

CHANGE IN PH AND RELEASE OF HEAVY METALS IN THE POLLUTED SEDIMENTS OF HAMBURG-HARBOUR AND THE DOWNSTREAM ELBE DURING OXIDATION

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ABSTRACT

Change in pH in a sediment-water system and its influence on release of Cu, Zn, Pb and Cd during the suspension of polluted sediments collected from Hamburg-Harbour and the downstream Elbe have been investigated. Heavy metals were released significantly from the anoxic polluted sediment with changes in pH and redox state. During the resuspension at stable pH (7.5) heavy metals in bottom sediment of the river Elbe were released slowly into the solution.

INTRODUCTION

Many investigations have shown that the sediments of the downstream Elbe have been seriously polluted by heavy metals and other pollutants during the last several decades (ref 1-3). The sediments of Hamburg-Harbour which is situated at the downstream Elbe is being dredged because of the needs of shipping. It results in 2 million m³ of dredged material per year (about 0.8 million m³ of sand and approximately 1.2 million m³ of contaminated harbour mud) (ref 4). The secondary pollution problem originating from the polluted sediments is concerned, whether metals bond in the sediments or adsorbed on solid surface of the sediments can be released into solution or transform into more bioavailable forms after the polluted sediments expose to atmosphere. In this work, change in pH caused by oxidation and its effects on the release of Cu, Zn, Pb and Cd in the polluted sediment of Hamburg-Harbour have been investigated. During a resuspension process under a stable pH condition release of Pb and Cd in the sediment collected from the downstream Elbe has been also observed.

MATERIALS AND METHODS

The first original sediment sample with a pH value of 6.43, no carbonate reaction and a low Eh value (-289 mV) was collected from Harburg section at Hamburg-Harbour. The sample was divided into 3 groups. The first group was fresh sample without any additional treatment. Natural water collected from Hamburg-Harbour or distilled water (1500 ml) was added to a subsample of 150 grams sediment (dry weight). Air was continuously pumped into the suspension according to the method of Charoenchamratchee (ref 5). The sediment was fully stirred with a magnetic stirrer. Redox potential and pH value were monitored at regular intervals. The experiment was carried out under dark condition. After the suspension was sampled, centrifuged and filtered with 0.45 µm membrane at regular intervals, the filtrates were acidified to pH 2 with concentrated nitric acid.

The second group was the subsample with artificial pollution at laboratory. The contents of Cd, Cu, Zn and Pb added to the sediment were 40, 200, 400 and 400 mg.kg⁻¹ in dry weight, respectively. The treated subsample was stirred for 1 hour and then stored under dark condition. After 30 days the subsample was treated and oxidised as the same as the first group.

The third group was the fractional polluted subsample which was smaller than 60 µm. The sediment was dried with the use of vacuum technique. After the sediment was sieved, heavy metals were added to the subsample < 60 µm. The pollution treatment was the same as before. The suspension was fixed at different pH values at oxidation stage or reduction stage. HCl and NaOH solutions were used to control the pH of the system. pH value in each stage was fixed for one week. At the beginning of the reduction stage nitrogen gas was pumped into the system. Redox potential was controlled lower than 100 mV at the reduction stage and higher than 450 mV at the oxidation

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stage, the treatment during the oxidation was the same as other two groups. To maintain a low redox potential glucose was added into the system at the reduction stage. Metals were analysed by the use of AAS techniques both flame and graphite furnace.

The second sediment was collected from Mühlenberger Loch where is situated at the downstream Elbe near Hamburg. The anoxic sediment at the depth 7-10 cm was moved into a 180 ml reaction-cell. 2 ml of non-complex buffer HEPES (2-[4-(2-hydroxyethyl)-1-piperasino]-ethansulfonic acid (Aldrich)) with a pH of 7.5 and 128 ml of artificial river water (2 mmol.l⁻¹ CaCl₂ and 5 mmol.l⁻¹ NaCl) were added into the reaction-cell. The ratio of solid to liquid in the suspension was about 1:50. Heavy metals were directly measured in the reaction-cell by DPASV/HMDE using a Metrohm VA646 Processor and VA663 electrode. This measurement system avoided any contamination from additional treatment. Stirring and oxygen pumping were controlled through the VA646 Processor connecting an additional device Drive Unite. pH was automatically adjusted with 0.1N NaOH or 0.1N HCl by a monitoring and adding solution system connecting with a Drive Unite.

