



Mercury contents in the green belts within the urban area

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Received 30 March 2018; Accepted 15 July 2018

ABSTRACT

Mercury as one of the trace metals has ability to cumulate in various environmental elements. Due to its high toxicity and derivatives, Hg making the significant risk for natural human environment results in the global problem of contamination. Mercury deposited on the surface largely retains in soils and vegetation increasing the hazard for remobilization to aquatic systems under certain conditions. The aim of the investigations was to quantify and assess the total mercury content in the surface layers of green belts originating from the urban district of the Polish capital, Warsaw, as well as to determine how the location points of the study area influence on the mercury contents. In this paper, the results of studies of mercury contents in the surface layer (0–20 cm) of municipal greenbelts zones in Warsaw's urban district Ursynów are presented. The total concentration of mercury was in the range of 0.012–0.058 mg Hg/kg dm. The concentrations of Hg in the studied samples did not exceed the permissible values established for urban soils (I category) at 5.0 mg/kg dm. It was observed that the street lawns, apparently exposed to the emissions from vehicles, did not show contamination with Hg as it was expected. Statistically significant correlation was found between soil grain size and mercury content. It was concluded that the source of mercury in the studied areas may not only be related to the transport but other anthropogenic factors resulting from the municipal activity as well as others that are difficult to identify and not considered in the studies. In order to avoid the uncontrolled re-emission and as a consequence possible accumulation of mercury in the other environmental compartments including water, it is recommended to further monitor the level of contamination with mercury, among others, in the soil within the urban areas.

Keywords: Mercury; Green belts; Pollution; Environment; Urban area

1. Introduction

Mercury as one of the most important trace metals emitting to the environment plays significant role in the influence on the environment quality, soils, and waters on urban areas [1]. Data coming from the European Environment Agency (EEA) report indicate that emission of mercury to the air ranged 37.8 tons in 2008 [2]. The activities undertaken by the EEA members that obligated to apply best available technologies (BAT) resulted in decline the burning of coal

(containing mercury) leading to the decrease the emission of Hg to the air of 61% within the period of 1990–2008. Despite the fact that BAT were employed in other countries outside the Europe and North America, it is estimated that the global emission of mercury, mainly from the combustion of fossil fuels will increase of 25% by 2020 [3]. The recent studies according to Xu et al. [4] confirm the increasing Hg concentration in soil by the factor of 3 to 10 indicating combustion of fossil fuels together with long-range atmospheric processes of transport are regarded as the main source of

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pollution. According to EEA report, the total wet and dry deposition of Hg in Europe varies from below 5 g/km²/y to more than 30 g/km²/y [3].

About 40% of global anthropogenic emission comes from East and Southeast Asia of which around 75% originates from China [5]. With respect to anthropogenic emissions, East and Southeast Asia create about 40% of the world mercury emissions. European countries emit to the air about 4.5% of the anthropogenic Hg. The mentioned humans' activity source of Hg in the environment increases the load of this compound in the surrounding areas overtime. As a result, the higher rates of re-emission of Hg appear leading to the longer time of emissions decrease including, among others, pathways of exposure to human. It was estimated that re-emission comprises about 60% of mercury emissions to the air. This process makes difficulty in the identification of the origin: natural or anthropogenic [6].

The contamination of soils, waters, and air with mercury comes from the natural occurrence in various ecosystems (trace amounts in rocks, not exceeding 00X ppm) as well as its anthropogenic application in the industry. Mercury is present in the waters and soils in ionic form, as a consequence of dry and wet deposition from the air or may be attached to the ash particles [7].

