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## Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

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V. M. Shulkin<sup>a</sup>; N. N. Bogdanova<sup>a</sup>

<sup>a</sup> Far Eastern Research Branch, Pacific Geographical Institute, Russian Academy of Science, Vladivostok, Russia

**To cite this Article** Shulkin, V. M. and Bogdanova, N. N.(1998) 'The Influence of Anthropogenic Contamination On Metals Release From Coastal Sediment Suspensions with Aerated Sea Water', *Chemistry and Ecology*, 15: 1, 87 – 102

**To link to this Article:** DOI: 10.1080/02757549808037622

**URL:** <http://dx.doi.org/10.1080/02757549808037622>

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# THE INFLUENCE OF ANTHROPOGENIC CONTAMINATION ON METALS RELEASE FROM COASTAL SEDIMENT SUSPENSIONS WITH AERATED SEA WATER

V. M. SHULKIN\* and N. N. BOGDANOVA

*Pacific Geographical Institute, Far Eastern Research Branch,  
Russian Academy of Science, Vladivostok 690041, Russia*

*(Received 11 April 1997; Revised 30 July 1997)*

The zinc, cadmium, copper and lead release from the uncontaminated and contaminated coastal sediments with aerated sea water was studied. The metals transfer to the dissolved forms was monitored during one–two months by differential pulse anodic voltammetry (DPASV). The sediments with different initial degree of contamination were sampled in the Peter the Great Bay, Sea of Japan around Vladivostok – the biggest city in Russian Far East. Sediment contamination by metals led to increased release to solution of zinc due to sulphide oxidation and cadmium on account of organic matter decomposition. The copper behaviour was complicated by strong binding with organic matter and enhancements of copper release can only be seen in sediment with a low organic matter content. Significant lead transfer to dissolved forms was not observed regardless of sediment contamination. The temperature affected the release of cadmium and copper through enhanced organic matter destruction. The dissolved metal fluxes from the sediment transformation are compared with metal fluxes towards bottom. Such comparisons show that second contamination by dissolved metals of the studied coastal environment may be important for cadmium only.

*Keywords:* Trace metals; contamination; bottom sediments; suspension experiments; metals release

## 1. INTRODUCTION

The removal of metals from the coastal waters to the sediments is the main trend in their migration at the sea (Santchi *et al.*, 1987). However

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\*Corresponding author.

the cycling nature of the most biogeochemical processes imposes the backward transfer of metals to the dissolved forms, particularly at the water–sediment interface. Increasing contamination of the bottom sediments through dumping, industrial and domestic sewage may lead to the water ecosystems secondary contamination by these released metals. The scale of secondary contamination is determined by the dynamics of the release from the sediments and backward scavenging. The dynamics and scale of the metals release from the sediments with near background metal contents have been investigated at the laboratory (Gerringa, 1990), mesocosms (Santschi *et al.*, 1987) and field studies (Westerlund *et al.*, 1986). The knowledge about metal release from the matter with elevated concentrations due to human activity is still limited and contradictory (Delaune and Smith, 1985; Galloway, 1979; Hoff *et al.*, 1982; Khalid *et al.*, 1981; Paulson *et al.*, 1991; Waldichuk, 1978).

The main goal of this paper is to determinate the contamination influence on the scale and dynamics of the zinc, cadmium, copper and lead release from sediment suspensions under laboratory conditions. Moreover, the influence of temperature and solid contents in suspensions on the metals release is investigated. In our study the dissolved electrochemically active (labile) metal forms were monitored in time during one–two months. Such a duration was chosen because backward removal to sediments prevails at longer times (Gerringa, 1990). The experiments were carried out in air saturated sea water because the studied metals are released more effectively at the aerobic conditions (Westerlund *et al.*, 1986). Besides, the bottom layers of water at the studied localities are oxygenated as a rule.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Sediment samples were taken in August 1994 at three localities in the coastal waters neighbouring Vladivostok, the biggest city of the Russian Far East (Fig. 1). Sampling was carried out by SCUBA diver in the glass tubes without sediment disturbance. Sampling station A was located 5 km off the shoreline in an uncontaminated area at 15 m depth. The sediment was oxidized (grayish–brown) in the top 7 cm

