Accepted Manuscript

Atmospheric deposition of trace elements at urban and forest sites in central Poland – Insight into seasonal variability and sources

Patrycja Siudek, Marcin Frankowski

Please cite this article as: Patrycja Siudek, Marcin Frankowski , Atmospheric deposition of trace elements at urban and forest sites in central Poland – Insight into seasonal variability and sources, *Atmospheric Research* (2017), doi: 10.1016/j.atmosres.2017.07.033

Atmospheric deposition of trace elements at urban and forest sites in central Poland – insight into seasonal variability and sources

Patrycja Siudek [a,b*], Marcin Frankowski[a]

[a] Department of Water and Soil Analysis, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b Street, 61-614 Poznań, Poland

[b] National Marine Fisheries Research Institute, Kołłątaja 1 Street, 81-332 Gdynia, Poland

[*] Corresponding author e-mail address: psiudek@mir.gdynia.pl, Tel. + 48 587 356 136

Abstract

This paper includes the results of chemical composition of bulk deposition samples collected simultaneously at urban (Poznań city) and forest (Jeziory) sites in central Poland, between April 2013 and October 2014. Rainwater samples were analyzed for trace elements (As, Zn, Ni, Pb, Cu, Cr, Cd) and physicochemical parameters. Overall, three metals, i.e. Zn, Pb and Cu were the most abundant anthropogenic constituents of rainwater samples from both locations. In Poznań city, the rainwater concentrations of trace elements did not differ significantly between spring and summer. However, they were elevated and more variable during the cold season (fall and winter), suggesting strong contribution from local high-temperature processes related to coal combustion (commercial and residential sector). In contrast to the urban site, relatively low variability in concentrations was found for Cu, Ni, Zn at the forest site, where direct impact of emission from vehicle traffic and coal-fired combustion (power plants) was much lower. The bulk deposition fluxes of Ni, As, Pb and Zn at this site exhibited a clear trend, with higher values during the cold season (fall and winter) than in spring and summer. At the urban site, the sums of total bulk deposition fluxes of Zn, Cu, Pb, Ni, As, Cr, Cd were as follows: 8460.4, 4209.2, 2247.4, 1882.1, 606.6, 281.6 and 31.4 $\mu g\ m^{-2}$. In addition, during the winter season, a significantly higher deposition fluxes of Cu and Zn were observed for rain (on average 103.8 and 129.4 $\mu g\ m^{-2}$, respectively) as compared to snow (19.7 $\mu g\ Cu\ m^{-2}$ and 54.1 $\mu g\ Zn\ m^{-2}$). This suggests that different deposition pattern of trace elements for rain, mixed and snow was probably the effect of several factors: precipitation type, changes in emission and favorable meteorological situation during rain events.

keywords: trace elements, bulk deposition, emission sources, rainwater, seasonal variation

Introduction

The input of trace elements (TEs) via dry and wet deposition is a large source of contamination for plants, soil and water systems. Therefore, the understanding of its seasonal variation is fundamental for the further development of local and regional policies related to urban air quality and ecosystem protection. Trace elements are emitted to the atmosphere mainly from different anthropogenic sources and they often exhibit toxic properties. Several recent measurement campaigns have provided evidence that urban areas play a key role in determining the impact of PM2.5-containing inorganic and organic compounds on the air quality, climate system and human health (Khan et al., 2016). The major hotspots of metallic compounds are linked to various industrial activities (i.e. fossil fuel and oil combustion, nonferrous metal smelting, iron/steel manufacturing, waste incineration, cement production), residential wood combustion and traffic (tire/brake wear).

The series of short- and long-term observations of trace elements has been performed at different sites across the globe (Connan et al., 2013, Gunawardena et al., 2012, 2013, Guo et al., 2015). These studies provided empirical evidence that changes in emission and meteorological conditions (i.e. mixing layer height, ambient temperature, precipitation amount, atmospheric circulation) can have a significant impact on the transport, transformation and deposition of trace elements. As a result, atmospheric deposition of trace elements is an important issue involved in the

1

assessment of the environmental risk in relation to surface water and terrestrial ecosystems. Knowledge of the atmospheric chemical and physical processes of TEs transformation in particulate and liquid phase (i.e. size distribution and composition of the particles, oxidation and dissolution states, reactivity and solubility, stability, advection) is also necessary to appropriately estimate the TEs atmospheric budget on regional and global scale.

So far, relatively few studies concerning the seasonal variability of trace elements deposition have been conducted in central Europe. Specifically, there is lack of comprehensive observations that would enable to quantify the sources, transport, deposition and impact of trace elements from the atmosphere over urban areas in Poland on the environment and human health. For this reason, the measurements of Cd, Zn, Ni, Cu, Pb, As, Cr in rainwater samples were performed at two different sites in central Poland, between April 2013 and October 2014. The goal of this study was to determine main sources of toxic metals deposited from the atmosphere to the urban and forest ecosystems. To our knowledge, this is the first long-term simultaneous observation focused on monthly fluxes of trace elements in this region, including more detailed analysis of main factors that control their inter-seasonal variability in rainwater. The contribution of local/regional sources of heavy metals in precipitation was studied using a multivariate analysis. This approach allowed to identify processes/environmental factors responsible for high concentrations of trace elements in rainwater samples. We also examined differences in concentrations and fluxes for three types of precipitation that occurred during the winter season. This study was part of the research project dedicated to the atmospheric pollution transfer to the ecosystem, which has provided evidence for significant differences in trace elements concentration and fluxes between urban and forest sites, depending on the season, strength of emission sources, metallic compounds loading, size distribution of particles, and source-receptor interactions. The obtained results could be used in comparative studies and might have implications for further evaluation of the relationship between trace elements deposition and environmental effects in this region.

