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STUDIES OF CONTRIBUTION OF METALS BONDED WITH ORGANIC MATTER OF SEAWATER TO THE FLUXES OF TOTAL DISSOLVED METALS ACROSS WATER–SEDIMENT INTERFACE AT VISTULA LAGOON OF BALTIC SEA

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Abstract

Investigations of fluxes of a dissolved element across the water-sediment interface in Vistula Lagoon (Baltic Sea) were carried out in August 2001 and 2002, using chamber experiments. Oxygen, iron(II), total dissolved iron, manganese, copper and lead fluxes were calculated. For the first time the fluxes of metals bonded with organic matter of sea water were studied. The contribution of metals bonded with organic matter to the total flux was varied depending upon conditions and may reach up to 70 %. It was found that metal fluxes at the coastal zone are larger than at the center of the lagoon by the factor of 2 – 4.

Keywords: Baltic Sea, chamber experiment, benthic fluxes, organic forms, manganese, iron species

1. Introduction

Studies of fluxes of some elements across the water-sediment interface were carried out in August 2001 and 2002 in Vistula Lagoon, Baltic Sea, using chamber technique. Elements of interest were oxygen and dissolved forms of manganese, iron, copper and lead.

Regions of studies reported in literature up to date are represented mostly by coastal waters with substantial anthropogenic pollution. In such conditions differences in metal concentrations and fluxes may be of several orders of magnitude: 20 – 1200 mmol m⁻² day⁻¹ for manganese; 1 – 150 for iron, 0.02 – 2 for copper (Berelson, 2003; Pakhomova, 2003; Sundby, 1986; Warnken, 2001; Westerlund, 1986; Zago, 2000). Direct measurements of fluxes of transitional and heavy metals at the water-sediment interface are represented mainly by dissolved inorganic forms. The environment in a coastal zone is usually under anthropogenic influence and loading by big amounts of organic matter. As a consequence, behavior of dissolved metals, especially bonded with organic substances, may become an important factor of exchange between sediment and water. However, studies of this kind are practically not present in literature.

The aim of this work was investigation of fluxes of dissolved forms of metals across water-sediment interface, namely, dissolved inorganic Fe(II), Fe(III), Mn, Pb, Cu, along with Fe, Mn, Pb, Cu bonded with organic matter of seawater. Two sites were selected for the estimation of anthropogenic influence in different regions of Vistula Lagoon, at the coast and at the center of the Lagoon. Studies were carried out

in 2001 and 2002 for finding out time changes in fluxes.

2. Materials and Methods

Within the framework of experiments carried out in August 2001, two stations were studied (stations 1.2001 and 2.2001) at the depth of 2 m in the central (by Nasypnoi island) and in the northern parts of Vistula Lagoon in Primorskaya Bight (Fig. 1). The chamber deployment lasted for four days. In August 2002 two stations were studied as well. The first study site was located at the same place as in 2001 (station 1.2002), and the second station was located in Primorskaya Bight, at the depth of 4 m (station 3.2002). Both deployments lasted the three days.

Sediments at all the stations were represented by aleurite silt. The uppermost (0 – 2 cm) sediment layer having brown tint was located over the layer of gray aleurite silt with admixtures of fine sand and lots of hydrotroilite additives. The odor of hydrogen sulfide was not observed on studied sediments.

2.1. Sampling and sample treatment

Four plastic cylindrical chambers (total height of 30 cm, working height of 25 cm, diameter of 30 cm) were deployed at the bottom. Two of them were working chambers, the third was blank chamber isolated from sediment. Cups with hydroquinone were placed inside and outside of the fourth chamber for obtaining the coefficient for recalculation from a closed chamber system to the real open system of seabed. Tracing the difference in dynamics of dissolution of hydroquinone inside and outside of the chamber allowed to account for changes of hydrodynamics inside the chamber. Water samples

were taken by divers every day using syringes (200 – 300 ml) and twice during the first day of deployment. The used chamber technique is described in details in (Vershinin, 1999, 2002).

All water samples were filtered through cellulose acetate filters, pore size 0.45 μm prior to the analyses.

Optical absorbance was measured using a KFK-3 spectrophotometer (Russia). Electrochemical measurements were carried out using electrochemical analyzer Ecotest-VA (SPE "Econics-Expert", Moscow, Russia) with a three-electrode cell. A thin-film mercury electrode served as a working electrode, a saturated silver chloride electrode served as a reference electrode, and platinum wire was used as an auxiliary electrode.