As Hg cycles through the environmental compartments, it can be deposited and re-emitted many times. Nevertheless, the combustion of mercury due to the human activity resulted in higher levels of re-emission. In the aquatic environment, re-mobilization of mercury occurs when mercury deposited on and accumulated in soils or sediments is re-mobilized by, for example, during rains or floods [8]. In the studies carried out by Li et al. [9], Hg contamination in the surface soil was considered with respect to possible migration of this compound to the area of potable water as a result of storm water runoff. It was estimated the moderate risk of Hg contamination in the investigated area. According to Li et al. [9], anthropogenic sources such as mining (33%–35%), vehicular emission (17%–27%), and coal combustion (11%–26%) were responsible for the presence of Hg and other heavy metals. Two broad categories of current anthropogenic sources are considered here: point sources of mercury release to water and diffuse releases of mercury, as a result of its remobilization from areas where it was previously deposited or accumulated due to human activity (i.e., contaminated sites).

At present, it is known that mercury does not play any biological function despite the fact of its high chemical activity. Mercury is highly toxic for living organisms due to the easy ability of cumulation in the organisms, Furthermore, Hg absorbs from the digestive system, through the biological blood-brain barrier, cross the placental barrier to the embryo and has strong carcinogenic properties [10,11].

In order to avoid the increase of mercury in the environment, the studies of determination in the individual components, fates, and toxicity to the living organisms of mercury should be carried out [10,11]. In the recent studies, the attention is paid into the bioaccessibility of soil-based mercury [12]. The studies have been carried out to determine the mercury concentration in soils in smelter community of Flin Flon, Manitoba (north Canada). The in-vitro tests of urinary inorganic mercury concentration conducted on children

between 2 and 15 years of age showed that the results can be valuable in predicting exposure to pollutants from soil ingestion pathways within risk assessment of human health. It was found that a mean bioaccessibility of 3.0% for mercury in soil did not influenced exposure levels to children. In another studies, Guney et al. [13] noticed that the bioaccessibility of soil-bound mercury was lowered when compared with more soluble forms.

Due to the actual, global problem of mercury pollution, the studies were undertaken in order to determine the mercury contents in the green belts originating from the Polish capital's urban district, Ursynów. It is commonly known that besides the combustion of fossil fuels the ground and surface water runs off can be regarded as the sources of mercury in the water. Acidic soil has lower pH which is the significant factor responsible for probable mercury leaching and increasing the water contamination.

Therefore, another reason was to assess the influence location of the urban area on the Hg content in soil, as a place where conditions may be conducive or inhibit the release of mercury from the soil into the water. Thus, the samples were taken from the green belts located in the neighborhood of transport routes expecting to determine the higher concentration of mercury compared with the samples located inside the residential areas. Additionally, samples were also taken from the area of Warsaw University of Life Sciences campus in order to investigate if soil samples are contaminated with mercury and if favorable conditions to the release of mercury from the soil to the water might occur.

2. Materials and methods

The soil samples were taken from the area belonging to the one among 16 urban boroughs of Warsaw (Map 1). Ursynów municipality is located in the southern part of Warsaw, on the left bank of the Vistula River. In the south of the borough, Ursynów is surrounded by the Piaseczno, Konstancin-Jeziorna municipal communes, as well as Leszowola rural commune. With a surface area of 44.6 km² (17.2 sq mi), it is the third largest district in Warsaw. The eastern section of Ursynów is heavily built up with blocks of flats, while its western and southern sections are often referred to as Green Ursynów due to its lower population density and broad open spaces as well as green areas. Ursynów's southern extremity comprises Kabaty Forest covering more than 9.2 km² (3.6 sq mi) as well as Natolin forest 1.02 km² providing natural filters of the district. The natural barrier of the Ursynów is Warsaw's embankment, with Warsaw plain behind above 100 m above sea level and 20–30 m above water level in the Vistula River. The area is built of postglacial material such as clay, sand, silt, and some minor, sand dunes [14]. The Ursynów area has been significantly modified by the anthropogenic activity affecting physical-chemical soils properties. The general monitoring studies, including the whole city, indicated that some areas differed in soil concentrations of trace metals, including Hg [15].