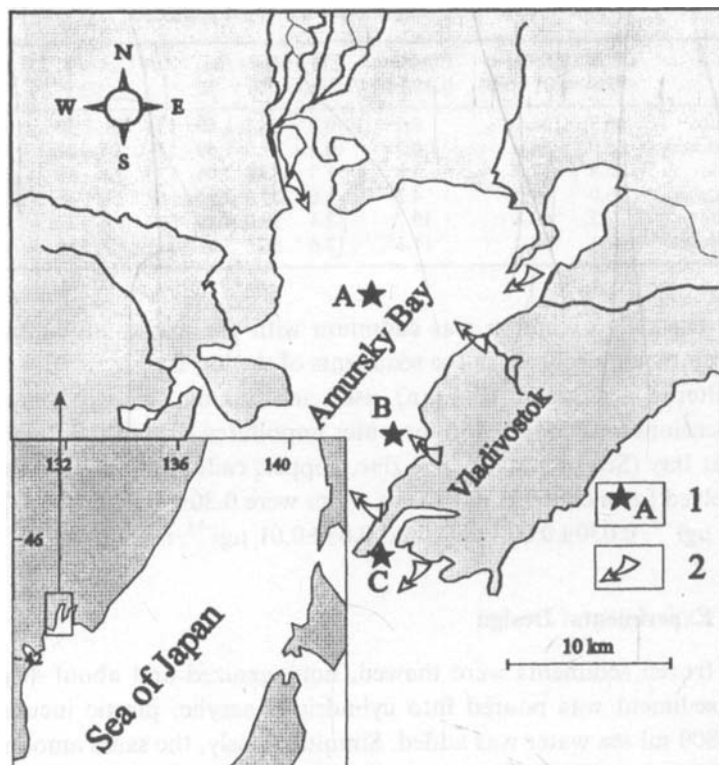


FIGURE 1 The studied area; 1. Sampling stations, 2. Main contamination inputs.

and reduced (black) deeper down. Sampling station B was located at 8 m depth near a large sewage outlet. The sediment was oxidized in the top 2 cm only and reduced deeper down. The most polluted sampling station C was located in the outer part of the Vladivostok harbour at 17 m depth. The upper 4 cm of this sediment are suboxic (black – grayish – brown) and due to strong reduced sediment situated below (black with  $H_2S$  smell). The oxidized and reduced parts of sediment are sampled separately. After careful homogenization and wet sieving over a 2 mm sieve, sediment was subsampled in polyethylene bags which were stored at  $-18^\circ C$ . Table I shows the sediment characteristics; sediment texture varied from silty clay mud (A) to silty mud with minor sand contents (C). The elevated metals and  $C_{org}$  concentrations enable the sediments characterized to be unpolluted (A), polluted (B) and heavily polluted

TABLE I Characteristics of the initial sediments

Station	Grain Size(mm)		Contents (%)	H <sub>2</sub> O (%)	C <sub>org</sub> (%)	Zn	Cu	Pb	Cd	
	< 0.01	0.01–0.05								0.05–0.1
A, oxic	66.3	33.1	0.2	0.4	58.1	1.69	131	28	30	1.01
A, reduced	65.0	34.0	0.7	0.3	57.9	1.69	121	27	27	0.62
B, oxic	25.8	67.7	4.8	1.7	53.8	2.06	170	39	46	2.68
B, reduced	26.0	68.2	4.2	1.6	53.6	2.05	169	37	48	2.36
C, oxic	7.5	69.4	10.7	12.4	59.0	4.84	300	89	127	1.51
C, reduced	7.1	69.2	11.1	12.6	58.5	5.85	311	100	154	1.72

(C). The only exception was cadmium with the maximum cadmium concentration occurred in the sediments of station B.

Filtered sea water (0.4 μm) used in making the experimental suspensions was collected in the outer unpolluted part of the Peter the Great Bay (Sea of Japan). The zinc, copper, cadmium and lead labile dissolved form contents in this sea water were  $0.30 \pm 0.05 \mu\text{g l}^{-1}$ ,  $0.25 \pm 0.04 \mu\text{g l}^{-1}$ ,  $0.030 \pm 0.009 \mu\text{g l}^{-1}$  and  $0.03 \pm 0.01 \mu\text{g l}^{-1}$ , respectively.

## 2.2. Experimental Design

The frozen sediments were thawed, homogenized and about 40 g of wet sediment was poured into cylindrical, acrylic, plastic incubator and 800 ml sea water was added. Simultaneously, the same amount of sediment was sampled for the water content. The sediment: water ratio was measured regularly during the experiments and averaged 1:50 (approx.  $20 \text{ g l}^{-1}$ ). Directly after thorough homogenization and mixing, the 60–100 ml of slurry was sampled and centrifuged at 4000 r.p.m. for 15 min. The water phase was decanted into a polyethylene vial. The pH of the water phase was measured immediately after centrifugation. The water samples were stored in the refrigerator before analysis. Sampled solids were returned to the experimental incubator with 60–100 ml of initial sea water. Thus, the experimental volume remained constant and dilution factor was taken into account at the metal content determinations. Air was pumped in continuously during the experiments to ensure air saturation within the incubator and additionally to keep the suspension mixed.

