When soils become sediments: large-scale storage of soils in sandpits and lakes and the impact of reduction kinetics on heavy metals and arsenic release to groundwater

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When soils become sediments: Large-scale storage of soils in sandpits and lakes and the impact of reduction kinetics on heavy metals and arsenic release to groundwater☆,☆☆

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ABSTRACT

Simulating the storage of aerobic soils under water, the chemical speciation of heavy metals and arsenic was studied over a long-term reduction period. Time-dynamic and redox-discrete measurements in reactors were used to study geochemical changes. Large kinetic differences in the net-complexation quantities of heavy metals with sulfides was observed, and elevated pore water concentrations remained for a prolonged period (>1 year) specifically for As, B, Ba, Co, Mo, and Ni. Arsenic is associated to the iron phases as a co-precipitate or sorbed fraction to Fe-(hydr)oxides, and it is being released into solution as a consequence of the reduction of iron. The composition of dissolved organic matter (DOM) in reducing pore water was monitored, and relative contributions of fulvic, humic and hydrophylic compounds were measured via analytical batch procedures. Quantitative and qualitative shifts in organic compounds occur during reduction; DOM increased up to a factor 10, while fulvic acids become dominant over humic acids which disappear altogether as reduction progresses. Both the hydrophobic and hydrophilic fractions increase and may even become the dominant fraction.

Reactive amorphous and crystalline iron phases, as well as dissolved FeII/FeIII speciation, were measured and used as input for the geochemical model to improve predictions for risk assessment to suboxic and anaerobic environments. The release of arsenic is related to readily reducible iron fractions that may be identified by 1 mM $CaCl_2$ extraction procedure. Including DOM concentration shifts and compositional changes during reduction significantly improved model simulations, enabling the prediction of peak concentrations and identification of soils with increased emission risk. Practical methods are suggested to facilitate the practice of environmentally acceptable soil storage under water.

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1. Introduction

The large-scale storage of contaminated soils and sediments in deep waterlogged former sand pits or in lakes has become a fairly common practice in recent years under the EU directive 2000/60/EC (EC, 2000). This disposal may have a restorative function in the sense that the depth of the lake is largely reduced from about 20 m to approximately 3 m, enabling the development of new ecosystems. Since the area-to-volume ratio in shallow lakes is much higher than in deep lakes, the conditions for rooted plants are much more favourable (Cooke et al., 2001). Increased plant settlement and growth promotes the feeding and breeding opportunities for insects and fish. In this study, we focus on the chemical effects of large scale soil storage in deep lakes on the anaerobic compartment, i.e., deep sediment layers and groundwater, induced by altered redox conditions.

It is often assumed that storage of soils under water leads to anaerobic conditions that will ensure immobilization of heavy metals through precipitation with sulphides. However, earlier studies (e.g., Du Laing et al., 2009a; Vink et al., 2010; Rinklebe, 2017) have clearly shown that various soils react very differently on

☆ This paper has been recommended for acceptance by Joerg Rinklebe.

☆☆ Soil reduction upon inundation results in compositional geochemical changes, Including dissolved organic compounds, Influencing fluxes to groundwater.

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reducing conditions. Sulphide phases may either be formed in insufficient amounts to bind all metals, or the formation of sulphide phases cannot prevent the net dissolution of heavy metals because of simultaneous metal binding to dissolved organic matter (DOM) that is released during reduction. Binding of heavy metals to DOM is of major importance in the overall metal mobility and has been subject of many previous studies. However, less data are available on the affinity of metals to specific DOM compounds released under anaerobic conditions, and quantitative data on the effect of time-dynamic redox reactions on the overall composition of DOM are rare. In order to calculate sorption of heavy metals to humic and fulvic substances, chemical models often use the NICA-Donnan approach (Kinniburgh et al., 1996). These individual organic substances have very different binding properties for metals, but since there is a serious lack of insight in the quantitative distribution of these compounds, the proportions are mostly estimated by assuming that DOM consists by 50% of humic and/or fulvic acids, while the remainder does not contribute to metal binding (e.g., Schröder et al., 2005). Deviations from this assumption directly influence calculation results and the assessment of risks (Kalis et al., 2006; Van Zomeren and Comans, 2007). Therefore, the characterization of DOM is of major importance to improve the performance of speciation models, as has often been suggested in literature (e.g., Tipping, 2002).

Iron plays a crucial part in remobilization of metals and arsenic under anaerobic conditions (Davison, 1993; Postma and Jakobsen, 1996; Van Cappellen et al., 1998; Bauer and Blodau, 2006; Francis and Dodge, 1990). The total amount of iron is however not a useful measure of potential mobilization of metals and arsenic that is bound in soils. In addition to organic matter, iron and aluminium (hydr)oxides are the major reactive surfaces that control the binding of metals by sorption processes in the soil matrix. The reactivity of these mineral surfaces varies strongly as a function of their specific surface area and crystallinity (e.g., Apul et al., 2005; Dijkstra et al., 2009). To simulate redox-induced mobility of metals and arsenic, the characterization of reactive surfaces for which thermodynamic adsorption parameters are available require selective methods. Analytical ISO standards have been developed for this purpose, and were used in this study to quantify the reactive iron and aluminium (hydr)oxides.

In this study, we aimed at the generation of redox-discrete kinetic data for the soil/pore water partitioning of heavy metals and arsenic during reduction of soils after storage under water over a long period of time (>17 months). We simulated anaerobic conditions in soil mesocosms, in order to perform kinetic measurements including the time-dynamic composition of DOM. The effect of DOM composition on the performance of geochemical modeling of the speciation and mobility of heavy metals was tested. Also, the role of iron in mobilization and remobilization processes was addressed. The evaluation of these measurements is focused on finding an operational method for assessment of the potential mobilization risks of metals and arsenic. The results are used to improve risk assessment for groundwater contamination resulting from large-scale storage of soils in sandpits and lakes.

2. Materials & methods

2.1. Selection and characterization of soils

Soils were selected on the basis of three main criteria:

- Soils have elevated levels of heavy metals;
- The solid phase composition (e.g., Fe-fractions, particulate organic matter (POM), particle size fraction <2 μm) displays a wide range between soils;
- Large amounts of these soils have actually been disposed in lakes, or have been planned to be stored in the near future.

Data on soil composition, including contamination, were acquired from commercial soil depots, civil sanitation projects, recycle facilities, and databases on local soil quality. Based on the mentioned criteria, seven locations were selected for sampling conform NEN-5740 protocol. After analyses of the solid phases, five soils were selected for further study.

Soil 1 originated from the banks of the Nieuwkoopse plassen (52°08′25”; 4°46′27″) and was sampled from a local storage facility in Duivendrecht. Soil 2 was a restoration site in De Brabantsche Kempen (51°20′44”; 5°36′40″). The area is known for its elevated levels of heavy metals, emitted from zinc smelters in the past century. Soil 3 was sampled from a redevelopment area on the east bank of the river IJssel (52°23′13”; 6°07′40″), of which large amounts were deposited in local lakes. Soil 4 was sampled from a soil sanitation site in the city of Utrecht, which was stored in the nearby lake Hooge Kampse Plas (52°06′50”; 5°09′45″). Soil 5 was sampled from a sanitation site in the urban area of Assendelft (52°29′23”; 4°45′25″) and was destined for storage in lake NoorderIJplas.

Approximately 75 kg of soil was sampled at each site. All soils were homogenized in a tumbler, sieved over 1 mm to remove debris, and stored in a cooling facility at 4 °C. Subsamples were taken for analyses. Three extraction procedures were applied:

1. Chemical destruction with *Aqua regia* (Berrow and Stein, 1983) providing total metal content including the inert, non-reactive pool;
2. Extraction with dilute nitric acid (0.43M HNO3), which is milder than *Aqua regia* and is regarded as the reactive pool of metals (Houba et al., 1985; Groenenberg et al., 2017). The procedure has recently been standardized as ISO 17586:2016 to be proposed in Dutch regulation.
3. Extraction with 1 mM CaCl2 (modified after Novozamsky et al., 1993), representing readily bioavailable fractions (Schröder et al., 2005).

2.2. Experimental design

Soils were incubated in SOFIE® cells (Vink, 2002, 2009; Düster et al., 2008), which were used as anaerobic incubators. These cells enable the time-dynamic sampling of pore water over redox transitions. Five kg of homogenized soils sample was brought into each cell, and groundwater of known composition (Supplementary Information Table S1) was slowly percolated from the bottom of each cell via a hydraulic potential of 5 cm to prevent air inclusion. Soils were inundated with a 7 cm water layer. Cells were then closed air-tight, and the 1-L headspace was flushed via a valve with grade-6 nitrogen gas to promote anaerobic conditions. Cells were placed in a 15 °C climate-controlled room which was darkened to prevent CO_2 production by algae. Pore water was sampled periodically from the core centre using integrated 0.1 μm-permeable polyethersulfone polymer probes which perform instantaneous microfiltration and yield sterile samples (Vink, 2002). Since microorganisms mediate many redox transformation processes, sterility ensures that reliable redox-discrete measurements could be performed. To prevent chemical transformation, pore water samples were not stored but analysed immediately after sampling.

