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*Original Research*

# Mercury Contamination of Surface and Ground Waters of Poznań, Poland

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**Abstract**

Poznań is a city in west-central Poland with over 500,000 inhabitants. Located by the Warta River, it is one of the oldest cities and the fourth largest industrial centers in Poland. The aim of this study was to determine the distribution of mercury in surface and ground waters in Poznań. Total mercury concentrations have been determined in surface waters (ponds, lakes, streams and rivers) and ground water collected in 2003 and 2004. Mercury was determined using the cold vapor atomic fluorescence spectrometry method (CV-AFS). The results of the study have shown that mercury distribution in the samples of surface and ground water collected from various sites in Poznań are relatively uniform. Total mercury concentration was 20 ± 8 ng/L (range 8 – 40) in the surface water and 1.3 ± 0.7 ng/L (range 0.8 – 4.1) in ground water.

**Keywords:** mercury pollution, surface water, ground water, Poznań, Poland

## Introduction

The main sources of mercury in urban areas are combustion facilities, including coal-fired power plants, municipal solid waste incineration and hospital incineration. Other sources of mercury contamination in urban areas are hazardous waste and sewage sludge [1]. Most anthropogenic mercury emissions are released to the atmosphere and water. Atmospheric mercury is deposited and accumulates in soils and, since cities often are located in connection to water, also in sediments. The transport and transformation processes by which mercury is delivered from contaminated soil to surface and ground waters reflect various factors, i.e. geological, hydrological, climatological, land use and soil characteristic [2, 3].

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In the atmosphere mercury mainly exists as an elemental Hg(0) in vapour phase, gaseous inorganic Hg(II) compounds and particulate phase mercury – Hg(p). In combustion processes (with no treatment systems), around 20-60 percent of mercury emissions occur in ionic form, the major part of which is probably bound to particles. Particulate mercury can be deposited at intermediate distances depending on particulate size and mass. Ionic mercury is deposited on a local-regional scale while elemental mercury is transported over long distances before oxidation and subsequent removal – the residence time Hg(0) in the atmosphere is about 1 year [4, 5]. Atmospheric concentrations of Hg(p) are about two magnitudes lower than those of total gaseous mercury subjected to both washout by precipitation and dry deposition. Although atmospheric mercury is dominated by Hg(0), gaseous Hg(II) is more soluble and is the dominant form in precipitation. Although concentrations of mercury

in precipitation vary widely, from < 1 to more than 1000 ng/L [6] the values are likely due to variations associated with sampling over short time periods or with samples collected near point sources of mercury. Generally, in industrialized urban areas volatile Hg and particulate mercury may be significantly higher. For example, in unpolluted areas in the arctic total gaseous mercury and total particulate mercury concentrations were 0.7-2 ng/m$^3$ and < 0.005 ng/m$^3$, respectively [7], but in contaminated areas total gaseous mercury and total particulate mercury concentrations were 8.2 and 1.9 ng/m$^3$, respectively [8].

Mercury deposited from the atmosphere is strongly bound in the soil and water suspension. It has been estimated that 90% of total mercury coming from the atmosphere is captured in the catchment area [9, 10]. Deposited mercury may become bound to dissolved organic carbon (DOC) and thus become mobile. Some of the mercury bound to DOC may be sorbed, some will be reduced to elemental mercury by both biotic and abiotic processes, and some of the mercury in soils may be leached into ground water and runoff water [11-13]. Surface runoff of mercury from rain or snow is a very important source of mercury contamination in aquatic systems in urban areas [3, 14]. For example, in the urban watershed of Anacostia River (Washington, USA), mercury concentrations in water during normal flow were less than 10 ng/L but were 3-5 times higher during storm flow, mainly as a result of high particulate loading [14]. Generally, the distribution of mercury in environmental media is related to pH, oxygen content, organic matter, reducing agents and microbial activity [15, 16].