Materials & Methods

Study area

In the present study, the measurements were carried out at two sampling sites located in the urbanized region of Wielkopolska Province, central Poland (Fig. 1), in the area of Poznań, which is a medium-sized city (area of 261.8 km^2, population of about 600 000), characterized by high industrial and urban emissions. The first sampling site (52.42°N 16.88°E) is in the Botanic Garden of Adam Mickiewicz University, situated in the northwestern part of the city. This site is dominated by commercial/residential buildings and roads. About 4 km east of the sampling site there is an international airport Poznań-Ławica, and about 10 km southwest – Karolin coal-fired power plant. Other local sources of urban particles in the vicinity of the first site are as follows: dumping grounds for municipal wastes, construction sites, domestic sewage, industrial units producing metals and paints, smelters, waste incinerators, domestic heating units and agricultural activities. The second sampling site is located at the Ecological Station of Adam Mickiewicz University in Jeziory, about 30 km southwest of the Poznań Agglomeration. This site is situated on the morainic plateau covered by mixed pine-oak forest. There are no major urban/industrial emission sources around the Ecological Station in Jeziory.
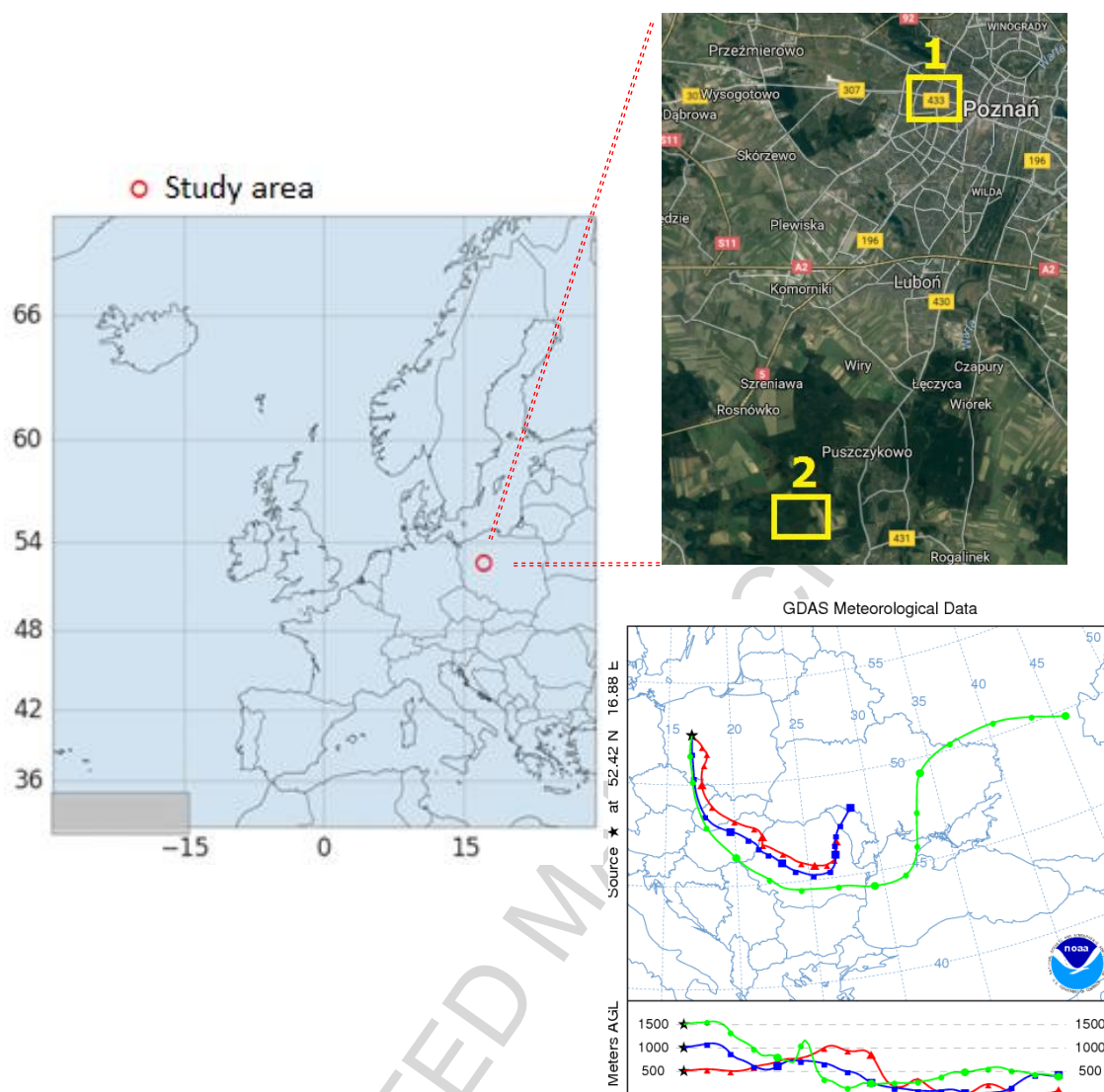
Fig. 1 Location of the sampling sites (urban – Poznań city, forest - Jeziory) in central Poland. The red circle refers to the study area in the urbanized region of Wielkopolska Province, whereas yellow open squares indicate: (1) urban site in Poznań city, and (2) forest site in Jeziory.

Sampling method

Atmospheric bulk deposition samples were collected at two locations between April 2013 and October 2014. The manually operated bulk deposition collectors were deployed at both sites, about 1.5 m above ground level, in open area, far from buildings and trees to avoid wind disturbances. The bulk rainwater sampler used in this study consisted of an acid-washed polyethylene funnel (36 cm in diameter and 0.0962 m^2 of reception surface) that was connected to an acid-cleaned borosilicate bottle by a Teflon adapter. In order to protect the collected samples against intense solar radiation, the sampling set was equipped with an outer wooden tube. Each experiment was finished immediately after precipitation event to reduce possible artifacts during sampling (i.e. leaves, insects) and storage (adsorption on the sampler walls). At both sites, the sampling system was changed manually after each precipitation event. Particular attention was paid to the collection surface (funnel), which was rinsed with double deionized water. Then, a new acid-cleaned bottle was loaded and the bottle with rainwater sample was transported directly to the analytical laboratory at the Adam Mickiewicz University in Poznań.

3

Sample analysis and quality control

In the present study, samples for trace elements analysis were not filtered. However, nitric acid (super-pure, 1% v/v) was used to adjust the pH to 1. All aliquots were shielded from light and stored at 4 °C until the main chemical analysis. The pH and electric conductivity (EC) of each rainwater sample were determined immediately after their collection, using a Mettler Toledo pH meter. The pH of rainwater samples collected in Poznań city varied from 3.61 (fall 2013) to 7.46 (spring 2013), with a mean ± SD value of 5.65 ± 0.72. In Jeziory, pH values ranged between 3.81 and 7.00. The minimum electric conductivity (EC) values of rainwater samples collected at the urban and forest sites were quite similar (5.38 and 5.61 $\mu S\ cm^{-1}$, respectively). The peak EC of 151.6 $\mu S\ cm^{-1}$ was measured in rainwater from Poznań city, and was significantly higher than the values recorded for Jeziory.

The rainwater samples for trace elements (Cr, Pb, Mn, Ni, Cd, As) were analyzed following the US EPA method 200.7:2001, using an atomic absorption spectrometer (AA-7000 Shimadzu, Japan) with graphite furnace atomization. The instrument was additionally equipped with ASC-7000 auto-sampler system. To quantitatively determine Zn concentration in collected samples, we applied the flame atomization spectrometry (AA-7000 Shimadzu, Japan). All details concerning the methods can be found elsewhere (Siudek et al., 2015). The quality assurance and control (QC/QA) procedures for the instrument were carried out using standards, duplicate blanks and procedural blanks (bottles filled with double deionized water). Generally, they represented less than 5% of the concentration measured in a sample. In addition, field blanks (bottles filled with deionized water) for precipitation samples were collected once per month and then analyzed in the same manner as rainwater samples. The results showed no contamination during sample handling and collection. The detection limit (*LOD*) and limit of quantification (*LOQ*) were calculated as 3 and 10 times the standard deviation of 10 blank samples. The *LOD* ($\mu g\ L^{-1}$) values were as follows: Cu (*0.03*), Cr (*0.02*), Cd (*0.003*), Pb (*0.03*), Ni (*0.1*), As (*0.1*) and Zn (*2*). The average relative standard deviation (*RDS*) for triplicate analysis of trace metals did not exceed 5% for GF-AAS and 7% for F-AAS.

The precipitation height (mm) was measured manually using a Hellman rain gauge. A total of 197 rainwater samples were collected. During the 19-month study period, the total precipitation amount in Poznań was 943.3 mm. The number of bulk deposition samples was 128 and 78, respectively for the urban and forest sites. At the urban site, the average monthly precipitation ranged between 5.6 mm (February 2013) and 109.8 mm (June 2013), with an average of 46.6 ± 27.2 mm per month. Additionally, during the winter season of 2013 and 2014, 26% of the collected samples were reported as snow, which depth ranged from 2.08 mm to 11.96 mm. Also, approximately 4% of rainwater samples were attributed to episodes with relatively small precipitation depth (< 0.2 mm).

