WATER RESEARCH 46 (2012) 2205–2214

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

The impact of increased oxygen conditions on metal-contaminated sediments part I: Effects on redox status, sediment geochemistry and metal bioavailability

M. De Jonge [a,*], J. Teuchies [b], P. Meire [b], R. Blust [a], L. Bervoets [a]

[a] Department of Biology, Ecophysiology, Biochemistry and Toxicology Group, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

[b] Department of Biology, Ecosystem Management Research Group, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium

ARTICLE INFO

Article history:
Received 5 December 2011
Received in revised form
17 January 2012
Accepted 28 January 2012
Available online 4 February 2012

Keywords:
Acid volatile sulfides (AVS)
Redox potential (Eh)
Sediment geochemistry
Diffusive Gradients in Thin films (DGT)
Metal pollution

ABSTRACT

In order to evaluate the effect of improved oxygen concentrations in overlying surface water on the redox status, sediment geochemistry and metal bioavailability in metal-polluted sediments a 54 days lab experiment with two different experimental treatments was conducted (90% and 40% O_2). Changes in redox potential (Eh) in the sediment were monitored over time. At 6 different time points (after 0, 2, 5, 12, 32 and 54 days) and at 4 sediment depths (0–1, 1–4, 4–8 and 8–15 cm), acid volatile sulfides (AVS), simultaneously extracted metals (SEM) and total organic carbon (TOC) were measured and metal release to overlying surface water was determined. Labile metal species in both water and sediment were measured using Diffusive Gradients in Thin films (DGT). Our results showed that elevated oxygen levels in overlying surface water led to an Eh increase in the sediment of the 90% O_2 treatment from 0 to ±200 mV while AVS concentrations in the upper sediment layer decreased by 70%. Following AVS oxidation metal availability in the pore water was highly elevated after 54 days. However, Cu remained strongly bound to the sediment during the whole experiment. Only a limited metal release to the overlying surface water was noticed, which was due to the fact that SEM_{tot} concentrations in the sediment did not yet exceeded AVS levels ($[SEM_{tot} - AVS]/f_{OC} = 0$) after 54 days. Additionally, adsorption on Fe and Mn hydroxides and particulate organic carbon also slowed down any potential metal release. Our results indicated that increasing oxygen concentrations due to general water quality improvements can enhance the mobility of trace metals which may result in the leaching of sediment-bound metals to overlying surface water, even in undisturbed watercourses.

1. Introduction

In the aquatic environment anoxic, organic rich sediments usually act as an important sink for metals and metalloids (Eggleton and Thomas, 2004; Kelderman and Osman, 2007) representing a large amount of metals in potentially bioavailable and toxic form (Luoma and Rainbow, 2008). This is due to the high affinity of cationic elements with sedimentary phases such as organic matter, Fe, Al and Mn oxides and, under anoxic conditions, acid volatile sulfides (AVS) (Yu et al., 2001; De Jonge et al., 2010). AVS are formed through the anaerobic reduction of sulfate (SO_4^{2-}) and are operationally

---

* *Corresponding author*. Tel.: +32 3 265 3533; fax: +32 3 265 3497.
E-mail address: maarten.dejonge@ua.ac.be (M. De Jonge).

0043-1354/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2012.01.052

defined as the amount of sulfides volatilized by the addition of 1 N HCl (Di Toro et al., 1990). In their reaction with trace metals, AVS can form thermodynamically stable metal-sulfide precipitates, resulting in a decreased concentration of metal ions in the sediment pore water and therefore reduced metal bioavailability. Metals which are associated with AVS are called Simultaneously Extracted Metals (SEM; Cu, Pb, Cd, Zn, Ni, Cr and Ag) (Di Toro et al., 1990; Luoma and Rainbow, 2008). The trace metal Cr does not form metal-sulfide complexes on itself, but its toxicity is decreased because the presence of AVS results in the reduction of the highly toxic Cr(VI) to form the less toxic and less mobile Cr(III) (Berry et al., 2004).

Recent water quality improvements in freshwater ecosystems are generally accompanied with an increase in oxygen concentration. These elevated oxygen levels can affect the redox potential (Eh) of the sediment drastically and lead to the oxidation of AVS (Zhuang et al., 1994; Peterson et al., 1996; Kelderman and Osman, 2007; Teuchies et al., 2011), resulting in an increased flux of metals to the overlying surface water (Teuchies et al., 2011). Furthermore, changes in sediment geochemistry can lead to the transformation of metals into more bioavailable and/or toxic forms (Zhuang et al., 1994; Guo et al., 1997; Eggleton and Thomas, 2004). However, to what extent increasing oxygen levels in the surface water can lead to an altered bioavailability and release of sediment-bound metals over time remains poorly investigated. Nevertheless, this information is crucial to understand and estimate the impact of metal-contaminated sediments on the aquatic environment. To our knowledge most studies investigating Eh related changes in sediment metal bioavailability used (re) suspension experiments (Caetano et al., 2003; Eggleton and Thomas, 2004), which resemble severe anthropogenic impacts on sediment like e.g. dredging. Therefore it is very important to use an undisturbed sediment/water interface in order to assess the impact of increasing oxygen levels on metal-contaminated sediments.