In natural waters, especially in marine water, mercury occurs at very low concentrations, which accurate determination makes difficult. The literature data on the concentration of mercury in natural waters are unreliably diverse not only as a consequence of the natural variation of the species and concentrations of this metal in water, but also analytical difficulties [15]. Recently established mercury levels in the aquatic system in Antarctica have been suggested as global values. Total mercury in surface water on Antarctic lakes and glacial streams ranged from 0.45 to 1.9 ng/L [17]. Uncontaminated freshwaters generally contain < 5 ng/L, although up to 10 or 20 ng/L can be found in humic-rich lakes or rivers rich in particulate mercury [2.9]. Background concentrations of mercury in unpolluted water range from 0.5 to 3.0 ng/L in the open ocean and from 2.0 to 15 ng/L in coastal estuaries and rainwater [11]. In strongly polluted waters the concentration of total mercury reaches a few tens µg/L [18, 19].

The sources and fate of mercury in Poznań remains poorly understood. The aim of this study was to determine a distribution of mercury in surface waters and ground water from Poznań and to identify potential sources of mercury pollution. Results of these studies are among the first in Poland.

## Materials and Methods

### Site Description

Poznań is a city in west-central Poland with over 570,000 inhabitants. Located by the Warta River, it is one

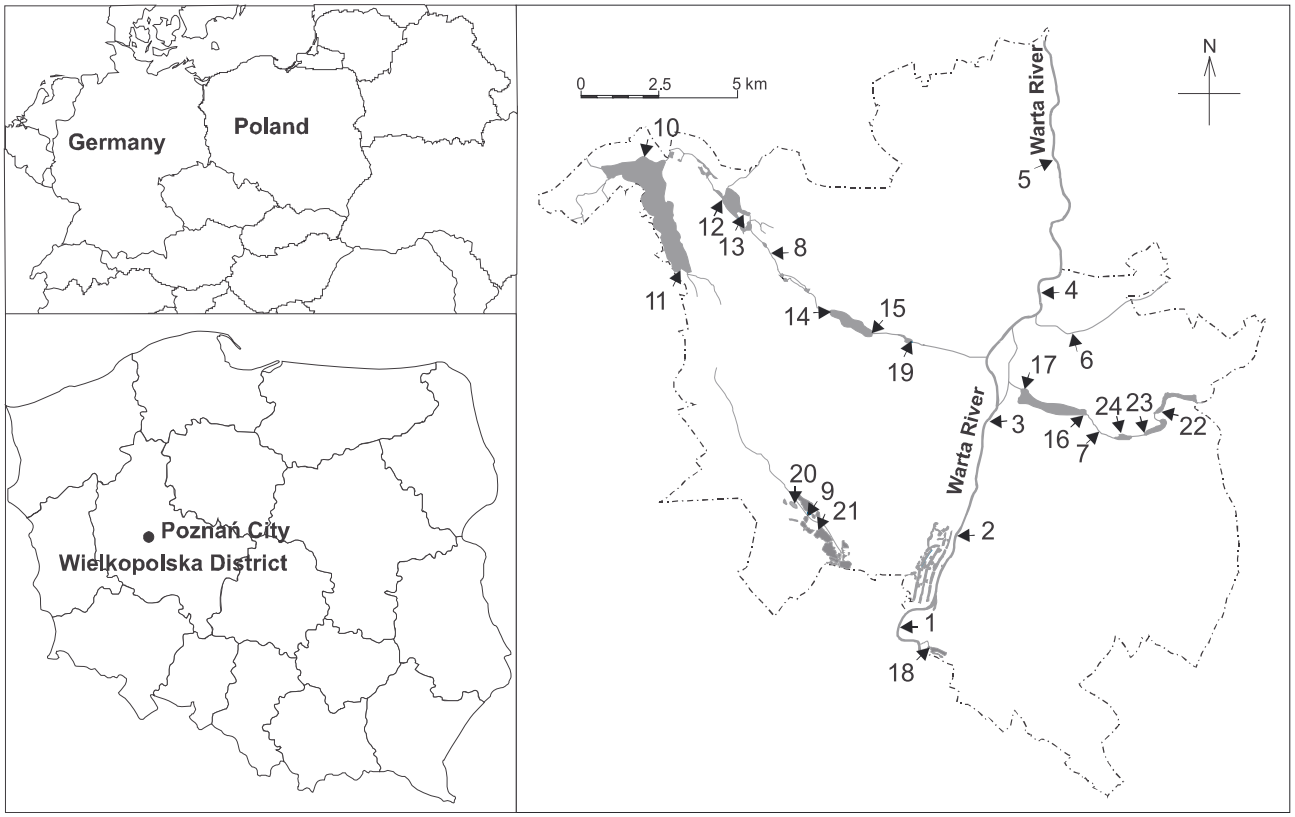


Fig. 1. Map of study area with surface water sampling points.

of the oldest Polish Cities, an important historical center and capital of the Wielkopolska District (Fig. 1). Poznań is the fourth largest industrial center in Poland featuring food, mechanical, electrotechnical, pharmaceutical and chemical industries. Buildings, green areas and arable grounds cover 106.7 km$^2$ (41%), 72 km$^2$ (27%) and 57.6 km$^2$ (21.6%) area of the city [20]. The number of rivers and streams flowing through the area is around 100, with a total length of ± 200 km. There are