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# Impact of anions on the heavy metals release from marine sediments

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**Abstract:** Marine sediments from Lianshan Bay in Huludao, China, were studied in laboratory. A series of simulated experiments were carried out to investigate the influences of three kinds of anions $Cl^-$, $SO_4^{2-}$ and $HCO_3^-$ on the release of Cd, Pb, Cu and Zn from the sediments. The results showed that the sequences about the impact of the three anions were $Cl^- > HCO_3^- > SO_4^{2-}$. The release potential of heavy metals in the presence of each anions was in the following order: Cd≫Cu>Zn≈Pb. The correlations were positive between $Cl^-$ content and the quantity of Cd released from the marine sediment, whereas there was no significant relationship between $Cl^-$ content and amount of Cu and Zn released. For $SO_4^{2-}$ and $HCO_3^-$, the release of the heavy metals from marine sediments was not obvious.

**Keywords:** marine sediments; anions; heavy metals; release

## Introduction

Heavy metal pollutants in the water usually transfer into sediments by physical, chemical and biological processes including ion-exchanging, precipitation, adsorption, hydrolyzation, complexation, flocculation and so on. When environmental conditions change as salinity, acidity, redox potential etc., heavy metals would be released from sediment to aqueous phase and lead to secondary pollution. So sediments could act both as sinks and sources of supplying for the elements to overlying water columns.

In offing or bay area, heavy metal concentrations in sediments are relatively high because they usually accommodate abundant heavy metal pollutants discharged from land pollution resources. So secondary pollution of heavy metal contaminated-sediments in these areas would cause severe danger to the environment and bring high ecological risk. So far, many researches have been reported about the distribution of main polluted elements in water columns and sediments along the offing areas (Goh and Chou, 1997; Willians *et al.*, 1999; Andrate *et al.*, 2001). Whereas investigation about transportation and transformation is less (Delavne and Smith, 1985; James, 1997), most of which focused on the impact of various environmental conditions on heavy metals release from sediments, for example, salinity, acidity and redox potential and so on. (Liao and Chen, 1994; Petersen *et al.*, 1997). Few studies were carried out about the effect of anions in seawater e.g. chlorid ion ($Cl^-$), sulfate ion ($SO_4^{2-}$), bicarbonate ion ($HCO_3^-$) on heavy metal release from sediments (Kazuo, 2005).

Lianshan Bay belongs to the Liaodong Gulf, and lies to Huludao City, China, in which the sediments are seriously contaminated by the heavy metal pollutants from industrial discharge including cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), mercury (Hg) and arsenic (As) (SOAC, 1984). According to the historical data (Peng *et al.*, 1981), an abundance of heavy metals has been discharged into the bay every year since 1951. The maximum amount discharged reached 3697 t of Zn, 102 t of Cd, 189 t of Pb and 286 t of Cu every year. Although the discharge amount decreased since 1980s, the bay has become one of the typical cases of heavy metals contamination in the world because of the long-term accumulation.

This work used the marine sediments from Lianshan Bay of Huludao City, Liaoning Province, China, and carried out a series of experiments in laboratory to investigate the influences of three kinds of anions $Cl^-$, $SO_4^{2-}$ and $HCO_3^-$ on the release of Cd, Pb, Cu and Zn from sediments. This study would provide some theoretical basis for ecological risk evaluation and environmental management.

## 1 Materials and methods

### 1.1 Sample collection and handling

Marine sediments were collected in Lianshan Bay (40°44′08.7″N and 120°59′01.4″E), Huludao City, northeast China. According to Peng *et al.* (1981), Cd and Zn were the main heavy metal pollutants in Lianshan Bay. Marine sediments were taken using plastic apparatus and stored in polyethylene sample bottles. Prior to collection, plastic apparatus and polyethylene sample bottles were pre-cleaned with detergent, soaked for 24 h in soap solution, acid washed for 24 h in 5% $HNO_3$ (68%), and rinsed by distilled-deionized water ($ddH_2O$). The samples were dried in air after eliminating impurity, including massive grits, shells and so on. Air-dried sample was ground in an agate mortar and passed through a 160-mesh nylon sieve (nominal sieve opening of 97 μm), then stored in vacuum airer at room temperature.

