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Mercury Fractions in Natural and Urban Soils of the Middle Amur, Far East Russia

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The dramatic increase of mercury (Hg) content - 10-50 times the background values, accompanied by Hg fractions redistribution in favor of the most labile ones has been revealed in the Middle and Lower Amur basin river and lake waters during separate monsoon water floods (Kot, 1996). The phenomenon remained still unexplained and is considered to be conditioned by natural mechanisms promoting Hg compounds to mobilize from the pedons and bottom sediments. The purpose of this work was to evaluate the Hg ability to mobilize from typical soils of the territory. Content of Hg bound to soil organic and inorganic matter fractions separated by routine chemical methods has been investigated.

MATERIALS AND METHODS

The samples were collected from mountain brown forest lessivated soil of a lowland setting and forest podbel (brown-podzolic) of flat clayey river terraces, as well as from their urban analogues within the City of Khabarovsk. Some related features of the soils can be found elsewhere (Trans-Siberia..., 1990).

The urban soils investigated, notwithstanding being subjected to anthropogenic influence and loss of their litter layer, still keep their natural profile structure. However, horizon A1 was sometimes also affected by anthropogenic influence. The urban soils were more consolidated and more hydromorphic, and they also had higher pH value and lower organic matter content compared to the pristine soils.

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The fractionation scheme was based on routine soil chemistry procedures (Kononova, Belchikova, 1961; Orlov, Grishina, 1981; Aleksandrova, 1980; Zyrin et al., 1981; Zvonarev, 1982; Dmitriw et al., 1995) (Table 1).

The analysis precision was 0.01 ppm, issued from the sensitivity of 0.002 ppm. Results were given on a dry weight basis.

RESULTS AND DISCUSSION

The results of the analysis (Table 2) revealed that the total Hg content varied greatly within the brown forest soil profile: it decreased significantly from horizon A1 to horizons A1B1 and B1, followed by increasing content in horizons Bm3 and BC. The increase was produced by the Hg-HA fraction, while the decrease was attributed to both Hg-humin and Hg-non-organic fractions. The total Hg content was more monotonous for the forest podbel soil profile, and was characterized by a maximum in horizon A1.

Organically bound Hg predominated for the entire soils' profile, accounting for 58-96% in the brown forest soil and 69-100% in the forest podbel: mostly owing to Hg-humin and, to a lesser degree, Hg-HA fractions.

The portion of mobile Hg fractions was significantly lower. For the brown forest soil Hg-FA accounting for 0% of total Hg in litter, 4% in A1, 5-6% in Bm and 2% in BC. A significant Hg portion was extracted with H_2O from the partly decomposed litter (L+F horizon) and horizon A1 - 0.01 and 0.005 ppm, respectively. Moreover, Hg was detected in the water extracts as soon as it was digested with the H_2SO_4+$KMnO_4$ mixture, indicating Hg binding to organic matter. A detective quantity of Hg for EDTA extracts was found for the partly decomposed litter of the brown forest soil, indicating Hg compounds uncomplexed or weakly complexed to the soil humus. Probably, the most labile Hg compounds are formed during decomposition of the forest litter. M.D. Stepanova (1976) observed a similar phenomenon for copper, boron, molybdenum (Cu, B, Mo) and, presumably, manganese (Mn) for chernozem and derno-podzolic soils of Western Siberia.

Table 1. Scheme of Hg fractionation analysis (steps A-E) and evaluation (steps F-G)

Step		Nominal fraction	Procedure
A		Hg-H_2O	H_2O, 3 hours, continuous agitation
B		Hg-EDTA	0.1 *M* $(NH_4)_2$-EDTA pH3, 3 hours, continuous agitation
C	1.	Hg-free (aggressive) fulvic acids (Hg-FFA)	0.1 *N* H_2SO_4, 8 hours, occasional agitation
	2.	Hg-fulvic acids (Hg-FA) Hg-humic acids (Hg-HA)	0.1 *M* $Na_4P_2O_7$ + 0.1 *N* NaOH, pH13, 8 hours, occasional agitation followed separation with 1 *N* H_2SO_4
	3.	(Hg residue content after steps C 1.-2.)	HNO_3(c) + H_2SO_4(c) + $HClO_4$(c) + 0.5 g $K_2S_2O_8$ + 0.2 ml 1 *M* $KMnO_4$, moderate heating during 15 min in Kjeldahl flask with reflux condenser
D	1.	Hg-non-organic (Hg-amorphous Fe(Mn) compounds)	1 *N* HCl, 8 hours, occasional agitation
	2.	(Hg residue content after steps D 1.)	As in step C 3.
E		Hg-total	As in step C 3.
F		Hg-organic (Hg-organic matter)	Evaluated as difference of Hg-total (step E) and Hg-non-organic content (step D)
G.		Hg-humin (presumably, Hg bound to refractory organic matter, sulfides and refractory Fe(Mn) compounds)	Evaluated as difference of Hg-organic and (Hg-FA + Hg-HA)

For the forest podbel soil a higher portion of Hg (0-9%) was bound to fulvic acids. A large Hg content was recognized for free fulvic acids - 0-6%. H_2O extracted insignificant quantity of organically bound Hg from horizons A2B and Btg2.