Oxygen was analyzed using Winkler titration technique. Dissolved inorganic manganese was determined spectrophotometrically using formaldoxyme (Marchenko, 1971). Concentration of iron(II) and total dissolved inorganic iron was determined spectrophotometrically using ferrozine (Kononets, 2003; Stookey, 1970).

2.2. Determination of Lead and Copper using anodic stripping voltammetry (SVA)

20 ml of sample was placed into the electrochemical cell, and 0.2 ml of 0.01 M mercury (II) chloride solution and 1 ml of 1:1 acetic buffer solution (pH 4.5) were added. Concentrations of metals were determined using standard addition technique. SVA measurements parameters: deposition and initial potential of sweep was – 900 mV, finishing potential of sweep was +200 mV, sweep rate 100mV s⁻¹, deposition time 300 – 900 s; differential pulse form of sweep was used with the pulse height of 30 mV and pulse frequency of 25 Hz.

2.3. Determination of metals after organic matter decomposition

For the determination of iron and manganese 20 ml of sample, 0.1 ml of concentrated nitric acid, and 0.06 ml of 30 % water solution of hydrogen peroxide were placed into a quartz test-tube. For the determination of copper and lead 20 ml of sample, 0.1 ml of concentrated nitric acid, and 0.06 ml of formic acid was placed into a quartz test-tube. Then, test-tubes were irradiated by UV lamp for 1 h. Following determination of metals was made as described above.

Studied forms of metals are denoted as follows: dissolved inorganic iron – Fe(II), total dissolved inorganic iron – Fe_{tot}, total dissolved iron after the decomposition of organic matter – Fe_{tot}*; total dissolved inorganic manganese – Mn_{tot}, total dissolved manganese after the decomposition of organic matter – Mn_{tot}*. Following forms were calculated as differences: dissolved inorganic iron(III): Fe(III)=Fe_{tot} – Fe(II), iron bonded with organic matter of seawater: Fe_{org}=Fe_{tot}* – Fe_{tot},

manganese bonded with organic matter of seawater: Mn_{org}=Mn_{tot}* – Mn_{tot}.

2.4. Calculation of fluxes

The detailed description of the calculation of fluxes was presented in (Vershinin, 1999). For evaluation of fluxes of dissolved elements on the base of chamber data we used linear approximation $J_{in} = -H\Delta C/\Delta t$, where H – working height of chamber, $\Delta C/\Delta t$ – rate of change (increase) of concentration of some form of an element (in this case only first day data used), the data for two working chambers were averaged. The resulting value was calculated as difference between flux in working and blank chambers. For recalculating chamber fluxes to open seabed system (Vershinin, 1999) we used equation $J_{open} = J_{in} \times k$, where $k = \Delta m_1 \times t_2 / (\Delta m_2 \times t_1)$; Δm_1 and Δm_2 – differences between a hydroquinone cup mass prior to deployment and after incubation inside (Δm_1) and outside (Δm_2) of chamber; t_1 and t_2 – time of stay of hydroquinone cups underwater inside and outside of chamber, respectively.

3. Results and discussion

Results of chemical analyses are presented in Table 1. Calculated values of fluxes are presented in Table 2. Positive flux value indicates that flux is directed into the sediment, negative - from the sediment into seawater. Obtained flux values are in accordance with previously reported data (Berelsona, 2003; Pakhomova, 2003; Sundby, 1986; Warnken, 2001; Westerlund, 1986; Zagoa, 2000).

3.1. Oxygen

Chamber fluxes of oxygen were close for stations 1.2001, 1.2002 and 2.2002, $J_{in}=14, 17$ and $24 \text{ mmole m}^{-2}\text{day}^{-1}$, respectively, that indicates similar biogeochemical conditions in chambers. Oxygen flux at the station 3.2002 was higher, $78 \text{ mmol m}^{-2}\text{day}^{-1}$. More intensive consumption of oxygen and higher fluxes of metals as will be shown further are essentially attributed to anthropogenic influence. The region of the station 3.2002 is affected by sewage of the Kaliningrad city and its harbor, and this load is subjected to tidal and weather as well as seasonal and annual changes.