Soils were incubated over a period of 17 months, since previous studies (Vink et al., 2010) have indicated that this is the time span over which major reduction processes occur.

2.3. Fe and Al reactivity; analytical

For the quantification of the reactive iron (FeIII) phases, we distinguished the amorphous and the crystalline phases. Amorphous iron oxides and hydroxides were extracted from homogenized soil samples with ascorbic acid according to ISO-12782-1. The extraction is based on the reduction of Fe(III) phases to the more soluble Fe(II) phases, as well as on the complexing affinity of ascorbate to extract iron from short-range ordered materials. The crystalline iron phases were determined via ISO-12782-2 using dithionite as an extractant. The extraction includes the complexing affinity of the chemicals to extract iron from crystalline materials. The amount of crystalline iron (hydr)oxides is determined by the dithionite extraction minus the amount of amorphous iron (hydr) oxides as obtained from ascorbate extraction. Aluminium (hydr) oxides were determined via ammonium oxalate/oxalic acid extraction according to ISO-12782-3, which is based on the complexing affinity of aluminium to acidic oxalate.

Aqueous concentrations of NO_3^-, SO_4^{2-}, PO_4^{3-}, and Cl^- were measured by ion chromatography using a High Capacity analytical column AS9-HC (Dionex), based on conductivity detection with chemical suppression (limit of detection (lod) min/max: 0.025 mg l^{-1} for NO_3^- to 0.05 mg l^{-1} for PO_4^{3-}). All anions were thus measured simultaneously under similar analytical conditions. Analysis of the elements As, B, Ba, Be, Ca, Cd, Co, Cu, Cr, Fe, Li, Mg, Mn, Mo, Ni, P, Pb, Se, V, and Zn were carried out with High Resolution ICP-MS (Thermo Scientific iCAP-Q; limit of detection (lod): min/max: 0.003 μg l^{-1} for Cd to 6.0 μg l^{-1} for Zn).

NH_4^+ analyses were done with a Skalar Segmented Flow analyser SAN+ 6250 matrix photometer (lod: 0.022 mg l^{-1}). All measurements in this study were checked with 6-point calibration curves from standard reference stock solutions, only allowing recovery between 90 and 110%.

Speciation of Fe(II/III) in pore waters was measured periodically with the Hach-Lange cuvette test, in which Fe(III) is reduced to Fe(II) to form stable complexes with added fenantroline. Colour intensity is measured photometrically.

Redox potential (Eh) was measured in sterile pore water immediately after sampling with a platinum electrode with reference.

2.4. DOM characterization

An analytical batch procedure (Van Zomeren and Comans, 2007) was applied to identify and quantify the reactive fractions of dissolved organic matter (DOM) in pore water samples. Four operationally defined organic fractions were measured, based on their physical and chemical properties: 1) Humic acids (HA); 2) Fulvic acids (FA); 3) Hydrophilic compounds (Hy); 4) Hydrophobic neutral organic matter (Hon).

The batch procedure is capable of isolating these operationally defined fractions. In the first step, dissolved humic acids were precipitated by adding 6 M HCl to the sample solution to adjust pH to 1. After 1 h, the suspension was centrifuged to separate precipitates from the liquid fraction. The supernatant was decanted, 0.45 μm filtrated, and subsampled for dissolved organic carbon (DOC) analysis (representing the sum of dissolved FA, Hy and HON). Next, 10 g of cleaned DAX-8 resin was added to the remaining supernatant to adsorb the FA and HON fraction. After 1 h of equilibration by continuous tumbling, the suspension was filtered and a subsample of the solution was taken for DOC analysis (=DOC HY). In order to desorb FA, the resin was equilibrated in four subsequent steps with 0.1 M KOH. DOC was analysed in the eluates, and HON was quantified as the difference between the amount of adsorbed FA + HON and the amount of desorbed FA. Meanwhile, the precipitated HA was dissolved in 0.1 M KOH and analysed for DOC (=DOC HA). To determine the DOC contribution from the resin, 10 g of moist DAX-8 was added to 50 mL of 0.1 M HCl after previous DOC analysis. After 1 h of equilibration by continuous tumbling, the resin was allowed to settle for 5 min and DOC was measured.

2.5. Modeling simulations

The numerical model BioChem-Orchestra (Vink and Meeussen, 2007) was used to simulate the reduction pathway in order to analyse the measured long term trends. The model calculates the solid-solution partitioning and speciation of heavy metals in soils as described by Schröder et al. (2005), by combining models for adsorption by clay and iron oxide surfaces (CD-MUSIC; Hiemstra and van Riemsdijk, 1996). Sorption to manganese oxide surfaces is described by a surface complexation model of Tonkin et al. (2004). Equilibrium constants for soluble species and mineral phases were used from the MINTEQA2 database version 4.0 (Allison et al., 1991). The activity of Fe^{3+} is assumed to be controlled by the presence of goethite, and the activity of Al^{3+} by gibbsite. Adsorption to the solid phase and dissolved organic matter (DOM) is calculated using the consistent non-ideal competitive adsorption model (NICA; Benedetti et al., 1995; Kinniburg et al., 1996) in combination with the generic sorption parameter sets of Milne et al. (2001, 2003) for fulvic and humic acids. The chemical module includes all minerals that are likely to occur in flood plain sediments. The redox potential is related to the water level through a gamma-function algorithm (Vink and Meeussen, 2007):

$$\Delta pe = \begin{bmatrix} pH + 6 - 8 \times dx_{wl}{}^{\gamma} & x < waterlevel \\ 12 \times e^{(-\alpha \times (x - waterlevel))} - pH & x \geq waterlevel \end{bmatrix}$$

with

$$dx_{wl} = \begin{bmatrix} x/waterlevel & waterlevel > 0 \\ 0 & waterlevel \leq 0 \end{bmatrix}$$

and α representing the rate of change of the redox potential:

$$\alpha = -\frac{1.1}{dx_n}$$

The characteristic distance dx_n is given by the distance between the water level and the layer with a *pe* of approximately −3. The *pe* at a given time t is calculated by:

$$pe_t = pe_{t-1} + \frac{10}{365} * (pe_{t-1} - \Delta pe)$$

with pe being defined as:

$$pe = \frac{F}{2.303RT} * Eh$$

with F=Faraday's constant (96.42 kJ V^{-1}.eq^{-1}); R = Nernst gas constant (8.31 J.K^{-1}.mol); T = temperature (Kelvin). At 20 °C, pe is expressed as pe = 16.9xEh (Eh in Volt).

Model simulations were performed to determine initial and endpoint thermodynamic equilibrium. To start reduction, a 1 m water layer was simulated over a 1 m aerobic soil layer. Time-dependent simulations were carried out using the measured speciation of Fe, pH, and the Ca-, Mn- concentrations measured in pore water. The reactive amorphous Fe fraction in soil rather than total content was used for parameterization of the model, adopting 600 m^2/g as a surface area for this phase from Luoma and Davis (1983). For arsenic, the 0.43M HNO_3 extracted amount was used.

The effect of the composition of DOM, which was measured with the method described in section 2.3, on the predictive performance of the model, was tested.

3. Results

3.1. Soil characteristics and metal availability

Major characteristics and the results of extractions of various Fe-fractions are summarized in Table 1. The extraction with *Aqua regia* is the most rigorous one and is a fairly complete destruction of the soil matrix. It represents the total amount of Fe, including the inert phases. The 0.43M HNO_3 extraction (further called *Aqua nitrosa*) is milder and yields the readily available fractions of Fe in the order of 10–30% of total Fe content. The operationally defined amorphous and crystalline phases are in a similar range. The relative contributions of amorphous and crystalline Fe fractions differ; soils 1 and 4 have a relatively large amorphous fraction compared to the crystalline fraction, the other soils show the opposite. The mildest extraction with 1 mM $CaCl_2$ represents the water-soluble Fe fraction. Due to its solubility, and accessibility to electron-transfer, this Fe fraction is subject to very fast reduction kinetics. In soil 4, this Fe fraction is significantly larger than in the other soils.

Ratios between extracted amounts with *Aqua nitrosa* (AN) and *Aqua regia* (AR) are shown in Table 2 (full data in Supp Info table S2). The contribution of the readily available amounts, compared to total amounts, differs per element (Ca = 100%, Cs = 1%). Most (priority) metals with Water Framework Directive (WFD) quality standards (e.g., Cd, Pb, Cu, Zn) are relatively weakly bound to the soil matrix (AN/AR>50%) and may be considered relatively mobile. In all cases, highest AN/AR ratio coincides with the highest observed pore water concentration for that soil (Fig. 1 and Fig S1).

Table 1
Solid phase composition (dry weight) of the five studied soils.

