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ORIGINAL ARTICLE

Bioavailability and mobility of mercury in selected soil profiles

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Abstract To understand the behaviour of mercury in soils and assess the risk of its toxicity, the forms in which the element is found in the environment must be detected. In the occurrence of favourable alkylation conditions (for example in floodplain soils), the content of methyl and ethyl mercury is higher. These Hg forms in comparison with mineral compounds are toxic for the same organisms in concentrations from 10 to 100 times lower. The research concerned eight selected soil profiles representing six different types of soils (*Endogleyic Phaeozem*, *Endogleyic Fluvisol*, *Eutric Fluvisol*, *Haplic Luvisols*, *Brunic Arenosol*, *Albic Podzol*) placed in croplands. The content of mobile (water soluble), available (DTPA-extractable) and bound with organic matter (NaOH-extractable) Hg forms was determined after thermal decomposition using AMA mercury analyser. The mobility as well as availability of mercury in the analysed soils was very low, with average percentage to 0.28 and 2.45 % of the total content of this metal, respectively. It was mainly dependent on texture, the amount of organic matter and soil pH. The percentage of mercury bound with organic matter ranged from 2.34 to 73.70 % of the total content of this metal and was correlated with amount of clay and Fe oxides. Considering these results, the hazard of migration of this element into deeper horizons of the soil profile and ground water is very low. Moreover, crops from the investigated area are not at risk from mercury contamination.

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Introduction

Mercury possesses unique physicochemical properties when compared to all chemical elements, and the variety of compounds it forms make it both a very difficult and interesting object of study (Fitzgerald 1995; Lindqvist et al. 1991; Schlüter 2000; Schuster 1991). Toxicity of mercury is linked to the form in which it is found in the environment. Organic Hg compounds (methyl mercury and ethyl mercury mostly), in comparison with mineral compounds, are toxic for the same organisms in concentrations from 10 to 100 times lower (Boening 2000; Gochfeld 2003). The form of the highest toxicity and at the same time of the highest bioaccumulation is methyl and dimethyl mercury (Alloway 1995; Gochfeld 2003). This element is very easily bioaccumulated. Plants accumulate relatively small amounts of Hg, much more in animals (especially water animals) and fungi (Boening 2000; Campbell et al. 2003; Kabata-Pendias and Pendias 2000; Tsuchiya et al. 2008). This metal is mainly accumulated in plant roots, from which it is transferred at different rates to the parts above the surface (Boening 2000; Gochfeld 2003).

Mercury undergoes very specific transformations in different ecosystems. It is crucial to observe the content of different forms of this metal in soils. This is correlated with the variety of structure and composition and the dynamics of the soil system. This results in different soil genesis, as well as a variety and variability of environmental conditions and human pressures, both spatially and temporally.

The aim of this study was to assess the influence of selected soil components and physicochemical properties

in mercury distribution, environmental mobility and potential toxicity of this element in different soil types of croplands.

Materials and methods

Study area

The study was carried out in three regions of Poludniowodbaltuckie Lake District, Northern Poland (Fig. 1). The parent materials of studied soils were glacial till deposited on Pomeranian phase of the Vistula glaciation period, fluvioglacial sands formed during the continental ice-sheet recession of the Pomeranian and Holocene phases, and also young fluvial deposits. The mean annual temperature in the study area is 8 °C, and the mean annual precipitation is 500 mm.

Sample collection

The research material was collected from 45 samples taken from eight selected soil profiles (Fig. 2) representing six types of soils: one profile of *Endogleyic Phaeozem*, one profile of *Endogleyic Fluvisol*, one profile of *Eutric Fluvisol*, three profiles of *Haplic Luvisols*, one profile of *Brunic Arenosol,* and one profile of *Albic Podzol* (IUSS Working Group 2014), formed form parent material of various origins. The analysed soils are arable soils (long-term cultivated) which are used for cultivating plants typical for the region (sugar beet, wheat, rye). Only Albic Podzol is a

forest soil located in the area of relatively limited anthropogenic influence. Soil samples were stored in plastic bags and kept in a refrigerator for mercury determination. The coordinates of sampling sites were recorded with GPS—profile (1) 53°12′25.7″N; 18°09′25.0″E, profile (2) 53°17′32.6″N; 18°04′29.9″E, profile (3) 53°17′31.4″N; 18°17′17.9″E, profile (4) 53°14′55.5″N; 18°16′13.7″E, profile (5) 53°13′54.4″N; 18°13′23.5″E, profile (6) 53°12′50.0″N; 18°03′49.1″E, profile (7) 53°15′48.1″N; 17°57′17.10″, profile (8) 53°11′10.6″N; 18°05′54.7″E.
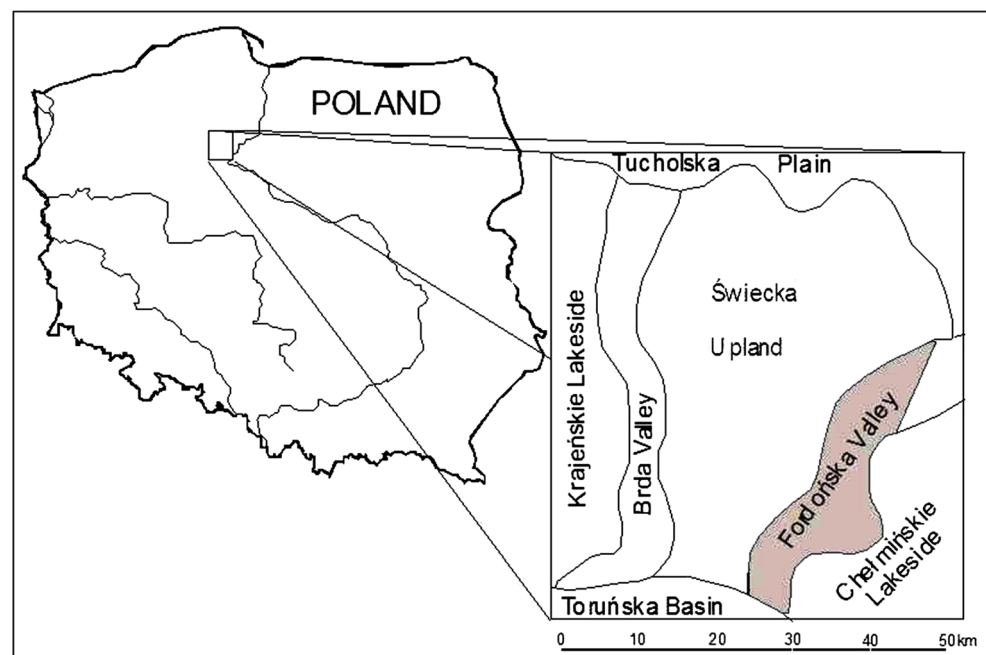
The results presented are a continuation and extension of research on the content of mercury in the soil environment presented by Różański (2009) together with complete data on composition, physicochemical properties, and the total content of mercury.