After recalculating chamber fluxes to the open seabed system using the coefficients ($k = 7.2, 6.5, 5.7, 6.9$ for stations 1.2001, 1.2002, 2.2001, 3.2002 respectively) obtained from the hydroquinone measurements flux values become sufficiently higher ($100, 160, 100$ and $540 \text{ mmol m}^{-2}\text{day}^{-1}$, respectively). Notably that after recalculation fluxes on stations 1.2001 and 1.2002 (same study site in two years) become equal.

Under the consumption of oxygen metal concentrations increased inside working chambers, and remained almost constant inside the blank chamber.

3.2. Iron

The concentration of dissolved inorganic iron in the near-bottom water at stations 1.2002 and 1.2002 was low ($< 0.07 \mu\text{M}$), while in Primorskaya Bight concentration of iron was noticeably higher ($0.1 - 0.4 \mu\text{M}$). Fe(II) was found to be the predominating form of dissolved iron (Table 1). During chamber

experiments concentrations of iron forms grew that allowed to evaluate fluxes of iron forms (Table 2).

The behavior of iron in the central and coastal parts of the Lagoon was different. On stations 1.2001 and 1.2002 (Fig. 3) increase of Fe(II) and Fe_{tot} was observed only for the first day of the chamber deployment.

Table 1
Concentration of elements in bottom water of Vistula Lagoon

Station	Element							
	O ₂	Mn	Mn _{tot} *	Fe(II)	Fe _{tot}	Fe _{tot} *	Cu	Pb
1.2001	224.1	0.29	–	0	0	0.23	–	–
2.2001	268.7	0.37	–	0.28	0.48	0.49	–	–
1.2002	283.5	0.7	3.80	0.05	0.07	0.44	14.4	2.88
3.2002	292.4	1.22	4.47	0.12	0.20	1.05	10.6	2.24

Table 2
Fluxes of dissolved elements across the water–sediment interface (J_{in}).

Element	Station			
	1.2001	2.2001	1.2002	3.2002
O ₂ , mmol m ⁻² day ⁻¹	14 ± 1	24 ± 1	17 ± 2	78 ± 8
Mn, □mol m ⁻² day ⁻¹	-270 ± 30	-410 ± 30	-300 ± 60	-770 ± 150
Mn _{tot} *, □mol m ⁻² day ⁻¹	–	–	-380 ± 20	-820 ± 200
Fe(II), □mol m ⁻² day ⁻¹	-90 ± 10	-50 ± 8	-26 ± 1	-170 ± 10
Fe(III), □mol m ⁻² day ⁻¹	-20 ± 8	-11 ± 5	-15 ± 6	-100 ± 30
Fe _{org} , □mol m ⁻² day ⁻¹	-30 ± 10	0	-100 ± 10	0
Fe _{tot} *, □mol m ⁻² day ⁻¹	-140 ± 10	-61 ± 5	-140 ± 10	-270 ± 20
Pb, nmol m ⁻² day ⁻¹	–	–	-90 ± 10	-1300 ± 400
Cu, nmol m ⁻² day ⁻¹	–	–	-950 ± 150	-2600 ± 300
k (recalculation coeff.)	7.2 ± 0.3	6.5 ± 0.8	5.7 ± 0.5	6.9 ± 1

