Influence of redox cycle on the mobilization of Fe, Zn, Cu and Cd from contaminated sediments: a laboratory investigation

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Abstract

An investigation was set up to elucidate the dynamics of metals flows from a contaminated and eutrophic lake. Two sediment layers were incubated in flow-cells to study the mobilization of Fe, Zn, Cu and Cd during the anoxic and oxic conditions. pH, inorganic carbon (IC) and dissolved organic carbon (DOC) were monitored to assess their influences on the metal mobilization. Under anoxic conditions, Fe was rapidly released to the solution, but taken up during the oxic conditions. The Fe-mobilization was not affected by pH, but positively correlated with the increase in DOC during the anoxic period. In contrast, Zn, Cu and Cd were removed from the solution during the anoxic period and released to the solution during the oxic conditions. The change in pH during the oxic period may have contributed to the increase in concentrations of Zn, Cu and Cd. The results of the experiment show that periodical redox changes likely are among the factors controlling the mobilization of Fe, Zn, Cu and Cd from the contaminated sediments.

Keywords: sediment, flow-cell, metal, mobilization, redox condition.

1 Introduction

Changes in redox conditions play a significant role in mobilization of heavy metals from sediments. Under anoxic conditions, heavy metals usually occur as stable sulfides buried in the sediment layers, which results in low concentrations of metals in the water phase Calmano et al [3]. Imposing oxic conditions, the
metal sulfides occurring under anoxic condition are oxidised and dissolved as ions or complexed by dissolved organic compounds. These may be transported or re-adsorbed on more reactive solid surface sites such as freshly-precipitated iron hydroxides or biotic material Calmano et al [2].

Lake Håcklasjön (250 km SE of Stockholm, Sweden) is a shallow, eutrophic lake and has elevated concentrations of Zn, Cu, Cd, Fe and organic matter in the sediment profile Eklund and Håkansson [6]. The contaminated lake sediments reflect the serious metal pollution history of the area, where the lake continuously and for a long period received the discharges from one of the biggest smelters in Sweden during the 18th and 19th centuries. The lake has been the recipient for untreated, but later treated sewage from town Åtvidaberg. The lake is now used as a dam for hydropower purpose. During operation periods, the power plant discharges about 4 m$^3$/s into the lake, causing strong water currents in the lake, resulting in the oxidation and resuspension of the surface sediments. During non-operation periods and, thus, low water flows the lake becomes stagnant and anoxic conditions are likely developed.

The main objective of our study was to examine the possible effects of a redox cycle caused by the hydropower plant on the mobilisation of the redox-sensitive metal Fe and the heavy metals Zn, Cu and Cd. As a part of this study, two sediment layers (the top 6-cm and the deeper 8-12 cm) were each set up in experimental flow-cells, where anoxic and oxic conditions were in turn introduced. The parameters pH, inorganic carbon (IC) and dissolved organic carbon (DOC) and redox were monitored to assess their influences on the mobilisation of the target metals.

2 Materials and methods

2.1 Field sampling

Sediment cores were collected from lake Håcklasjön into acrylic cylinders in July 2005. The collected cores were sealed with 20-cm height of overlying water and rubber stoppers on top to avoid intrusion of air. Lake water was taken at ~1 m depth by a water sampler to a 15-l plastic carboy. All the samples were kept airtight and cool during transport to the laboratory. Upon arrival, the lake water and sediment samples were stored dark in a refrigerator at 4°C until they were treated and used.

2.2 Flow-cell design

Three-compartment flow-cells (l×w×h=36×11×11 cm, fig. 1), made of unstained polypropylene, were filled with sediment material in the middle compartment (22×6×11 cm). The two outer compartments functioned as reservoirs for an even flow of water above the sediments when used in circulation mode. Sediments were confined in the middle compartment (22×6×11 cm). A peristaltic pump was connected to each flow-cell via PVC tubing equipped with a Luer-lock joining
with a 60-ml syringe for collection of overlying water. Each flow-cell was sealed with an airtight lid, followed by silicone gluing at the conjunctions.

Figure 1: Schematic drawing of the flow-cell setup for the experiment. Platinum wires (1-4) and calomel reference electrode (5) connected to a standard pH-meter (PHM 83, Radiometer) were constructed and immersed in the overlying water (at 1-cm depth above the sediment surface) and in the sediments at 0.5-1, 1.5-2 and 3-3.5 cm.