The Warsaw's municipal climate is humid continental, and it varies slightly from the climate of surrounding area. It is due to the fact that area of well-knit buildings favors to form the islands of warmer and colder air, and the average annual temperature is higher of about 1°C. In the area

of Warsaw, the humidity of the air and insolation decreases whereas the cloudiness increases. The higher precipitations, about 500–550 mm, have been noted as well as the increase of particulates amount in the air has been found. On the Warsaw’s agglomeration, western and south-west winds preponderate [16]. The location of sampling points is given in Fig. 1.

Soil samples were taken from the surface soil layer (0–20 cm) in the Ursynów district. The area of sample taking is covered by the birches. The samples were taken during autumn season. In the studied area 15 squares of 1.5 × 1.5 m were chosen. Five samples were taken from

each square, that were homogenized and average sample of 1 kg was taken for analyses of soil properties and mercury content. The studied material was initially prepared by removing plants, stones, and visible invertebrate parts for further analytical steps. Then, the samples were dried under the room temperature within 5 weeks in order to obtain air stable dry mass. Afterwards, the granulometric composition and other physical-chemical soil properties were determined according to known soil procedures [17]: pH in 1 mol/dm³ KCl—potentiometric method using pH meter with glass combine electrode, hydrolytic acidity (Hh)—Kappen’s method, sum of alkalinity exchangeable



Fig. 1. Location of sampling points.

cations (S)—Kappen's method, cation exchange capacity of soil (T)—sum of hydrolytic acidity and sum of alkalinity exchangeable cations, organic matter (OM) content by losing mass during anneal.

The concentration of the total mercury in this study was determined using the atomic absorption spectroscopy method, and the analysis was performed on an AMA 254 mercury analyzer (Altec, Czech Republic). The analyzer used allows the determination of mercury in biological samples (both fresh and dried to a constant mass) and environmental tests, without the necessity of their earlier mineralization in acids, under conditions of high temperature and pressure.

For analysis, 100–300 mg of sample was taken, which was placed in a nickel cuvette, where it was automatically weighed and dried. The sample was then subjected to thermal decomposition in the oxygen stream to the gaseous form, and its decomposition products were transferred to the amalgamator for the selective capture of mercury. Mercury in the form of steam is released from the amalgamator by its short heating. The amount of mercury released was measured by the atomic absorption method (the detector in the AMA 254 analyzer is a silicon UV diode) at a wavelength of 254 nm, in a system of two measuring cells. The samples were analyzed at specific cycle parameters: 60/160/60, which in turn means the times (in seconds) of drying, decomposition (at 550°C), and waiting for the measurement. The mercury detection limit for this apparatus is 0.01 ng. For each sample, two replicates were made and the obtained mean concentration result was given in mg/kg of dry matter.

During the determination of the mercury content in soils, to control the correctness of the analytical procedure it was used Certified Reference Standard EnviroMAT Contaminated Soil (SS-1) with reference value of mercury 0.41 mg/kg.

Correlations between Hg concentrations in soil samples and the parameters characterizing soil properties were determined by a simple regression analysis. All the statistical calculations were performed using Statistica 6.0 software.

3. Results and discussion

The results of granulometric composition of studied soil samples did not differ significantly. According to Polish Soil Society soil standards that are compatible with U.S. Department of Agriculture standards, soil samples were qualified to mechanical group sandy loam and loam (Table 1). According to Gworek et al. [18], in sandy loams the leaching of mercury and its compounds to the deeper soil layers occurs faster, that may result in the decrease of mercury concentration in the surface layer.

The results of physical-chemical properties of studied soils are included in Table 2. The pH in the studied soil samples proved that soils originating from the Ursynów area are rather acidified, as pH was in the range of 4.47–6.50. In six investigated samples, pH in the range of 6.75–7.25 indicated the neutral soil. According to studies of Dusza-Dobek [19], the soils neutralization is related to the debris anthropogenic layers embankments including the remaining of carbonate mortar. As a consequence, the natural soil acidification takes place together with the alkaline particulates emitting from the electrical power and heating plants. In order to determine the values of cation capacity exchange (T), the values of hydrolytic acidity (Hh) and sum of exchangeable cations (S) were calculated and then the obtained values were added. The investigated soil samples were characterized by diversified Hh values. The highest value equal to 1.41 cmol(+)/kg was found in Sample 12, whereas the lowest equal to 0.44 cmol(+)/kg was obtained in Sample 4. Values of the S were also diversified. The highest value equal to 48.97 cmol(+)/kg appeared in Sample 5, whereas the lowest value equal to 1.76 cmol(+)/kg was found in Sample 5. Cation capacity exchange (T) was in the range of 3.17–49.66 cmol(+)/kg.

