

TRACE METALS OF BOTTOM SEDIMENTS OF THE AMUR RIVER AND ITS ESTUARY: SAMPLING 1994-95

KOT FYODOR S. *

Institute of Water and Ecology Problems, Far Eastern Branch of the Russian Academy of Sciences

INTRODUCTION

The sediments existing at the bottom of the water column play a major role in the biogeochemical/pollution scheme of the river systems by metals. They reflect the current and historical situation of the water system and can be used to detect the presence of contaminants that do not remain soluble after discharge into surface waters. Moreover, sediments act as a carrier and possible source of pollution because trace metals can be released back to the water column by changes in environmental conditions. Therefore, the analysis of trace metals in bottom sediments permits us to detect pollution that could escape water analysis, and also provides information about the critical sites of the water system under consideration (Förstner and Salomons, 1980).

According to Förstner and Wittmann (1983) trace metals in recent sedimentary deposits can generally be divided into two categories: in accordance with their predominant source of origin, either as “geochemical” or “man-made” (“civilisational”). Metals such as Zr, Rb, and Sr, which are derived from rock material by natural weathering processes, constitute the first group. The second group is made up of metals which have become enriched chiefly as a result of man’s activities, and includes among others Cr, Co, Ni, Cu, Zn, Cd, Hg, and Pb. Between these two groups there are combinations; for example, the enrichment of mobile elements such as Mn and Fe, which may well have had civilisational origins such as extreme eutrophication. By their own accumulation, these metals can cause other elements to accumulate.

Few works have been published on trace metals biogeochemistry/pollution of the spacious Amur River basin (*see* Kot, 1996, Goryachev and Kot, 1997, Chen et al., 2000). The present work was intended to evaluate to a first approximation: (1) trace metal background abundances of recent bottom sediments of the middle and lower Amur River stream and its outflow in the Sea of Okhotsk, (2) forms and behaviour of trace metals bound to suspended matter, and (3) possible human-impacted metal enrichment along the Amur River.

* Present address: Biogeochemical Professional Findings Independent, 17-14 Almagor Street, Tel Aviv, 69187, Israel; e-mail: kits@front.ru.

OBJECTS AND METHODS



Fig. 1. Survey location map showing sampling sites.
SB - Sakhalinski Bay
NES - by NE Sakhalin I.

The area surveyed comprised: (1) the Amur River section downstream Blagoveshchensk to the mouth, and (2) two areas in the Amur River estuary, namely (2.1) the Sakhalin Bay (the survey area confined to 53°40.0'N, 141°30.3'E; 53°39.7'N, 142°04.0'E; 53°52.6'N, 142°21.0'E; 54°19.8'N, 142°04.1'E, and 54°20.0'N, 141°11.9'E), and (2.2) by the NE Sakhalin Island by the Piltun Firth (52°34.8'N, 143°22.4'E; 53°03.8'N, 144°06.1'E; and the island shore) (Fig. 1). The suspended and soluble matter carried by the Amur River originates from the vast and highly

varied in geochemical and ecosystem patterns territory. The terrigenous sediments of the Amur River origin occupy vast areas of the SW Sea of Okhotsk, reflecting the main direction of the Amur River plume during the summer and autumn monsoons (Petelin and Ostroumov, 1961).

The Amur River sediment cores were collected with a PI-2 corer during three cruises of the R/V *Ladoga* in 1994-95. The outflow zone sediments were collected with modified dredges during the 19th and 20th voyages of the R/V *Akademik A. Nesmeyanov* in 1992-92. Samples to be analyzed were drawn from the inner portion of the collected mass which had not been in contact with metallic parts of the sampler, and air-dried. Special measures were taken to avoid both "positive" and "negative" contamination of samples (Kralik, 1999).

