



Atmospheric deposition of mercury in central Poland: Sources and seasonal trends



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ABSTRACT

Atmospheric deposition of total mercury was studied at two sites in central Poland, between April 2013 and October 2014. Hg in rainwater (bulk deposition) was analyzed in relation to meteorological parameters and major ions (H^+ , NO_3^- , Cl^- , SO_4^{2-}) in order to investigate seasonal variation, identify sources and determine factors affecting atmospheric Hg chemistry and deposition. Total mercury concentrations varied between 1.24 and 22.1 $ng\ L^{-1}$ at the urban sampling site (Poznań) and between 0.57 and 18.3 $ng\ L^{-1}$ in the woodland protected area (Jeziory), with quite similar mean values of 6.96 and 6.37 $ng\ L^{-1}$, respectively. Mercury in precipitation exhibited lower spatial variability within the study domain (urban/forest transect) than the concentrations determined during other similar observations, reflecting the predominant influence of the same local sources. In our study, a significant seasonal pattern of Hg deposition was observed at both sampling sites, with higher and more variable concentrations of Hg reported for the urban area. In particular, deposition values of Hg were higher in the samples attributed to relatively large precipitation amounts in the summer and in those collected during the winter season (the result of higher contributions from combustion sources, i.e. intensive combustion of fossil fuels in residential and commercial boilers, individual power/heat-generating plants). In addition, a significant relationship between Hg concentration and precipitation amount was found while considering different types of wintertime samples (i.e. rain, snow and mixed precipitation). The analysis of backward trajectories showed that air masses arriving from polluted regions of western Europe and southern Poland largely affected the amount of Hg in rainwater. A seasonal variation in Hg deposition fluxes was also observed, with the maximum value of Hg in spring and minimum in winter. Our results indicated that rainwater Hg and, consequently, the wet deposition flux of Hg are related to seasonal differences in precipitation (type, intensity, amount) and the emission source.

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1. Introduction

Transformation, transport pathways and fate of mercury in the atmosphere are linked to different natural and anthropogenic sources, among which local and regional industrial/urban activities play a key role (Pacyna et al., 2010). Mercury is a hazardous global pollutant with residence time of 0.5–2 years. It exists in the atmosphere predominantly in the gaseous elemental phase (GEM or $Hg > 95\%$ of total gaseous mercury; TGM) (Schroeder and Munthe, 1998). Atmospheric mercury in the ambient air also includes gaseous oxidized mercury (GOM or RGM) and particulate-phase mercury (TPM, PHg), which together constitute less than 5% of total atmospheric Hg. Both GOM and TPM are more water-soluble, less volatile and have much shorter atmospheric residence times than the GEM. In addition, vertical distribution of TPM and RGM in the lower atmosphere is limited to the areas of

their emission due to rapid removal via dry and wet deposition (Lindberg et al., 2007).

Wet deposition is a crucial process responsible for the incorporation of mercury compounds into aquatic and land surfaces, as well as for the increase in Hg potential bioavailability and interactions with other chemical compounds and biota (Downs et al., 2007; Mason et al., 2012). A number of studies have shown that Hg wet scavenging is a very complex mechanism and involves numerous factors, i.e. size distribution of particles, Hg speciation, oxidation and dissolution states, other chemical compounds and their reactivity and solubility, as well as a broad range of meteorological parameters (air temperature, variability in the boundary layer height, thermal inversion, mixing height, relative humidity, wind speed and direction, solar radiation, cloud microphysics, precipitation type and time, small-scale atmospheric processes, etc.) (Mao et al., 2012). Some authors have highlighted that kinetics and chemical reactions of Hg in the aqueous phase are also important for its deposition (Xie et al., 2008).

Total mercury concentration in precipitation and wet deposition fluxes at many urban sites are regarded as hotspots in regional and

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global budgets of Hg. Based on previous observations from Asia (Guo et al., 2008; Liu et al., 2011; Kim et al., 2013; Huang et al., 2013; Wang et al., 2014; Zhao et al., 2015; Fu et al., 2015), North America (Sigler et al., 2009; Caffrey et al., 2010; Lombard et al., 2011; Lynam et al., 2013; Yu et al., 2013; White et al., 2013), South America (Hensen and Gay, 2013) and Europe (Li et al., 2008), as well as model outputs (Chen et al., 2013), the fluxes of Hg wet deposition have been calculated and significant spatial and seasonal variability in mercury concentrations have been confirmed. It has been observed that aerosol loading and Hg emission during winter period is increased as an effect of primary sources activity, such as industrial emission, power and chemical plants, domestic heating, iron/steel manufacturing and coal-fired utilities. Therefore, to better understand the atmospheric chemistry of Hg and to assess the impact of individual emission sources, factors and transport processes on the local, regional and global-scale cycle of Hg, the data provided systematically from ongoing field measurements and modeling are needed.

The studies concerning Hg in central and eastern Europe are still limited. Recent results by Muskała et al. (2015) showed some regional air quality problems in Poland. So far, the long-term observations of atmospheric mercury in Poland have been undertaken within a few national programs, i.e. in the urbanized coastal zone of the southern Baltic (Beldowska et al., 2012; Siudek et al., 2011; Siudek et al., 2015a), in the Upper Silesia region (Pyta et al., 2009; Nowak et al., 2014) and at a rural monitoring site in southern Poland (Zielonka et al., 2005). However, the seasonal differences in Hg concentration in rainwater and Hg deposition have not been described well enough for most of the sites.