In the studied soil samples, the organic content was in the range of 2.2%–6.3%. As reported by various researchers in municipal soils, the significant impact on the OM concentration has open cut activities that are carried out constantly during housing development [20]. Mercury has affinity to the

Table 1
Granulometric composition of studied fractions (%)

Sample no.	Granulometric fractions diameter in millimeters (%)											Mechanical group
	2	2–1	1–0.5	0.5–0.25	0.25–0.1	0.1–0.05	0.05–0.02	0.02–0.006	0.006–0.002	<0.002		
1	5	14	5	15	8	16	9	4	2	10	Loam	
2	5	2	7	15	6	16	20	7	3	10	Sandy loam	
3	2	2	10	23	8	15	13	7	2	11	Sandy loam	
4	10	6	8	21	8	10	14	6	3	8	Loam	
5	4	2	6	14	6	17	22	9	2	10	Sandy loam	
6	13	4	4	13	8	11	18	8	2	10	Sandy loam	
7	3	2	7	17	6	12	21	9	3	13	Sandy loam	
8	10	1	11	26	8	8	13	6	1	12	Loam	
9	2	1	6	18	6	13	25	9	2	10	Sandy loam	
10	10	6	6	17	8	16	14	6	3	9	Sandy loam	
11	3	2	8	22	8	14	15	6	2	11	Sandy loam	
12	10	3	10	24	9	9	13	7	2	9	Loam	
13	11	5	6	20	8	12	16	4	3	13	Sandy loam	
14	13	4	12	28	7	5	11	4	2	9	Loam	
15	7	2	7	16	6	11	24	8	4	9	Sandy loam	

Table 2
Physical-chemical properties and total Hg content of green belts samples

Sample no.	Fractions (mm)			OM %	pH KCl	Hh (cmol[+]/kg)	S	T	Hg (mg/kg dm)
	2–0.05 %	0.05–0.002	<0.002						
1	62	15	10	5.20	5.38	1.05	12.34	13.39	0.027
2	51	30	10	6.30	7.05	0.67	28.72	29.39	0.030
3	59	22	11	4.50	7.02	0.52	29.65	30.17	0.026
4	63	23	8	5.00	7.25	0.44	45.39	45.83	0.024
5	49	33	10	3.20	6.50	0.69	48.97	49.66	0.029
6	52	28	10	3.90	7.09	0.46	24.84	25.30	0.058
7	47	33	13	4.10	4.68	1.25	10.64	11.89	0.031
8	63	20	12	5.70	6.75	0.78	25.50	26.28	0.022
9	46	36	10	5.60	5.38	0.93	14.98	15.91	0.031
10	63	23	9	2.20	4.47	1.06	8.32	9.38	0.014
11	56	23	11	3.20	5.22	0.89	10.04	10.93	0.033
12	63	22	9	2.70	4.73	1.41	1.76	3.17	0.012
13	60	23	13	3.50	6.78	0.53	17.39	17.92	0.011
14	68	17	9	3.50	6.18	0.72	12.56	13.28	0.017
15	49	36	9	2.90	4.73	1.05	5.80	6.85	0.045

OM content in the soil that favors to cumulate the mentioned trace metal in surface humus-rich soil layers [21].

