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[☆,☆☆]

Jos P.M. Vink [a, *], Andre van Zomeren [b], Joris J. Dijkstra [b], Rob N.J. Comans [c]

[a] Deltares, Unit Subsurface & Groundwater Systems, PO-box 85467, 3508 AL Utrecht, The Netherlands
[b] Energy Research Centre of the Netherlands, PO-box 1, 1755 ZG Petten, The Netherlands
[c] Wageningen University, Dept. Soil Quality, PO-box 47, 6700 AA Wageningen, The Netherlands

ARTICLE INFO

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.

© 2017 Elsevier Ltd. All rights reserved.

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

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.