Concentration of Zn, Cu, Pb, Sn, Bi, Sr, Rb, Ba, Y, Th, U, Zr, and Nb were determined by X-ray fluorescence spectroscopy, Hg by cold-vapour atomic absorption spectrometry; and Mn, Mo, V, Be, Ga, Co, Ni, Cr, Ti, Li, Al, and Fe by semi-quantitative atomic emission spectrometry. The organic matter content was accounted for by the loss on ignition at 600 °C during 4 hrs. The analytical accuracy was controlled by duplicate determinations and with standard samples from the Ministry of Geology of the Russian Federation, and RSO-3497 standards for Hg from Ukrainian Physico-Chemical Institute, NAS (Odesa). Intercalibration measurements with the Analytical Laboratory of the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements (IMGRE, Moscow) were satisfactory.

RESULTS AND DISCUSSION

Geochemical background. The obtained bulk-sediment concentrations of trace metals have been re-estimated into contents of pelitic fraction by normalizing procedure to Al abundances to compensate for the coarse-grained sediment fraction dilution (Table 1).

Table 1. Normalised trace metal concentration in bottom sediments of the Amur River, $\mu\text{g g}^{-1}$ d.w., noted otherwise.

Element	$\bar{x} \pm S_x$	max	References		
			Peterson and Boughton (2000) [n=24]	Average shale (Turekian and Wedepohl, 1961)	Upper Amur River and its tributaries (Chen et al., 2000) [n=5]
As	8.5 ± 5.1	18.6	8.7	13	
Ba	330 ± 180	690	820	580	
Be	2.3 ± 1.1	5.4	1.8	3	
Co	8.5 ± 2.6	13.9	13.1	19	
Cr	48 ± 23	96	92	90	
Cu	27.0 ± 11.1	53.6	27.9	45	11.5-21.2
Ga	21 ± 10	41	15	19	
Hg	0.28 ± 0.22	0.75	0.04	0.4	
Li	-	30	-	66	
Mn	580 ± 260	1200	540	850	790-990
Mo	3.1 ± 2.8	13.9	0.8	2.6	
Nb	11.9 ± 5.5	22.7	11.8	11	
Ni	20.0 ± 9.1	40.5	34.5	68	
Pb	22.9 ± 6.6	35.3	21.5	20	22.6-36.6
Sc	5.8 ± 1.2	7.1	9.9	1.3	
Sn	11.3 ± 10.8	36.9	2.0	6	
Sr	313 ± 112	558	328	300	
Th	9.0 ± 3.9	17.7	11.1	12	
Ti, %	0.30 ± 0.11	0.54	0.35	0.46	
U	2.7 ± 1.2	5.9	2.8	3.7	
V	83 ± 52	280	99	130	
Y	21.3 ± 8.1	35.4	20.2	26	
Yb	1.7 ± 0.5	2.7	2.2	2.6	
Zn	55.9 ± 36.7	117.0	82.4	95	68.3-91.6
Zr	271 ± 117	611	-	160	
C _{org} , %	5.40 ± 3.01	11.9	2.00	-	0.40-2.33
Al, %	7.24 ± 2.30	11.3	6.75	8.0	
Fe, %	3.6 ± 0.89	6.0	3.2	4.72	2.74-3.19

Al is assumed to have had a uniform flux to the sediments over the past century from crustal rock sources. Consequently, changes in the water, CaCO₃ or organic matter content, especially in the upper layers, can be compensated (Bruland et al., 1974; Förstner, 1981). The obtained values were compared to the average abundances in sedimentary rocks (average shale) after Turekian and Wedepohl (1961) (Fig. 2).