Parameter	Unit	Soil				
		1	2	3	4	5
pH	-	6.8	7.2	7.4	6.5	7.4
<2 μm	%	8.3	7.4	25.2	6.1	5.6
<16 μm	%	13.1	10.9	37.4	7.5	12.5
<63 μm	%	15.0	21.1	47.4	8.3	15.5
POC	%	15.0	1.7	1.8	4.0	4.2
$CaCO_3$	%	0.3	0.4	6.6	0.02	6.7
Aqua regia						
Al	$g.kg^{-1}$	13.8	5.6	21.7	9.2	10.4
As	$mg.kg^{-1}$	14.5	5.1	12.9	14.1	15.3
Ba	$mg.kg^{-1}$	103	31.2	167	76.9	856
Be	$mg.kg^{-1}$	0.67	0.24	1.08	0.39	0.72
Ca	$g.kg^{-1}$	17.6	3.2	25.9	3.2	30.4
Cd	$mg.kg^{-1}$	0.34	0.57	0.92	0.16	1.88
Co	$mg.kg^{-1}$	4.68	2.30	9.25	2.18	8.15
Cr	$mg.kg^{-1}$	23.9	18.3	47.3	12.7	78.0
Cu	$mg.kg^{-1}$	21.0	41.2	26.0	13.3	195
Fe	$g.kg^{-1}$	16.5	5.4	19.8	6.8	19.2
Hg	$mg.kg^{-1}$	0.21	0.04	0.43	0.11	4.54
Mg	$g.kg^{-1}$	4.04	0.51	6.96	1.17	2.91
Mn	$mg.kg^{-1}$	486	231	636	119	578
Mo	$mg.kg^{-1}$	1.86	0.49	0.36	0.44	2.44
Ni	$mg.kg^{-1}$	17.7	9.88	29.8	8.63	32.9
Pb	$mg.kg^{-1}$	162	47.9	49.7	51.4	514
S	$g.kg^{-1}$	16.9	0.16	0.25	0.62	1.42
V	$mg.kg^{-1}$	27.5	16.6	39.0	14.0	36.7
Zn	$mg.kg^{-1}$	121.8	607.5	185.7	39.9	1064
Fe + Al extractions						
Fe-Amorphous	$g.kg^{-1}$	4.4	1.4	2.0	2.4	1.6
Fe-Crystalline	$g.kg^{-1}$	1.6	2.4	6.3	1.0	6.4
Al-Amorphous	$mg.kg^{-1}$	449	223	51	342	111
Fe-Amorph/crystalline		2.8	0.6	0.3	2.5	0.3

Although exceptions occur, the AN/AR ratio between soils is surprisingly similar for the majority of elements (standard error < 20% of mean), potentially providing the means to estimate data between these two extraction procedures in cases of missing data.

3.2. Reduction kinetics

Time-dynamic measurements of redox sensitive parameters in reducing pore waters of all soils are summarized in Fig. 1 and Fig S1 (supplementary section). After inundation, redox potentials (Eh) in pore water dropped rapidly mainly as a result of microbial respiration, reaching sulfate-reducing conditions within 20–30 days in all soils. Since reduction rates were quite uniform between soils, we assume that organic matter was not a limiting factor for microbial respiration in any of these soils. Respiration causes a temporal rise in pCO_2, resulting in the dissolution of calcite and alkalinity production:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad \left(K = 10^{-5.8}\right)$$

After inundation, pH increases and reaches a stable value after approximately 6 months, which is 0.4–0.8 unit higher than the starting value. Nitrate disappears within 2 weeks in all soils (Fig S1

Table 2
Extraction ratios for *Aqua nitrosa* (AN) and *Aqua regia* (AR). SE = standard error of mean.

	AN/AR ratio					SE
	Soil 1	2	3	4	5	
Ag	0.07	0.03	0.04	0.10	0.01	0.03
Al	0.11	0.11	0.06	0.09	0.23	0.07
As	0.56	0.41	0.11	0.28	0.47	0.17
Ba	0.06	0.56	0.55	0.54	0.10	0.26
Be	0.39	0.42	0.32	0.49	0.32	0.07
Ca	1.26	0.94	0.97	0.96	1.05	0.13
Cd	0.70	0.92	0.82	0.76	0.77	0.08
Ce	0.28	0.26	0.26	0.26	0.28	0.01
Co	0.44	0.46	0.29	0.31	0.50	0.09
Cr	0.05	0.13	0.08	0.03	0.26	0.09
Cs	0.002	0.007	0.000	0.001	0.008	0.00
Cu	0.49	0.83	0.58	0.55	0.68	0.13
Fe	0.38	0.25	0.11	0.21	0.15	0.11
Ga	0.06	0.08	0.04	0.03	0.12	0.03
Gd	0.40	0.38	0.40	0.41	0.32	0.04
K	0.07	0.12	0.02	0.04	0.21	0.08
La	0.27	0.23	0.26	0.25	0.30	0.02
Li	0.03	0.02	0.02	0.00	0.12	0.05
Mg	0.47	0.13	0.32	0.09	0.35	0.16
Mn	0.80	0.50	0.51	0.53	0.39	0.16
Mo	0.01	0.14	0.03	0.02	0.05	0.05
Nb	0.01	0.15	0.02	0.02	0.06	0.06
Nd	0.36	0.31	0.36	0.32	0.33	0.02
Ni	0.33	0.59	0.15	0.24	0.26	0.16
P	0.35	0.69	0.41	0.30	0.63	0.18
Pb	0.38	1.30	0.66	0.77	0.71	0.34
Pr	0.31	0.26	0.31	0.29	0.30	0.02
Rb	0.02	0.04	0.00	0.01	0.07	0.03
S	0.69	0.32	0.12	0.22	0.42	0.22
Sb	0.06	0.23	0.12	0.07	0.09	0.07
Sn	0.01	0.07	0.01	0.01	0.06	0.03
Sr	0.75	0.58	0.74	0.56	0.52	0.11
Th	0.01	0.01	0.01	0.01	0.02	0.01
Ti	0.06	0.07	0.01	0.02	0.06	0.03
Tl	0.09	0.09	0.01	0.01	0.19	0.08
U	0.30	0.26	0.22	0.35	0.28	0.05
V	0.29	0.50	0.13	0.17	0.44	0.16
W	0.01	0.17	0.01	0.03	0.08	0.07
Zn	0.58	0.92	0.35	0.32	1.02	0.32
Zr	0.02	0.15	0.07	0.08	0.09	0.05

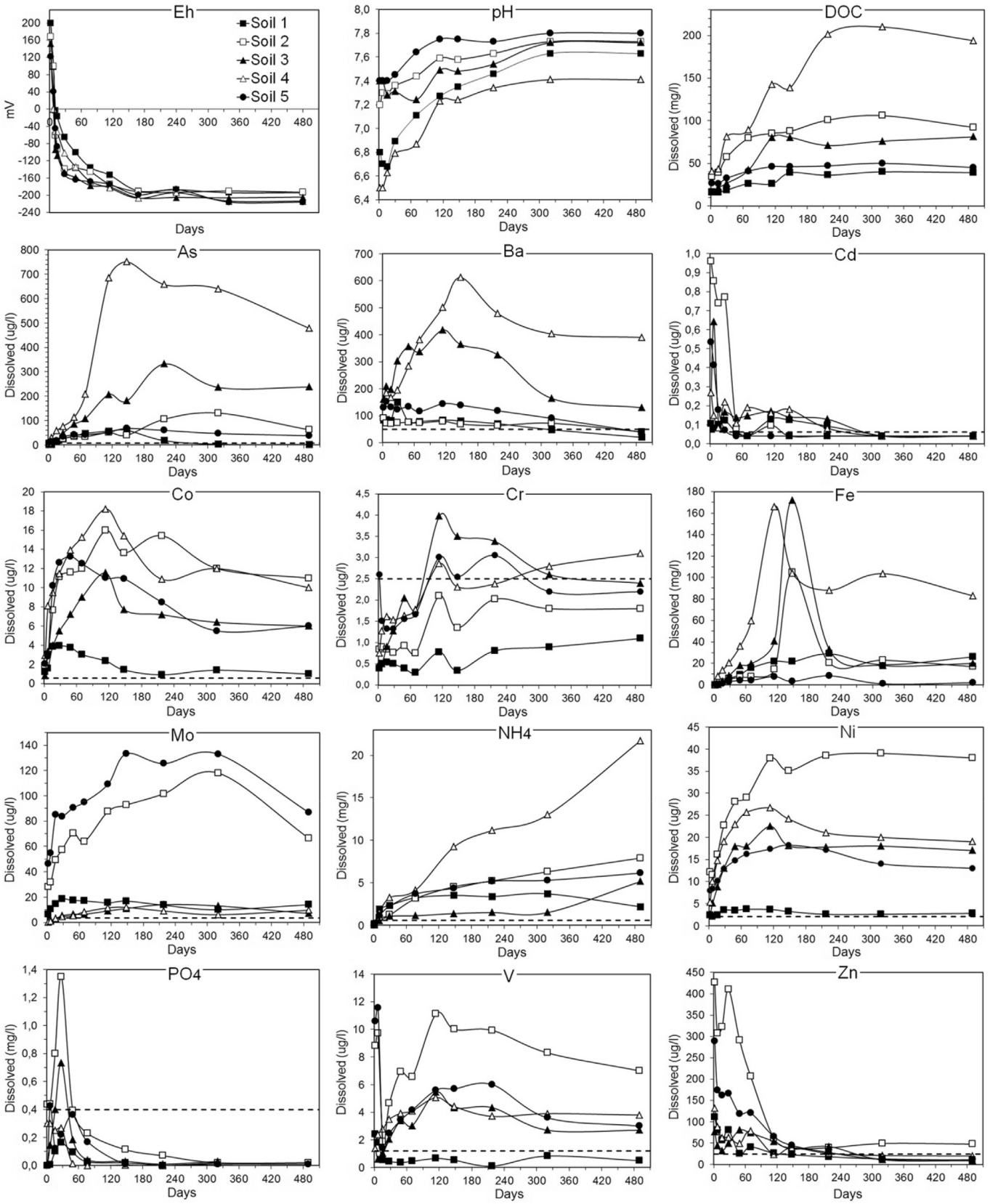

Fig. 1. Reduction kinetics of five soils over 16 months. Dotted lines are WFD-quality standards for groundwater, if available.