### 1.2 Sediments analysis

1.0000 g dry weight samples ($n$=4) were accurately weighed in beakers and digested with 12 ml of concentrated $HNO_3$ (68%)/$HClO_4$ (72%) (3:1). The samples were let in contact with the acid solution

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overnight before digesting. The concentration of each heavy metal was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (PE OPTIMA 3000, USA) in the Testing Laboratory of Institute of Applied Ecology, Chinese Academy of Sciences.

The organic matter was determined by heating the dried samples in a muffle furnace at 450℃ for 8 h.

The speciation distribution of each heavy metal was determined by five steps of sequential extraction (Tessler *et al.*, 1979).

### 1.3 Experimental design

Seawater contains many kinds of anions in which $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ are the major. Usually in the seawater the alleged $SO_4^{2-}$ is mainly exist in the forms of $SO_4^{2-}$, $NaSO_4^-$ , and the alleged $HCO_3^-$ is mainly $HCO_3^-$, $CO_3^-$, $CO_2$. When the value of salinity is 35‰, the concentrations of $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ in the seawater are 19350, 2712 and 142 mg/L respectively (Chinese Encyclopaedia). Contents of each anions in simulating experiment were designed from 0 mg/L to the concentrations in the natural seawater. The zero concentration is control experiment. Ions in the simulated solution were all simplified in the forms of $Cl^-$, $SO_4^{2-}$, $HCO_3^-$, which was convenient to control in the laboratory experiment.

#### 1.3.1 Effect of $Cl^-$ on the release of heavy metals

2.5000 g dry weight samples ($n$=6)were immersed in 50 ml NaCl and $NaNO_3$ solution in centrifugal tubes. The concentration of $Cl^-$ was 0 mg/L (0 mol/L), 710 mg/L (0.02 mol/L), 5325 mg/L (0.15 mol/L), 10650 mg/L (0.30 mol/L), 15975 mg/L (0.45 mol/L) and 19170 mg/L (0.54 mol/L) respectively. The concentration of $Na^+$ was 0 mg/L (0 mol/L), 460 mg/L (0.02 mol/L), 3450 mg/L (0.15 mol/L), 6900 mg/L (0.30 mol/L), 10350 mg/L (0.45 mol/L) and 12420 mg/L (0.54 mol/L) respectively. Three samples of each treatment were kept still for 24 h, while the other three were agitated continuously for 24 h. The solid and liquid were separated by centrifuge at 4000 r/min. The concentrations of Cd, Cu, Zn and Pb were determined by ICP-AES after being acidified by $HNO_3$ (68%).

#### 1.3.2 Effect of $SO_4^{2-}$ and $HCO_3^-$ on the release of heavy metals

The method was the same as Section 1.3.1. The concentration of $SO_4^{2-}$ was 0 mg/L, 500 mg/L, 1000 mg/L, 1500 mg/L, 2000 mg/L and 2700 mg/L respectively. The concentration of $HCO_3^-$ was 0, 30, 60, 90, 120 and 142 mg/L respectively.

## 2 Results and discussion

### 2.1 Characteristics of the sediments

Heavy metal in sediments come from natural as well as anthropogenic source. Naturally occurring metals come from rock weathering, soil erosion, and the dissolution of salts (Huang *et al.*, 2006). Anthropogenic sources of Lianshan Bay metals come mainly from the metallurgical industry pollution.

The concentration of major heavy metals Cd, Cu, Pb and Zn in sediment samples were 204 mg/L, 282 mg/L, 501 mg/L and 4167 mg/L respectively. While according to the assessment standard for sediments, concentrations of Cd, Cu, Pb and Zn in sediments were 0.5 mg/L, 30 mg/L, 80 mg/L, 25 mg/L respectively (Li *et al.*, 2005).