This work is based on the first long-term research on Hg in Wielkopolska district (central Poland), with the focus on urban-forest study domain that is under constant influence of different anthropogenic sources (coal-burning heat and power plants, commercial heat-generating stations, coal-fired DHUs, municipal wastes, different industrial units producing metals and paints, chemical industry, motor vehicle emission, international airport). The main purpose of this research was to determine total mercury concentration and Hg wet deposition fluxes, including various types of precipitation, i.e. rain, snow and mixed rain and snow collected during wintertime. Additionally, a seasonal trend in rainwater Hg concentrations at both sites was examined in the context of different meteorological (precipitation amount, air temperature, wind direction and speed) and environmental (H^+ , SO_4^{2-} , NO_3^- , Cl^- , pH, conductivity) factors. Taking into account a strong influence of the long-range transport, we also considered our results in relation to potential source regions, using backward trajectory analysis from the HYSPLIT model.

2. Materials and methods

2.1. Study domain

Poznań is a medium-sized city in Wielkopolska Province (central Poland) with an area of 261.8 km² and a population of about 600,000, characterized by high industrial and urban emissions. It is a well-situated city to examine local and regional pollutants as well as to investigate aerosol properties and long-range transport of Hg species originating from the surrounding countries, e.g. Germany, Belarus, Ukraine, Lithuania, Russia, Czech Republic, Slovakia and the Scandinavian Peninsula.

Two sampling sites located in the urbanized and industrialized region (Wielkopolska district) of central Poland were selected for this study. The first sampling site (POZ) was located in a residential area of Poznań City, in the Botanic Garden of Adam Mickiewicz University (AMU, Fig. 1). The AMU garden is situated in the northwestern part of the urban area, about 4 km east of the international airport Poznań Ławica and about 10 km southwest of the Karolin power plant. Other local point sources in the vicinity of the POZ site (radius of 20 km) were as follows: dumping grounds for municipal wastes, hospital and domestic sewage, industrial units producing metals and paints, smelters, waste incinerators, domestic heating units (DHUs) and agricultural activities.

The second sampling site was located at the Ecological Station of Adam Mickiewicz University in Jeziory, on the morainic plateau covered by mixed pine-oak forest. This site was located about 30 km southwest of the Poznań Agglomeration. There were no major urban/industrial sources within the Jeziory area at that time. Therefore, the forest site could be regarded as a representative regional background site for atmospheric mercury measurements in the study domain.

2.2. Sampling method

A total of 196 precipitation events were registered during the period from April 2013 to October 2014. Rainwater samples were collected simultaneously at both sampling sites, using a manually operated rain collector that was mounted 1.5 m above ground level in an open area. The bulk Hg sampler (wet + dry) consisted of an acid-washed polyethylene funnel (36 cm in diameter, reception surface of 0.0962 m²) connected by a Teflon adaptor to an acid-cleaned borosilicate bottle. In addition, the whole sampling set was equipped with an outer wooden tube to protect collected samples from solar radiation. Samples were collected after precipitation events to prevent artifacts associated with background contamination (leaves, insects), Hg adsorption on the sampler walls and to maintain a low value of field blanks.

At each site, the sampling set was manually changed after each precipitation event, i.e. collection surface (funnel) was rinsed with DDW, a new acid-cleaned bottle was loaded and the bottle with a collected rainwater sample was directly transported to the analytical laboratory at the Faculty of Chemistry of Adam Mickiewicz University in Poznań. In the laboratory, samples (rain or melted snow) were pre-acidified using HCl (Fluka, Switzerland) in the amount of 0.5% per volume, in order to minimize Hg losses and stabilize pH to the value of <2. All preserved samples were stored at 4 °C in borosilicate glass bottles prior to the main analysis and quantification. Snow samples were melted thoroughly at room temperature and then stored in the same manner as rainwater samples. To assure high-quality data and estimate uncertainties of the collection system, the sampling procedure, storage period and field blank (bottle blank + transport blank) values were controlled monthly. The tests of the abovementioned procedures (transport, calibration, preservation) confirmed no evidence for contamination of the samples during system handling. The values for background samples were not higher than 10% of Hg concentration measured for individual cases. The bottle blanks were processed in parallel to the environmental samples and their mean value was <0.5 ng L⁻¹. All steps of the abovementioned sample treatment and further analytical procedures were carried out in a clean laboratory meeting the standards specified for trace analyses (particle-free gloves, protective clothing, laminar flow chamber), where Hg concentration in the air was relatively low.

2.3. Sample analysis and quality control

Total mercury in unfiltered rainwater samples was quantitatively determined by cold vapor atomic fluorescence spectrometry (CVAFS) on a PSA Millennium Merlin mercury analyzer (UK), according to Method 1631 (US EPA) based on oxidation (0.5 mL 0.2 N BrCl), neutralization (0.25 mL 20% NH₂OH · HCl) and reduction to Hg⁰ (20% SnCl₂). The method detection limit (MDL as 3 times the standard deviation of 10 blank samples) was 0.1 ng L⁻¹ (or 0.01 ng of mercury in absolute mass units). The percentage recovery of Hg from duplicate spike standard solutions ranged from 98% to 103%. Additionally, to verify and control the applied method, a certified reference material was used (ORMS-3, National Research Council, Canada). The method recovery was 98 ± 5%. Reagents and sub-standard solutions for 5-point calibration curves (DDW with Hg(NO₃)₂ in the concentration range from 0 to 50 ng L⁻¹ plus reagent blanks) were ultrapure and of high quality grade (Sigma Aldrich, USA). Sub-standards were prepared from a 1 g L⁻¹ stock mercury standard (Merck) to obtain 0.1, 0.5, 1.0, 2.5 and 5 ng of Hg (1.0, 5.0, 10.0, 25.0 and 50.0 ng L⁻¹, respectively).

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