During the first 4–5 days of the experiment, samples were taken once a day; then once every two days, and after two weeks of the

experiment once every three days. The overall incubation time was 32–35 days. The experiments were carried out in a dark room at 20–22°C, the typical temperature for the warmest period of year in the studied coastal zone.

Additional experiments were carried out with a reduced sediment:water ratio (1:1000, i.e.  $1\text{g l}^{-1}$ ) at 20–22°C and with sediment:water ratio 1:50 but at 2–3°C, the typical temperature for the winter conditions of the studied region.

### 2.3. Analysis

Determination of the dissolved metals in water was performed by differential pulse anodic stripping voltammetry (DPASV) with a thin mercury film rotating glassy carbon disk electrode (TMF-RGCDE). The analysis system consisted of polarograph PU-1 with XY chart recorder and electrochemical cell. The cell had rotating polished glassy carbon disk electrode  $3\text{ mm}^2$  square embedded in a TFE electrode body. Platinum wire and AgCl/KCl electrodes served as the counter and reference electrodes, respectively. The degassing was performed by oxygen-free argon bubbling through a capillary tube.

Before analysis, the working electrode was polished with  $0.05\text{ }\mu\text{m}$  aluminium oxide, then rinsed with 2%  $\text{HNO}_3$  and double-distilled water. The 20–25 ml sample was added together with  $50\text{ }\mu\text{g}$  mercury in  $\text{HgNO}_3$  form and degassed with argon for 10 min. Then the working electrode rotation began (3000 rpm) at a deposition potential of  $-1.25\text{ V}$ . The deposition time varied from 90 to 300 s depending on metal content. The rotation and argon bubbling were stopped 30 s before stripping to allow the systems to settle. The mercury film with the deposited metals was stripped by scanning the potential towards  $+0.3\text{ V}$  in the differential pulse mode (scan rate  $30\text{ mV s}^{-1}$ ; pulse modulation 30 mV) with 30 s electrochemical cleaning at  $+0.3\text{ V}$ . The cycle was repeated (3–4 times) for reproduction peak heights. The zinc, lead and cadmium spikes were added and analysis was repeated. Two additions were performed usually and results were averaged. The copper contents were determined separately at a deposition potential  $-0.95\text{ V}$  due to zinc–copper intermetallic compounds forming. Detection limits of the DPASV analysis were  $0.01\text{ }\mu\text{g l}^{-1}$  for zinc, lead and cadmium and  $0.05\text{ }\mu\text{g l}^{-1}$  for copper. The accuracy of our DPASV

method was checked by the analysis of filtered sea water with metal spikes 1 and 5  $\mu\text{g l}^{-1}$  for zinc and copper, and 0.1, 1 and 5  $\mu\text{g l}^{-1}$  for cadmium and lead. The accuracy of spikes determination was within 10%. The reproducibility of the metals determination in the water samples (triplicate analysis) was within 10–20%.

Metal concentrations in the initial sediments (Tab. I), were determined after acid ( $\text{HF-HNO}_3\text{-HClO}_4$ ) digestion by atomic absorption spectrometry using Hitachi 180 AAS with reproducibility 5–8%. Accuracy was determined by analysing reference sediments NBS 646, where we found  $130\pm 5 \mu\text{g g}^{-1}$  zinc,  $17\pm 2 \mu\text{g g}^{-1}$  copper,  $25\pm 2 \mu\text{g g}^{-1}$  lead and  $0.40\pm 0.03 \mu\text{g g}^{-1}$  cadmium in comparison with certified concentrations 138, 18, 28.2 and  $0.36 \mu\text{g g}^{-1}$ , respectively.

### 3. RESULTS AND DISCUSSION

The variation of pH and dissolved copper, lead, cadmium and zinc during experiments are shown on Figures 2–4. The change in concentration of the dissolved metals in the suspension was the result of two opposing processes; on one side, the organic matter and sulphide compounds decomposition is accompanied by a release of metals to the sea water. On the other side, the released metals may be reabsorbed back to the solids, such as Fe–Mn hydroxides. Dissolved organic substances may also play a significant role due to their ability to bind metals, first of all copper, in strong dissolved complexes not detectable by DPASV (Coale and Bruland, 1988; Gerringa *et al.*, 1991).