Chemical analysis

Each soil sample was air-dried at room temperature until constant mass, crushed, and sieved to separate the <2 mm fraction from any gravel or larger detritus.

The following soil properties and components were determined: texture (Bouyoucos hydrometer method), TOC—total organic carbon content (SKALAR analyser), $Fe_{tot.}$—total iron content (ISO 14869-1:2001), Fe_d—content of free iron oxides (Mehra and Jackson 1960), Fe_o—content of amorphous iron oxides (Schwertmann 1964), pH in H_2O and in 1 M solution of KCl (ISO 10390:1994), total content of exchangeable hydrogen cations (Kappen method in 1 M CH_3COONa), and CEC—cation exchange capacity (ISO 11260:1994).

Fig. 1 Location of sampling area

**Haplic Luvisol
(profile no 1.)**

Ap
- 0-22 cm, texture SL, colour 10YR6/3; 10YR3/3, OM content 1.66%, structure GR

Bt
- 22-61 cm, texture L, rare stones (to 8 cm ø), colour 10YR5/6; 10YR4/4, OM content 0.51%, structure SB, carbonates at 60-63cm

Ck1
- 61-95 cm, texture L, colour 10YR6/4; 10YR4/4 with mottles of carbonates, OM content 0.52%, structure AB

2Ck2
- <95 cm, texture L, colour 10YR6/4; 10YR4/6, with mottles of carbonates, OM content 0.31%, structure AB

**Haplic Luvisol
(profile no 2.)**

Ap
- 0-26cm, texture SL, colour 10YR6/2; 10YR3/3, OM content 1.10%, structure GR

E
- 26-36cm, texture SL, colour 10YR6/2; 10YR3/3, OM content 0.95%, structure SB

E/B
- 36-57cm, texture SL, colour 10YR6/3; 10YR4/4, OM content 0.22%, structure AB

Bt1
- 57-90cm, texture SCL, rare stones (5-100 cm ø), colour 10YR6/4; 10YR4/4, OM content 0.23%, structure PR

Bt2
- 90-120cm, texture SCL, rare stones (5-100 cm ø), colour 10YR6/4; 10YR4/4, OM content 0.12%, structure PR

Ck
- <120 cm, texture SL, colour 10YR6/3; 10YR4/4, OM content 0.61%, structure SB,

**Haplic Luvisol
(profile no 3.)**

Ap
- 0-27cm, texture SL, colour 10YR6/2; 10YR3/3, OM content 0.65%, structure GR

Eg
- 27-40cm, texture SL, colour 10YR7/2; 10YR5/2, OM content 0.18%, structure SB

Btg1
- 40-76cm, texture L, many stones (to 140 cm ø), colour 10YR6/4; 10YR4/6, OM content 0.23%, structure SB

Bt2
- 76-105cm, texture SL, colour 10YR6/6; 10YR4/6, OM content 0.17%, structure SB

BC
- 105-135cm, texture SL, colour 10YR6/4; 10YR4/6, OM content 0.08%, structure SB

Ck
- <135 cm, texture SL, colour 10YR6/4; 10YR4/6, OM content 0.62% structure AB,

**Eutric Fluvisol
(profile no 4.)**

Ap
- 0-15cm, texture LS, colour 10YR5/2; 10YR3/3, OM content 3.10%, structure GR

C1
- 15-55cm, texture SL, colour 10YR5/3; 10YR3/4, OM content 1.49%, structure PR,

C2
- 55-73cm, texture L, colour 10YR5/4; 10YR3/4, OM content 1.18%, structure PR

C3
- 73-90cm, texture L, colour 10YR5/4; 10YR3/3, OM content 1.70%, structure PR

C4
- <90cm, texture S, colour 10YR7/3; 10YR5/4, OM content 1.26%, structure SG,

**Endogleyic Fluvisol
(profile no 5.)**

Ap
- 0-20cm, texture SiC, colour 7.5Y5/2; 7.5Y3/2, OM content 4.04%, structure GR