The organic matter content in sediments was 2.46% which was higher than usual values. This would be the cause of the relatively higher concentrations of heavy metals accumulated in the sediments.

The speciation distribution of each heavy metals are shown in Table 1. The values of exchangeable fraction indicated that Cd was the most active element and prone to vary with the change of environment condition. Compared with the values, the speciation of Cu and Pb were relatively safe which were mainly bound to Fe, Mn oxides and bound to organic matter and sulfides. Whereas, Zn bound to carbonates and Fe, Mn oxides were major fraction.

**Table 1 Speciation distribution of heavy metals**

| Fractions | Cd, mg/L | Zn, mg/L | Cu, mg/L | Pb, mg/L |
|---|---|---|---|---|
| Exchangeable | 154.64 | 98.04 | 3.06 | 0.60 |
| Bound to carbonates | 29.02 | 1093.35 | 3.04 | 46.66 |
| Bound to Fe, Mn oxides | 7.68 | 2957.84 | 1.30 | 235.70 |
| Bound to organic matter and sulfides | 6.32 | 430.88 | 217.65 | 46.48 |
| Residual | 1.62 | 171.29 | 38.06 | 80.48 |

### 2.2 Factors influencing heavy metal release

Researchers (Ke, 1991; Lindstrom *et al.*, 2001) found that the concentrations of Pb, Cu, Zn in the water column gradually decreased from mainland to coastal area, but Cd behaved in an opposite way (Huang *et al.*, 2001; Massoud *et al.*, 2002). The reason of the trend may rest with the gradually increasing quantity of ions in the aqueous phase which could be measured as salinity. Along mainland to coastal area, heavy metals in the sediment were susceptible to the variety of salinity and could be frequently shifted at the water/sediment interface.

#### 2.2.1 Effect of $Cl^-$ on the release of heavy metals

It is commonly considered that Cd could exist by formation of complexes with chlorine in the sea. So the abundance of $Cl^-$ could accelerate the release of Cd from sediments (Chen *et al.*, 2001). Few investigations have been done on the relationship between amount of Cd released from sediments and $Cl^-$ content in the water. And it is still not clear whether it impacts on the release of other heavy metals such as Zn, Cu and Pb. Thus, series of $Cl^-$ content with NaCl were designed to investigate the release of Cd, Zn, Cu and Pb. Contrast experiment was carried out with $NaNO_3$

to detect whether the $Na^+$ affect the release. Results are shown in Fig.1.

There was no curve for Pb in the figure as Pb concentration was undetectable in the solution. The reason may be due to its speciation distribution and the distribution coefficient between the sediment and the water column. According to Ye (1990), the distribution coefficient of Pb was almolst ten times higher than that of Cu, Cd and Zn, and the exchange potential of Pb was also less than that of the other three heavy metals. Otherwise, in the sediment we used, exchangeable fraction of Pb was just 0.60 mg/L which also restricted the release (Table 1). Whereas, the fact of undetectable Pb indicates that $Cl^-$ ions hardly affect Pb release from sediment.