supplementary information), and the production of ammonium increases significantly due to a combination of enhanced organic matter mineralization (Lamers et al., 1998) and the catalytic effect of released Fe which acts as an electron donor to reduce nitrate

(e.g., Devlin et al., 2000).

Initially, soils release Fe(II), but not in comparable amounts and rates, which will be discussed below. Reductive ferrihydrite dissolution occurs primarily via:

$$Fe^{III}(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \quad \left(K = 10^{16.8}\right)$$

Ferric phases in soils have a high binding capacity to many heavy metals, but also anionic species may be highly associated with Fe(III) phases (Pedersen et al., 2006). The reduction of ferric phases consequently results in the release of these contaminants. Thermodynamically, the release of heavy metals such as Cd, Cu, Pb, and Zn (but also Fe itself) is counteracted by the formation of sulphides as a result of microbially mediated reduction of SO_4 from solution (Salomons et al., 1987; Du Laing et al., 2009a). Fisher and Peters (1970) ranked the stability constants K in the sequence Cu > Pb > Cd > Zn > Fe > Ni. Fig. 1 and Fig S1 indeed show that Cu and Pb are almost completely sequestrated from solution via sulfide complexation, whereas Ni is not. The formation of (Fe)-sulphides occurs over various stages (Morse and Luther, 1999), but the overall co-precipitation reaction for copper, for example, can be written as:

$$Cu^{2+} + Fe^{2+} + 2HS^- \rightarrow CuFeS_2 + 2H^+ \quad \left(K = 10^{35.3}\right)$$

Kinetically however, there are large differences in the net-complexation quantities of heavy metals with sulfides, and elevated pore water concentrations may remain for a prolonged period. This was observed specifically for As, B, Ba, Co, Mo, and Ni (Fig. 1 and Fig S1). Arsenic is associated to the iron phases as a co-precipitate or sorbed fraction to Fe-(hydr)oxides, and it is being released into solution as a consequence of the reduction of iron (Pedersen et al., 2006), possibly facilitated by metabolic activity of specific microbial populations (Macur et al., 2004). We observe in our reduction experiments a significant release of As in all studied soils. In all cases, the WFD (EC, 2000) quality standard for groundwater, and the WHO drinking water limit (both 10 μg/l), are exceeded by far. In soil 4, porewater concentrations even exceed 700 μg/l. Since As(III) and Cr(III) are practically inert to reaction with sulfides (Morse and Luther, 1999), their concentrations generally remain elevated over prolonged periods. This was also observed for barium, which displays comparable behaviour as arsenic. It has been suggested that Ba is mainly coprecipitated with iron and manganese (hydr)oxides in aerobic conditions (Coffey et al., 1997), while Frohne et al. (2015) suggested strong Ba-DOC interaction during redox alterations.

Concentrations of cobalt and nickel are significantly elevated over long periods as well. Van Hullebusch et al. (2005) found that the presence of iron negatively affected cobalt and nickel to accumulate in the organic and sulphide fractions, thus suggesting a higher binding affinity to reactive iron than to organic matter (Shaheen et al., 2014a).

Molybdenum is a redox sensitive trace metal, but the microbial reducing activity can be inhibited in the presence of metal ions such as Cd, Cr, Cu, Ag by approximately 75%, as was observed by Shukor et al. (2009). Binding to sulphides in lake sediment was studied by Dahl et al. (2013), showing that Mo is scavenged from sulphide-containing porewater as reactive Mo(IV)-polysulfide species. We indeed observe declining pore water concentrations of Mo, but only after a prolonged period (>300 days). This implies that the transition of Mo to sulphide phases occurs only slowly.

Vanadium reduces from V(V) to V(IV) and is mobilized. Different redox pairs such as NO_3^-/NH_4^+, Fe^{3+}/Fe^{2+}, MnO_2/Mn^{2+}, and SO_4^{2-}/H_2S play a role in the electron transfer following vanadium speciation (Sadiq, 1988; Wang and Wilhelmy, 2009). V(IV) probably remains in solution at elevated concentrations due to sorption to DOM (Emerson and Huested, 1991) as was demonstrated by Dijkstra et al. (2009) for a wide pH-range.

Prolonged and significant elevated concentrations of Boron occur in all soils. Boron may be associated to iron as borohydride (Glavee et al., 1995), but very little is known about redox speciation. Goldberg (1997) identified Boron in soils mainly as hydroxyl-ion accepting borate ions which may be very soluble depending on pH.

Phosphorous concentrations follow the transition pathway of Fe(III)- to Fe(II)-phosphate minerals (described in detail by Nriagu and Dell, 1974). The reduction of a Fe(III) mineral such as strengite ($FePO_4$) releases Fe(II) in solution, which is followed by the formation of Fe(II) minerals such as vivianite ($Fe_3(PO_4)_2$) via:

$$FePO_4 + e^- \rightarrow Fe^{2+} + H_2PO_4^- \quad \left(K = 10^{5.7}\right)$$

$$3Fe^{2+} + 2H_2PO_4^- \rightarrow Fe_3(PO_4)_2 + 4H^+ \quad \left(K = 10^{-3.1}\right)$$

Generally, kinetics for these reactions is relatively fast since the reduction of iron or the formation of Fe-P minerals is not thermodynamically hindered by other phases. Typically, phosphorous peak concentrations occur for some weeks, and are followed by a swift decline due to precipitation in ferrous phases. Significant emissions to groundwater may be restricted when the molar amount of reactive iron at least equals the amount of phosphorous.

3.3. DOM composition over time

DOM consists of an array of organic compounds with various alternating characteristics, but can be functionally grouped into compounds with comparable characteristics, such as hydrophilic, fulvic, and humic compounds (e.g., Stevenson, 1982; Egeberg et al., 2002; Sutton and Sposito, 2005). Humin compounds are insoluble and not regarded to take part in DOM. In the order presented here, these compounds increase in molecular weight, and decrease in solubility.

Time-dynamic concentrations of DOC in reducing pore water are shown in Fig. 1. DOC increased significantly to up to a factor of 10 compared to the initial aerobic state. The production of DOC was described in detail by Vink et al. (2010) and could be linked to the reductive release of Mn from oxides. Mn is an essential element for microbial synthesis, and its release results in a short-term metabolic boost of particulate organic matter degrading microorganisms. Consequently, soil particulate organic matter is degraded at a temporal increased rate, and associated metals are released (Dijkstra et al., 2004, 2009) and redistributed over particulate organic carbon (POC) and DOC. In particular Soil 4 produces large amounts of DOC (over 200 mg/l in pore water). In the linear part of the time-dependent concentration curve, a DOC production rate of 25 mg/kgC_{soil}/day was calculated. During reduction, metals are also released from the reactive Mn-oxide and Fe-(hydr)oxide sorption phases. Alternative binding capacity is provided by DOM which consequently keeps metals into solution. DOM releases metals only slowly, therefore kinetically hindering the phase shifting to stable metal sulfide precipitates.

As reduction progresses, the amount as well as the composition of DOM changes gradually. Fig. 2 shows examples of the compositional changes of DOM during reduction. Results clearly show that quantitative and qualitative shifts take place; fulvic acids become dominant over humic acids which disappear altogether as reduction progresses. Both the hydrophobic (Hon) and hydrophilic (Hy) fractions increase and may even become the dominant fraction (e.g., soil 5). The effect of these transitions on chemical modeling performance is discussed below.