In the present study, the atmospheric bulk deposition fluxes of trace elements ($\mu g\ m^{-2}$) were obtained by multiplying the TEs concentrations measured in each sample ($\mu g\ L^{-1}$) by precipitation depth (mm) and dividing by reception surface the collection funnel (0.0962 m^2).

Data analysis

The statistical analysis of all data obtained from both measurement locations was performed using Statistica 10.0 software. First of all, the collected data were checked for normality (Shapiro-Wilk test), outliers (Grubbs test) and distribution pattern (Levene'a test). Subsequently, the differences in mean concentration were estimated using parametric (ANOVA) or non-parametric (Kruskal-Wallis) tests. The Spearman's correlation (p<0.05) was used to establish statistically significant dependencies between trace elements concentrations in rainwater samples. The basic meteorological parameters, i.e. air temperature, atmospheric pressure, relative humidity, wind speed and direction, were registered simultaneously by a local weather station.

In the present study, the principal factors corresponding to sources/processes associated with trace elements and physicochemical variables such as pH and EC were determined by Principal

4

Component Analysis (PCA) for two independent databases, i.e. urban and forest. This multivariate approach allowed to identify the dominant component controlling variability of trace elements in bulk deposition. The PCA method have been previously applied to similar observations (Montoya-Mayor et al., 2013). Here, data were standardized prior to the PCA analysis, and then positive/negative correlations of 7 variables, i.e. As, Cd, Pb, Ni, Zn, Cu and Cr with H^+ and pH were computed. By creating the standardized database we were able to find the distribution of variability for both sites separately. These aspects will be discussed in details in the next section.

Results and discussion

Seasonal variability of trace elements in rainwater

Fig. 2 shows the seasonal variability in As, Ni, Pb, Cu, Zn, Cd and Cr concentrations at the urban and forest sites during the 19-month field measurement campaign. In Poznań city, all trace metals exhibited relatively large differences in concentrations between sampling seasons (spring 2014, summer 2013, fall 2013, winter 2013/2014, spring 2014, summer 2014, fall 2014), with a median ranging from 0.02 µg L^{-1} (Cd) to 18.0 µg L^{-1} (Zn). The maximum concentrations of 137.1 µg L^{-1} and 49.1 µg L^{-1} were found in spring 2014 and winter 2013/2014 for Zn and Cu, respectively. In addition, the largest discrepancies for Zn were observed in fall 2013. The median concentrations of Zn, Pb and Cr in rainwater samples were significantly higher in spring 2013 than in spring 2014 when median concentrations of these elements did not exceed 9, 2 and 1 µg L^{-1}, respectively. The highest median concentration for Ni (3.70 µg L^{-1}) and for As (1.48 µg L^{-1}) was observed respectively in fall 2014 and fall 2013. During summer 2013, the highest peak concentration was observed for Zn (37.0 µg L^{-1}), followed by Pb (13.23 µg L^{-1}), Cu (11.94 µg L^{-1}), Ni (6.42 µg L^{-1}), Cr (1.64 µg L^{-1}), As (1.12 µg L^{-1}) and Cd (0.14 µg L^{-1}). In contrast to summer 2013, from 2 to 4 times higher concentrations for As, Ni and Cu were observed in summer 2014.
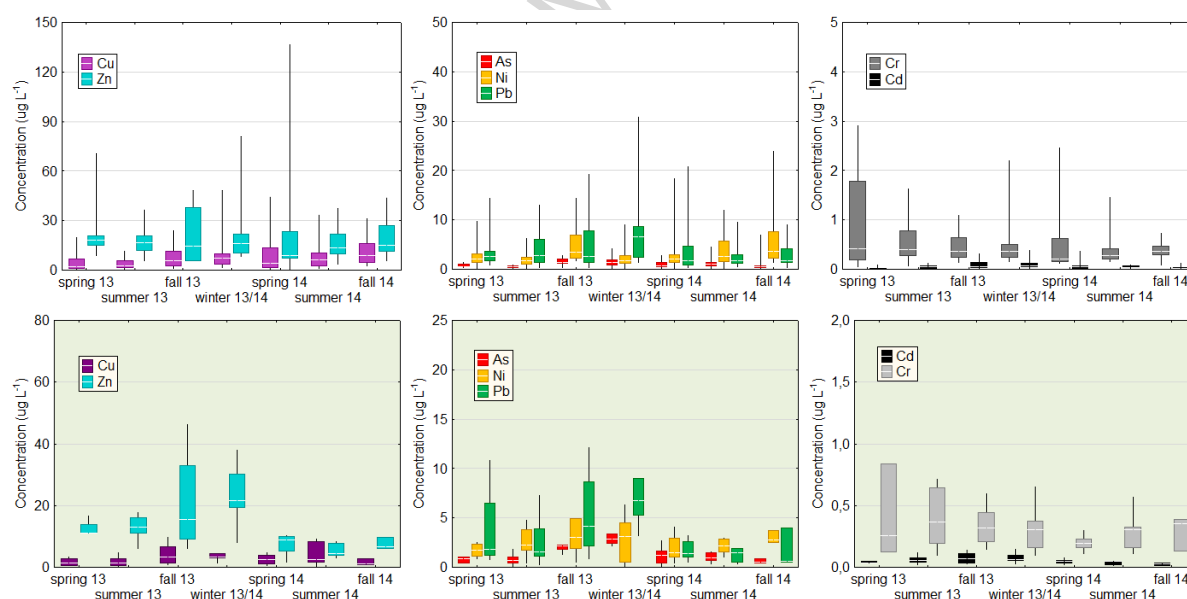

Fig. 2. The box-and-wishers plots displaying the variability of seven trace elements during the sampling seasons in Poznań city (top panel) and Jeziory (lower panel). The upper and lower box bounds represent the upper/lower 25 % values. The upper and lower whiskers represent the maximum/minimum values. White line in the middle of the boxes represents the median value. The Kruskal-Wallis test was used to find differences between seasons. The differences between the plotted median values for urban database were statistically significant for As: p = 0.00, Ni: p = 0.00, Pb: p = 0.02, Cu: p = 0.00, Cd: p = 0.00, while in case of the forest database the statistically significant values were obtained for As and Pb (p = 0.00)

Atmospherically deposited As species might be a product of fossil fuel combustion, or originate from contaminated soil and re-suspended road dust (Pacyna and Pacyna, 2001). At the urban site, the elevated concentrations of As, Ni and Pb in fall 2014 and winter 2013/2014 were

5

predominantly associated with intensive emission from residential and industrial sectors (Fig. 2). However, the highest concentrations during the entire sampling period in Poznań city were observed for Zn. In this study, the urban site was in close proximity to several roads, thus traffic emission was a significant source of Zn. This finding is consistent with previous studies by Gunawardena et al. (2013), who also found a significant correlation between this element and traffic volume. It has been previously documented by some authors that Zn in the urban atmosphere is mainly associated with vehicular traffic (Kemp, 2002), as well as with industrial and domestic heating.

