**GEOGRAPHY**

## **Behavior of Metals in the Amur River Estuary**

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Presented by Academician P.Ya. Baklanov January 11, 2006

Received January 11, 2006

**DOI:** 10.1134/S1028334X06080216

Biogeochemical processes in estuaries determine to a significant extent the further life of chemical compounds, including metals transported by rivers. Therefore, the characteristics of the behavior of metals in waters with intermediate salinity at the river–sea interface have both scientific and practical significance [1–5]. In terms of estimation of the concentrations of dissolved metals, the estuary of the Amur River, the largest river in the Russian Far East, has not been studied thus far by modern methods. During the complex expedition of the Far East Division of the Russian Academy of Sciences organized to study the ecosystem of the Amur River estuary in July 2005, we studied the distribution of dissolved and suspended forms of Fe, Mn, Zn, Cu, Pb, Cd, and Ni in the estuary and adjacent waters of Sakhalin Bay and the northern Tatar Strait (Fig. 1). In order to prevent pollution, sampling was carried out using a plastic boat and samples were immediately filtered through GWV Pall Gelman capsule filters (mesh 0.45 µm). The replicate water sample was filtered through a membrane filter (mesh  $0.45 \mu m$ ) to obtain suspended particles for further determination of their microelement composition. The technique of measure-





Note: (–) No data; (\*) example of highly polluted river.

**Table 2.** Concentration of suspended matter (*D*, mg/l) and metals therein in the Amur and some other rivers

River	D	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Source
Amur	$33 - 40$	4.17	$1307 - 1442$	$89 - 104$	$22 - 24$	$22 - 23$	$0.34 - 0.38$	$33 - 35$	This work
Lena	29	5.5	1243	180-217	$26 - 39$	$31 - 37$	$0.14 - 1.4$	$24 - 37$	[1]
Gironda	42.5	4.89	880	229	55	46	1.90	53	$^{[3]}$
Mississippi	200	5.0	1620	130	38	33	0.65	45	[4]
Shelda*	$20 - 85$			540-1133	125–192	$125 - 132$	$6.3 - 12.7$	$33 - 67$	[5]

Note: (\*) Example of highly polluted river; Fe is given in %, other metals, in  $\mu g/l$ ; (-) no data.

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**Fig. 1.** The study area, distribution of salinity (‰) in surface waters, and changes in concentrations of dissolved metals (µg/l) in waters with different values of salinity. (*1, 2*) Sampling stations in the northern and southern parts, respectively, of the study area.

ment of metal concentrations in water and suspended matter is described in [6].

In the summer low-water period (July 2005), waters with intermediate salinity occupied the northern part of the Amur estuary confirming the dominant summer river runoff to Sakhalin Bay [7]. The southern part of the estuary was occupied by waters with salinity of 28– 29‰. Waters in the northern part of the Tatar Strait had a salinity of 29–31‰.

As compared with other large rivers, the Amur River shows no significant pollution by dissolved metals, as is evident from their concentrations in waters in the lower



**Fig. 2.** Concentration of metals in suspended matter of the Amur estuary with different Al contents. (*1, 2*) Northern part and southern parts, respectively, of the study area.

course of the river (Table 1). The exception is dissolved Fe forms with concentrations being substantially higher than in most large rivers, which is probably explained by the wide development of boggy landscapes and elevated content of organic matter in the lower reaches.

The content of suspended matter in the Amur water during the summer low-water period varied from 33 to 40 mg/l against the background of its annual mean values of 65–107 mg/l [7].

The concentrations of metals in the suspended matter in waters at lower reaches of the Amur are practically similar to their background values, indicating an insignificant human impact (Table 2). Thus, the concentrations of metals in solution and suspended matter in the lower course of the Amur during the summer low-water period of 2005 were comparable with their minimal values in other large rivers.

Figure 1 demonstrates the distribution of dissolved metals in waters of the Amur estuary with different values of salinity. Like in the majority of other estuaries [1, 2], Fe is rapidly removed from solution in waters with salinity up to 5‰. Changes in concentrations of Cu and Ni in waters with intermediate salinity are best approximated by the linear function, which points to conservative dilution as the main controlling agent. A similar trend is observed for dissolved Pb, although the scatter of data is greater. The distribution of dissolved Cd and Mn is characterized by distinct concentration maximums in waters with salinity of 10–25‰ (Fig. 1, diamonds), indicating an additional influx of these metals due to their desorption from suspended matter and/or bottom sediments [2, 3]. The dissolved Zn content in waters with intermediate salinity shows irregular variations from  $0.24$  to  $0.68 \mu$ g/l.

In the southern part of the Amur estuary and adjacent waters of the Tatar Strait, variations in the contents of dissolved metals are also significant (Fig. 1, boxes), although salinity during the summer low-water period shows a narrow variation range (29.30–31.51‰).

A significant correlation with salinity variation in this interval was observed only for dissolved forms of Cu and Mn.

Changes in the microelement composition of suspended matter in the Amur estuary are controlled by proportions of riverine (terrigenous) and marine (biogenic) components, rather than by salinity. These proportions are determined, in turn, by the distribution of terrigenous suspended matter along the estuary and by plankton productivity. Judging from the high (over 5%) content of Al (typomorphic metal for terrigenous aluminosilicate material), the role of the biogenic component in the Amur estuary is insignificant. Input of the biogenic constituent increases in the southern part of the estuary and northern part of the Tatar Strait. Nevertheless, the Al concentration in these waters averages 3.65%; i.e., more than one-half of the suspended matter is represented by terrigenous material.

Among the metals under consideration, Fe and Ni demonstrate significant positive correlation with the Al concentration in suspended matter. Cu, Mn, and Cd show a negative correlation (Fig. 2); i.e., they are most intensely concentrated in the biogenic component of material suspended in waters adjacent to the Amur estuary. Zn and Pb lack any correlation with the content of terrigenous material.

Thus, the content of dissolved Fe in the Amur estuary and adjacent waters is controlled by its accelerated removal from solution at a salinity up to 5‰. The concentrations of Cu, Ni, and, probably, Pb are governed by the mixing of riverine and sea waters with different contents of these metals in solution. The elevated concentrations of dissolved forms of Cd and Mn in waters with intermediate salinity suggests desorption of these metals from suspended matter transported by rivers and/or bottom sediments into solutions. Because of the initial low content of dissolved Zn in Amur water comparable with that in coastal-marine waters, this metal shows no significant trend in changes of its concentrations in the course of water mixing.

Terrigenous material is enriched in Al, Fe, and Ni, while biogenic material is enriched in Cu, Mn, and Cd. Therefore, changes in the metal concentrations in suspended matter of the Amur estuary are primarily controlled by the ratios between its terrigenous and biogenic components.

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