The highest concentration of mercury equal to 0.05703 mg Hg/kg dm was found in Sample 6. However, it is not possible to conclude whether the determined concentration resulted from the neighborhood of transport route, as in the Sample 11 originated from the area of Kabacki Forest the content of mercury was lower and equal to 0.03292 mg/kg dm. The lowest concentration of Hg equal to 0.01109 mg/kg dm occurred in sampling point no 12. According to the legislation considered, soils can be treated as unpolluted [22]. The determined contents of the mercury are similar to the results obtained by Pasiieczna et al. [23] during monitoring studies carried out, among others in Ursynów. Dradrach and Karczewska [24] investigated Hg content in the surface soil layers coming from the city of Wrocław. The Hg content in Wrocław was slightly higher and varied from 0.046 to 1.144 mg/kg dm, and it did not exceed the quality standard for the surface soil specified by the Polish law [22].

The other available literature sources indicate that the average mercury content are in the range of 0.08–1.5 mg/kg dm, whereas the world average Hg concentration is equal to 1.1 mg/kg dm [25]. Usually, the range of 0.05–0.3 mg/kg dm is regarded as a background of Hg in soils. Other source indicates that the concentration of Hg in soil may be in the range of <0.01–1800 mg/kg dm [26] with the regulatory limits 270 mg/kg dm [27]. According to Environmental Agency, the United Kingdom Soil and Herbage Survey gives brief overview of the concentrations of significant pollutants across Great Britain indicating that total contents of mercury in urban soils varied from 0.07 to 1.53 mg kg dm (mean of 0.35 mg/kg dm) [28]. In the studies carried out by Rodrigues et al. [29], the total mercury concentration was determined in urban soils originating from six parks of the following European countries: Portugal (Aveiro), Scotland (Glasgow), Slovenia (Ljubljana), Spain (Sevilla), Italy (Torino), as well as Sweden (Uppsala).

Samples were taken at depths (0–10 cm and 10–20 cm, respectively). The lowest Hg contents were determined in Portugal, at depth 0–10 cm Hg was equal to 0.055 mg/kg dm, whereas at the depth of 10–20 cm Hg was equal to 0.054 mg/kg dm, respectively. The highest median mercury concentration occurred in soil samples coming from Scotland in surface and sub-surface layers (1.2 and 1.3 mg/kg dm), respectively. It was concluded that the observed high differences of mercury content were due to the several sources, such as contribution from the natural background, former human activities and differences in the origin of cities and land application, local environmental conditions and the impact of their place within the urban area.

Taking into considerations the European Union Legislations dealing with contaminated soils including Hg, the following Directives and documents exist: Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment [30], and in particular of the soil when sewage sludge is used in agriculture, Council Directive 91/156/EEC of 18 March 1991 establishes the obligation to draw up inventories of contaminated sites [31], the Strategy for soil protection, Communication COM [2006] 231 including concept to prevent and apply soil sustainable, to identify risk area and to restore contaminated soils and implementation of the Strategy in a document COM (2012) 46 final [32], Directive 2010/75/EU on Industrial Emissions (IPPC) [33] as well as Directive 99/31 on landfill of waste dealing with maintenance, monitoring, and control of the polluted soils [34].

Additionally, statistically significant correlation between the properties of the soil and the content of Hg was analyzed. It was found statistically significant correlation only between soil grain size and mercury content at the confidence level of 95%. Fig. 2 shows negative correlation between the Hg concentration and soil grain size-sand (2.0–0.05) content in the tested samples; whereas Fig. 3 shows positive correlation between the concentration of mercury and soil grain size – the silt (2.0–0.05) content in the studied soils.

