Environ Monit Assess (2010) 168:133–140
DOI 10.1007/s10661-009-1097-0

Mercury in bottom sediments of the Amur River, its flood-plain lakes and estuary, Eastern Siberia

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Received: 10 January 2009 / Accepted: 2 July 2009 / Published online: 24 July 2009

Abstract Mercury (Hg) is an element of a special concern in the Amur River basin, where numerous cinnabar deposits and manifestations have been prospected. Moreover, the territory is under heavy anthropogenic pressure due to intensive economic development that includes activities accompanied by noticeable emissions of Hg to the environment through poor waste management practices and accidental emergency discharges. Yet, information on Hg distribution and behavior in this region is scarce and inadequate. In order to evaluate Hg levels and fate in this vast territory, surveys of river, lake, and estuarine bottom sediments, as integral indicators of environmental status, were carried out in 1990, 1991, 1997, and 2004. The results showed the following: (1) stagnation of the Russian economy in the 1990s has resulted in a noticeable decrease of the Hg content in the Amur River sediments to the basin pristine level of about 0.05 mg kg^{-1}; (2) Hg distribution in the sediment depth proves the element redox-dependent behavior; (3) in some cases, Hg enrichment may be related to the long-term anthropogenic emission; (4) Hg concentration in bottom sediments was found to increase in the following order—the Amur River mouth, the estuary, and the Sea of Okhotsk, showing the weakly non-conservative Hg behavior during estuarine water mixing.

Keywords Mercury · River · Lake · Estuary · Bottom sediments · Contamination · Economic stagnation · Amur River

Introduction

The Amur River (Heilongjiang) is one of the world's largest rivers. It drains a 1,855,000 km^2 area of Eastern Asia that varies in geological, geochemical, and climate–landscape features. The region's environment is strongly affected by rapid economic development, boosted since the

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1930s in the Russian and since the 1950s in the Chinese parts of the basin. Mercury (Hg) is a typical element of the region's mineralization; many cinnabar deposits and manifestations have been prospected here. Secondly, numerous industrial enterprises, including large paper mills, are situated in both the Russian and Chinese regions. Their poor waste management and obsolete technologies are responsible for significant enduring Hg emissions and disastrous emergency discharges (Wu et al. 1994; Laperdina 2002; Kot and Matyushkina 2002; Zhang and Wong 2007; Lin et al. 2007). Unfortunately, government authorities of both countries tend to underestimate ecological problems or/and are often unable to take appropriate measures when dealing with emergency situations and their consequences. Despite the obvious necessity of relevant environmental monitoring, a regular and systematic investigation of geochemical and toxicological behavior of Hg in the basin only commenced recently, and information on Hg distribution here is still scarce and fragmented. Besides, some available published data is often considered untrustworthy due to the questionable reliability of instruments and poor quality control that is common in Russian environmental monitoring practice (Tsirkunov 1998).

It is well known that sediments at the bottom of water column play a key role in the biogeochemical cycle of Hg in water ecosystem by accumulating and storing the metal. Thanks to this ability, bottom sediments may reflect both short-term and long-term biogeochemical conditions of any particular water system ("memories of chemical exposure") and therefore can be used to detect the presence of contaminants, which do not remain soluble after discharge. Moreover, bottom sediments are an integral product of the processes of weathering and transport of soil/rocks and reflect a real biogeochemical situation of the draining area (Förstner and Wittmann 1983). In addition, usual metal contents in bottom sediments of up to two to three orders of magnitude greater than their level in water that simplifies the procedures of sampling, storage, and analysis for metals. Analytical processes are thus less demanding of the strict precautions required for studies of trace metals in dynamic water phase. This may extend the research abilities of many relatively poorly equipped Russian and Chinese laboratories unable to implement the "clean room" procedures (Cossa et al. 1996).

The presented work pursued the following purposes:

1. to survey the level and distribution of Hg in bottom sediments of the Amur River middle and lower stream, its flood-plain lakes and the estuary, and, thus
2. to assess the extent of technogenic Hg contamination in the basin
3. to examine Hg behavior and fate in the sediment environment

Results from the 1991, 1997, and 2004 sampling campaigns of the Amur River, along with data obtained in a 1990 marine research cruise to the Amur River estuary, have been summarized and reported.