#### 3.1. Zinc

The zinc mobilisation to sea water is very different between polluted and unpolluted sediment suspensions and between oxidized or reduced initial status of sediments (Fig. 2). For unpolluted oxidized sediments rapid (within 1 h) zinc transfer to solution is observed (up to  $3.9\text{--}9.2 \mu\text{g l}^{-1}$ ). The fast zinc leaching from sediments by sea water was established at mesocosm experiments (Santschi *et al.*, 1987) and at aerobic destruction of organic debris (Lee and Fisher, 1992a,b). The later decrease in concentration indicates a zinc mobility in the sediment:water ecosystem with a rapid zinc reabsorption on the solid

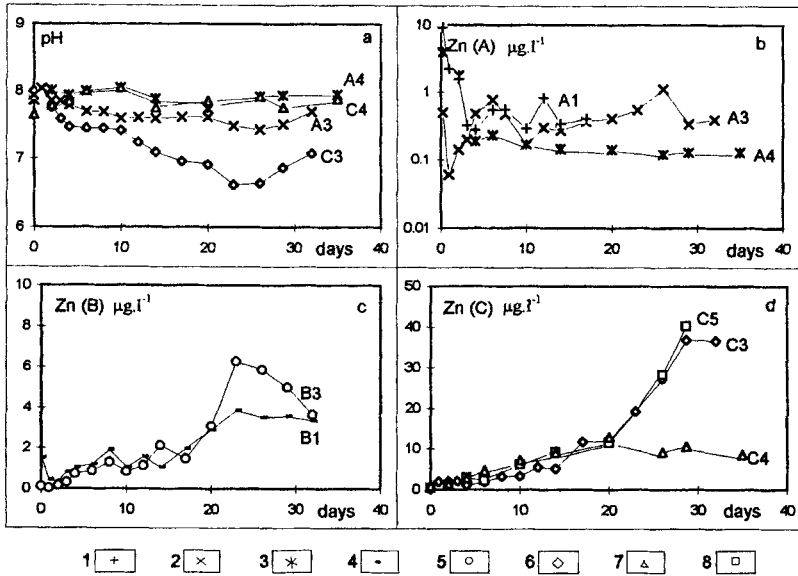


FIGURE 2 The change during experiments pH (a) and dissolved zinc contents ( $\mu\text{g.l}^{-1}$ ) in the unpolluted suspensions (b), polluted (c) and heavily polluted ones (d); 1. Unpolluted oxidized sediment at  $20 \text{ gl}^{-1}$  solid content (A1). 2. Unpolluted reduced sediment at  $20 \text{ gl}^{-1}$  (A3). 3. Unpolluted reduced sediment at  $1 \text{ gl}^{-1}$  (A4). 4. Oxidized polluted sediment at  $20 \text{ gl}^{-1}$  (B1). 5. Reduced polluted sediment at  $20 \text{ gl}^{-1}$  (B3). 6. Heavily polluted sediments at  $20 \text{ gl}^{-1}$  (C3). 7. The same sediment at  $1 \text{ gl}^{-1}$  and  $22^\circ\text{C}$  (C4). 8. The same sediment at  $20 \text{ gl}^{-1}$  and  $2^\circ\text{C}$  (C5).

phases and the absence, in the unpolluted sediments, substances which can transfer zinc to the sea water over the one month experiment. After 10 days, the dissolved zinc concentration was reduced to  $0.12\text{--}0.13 \mu\text{g.l}^{-1}$  at the solids content  $1 \text{ gl}^{-1}$  and to  $0.27\text{--}0.54 \mu\text{g.l}^{-1}$  at the  $20 \text{ gl}^{-1}$  (Fig. 2b). This can be explained by "particle concentration effect": increase in solid phases content in suspension leads to a decrease of the adsorption efficiency (Honeyman and Santschi, 1988). The initial zinc mobilization into solution was restricted in the suspension of reduced unpolluted sediments (Fig. 2b). This indicates complete transfer of the zinc to dissolved forms at the oxidized top layer of the sediments.

A more gradual zinc mobilization to the solution was observed in the polluted sediments suspension. The mobilization scale was proportional to the degree of contamination (Fig. 2c,d). Metal transfer to dissolved