Soil	Days	DOC mg C/l	HA	FA	Hy	HON	Mass (%)
1	7	21,7	1,0	10,2	10,7	0,0	123
	70	30,8	0,3	11,0	7,6	12,1	118
	210	30,6	0,2	11,9	10,1	8,7	101
2	7	39,3	2,0	13,3	7,6	16,3	115
	70	102,7	5,8	61,3	25,7	16,3	129
	210	100,7	0,5	55,0	17,5	29,7	95
3	7	19,2	0,4	8,9	6,1	3,8	119
	70	49,1	0,0	19,4	13,3	16,4	117
	210	71,0	0,0	32,2	18,7	20,1	93
4	7	62,1	4,7	36,1	8,9	12,5	152
	70	83,2	4,8	46,4	16,1	15,9	93
	210	201,6	1,5	109,9	37,9	52,3	115
5	7	31,8	2,1	7,0	8,6	14,1	121
	70	39,7	0,5	18,2	11,8	9,2	97
	210	47,0	1,1	19,6	11,8	14,4	103

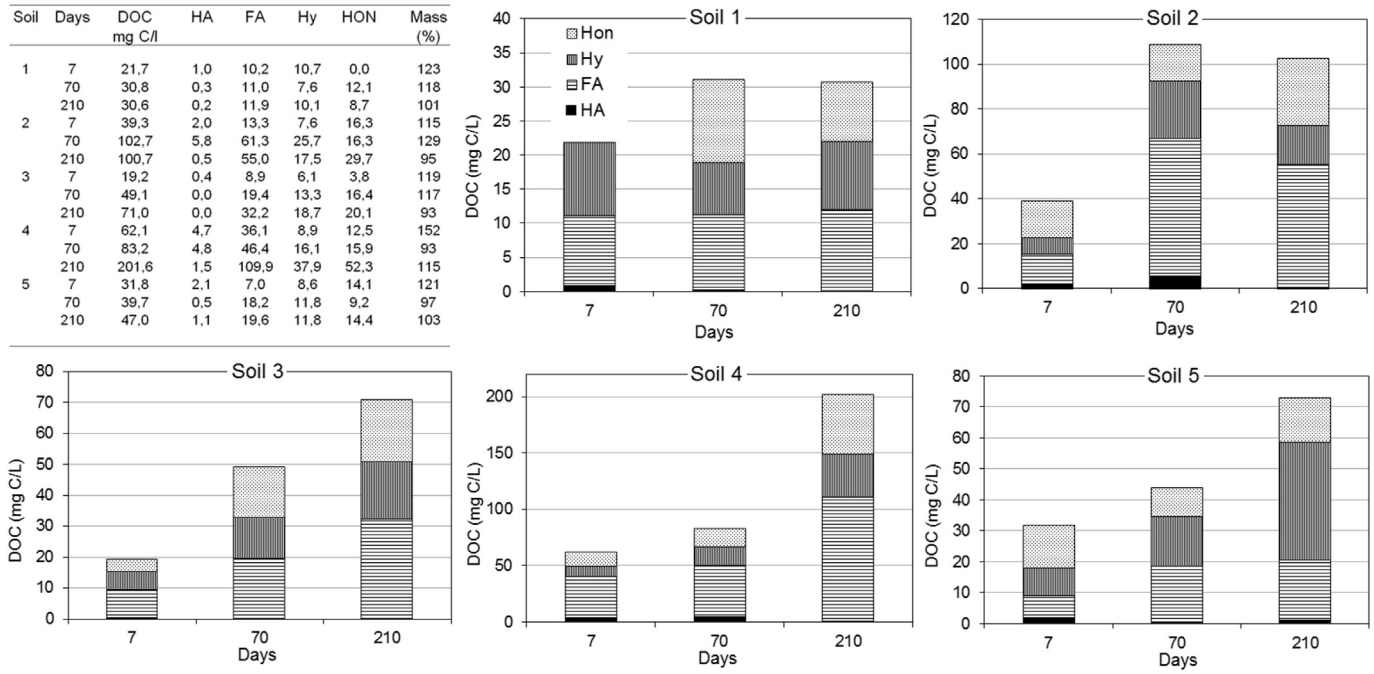

Fig. 2. Amount and composition of DOM during reduction. Hon = Hydrophobic neutral organic matter; Hy = Hydrophylic compounds; FA=Fulvic acids; HA=Humic acids.

3.4. Modeling simulations

Equilibrium - The geochemical conditions in the initial aerobic state, and the conditions after 17 months of reduction, are assumed to be at thermodynamic equilibrium. The speciation of the dominant controlling Mn and Fe phases can therefore be illustrated by pe-pH stability diagrams (Brookins, 1988; Patrick and Verloo, 1998) which show the dominant minerals that control metal and arsenic speciation as a function or redox potential and alkalinity. The boundaries between phases were calculated by using the relevant mineral solubility products and the measured concentrations of the dissolved species at the aerobic and anaerobic steady state (FeIII, FeII, MnIV and MnII, Fig. 1 and Fig S1.). We focused on the Fe/Mn-C-S-O-H system and excluded Si and the many dissolved Fe/Mn ionic species other than Fe^{2+} and Mn^{2+}. Hematite (Fe_2O_3) is excluded because of the very slow kinetic formation of this crystalline phase, considering the time frame of the experiments.

Fig. 3 shows that the initial aerobic conditions in all soils are controlled by stable phases of ferrihydrite ($Fe(OH)_3$) and MnO_2. Below neutral pH, Fe can only exist in solution at low redox potentials or as a soluble organic complex. At near neutral conditions and low redox potentials, the boundary for Fe^{2+} is primarily controlled by:

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3(s) + H^+ \quad \left(K = 10^{-5.9}\right)$$

$$Fe^{2+} + HS^- \rightarrow FeS(s) + H^+ \quad \left(K = 10^{14.0}\right)$$

And for Mn:

$$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad \left(K = 10^{41.4}\right)$$

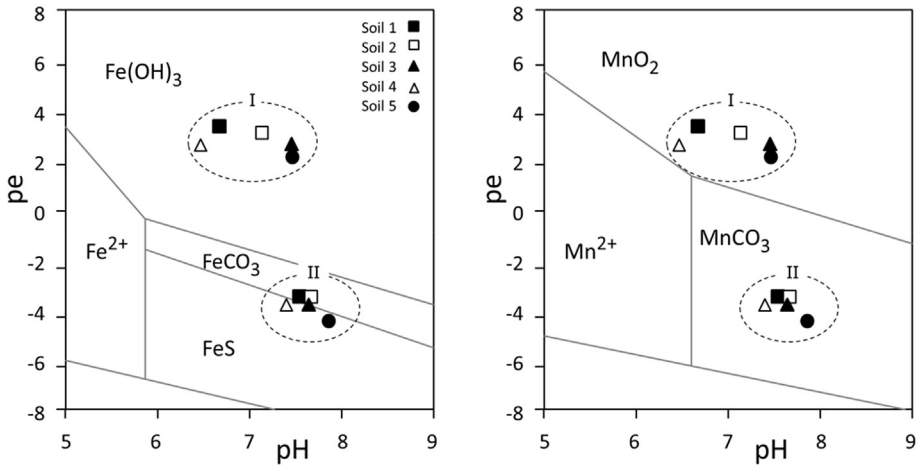

Fig. 3. Stability diagrams of Fe and Mn species and the position of the five soils prior to (I) and 17 months after (II) inundation.

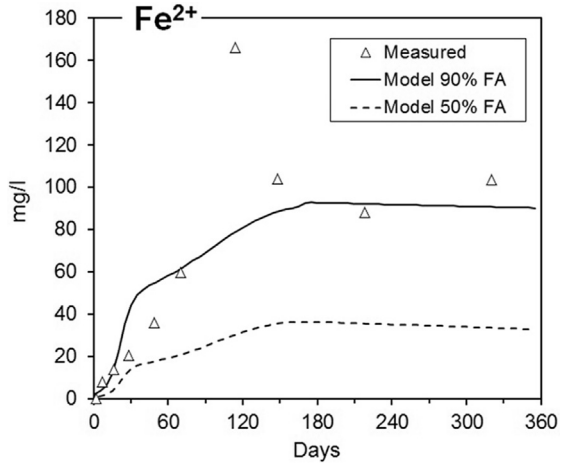

Fig. 4A. Results of model simulations. The effect of FA-contribution to total dissolved organic matter (DOM) on iron Fe(II) concentrations for soil.

$$Mn^{2+} + HCO^{3-} \rightarrow MnCO_3(s) + H^+ \left(K = 10^{0.8}\right)$$

Fig. 3 shows that at the transition from aerobic to anaerobic conditions, the solubility of Fe and Mn is controlled by different mineral phases, which may occur simultaneously during non-equilibrium periods. The prevailing dominant iron phase is rather sensitive, given the close position of the soils near the thermodynamic stability boundaries. The endpoint conditions are controlled by $FeCO_3$ and FeS phases rather than ferrihydrite, and affect the speciation and consequently the mobility of metals and arsenic.