AC
- 20-45cm, texture SiCL, colour 5Y5/3; 5Y3/2, OM content 3.51%, structure SB,

Cg1
- 45-70cm, texture SiL, colour 5Y5/3; 5Y3/2, OM content 2.42%, structure SB

Cg2
- 70-100cm, texture SiL, colour 5Y5/3; 5Y4/3, OM content 2.01%, structure SB

Cg3
- <100cm, texture SiL, colour 5Y5/2; 5Y4/2, OM content 2.01%, structure SB,

**Endogleyic Phaeozem
(profile no 6.)**

Ap
- 0-35cm, texture LS, colour 10YR2/1; 10YR1,7/1, OM content 3.23%, structure GR

AC
- 35-48cm, texture SCL, colour 5Y4/1; 5Y2/1, OM content 0.84%, structure SB,

Cg1
- 48-95cm, texture SCL, colour 5Y6/3; 5Y4/4, OM content 0.34%, structure SB

Cg2
- 95-140cm, texture SCL, colour 5Y6/2; 5Y4/3, OM content 0.02%, structure SB

Cgk3
- <140cm, texture SL, colour 5Y6/3; 5Y4/4, OM content 0.31%, structure SB,

**Brunic Arenosol
(profile no 7.)**

Ap
- 0-29cm, texture LS, colour 10YR5/3; 10YR2/3, OM content 1.47%, structure GR

A/B
- 29-37cm, texture S, colour 10YR5/4; 10YR3/4, OM content 0.84%, structure SG

Bs
- 37-65cm, texture S, colour 10YR6/4; 10YR4/6, OM content 0.50%, structure SG

BC
- 65-77cm, texture S, colour 10YR6/4; 10YR4/6, OM content 0.22%, structure SG

C
- <77 cm, texture S, colour 10YR6/3; 10YR4/4, OM content 0.06%, structure SG,

**Albic Podzol
(profile no 8.)**

AE
- 0-12cm, texture S, colour 10YR5/1; 10YR2/1, OM content 2.85%, structure SG

Bh
- 12-18cm, texture S, colour 10YR6/3; 10YR3/3, OM content 1.63%, structure SG

Bs
- 18-36cm, texture LS, colour 10YR6/4; 10YR4/4, OM content 1.15%, structure SG

B/C
- 36-84cm, texture S, colour 10YR7/3; 10YR5/4, OM content 0.28%, structure SG

C1
- 84-125cm, texture S, colour 10YR7/4; 10YR6/3, OM content 0.05%, structure SG,

C2
- <125cm, texture S, colour 10YR8/1; 10YR6/1, OM content 0.23%, structure SG,
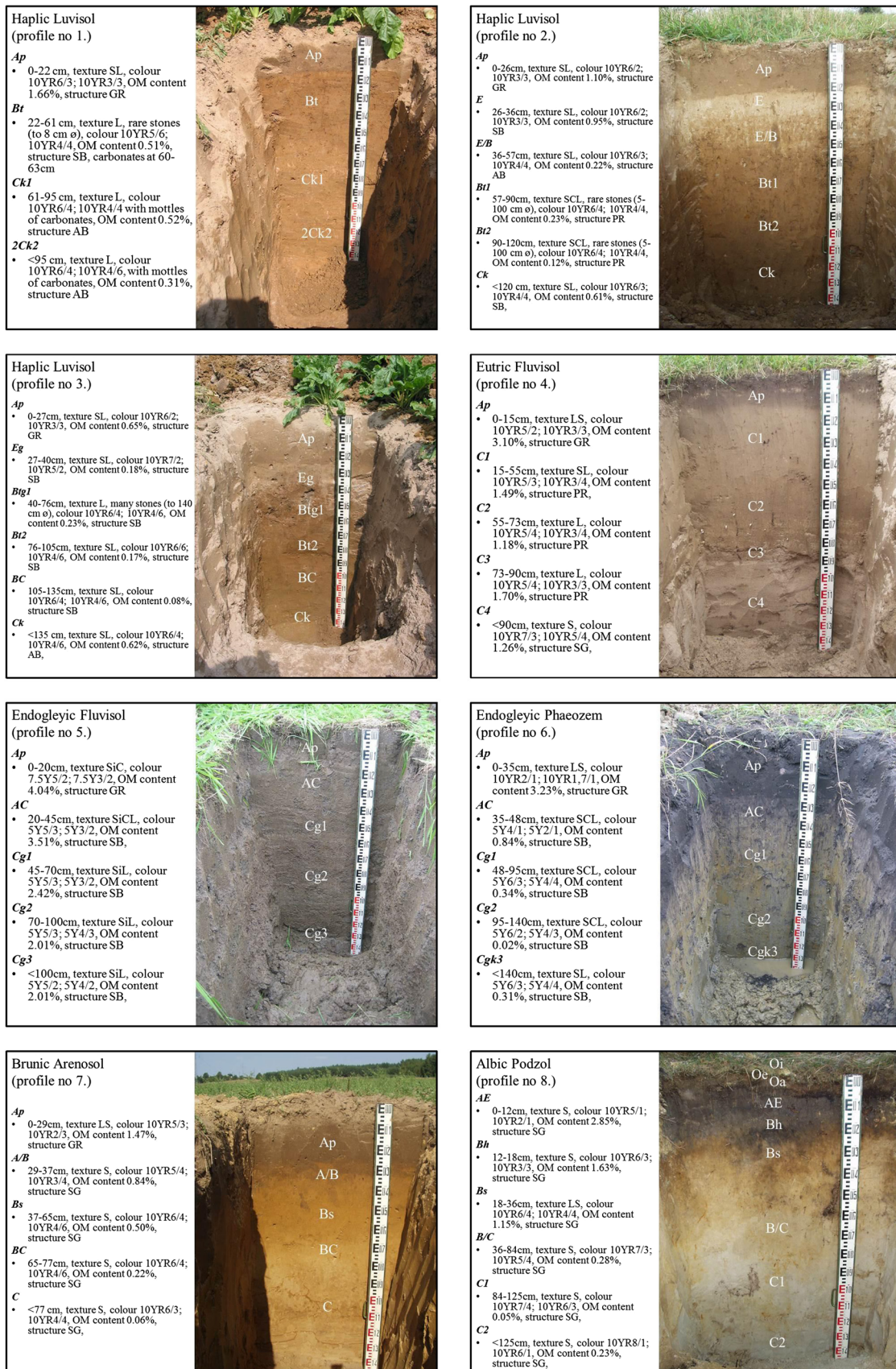