around 200 aquatic reservoirs [21, 22]. Average annual temperature (1951–1980) is 8.0°C. The warmest months are June, July and August with an average temperature of 17.4°C; the coldest are December, January and February with an average temperature of 1.2°C. Average annual precipitation (1951–1980) is 528 mm. The highest amount falls in July (average 71 mm) and the lowest in March (average 26 mm) [23]. Poznań in the Mesozoic structural plane lies at the border of the Foresudetic Monocline and Lódź Synclinorium, while in the Cainozoic structural plane it lies in the centre of the Neogen Wielkopolska Trough, characterised by deep tectonic faults affecting the mutual relation of the aquifers in the area [44]. The hydraulic relations between the surface and groundwater are realised through the drainage zones of the Warta river valley and postglacial trough with lakes and smaller rivers being the Warta river tributaries [44].

## Sampling Procedure

Samples of surface water were collected from 24 sites (ponds, lakes, streams and rivers) during September and October of 2003 from sub-surface layer of water (~20 cm) about 2 meters from the bank (Fig. 1). Samples of ground water were collected during October and November of 2004 from 26 drilled wells used as alternative source of drinking water for the citizens of Poznań in case of disturbances to the standard water supply system (Fig. 2). Depths of wells ranged from 6 to 25 meters and only sample No. 21 is over 100 m deep. The yield of the wells is a few m$^3$/day. They are equipped with a screen at a depth from 15 to about 40 m. The screens are in the layer of fluvioglacial deposits of sands and gravels, covered by a few metres of glacial tills. The groundwater from the Quaternary deposits is characterized by tense or locally free table. Ground water was collected after the well was flushed with at last 3 well volumes. The geographical coordinates were measured using GPS (Garmin eTrex Summit).

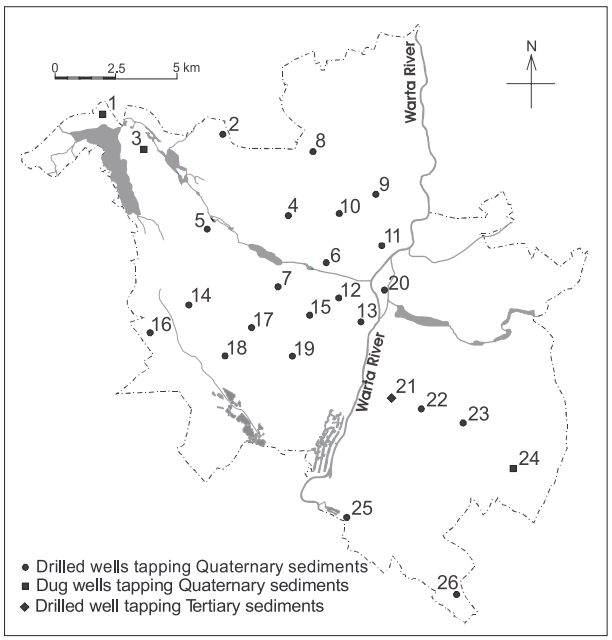


Fig. 2. Map of study area with ground water sampling points.