Materials and methods

Study area

The middle and lower Amur River basin is influenced by summer–autumn monsoons creating wet subtropical-like conditions. These alternate with severe and frosty winters. Such unique conditions, called "monsoon-frost hydromorphism", facilitate intensive weathering processes (Zimovets 1976). Much of the water stream runs between low, often overflowing banks into vast marshes broken by numerous channels and dotted with lakes and ponds. The river is fed primarily by summer and autumn monsoon rains. During the high-water season from May to October, the vast areas of the floodplain often join together forming enormous lakes.

The area surveyed encompassed (Fig. 1):

1. the Amur River downstream of Khabarovsk to the mouth at the port of Mago, with two sites upstream
2. the lakes of the Amur flood-plain, along with lakes Chukchagirskoye and Evoron situated above the flood-plain

Fig. 1 Schematic map of the middle and lower Amur and its estuary showing sampling sites. River sites sited: *SA* Sikachi-Alyan, *K* Kafa, *T* Tyr, *M* port of Mago

3. two areas in the Amur River estuary—the mixing zone in the Sea of Okhotsk, namely the Sakhalinsky Bay and the north-eastern shelf of the Sakhalin I. Terrigenous sediments, originating from the Amur River, compose vast areas of the south-western Sea of Okhotsk, reflecting the Amur River plume during monsoon floods (Petelin and Ostroumov 1961).

Sampling

Four sampling campaigns along the Amur River and its flood-plain lakes have been carried out—in 1991 (two cruises), 1997, and 2004. The river and the bottom sediments of the lakes, as well as the river fresh sediment material left by the high water flood were sampled in 2004. The corer *PI-2* was used for the river and lake sediment sampling. The river samples considered in this work were collected from the same sites in 1991, 1997, and 2004. Soil corers were utilized for lake sediment sampling during extremely low water in 2004. Samples of the surface 0–5 cm bottom sediments in the estuary were taken with a modified dredge from on board the R/V *Akademik A. Nesmeyanov* (Pacific Institute of Oceanography, Vladivostok) in 1990.

The matter to be analyzed was drawn from the inner portion of the collected mass, which had not been in contact with the metallic parts of the samplers. Air-dried samples were crushed in an agate mortar and sieved through a 1 mm mesh. In order to compensate for the coarse dimensions and maintain homogeneity of the samples, large aliquots of 3 g were taken for analysis.

Analytical methods

The aliquots of the dry sediment material were first wetted before being soaked in concentrated HNO_3 overnight, followed by a wet-digestion by cautious simmering for 15 min with $HNO_3 + H_2SO_4$ (4:1) in Kjeldahl flasks with a reflux condenser. The analysis was carried out with cold vapor AAS technique using a *Yuliya-5K* analyzer (*Metrologiya*, Russia). The accuracy of Hg measurements was verified using DSZ-MSO-0028:1998 reference sample for Hg provided by O.V. Bogatsky' Physico-Chemical Institute (Odesa, Ukraine). The detection limit, calculated as a triple standard deviation of the procedural blank, was 0.004 mg Hg kg^{-1}. The corresponding reproducibility of replicated analysis was better than ±10% for samples with ≥ 0.01 mg kg^{-1} Hg content. Reagents and distilled water were tested for Hg content. The laboratory glassware, equipment, and supplies that came directly in touch with samples were pre-cleaned by filling up with or soaking in 2% HNO_3 for 48 h.

As many authors stress, the fine-grained sediments, in which most of the substances active in metal bonding are enriched, should be separated from the coarser-grained (mostly quartz), more or less inert (with regard to metal accumulation) sediment fractions (Förstner and Wittmann 1983). The diluting effect of the coarse sediment fraction was corrected by normalization (quartz compensation) to the content in fine (pelitic) fraction by comparing with the content of aluminum.