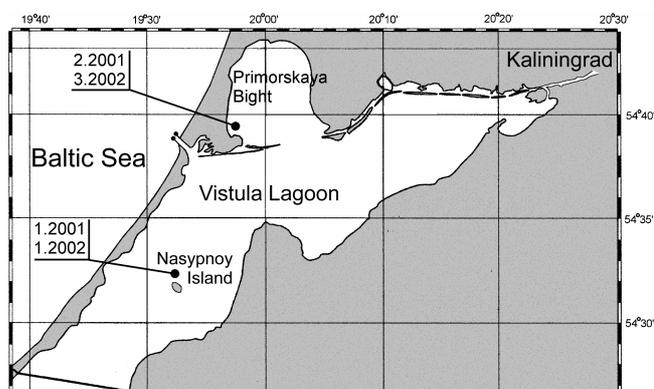


Fig. 1. Map of study sites

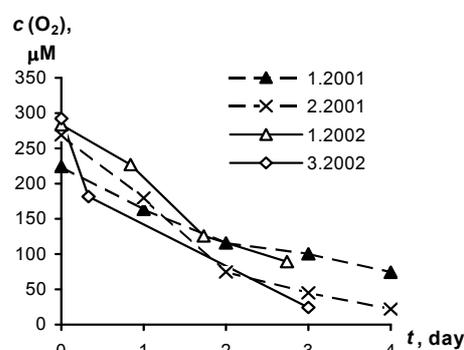


Fig. 2. Decrease of oxygen in chamber

Then, the increase stopped and iron concentration changed insignificantly during the rest time of deployment. On station 1.2001 in the initial time concentrations of Fe(II) and Fe_{tot} were below the detection limit (which is equal to $0.04 \mu\text{M}$), so the initial concentrations of these forms were considered as equal to zero when calculating fluxes. Evidently that this approximation does not affect fluxes of Fe(II) and Fe_{tot} , but does affect the flux of Fe(III) and may be the source of error leading to some overestimation of Fe(III) flux. On station

1.2002 Fe(III) flux appears more reliable because the concentrations of Fe(II) and Fe_{tot} in the initial time exceeded remarkably the detection limit and were equal to 0.05 and $0.07 \mu\text{M}$, respectively. On both stations at the beginning of chamber experiment concentration of Fe_{org} was quite high, 0.27 and $0.44 \mu\text{M}$ for 1.2001 and 1.2002, respectively.

In 2001 on station at the central part of the Lagoon the flux of Fe_{org} was low, $30 \mu\text{mol m}^{-2} \text{day}^{-1}$, and increased up to $100 \mu\text{mol m}^{-2} \text{day}^{-1}$ in 2002. It is

interesting that the flux of Fe_{tot}^* was equal to $140 \mu\text{mol m}^{-2} \text{day}^{-1}$ for both years, but in 2001 predominating form of iron was Fe(II), and in 2002 – Fe_{org} . The flux of Fe(III) was low ($15 - 20 \mu\text{mol m}^{-2} \text{day}^{-1}$).

The flux of Fe_{org} was not detected on stations 2.2001 and 3.2002 (Fig. 4). On station 2.2001 Fe_{org}

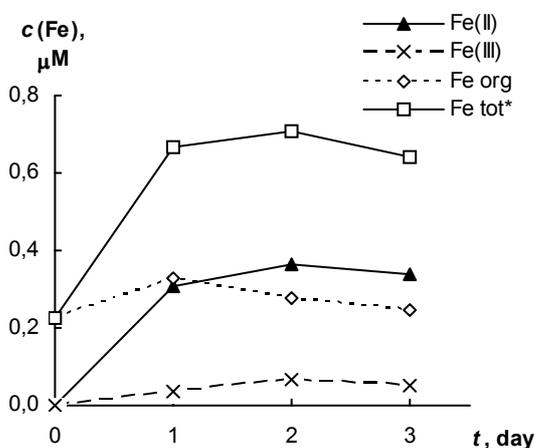


Fig. 3. The release of iron in chamber on station 1.2001

The increase of concentrations of iron forms was linear during the whole experiment on station 2.2001. Evaluating the fluxes from the sediments into the water in Vistula Lagoon one can consider that the flux of Fe(II) forms the major fraction of iron flux. The second (by the value) fraction is Fe_{org} , although the release of Fe_{org} may be hardly detectable under high concentrations of Fe_{tot} and Fe_{tot}^* .

3.3. Manganese

The behaviour of Mn_{tot} is alike to Fe_{tot} for all stations. On stations 1.2001 and 1.2002 in the central part of the Lagoon fluxes of Mn_{tot} are similar and are equal to 270 and $300 \mu\text{mol m}^{-2} \text{day}^{-1}$, respectively (Fig. 5). Stations 2.2001 and 3.2002 have considerably higher fluxes of Mn_{tot} , 410 and $770 \mu\text{mol m}^{-2} \text{day}^{-1}$, respectively, which may be attributed to anthropogenic influence. On both stations in 2002 Mn_{org} fluxes were also investigated. Bottom water both at the central part of the Lagoon and in the Primorskaya Bight was found to contain high concentration of Mn_{tot} ($3.8 - 4.5 \mu\text{M}$). The major part of manganese is bonded with the organic matter of seawater, about $3 \mu\text{M}$ (stations 2.2001 and 3.2002, Table 1). On the contrary, the contribution of Mn_{org} to the total flux of dissolved manganese

was almost not detectable. On station 3.2002 Fe_{org} was quite high ($0.9 \mu\text{M}$) and remained constant, so flux value was insignificant. The behavior of Fe(II) and Fe_{tot} on station 3.2002 was similar to 1.2001 and 1.2002. The increase of these forms was not linear and slowed down during the chamber experiment.