Gunawardena et al. (2013) have pointed out that Zn is a good marker for traffic volume as it primarily originates from the wear of vehicle components, whereas heavy metals such as Ni, Pb, Cu and Cd correlate well with traffic congestion. As shown in the lower panel of Fig. 2, the seasonal variation in concentrations of Zn and Cu in rainwater collected at the forest site was more pronounced. Specifically, slightly elevated concentrations of these metals were found in fall 2013 and winter 2013/2014. Due to the fact that our forest site was located far from heavy-traffic roads, it seems that other point emission sources related to combustion processes could contribute to high concentrations of both (Zn and Cu) metals in rainwater samples. The meteorological data analysis, including local wind and direction pattern and backward trajectory, showed that the forest site was affected by different air mass types. In particular, it was recognized that the regional sources located south and west from this forest area might have been of primary interest for the whole sampling period. Therefore, it was possible that some amount of Zn and Cu could have been transported from distant emission sources. For example, the transport from S direction typically brought polluted air masses to the forest site (Fig. 1), which resulted in high concentrations of Pb, Zn and Cu in rainwater samples collected during fall and winter. This hypothesis has been previously confirmed in relation to atmospheric mercury based on the backward trajectories analysis (Siudek et al., 2015). For the other elements, seasonal differences were not statistically significant ($p < 0.05$). In Jeziory, the wintertime peak concentration of Cu was 10 times lower than that observed in Poznań city. During the winter of 2013/2014, we observed an opposite trend for As, i.e. concentrations of this metal ranged from 2.46 to 5.36 µg L^{-1} at the forest site, whereas for the urban site the median value did not exceed 2.1 µg L^{-1}. For the forest site, the Spearman's correlation analysis showed the statistically significant correlation between Pb and Cd ($R^2 = 0.70$, $p < 0.05$, Fig. 3).
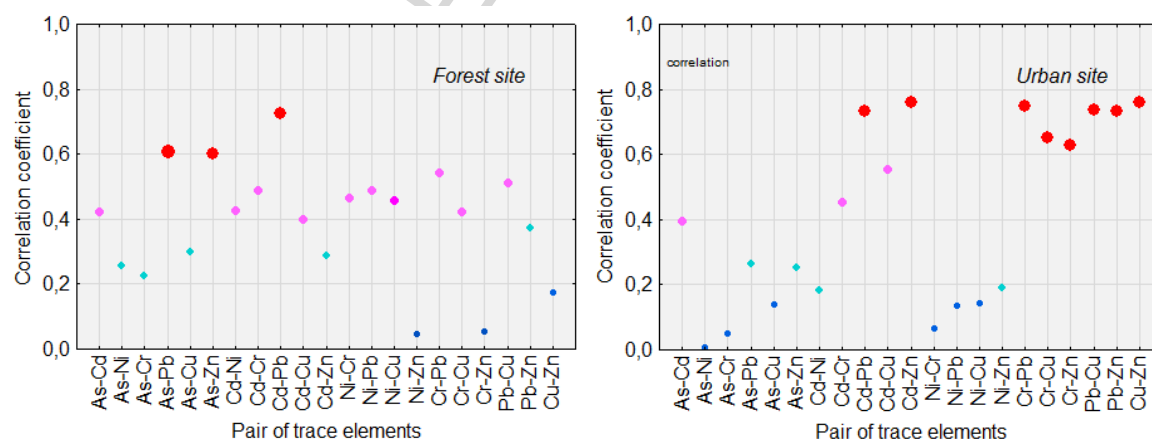
Fig. 3. Results of trace elements correlation analysis at the forest (left) and urban (right) sites. In both plots, the red dots indicate strong correlation ($R^2 > 0.60$), pink dots represent relatively medium correlation (R^2: 0.40 - 0.60), whereas blue dots are referred to a weak correlation ($R^2 < 0.40$).

This finding might indicate the same sources for these two metals, but also similar geochemical behavior and/or transport processes. There were also positive correlations found for As-Zn, As-Pb ($R^2 = 0.60$) and Pb-Cr ($R^2 = 0.55$), however, correlations between As-Cr, As-Ni, Pb-Zn, Cd-Zn and As-Cu were higher than for Ni-Zn , Cr-Zn and Cu-Zn (Fig. 3). Comparing the results from our forest site with other non-urban locations, we found that majority of trace elements measured in rainwater samples collected in Jeziory had higher concentrations in comparison with the values registered by

Connan et al. (2013) for the wetland site of Marais Vernier in France. For example, mean concentrations of rainwater Zn, Ni and Pb from the Connan et al. (2013) investigations were 5.4, 0.6 and 0.2 µg L^{-1}, respectively, which was about 3, 8 and 20 times lower than the average concentrations measured at the forest site in Jeziory.

A slightly wider range of the coefficients of correlation between trace elements in rainwater samples was found at the urban site, indicating different anthropogenic sources of pollutants (Fig. 3). A strong positive correlation ($R^2 > 0.7$) was observed for Cd-Pb, Cd-Zn, Cr-Pb, Pb-Zn, Pb-Cu and Cu-Zn. This finding suggests significant contribution from a variety of local/regional sources mainly associated with coal combustion, road traffic, ferrous and non-ferrous metal production, but also with atmospheric distribution, transformation and transport processes of these elements.

Trace metal concentration vs. precipitation amount

Previous studies by Lynam et al. (2013) have shown that linear relationship between ln(Hg) concentration and precipitation height (H) was not strong. Similarly, the dilution effect was of relatively minor importance at several other sites (Wang et al., 2012, Shi et al., 2015). Also, White et al. (2013) have found low value of the slope of linear fit and low regression coefficient for samples collected nearby major anthropogenic sources. Our results were quite similar to those from the abovementioned works. For example, negative coefficients of -0.50 and -0.14 were determined in rainwater samples for Zn and Cu, while Ni, Pb and Cd exhibited much smaller values of -0.07, -0.06 and 0.00, respectively (Fig. 4). This finding suggests that local anthropogenic sources related mostly to high-temperature combustion (coal-fired power plant Poznan-Karolin, smelting, domestic heating), traffic and industrial activities, played a significant role in distribution of Zn and Cu with precipitation depth. However, it is important to highlight that only a small percentage of the total variation in concentrations of these two metals was attributed to the precipitation depth at this site. Specifically, the R^2 for ln(Zn) vs. H was found to be 0.04, whereas for Cd it was 0.01.
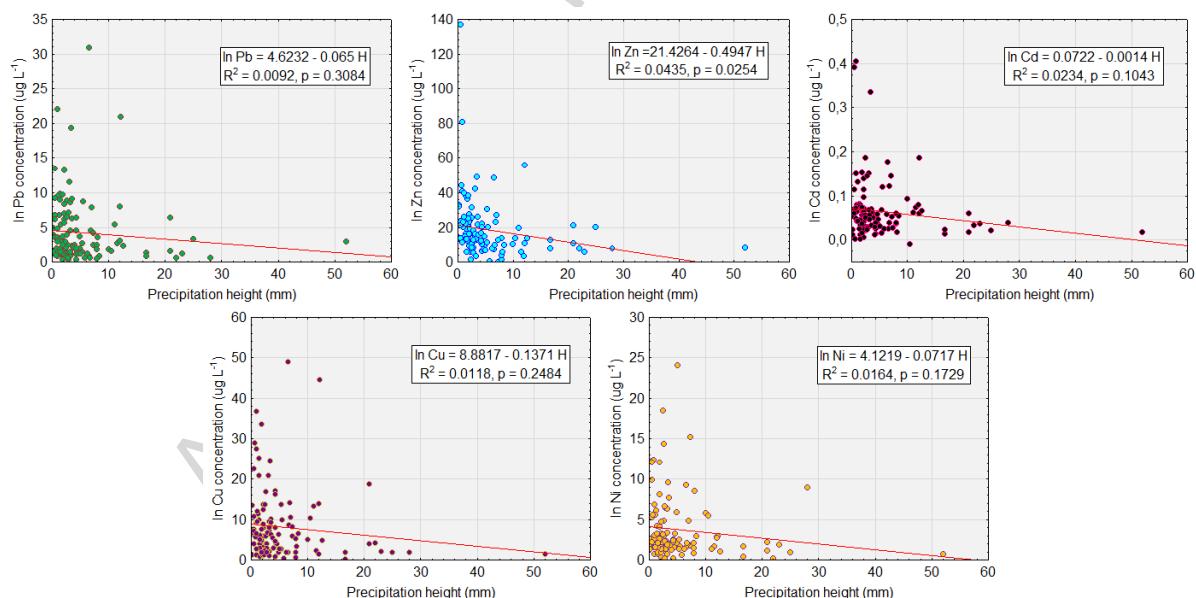
Fig. 4. The natural log concentration of trace elements (µg L^{-1}) vs. precipitation depth (mm) at the urban site, between April 2013 and October 2014, Poland