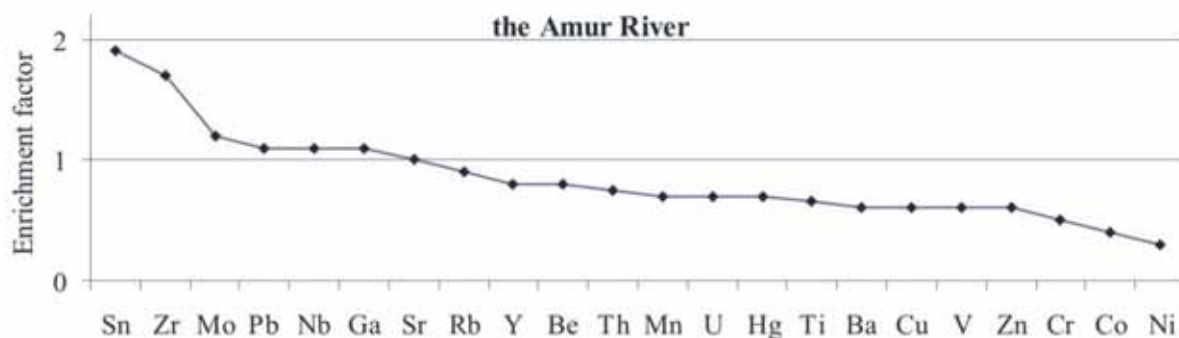


Fig. 2. Trace metal geochemical spectre for the Amur River

From this we can ascertain that the Amur River bottom sediments are relatively enriched in Sn (enrichment factor, 1.9), and Zr (1.6), while depleted in Ni (0.3), Co (0.4), Cr, Cu, Hg (0.5), and V, Ti (0.6). Other metals, i.e. Mo, Pb, Nb, Ga, Sr, Rb, Y, Be, Th, Mn, and U could be supposed to be on the average abundance level. On the whole, this spectrum agrees well with the character of mineralization of the basin (Smirnov, 1946; Radkevich, 1977) and corresponds to the trace element spectrum of acidic (granite) rocks. Hg and Zn, typical elements of mineralization, are an exception. The high abundance of lithogenic Sn and Zr might indicate the high weathering rate in the basin.

Evaluation of human impact. In many respects, bottom sediments are a more advantageous object for environmental testing compared to water or water biota. First, sediments have a reasonably constant chemical composition. Second, they are relatively inert and have long memory of chemical impact. Third, they usually require simpler procedures of sampling, storage, preparation and analyzing for trace elements than water and biological material does. This last advantage is especially important in view of the equipment and techniques commonly at hand at domestic laboratories and the skill of the personnel occupied in scientific and environmental protection services.

Estimation of the contamination level of sediments by a certain element requires knowledge of the natural, pre-industrial concentration, in order to compute a sediment enrichment factor (EF). Quite often background values used to compute these factors are simply taken from a compilation of the average shale composition (Turekian and Wedepohl, 1961). The advantage of this standard is that it is free from any anthropogenic admixtures; disadvantages are, however, that regional geochemical characteristics are not taken into account, and that the shale has a nominal grain-size range of $<2 \mu\text{m}$. The problem at hand is, therefore, to estimate the natural background levels as a function of the mineralogy. Since use of baseline levels is appropriate only if the granular composition of both sediments is the same, the values from the Amur River had to be used corrected for the enrichment factor (EF) (Förstner, 1981):

$$EF = (X/A)_{\text{sample}} / (X/A)_{\text{reference}},$$

where (X/A) is the ratio of the concentration of trace elements X to a conservative reference element (such as Al) in sample and reference material.

The averaged data obtained (Table 2) prove that the trace metal levels of the Amur River bottom sediments are far from those measured in old industrialised regions. Moreover,

they should be rating to Class 1 of pollution classes after European Water Association, i.e. they are virtually clean (Shaping..., 2002).

Table 2. Trace metal abundances in pelitic fraction of bottom sediments of the Amur River and some old industrial regions, $\mu\text{g g}^{-1}$ dry weight.

Element	Amur River	Unpolluted muddy sediments (Förstner, 1981)	Upper Vistula River (Rybicka, Watras, 1989)	Rhine River (Müller, 1985)	
				1972	1985
Hg	0.28	0.2	-	1.1-13.9	0.2-17.0
Cu	27.0	30	440	55-287	76-361
Pb	22.9	19	600	112-357	58-190
Cr	48	50	130	134-405	87-325
Zn	55.9	124	4200	542-1572	365-1818
Co	8.5	17	-	-	-
Ni	20.0	55	130	-	-