Non-equilibrium - Redox potentials over time were simulated using the pe-gamma functions and initial parameterization settings described earlier. For sorption to DOM, the often used NICA 50-50 contribution of HA-FA was replaced by a 10–90 distribution assuming that the metal binding affinity of hydrophilic (Hy) fractions approximates those of FA (Tipping, 1994, 2002; Kinniburg et al., 1996; Smith and Martell, 1976). POM was assumed to be HA-dominant. Since measurements indicated that the release of arsenic during reduction poses a serious potential threat to groundwater, modeling focused on the reductive release of iron, its sorption to DOM and the resulting effect on As concentration. Results are shown in Fig. 4B. Redox potentials were predicted quite adequately, but kinetic improvements are desired since reduction appears to occur somewhat faster in reality. The predicted mobility of As shows good agreement with measured concentrations both in terms of magnitude and ranking between soils. The significant increase in As mobility in soil 4, followed by soil 3, is convincingly predicted (see also Fig. 1). Nevertheless, an underestimation of predicted concentrations of approximately 30% still occurs for soil 4. Possibly, the (microbial) transition of Fe-crystalline to amorphous phases over the studied time period may play a role, thus underestimating the total reducible Fe pool. Also, the binding affinity of arsenic species to organic compounds is a source of uncertainty (Bauer and Blodau, 2006).

The quantitative effect of altering the composition of DOM to speciation in pore water is quite large. Increasing the fraction of FA from 50 to 90% of total DOM increases the match between measured and predicted concentrations. Fig. 4A + B show examples of simulated concentrations of dissolved Fe^{2+} and associated As(III)-species ($H_2AsO_3^-$ and $H_3AsO_3^0$ being the dominant species at the specified conditions). Still, peak concentrations are not fully reproduced, and some underestimation remains due to the suggested mechanisms described earlier.

4. Discussion and conclusions

Mesocosm experiments and geochemical modeling simulations of soil reduction yielded valuable kinetic data on mobility of compounds that may pose a threat to groundwater quality. Redox-discrete measurements over long-term reduction of aerobic soils showed a range in mobilization rates despite comparable reduction rates. A qualitative indication of potential risks is shown in Table 3.

Table 3
Qualitative indication of mobilization risks for compounds based on compliance check with WFD quality standards for groundwater (magnitude and time period of exceedance).

Low[a]	Moderate	High[b]
Cd	Cr	As
NO_3	Cu	B
Pb	NH_4	Ba
PO_4	Se	Co
	V	Mo
	Zn	Ni

[a] > EQS, but < 60 days.
[b] > 10xEQS, for > 100 days.

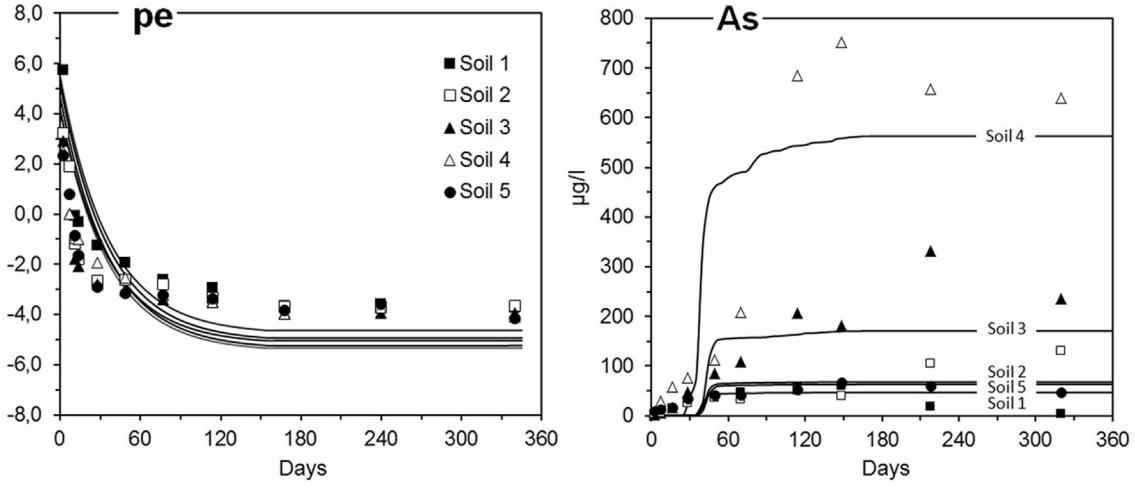

Fig. 4B. Results of model simulations. The kinetic development of redox potential (left) and arsenic release (right) over time.

Categories are based on the WFD quality standard for groundwater of each compound and the rate of release from sediment to pore water (magnitude and time period of exceedance). Compounds in the low category may exceed environmental quality standards (EQS), but by less than 60 days. These compounds include the heavy metals Cd and Pb, which form sulfide complexes with stability constants K of at least 10^{-27} (Fisher and Peters, 1970). Cu meets this criterion too, but competition with DOM decreases the sulfide reaction rate (Römkens and Dolfing, 1998; Shi et al., 1998; Vink et al., 2010) and remains in solution for a prolonged period. Compounds in the high risk category include As, B, Ba, Co, Mo, and Ni, and exceed their EQS by a factor >10, and for >100 days, in at least two cases. These compounds may require priority attention when risk predictions are performed for soils that are stored under water.

4.1. Fe speciation

Speciation of iron plays a crucial role in the mobilization of associated compounds. Amorphous and crystalline iron phases were quantified with chemical extractions to identify reactive or readily reducible phases. The reduction of Fe (hydr)oxides and the stability of Fe^{2+} in solution primarily depends on a combination of Eh and pH of the sediment. The nearly amorphous $Fe(OH)_3$ minerals (ferrihydrite) are reduced faster than the more crystalline forms like FeOOH (goethite) or Fe_2O_3 (hematite) (Wahid and Kamalam, 1992; Du Laing et al., 2009b). Davis and Leckie (1978) estimated that the specific surface area of amorphous Fe was approximately 20–30 times higher than the crystalline Fe. However, Wahid & Kamalam, 1992 found that during reduction the crystalline Fe(III)oxides were converted into the amorphous form, probably due to microbial hydration. This would mean that the readily reducible Fe fraction could include some part of the crystalline phase if reduction progresses. The relative contribution of these iron phases may therefore largely affect computations of reduction and mobilization reactions for associated compounds. Fig. 5 shows the relative contributions of these phases in the studied soils. The combined amorphous + crystalline phases contribute 36–70% to total Fe extracted with *Aqua regia*. The residual part is not readily reducible and non-reactive.

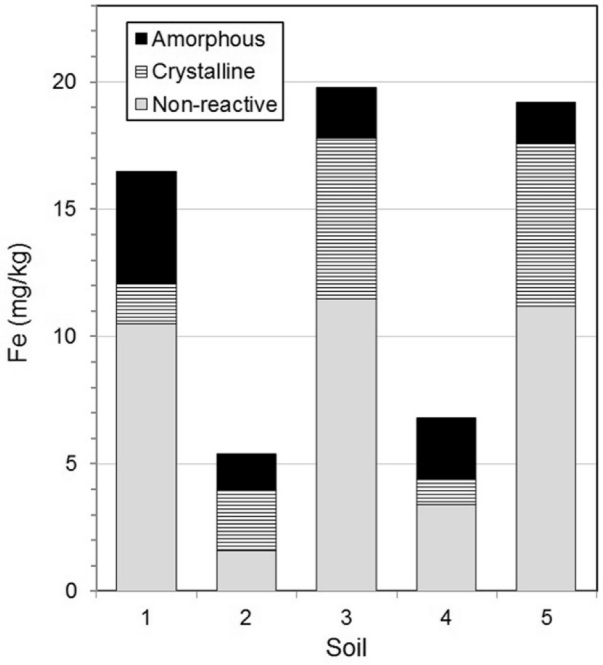

Fig. 5. Distribution of Fe-phases in soils.

The exceptionally high release of arsenic in soil 4 during reduction experiments is not reflected by its contamination level (i.e., conventional extraction with *Aqua regia*). However, a relatively large amount of 1 mM $CaCl_2$ extractable Fe was found in this soil. Since this extraction is performed at neutral conditions at the pH of the soil itself, this Fe fraction resembles the Fe^{3+} concentrations in pore water of which a large part is most probably associated to DOM. Combined with a low acid buffering capacity (pH = 6.5, $CaCO_3$<0.02%), this soil releases Fe and associated compounds very easily upon reduction. The partitioning of Fe between the solid and dissolved phase may be approximated by using the defined phases that are determined by the various extractions. Table 4 shows the partitioning coefficients of Fe, calculated from these extractions. The expression is written as Kp = reactive solid Fe/dissolved Fe (l/kg). The Kp for soil 4 is a factor of 10–100 lower than for the other soils, showing its capability to release Fe and associated compounds relatively easily.