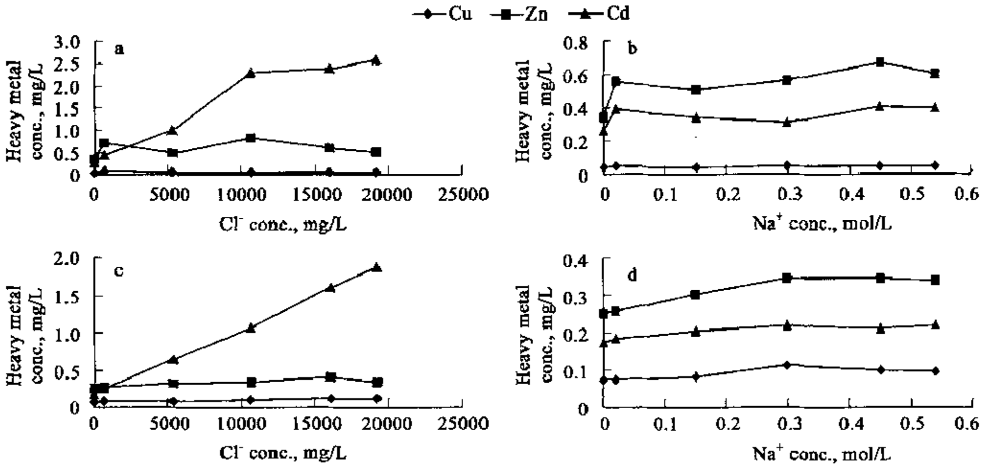


Fig.1 The impact of $Cl^-$ on the release of heavy metals
a. NaCl, stillness; b. $NaNO_3$, stillness; c. NaCl, agitation; d. $NaNO_3$, agitation

For $NaNO_3$, heavy metal concentrations in the water are almost constant with $Na^+$ increasing. In the state of stillness, concentrations of Cd, Zn and Cu in the water were within the range of 0.26—0.39 mg/L, 0.35—0.61 mg/L and 0.04—0.05 mg/L respectively (Fig.1b). In the state of agitation, the concentrations were within the range of 0.17—0.22 mg/L, 0.25—0.34 mg/L and 0.07—0.09 mg/L respectively (Fig.1d). The values show that $Na^+$ play little role in the release of Cd, Cu and Zn from the sediments. Then, heavy metal content released into solution of NaCl could be considered mainly for the presence of $Cl^-$ ions.

The results showed that the amount of Cd released from the sediment increased with $Cl^-$ content in the water increasing (Figs.1a and 1c). Especially, in the state of agitation, concentration of Cd in the solution is almost linear increase as the $Cl^-$ content increasing. But for the release of Cu and Zn, the correlativity with the $Cl^-$ concentration was not obvious. In the state of stillness, the concentrations of Cd, Zn and Cu in the solutions were within the range of 0.26—2.58 mg/L, 0.35—0.83 mg/L and 0.04—0.09 mg/L respectively. And when being in the state of agitation, the concen- trations of Cd, Zn and Cu in water were within the range of 0.17—1.88 mg/L, 0.25—0.41 mg/L and 0.07—0.12 mg/L respectively. The content of Cd released into the water is much higher than Cu and Zn at the same condition when $Cl^-$ concentration was more than 700 mg/L. Values of the maximum release concentration indicated that Cd release from the sediment was much more intense.

The result illuminates that the marine sediment accumulated with Cd was prone to form secondary pollution in seawater. Comparison of the values of the four heavy metals released from the marine sediment shows that Cd has the highest ecological risk. So it is not appropriate to discharge the waste containing Cd into the sea area.

#### 2.2.2 Effect of $SO_4^{2-}$ on the release of heavy metals

Sulfate ions are major anions in seawater. Furthermore, a large amount of waste containing sulphide was introduced into the Lianshan Bay every year, which would lead to variation of the $SO_4^{2-}$ content in the seawater. Hence it makes sense to study the impact of the $SO_4^{2-}$ on heavy metals release from marine sediments. The simulating experiments using $Na_2SO_4$ in the state of stillness and agitation were carried out to investigate the influence of the $SO_4^{2-}$ on the heavy metal release under different conditions. The contents of Cd, Zn, Cu and Pb released are showen in Fig.2.

Either in the state of stillness or agitation, the amount of Cd and Zn released into the water was larger than Cu and Pb. While the release trends in the two states were different. In the state of stillness, each metal released into the water fluctuates as the $SO_4^{2-}$ increasing. While in the state of agitation, except Pb, other metal concentrations in the water increased to a certain extent as the $SO_4^{2-}$ increasing. As a whole, the impact of $SO_4^{2-}$ is not significant on the four heavy metals release from the sediment.