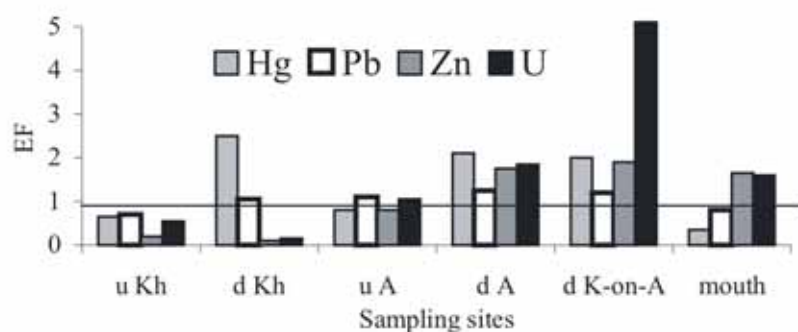


Fig. 3. Trace metal enrichment factor values for some sites along the Amur River:

u Kh, d Kh - upstream and downstream Khabarovsk,

u A, d A - upstream and downstream Amursk,

d K-on-A - downstream Komsomolsk-on-Amur

Meanwhile, the enrichment factor calculated for selected sampling sites shows that the Amur bottom sediments – sampled in 1994-95 – downstream from large industrial centres are enriched in metals (Fig. 3). At present, trace metal loading to the Amur River is expected to decrease due to the Russian

Far East economical activity decline last years. On the other hand, the growing industrial and agricultural activity in the Chinese part of the basin may become the main source of contamination.

To trace metal migration forms. As Duinker stresses (1986) transformation of element species in estuaries has a complex character and the popular plots of dissolved concentrations vs. salinity used to decide how a given element behaves are usually insufficient. While, the chemical composition and distribution of trace elements in sediments can be used for distinguishing depositional environment and sources of weathering (Krejci-Graf, 1964, 1972).

From the comparative data for the bottom sediments of the Amur River and its estuary one can conclude that most carrying by the Amur River Be and Li (up to 100%), Sn (about 70-80%), organic matter (as $C_{org.}$, 50-90%), considerable part of U (30-60%), Th (up to 50%), Mn (30-60%), Zn (about 50%) settles from the river water column to sediments of the Sakha-

linski Bay (Fig. 4; concentration values for the Amur River have been taken as 1). Concentration of others – Al, As, Co, Ni, Mo, Rb, Ba, Y, and Yb does not change.

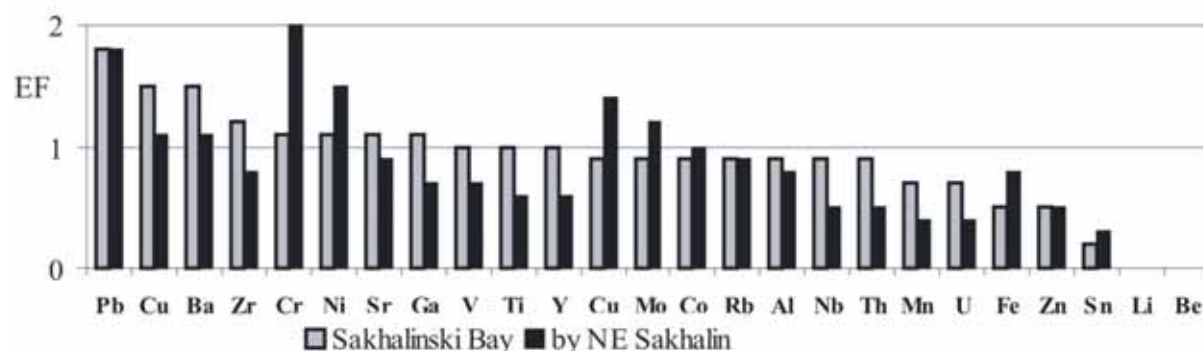


Fig. 4. Trace metal enrichment factor for the Amur River estuary bottom sediments

