in these groups are controlled by the same kinetic processes,

Table 3 Summary of some key results for As, Cd, Pb, and Zn during the 120-h or 160-h experiments: maximum concentration; corresponding duration of resuspension; ratio between maximum amount of dissolved element and total amount of metal in suspended sediment

Trace element	Resuspension experiment	Maximum concentration (mmol L^{-1})	Time of maximum concentration	Maximum dissolved/total suspended (%)
As	2.7 g L^{-1} for 120 h	2.72E-04	120 h	18
	5.0 g L^{-1} for 120 h	3.67E-04	120 h	9.3
	9.4 g L^{-1} for 160 h	2.55E-04	2 h	3.8
Cd	2.7 g L^{-1} for 120 h	1.17E-06	t0	0.84
	5.0 g L^{-1} for 120 h	5.69E-07	t0	0.20
	9.4 g L^{-1} for 160 h	6.05E-07	t0	0.06
Fe	2.7 g L^{-1} for 120 h	4.68E-03	2 min	0.54
	5.0 g L^{-1} for 120 h	4.63E-03	30 min	0.27
	9.4 g L^{-1} for 160 h	8.87E-03	30 min	0.28
Mn	2.7 g L^{-1} for 120 h	7.10E-04	2 min	3.8
	5.0 g L^{-1} for 120 h	9.55E-04	5 min	3.5
	9.4 g L^{-1} for 160 h	1.03E-03	5 min	1.6
Pb	2.7 g L^{-1} for 120 h	4.04E-06	5 h	1.2
	5.0 g L^{-1} for 120 h	3.69E-06	5 h	0.66
	9.4 g L^{-1} for 160 h	4.04E-06	5 h	0.43
Zn	2.7 g L^{-1} for 120 h	2.96E-06	t0	0.81
	5.0 g L^{-1} for 120 h	1.49E-05	24 h	0.45
	9.4 g L^{-1} for 160 h	5.03E-05	t0	0.16

involving rapid but also slow exchange processes between the solid and dissolved phases (adsorption/desorption and precipitation/dissolution).

Indeed, our results illustrate that the concentrations of trace elements in the dissolved phase vary during the first minutes and hours of sediment resuspension (during sharp variations of pH and Eh) but also up to 1 week. These two timescales are useful to prove the release and removal of dissolved trace elements over the typical duration of a draining operation.

The contents of As, Cd, Pb, and Zn in the sediment were above the probable effect concentrations defined in MacDonald et al. (2000), due to past mining activities. The laboratory resuspension experiments showed that the risk of metal remobilization from the solid to the dissolved phase due to the sediment resuspension would be higher for As than that for the other contaminants. Indeed, Cd and Zn are not released in the dissolved phase, and Pb showed a fast desorption stage followed by re-adsorption. The oxidation and precipitation of Fe and Mn oxyhydroxides, resulting in the co-precipitation of Pb, were allowed by the rise of dissolved oxygen in the slurries after a few minutes of aeration. Unlike Pb, the As concentration increased almost continuously, and the later precipitation of oxyhydroxides did not lead to its removal from the solution. This is probably due to its speciation (anionic or organic complexes), promoting the As mobilization. The As reached a maximum of $30 \mu\text{g L}^{-1}$ at the end of the resuspension, a concentration that remained well below the acute toxicity levels reported in the literature for fish.

Furthermore, the results from the sequential extraction procedure were not consistent with the observations from the resuspension experiments and cannot be used to predict the remobilization of pollutants.

Laboratory resuspension experiments allow easier measurements of ETM remobilization with varying parameter values (in our case the mass of suspended sediments), as well as a close monitoring of the reaction kinetics. They do not permit to take into account the variability of sediment amounts and characteristics that may be resuspended in a real case, which could depend on the thickness of the resuspended layer or the location within the reservoir. In the case of a reservoir drawdown, the resuspended particles will also be transported downstream with or without dilution depending on the site configuration. However, the chemical processes evidenced here as well as the kinetics of the remobilization of trace elements may be representative of in situ studies. The experiments provide an idea of what can be expected in terms of risk for the environment.

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