Results and discussion

The Amur River

Hg concentrations in the bottom sediments of the middle and lower Amur River, obtained in all sampling campaigns, were relatively low (Table 1). This may lead us to the conclusion that neither the mercuric mineralization nor specific weathering processes contributed significantly to the territory environment background of Hg. Nevertheless, Hg concentrations in the 1991, 1997, and 2004 samplings differ noticeably. The 1991 values are up to three to four times higher than the 1997 and 2004 ones (0.23 ± 0.15, 0.07 ± 0.04, and 0.05 ± 0.02 mg kg^{-1}, correspondingly; Table 1, Fig. 2). Moreover, the highest Hg levels in 1991 were registered downstream from large industrial centers such as Khabarovsk, Amursk, and Komsomolsk-on-Amur. The sediment cores collected from the same sites during 1997 survey have not shown any noticeable Hg enrichment. The authors believe that this indicates a substantial drop in Hg emissions due to the general stagnation of the Russian economy in the 1990s. In 1991 the (Far East) Russian economy was at its peak, generating substantial technogenic impact. Since 1991, the contaminated sediments might have been re-suspended during water floods and/or capped by more recent sediment material, depending on the local

Table 1 Hg content in pelitic fraction of surface bottom sediments of the middle and lower Amur River and its estuary, Eastern Siberia, mg kg^{-1}, dry weight basis (average, standard deviation, and range)

Bottom sediments	$x \pm Sx$	($x$min–$x$max)
Amur River		
(1) Sampling 1991 ($n = 20$), including	0.23 ± 0.15	0.05–0.79
Upstream industrial centers	–	0.05–0.30
Downstream industrial centers	–	0.13–0.79
(2) Sampling 1997 ($n = 25$)	0.07 ± 0.04	0.02–0.17
(3) Sampling 2004, high flood ($n = 9$)	0.05 ± 0.02	0.02–0.07
Lakes of the Amur floodplain, 2004 ($n = 55$)	0.05 ± 0.01	<0.02–0.14
Amur estuary		
Sakhalinsky Bay ($n = 26$)	0.19 ± 0.18	0.13–0.34
NE Sakhalin I. Shelf ($n = 30$)	0.26 ± 0.09	0.13–0.47
Comparative data		
Soils of the Middle Amur Lowlands ($n = 30$)[a]	–	0.02–0.10
2nd Songhua River[b], background	–	0.01–0.02
Actual content	–	0.01–1.27
Thur River, background (NE France) ($n = 50$)[c]	0.23	0.03–0.41
Madeira River	0.045	(0.04–0.05)
Its floodplain lakes (Amazon, Brazil)[d]	–	0.06–0.12
Great Lakes ($n = 1885$)[e], background	0.04 ± 0.09	0.00–0.37
Contaminated	0.19 ± 0.59	0.00–1.40
Gulf of the St. Lawrence River ($n = 445$)[f]	0.39	0.01–12.3
Seine River ($n = 9$)[g]	0.41 ± 0.10	–
Estuary	0.58 ± 0.20	–
Marine	0.38 ± 0.08	–
Average shale (argillaceous material)[h]	0.4	–