2.3 Experimental procedure

The lake water was purged with N\textsubscript{2} gas (<1 ppm (v) O\textsubscript{2}, AirLiquide, Sweden) over night to decrease dissolved O\textsubscript{2} before the start of the anoxic incubation and a continuous N\textsubscript{2} gas flow (20 ml/min) was applied to the flow-cells cf. fig. 1 to employ anoxic conditions. The gaseous content of oxygen was regularly checked with an oxygen analyzer (Servomex 570 A) via the gas outlet and stayed <0.1% during the anoxic experiment. All sample preparations were carried out in a glove box flushed with N\textsubscript{2} gas resulting in <0.4% O\textsubscript{2}. The cells were incubated at 15\textdegree C in the dark. Construction for redox electrodes and measurements followed the procedure by Svensson and Rosswall [13].

Water standing above the sediment surface was siphoned off and the cores were sliced into: 0-0.5, 0.5-1.5, 1.5-2.5, 2.5-4, 4-6 and 8-12 cm sections. Slices from each level were lumped together in airtight N\textsubscript{2} pre-filled plastic containers, followed by homogenization under O\textsubscript{2}-free condition. The top sediment layers (0-6 cm) were transferred in depth-order into one cell, while the deeper mixed-layer (8-12 cm) was placed into another cell to give 6-cm height. The cells were then filled with de-oxygenated water to a height of 3-cm above the sediments and the lids were sealed to the cells. While being at anoxic stagnant conditions for 21 days, water samples (60 ml each) were withdrawn on 6 occasions: at 3 h and 1, 3, 4, 11 and 21 days. In order to mix the stagnant water before sampling, a slow recirculation (~50 ml/min) was applied for about 10 minutes in both cells. Thereafter, oxic conditions were applied to both flow-cells by exchanging the N\textsubscript{2}-flow for technical air (AirLiquide, Sweden). Simultaneously, water recirculation was applied in the two cells at a rate of ~1.4 l/min. Overlying water
samples were sampled at 6 occasions at 1, 2, 4, 6, 8 and 11 days after the aeration start. Before sampling, the pumps were stopped for 4-5 minutes to enable stable redox readings and to let the suspended particles settled. After withdrawal of overlying water, an equivalent volume of filtered-lake water (deoxygenated during the anoxic and oxygenated during the oxic periods, respectively) was supplied to the flow-cells to conserve the initial solid/liquid ratio.

2.4 Sample analysis

Total contents of Fe, Zn, Cu and Cd in the sediments were determined using ICP-OES (Al-Control Laboratories, Sweden) after digestion in aqua regia according to standard method [18]. Blanks using Milli-Q water and certified reference samples using PACS-2 (National Research Council, Canada) were prepared in the same way as the samples to evaluate the analytical procedures and the quality of the obtained data. The accuracy was within 15% of the certified concentrations for all elements of interest. The concentrations of target elements in the blanks were below the detection limits of the analytical technique used. The water contents and estimation of organic matter contents (LOI) in the sediments were determined following standard methods [16, 17].

As soon as collected, the overlying water was filtered through 0.4 µm polycarbonate filters (Millipore) to determine the concentrations of dissolved Fe, Zn, Cu and Cd, dissolved organic carbon (DOC) and inorganic carbon (IC). All samples for metal determinations were preserved with concentrated HNO₃ to pH <2 and stored dark at 4°C until analysis. The pH of the overlying water was determined using a pH-meter (PHM 83, Radiometer). Concentrations of IC and DOC were obtained using a TOC analyser (TOC-500, Shimazu). Concentrations of Fe and Zn were determined using flame atomic absorption spectrometry (AAS, Perkin Elmer 1100), whereas Cu and Cd were determined using AAS with furnace. Blanks were prepared and analysed in the same way as the samples to control the obtained data. The concentrations of the metals of interest in the blanks were below detection limits of the analytical technique used.

2.5 Statistical analysis

Pearson’s correlation coefficients (r) were calculated and used in the correlation analyses to check the relations between the target parameters, using SPSS 11.5 for Windows (SPSS Inc., USA). The correlations were considered to be statistical significant at \( r \geq 0.7 \) at the set \( p \leq 0.05 \) level, using a 2-tailed test with \( n=6 \).

3 Results and discussion

The original sediments showed lower pH-levels with depths (from pH 7.1 to 6.8, table 1) and the metal concentrations of Zn, Cd and Cu were high \( i.e \) class 4 to very high \( i.e \) class 5 according to the 5-level scale classified by Swedish
The water content and organic matter content (LOI) of the sediments decreased slightly with depths, table 1.

The lake water shows high pH (pH 8.9), which is probably induced by the photosynthesis or chemosynthesis of aquatic plants during the sampling occasion in July Mayer et al [8]. This eutrophic lake Håcklasjön’s water shows high concentration of DOC, about 2- to 6-fold more elevated than the average DOC concentrations in eutrophic lakes Drever [4]. The concentrations of Cd, Zn and Cu in the lake water were moderately high, falling into class 3 on the 5-level scale classified by Swedish Environmental Protection Agency [15].