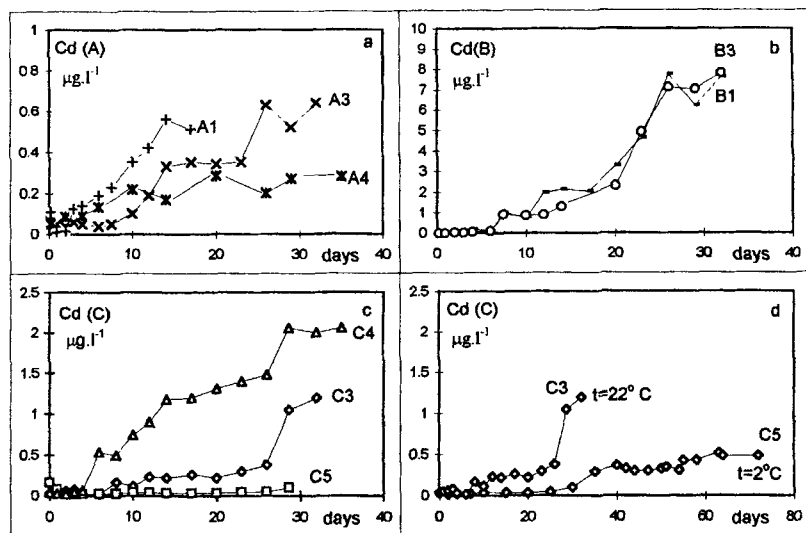


FIGURE 3 The dissolved cadmium concentration ( $\mu\text{g.l}^{-1}$ ) in the sediment suspensions by sediment type (a,b,c) and by temperature (d). The symbol definition see Figure 2.

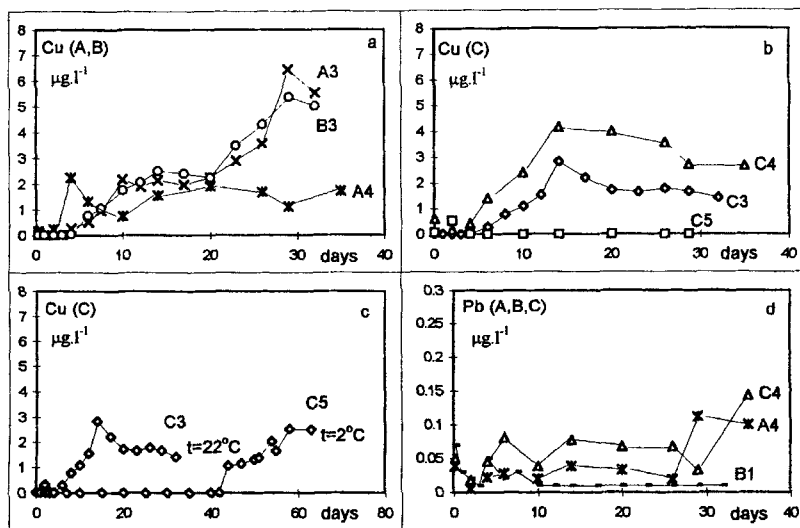


FIGURE 4 The change in copper concentration ( $\mu\text{g.l}^{-1}$ ) in the sediment suspensions by sediment type (a,b), at two temperatures (c) and the dissolved lead concentration (d). For symbol definition see Figure 2.

forms is caused by decomposition of organic matter and/or oxidation of the sulphide compounds. The first process can be microbiologically mediated and therefore would be dependent from temperature (Lee and Fisher, 1992a,b). The sulphides oxidation is chemical in the main (Berner, 1980) and temperature influence would be restricted. The dynamics of the dissolved zinc elevation in the polluted suspensions is similar at 20–22°C and at 2°C (Fig. 2d, C3 vs C5). Therefore, it can be concluded that in polluted suspensions zinc release was from the oxidation of sulphide.

There was different response in the dissolved zinc concentration in the polluted suspensions during the second half of the experiments with different solid contents (Fig. 2d, C3 vs C4) due to the effect of pH. Sulphide oxidation is accompanied by a pH decrease (Berner, 1980; Cai and Reimers, 1993). At low solid contents ( $1 \text{ gl}^{-1}$ ) the buffer capacity is sufficient to maintain the pH at 7.76–8.05 during the entire experiment (Fig. 2a), and zinc had been desorbed to the solution during the first 2 week sulphide oxidation, and is gradually re-adsorbed later on the other solid phases with a corresponding decrease in the dissolved zinc concentrations (Fig. 2d, C4). At high solid contents ( $20 \text{ gl}^{-1}$ ) with greater associated metal sulphide concentrations, the water buffer capacity was depleted and pH decreased to 6.8 (Fig. 2a). Such a pH reduction has not infrequently been observed in nature (Cai and Reimers, 1993) and in this case leads to intensification of zinc release, up to  $35\text{--}40 \text{ }\mu\text{gl}^{-1}$  (Fig. 2d).

### 3.2. Cadmium

Unlike zinc, cadmium transfer in the solution was prevailed in the uncontaminated suspensions (Fig. 3a), though slight initial rise with followed decrease of dissolved cadmium were observed during first three days in suspension of uncontaminated oxidized sediment (Fig. 3a, A1). The rate of subsequent (up to 13 days) mobilization from oxidized uncontaminated sediments was more than from reduced sediments (Fig. 3a, A1 vs A3). By day 25 the dissolved cadmium concentration was equilibrated on  $0.5\text{--}0.6 \text{ }\mu\text{gl}^{-1}$  in the uncontaminated suspension at solid content  $20 \text{ gl}^{-1}$ . The equilibrium dissolved cadmium concentration was  $0.2 \text{ }\mu\text{gl}^{-1}$  and at a solid content  $1 \text{ gl}^{-1}$  (Fig. 3a, A4 vs A3). With a higher solid content ( $60\text{--}70 \text{ gl}^{-1}$ ), the final

dissolved cadmium concentration was 2–2.5  $\mu\text{gl}^{-1}$  (Gerringa, 1990). The increase of the equilibrium dissolved cadmium concentration with enlargement of solid content in suspension is consistent with “particle concentration effect” (Honeyman and Santschi, 1988).