Samples were collected using ultraclean sampling techniques into borosilicate bottles of 0.25 L volume which were soaked in 10% nitric acid rinsed with deionized water (Milli-Q system, Millipore, < 1 μS). Water samples were acidified to pH=2 with concentrated nitric acid and were transported to the laboratory in 4°C in mobile refrigerator. Samples of surface water prior to analysis were filtered in borosilicane set (Sotarius, NC 0.45 μm).

## Analytical Method

Mercury content was determined by cold vapour atomic fluorescence spectroscopy (CV-AFS) using Millenium Merlin Analyzer (PS Analytical, England). Calibration was made with mercury standard HgNO3 (Merck) with the nominal mercury content of 980 ± 020 ng/L diluted to 1 ng/L–200 ng/L. Procedural blanks were run with each set of sample analyses. Recoveries for spiked samples (n=4) averaged 100.2%. Precision of determination was from 0.02% to 0.14%. The limit of detection and quantification of the method depends on the purity of the reagents used. The value of the limit of quantification (LOQ) of the method reached 0.3 ng Hg/L and was calculated according to the formulas presented by Konieczka et al. [42].

Along with determination of the total mercury, routinely analysis was made of the certified materials, including: SRM 2711 (Montana Soil), SRM 2709 (San Joaquin Soil) and LGC 6137 (Estuarine Sediment). The total mercury concentrations, taking into regard the values of expanded uncertainty [42], 6060 ± 351 ng/g (SRM 2711, n = 5), 1440 ± 98 ng/g (SRM 2709, n = 6), 370 ± 21 ng/g (LGC 6137, n = 7) correspond well with those obtained for the certified materials of 6250 ± 190 ng/g, 1400 ± 80 ng/g and 340 ± 50 ng/g, respectively [43]. The method for determining mercury in environmental samples is characterized by good recovery and reproducibility [24, 43].

# Results

## Surface Water

Mean total mercury concentration in the surface water of Poznań was 20 ± 8 ng/L (range 8–40) (Ta-

ble 1). The highest average concentration was noted in water from the Warta River 27 ± 7 ng/L (range 20–36). Other rivers and streams were 23 ± 12 ng/L (range 12–40) and pond water was 20 ± 6 ng/L (range 16–31). The relatively lowest average concentration of mercury was noted for water collected from lakes 15 ± 5 ng/L (range 8–24). The variance analysis (ANOVA) showed statistically significant differences ($p<0.05$) only between mean concentration of mercury in water from Warta river and lakes ($F(3.24)=3.4718$; $p=0.035390$).

## Ground Water

Total mercury concentrations in ground water from Poznań were low 1.3 ± 0.7 ng/L (range 0.8 – 4.1) (Table 2). The highest mercury concentration was observed in ground water collected from the well drilled in Tertiary sediments 4.1 ng/L, while the next lower one was from wells dug in Quaternary sediments 1.6 ± 0.7 ng/L (range 1.0–2.4) and the lowest was from wells drilled in Quaternary sediments 1.1 ± 0.4 ng/L (range 0.8–2.5) (Table 2, Fig. 2). A relatively high average concentration was noted in the ground water from the Nowe Miasto District 1.7 ± 1.3 ng/L (range 0.9–4.1), and from Jeżyce District 1.3 ± 0.6 ng/L (range 0.8–2.5). The lowest average concentration of mercury was noted for the ground water collected from Stare Miasto District 1.1 ± 0.1 ng/L (range 0.8–1.2) and from Grunwald District 1.1 ± 0.2 ng/L (range 0.9–1.5). The variance analysis (ANOVA) did not show statistically significant differences ($p > 0.05$) in the mean concentration of total mercury in ground water collected from different districts of Poznań and between wells dug and drilled in Quaternary sediments.