RESULTS AND DISCUSSION

Change in pH

During the oxidation for 30 days pH value of the suspension decreased gradually from about 7 to about 3.4 (Fig. 1). The first and the second groups of the experiment showed this similar tendency. Charoenchamratcheep *et al.* found that pH in 4 groups of the suspension decreased 1 to 3 units after oxidation for 35 days (ref 5). The studies of Calmano showed that the oxidation of some sediments resulted in decrease for several units of pH in the system (ref 6). These results suggest that acidification of a suspension may occur when anoxic sediment with low buffer capacity exposes to atmosphere and undergoes continuous oxidation.

Compounds containing Fe, N and S in lower oxidation states in sediment are ultimately oxidised to Fe³⁺, NO₃⁻ and SO₄²⁻, thereby releasing equivalent amounts of hydrogen ions into the environment. Acid-producing coefficient of compounds has been developed and used to assess their acid producing potential (ref 7,8). APP_{-apparent} (apparent acid producing potential) indicates how many hydrogen ions per unit weight sediment contribute to the change in pH after overcoming acid neutralising capacity. The APP_{-apparent} of the several samples are between 3.89 and 6.16 mmol.kg⁻¹.

Release of heavy metals during the oxidation

Oxidation of both the original sediment and the treated sediment led to release of heavy metals

Table 1 Release concentrations of metals at the end of the oxidation (mg.kg⁻¹)

	Original sample				Treated sample			
	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
Total content*	309.0	775.0	412.0	5.50	496.0	1162.0	753.0	38.0
Release Concentration	20.9	191.0	6.5	1.96	41.1	335.0	15.5	11.6
Release percentage(%)	6.8	24.6	1.6	35.6	8.3	28.8	2.1	30.5

* Not including metal content in residual fraction (ref 9).

(Fig.2, 3). The release of Zn and Cd was rather quickly. On the third day it had reached a very high level. Contrary, the release of Pb and Cu was slow (Fig.2). Release concentrations of heavy metals at the end of the 30-day-oxidation are listed in Table 1. The order of metal release percentage is as follows: Cd (35.6%) > Zn (24.5%) > Cu (6.8%) > Pb (1.6%). The release of Cd could reached 35.6% of total content (not including metal content in residual fraction); while for Pb it was only 1.6% under the same oxidation condition.

It is undoubted that release of metals in sediment is accompanied with decrease in pH. The results showed that the concentration of heavy metals in the suspension responded to the change in pH

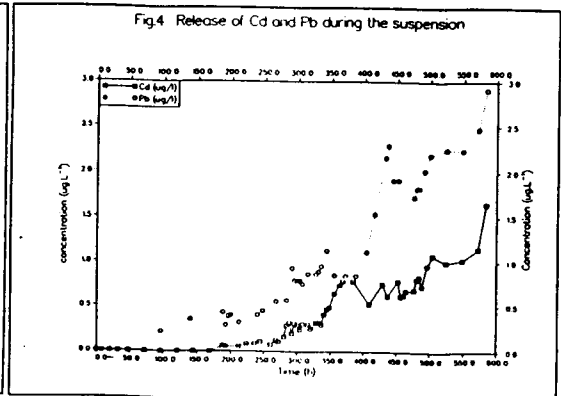
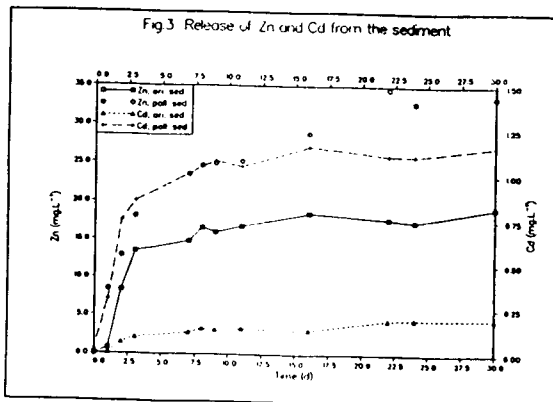
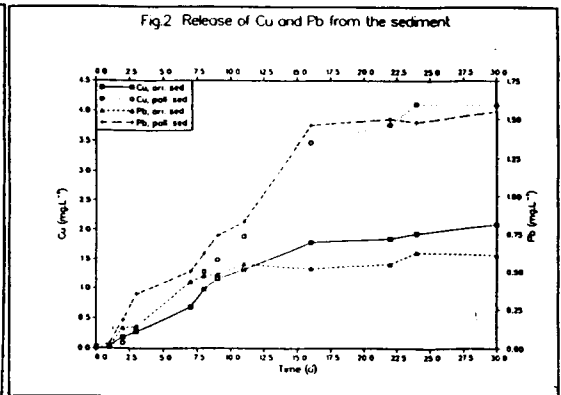
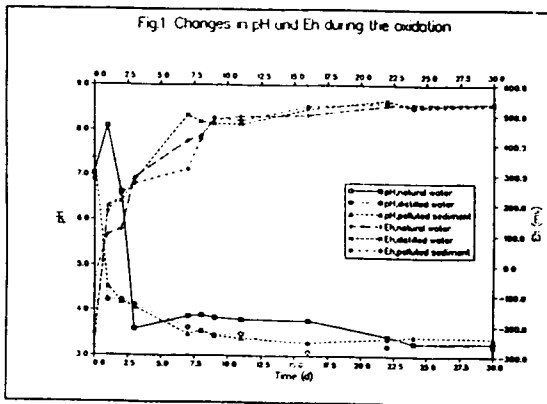
(Fig.1-3). The acidification of the suspension caused by the oxidation led to the release of heavy metals in the sediment samples.