The portion of Hg bound to the non-organic fraction increased significantly within the lower part of all the profiles.

Table 2. Content (ppm, dry weight) of Hg in extracting fractions of soils.

			Fractions/extracts						
Material	Horizon	Depth (cm)	Free FA	FA	HA	Humin	Org. matter	"Non-org."	Total
	Pristine soils								
Brown forest									
Litter	L + F	0-2(3)	0.00	0.00	0.05	0.14	0.19	0.01	0.20
	H	2(3)-3(4)	0.00	0.00	0.08	0.21	0.29	0.01	0.30
Soil	A1	3(4)-11(13)	0.00	0.01	0.06	0.15	0.22	0.01	0.23
	A1B1	11(13)-14(16)	0.00	0.01	0.06	0.08	0.17	0.01	0.18
	Bm1	14(16)-24	0.00	0.01	0.05	0.10	0.16	0.02	0.18
	Bm2	24-48	0.00	0.01	0.05	0.09	0.15	0.05	0.20
	Bm3	48-65	0.00	0.02	0.07	0.23	0.32	0.06	0.38
	BC	65-87	0.00	0.01	0.05	0.28	0.34	0.22	0.56
	BC	87-below	0.00	0.01	0.05	0.26	0.32	0.23	0.55
Forest podbel (brown-podzolic)									
	A1	1-7	0.01	0.02	0.07	0.13	0.22	0.01	0.23
	A2g	7-19(25)	0.00	0.01	0.04	0.10	0.15	0.00	0.15
	A2B	19(25)-38	0.00	0.01	0.03	0.11	0.15	0.00	0.15
	Btg1	38-64	0.01	0.00	0.05	0.11	0.16	0.00	0.16
	Btg2	75-85	0.01	0.01	0.04	0.09	0.14	0.03	0.17
	Cg	120-130	0.01	0.01	0.04	0.06	0.11	0.05	0.16

Table 2. Content (ppm, dry weight) of Hg in extracting fractions of soils (cont.).

Material	Horizon	Depth (cm)	Fractions/extracts						
			Free FA	FA	HA	Humin	Org. matter	"Non-org."	Total
	Urban soils								
Brown forest, forest park, recreation zone									
	A1	0-7(8)	0.02	0.02	0.12	0.18	0.32	0.01	0.33
	A1A2	7(8)-12	0.02	0.02	0.11	0.19	0.32	0.00	0.32
	B	12-25	0.01	0.01	0.05	0.05	0.11	0.03	0.14
Brown forest, cultivating for kitchen-gardens									
	A1	0-15	0.01	0.01	0.07	0.17	0.25	0.03	0.28
	AB	15-30	0.02	0.02	0.06	0.19	0.27	0.02	0.29
	B	30-40	0.01	0.02	0.04	0.06	0.12	0.04	0.16
Brown forest, suburban forest, recreation zone									
Litter	L	0-7	0.04	0.07	0.16	0.15	0.38	0.01	0.39
Soil	A1	7-12(13)	0.02	0.03	0.11	0.16	0.30	0.01	0.31
	B	12(13)-27	0.01	0.01	0.04	0.00	0.05	0.05	0.10
Forest podbels (brown-podzolic), with surface affected by urban building									
	A1A2	0-17	0.01	0.02	0.06	0.11	0.19	0.03	0.22
	A2g	17-38	0.01	0.01	0.06	0.03	0.10	0.03	0.13
	Bg	38-50	0.00	0.00	0.02	0.00	0.02	0.04	0.06

Thus, most of Hg in the investigated soils was found to be bound to the organic matter, primarily to humin, as well as to humin acids. The most mobile forms were bound to fulvic acids in the brown forest soil, and fulvic acids and free fulvic acids for the forest podbel soil. Presumably, the most labile Hg compounds were extracted with H_2O and $(NH_4)_2$-EDTA pH3 from the partly decomposed forest litter.

It is important to emphasize that the observed strong Hg binding capacity with respect to the soil organic matter is unique. For example, according to Stepanova (1976) only Cu (but not Zn, Mn, Mo and B) indicated a comparable, though much lesser binding capacity to the soil organic matter.