The observed linear decline in rainwater trace metals concentrations was significantly lower compared to the values obtained by Lynam et al. (2013) during the mercury measurements at 8 monitoring stations in the USA. Hence, we concluded that probably some other parameters influenced the inter-annual variation in trace elements in precipitation at the urban site in central Poland. In addition, as shown in Fig. 4, the concentrations of trace elements were relatively low for single episodes with extremely high precipitation depth (H> 50 mm), indicating the effective below-

7

cloud scavenging of metals in airborne particles of different size mode. This observation was similar to previous studies by Montoya-Mayor et al. (2013).

Bulk deposition fluxes of TEs vs. precipitation amount

The relationship between trace elements deposition (wet plus dry) and precipitation amount at the urban sampling site is shown in Fig. 5. Results of bulk deposition presented in this study were representative for the sum of dry and wet scavenging of particle-bound trace elements, including in-cloud and below-cloud processes. In Poznań city, the linear correlation between Zn deposition fluxes and rainfall depth was strong (R^2 = 0.51) and statistically significant at the 5% level (Fig. 5, middle one). However, for other metals, positive but slightly weaker correlations (R^2 < 0.40, p < 0.05) were observed. Specifically, weak correlations for the deposition fluxes of Cu, Cr, Ni and Pb vs. precipitation amount might suggest more complex mechanism of these metals transformation in rainwater, which is controlled by various environmental factors. Previous studies by Gunawardena et al. (2013) have explained that significantly higher Zn wet deposition fluxes compared with Cr or Ni were mainly caused by enhanced solubility of Zn in rainwater. Morselli et al. (2003) have also found higher solubility of Zn in wet deposition in relation to other heavy metals, which rainwater dilution potential decreased in the following order: Cd > Cu > Ni > Pb > Cr. In addition, measurements by Gunawardena et al. (2013) have shown that Cr is more effectively scavenged via dry than wet deposition. All the above mentioned findings are consistent with the results of this study.

During the heavy rain episode (H> 50 mm) in July 2013, relatively high values of bulk deposition fluxes of Zn (431.5 μg m^{-2}) and Pb (150.5 μg m^{-2}) in relation to other trace elements were obtained (Fig. 5). It should be highlighted that anthropogenic sources of Zn during summer period included mainly industrial activities (those associated with paints, galvanized coated roofing, gutters, storm water pipes) and traffic emission. Therefore, the contribution from local emission sources associated with construction works may be significant for the Zn atmospheric budget within our urban study domain.
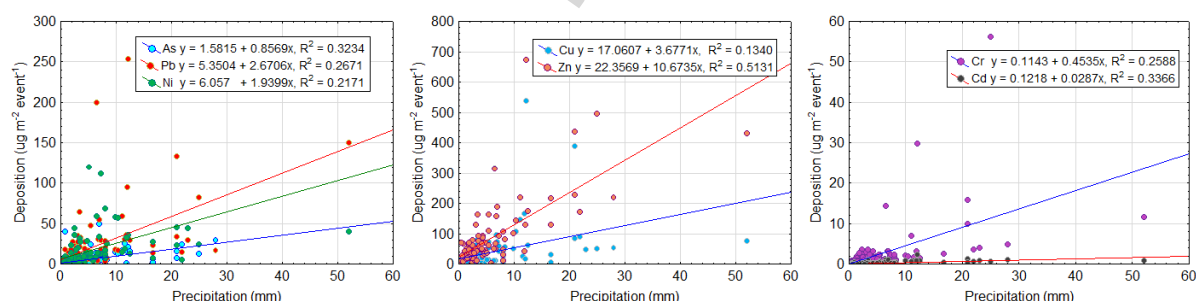
Fig. 5. Linear regression analysis between bulk deposition fluxes (μg m^{-2} event^{-1}) of As, Pb and Ni (left picture), Cu, Zn (middle picture), Cr, Cd (right picture) and precipitation amount (mm) at the urban site, between April 2013 and October 2014. The bulk deposition fluxes of TEs were obtained by multiplying metal concentration in rainwater sample and precipitation depth for a single rain episode

Seasonal variation in TEs deposition fluxes and comparison with other studies

Generally, higher and much variable values of bulk deposition fluxes in this study were observed at the urban site. Specifically, the mean deposition fluxes of Zn, Cu, Pb, Ni, As, Cr, Cd, from April 2013 to October 2014, were as follows: 8460.4, 4209.2, 2247.4, 1882.1, 606.6, 281.6 and 31.4 μg m^{-2} (Table 1). At the forest site, mean deposition fluxes of trace elements increased in the following order: Zn < Cu < As < Pb < Cr < Ni < Cd (Table 1). Such results suggested that local urban activities had a significant contribution to air pollution in Poznań city. As can be seen in Table 1, the bulk deposition fluxes of Zn and Pb measured at both sites in this study were higher in comparison to the values reported for a rural site in France (Connan et al., 2013). The deposition fluxes of Cd registered in this study at the forest site were slightly lower than the annual deposition fluxes obtained at the Marais Vernier, France (Connan et al., 2013) and Lhasa, Tibet (Guo et al., 2015). At

8

the urban site, the deposition fluxes of Zn, As, Cr, Cd, Pb were higher than those in France (Connan et al., 2013), Lhasa (Guo et al., 2015) and Canada (Lynam et al., 2015), but lower than the results obtained at the remote site along the Japan Sea coast (Sakata and Asakura, 2009). The elevated deposition fluxes of trace elements measured at the Nakanato site, Japan, were associated with large contribution of long-range transport of air pollutants from Asian regions (Sakata and Asakura, 2009). Pan and Wang (2015) found extremely high values of bulk deposition fluxes of trace elements at the urban site in northern China. The total annual deposition fluxes of Zn (up to 245 000 μg m^{-2}), Pb (31 100 μg m^{-2}) and Cu (19 400 μg m^{-2}) in Tianjin, China were 5-29 times higher than the mean values of these elements observed in bulk deposition samples collected in Poznań city.

Table 1 Comparison of mean bulk deposition fluxes of trace elements from this study (April 2013 and October 2014) and from studies focused on other regions. All data are given in μg m^{-2}.