4.2. Reduction/release rates of Fe and associated compounds

The time dynamic data of $[Fe^{2+}]$ enable the calculation of reduction rates for reducible iron phases (as suggested by Postma, 1993), and the release rates of associated compounds like arsenic and barium (see Table 5). Although many authors found empirical relations between As and Fe concentrations in groundwater, suggesting a direct link to Fe-reduction (e.g., Nickson et al., 2000; Cherry et al., 1979; Pierce and Moore, 1982; Frohne et al., 2014; Shaheen et al., 2014b), this relation is disputed by e.g., Pedersen et al. (2006). These authors suggest a redistribution of As over Fe phases during reduction, allowing a shift of As from unstable amorphous iron(hydr)oxides to crystalline phases. Our data indeed show a slow decline in As concentrations after approximately 200 days after reduction. Since we exclude sulfide complexation with As, this observation may be explained by secondary sorption of released As to (transformed) reactive surfaces of crystalline Fe phases. The presence of other anionic species may however interfere with arsenate sorption to iron(hydr)oxides. Competitive anion exchange with phosphate (Acharyya et al., 1999), carbonate (Appelo et al., 2002), as well as DOM (Burton et al., 2008; Frohne et al., 2014) can mobilize arsenic from these reactive surfaces.

4.3. The role of dissolved organic matter

During reduction, DOM changes in magnitude and composition, and fulvic acids dominate humic acids by far. Hydrophobic and

Table 4
Fe partition coefficient calculated from operationally defined extractions.

Log Kp (l/kg)	Soil				
	1	2	3	4	5
Fe-HNO_3/Fe-$CaCl_2$	6.20	5.16	5.53	4.27	5.66
Fe-am + cryst/Fe-$CaCl_2$	6.17	5.60	6.13	4.65	6.11

Table 5
Fe reduction rate and release rates of associated arsenic and barium.

Element	Unit	Soil				
		1	2	3	4	5
Fe	$mg/m^2/day$	4.4	2.4	5.0	48.1	1.3
As	$\mu g/m^2/day$	13.5	16.0	50.3	198	15.1
Ba	$\mu g/m^2/day$	24.3	23.0	121	145	41.8

hydrophilic fractions show the tendency to increase and even become dominant, depending on the type of soil. The inclusion of the quantitative and qualitative transitions of DOC in geochemical modeling demonstrated a large impact on model performance and the ability to predict solute concentrations of Fe and As. Williams et al. (2011) also showed that DOC has a strong potential to mobilize arsenic in paddy fields, with DOC influencing arsenite/arsenate interconversion. They concluded that DOC was the strongest determinant of arsenic solid-solution phase partitioning. Buschmann et al. (2006) reported on the influence of the type of humic acid on arsenate mobilization, observing differences of binding affinities of a magnitude 3 between aquatic and terrestrial humic types via ligand exchange with carboxylic functional groups. Weng et al. (2009) linked As binding and type of DOC to sorption to Fe-phases, e.g, goethite.

A good agreement was observed between dissolved [Fe] and [DOC]. Data for all soils give an empirical relation that can be described with

$$Fe_{diss} = 0.45 \times DOC \quad \left(r^2 = 0,67;\ n = 55\right)$$

Dissolved organic matter is able to mobilize arsenic from solid phases (Buerge and Hug, 1998; Burton et al., 2008). Bauer and Blodau (2006) demonstrated that addition of DOM lead to enhanced reduction of arsenic and the appearance of arsenite in the aqueous phase of soil samples. The underlying mechanism is competition between arsenic and organic anions for sorption sites. Including this mechanism in a multisurface approach (e.g., Filius et al., 2003) could further improve modeling performances.

4.4. Outlook for practical, descriptive methods

This study yielded several insights to improve the predictive risk assessment for contaminated soils after reduction during under water disposal or storage. Next to improving geochemical computations by using advanced redox modeling and sorption by reactive phases of iron and DOM, some practical methods are suggested here.

The use of operationally defined extraction techniques may provide useful alternatives for conventional destructions that aim at total content of compounds in soil. Examples are:

- The ratio of *Aqua nitrosa* over *Aqua regia* extracted concentrations proved a useful indicator for binding strength to the soil matrix, and hence, mobility. The highest pore water concentrations for Cd, Cu, Ni, P, V, and Zn were observed in soils that had a high ratio of AN/AR.
- The amorphous Fe fraction in soils could well be approximated with an *Aqua nitrosa* extraction, and not with *Aqua regia.* Modeling results improved using AN-measurements as input.
- The amount of readily reducible Fe is a potential indicator for release rates of As, Ba, P, and possibly other metals. This Fe-fraction could well be approximated with a mild 1 mM $CaCl_2$ extraction.
- Soil-specific partitioning coefficients can be derived from extraction ratios that relate reactive solids to dissolved compounds. A proxy value for Fe of log Kp < 5 may be used as a first tier indicator for potential mobilization risks of redox sensitive compounds.

In order to improve the identification of soils that display high emission potential of toxic metals to environmental compartments, future regulative procedures may include the use of targeted extraction techniques as better indicators for chemical availability. Improved geochemical modeling is not only beneficial to general scientific underpinning of chemical processes; especially in cases of site-specific risk assessment it is often the only means of addressing uncertainty around large-scale soil applications and pollution of surroundings. In cases of groundwater risks, the effect of eventual dilution should also be considered, since the legal compliance check with environmental quality standards is concentration based.

Acknowledgement

This research was performed to improve risk assessment of large scale soil applications and the implementation of practical methods in a legal framework. We thank the Dutch ministry of Infrastructure and Environment (I&M), Rijkswaterstaat, and the National Institute for Public Health and the Environment (RIVM) for their support. Three anonymous reviewers are greatly acknowledged for their critical review of the manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.04.016.

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SUPPLEMENTARY INFORMATION

When Soils Become Sediments: Large-scale Storage of Soils in Sandpits and Lakes and the Impact of Reduction Kinetics on Heavy Metals and Arsenic Release to Groundwater.

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Table S1. Groundwater composition (SD=standard deviation).

Parameter	Unit	Mean n=5	SD
T	ºC	16	0
pH	-	8.3	0.1
Eh	mV	+218	4
DOC	$mg.L^{-1}$	1.33	0.10
Cl	$mg.L^{-1}$	26.9	0.53
NH_4	$mg.L^{-1}$	0.03	0.01
NO_3	$mg.L^{-1}$	2.82	0.14
PO_4	$mg.L^{-1}$	0.08	0.01
SO_4	$mg.L^{-1}$	18.1	0.21
As	$\mu g.L^{-1}$	1.62	0.09
B	$\mu g.L^{-1}$	33	0.97
Ba	$\mu g.L^{-1}$	11.6	0.2
Be	$\mu g.L^{-1}$	<0.3	0
Ca	$mg.L^{-1}$	37.7	1.3
Cd	$\mu g.L^{-1}$	0.34	0.13
Co	$\mu g.L^{-1}$	0.69	0.21
Cr	$\mu g.L^{-1}$	0.87	0.06
Cu	$\mu g.L^{-1}$	14.7	6.93
Fe	$\mu g.L^{-1}$	<30	0
Li	$\mu g.L^{-1}$	4.09	0.06
Mn	$\mu g.L^{-1}$	2.38	0.15
Mo	$\mu g.L^{-1}$	<0.5	0
Ni	$\mu g.L^{-1}$	0.75	0.28
Pb	$\mu g.L^{-1}$	<0.7	0
V	$\mu g.L^{-1}$	0.81	0.05
Zn	$\mu g.L^{-1}$	30.2	7.73

Table S2. Element concentrations (mg/kg dw) determined with three extraction procedures.