Fig. 2 Morphological description of studied soil profiles

Total Hg concentrations and its forms were analysed according to the following procedure. The content of water-soluble, mobile mercury forms (Hg_{H2O}) was extracted using deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} at 25 °C) in a soil/water ratio 1:2 during 16 h. The content of available mercury was extracted by 1 M diethylene triamine pentaacetic acid (Hg_{DTPA}) (Lindsay and Norvell 1978) in a soil/DTPA ratio 1:2 during 2 h, and the content of mercury bound to the soil organic matter by 1 M NaOH (Hg_{NaOH}) in a soil/NaOH ratio 1:20 during 2 h (Schnitzer and Khan 1978). Mercury was determined on advanced mercury analyser, the AMA-254 in solid (Hg_{tot}) and liquid (Hg_{H2O}, Hg_{DTPA}, and Hg_{NaOH}) samples. The system allows for the thermal heating (750 °C) of the sample in flow of oxygen to decompose the sample in quartz tube and release mercury, which is concentrated in a gold amalgamator. The mercury vapours are measured at 253.65 nm by a silicon diode UV detector. The AMA-254 has a 0.01-ng Hg detection limit, a working range from 0.05 to 600 ng Hg, reproducibility smaller than 1.5 %. Hg_{tot} was determined in solid 300 mg samples in five replications, and Hg_{H2O}, Hg_{DTPA}, and Hg_{NaOH} were determined in liquid samples in three replications the volume from 1000 to 1500 μL, depending on the mercury concentration in the extract.

All the results of the mercury content in soil samples were verified using certified material (reference soil sample TILL-3 and SO-4, Canada Center for Mineral and Energy Technology).

Results and discussion

Content of water-soluble mercury

It is assumed that the water-soluble mercury compounds are mainly salts—e.g. $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, $Hg_2(C_2H_3O_2)_2$ (Barnett and Turner 2001; Han et al. 2003; Schroeder and Munthe 1998), and also low-molecular-weight organic Hg compounds (Wallschläger et al. 1998a). It should, however, be noted that the solubility of mercury compounds depends to a great extent on the composition and properties of the soil solution. For example, cinnabar (HgS), which is sparingly soluble, may dissolve in solutions containing dissolved organic matter (fulvic acids) or compounds with thiol ligands (Jacobson et al. 2005). The content of soluble fractions in soils does not usually exceed 4 % of the total organic matter content (Henderson et al. 1998).

The content of mobile, water-soluble mercury forms was very low in the examined soils and ranged between 0 and 0.82 μg·kg^{-1} (Table 2). The percentage of Hg_{H2O} in the total content of this metal was on average 0.28 %. Low

share of readily soluble Hg compounds indicates that their migration into the deeper soil horizons is low. The highest content of Hg_{H2O} was found in surface horizons, especially organic horizons of *Albic Podzol* (profile 8). Slightly different results were found for the polluted soils of Europe, where the highest content of mobile mercury forms was found in subsurface horizons (below 20 cm). This was linked with Hg being washed together with humus acids from surface horizons to subsurface horizons, where these were sorbed by mineral components of soil sorption complex (Biester et al. 2002a, b).

Forest soils of northern Poland were characterized by higher content of Hg than the content found in this research (Malczyk 2000), while in the mercury-polluted soils of Great Britain, the concentration of Hg_{H2O} was so low that it did not exceed the detection level in the analytic method used (Panyametheekul 2004). In the soils of central Spain, the content of Hg_{H2O} did not exceed the level of 0.025 μg·kg^{-1} (using both the AMA and ICP-MS method) (Sánchez et al. 2005).

The content of readily soluble mercury compounds was positively correlated with the content of organic carbon ($r = 0.51$; $p < 0.05$, Table 3). The highest content of Hg_{H2O} was determined in surface horizons of the analysed soils, rich in organic matter (except profile 3 and 7, Tables 1, 2). The greatest percentage of water-soluble forms in the total content of Hg was found in horizons with considerably low content of organic matter and poor in clay fraction (especially in *E* horizons of *Haplic Luvisols*, profiles 2 and 3). Such results indicate considerable influence of both organic matter and clay fraction on the content of Hg_{H2O}.

These results indicate that the amount of readily soluble Hg forms was relatively low in relatively fine-textured soil, rich in clay minerals (profile 5). When comparing the content of Hg_{H2O} in surface horizons in both analysed *Fluvisols* (profiles 4 and 5), it could be concluded that the percentage of these Hg forms, despite comparable content of organic carbon, and considerably high total content of mercury in fine-textured *Endogleyic Fluvisol* (profile 5), was significantly higher in coarse-textured *Eutric Fluvisol* (profile 4, Tables 1, 2). Therefore, it seems that clay fraction was very influential for binding mercury in these soils. Moreover, the content of the analysed *Fluvisols* suggests that in soils enriched in humus and clay minerals, as a result of adsorption of positively charged mercury cations on the negatively charged surface of humus compounds and clay minerals, sparingly soluble in water complexes Hg-humus-clay minerals may be formed. Mercury is hence bound to the solid phase of the soil. This could account for a relatively high content of Hg_{H2O} in organic horizons (*Oi, Oe,* and *Oa*) of the *Albic Podzol* (profile 8), in which no clay minerals were found. The above hypothesis stating the