	Poznań city Poland *Urban* A	Jeziory Poland *Forest* B	Lhasa Tibet *Urban* C	Tianjin China *Urban* D	Marais Vernier France *Rural* E	Nakanato Japan *Remote* F	Patricia McInnes USA *Air quality monitoring station* G
As	606.6	465.3	233	5510	-	1600	-
Cd	31.4	7.3	9.5	560	9	310	-
Cr	281.6	132.3	118	9770	-	400	-
Ni	1882.1	19.2	171	7390	362	1400	-
Pb	2247.4	160.6	516	31 100	142	10 000	-
Cu	4209.2	1904.0	584	19 400	-	1800	-
Zn	8460.4	6654.7	5211	245 800	2980	27 000	1033

A and B   This study
C   Guo et al., 2015
D   Pan and Wang, 2015
E   Connan et al., 2013
F   Sakata and Asakura, 2009
G   Lynam et al., 2015

It should be noted that such large discrepancies in atmospheric deposition fluxes, which have emerged from the abovementioned studies, were the result of the strength of emission sources, differences in the acidity of samples, chemical reactivity and water solubility of trace elements. The differences could be also attributed to meteorological conditions during measurement campaigns.

In the present study, we observed strong seasonal variability in deposition fluxes of seven trace elements at both sites (Fig. 6). The highest cumulative deposition flux of the measured TEs at the urban site was observed in spring 2014 (4100 μg m^{-2}), followed by fall 2014 (2813 μg m^{-2}) and summer 2014 (2704 μg m^{-2}). This indicates that differences in deposition fluxes of elements were mostly associated with concentration of pollutants in rainwater and precipitation depth, which confirmed the findings of several other works (Connan et al., 2013, Guo et al., 2015). In this study, the total deposition flux of selected elements was much lower in spring 2013 than in spring 2014. Namely, Cu contribution to the total bulk deposition was significantly small (< 10%) in spring 2013 compared with spring 2014. This was due to 2 times lower precipitation depth measured in spring 2013 as compared to spring 2014. On the other hand, the increase in the bulk deposition fluxes of trace elements at the urban site during the winter season of 2013/2014 was mainly the effect of local/regional emission of pollutants from coal combustion in domestic heating units. Due to fact that the monthly sum of precipitation depth in winter varied from relatively low (5.6 mm in February 2014) to medium (47.9 mm in January 2014), this parameter had rather minor contribution to the observed intraseasonal variability in TEs bulk deposition fluxes (Fig. 6).

As for our forest site, the obtained bulk deposition fluxes of trace elements in winter 2013-2014 compared with other seasons were relatively high, indicating large impact of regional

anthropogenic emission on concentration levels of TEs. In analogy with the urban site, the peak values were observed for Zn and Cu in Jeziory during the winter of 2013/2014 (Fig. 6).
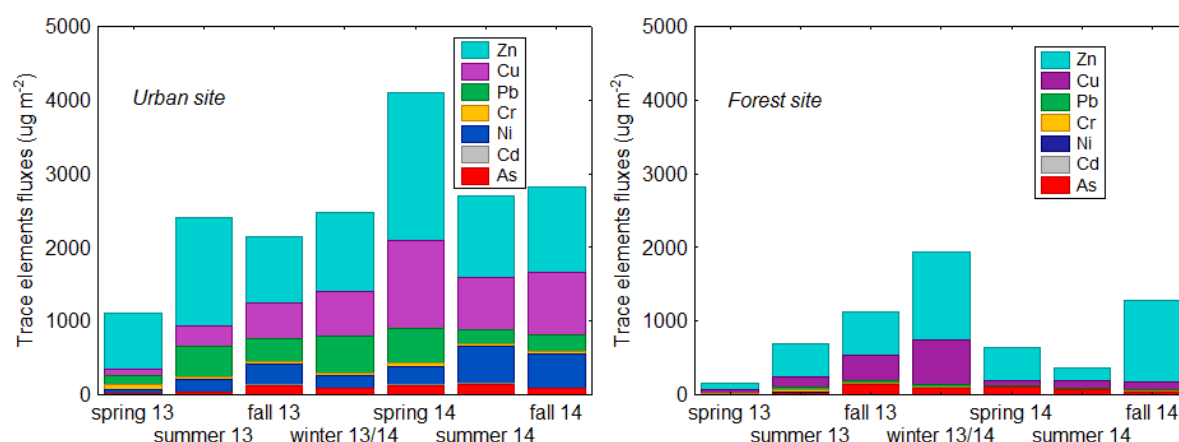

Fig. 6. The stacked seasonal bulk deposition fluxes of trace elements in Poznań (left) and Jeziory (right)

It has been found in some previous studies that the influence of non-urban environments (i.e. forest, rural, remote) on trace elements emission is disproportionately lower in relation to industrially-impacted regions (Connan et al., 2013, Shi et al., 2015). Comparing the results from this study, it can be concluded that transport of pollutants from regional industrial and commercial sources was an important factor that contributed to higher wintertime deposition of trace elements. The results of backward trajectories showed that on average ca. 57% of precipitation events collected from November 2013 to February 2014 were associated with south-to-southwestern wind regime, including highly polluted southern parts of Poland (upper Silesia) and Europe (Czech, Germany, France). For example, Fig. 1 displays a backward simulation of air masses that travelled from the S direction over European industrialized regions. In contrast, during the northern advection a large fraction of toxic TEs deposited in Jeziory could be associated with particles that were emitted from various industrial processes/residential heating in Poznań Agglomeration and distant European regions. This finding was in agreement with past studies conducted by Siudek et al. (2016 a,b) and Walna (2015), carried out in Jeziory, which indicated several major point sources from Poznań Agglomeration as effective factors controlling the loading of anthropogenic aerosol and seasonal variation of major inorganic ions in precipitation.

It should be noted that the seasonal pattern of bulk deposition fluxes of trace elements in Poznań city was quite different from the patterns registered for other urban areas, especially those in Asia. For example, the maximum deposition fluxes of trace elements, observed at the several sites in Northern China coincided with the rainy season and were observed in summertime (Pan and Wang, 2015). In the present study, the ∑F-urban vs. ∑F-forest calculated for all metals was on average 18.7, ranging from 1.3 to 100.8.

Trace metals deposition via wintertime precipitation (rain, snow and mixed phase)

Considering different types of precipitation in the winter period, we observed statistically significant differences in mean concentrations of trace elements, between snow, rain and mixed phase ($p < 0.05$). Trace elements concentrations ranged between < MDL and 81.3 μg L^{-1}, and the trend was as follows: mixed phase > rain> snow (Fig. 7). The mean pH values for snow, rain and mixed samples were 4.80, 5.05 and 4.76, respectively. The highest mean concentrations were found in mixed precipitation: Zn (46.6 μg L^{-1}), Cu (19.8 μg L^{-1}) and Pb (12.3 μg L^{-1}), whereas the lowest mean concentrations were measured in snow samples, for Cd and Cr (Fig. 7a). Results obtained by Lynam et al. (2015) for snow, rain and mixed samples collected at the Patricia McInnes site in Canada, revealed quite similar trend for some trace elements. They found slightly higher volume-weighted