The cadmium mobilized from the polluted suspension was proportional to the initial sediment cadmium concentration (Figs. 3b,c). Cadmium begins to desorb exponentially after 1 week incubation. The dissolved cadmium concentration was similar to the unpolluted suspensions prior to this time. After 25 days, the dissolved cadmium had stabilized at 6–8  $\mu\text{gl}^{-1}$  with a sediment suspension from station B and 1.2–2.4  $\mu\text{gl}^{-1}$  with sediment from station C (Fig. 3 b,c). It should be noted that the “particle concentration effect” does not work with the polluted suspensions: the cadmium released diminished with an increase in the solids (Fig. 3c, C4 vs C3). The cadmium transfer to solution was independent of observed pH changes (from 7.8 to 6.8, Fig. 2a), but was dependent upon temperature; at 2°C the dissolved cadmium increased later and was less than at 22°C (Fig. 3c). Thus we can suppose that cadmium desorbs due to decomposition of the organic matter containing cadmium by micro-organisms.

### 3.3. Copper

The main feature of copper desorption in the aerated suspensions was the absence of a direct connection between mobilization scale and initial contamination which was observed for zinc and cadmium (Fig. 4). At the same time the copper release was dependent on the solid contents. In the unpolluted suspensions with low solid content (1  $\text{gl}^{-1}$ ) the final copper concentration was varied from 1.1 to 2.2  $\mu\text{gl}^{-1}$ , but increased to 5–7  $\mu\text{gl}^{-1}$  with a solid content of 20  $\text{gl}^{-1}$  (Fig. 4a, A3 vs A4). In experimental unpolluted slurries containing 60–70  $\text{gl}^{-1}$  solids (Gerringa, 1990) the equilibrium copper concentration reaches 15  $\mu\text{gl}^{-1}$ . Therefore “particle concentration effects” (Honeyman and Santschi, 1988) has influence on copper behaviour in the unpolluted suspensions with zinc and cadmium. It should be noted that copper release begins with 4–5 days delay at the high solid contents (Fig. 4a).

In the contaminated sediment suspensions with low solid contents, the dissolved copper increase begins after 2–3 days and reaches up 4  $\mu\text{gl}^{-1}$  after 10 days (Fig. 4b). However at high solid contents, the

copper release begins after 4–6 days and does not exceed  $2-3 \mu\text{gl}^{-1}$  compared with  $5-7 \mu\text{gl}^{-1}$  in the unpolluted suspensions containing the same  $20 \text{ gl}^{-1}$  solid phase. The limited nature of copper desorption in contaminated sediment suspensions with a high solid content may be explained by the increase of organic matter (Tab. I), which binds copper in strong complexes (Coale and Bruland, 1988; Gerringa, 1990; Donat *et al.*, 1994). The connection between copper release and organic matter decomposition is confirmed through temperature experiments at  $2^\circ\text{C}$  where the dissolved copper concentration remained below  $0.01 \mu\text{gl}^{-1}$  for one month, and then mobilization was observed similar to that at  $22^\circ\text{C}$  (Fig. 4c). It is likely that copper dissolves through organic matter degradation, similar to cadmium but more slowly due to the stronger affinity with organic matter especially at the high  $C_{\text{org}}$  contents.

### 3.4. Lead

The concentration of lead in solution (the uncontaminated and contaminated suspensions) varied in a non-sequential manner from  $0.01$  to  $0.1 \mu\text{gl}^{-1}$  and in heavily contaminated sediment suspensions ranging from  $0.04$  to  $0.19 \mu\text{gl}^{-1}$ . Lead behaviour was not influenced by the solid content nor the temperature. It may be pointed out that only slight increase of dissolved lead is found at the end of experiments (Fig. 4d). The absence of significant lead release in the suspensions regardless to the initial contamination may be explained by the dominance of precipitation–dissolution reactions controlling lead beside adsorption–desorption reactions controlling zinc, cadmium and copper (Salomons, 1985). The weak lead mobility has been confirmed by other investigators (Gerringa, 1990; Westerlund *et al.*, 1987).