Effects of pH on metal release under different redox states

In order to assess the decline in pH on release of heavy metals in the sediment, the results from the third group have been listed in Table 2. Under the same pH condition the metals was released with higher concentration from the sediment at the oxidation stage than that at the reduction stage. If pH of the system is greater than 4.5, redox state will pay an important role in metal release. When pH of the system decreased down 4.5 or lower, release of metals in the sediment at both the reduction stage and the oxidation stage will increase significantly.

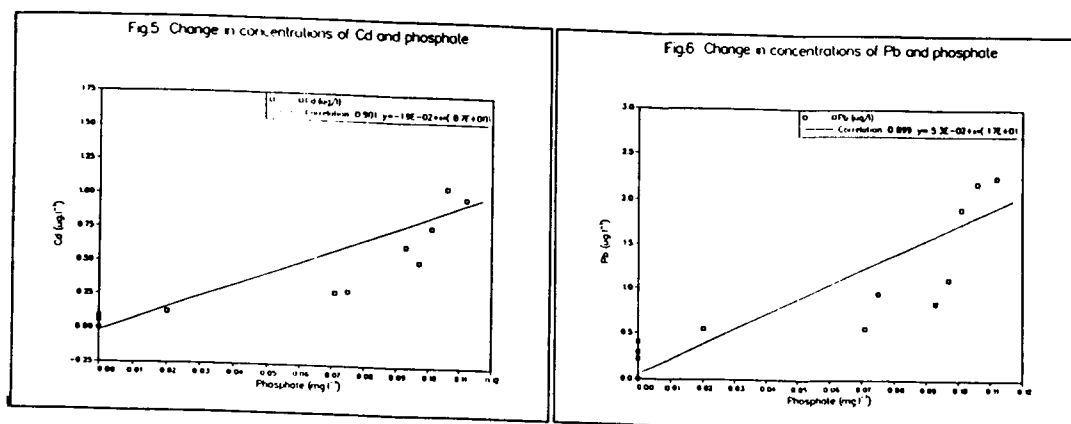
Table 2 Release of metals from the sediment at different pH values (mg.kg⁻¹)

pH	Reduction stage				Oxidation stage			
	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
6.0	<1	2.2	0.04	0.3	1.2	7.1	0.05	0.41
5.5	<1	6.2	.05	0.5	3.1	18.3	0.06	0.88
5.0	<1	18.9	.06	0.78	4.6	39	0.08	1.75
4.5	2.6	31.0	1.1	0.98	8.9	77	2.20	2.15
4.0	2.7	55	2.1	2.44	19.0	114	8.80	7.85
3.5	3.1	89	3.2	5.07	32.5	186	10.5	10.45
3.0	9.8	170	3.9	15.17	99.8	385	30.3	27.10



Metal release during the resuspension under stable pH condition

During the resuspension release of Cd and Pb from the sediment at pH 7.5 which is a normal value in the Elbe waters has been shown in Fig.4. No Cd²⁺ could be found in the solution until about the 180th hour during the suspension. From the 200th hour release of Cd increased quickly. At the end of the experiment Cd release from the sediment reached 87 $\mu\text{g.kg}^{-1}$. Pb release was also very limited during the first 200 hours. Similar to Cd from about the 200th hour Pb release increased rapidly. A relationship between metals and phosphate was observed and shown in Fig.5 and Fig.6. The resulting metal-PO₄ correlations were 2.4×10^{-3} mol Cd/mol PO₄ ($r = 0.901$) and 2.54×10^{-3} mol Pb/mol PO₄ ($r = 0.899$). Cd-PO₄ relationship was also found in some lake water and seawater samples (ref 10,11). The origin of the increase in PO₄ and metals is probably due to decomposition of organic matter containing metals or mineralisation of biological particle in the suspension. Prause *et al.* observed that after adding antibiotics to a suspension the release of Cd was interrupted (ref 12). These results suggest that the metals had participated in the cycle of biogeochemistry and their release was also influenced by microbiological process in the suspension.



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