mean concentrations for As and Cd in rainwater samples than in snow and mixed precipitation, whereas for the most abundant anthropogenic elements such as Cu and Zn, the highest concentrations were measured in snow (Lynam et al., 2015).
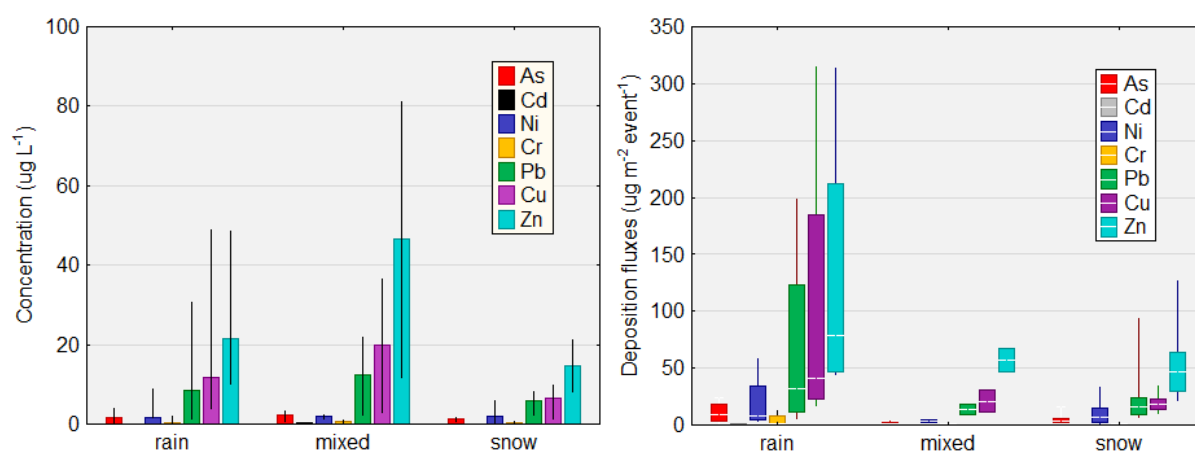
Fig. 7. Examples of (a) concentrations of trace elements, and (b) deposition fluxes of trace elements, for three types of precipitation collected during winter 2013/14 in Poznań city. The term 'mixed' was referred to the precipitation type that included both snow and rain component.

As mentioned before, deposition fluxes of trace elements are primarily determined by precipitation amount and the concentration of pollutants in rainwater samples. In Poznań city, higher deposition fluxes of As, Ni, Cr, Pb, Cu and Zn were more often observed in the case of rainfall samples than in other types of the samples (Fig. 7). Interestingly, the peak Zn concentration of 81.3 µg L^{-1} was observed for a mixed sample and corresponded to a deposition flux of 67.6 µg Zn m^{-2}, while the maximum flux of 315.3 µg Zn m^{-2} was observed for the rain episode with about 2 times lower concentration of Zn. The lowest deposition values were found for Cr in snow samples, followed by mixed phase and rain (Fig. 7b), but the differences were not statistically significant ($p < 0.05$). Similar deposition trend was reported by Lynam et al. (2015) for Ni and Pb. They indicated a strong influence of meteorology and local sources of emission. The results from our study, similarly to Lynam et al. (2015), suggested less effective uptake of trace elements by snow than by rain. However, higher fluxes observed for rain could be also attributed to several other factors, e.g. emission source strength, preceding dry period and precipitation depth (in particular: its frequency, intensity and type). It should be mentioned that above and below cloud scavenging of particles has been identified as another crucial mechanism for pollutants removal from the polluted atmosphere (Andronache, 2003). The effect of trace elements scavenging from cloud is difficult to distinguish based on snow and rain data. It should be further investigated during a more detailed study, which is beyond the scope of this work. Croft et al. (2009) have emphasized that scavenging efficiency of gaseous and particulate phase species depends primarily on two parameters, i.e. precipitation intensity and particle size distribution. Based on their semi-empirical parameterization of below-cloud scavenging, they have shown that in case of relatively low precipitation intensity both fine and ultrafine particles can be more intensively scavenged under snow conditions as compared to rain (Croft et al., 2009). The results obtained in this study can be partly explained by significant differences in atmospheric conditions during the sampling days, especially by lower intensity of snowfalls compared to rainfalls. As already mentioned, Zn, Cu and Pb in winter samples collected at the urban site in Poznań city might have originated mainly from local industrial sources and residential sector, which both emitted mostly smaller particles.

Principal Component Analysis of trace elements in rainwater samples – urban vs. forest site

As shown in Table 2, the sum of individual principal components accounted for quite similar percentage of the total variance for both sites, i.e. 68% for urban (**PC-u**) and 71% for the forest (**PC-f**) site.

At the urban site, first factor **PC1-u** showed that the major component of overall variance (33%) was formed by three variables (Cu, Zn and Pb) with loadings greater than 0.8, whereas at the forest site, the **PC1-f** was different (Table 2). Specifically, the group of correlated variables included three ions with high loadings (Pb and Zn: 0.879, As: 0.870) that explained 38% of the total variation in Jeziory. The **PC1-f** could be assigned to the regional transport from traffic-related sources and industrial activities, due to the fact that there were no major anthropogenic sources in Jeziory. As mentioned before, Zn, Ni, Pb, Cd and Cu are good markers of traffic volume and congestion. Hence, the contribution from traffic sources (vehicle exhaust, tire and brake wear) to the total trace elements budget at the urban site was high during the whole sampling period. At the urban site, EC and H^+, with high loadings of 0.688 and 0.906, were identified as important variables controlling the overall variance of **PC2-f,** similarly to the results obtained for **PC2-u**. Therefore, it can be supposed that both parameters had equally important impact on rainwater composition in the urban environment and forest ecosystem. As can be seen in Table 2, there were no statistically significant correlations between pH, EC and trace elements.

Also, an additional regression analysis (data not shown) between trace elements and pH did not reveal strong correlation ($p < 0.05$) at any of the selected sites during the whole study period. At the forest site, only Pb showed weak and negative relationship with pH ($R^2 = -0.38$, $p < 0.05$), whereas slightly similar correlations were observed for Cu -pH ($R^2 = 0.23$) and Cr-pH ($R^2 = 0.21$) at the urban site. This finding suggested that acidity of rainwater samples was not a limiting factor for trace elements variability. The pH level also depended on other ions. This could also point to the significant role of emission sources, which is in agreement with other studies (Shi et al., 2015). As for the relationship between EC (electric conductivity) and trace elements, a significant correlation was found for Zn-EC (0.58) and Cu-EC (0.51) at the urban site. A correlation of other elements with EC was also positive but insignificant, i.e. Cd-EC (0.37), Cr-EC (0.33) and Pb-EC (0.33) at this site. When comparing the results of EC from the urban site with those from the forest observations, we found out that the impact of air quality on TEs concentration level in rainwater was significant and more pronounced at the urban site. These differences suggested that anthropogenic emission of Zn, Cu and other elements from a variety of local sources was enhanced in Poznań city as compared to Jeziory. The effect of EC and pH on cloud/fog water composition has been previously studied by Liu et al. (2012) at the mountain site in China. The authors indicated elevated concentrations of trace elements in a highly acidic sample (pH = 2.56, EC up to 2680 μS cm^{-1}). Moreover, they explained the large content of Mn, Fe, Zn and Pb in first samples of cloud/fog events as a combined impact of below-cloud scavenging efficiency of particulate phase tracers, meteorological conditions and strong impact of emission and transport of pollutants from different sources on the atmospheric chemistry.