[a] Kot and Matyushkina 2002

[b] Lin et al. 2007

[c] Remy et al. 2003

[d] Bastos et al. 2006

[e] Marvin et al. 2004

[f] Loring 1975

[g] Mikac et al. 1999

[h] Turekian and Wedepohl 1961

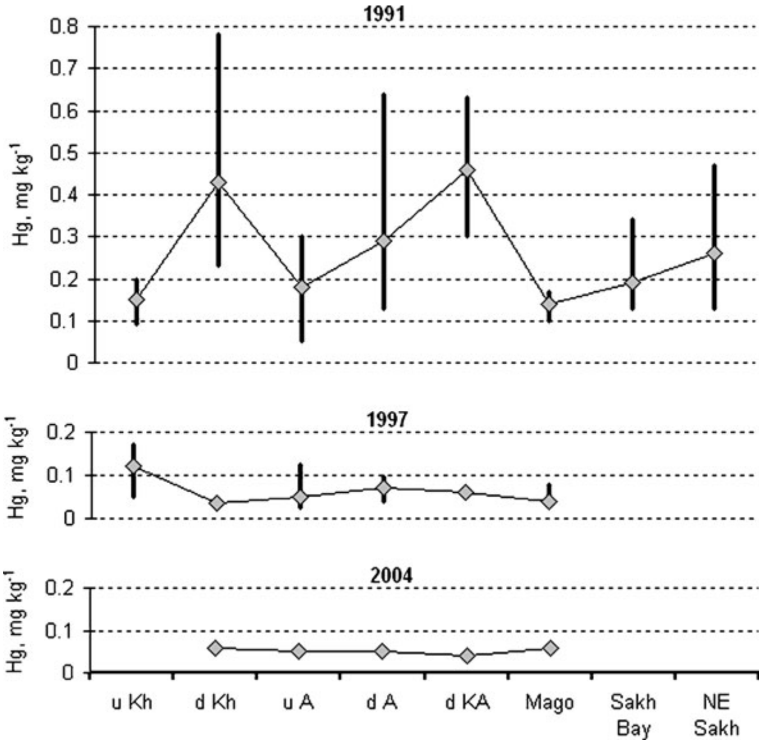


Fig. 2 Contents of Hg of bottom sediments of the middle and lower Amur River (sampling 1991 and 1997) and its estuary (1991), and the river flood silts (average 2004): *u Kh* and *d Kh* upstream and downstream Khabarovsk, *u Am* and *d Am* upstream and downstream Amursk, *d KA* downstream Komsomolsk-on-Amur, *Mago* the mouth at the port of Mago, *SB* Sakhalinsky Bay, *NES* north-eastern shelf of Sakhalin I. by the Piltun inlet

situation. As an example, Laszlo et al. (1977), in studying the Sajo River, Hungary, found that 3 months after a flood, the Hg concentration in the bottom sediments had been reduced to approximately one-quarter of the values found immediately before the flood. Intensive water circulation, strong current, and high water discharge are main factors contributing to this self-restoration. In this connection, it is important to point out that Hg concentrations found for the basin pristine soils, namely 0.05–0.10 mg kg^{-1} (Kot and Matyushkina 2002), correspond well to Hg content in bottom sediments collected in 1997 and 2004.

Analysis of sediment cores collected in the Amur River revealed a noticeable variation of Hg distribution and pattern in depth (Fig. 3). Mercury concentration peaks, coinciding with layers of light ochre-rust colors of ferric Fe hydro-oxides, were found in the cores sampled at Tyr (9–17.5 cm) and Kafa (11–13.5 cm). This indicates Hg redox-dependent post-sedimentation redistribution as has previously been found in the pelagic sediments of the Sea of Japan (Kot 2004). An indicative core No. 76 was taken at Tyr in the lower Amur River stream, in 1991. The sampling was carried out in deep and calm waters beneath the Tyr cliff where Amur River fine-grained suspended matter has slowly accumulated for centuries sheltered from river turbulence by the cliff. Thanks to these unique conditions, this

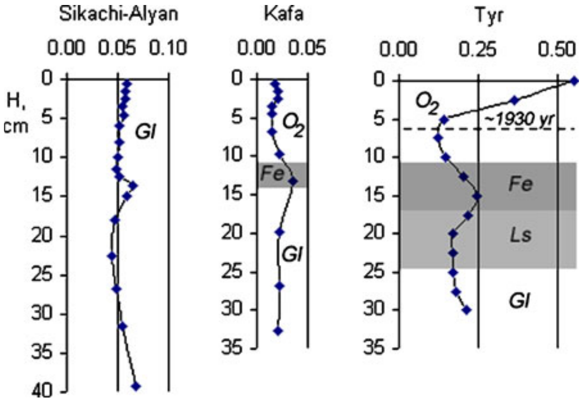


Fig. 3 Contents of Hg of some sediment cores of the Amur River. Symbols *Fe* and *Ls* indicate strata mottled with Fe^{3+} hydro-oxides and lilac spots efflorescence, *Gl* gley strata

sample may represent the long-term continuous sedimentation and contamination trends of the Amur River. Classic sharply shaded sediment facies strata were marked within the core's well-consolidated material in the following order of depth:

1. the upper light brown and hazel colored, oxic (0–9 cm)
2. ochre-rust spot-efflorescence of ferric Fe hydro-oxides (9–17.5 cm)
3. deep-lilac colored large spots of an uncertain nature (17.5–25 cm)
4. below 25 cm—a monotonous faded-olive and gray colored, gley

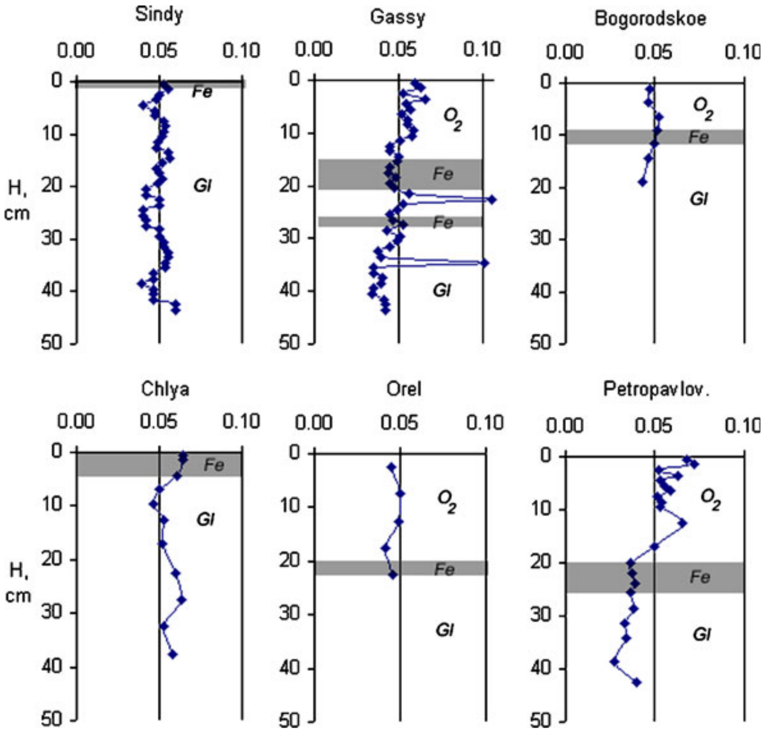
The average sedimentation rate in this part of the basin was evaluated as about 1 mm year^{-1} (Makhinov 1995). Based on this rate, the dramatic surface Hg concentration peak in the 0–6(7) cm sediment layer may correspond to 1920/1930–1990 years that coincides with the start of active industrial development in the Russian part of the basin.

Lake bottom sediments

Hg contents in bottom sediments of the lakes of the Amur River flood-plain corresponded well to those in the Amur River sediments of the 1997 and 2004 samplings (Table 1). Inasmuch as the flood-plain lakes' sediments are formed with a major contribution of material brought from the Amur River (Shamov et al. 1999), the average Hg value of 0.05–0.10 mg kg^{-1} may serve as a natural background level of Hg in sediments and soils of the basin.

Mercury concentration varies with depth in the lakes' sediment cores. For lakes Sindi, Bogorodskoye, Chlya, and Orel, it fluctuates around background average, but in sediments of Lake Gassi and in the upper core from Lake Petropavlovskoye, it increases steadily towards the surface (Fig. 4). The increase in Hg content of Lake Petropavlovskoye is most likely linked to industrial and municipal waste discharge from the City of Khabarovsk via the urban rivers of Chernaya and Berezovaya, along with wastes from commercial cattle farms situated on the lake