Table 1 Determined components and properties of studied soil profiles (Różański 2009)

Profile no	Horizon	Depth (cm)	Clay (%)	TOC (g kg^{-1})	pH H$_2$O	pH KCl	H$^+$ (mmol kg^{-1})	CEC (mmol kg^{-1})	Fe$_{tot.}$ (g kg^{-1})	Fe$_d$ (g kg^{-1})	Fe$_o$ (g kg^{-1})
Haplic Luvisol											
1	Ap	0–22	15	9.7	6.5	5.9	5.2	68.2	12.93	4.3	1.4
	Bt	22–61	22	3.0	6.3	4.9	5.0	116.0	24.55	8.0	1.7
	Ck1	61–95	17	1.2	8.0	7.3	0.8	100.7	17.53	4.5	0.7
	2Ck2	<95	26	1.0	8.0	7.3	0.8	81.5	20.02	6.0	0.6
Haplic Luvisol											
2	Ap	0–26	7	6.4	5.7	4.7	13.5	43.9	7.91	2.1	0.8
	E	26–36	5	5.5	5.8	4.6	6.9	39.1	8.58	1.8	0.5
	E/B	36–57	18	1.3	6.3	4.9	4.8	82.6	18.19	4.5	1.0
	Bt1	57–90	22	1.4	6.7	5.2	4.5	112.1	25.43	6.9	1.3
	Bt2	90–120	23	0.7	7.1	5.9	3.4	124.5	22.78	6.2	1.0
	Ck	<120	17	0.7	8.0	7.3	0.7	103.5	18.07	4.2	0.5
Haplic Luvisol											
3	Ap	0–27	4	3.8	6.8	6.6	1.8	28.0	7.17	2.1	0.9
	Eg	27–40	1	1.1	6.6	5.6	2.8	25.0	7.66	1.7	0.8
	Btg1	40–76	20	1.4	6.9	5.3	5.4	145.4	29.03	7.6	2.6
	Bt2	76–105	18	1.0	6.5	5.0	4.5	107.0	21.88	6.1	1.4
	BC	105–135	16	0.5	7.3	6.5	2.2	93.2	19.20	5.3	1.2
	Ck	<135	13	0.4	8.0	7.4	0.6	84.6	16.45	4.6	0.4
Eutric Fluvisol											
4	Ap	0–15	7	18.0	7.0	6.7	3.2	93.3	9.65	3.7	2.0
	C1	15–55	10	8.7	7.4	7.2	1.7	98.6	12.47	4.4	2.5
	C2	55–73	15	6.9	7.6	7.2	1.6	153.1	18.07	7.0	3.8
	C3	73–90	13	9.9	7.7	7.3	1.4	139.7	16.72	6.1	3.4
	C4	<90	2	7.3	7.8	7.4	2.0	19.6	2.34	0.9	0.4
Endogleyic Fluvisol											
5	Ap	0–20	42	23.5	7.5	7.1	2.3	317.2	39.59	18.9	8.1
	AC	20–45	29	20.4	7.6	7.0	1.8	252.1	33.65	15.1	6.4
	Cg1	45–70	26	14.1	7.7	7.1	1.6	236.7	30.22	13.5	5.9
	Cg2	70–100	21	11.7	7.8	7.2	1.9	198.6	24.03	10.6	4.7
	Cg3	<100	20	11.7	7.8	7.2	1.6	196.9	24.48	10.1	3.4
Endogleyic Phaeozem											
6	Ap	0–35	8	18.8	6.2	5.8	7.5	138.3	7.17	1.8	0.7
	AC	35–48	23	4.9	7.0	5.8	4.2	150.9	15.63	2.3	0.3
	Cg1	48–95	22	2.0	7.5	6.4	2.1	132.1	23.17	10.5	0.5
	Cg2	95–140	20	0.1	7.6	6.5	2.3	107.0	18.76	5.3	0.4
	Cgk3	<140	19	0.3	7.9	7.3	1.4	106.8	18.33	5.3	0.6
Brunic Arenosol											
7	Ap	0–29	3	8.5	4.8	4.1	20.9	30.3	5.90	2.3	1.1
	A/B	29–37	4	4.9	5.3	4.5	12.0	18.6	5.21	2.2	1.6
	Bs	37–65	5	2.9	5.7	4.8	13.4	25.3	5.15	2.3	1.4
	BC	65–77	2	1.3	6.3	5.1	7.3	20.2	5.12	1.4	0.6
	C	<77	3	0.4	6.6	5.2	6.1	21.7	3.94	1.1	0.4

Table 1 continued

Profile no	Horizon	Depth (cm)	Clay (%)	TOC (g kg^{-1})	pH H$_2$O	pH KCl	H$^+$ (mmol kg^{-1})	CEC (mmol kg^{-1})	Fe$_{tot.}$ (g kg^{-1})	Fe$_d$ (g kg^{-1})	Fe$_o$ (g kg^{-1})
Albic Podzol											
8	Oi	10–9	–	448.2	4.7	4.3	104.3	852.5	1.94	1.0	0.4
	Oe	9–3	–	485.2	4.3	3.7	189.0	816.9	5.17	2.7	1.4
	Oa	3–0	–	216.9	4.2	3.5	144.0	515.3	5.58	3.5	1.8
	AE	0–12	5	16.6	4.4	3.9	48.8	55.1	2.82	1.4	0.9
	Bh	12–18	6	9.5	4.7	4.3	25.2	27.4	2.82	1.5	1.2
	Bs	18–36	8	6.7	4.6	4.5	18.3	19.8	3.10	1.7	1.4
	B/C	36–84	4	1.6	4.8	4.6	12.3	14.4	2.59	0.8	0.4
	C1	84–125	4	0.3	4.8	4.7	7.5	13.0	2.99	0.8	0.4
	C2	<125	3	1.4	5.1	4.7	6.7	14.0	2.77	0.4	0.1

role of clay minerals in binding mercury in soil has also been confirmed by other authors (Biester et al. 2002a; Boszke et al. 2004; Inácio et al. 1998).