The main disadvantage of these laboratory experiments is the unknown relationships with hydrodynamic and physico-chemical reactions in nature. It may be that the mechanisms, direction and relative scale of the metals release has been identified, but the scale of the real influence on the dissolved metal contents is uncertain. The significance of these metals release in the sedimentation cycle is also unknown. Nevertheless, the stabilization of the dissolved metal contents is observed after 30–70 days has been observed in our experiments such as in other similar investigations (Gerringa, 1990;

Paulson *et al.*, 1991). This indicates the achievement of some quasi-stationary equilibration between the metal release due to organic matter degradation and/or sulphide oxidation and re-adsorption on to other solid phases. Thus we can roughly estimate the resulting fluxes ( $F$ ) of dissolved released metals in our experiments, accepting the quasi-stationary metal distribution at the end of the incubation and affinity of the conditions in the experimental vessels to natural sediment-water interface:

$$F = (C_i - C_0) \cdot V/S \cdot t \text{ [}\mu\text{g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}\text{]}$$

where  $C_i$  is the quasi-equilibrium dissolved metal concentration in suspension,  $\mu\text{gm}^{-3}$ ,  $C_0$  is the initial dissolved metal concentration in suspension,  $\mu\text{gm}^{-3}$ ,  $t$ , is time to equilibrium in days,  $V$ , is volume of suspension,  $0.0008 \text{ m}^3$ ,  $S$ , is area of experimental vessel bottom,  $0.0063 \text{ m}^2$

The results are shown in Table II together with dissolved metal fluxes from bottom sediments that have been observed during *in situ* experiments in benthic chambers in unpolluted fjords (Westerlund *et al.*, 1986).

There is a reasonable agreement between the cadmium and copper fluxes from the unpolluted sediments at a solid content in suspension  $1 \text{ gl}^{-1}$  and flux values obtained by a different method more closely related to nature. At the same time, the zinc fluxes from unpolluted

TABLE II The resulting dissolved metal fluxes  $F$  ( $\mu\text{g m}^{-2}\text{day}^{-1}$ ) from the sediment suspensions after  $t$  days of the experiment

Station, Solids content,	Temperature	$t$	Cu		Zn		Cd		Pb	
			$F$	$t$	$F$	$t$	$F$	$t$	$F$	$F$
A,	$1 \text{ gl}^{-1}$ ,	$22^\circ \text{C}$	25	$7.3 \pm 1.6$	25	$-19.3 \pm 2.0$	25	$1.3 \pm 0.3$	25	$0.2 \pm 0.1$
A,	$20 \text{ gl}^{-1}$ ,	$22^\circ \text{C}$	30	$26.7 \pm 3.5$	25	$3.1 \pm 1.3$	30	$2.5 \pm 0.2$	30	$-0.1 \pm 0.3$
B,	$20 \text{ gl}^{-1}$ ,	$22^\circ \text{C}$	30	$22.0 \pm 4.1$	25	$10.4 \pm 1.1$	25	$36.9 \pm 7.1$	30	$0.2 \pm 0.1$
C,	$1 \text{ gl}^{-1}$ ,	$22^\circ \text{C}$	30	$10.6 \pm 1.5$	25	$47.8 \pm 8.9$	30	$8.6 \pm 1.4$	30	$0.2 \pm 0.1$
C,	$20 \text{ gl}^{-1}$ ,	$22^\circ \text{C}$	25	$8.8 \pm 2.0$	30	$155 \pm 12$	30	$4.6 \pm 0.4$	30	$-0.2 \pm 0.3$
C,	$20 \text{ gl}^{-1}$	$2^\circ \text{C}$	60	$5.2 \pm 0.6$	60	$84.4 \pm 21.1$	60	$0.9 \pm 0.1$	60	$0.2 \pm 0.1$
(Westerlund	$10^\circ \text{C}$			7.5		124		1.5		
<i>et al.</i> , 1986),	$1^\circ \text{C}$			1.7		91		1.2		

\* - the error of the  $F$  estimation is determined by the error of the dissolved metal analysis (10-20% in depending of concentration) and by the variation of metal concentration on the quasi-equilibrium level at the end of experiment.

\*\* - the negative value of zinc and lead fluxes correspond to a transfer from the dissolved to the solid phase.

sediments *in situ* research were one order of magnitude greater than ours (Tab. II). This confirms the suggestion about early zinc release and high mobility during sedimentation, and implies that zinc had been mobilized from unpolluted sediments, especially reduced ones, used for the experiments. On the contrary, contaminated sediments were a more persistent source of dissolved zinc through the process of sulphide oxidation, which have been equilibrated after 20–30 days of the experiments (Fig. 2c,d).