#### 2.2.3 Effect of $HCO_3^-$ on the release of heavy

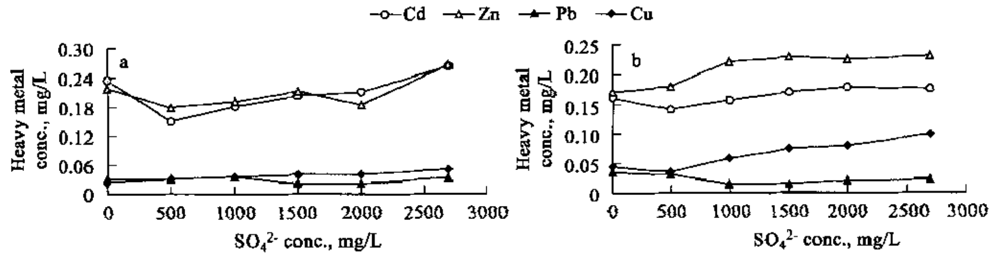


Fig.2 Impact of $SO_4^{2-}$ on the release of heavy metals
a. stillness; b. agitation

**metals**

In seawater $HCO_3^-$ content is relatively high among the anions. It is also a relatively special ion for its speciation in the seawater. Although it is measured in the form of $HCO_3^-$, the main speciation existing in the seawater is $HCO_3^-$, $CO_3^{2-}$ and $CO_2$. Theoretically, when $HCO_3^-$ prevails in the seawater, heavy metals accumulated in marine sediments are prone to form soluble complexes with $HCO_3^-$, which leads to the release of the heavy metals from the sediments. While the dominating species is $CO_3^{2-}$, the heavy metals tend to form insoluble carbonate salts. This process could wipe off the heavy metals from the seawater to reduce the pollution of the seawater to some extent. It is necessary to make clear whether $HCO_3^-$ affects the heavy metal release, and to what extent when it really impacts the release. Fig.3 shows the release of heavy metals from the sediments.

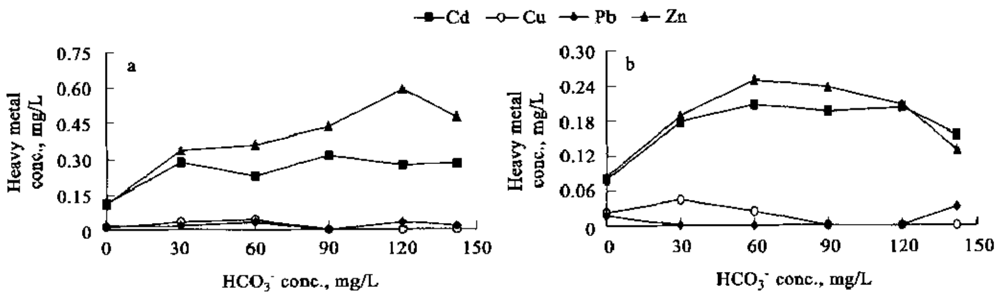


Fig.3 Impact of $HCO_3^-$ on the release of heavy metals
a. stillness; b. agitation

The release of Cd, Zn, Cu and Pb from the marine sediments occurred to a certain extent in the solution of $NaHCO_3$. Comparing with the amounts released into the water, they are following the order: Zn > Cd > Cu ≈ Pb both in the state of stillness and agitation. While compared with the release trends between stillness and agitation, there are very different between Cd and Zn release. In the state of stillness, Cd and Zn concentrations in the water increased as the $HCO_3^-$ content increasing, while in the state of agitation, concentrations of Cd and Zn in the water firstly increased then decreased as the $HCO_3^-$ content increasing. The difference may be caused by the equilibrium transition for the agitation.