Table 1. Mercury concentration in samples of surface waters from Poznań.

| Number of sample | Sampling sites and description | Geographical coordinates | | Hg [ng/L] |
|---|---|---|---|---|
| 1 | Warta River – 500 meters south from the recharge water-work | N 52° 22’ 25.3’’ | E 16° 53’ 58.9’’ | 26 |
| 2 | Warta River – 500 meters north from the recharge water-work | N 52° 21’ 56.3’’ | E 16° 55’ 36.8’’ | 20 |
| 3 | Warta River – Królowa Jadwiga Bridge | N 52° 23’ 58.0’’ | E 16° 56’ 31.4’’ | 22 |
| 4 | Warta River – Lech Bridge | N 52° 25’ 52.1’’ | E 16° 57’ 59.3’’ | 32 |
| 5 | Warta 500 meters after wastewater treatment plant | N 52° 28’ 29.6’’ | E 16° 58’ 17.6’’ | 36 |
| 6 | Główna River – Bridge on Gdyńska Street | N 52° 25’ 24.5’’ | E 16° 58’ 34.4’’ | 40 |
| 7 | Cybina River – between Olszak Pond and Maltańskie Lake | N 52° 23’ 40.3’’ | E 16° 59’ 46.7’’ | 12 |
| 8 | Bogdanka River – Biskupińskia Street | N 52° 26’ 50.5’’ | E 16° 50’ 24.2’’ | 21 |
| 9 | Junikowski Stream – Wykopy Street | N 52° 22’ 21.2’’ | E 16° 51’ 25.6’’ | 17 |
| 10 | Kierskie Lake – northern waterside | N 52° 28’ 26.6’’ | E 16° 46’ 57.1’’ | 16 |
| 11 | Kierskie Lake – southern waterside | N 52° 26’ 30.2’’ | E 16° 47’ 50.9’’ | 24 |
| 12 | Strzeszyńskie Lake – northern waterside | N 52° 27’ 50.9’’ | E 16° 49’ 11.5’’ | 13 |
| 13 | Strzeszyńskie Lake – southern waterside | N 52° 27’ 27.0’’ | E 16° 49’ 44.9’’ | 11 |
| 14 | Rusałka Lake – outflow Bogdanka River | N 52° 25’ 48.7’’ | E 16° 52’ 7.3’’ | 9.0 |
| 15 | Rusałka Lake – south-eastern waterside | N 52° 25’ 24.4’’ | E 16° 53’ 16.4’’ | 8.0 |
| 16 | Malta Lake – outflow Cybina River | N 52° 24’ 27.9’’ | E 16° 57’ 32.3’’ | 15 |
| 17 | Malta Lake – inflow Cybina River | N 52° 23’ 59.7’’ | E 16° 59’ 14.3’’ | 15 |
| 18 | Czapnica Lake | N 52° 20’ 6.6’’ | E 16° 54’ 52.5’’ | 21 |
| 19 | Sołacki Pond | N 52° 25’ 17.4’’ | E 16° 54’ 21.9’’ | 18 |
| 20 | Stara Baba Pond | N 52° 22’ 33.4’’ | E 16° 51’ 5.5’’ | 31 |
| 21 | Rozlany Pond | N 52° 22’ 4.9’’ | E 16° 51’ 41.9’’ | 16 |
| 22 | Młyński Pond | N 52° 24’ 3.9’’ | E 17° 01’ 18.5’’ | 22 |
| 23 | Borowik Pond | N 52° 23’ 42.1’’ | E 17° 00’ 56.9’’ | 17 |
| 24 | Olszak Pond | N 52° 23’ 36.0’’ | E 17° 00’ 19.6’’ | 16 |