The magnitude of the dissolved copper and cadmium fluxes from the suspensions with a solid content of  $20 \text{ gl}^{-1}$  disagreed with the results of Westerlund *et al.* (1986) (Tab. II). If a similar solid content  $60–70 \text{ gl}^{-1}$  is used (Gerringa, 1990), the coincidence will be even worse. It is probable that the transformation of the metals on the sediment–water interface take place at a solid content of  $1 \text{ gl}^{-1}$  rather than  $20 \text{ gl}^{-1}$  or more.

The significance of the metal content release as a part of the sedimentation cycle may be evaluated by comparison of the dissolved metal fluxes from the sediments and metal fluxes towards the bottom associated with settling matter. Such assessments of the metal fluxes towards the bottom in the coastal zone with data by sedimentation traps are shown in Table III. The significance of the copper and cadmium release from the sediments reaches up 11–15% and 3–9% fluxes towards the bottom with uncontaminated settling matter. The lead and zinc released from the sediments in the aerated sea water does not exceed 1–2% of fluxes toward the bottom. Contamination increases of the cadmium release up to 30–60% of the fluxes towards

TABLE III Metal fluxes towards the bottom by sediment traps

Region, reference season,	Settling matter $\text{gm}^{-2} \cdot \text{day}^{-1}$	Cu	Zn $\mu\text{gm}^{-2} \cdot \text{day}^{-1}$	Cd	Pb
Sea of Japan, Vostok Bay (Shulkin, 1990)					
April-July	2.6	179	606	7.9	150
August-September	5.0	240	755	16.3	335
Stockholm Archipelago (Broman <i>et al.</i> , 1994)	1.50–7.55	100–2000	500–5000	1–20	100–2000
Puget Sound					
(Feely <i>et al.</i> , 1986) winter	1.65	120	260	n.d.	130
summer	2.72	174	424	n.d.	141

bottom. The copper release does not exceed 10% as before, though experiments with sewage matter in the Puget Sound showed copper releases up to 25% of the fluxes towards the sediments (Paulson *et al.*, 1991). The contaminated sediments with zinc leads to an elevation of the metal release (Table II), but the zinc flux towards the sediments increases simultaneously, and the slight significance of the zinc mobilization is maintained. The lead release is also negligible in the contaminated sediments (Tabs. II and III). The assessment of the metal fluxes in Puget Sound based on the sedimentary role of the metal release from the settling matter: 20% copper, 34% zinc and 39% lead of the buried quantities (Feely *et al.*, 1986). The main reason for such a discrepancy with these results is the use in our experiments of settled sediments, i.e. solid phases, may have been transformed during settling.

#### 4. CONCLUSIONS

The partial transfer of the zinc, cadmium and copper to dissolved forms is observed during one–two months mixing of coastal sediments with aerated sea water.

The zinc release in the polluted suspensions occurred due to the gradual oxidation of sulphide and the scale of mobilization is proportional to the initial degree of contamination. In the uncontaminated sediments, zinc release is observed mainly during the settling stage.

The cadmium release took place during sedimentary organic matter decomposition and the magnitude of the release was determined by the initial cadmium content of the sediments and by the temperature during the experiment.

The copper transfer to the dissolved forms is gone at organic matter decomposition too, but the strong copper binding with organic matter restricts and delays the copper release. The contamination of the sediment by metals was accomplished by arranging increase in the  $C_{org}$ . Therefore the contamination influence on the copper release was veiled and was only observed at the low solids content ( $1 \text{ gl}^{-1}$ ). The lead release was negligible regardless of the sediment degree of contamination.

The effect of temperature was expressed as a reduction in cadmium and copper release due to their connection with decomposing organic matter.

Increasing the solid content in the uncontaminated sediment suspension was accompanied by an increase in metals release, but contaminated sediments led to backwards dependence by an unknown reason. Perhaps in the contaminated sediment suspensions with high solid contents the organic matter and sulphide oxidation were decelerated.

The resulting dissolved metal fluxes due to the destruction and oxidation of uncontaminated sediments were equal to 11–15% cadmium, 3–9% copper, 1–2% zinc and less than 1% for lead of the fluxes towards the bottom. For contaminated sediments, the significance of the cadmium release reached 60–80% of the input to the bottom. The role of the other metal released remained similar. Therefore, the substantial second pollution of waters by dissolved metals is possible by cadmium only.

### *Acknowledgments*

This work was possible due to International Science Foundation (ISF) grant N RJN000 and joint grant N RJN300 of ISF and Russian Foundation for Fundamental Research. The presentation of this paper at the 3<sup>rd</sup> International Ocean Pollution Symposium was supported by the travel grant of MacArthur Foundation (46462A FSU/EKP). Special thanks to Dr.G. Howells and reviewers for helpful comments and suggestions which have improved the manuscript significantly.

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