The main objective of the present study was to evaluate the effect of elevated oxygen concentrations in overlying surface water on the redox status, sediment geochemistry and metal bioavailability from metal-contaminated sediments over time under experimental conditions. A companion paper discusses to what extent Eh induced changes regarding the bioavailability of sediment-bound metals can affect both metal accumulation and toxicity in aquatic invertebrates (De Jonge et al., 2011).

2. Materials and methods

2.1. *Sediment sampling*

Natural sediment was sampled in November 2009 from the Moerbeek, a slow-flowing lowland creek near the town of Nazareth, Belgium (x/y-coordinates; x: 101249; y: 183807). This sample point was chosen based on both its high organic matter and AVS content and its high metal contamination (De Jonge et al., 2010).

Subsurface sediment samples (1–10 cm depth) were collected using a stainless steel Petit Ponar grab sampler (Wildco cat. No. 1728; 235 cm^2). Immediately after sampling the sediment was transferred to sealed polypropylene containers (10 L). At the laboratory, the sediment was carefully homogenized and placed under a N_2 atmosphere at 4 °C for one week until the start of the experiment.

2.2. *Experimental setup and sampling design*

A 54 days lab experiment using the collected sediment was conducted in 2 experimental treatments, each consisting of a polypropylene container (60 cm × 80 cm × 40 cm) connected to a lower water basin (Fig. 1). In each upper container a volume of 72 L sediment was placed and 34 L medium-hard reconstituted freshwater (OECD; 294 mg/L $CaCl_2.2H_2O$; 123.25 mg/L $MgSO_4.7H_2O$; 64.75 mg/L $NaHCO_3$; 5.75 mg/L KCl) (OECD, 2004) was added. In order to create natural flowing conditions and subsequent sediment/water interactions, water was pumped at 10 L/min from the lower basin into the upper container. The surface water of both treatments was nitrogen purged and held under N_2 atmosphere for 10 days. After this equilibration period the oxygen level in the water of treatment 1 was raised to 90.0 ± 3.0% O_2 saturation, while O_2 in the surface water of treatment 2 was held at 40.7 ± 6.9% O_2 (Table 1). Oxygen levels were monitored and held constant during the entire period of the experiment using an O_2-stat system (R362, Consort, Turnhout, Belgium). Temperature was kept at 20 ± 1 °C by conducting the experiment in a climate chamber (Type WT15′/+5DU-WB, Weiss Technik, Reiskirchen-Lindenstruth, Germany).

Changes in sediment Eh were automatically measured in time at 4 different depths without disturbance using a newly developed continuous Eh and temperature data logger (Hypnos III; MHV Consult, the Netherlands) (Vorenhout et al., 2004). The data logger was connected to probes with 4 Eh sensors (at 1, 4, 8 and 15 cm depth) and 2 temperature sensors (at 1 and 15 cm depth) and a separate calomel reference electrode. Eh values and temperature were automatically recorded in duplicate in both treatments every 30 min during 54 days. Each day pH, temperature, dissolved oxygen and electrical conductivity (EC) of the surface water was measured *in situ*

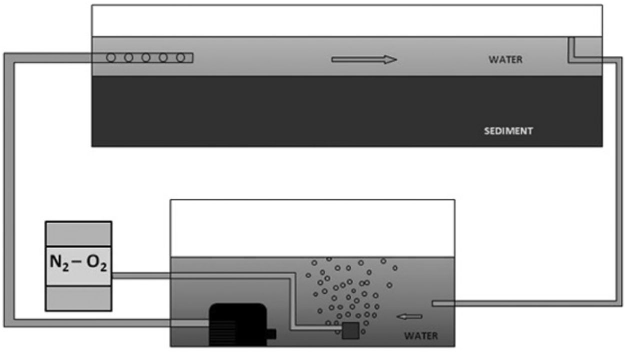

Fig. 1 – Overview of the experimental set-up in one treatment. Water is aerated/N_2-purged in the lower reservoir. Subsequently it gets pumped into the upper basin, which contains the experimental sediment/water interface. Overflowing water is removed to the lower reservoir. The black box indicates a 10 L/min water pump.