## Discussion

The spatial distribution of mercury in surface and ground waters from Poznań are relatively uniform. The maximum mercury concentrations in surface water were in the Główna (40 ng/L) and Warta rivers (36 ng/L). Samples of water from the Warta were collected 500 meters after the wastewater treatment plant. Sediment collected from this site has 283 ng Hg/g and it was maximum mercury concentration determined in sediments from the Warta within city limits [25]. Generally, mercury concentrations in sediments of Poznań are low and range from 29 to 283 ng/g (average 97 ± 70 ng/g) [25]. The sewage treatment plant may be possible source of mercury in the Warta in Poznań. For example, in water from the Chattahooche River (USA) average mercury concentration was 0.4 ng/L above Atlanta to an average of 1.6 ng/L at Atlanta sewage treatment plant [26]. Measured mercury inputs from wastewater treatment plants represented less than 4% of the annual river mercury loading from watershed [27]. Generally, mercury concentrations in surface waters of Poznań are rather typical for other urban systems. For example, in the urban and industrially area in Wisconsin in the water of Fox River, the mean concentration of mercury was 22 ng/L [28]. Higher mercury concentrations in surface water was noted in Changchun, China, from 56.7 to 192.6 ng/L [29]. In less urban areas, the elevated concentrations noted during periods of high flow are more likely due to the flushing of mercury from storage in association with

Table 2. Mercury concentration in samples of ground water from Poznań.

| Number of sample | Sampling sites and description | | Geographical coordinates | Hg [ng/L] | |
|---|---|---|---|---|---|
| 1 | Jeżyce District | Chojnicka Street | N 52° 28’ 39.5” | E 16° 47’ 04.1” | 1.3 |
| 2 | | Borówkowa Street | N 52° 28’ 16.4” | E 16° 51’ 21.0” | 2.5 |
| 3 | | Koszalińska Street | N 52° 28’ 23.4” | E 16° 48’ 12.4” | 1.0 |
| 4 | | Szczawnicka Street | N 52° 26’ 21.3” | E 16° 53’ 24.1” | 1.8 |
| 5 | | Chodzieska Street | N 52° 26’ 09.4” | E 16° 50’ 34.6” | 0.9 |
| 6 | | Generała Maczka Street | N 52° 25’ 24.9” | E 16° 55’ 00.4” | 1.0 |
| 7 | | Nowy Świat Street | N 52° 24’ 54.5” | E 16° 52’ 57.4” | 0.8 |
| 8 | Stare Miasto District | Sobieskiego Quarter | N 52° 27’ 48.8” | E 16° 54’ 48.6” | 1.1 |
| 9 | | Władysława Łokietka Quarter | N 52° 27’ 03.9” | E 16° 56’ 34.5” | 1.1 |
| 10 | | Zwycięstwa Quarter | N 52° 26’ 27.9” | E 16° 55’ 23.4” | 1.1 |
| 11 | | Pod Lipami Quarter | N 52° 25’ 49.0” | E 16° 56’ 35.5” | 1.2 |
| 12 | | Aleje Niepodległości | N 52° 24’ 40.1” | E 16° 55’ 06.7” | 0.8 |
| 13 | | Krakowska Street | N 52° 24’ 02.0” | E 16° 55’ 54.0” | 1.1 |
| 14 | Grunwald District | Tuwima Street | N 52° 24’ 24.3” | E 16° 50’ 14.9” | 1.0 |
| 15 | | Konopnickiej Street | N 52° 24’ 12.2” | E 16° 54’ 10.4” | 1.2 |
| 16 | | Złotowska Street | N 52° 23’ 56.9” | E 16° 48’ 35.4” | 1.5 |
| 17 | | Huzarska Street | N 52° 24’ 05.5” | E 16° 52’ 24.2” | 0.9 |
| 18 | | Galileusza Street | N 52° 23’ 16.8” | E 16° 51’ 40.5” | 1.1 |
| 19 | | Winklera Street | N 52° 23’ 23.1” | E 16° 53’ 23.1” | 0.9 |
| 20 | Nowe Miasto District | Wieżowa Street | N 52° 24’ 29.7” | E 16° 56’ 50.7” | 1.0 |
| 21 | | Armii Krajowej Quarter | N 52° 22’ 39.7” | E 16° 57’ 18.8” | 4.1 |
| 22 | | Orła Białego Quarter | N 52° 22’ 36.4” | E 16° 57’ 40.5” | 1.0 |
| 23 | | Szczepankowo Stret | N 52° 22’ 18.0” | E 16° 59’ 428” | 1.2 |
| 24 | | Spławie Street | N 52° 21’ 05.7” | E 17° 01’ 30.4” | 2.4 |
| 25 | | Rzewuskiego Street | N 52° 19’ 55.4” | E 16° 55’ 27.4” | 1.0 |
| 26 | | Sypniewo Street | N 52° 18’ 38.2” | E 16° 58’ 39.4” | 0.9 |