Table 1: Physio-chemical compositions of the original samples used in the experiment. The metal contents in the sediments were calculated on dry weight basis.

<table>
<thead>
<tr>
<th>Filtered lake water</th>
<th>pH</th>
<th>IC (mg/l)</th>
<th>DOC (mg/l)</th>
<th>Fe (µg/l)</th>
<th>Zn (µg/l)</th>
<th>Cu (µg/l)</th>
<th>Cd (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.9</td>
<td>10</td>
<td>12</td>
<td>380</td>
<td>42</td>
<td>6</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sediments</th>
<th>Depth (cm)</th>
<th>pH</th>
<th>Water cont. (%)</th>
<th>LOI (%)</th>
<th>Fe (µg/g)</th>
<th>Zn (µg/g)</th>
<th>Cu (µg/g)</th>
<th>Cd (µg/g)</th>
<th>S (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.5</td>
<td>7.1</td>
<td>82</td>
<td>33</td>
<td>44900</td>
<td>3930</td>
<td>640</td>
<td>17</td>
<td>21800</td>
<td></td>
</tr>
<tr>
<td>0.5-1.5</td>
<td>7.0</td>
<td>82</td>
<td>32</td>
<td>43500</td>
<td>2560</td>
<td>630</td>
<td>9</td>
<td>20600</td>
<td></td>
</tr>
<tr>
<td>1.5-2.5</td>
<td>6.9</td>
<td>80</td>
<td>32</td>
<td>44600</td>
<td>3850</td>
<td>690</td>
<td>16</td>
<td>22000</td>
<td></td>
</tr>
<tr>
<td>2.5-4</td>
<td>6.8</td>
<td>80</td>
<td>32</td>
<td>42200</td>
<td>4210</td>
<td>720</td>
<td>30</td>
<td>21200</td>
<td></td>
</tr>
<tr>
<td>4-6</td>
<td>6.8</td>
<td>81</td>
<td>32</td>
<td>45300</td>
<td>4280</td>
<td>730</td>
<td>20</td>
<td>24600</td>
<td></td>
</tr>
<tr>
<td>8-12</td>
<td>7.1</td>
<td>79</td>
<td>30</td>
<td>48100</td>
<td>5560</td>
<td>1220</td>
<td>29</td>
<td>29600</td>
<td></td>
</tr>
</tbody>
</table>

The results of the experiment are presented in fig. 2 and fig. 3. During 21 days of the anoxic stagnant incubation, the pH-pattern was similar for both sediment layers, fig. 2. However, once shifted to oxic conditions, the pH for the top layer decreased from 7.6 to 6.9, suggesting that oxidation of sulphides occurred, whereas the pH for the deeper layer increased from 7.5 to 8.

During the anoxic event, the concentrations of IC gradually increased from ~8 to ~20 mg/l in both sediment layers, fig. 2, suggesting that a decomposition of organic matter or a dissolution of carbonate minerals occurred. In contrast, the IC concentrations rapidly dropped from 18 to 4 mg/l for the top layer and from 20 to 9 mg/l for the deeper layer during the first two days after air introduction to remain stable for the rest of the experiment, fig. 2.

As for IC, the concentration of DOC for both layers gradually increased during the anoxic incubation, fig. 2, indicating that anaerobic degradation of organic matter was likely occurred in the sediments, cf. Salomons [10]. The concentrations of DOC rapidly decreased upon the initiation i.e. within the first 2 days of aeration.
Figure 2: Evolution of pH, inorganic carbon (IC) and dissolved organic carbon (DOC) in solution during the experiment. Solid lines represent the top layer and dashed lines represent the deeper layer.

The Eh values were unfortunately not recorded during the anoxic period and the first sampling during the oxic conditions. However, after one day of aeration, the Eh value of the overlying water was recorded at +420 mV and remained stable between +410 and +480 mV during the rest of the oxidation, table 2. The Eh values of three sediment depths (0.5-1, 1.5-2 and 3-3.5 cm) showed a gradual increase from day 2 to day 8 after when they stabilised. Thus, the Eh readings showed that the sediment profiles were gradually oxidised after the introduction of air.