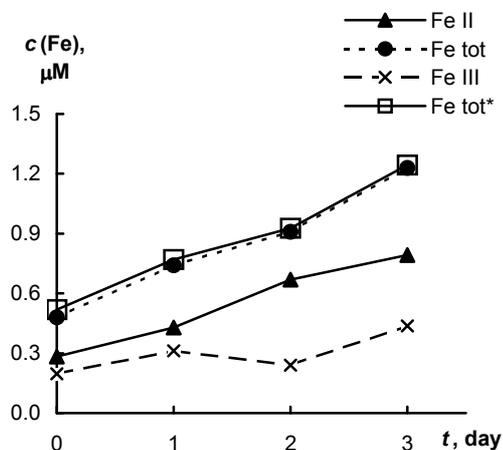


Fig. 4. Release of iron in chamber on station 2.2001

was low, 21 % and 6 % for stations 1.2002 and 3.2002 respectively (Table 2). The behavior of Mn_{org} is similar to the behavior of Fe_{org} for all studied stations.

3.4. Copper

Concentration of Cu_{tot} in the chambers on station 1.2002 increased linearly throughout the chamber experiment beginning from its initial value of 14 nM which is common value for near-bottom water (Fig. 6). On station 3.2002 behavior of copper is similar to other metals, which means initial increase followed by its slow down or change to the constant value. After the decomposition of organic matter concentration of copper (Cu_{tot}^*) increased by three orders of magnitude from 7 nM to $10 \mu\text{M}$ and remained constant over the experiment, so flux of Cu_{tot}^* was insignificant.

3.5. Lead

The increase of lead was linear for stations 1.2002 and 3.2002 (Fig. 6). Concentration of lead did not change after decomposition of organic matter ($3 - 8 \text{ nM}$), so the flux of this toxic element bonded with organic matter is practically absent.

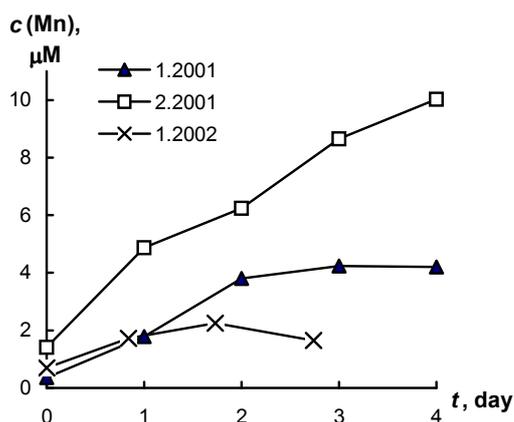


Fig. 5. Release of manganese in chamber

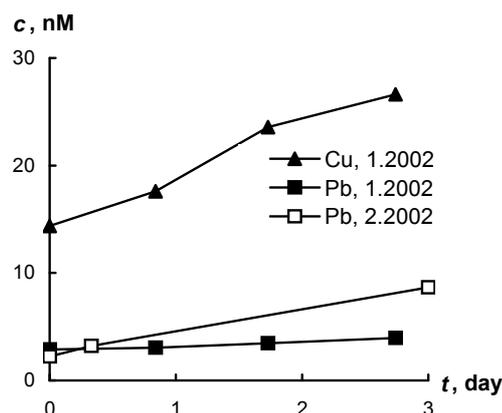


Fig. 6. Release of copper and lead in chamber

4. Conclusions

Thus, the fluxes of dissolved forms of iron, manganese, copper and lead across the bottom water-sediment interface were studied. For the first time fluxes of these metals bonded with organic substances of seawater were studied. It was found that a significant part of iron and copper, and manganese may be bonded with the organic matter of seawater. The contribution of the organically bonded form to the flux of manganese constitutes up to 20 %. On stations at the center of the Lagoon iron bonded with organic matter of seawater contribute to the exchange of iron, and the contribution of Fe_{org} to the total flux of iron increased from 21 % in 2001 to 71 % in 2002 due to the decrease of Fe_{org} contribution from 64 % to 18.5 %. Copper was found to be almost completely bonded with the organic matter and its flux is insignificant. Lead is not complexed with organic matter. On stations located at the coastal zone under strong anthropogenic influence fluxes are 2 – 4 times higher compared to the stations in the center of Vistula Lagoon.

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