DOC during periods of high runoff [13, 27]. The hydrological flushing of mercury is likely due to the release of mercury accumulated from atmospheric deposition rather than from a geological source [13]. Baseline wintertime mercury concentrations are generally less than 1 ng/L, reflecting primarily ground water input [27]. Low mercury concentrations were detected in surface water in South Florida 1.0 ± 0.7 ng/L [30] or water from Lake Balaton, Hungary (1.4 – 6.5 ng/L) [31].

Mercury concentrations in ground water from Poznań are low and typical for background values for marine and freshwaters [11, 17]. In ground water from remote areas, mean mercury concentration was 16.5 ng/L (median – 2.0 ng/L) in Sweden [32] and 2–4 ng/L in Wisconsin (USA) [33]. In other parts of the USA, average ground water concentrations of mercury ranged from 0.7 ± 0.5 ng/L (range 0.5–1.0) to 1.4 ± 1.1 ng/L (range 0.8 – 2.7) in South Florida [30]. Higher mercury concentrations were noted in ground water from the Nevada region: unfiltered samples were 11.9 ± 10.7 ng Hg/L (0.4–36.7) and filtered samples were 5.4 ± 4.3 ng Hg/L (< 15.7) [34]. Much higher mercury concentrations were detected in samples of ground water from Stockholm agglomeration – the mean concentration was 121 ng/L (range 0.26 – 4566 ng/L, median – 15.6 ng/L) [35]. Mercury in the ground water of Stockholm has median concentrations exceeding 'background' median 8 times [35]. It seems that leaching from soils and old deposits might be an important source of mercury in ground water of Poznań. Total mercury concentration in the soil from Poznań ranged from 17 ng/g to 746 ng/g dry weight and samples collected from Poznań city centre showed higher mercury concentrations [25, 36]. The spatial distributions of mercury in surface water and ground water have different patterns – they are relatively uniform. This indicates that the buffering properties of soils from Poznań were not exceeded. For example, maximum concentration of mercury in leachate (artificial rainwater) from very highly contaminated soil (waste land – 2730 ng/g) from Stockholm region was 90 ng/L [37]. Mercury concentration in leachate was only 2% (50 times lower) of the maximum concentration reported from Stockholm ground water, indicating the existence of other probable sources of mercury in ground water in the Stockholm region [37].

## Conclusions

The results of the study have shown that mercury distribution in the samples of surface and ground water collected from various sites in Poznań is relatively uniform. Much higher differences in mercury concentrations (0.9–340 ng/L) were noted for wet precipitation [41]. The mercury concentration in samples of surface water from Poznań agglomeration obtained in this study do not exceed acceptable legally admissible values (500 ng/L) for mercury in surface water and drinking water in Poland [38, 39] and in drinking water in the world [40]. Generally, the total mercury concentrations in water from Poznań are typically for urban waters not strongly polluted with mercury. Although at present the state of Poznań city pollution with mercury is below acceptable regulatory limits, taking into regard the extreme toxicity of some of its species and the fact that the buffer properties of Poznań's ecosystem are unknown, monitoring of this metal in the city should continue.

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