Content of bioavailable mercury

The content of DTPA-extractable metals in soils are considered as fractions available for plants (Kabata-Pendias and Pendias 2000; Lindsay and Norvell 1978). The percentage of Hg$_{DTPA}$ in the total content of mercury was low and ranged between 0.01 and 13.26 % (2.45 % on average, Table 2). A comparable participation of available forms was found by Barnett and Turner (2001) in soils polluted by this metal (0.3–14 %, 3.2 % on average). However, these cited authors found that higher available mercury values were in the subsurface horizons, which contrasts with the results of this study since in this case the highest values of available mercury appeared mostly associated with both surface (profiles 1, 2, 4, 7 and 8) and subsurface (usually the parent material horizons—profiles, 3, 5, and 6) horizons.

The concentration of bioavailable forms of Hg in the examined soils ranged between 0.09 and 2.20 µg kg^{-1} in mineral horizons (0.39 µg kg^{-1} on average) and from 1.21 to 6.83 µg kg^{-1} in organic horizons (4.50 µg kg^{-1} on average, Table 2). The profile distribution for Hg$_{DTPA}$ was not homogeneous. No statistically significant correlation was determined between the content of this mercury fraction and total content of the metal. Significant correlations were stated for Hg$_{DTPA}$ with acidity (pH in H$_2$O and in KCl), total content of exchangeable H$^+$ cations, total content of Fe and content of the clay ($r = -0.72$, $r = -0.58$, $r = 0.81$, $r = -0.59$, $r = -0.49$; $p < 0.05$, respectively, Table 3).

In the study of the content of available, DTPA-extractable, mercury forms in soils with acid reaction (*Brunic Arenosol* and *Albic Podzol*, profiles 7 and 8, Table 1), the

content of these forms was higher in comparison with soils with neutral reaction (*Fluvisols* and *Endogleyic Phaeozem*, profiles 4, 5, and 6). Higher content of Hg$_{DTPA}$ in these acidic soils may be the result of the release of mercury from Fe and Al complexes (Schlüter 1997). Regarding this, it must be taken into account that the acid reaction increases the content of soluble, low-molecular-weight fulvic acids, mainly responsible for binding of Hg in the soil solution (Biester et al. 2002a; Wallschläger et al. 1998a). Another important fact in this regard is the important role of pH fluctuations, which influence the methyl mercury sorption more than Hg^{2+} sorption (Boszke et al. 2003).

A relatively low content of DTPA-extractable mercury should be noted in *Fluvisols* and *Bt* horizons of *Luvisols* (profiles 1–3). These soils were characterized by considerably high content of clay and amorphous Fe oxides in comparison with other examined samples (Table 1). High content of clay fraction and Fe$_o$, which forms soil sorption complex, leads to binding of mercury by the solid phase of the soil (Boszke et al. 2003; Dreher and Follmer 2004). This fact does not limit mercury bioavailability when soil shows low amount of organic matter (Biester et al. 2002a; Wang et al. 1997). The process of mercury binding by clay minerals has been observed in soils containing a minimum of 15 % of clay (Wang et al. 1997).

Toxicity of mercury depends on formation of compounds with alkyl groups (mostly methyl group), and therefore alkylation is a very important process from this point of view. It usually takes place in alluvial soils, in which this process, due to high content of organic matter, high level of ground water and seasonal floods, may occur quite fast (Montgomery et al. 2000). Such a direction in transformation of mercury compounds may have influenced the distribution of DTPA-extractable mercury forms in the profiles of *Fluvisols* and *Endogleyic Phaeozem* (profiles 4, 5, and 6). In horizons of gleyic characteristics