According to Petelin (1961) Zr is contained in the Amur mixing zone sediments as clastic zircon associated with the aleuric fraction, mainly, coarse-grained aleurite of 100 to 10 μm . From this, one can conclude that these coarse-grained aleuric particulates overcome the mixing barrier of the Amur River-the Sea of Okhotsk waters (Fig. 4). Therefore, particulate Sn, U, Th, Be, Li, and Mn, which fail to overcome the mixing zone, might be associated with coarser (>100 μm) particulates. Consequently, the trace metals can be divided to a first approximation into the following groups:

1. terrigenous, bound to the coarse-grained suspended particles – Sn, Zn, U, Mn, Be, and Li;
2. terrigenous, bound to the fine-grained suspended particles/coagulating matter – Zr, Ga, V, Ti, Y, Nb, Th, Mn, U;
3. talassophilic – Pb, Cr, Ni, Cu, Mo;
4. conservative – Sr, Co, Rb, Al;

As a whole, the trace metal distribution in the Amur River estuary corresponds well to the earlier established patterns, excepting Ga, and V. Krejci-Graf (1964, 1972) discusses that Sn, U, Ti, and Th are characteristic of sediments which have undergone a long period of subaerial weathering. They are typically a continent element, and their content decreases with increasing distance from the land. Cr, Cu, Ga, Ni, and V are usually more enriched in marine than in the continental sediments. Cr is concentrated in sediment of gyttja (slightly anaerobic) facies, while V is concentrated in sediment of sapropel (dygyttja or highly anaerobic) facies. Concentration of Pb, Ni, and Co always takes place with increasing of reducing conditions. Ni, and Cu sometimes become enriched in organic matter in the deposits of reducing environment (Krejci-Graf, 1964; Degens, 1965; Ernst, 1974). Goryachev and Kot (1997) located the increased Pb, Ni, Co, and Cu concentrations in sediments of the Sakhalinski Bay in conditions of slowed near-bottom water circulation and organic matter accumulation.

To trace metal diagenesis. All the investigated trace metals exhibit variable profiles of concentration in the Amur River sediment cores, as it is shown by a representative sediment core No. 76 (Fig. 5). The core site, somewhat downstream the Tyr Cliff, has the long-term water

dead-space condition where the Amur River fine-grained silty suspended matter accumulation takes place. “Classic” sharply shaded sediment facies strata has been marked out within the core depth, namely – successively downward: (1) the upper light brown and hazel coloured, oxidising (0-9 cm), (2) ochre-rust spot-efflorescence of Fe oxidation (9-17.5 cm), (3) lilac spotty Mn oxidation (17.5-25 cm), and (4) the downmost monotonous faded-olive and grey, gley (25 cm and below).

Thus, the investigated trace elements exhibited a redox-dependant distribution within the core (Fig. 5). At that most trace metals conformed clearly to one or more patterns: (1) enriched in Fe-oxidation slices – Hg, Sr, Co, and U; (2) enriched in Mn-oxidation slices – Zn, As, Rb, Nb, U, and Th; (3) enriched within gley slices – V, Fe, Hg, Sr, Co, and, probably, Zr; (4) Hg, Co, U, Cu, Ga, Y, As, and, probably, Zn and Rb exhibited obvious accumulation in the core uppermost oxidative strata. These patterns are inferred to represent different responses to the existing redox conditions.

From the data obtained one can resume that there are no evidences of major substantial trace metal enrichment during the industrial development in the basin have been revealed. The effects of anthropogenic and natural inputs *vs.* diagenetic redistribution on Hg, Co, U, and, Zn enrichment of the near-surface strata warrant further research.