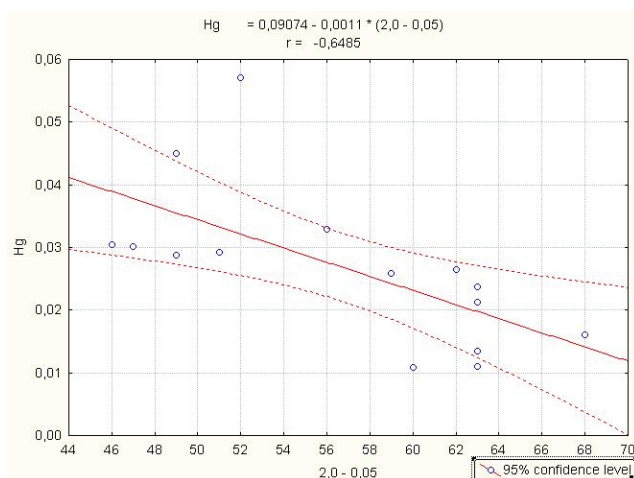


Fig. 2. The correlation between Hg concentrations in the soil and soil grain size (2.0–0.05) ($p < 0.05$, $n = 15$).

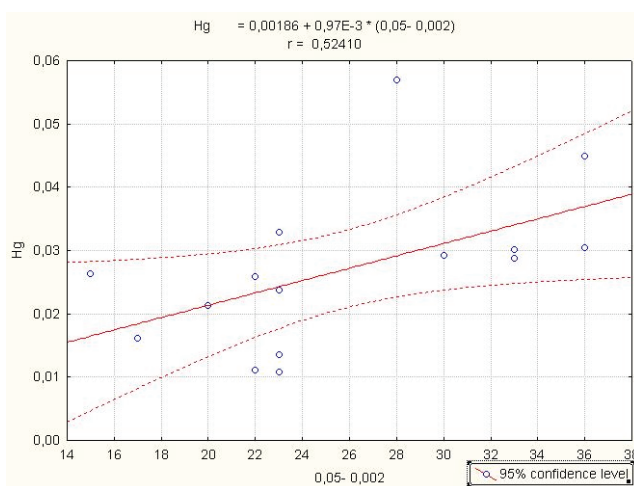


Fig. 3. The correlation between Hg concentrations in the soil and soil grain size (0.05–0.002) ($p < 0.05$, $n = 15$).

Considering the obtained results, it can be noted that the lowest Hg content was found in the samples including the lowest amount of sand. This indicates that soils containing higher amounts of silt may contain more mercury, while in soils containing larger amounts of sand, a lower mercury content may be expected. That confirms the former studies of Gworek et al. [18] indicating that the soil composition influences on the Hg binding. In the studied soils, the fractions of clay and silt were much lower than the sand fraction, that influence on the water–air conditions resulting in the low mercury content in the surface soil layers [18].

pH is another significant parameter that has influence on the mercury concentration in the soil. In acid soils, the main mercury absorbent is OM, whereas in slightly alkaline or neutral soils clay minerals and iron, manganese and aluminum oxides have the higher sorptive properties [20]. It should be stressed that the street lawns, apparently exposed to the emissions from vehicles, did not show soil contamination with Hg, and in fact contained its lowest concentrations. Several other authors, who examined the roadside soils in Stockholm [35] and Dortmund [36], did not found any

dependence of soil Hg on the distance from the road, either. Some reports stress the crucial role of OM in that effect and negate the importance of mineral components, particularly in acidic conditions [37].

4. Conclusions

The carried out soil studies in the Ursynów district indicated that soils can be classified mainly to sandy loam and loam mechanical group, and the granulometric composition did not vary significantly. The investigated soils varied in the cation exchange capacity of soil (T) with exceeding sum of the of alkalinity exchangeable cations (S). The analysis of the OM decomposition in Ursynów soils did not differ significantly and was in the range of 2.2%–6.3% resulting in the mercury accumulation in surface layers of studies soils and possess potential source of the mercury re-emission to the other environmental compartments. It should also be pointed out that it is usually difficult to identify the sources of soil pollution in the cities due to the fact that the emissions from the linear, point, and areal sources overlap.

The total concentration of mercury determined in the studied soils varied from 0.01109 to 0.05703 mg/kg dm allows to treat that studied soils as unpolluted according to the Polish regulation.

However, the further monitoring is required in order to control the levels of mercury in soils due to its long cycle in the environment resulting in mercury extension in the individual environmental elements, especially water.

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