Table 2 Total mercury content and its forms

Profile no	Horizon	Depth (cm)	Hg$_{tot.}$* (μg kg^{-1})	Hg$_{H2O}$ (μg kg^{-1})	Hg$_{DTPA}$ (μg kg^{-1})	Hg$_{NaOH}$ (μg kg^{-1})	Hg$_{H2O}$ (%)	Hg$_{DTPA}$ (%)	Hg$_{NaOH}$ (%)
Haplic Luvisol									
1	Ap	0–22	48.62	0.23	0.27	35.83	0.47	0.56	73.70
	Bt	22–61	36.26	0.06	0.13	16.68	0.17	0.36	46.01
	Ck1	61–95	19.07	0.02	0.15	8.99	0.10	0.78	47.13
	2Ck2	<95	19.50	0.05	0.12	7.86	0.26	0.64	40.31
Haplic Luvisol									
2	Ap	0–26	26.93	0.13	0.61	15.62	0.48	2.26	57.99
	E	26–36	16.01	0.08	0.28	6.51	0.50	1.76	40.68
	E/B	36–57	21.60	0.04	0.21	9.06	0.18	0.97	41.96
	Bt1	57–90	22.15	0.04	0.10	7.32	0.18	0.47	33.04
	Bt2	90–120	33.04	0.01	0.09	8.77	0.03	0.26	26.54
	Ck	<120	17.67	0.01	0.11	4.64	0.06	0.62	26.26
Haplic Luvisol									
3	Ap	0–27	26.61	0.09	0.30	14.01	0.34	1.13	52.66
	Eg	27–40	14.19	0.10	0.34	4.90	0.70	2.36	34.53
	Btg1	40–76	36.85	0.08	0.08	10.79	0.22	0.22	29.28
	Bt2	76–105	29.38	0.09	0.09	6.68	0.31	0.31	22.74
	BC	105–135	31.30	0.02	0.09	7.73	0.06	0.29	24.71
	Ck	<135	17.08	0.02	0.16	4.02	0.12	0.94	23.52
Eutric Fluvisol									
4	Ap	0–15	142.90	0.42	0.49	76.00	0.29	0.35	53.18
	C1	15–55	80.60	0.08	0.12	43.97	0.10	0.15	54.56
	C2	55–73	88.93	0.04	0.12	48.36	0.04	0.14	54.38
	C3	73–90	71.90	0.03	0.14	35.23	0.04	0.19	49.00
	C4	<90	3.73	0.04	0.38	1.18	1.07	10.19	31.59
Endogleyic Fluvisol									
5	Ap	0–20	1438.00	0.18	0.20	33.70	0.01	0.01	2.34
	AC	20–45	280.50	0.05	0.21	113.82	0.02	0.07	40.58
	Cg1	45–70	384.70	0.08	0.19	159.37	0.02	0.05	41.43
	Cg2	70–100	292.00	0.04	0.24	142.49	0.01	0.08	48.80
	Cg3	<100	238.40	0.04	0.24	96.70	0.02	0.10	40.56
Endogleyic Phaeozem									
6	Ap	0–35	36.66	0.20	0.39	23.46	0.54	1.07	63.99
	AC	35–48	21.66	0.09	0.28	8.83	0.41	1.29	40.77
	Cg1	48–95	23.26	*bdl*	0.31	9.46	*bdl*	1.32	40.65
	Cg2	95–140	17.60	0.01	0.44	6.43	0.06	2.52	36.51
	Cgk3	<140	18.13	0.02	0.32	3.82	0.11	1.74	21.07
Brunic Arenosol									
7	Ap	0–29	24.64	0.09	2.20	14.36	0.37	8.92	58.26
	A/B	29–37	22.20	0.11	0.53	13.03	0.50	2.40	58.71
	Bs	37–65	21.71	0.05	0.36	11.55	0.23	1.64	53.19
	BC	65–77	8.95	0.09	0.29	2.75	1.00	3.21	30.68
	C	<77	6.98	0.10	0.28	0.78	1.43	3.96	11.22

Table 2 continued

Profile no	Horizon	Depth (cm)	Hg$_{tot.}$* (μg kg^{-1})	Hg$_{H2O}$ (μg kg^{-1})	Hg$_{DTPA}$ (μg kg^{-1})	Hg$_{NaOH}$ (μg kg^{-1})	Hg$_{H2O}$ (%)	Hg$_{DTPA}$ (%)	Hg$_{NaOH}$ (%)
Albic Podzol									
8	Oi	10–9	126.50	0.59	5.45	58.40	0.46	4.31	46.17
	Oe	9–3	266.70	0.38	1.21	85.86	0.14	0.46	32.19
	Oa	3–0	322.00	0.82	6.83	76.06	0.25	2.12	23.62
	AE	0–12	21.12	0.09	1.46	9.93	0.43	6.93	47.00
	Bh	12–18	19.56	0.01	0.99	8.82	0.05	5.08	45.11
	Bs	18–36	23.11	0.02	0.73	12.57	0.09	3.14	54.38
	B/C	36–84	7.40	*bdl*	0.98	1.81	*bdl*	13.26	24.52
	C1	84–125	6.88	*bdl*	0.74	1.40	*bdl*	10.79	20.39
	C2	<125	5.56	0.01	0.61	0.85	0.18	10.98	15.34

bdl below detection limit

* Różański (2009)

Table 3 Statistically significant relationship between mercury forms and main soil properties

Hg form	Hg$_{tot.}$	TOC	pH H$_2$O	pH KCl	H$^+$	Fe$_{tot.}$	Fe$_d$	Fe$_o$	Clay	CEC
Hg$_{H2O}$		0.51								
Hg$_{DTPA}$			−0.72	−0.58	0.81	−0.59				−0.49
Hg$_{NaOH}$	0.90	0.77					0.44	0.74	0.40	0.66

Significant correlation coefficients ($p < 0.05$)

(g) in *Endogleyic Phaeozem* (profile 6), fine-textured *Endogleyic Fluvisol* (profile 5) and in *Haplic Luvisol* (profile 4), the percentage of Hg$_{DTPA}$ forms was greater in the entire profile. This could be the result of in situ formed alkyl mercury compounds, and the migration of mobile mercury forms from higher horizons (Barnett and Turner 2001; Montgomery et al. 2000). The consequence of the occurrence of favourable alkylation conditions may be the increase in the content of especially toxic methyl and ethyl mercury, which as bioavailable forms constitute greater danger for all living organisms (Boening 2000; Han et al. 2003; Tsiros and Ambrose 1999). According to Gilmour and Henry (1991) and Paterson et al. (1990) even in such conditions, the share of alkyl mercury forms usually does not exceed 3 % of the total content of this metal in soils.

Mercury bound to organic matter

According to some authors (Biester et al. 2002a; Dmytriw et al. 1995), the forms of mercury extractable by NaOH are mainly typical humus compounds.