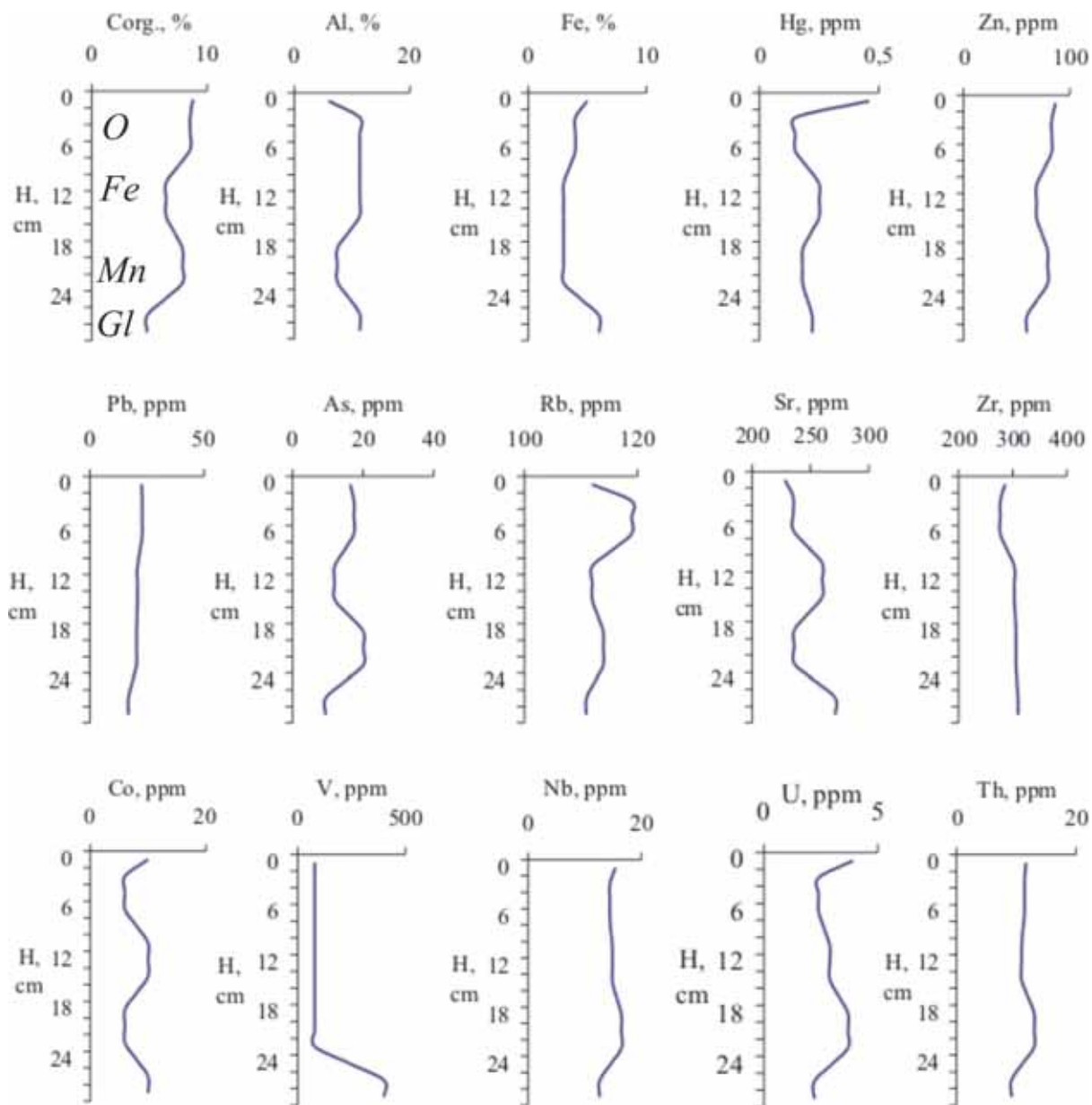


Fig. 5. Trace metal epures within the core No. 76 depth

O - oxidizing strata
Fe - Fe oxidation strata
Mn - Mn oxidation strata
Gl - gley strata

CONCLUSIONS

In general outline the Amur River bottom sediment trace metal geochemical spectrum agrees well with the character of mineralization of the basin and corresponds to the spectrum of acidic (granite) rocks.

General trace metal redistribution takes place in the geochemical barrier of the Amur River estuary.

All the investigated trace metals exhibit redox-dependant behaviour within the sediment depth. The effects of anthropogenic and natural inputs vs. diagenetic redistribution on trace metal enrichment of the near-surface strata warrant further research.