Fig. 4 Hg contents of some sediment cores of lakes of the Amur River flood-plain. Symbol *Fe* indicates strata mottled with Fe^{3+}, *Gl* gley strata



banks. Mercury distribution in the sediments of lakes Gassi and Sindi is most probably shaped by internal diagenetic processes. It is interesting to compare these neighboring 100 km lakes. Both lakes are similar in their sizes and hydrometric features and they are believed to be comparable in hydrologic characteristics. There are no substantial contamination sources affecting this area, except for the Khabarovsk-Komsomolsk-on-Amur motorway. Nevertheless, in spite of the fact that the average Hg concentration in sediments of both lakes is close, Hg distribution within their depths has significantly different patterns. Lake Sindi's bottom sediments are of monotonous gray-olive "reducing" colors, mottled with ferric Fe hydroxides spots in the uppermost 2 cm. Whereas, the sediments of Lake Gassi showed a variegated picture of alternated strata with Hg concentration peaks in the upper light-brown oxic layers (0–11 cm), two sharp peaks on 22 cm depth just beneath the Fe-mottled strata and on 34 cm depth within the lightened (bleached) horizon. This dissimilarity between two lakes may be explained by different water and oxygen dynamics and differing unload regimes of suspended matter.

Thus, Hg distribution in bottom sediments of the river-bed lakes is determined by either anthropogenic pollution or internal sediment processes of diagenetic redistribution.

Estuarine sediments

Approximately nine of ten of the Amur River water discharged into the sea during the warm (high discharge) season goes in a northerly direction and spread from the surface in the Sakhalinsky Bay, mostly in the central–eastern part. Then the current turns around the north of Sakhalin Island and moves southward along the eastern coast of the island (Petelin and Ostroumov 1961). In the central–eastern part of the Sakhalinsky Bay, slow water-exchange at the bottom favors accumulating of fine and rich in organic matter suspended material brought by the Amur stream. Anoxic conditions are developed there (Goryachev and Kot 1997). Mercury enrichment was found in two distinctive estuarine zones—firstly, an area dominated by the Amur River discharge and forming sediments with higher content of organic matter and fine particles, and secondly, a zone influenced by the marine counter-current, of coarser sediments impoverished with C_{org} and fine earth (Goryachev and Kot 1997).

The Hg content in bottom sediments of the Amur River estuary/mixing zone revealed a tendency to increase marine-ward in the following order (the data of 1990–1991): the mouth, Sakhalinsky Bay and the north-eastern Sakhalin Island shelf, by a ratio of 1.0:1.4:1.9, correspondingly, showing the weakly non-conservative Hg behavior, that is the Hg content does not correlate directly to the river–sea water mixing gradient. This phenomenon in river estuaries has been described earlier, for example, in the estuaries of the St. Lawrence River (Cossa et al. 1988), the Scheldt River (Leermaker et al. 1995), and the Patuxent River (Benoit et al. 1998), and is consistent with the removal of dissolved, colloidal, and particulate Hg from the water column.

Conclusions

Hg contents in the bottom sediments of the Amur River downstream large industrial centers have noticeably decreased down to a background level of 0.05 mg kg^{-1} during the period of Russian economical stagnation in the 1990s. This value corresponds to the Hg concentrations in the basin pristine soils.

Hg in the river and the lakes' bottom sediments showed redox-dependent behavior, with concentration peaks registered in the surface oxic and by Fe oxidation strata. Some Hg concentration peaks in the surface layers are most likely linked to long-term industrial pollution.

Hg concentration in bottom sediments of the Amur River estuary/mixing zone increased in the order: the Amur River mouth, the estuary, the sea of Okhotsk, showing the weakly non-conservative Hg behavior.

Acknowledgements The authors are grateful to Prof. Pyotr V. Ivashov for the productive discussion of the materials, Dr. Sergey Ye. Sirotskiy, Dr. Dmitriy N. Yur'yev, Sergey N. Belotskiy, Dr. Vladimir V. Shamov, the crew of R/V *Ladoga,* all are from the Institute of Water and Ecology Problems, Khabarovsk, and Erick F. Kot, my son for their kind support in the fieldwork. Mrs. Louisa Herd, Biosecurity Service, Ministry of Agriculture and Forestry, Auckland, New Zealand, is greatly appreciated for the English text editing. Comments from the anonymous referees considerably improved the final manuscript. Partial support provided by The Ministry of Absorption, State of Israel, is appreciated.

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