	Aqua regia					0.43M HNO3					1mM CaCl2				
	Soil 1	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
Ag	0.15	0.30	0.26	0.10	0.98	0.01	0.01	0.01	0.01	0.01	8.34E-05	8.34E-05	3.66E-05	9.83E-05	2.90E-05
Al	13754	5644	21722	9228	10422	1470	631	1221	814	2415	0.104	0.322	6.27E-02	3.25	0.781
As	14.5	5.1	12.9	14.1	15.3	8.06	2.1	1.43	3.92	7.18	8.48E-03	3.95E-02	1.01E-02	1.46E-02	5.45E-02
Ba	103	31	167	77	856	5.8	17.4	92	41.9	87.8	0.502	0.144	0.542	0.655	0.699
Be	0.67	0.24	1.08	0.39	0.72	0.26	0.10	0.35	0.19	0.23	2.32E-05	2.58E-05	1.65E-05	2.31E-04	2.80E-05
Ca	17607	3215	25909	3193	30408	22151	3028	25037	3065	31785	nd	nd	nd	nd	nd
Cd	0.34	0.57	0.92	0.16	1.88	0.238	0.522	0.753	0.122	1.45	5.19E-04	1.01E-03	3.68E-04	4.77E-04	5.94E-04
Ce	19.20	18.84	34.29	10.67	16.69	5.28	4.87	8.94	2.73	4.66	5.26E-05	2.27E-04	1.61E-04	1.91E-03	5.64E-05
Co	4.68	2.30	9.25	2.18	8.15	2.07	1.05	2.72	0.685	4.11	6.14E-04	6.08E-04	2.66E-04	1.47E-03	1.21E-03
Cr	23.93	18.32	47.27	12.71	77.97	1.12	2.31	3.55	0.38	20.6	9.92E-04	2.83E-02	1.40E-02	5.58E-03	0.220
Cs	2.88	0.59	4.74	1.79	1.66	0.005	0.004	0.001	0.002	0.013	9.20E-05	5.61E-05	5.01E-05	5.58E-04	2.64E-04
Cu	21.02	41.21	25.98	13.26	194.91	10.2	34.2	15.1	7.3	132	1.20E-02	8.09E-02	3.29E-02	4.02E-02	0.115
Fe	16513	5438	19829	6843	19225	6344	1385	2106	1428	2813	4.04E-02	9.64E-02	6.16E-02	2.14	6.17E-02
Ga	3.77	1.76	6.36	2.58	4.10	0.22	0.14	0.27	0.08	0.48	9.73E-04	1.33E-03	1.16E-04	8.20E-04	1.64E-03
Gd	1.68	1.25	3.12	0.82	1.61	0.67	0.48	1.25	0.34	0.52	4.59E-05	6.37E-05	4.08E-05	2.49E-04	2.14E-05
K	2866	886	4649	1278	2350	187	110	76	46	502	nd	nd	nd	nd	nd
La	9.23	8.84	16.27	5.25	8.11	2.50	2.06	4.31	1.33	2.40	4.01E-05	1.22E-04	9.50E-05	8.83E-04	4.32E-05
Li	17.34	5.25	31.14	11.12	13.32	0.55	0.10	0.55	0.01	1.65	6.91E-02	6.04E-03	1.52E-02	6.78E-03	0.170
Mg	4036	515	6964	1168	2908	1901	67.8	2207	103	1025	nd	nd	nd	nd	nd
Mn	486	232	637	119	578	391	116	322	63.4	223	0.119	4.04E-03	1.55E-03	7.63E-02	5.29E-03
Mo	1.86	0.49	0.36	0.44	2.44	0.02	0.07	0.01	0.01	0.11	0.132	3.25E-02	1.42E-02	8.79E-03	5.68E-02
Nb	0.72	0.41	0.62	0.41	0.65	0.01	0.06	0.01	0.01	0.04	6.76E-05	6.79E-05	3.58E-04	4.09E-04	1.10E-04
Nd	9.03	8.41	16.43	5.12	8.33	3.21	2.57	5.97	1.65	2.73	3.66E-05	1.79E-04	1.01E-04	9.78E-04	3.87E-05
Ni	17.7	9.9	29.7	8.6	32.9	5.8	5.8	4.5	2.1	8.4	5.94E-03	1.93E-02	4.46E-03	1.55E-02	1.60E-02
P	454	447	590	214	1313	159	309	240	63.8	831	0.881	1.880	0.713	0.944	2.06
Pb	156.6	47.9	49.7	51.4	514.1	59.3	62.3	32.9	39.6	363	1.84E-03	1.54E-03	4.83E-04	2.20E-02	5.30E-03
Pr	2.33	2.24	4.24	1.32	2.07	0.72	0.59	1.31	0.38	0.62	7.13E-06	3.80E-05	2.54E-05	2.37E-04	9.20E-06
Rb	22.3	7.12	38.3	11.6	16.9	0.42	0.31	0.07	0.06	1.10	4.10E-02	3.68E-02	1.05E-03	7.83E-03	9.65E-02
S	16913	157	254	617	1419	11635	51	31	137	590	nd	nd	nd	nd	nd
Sb	0.36	0.99	0.26	0.27	3.35	0.02	0.23	0.03	0.02	0.29	8.11E-03	5.49E-02	3.60E-03	5.08E-03	7.76E-02
Sn	3.35	2.61	1.61	1.27	19.13	0.03	0.19	0.02	0.01	1.07	1.55E-04	1.07E-04	1.09E-04	6.84E-04	2.77E-04
Sr	83.6	10.1	83.0	19.0	116.9	62.32	5.86	61.60	10.65	60.31	20.7	0.87	1.62	1.66	2.70
Th	3.22	2.17	5.39	1.71	2.07	0.04	0.02	0.04	0.01	0.05	7.10E-05	4.58E-05	1.49E-03	4.24E-04	1.70E-04
Ti	258.5	138.0	392.8	140.4	1090.7	15.6	9.9	4.8	3.5	65.9	1.40E-03	2.78E-03	2.70E-03	6.17E-02	2.44E-03
Tl	0.22	0.08	0.37	0.12	0.27	0.019	0.007	0.002	0.001	0.052	2.86E-04	1.81E-04	2.01E-05	6.52E-05	3.43E-04
U	2.33	0.34	0.64	0.96	0.76	0.69	0.09	0.14	0.34	0.21	5.59E-04	1.20E-03	1.07E-03	4.67E-04	1.09E-02
V	27.49	16.63	39.04	13.99	36.71	8.04	8.25	5.27	2.35	16.09	6.81E-03	6.60E-02	3.93E-03	8.25E-03	9.51E-02
W	0.12	0.25	0.11	0.08	0.62	0.001	0.042	0.001	0.002	0.050	9.10E-04	1.09E-02	5.33E-04	1.58E-04	1.25E-02
Zn	121.8	607.5	185.7	39.9	1064.0	70.6	561	64.2	12.8	1085	0.125	0.293	0.229	0.115	0.128
Zr	8.85	1.69	9.14	3.88	7.52	0.18	0.26	0.64	0.32	0.70	4.10E-04	6.87E-04	7.73E-04	4.10E-03	9.11E-04

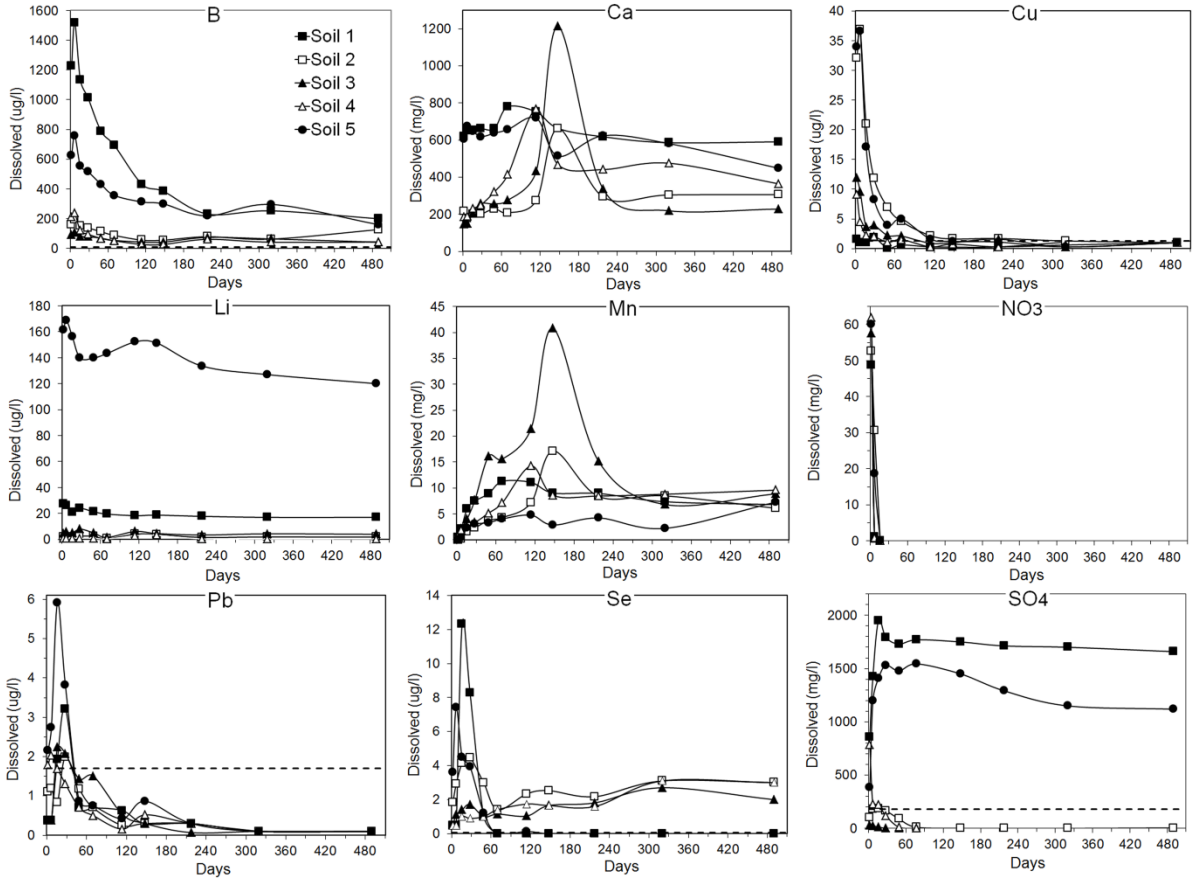

Figure S1. Reduction kinetics for borium, calcium, copper, lithium, manganese, nitrate, lead, selenium, and sulphate for five soils. Despite anaerobic conditions, elevated sulphate concentrations occur for soils 1 and 5 which result from dissolution of autogenic gypsum.

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