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

For agitation could accelerates the reaction rate, when $HCO_3^-$ concentration was more than 90 mg/L, the $CO_3^{2-}$ content gradually increases, and part of metals released into the water deposited again, which lead to the content of Cd and Zn decrease in the water.

### 2.3 Influence of the three anions on the release rate of heavy metals

In different solution each heavy metal was released from marine sediments to some extent. But heavy metal concentrations released into the aqueous phase could not totally explain the release capacity for the variable contents accumulated in the marine sediments. Then the release rate of each heavy metal was calculated as a measurement to access the release potential under different conditions.

$$r = \frac{c_1 v}{m c_2}$$

Where $r$ is the release rate, $c_1$ is the heavy metal concentration in water, $v$ is the water volume, $m$ is the mass of sediment, $c_2$ is the heavy metal content in sediment. Release rate values are listed in Table 2.

The proportion among the three anions is nearly 998:140:7 (Chinese Encyclopaedia). In this paper all the anion contents were designed evenly from 0 mg/L to the content in natural seawater. Hence it is proper to compare the contributions of the anions to the heavy metal release by the release rate. Comparing the release rates of each heavy metal, the sequences about the contributions of the three anions to the release are $Cl^-$ > $HCO_3^-$ > $SO_4^{2-}$. When under the condition of the same anion, the release rate values, as a whole, indicate that the release potential varies in the following order: Cd≫Cu > Zn ≈Pb. From their speciation distribution values we could find that the exchangeable fractions of the four metals follow the similar sequence (Table 1). For each heavy metal, the release potential is not the same for the state of stillness and agitation. The release rate of Cd and Zn is larger in the state of stillness than in agitation, whereas the release rate of Cu is higher for the agitated system.

**Table 2 Release rate of the heavy metals**

| | Cd, % | | Zn, % | | Cu, % | | Pb, % | |
|---|---|---|---|---|---|---|---|---|
| | Stillness | Agitation | Stillness | Agitation | Stillness | Agitation | Stillness | Agitation |
| $Cl^-$ | 2.60—25.3 | 1.69—18.5 | 0.17—0.40 | 0.12—0.20 | 0.27—0.65 | 0.52—0.85 | — | — |
| $SO_4^{2-}$ | 2.30—2.60 | 1.68—1.74 | 0.086—0.13 | 0.017—0.11 | 0.18—0.35 | 0.31—1.36 | 0.087—0.14 | 0.063—0.93 |
| $HCO_3^-$ | 2.30—3.08 | 1.68—2.03 | 0.16—0.28 | 0.063—0.12 | — | — | — | — |

## 3 Conclusions

The quantity of Cd released from the marine sediments had an obvious positive relationship with the $Cl^-$ content in the water, whereas the relationship was not significant between the release of Cu, Zn in the sediments and the $Cl^-$ content in the water. Concentration of Cd released into the water was almost linear increase as the $Cl^-$ content increasing in the water, while concentrations of Cu and Zn varied little. The quantity of Cd released from the sediments was much higher than Cu and Zn in the same conditions.

$SO_4^{2-}$ and $HCO_3^-$ play little role in the release of Cu and Pb in the marine sediments. While for Cd and Zn, the influence of $SO_4^{2-}$ and $HCO_3^-$ was a little difference between the state of stillness and agitation. As a whole, impact of these two anions was not obvious on the release of Cd and Zn.

The three anions play different roles in the release of heavy metals Cd, Zn, Cu and Pb from marine sediments. But compared with the release rates of each heavy metal from the marine sediments, as a whole, the influence potential was in the following order: $Cl^- > HCO_3^- > SO_4^{2-}$.

When the sediment accumulated with heavy metals was under the condition of the same anion , the release ratio of the heavy metals was in the following order: Cd≫Cu >Zn ≈Pb. It was to say that for the marine sediments accumulated with the heavy metals Cd, Zn, Cu and Pb, Cd was inclined to release into the water best of all. Hence the waste containing Cd should not be discharged into the aquatic environment especially the sea.

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