Table 2: Redox measurements (in mV) of overlying water and sediments during the oxidation period in the top 6-cm sediment layer.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Overlying water</th>
<th>Sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day 1</td>
<td>Day 2</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>420</td>
</tr>
<tr>
<td>0.5-1</td>
<td>-</td>
<td>150</td>
</tr>
<tr>
<td>1.5-2</td>
<td>-</td>
<td>-150</td>
</tr>
<tr>
<td>3-3.5</td>
<td>-</td>
<td>-350</td>
</tr>
</tbody>
</table>
3.1 Evolution of iron

Similar dissolved concentration patterns of increasing Fe were observed for both sediment layers, fig. 3. Within 21 days of anoxic incubation, the Fe concentrations gradually increased ~7- and 5-fold for the top and deep sediments, respectively. It is likely that a reductive dissolution of Fe oxides/hydroxides in the particulate phase occurred in both layers cf. Mitsch and Gosselink [9]. Also, in the presence of organic matter, ferric Fe could be removed by reductive reactions cf. Salomons and Förstner [11], which, thus, may be part of the picture in our experiment. This is supported by the correlation ($r=0.80$) found for the simultaneous increase in the Fe- and DOC-concentrations for both sediment layers. The changes in pH (pH 7.2-7.7 in the top and pH 7.2-8.3 in the deeper layers) did not seem to affect the release of Fe during the anoxic incubation, c.f. fig. 2 and fig. 3.

In contrast, Fe of both sediment layers (the top and the deeper) was rapidly removed from the solution within 11 days of the aeration, fig. 3. The dissolved Fe concentrations decreased ~16-fold in the top layer and ~22-fold in the deeper layer. Iron in solution is known to form a particulate phase through the oxidation reactions or the bacteria activities in presence of O$_2$ cf. Sunby et al [14].

Figure 3: Evolution of Fe, Zn, Cu and Cd in solution during the experiment. Solid lines represent the top layer and dashed lines represent the deeper layer.
However, opposite result was found in the laboratory investigations conducted by Saulnier and Mucci [12], who observed an outflux of Fe when Fe monosulphides were oxidised. Nevertheless, within a matter of days, Fe in their studies was rapidly removed from the solution, probably due to depletion of Fe monosulphides occurring in parallel with the fast oxidation of ferrous Fe through contact with O₂.

3.2 Evolution of zinc, copper and cadmium

Under the anoxic condition, Zn, Cu and Cd behaved differently to Fe, i.e. they were generally low, fig. 3. Zinc ranged ~10 and ~30 µg/l and ~15 and ~70 µg/l for the top and the deeper layers, respectively. The corresponding ranges for Cu were ~2 to 10 µg/l and ~6 and ~14 µg/l, and for Cd ~0.04 to ~0.1 µg/l and ~0.05 to ~0.2 µg/l. It is known that the formation of sulphide metals such as ZnS, Cu₂S and CdS probably occur in the presence of sulphur in the anoxic systems cf. Salomons and Förstner [11]. This is consistent with our finding as our sediment layers contain high S contents cf. table 1, which may govern the precipitation of the freshly-formed metal sulphides. The pH range (pH 7.2-8.3) within the anoxic conditions in both the top and the deeper layers seems not influence the removal of Zn, Cu and Cd from the solution to the particulate phase, fig. 2 and fig. 3.

In opposite, the concentrations of Zn, Cu and Cd for both the top and deeper layers increased throughout 11 days of the aeration, fig. 3. For the top layer, the dissolved metal concentrations rapidly increased ~6-fold for Cu and ~16-fold for Cd, whereas a progressive increase up to 60-fold was observed for Zn. The same pattern was observed for the deeper layer but at a lower extent, i.e. 2-fold increase for Cu, 5-fold for Cd and 17-fold for Zn. This is in agreement with Caetano et al [1], who observed a release of the sorbed-Cd and -Cu on Fe sulphides upon oxidation of these sulphides. In another study on re-oxidation of anoxic sediments, Fajtl et al [7] recorded a flux of Zn in the water phase as a result of the oxidation of Zn sulphides or its desorption from organic/mineral sorption sites during oxidation. On the other hand, Dutrizac and MacDonald [5] found that ferric iron resulting from the oxidation of ferrous Fe is a powerful oxidising agent. The agent can attack most of metal sulphides like ZnS, Cu₂S and CdS in the presence of bacteria and, as a consequence, the metals Zn, Cu and Cd were generated to the solution. Our experimental results agreed with their findings.

According to the correlation analyses, the pH decrease (from 7.5 to 6.9) in the top layer may have affected the release of Zn (r=-0.72), Cu (r=-0.91) and Cd (r=-0.76). No correlation was found between the pH and the dissolved metal concentrations for the deeper layer. The rapid release of Zn, Cu and Cd from both sediment layers is also likely enhanced by the water flow, which may have increased the diffusion rate of O₂ into the sediment depths as indicated by the evolution of redox conditions in the top layer, table 2. As soon as the sediments were in contact with O₂, the oxidation reactions occurred and the sediment pore-water become the medium for exchanging the resultant released ions from the sediment phase to the water phase cf. Saulnier and Mucci [12].
References