The concentration of Hg$_{NaOH}$ in the analysed soils ranged between 0.78 and 159.37 μg kg^{-1}, and the profile distribution was proportionally close to the distribution of total Hg content (Table 2). It confirms the positive significant correlation coefficient between Hg$_{tot.}$ and Hg$_{NaOH}$ ($r = 0.90$; $p < 0.05$, Table 3). Similar results were

determined by Malczyk (2000) in unpolluted forest soils. This indicates that organic matter plays a dominant role in binding of mercury in soils. Mercury often forms stable complexes with organic ligands with a stability constant ranging from 18.4 to 22.1 (Stein et al. 1996).

Due to the complexity of the organic matter transformations in soil, scientific reports give contradictory information in this aspect. Wang et al. (1997) observed that the increase of humus in soils affects the decrease of Hg content in plants, which could indicate strong binding of this element by organic matter. Montgomery et al. (2000), however, found relatively high concentration of mobile and available mercury forms in soils with comparatively high amount of organic matter. Furthermore, the influence of soil humus on binding of mercury is dependent on the clay content, and whether clay is high may even play the dominant role in this process (Inácio et al. 1998; Wang et al. 1997).

The proved lack of pH influence on the content of Hg$_{NaOH}$ in the analysed soils (no significant correlation coefficient) may be caused by either the binding of mercury by organic matter regardless of pH value, or by the fact that determined pH range favoured such complexation. Gabriel and Williamson (2004) noticed the dominant influence of organic matter on binding mercury in soils, in which pH was lower than 7. This process occurred in both aerobic and anaerobic conditions.

The percentage of Hg_{NaOH} forms in the examined soils ranged from 2.34 to 73.70 % of the total content of mercury (Table 2). Other authors indicated that in some soils the organic matter binds about 30 % (Munthe et al. 2001), and even 80–85 % of total mercury content (Dmytriw et al. 1995; Henderson et al. 1998; Renneberg and Dudas 2001).

The highest percentage of Hg_{NaOH} in the total content of mercury was determined in surface horizons of the studied soils. The share decreased with the depth in the soil profiles. Such Hg_{NaOH} distribution was mainly connected with the content of organic carbon in profiles of soil horizon, which is confirmed by a significant positive correlation coefficient between this form of mercury and total organic carbon content ($r = 0.77$; $p < 0.05$, Table 3). A rather low percentage content of mercury bound with organic matter in enrichment horizons (Bt) of *Luvisols* (profiles 1, 2 and 3) could be a result of formation of Fe-clay complexes responsible for binding mercury in these horizons, and not of greater Fe-humus-clay or humus-clay complexes (Dmytriw et al. 1995; Schlüter 1997).

In *Fluvisols,* the percentage of Hg_{NaOH} in the total content of mercury in separate layers, despite its varied concentration, was relatively even. An exception was the surface horizon of *Endogleyic Fluvisol* (profile 5), in which the percentage of this mercury form (2.34 %) was the lowest in all of the horizons of the examined soils, showing, however, high values in the remaining subsurface horizons (40.56–48.80 %). Also, a considerably lower percentage of Hg_{NaOH} as compared with the remaining part of the profile was determined in the deepest horizon of the *Eutric Fluvisol* (31.59 %), with content in the remaining part of the profile of 49.0–54.56 % (profile 4). This was most probably due to different texture of these horizons in comparison with the rest of the profile (especially varied content of clay fraction, Table 1), or the difference in humus composition (Boszke et al. 2004; Wallschläger et al. 1998b).

After statistical analysis, correlations between the content of Hg_{NaOH} and the content of clay as well as free (Fe_d) and amorphous (Fe_o) ferric oxides ($r = 0.40$, $r = 0.44$, $r = 0.74$; $p < 0.05$, respectively, Table 3), has been confirmed. This may be due to the fact that during extraction procedure (1 M NaOH), the solution contained exchangeable forms of mercury, bound to these soil elements (Wang et al. 1997). Even taking this into account, their percentage in soils does not usually exceed 3 % of the total content of mercury (Panyametheekul 2004). Moreover, the application of 1 M NaOH solution, in comparison with other reagents used for extraction of typical humus fractions (e.g. $Na_4P_2O_7$), allows us to assess mercury bound to organic matter, obtaining by this way the fraction more similar to the actual content of this Hg form in soil (Hall and Pelchat 1997; Schnitzer and Khan 1978).

The content of Hg_{NaOH} forms was significantly, positively correlated with cation exchange capacity ($r = 0.66$; $p < 0.05$, Table 3), which is linked with high sorption capacity of organic matter (Gabriel and Williamson 2004) and high affinity of Hg to functional groups containing sulphur (Kabata-Pendias and Pendias 2000; Skyllberg et al. 2003; Xia et al. 1998) proved in their research that from 50 to 70 % of the total sulphur content in soils was included in the functional groups (mainly thiol) of organic matter, which bind metallic mercury as well as alkyl compounds very easily.

Conclusions

The availability of mercury for plants in the analysed soils was very low, on average amounting to 2.45 % of the total content of this metal. It was mainly dependent on texture, the amount of organic matter and soil pH. In the horizons enriched in both organic carbon and clay fraction, the share of water-soluble Hg and DTPA-extractable forms was the lowest. Considering low percentage of mobile mercury forms in total content, the risk that the metal shall migrate into deeper horizons of the soil profile and ground water is rather small. Moreover, even in soils with comparatively high total content of mercury, its availability for plants is very low. Only considerable decrease of pH value simultaneously with more intensive mineralization of organic matter, responsible for binding majority of mercury in the analysed soils (up to 73.7 %), could significantly affect mobility and/or toxicity of this metal.

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