The Amur River bottom sediment trace metal concentration level is far from those measured in old industrialised regions. Meanwhile, the sediments downstream large industrial centres are considerably enriched in metals.

Acknowledgements. The author kindly thanks Dr. Konstantin G. Bakanov, as well as the crew of the R/V *Ladoga* and colleagues from Laboratory of Biogeochemistry, Pacific Institute of Oceanography, Vladivostok for their help in the field works.

REFERENCES

- Bruland K.W., Bertine K., Koide M. and Goldberg E.D. // *Environ. Sci. Technol.*, 1974. V. 8. P. 425-432.
- Chen J.S., Wang F.Y., Li X.D. and Song J.J. // *Environ. Geol.*, 2000. V. 39. P. 1334-1340.
- Collection and Preparation of Bottom Sediment Samples for Analysis of Radionuclides and Trace Elements. IAEA, Vienna, 2003.
- Degens E.T. *Geochemistry of Sediments: A Brief Survey*. New Jersey, Prentice-Hall, 1965.
- Duinker J.C. In: *The Importance of Chemical "Speciation" in Environmental Processes* (Bernhard M., Brinckman F.E. and Sadler P.J., eds.). Dahlem Konferenzen, 1986. Springer-Verlag, Berlin, Heidelberg. P. 365-384.
- Ernst W. *Schwermetallvegetation der Erde*. Stuttgart, 1974.
- Förstner U. // *Chemiker Zeitung*, 1981. B. 105. S. 165-174.
- Förstner U. and Salomons W. // *Environ. Technol. Letters*, 1980. V. 1. P. 494-505.
- Förstner U. and Wittmann G.T.W. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin et al., 1983.
- Goryachev N.A. and Kot F.S. In: *Complex Investigations of Ecosystems of the Sea of Okhotsk/ Ecology of the Russian Seas*. VNIRO Publish, Moscow, 1997. P. 188-198. (in Russian)
- Kot F.S. // *Geochem. Int.*, 1996. V. 36. No. 1. P. 91-96.
- Kralik M. // *Appl. Geochem.*, 1999. V. 14. P. 807-816.
- Krejci-Graf K. // *Proc. Yorkshire Geol. Soc.*, 1964. V. 34. P. 469-521.
- Krejci-Graf K. In: *The Encyclopedia of Geochemistry and Environmental Sciences* (Fairbridge R.W., ed.). Dowden, Hutchinson & Ross, Stroutsburg, 1972. P. 1201-1209.
- Müller G. // *Proc. Int. Conf. "Heavy Metals in the Environment"*, Athens, Sept., 1985. V. 1. P. 110-112.
- Petelin V.P. In: *Recent Marine and Oceanic Sediments*. AN SSSR Publish, Moscow, 1961. P. 368-379.
- Petelin V.P. and Ostroumov E.A. In: *Recent Marine and Oceanic Sediments*. AN SSSR Publish, Moscow, 1961. P. 380-430.

- Peterson D.A. and Boughton G.K. Organic Compounds and Trace Elements in Fish Tissue and Bed Sediments from Streams in the Yellowstone River Basin, Montana and Wyoming. Water-Resources Investigations Rep. 00-4190. U.S. Department of the Interior/U.S. Geological Survey. Cheyenne, Wyoming, 2000.
- Radkevich E.N. Metallogenic Provinces of the Pacific Ore Belt. Nauka, Moscow, 1977. (in Russian)
- Rybicka E.H., Watras M. // Przegląd Geologiczny, 1989. No. 6. P. 307-339. (in Polish)
- Shaping the Environment: Aquatic Pollution and Dredging in the European Community (Donze M., ed.). Delwel, The Hague, 1990.
- Smirnov S.S. // Vestnik AN SSSR, 1946. No. 3. P. 15-26. (in Russian)
- Turekian K.K. and Wedepohl K.H. // Bull. Geol. Soc. Am., 1961. V. 72. P. 175-192.