Mean total Hg content in A1-B horizons of soils sampled within the City of Khabarovsk area did not exceed that for pristine soils. Mercury content in horizon A1 of the urban brown soils was 1/3 higher than in forest soils. According to the data obtained by Kot (1996) and Kot and Dugina (1999) Hg deposition with both precipitation and aerosols onto the surface of Khabarovsk urban soils was 14.5-22.5 and 20.0-31.0 $\mu g \cdot m^{-2} \cdot yr^{-1}$, respectively. This is approximately 20-30% higher than the deposition onto background areas of the Middle Amur Lowland - 14.3-18.8 and 15.4-23-8 $\mu g \cdot m^{-2} \cdot yr^{-1}$, respectively. The uppermost organic horizon of the urban soils has been the most impacted. The pollution of the urban soils must occur owing to polluted wet and dry deposition. The precipitation seemed to be Hg enriched within the urban milieu, presumably as the result of Hg sorption from the "urban atmosphere".

No increase in the Hg content of the H_2O and $(NH_4)_2$-EDTA extracts was detected. All the urban soils had higher a Hg content connected with extractable humus acids - both humic and fulvic. The fraction of Hg bound to free fulvic acids was significantly higher compared to the pristine soils. The highest content of inorganic Hg fraction was observed in the urban profile, which accounted for 9-94 - 14-67% of the total element content. It is assumed that the physico-chemical conditions in the urban soils impacted by technogenic influence promoted a higher mobilization of the Hg-containing compounds, including such relatively active migrants as Hg-fulvates and Hg-free fulvates.

Table 3. Specific Hg content (ppm, w/w) in fractions of forest podbel (brown podzol type)

Horizon	H, cm	FFA	FA	HA	Humin	Total org. Hg	Total
A1	1-7	5.0	1.2	3.7	5.4	3.7	0.23
A2g	7-22	-	4.6	36.4	25.6	20.8	0.15
Btg2	75-85	16.7	5.3	80.0	37.5	29.2	0.17

Thus, Hg compounds were more mobile and therefore more toxicologically dangerous in the urban soils. Although the urban soils were not significantly higher in the total Hg content than the pristine soils there were more labile forms of Hg activity than in the urban soils. The fractionation scheme presented in this work has partly allowed the revelation of this phenomenon. The specific Hg content for the humus fractions of the pristine forest podbel has been also evaluated (Table 3).

The data obtained demonstrated that the most specific Hg content was observed for the organic matter in horizon Btg2, the lowest one - in horizon A1. This is assumed to be a consequence of the relative abundance of the organic matter compared to Hg content in organic horizons. The Hg concentration level for the whole organic matter content and the content in the separated fractions were of 1-2 order of magnitude compared to the bulk soil. According to the bonding capacity for Hg the soil organic matter fractions may be arranged as follows:

Horizon	
A1	Hg-humin ≅ Hg-FFA ≅ Hg-HA > Hg-FA
A2g	Hg-HA > Hg-humin >> Hg-FA
BC	Hg-HA > Hg-humin > Hg-FFA >> Hg-FA.

According to the published data on humic acids' complexing capacity for Hg (Varshal et al., 1998) and the data obtained in this work, the Khabarovsk urban soils preserved their high buffer capacity for Hg bonding.

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REFERENCES

Aleksandrova LN (1980) Soil organic matter. Nauka, Leningrad (in Russian)

Dmitriw R, Mucci A, Lucotte M, Pichet P (1995) The partitioning of mercury in the solid components of dry and flooded forest soils and sediments from a hydroelectric reservoir, Quebec (Canada). Wat Air Soil Poll: 80: 1099-1103

Kononova MM, Belchikova NP (1961) Rapid method of humus composition determination in mineral soils. Soviet Soil Sci: 10: 1112-1121

Kot FS (1996) Mercury in waters, bottom sediments and ichthyofauna of Lower Amur and its mixing zone. Vestnik DVO RAN: 2: 98-104 (in Russian)

Kot FS, Dugina IO (1999) On Hg fluxes balance for the Amur River basin. Int Conf Mercury As A Global Pollutant, 24-29 May, Rio de Janeiro, Brazil

Orlov DS, Grishina LA (1981) Manual for chemistry of humus. Moscow State Univ Publish, Moscow (in Russian)

Stepanova MD (1976) Microelements in soil organic matter. Nauka, Novosibirsk (in Russian)

Trance-Siberia Pri-Congress Field Study Tour (A Guide-Book of Field Excursions) (1990). Scientific Centre for Biologic Investigations of USSR Academy of Sciences in Pushchino, Pushchino

Varshal GM, Koshcheyeva IYa, Khushvakhtova SD, Kholin YuV, Tyutyunnik OA (1998) On mechanism of mercury(II) sorption with humic acids. Eurasian Soil Sci: 9: 1071-1078

Zvonarev BA (1982) On extractability of Hg from soil // Vestnik MGU: 2: 54-56 (in Russian with English summary)

Zyrin NG, Zvonarev BA, Sadovnikova LK, Voronova NI (1981) Profile distribution of mercury in soils of flat part of North Osetiya. Eurasian Soil Sci: 9: 40-48