Table 2 Principal Component Analysis for trace elements in rainwater samples collected at the urban and forest sites in central Poland, between April 2013 and October 2014. The Varimax normalized rotation and Kaiser criterion (eigenvalues > 1) was used to extract the principal components. Data in bold font represent correlation of variables greater than 0.650

Variables	*PC1-u*	*PC2-u*	*PC3-u*	*PC4-u*	*PC1-f*	*PC2-f*	*PC3-f*
H^+	-0.009	**0.906**	0.024	0.026	-0.003	**0.841**	0.174
EC	0.523	**0.688**	0.043	0.045	0.028	**0.875**	0.022
As	-0.137	-0.138	**-0.720**	0.237	0.229	0.043	**0.854**
Cd	-0.022	-0.084	0.026	**-0.928**	**0.665**	0.129	0.373
Ni	0.328	-0.182	0.258	0.271	**0.800**	0.064	0.031
Cr	-0.138	-0.053	**0.675**	0.185	**0.792**	-0.100	0.083
Cu	**0.862**	0.049	-0.051	0.019	0.352	-0.015	**0.845**
Pb	**0.919**	0.049	0.001	0.016	**0.711**	-0.009	0.182
Zn	**0.881**	0.207	0.035	0.013	-0.030	0.241	**0.852**
% Variance	33	13	11	11	38	19	14
Eigenvalue	3.01	1.21	1.03	1.02	3.39	1.73	1.22

In Poznań city, the third and fourth factor contributed to the same percentage of the total variance (11%), however these two components were represented by different variables, i.e. As and Cr in *PC3-u* and Cd in *PC4-u*. It seemed that *PC3-u* could be related to the local power and industrial sectors, which have high potential to produce small particles containing As and Cr during fossil fuel combustion (i.e. emission from local power plants and residential heating, vehicular emission, construction activities, use of pigments, pesticides, waste incineration). The *PC4-u* revealed high loading for Cd (-0.928), which suggested strong contribution of this heavy metal from various industrial activities, including construction and steel works, waste incineration, vehicle emission, traffic-induced resuspension, road dust transport under different wind conditions as well as emission from contaminated soils. Unlike *PC3-u*, the *PC3-f* with a 14% contribution to the total variance showed three positively correlated variables, i.e. As, Cu, Zn, with the loading greater than 0.8 (Table 2). These elements originate from different anthropogenic sources. For example, As – from steel manufacturing and chrome plating (Majestic et al., 2007), while Pb can be emitted from oil combustion, motor vehicle exhausts, smelting and waste incineration (Pacyna and Pacyna, 2001). The Zn, in turn, originates from fossil combustion, tire abrasion, processing of non-ferrous metals and steel production (Pacyna and Pacyna, 2001). The results obtained in the present study for *PCA-u*, together with positive correlations of Pb-Cu, Pb-Zn and As-Cr, were consistent with the results presented by Montoya-Mayor et al. (2013) for the urban-traffic site in Sevilla (Spain). Based on sequential PCA, they found a clear relationship between high TEs concentration in rainwater samples and factors representing sources such as acid rain, regional pollution, intense traffic, contaminated soil and mixed soil-traffic.

The main conclusion from the abovementioned multivariate analysis is that different factors might influence trace elements concentration levels in rainwater at the urban and forest locations. In particular, the obtained *PCA-u* and *PCA-f* results showed clear differences in the impact of anthropogenic emission. At the urban site, due to numerous sources of pollutants and their time-varying emission strength, we observed more significant variability in rainwater heavy metals concentration compared to the forest site. Previous studies by Siudek et al. (2016 a,b) have also showed that the contribution from local coal-combustion processes (fuel-based domestic heating) was typically higher during winter and lower during summer season.

Conclusions

The bulk deposition fluxes of trace elements (As, Cd, Cr, Ni, Cu, Pb, Zn) were investigated at the urban and forest sites in central Poland, between April 2013 and October 2014. The variability in rainwater concentrations of trace elements was analyzed in relation to season, precipitation type, emission sources and meteorological factors. A clear seasonal trend in trace elements concentration in rainwater was attributed to local/regional sources and transport processes. At the urban site, the elevated concentrations and deposition of As, Ni, Zn and Pb in fall 2014 and winter 2013/2014 were predominantly associated with intensive emission from residential and industrial sectors (i.e. coal combustion) and traffic emission. Comparison of bulk deposition fluxes of TEs at the urban and forest sites indicated that precipitation depth and transport of pollutants can play a significant role in trace elements distribution. A detailed analysis of winter samples showed significant variability in trace elements concentrations. In particular, a vast majority of selected elements revealed higher concentrations in mixed phase samples, followed by rain and snow. The observed trend was probably the effect of several factors: precipitation type, changes in emission and favorable meteorological situation during rain events.

References

1. Andronache, C., 2003. Estimated variability of below-cloud aerosol removal by rainfall for observed aerosol size distributions. Atmospheric Chemistry and Physics 3, 131-143.

2. Connan, O., Maro, D., Hébert, D., Roupsard, P., Goujon, R., Letellier, B., Le Cavelier, S., 2013. Wet and dry deposition of particulate associated metals (Cd, Pb, Zn, Ni, Hg) in a rural wetland site, Marais Vernier, France. Atmospheric Environment 67, 394-403.

3. Croft, B., Lohmann, U., Martin, R.V., Stier, P., Wurzler, S., Feichter, J., Posselt, R., Ferrachat, S., 2009. Aerosol size-dependent below-cloud scavenging by rain and snow in the ECHAM5-HAM, Atmospheric Chemistry and Physics 9, 4653-4675.

4. Gunawardena, J., Egodawatta, P., Ayoko, G.A., Goonetielleke, A., 2012. Role of traffic in atmospheric accumulation of heavy metals and polycyclic aromatic hydrocarbons. Atmospheric Environment 54, 502-510.

5. Gunawardena, J., Egodawatta, P., Ayoko, G.A., Goonetilleke, A., 2013. Atmospheric deposition as a source of heavy metals in urban stormwater. Atmospheric Environment 68, 235–242.

6. Guo, J., Kang, S., Huang, J., Zhang, Q., Tripathee, L., Sillanpää, M, 2015. Seasonal variations of trace elements in precipitation at the largest city in Tibet, Lhasa. Atmospheric Research 153, 87-97.

7. Khan, M.F., Latif, M.T., Saw, W.H., Amil, N., Nadzir, M.S.M., Sahani, M., Tahir, N.M., Chung, J.X., 2016. Fine particulate matter in the tropical environment: monsoonal effects, source apportionment, and health risk assessment. Atmospheric Chemistry and Physics 16, 597-617.

8. Kemp, K., 2002. Trends and sources for heavy metals in urban atmosphere. Nuclear Instrumental Methods in Physics Research B: Beam Interactions with Material and Atoms 189, 227-232.

9. Liu, X., Wai K-M., Wang Y., Zhou J., Li P., Guo J., Xu P., Wang W., 2012. evaluation of trace elements contamination in cloud/fog water at an elevated, mountain site in Northern China. Chemosphere 88, 531-541.

10. Lynam, M.M., Dvonch, J.T., Hall, N.L., Morishita, M., Barres, J.A., 2013. Spatial patterns in wet and dry deposition of atmospheric mercury and trace elements in central Illinois, USA. Environmental Science and Pollution Research 6, 4032–4043

11. Lynam, M.M., Dvonch, J.T., Barres, J.A., Morishita, M., Legge, A., Percy, K., 2015. Oli sands development and its impact on atmospheric wet deposition of air pollutants to the Athabasca Oil Sands Region, Alberta, Canada. Environmental Pollution 206, 469-478.

12. Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emission of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Review 9, 269-298.

13. Pan, Y.P., Wang, Y.S., 2015. Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. Atmospheric Chemistry and Physics 15, 951-972.

14. Montoya-Mayor, A., Fernandez-Espinosa, A.J., Seijo-Delgado, I., Ternero-Rodriguez, M., 2013. Determination of soluble-trace metals and metalloids in rainwater and atmospheric deposition fluxes: A 2-year survey and assessment. Chemosphere 92, 882–891.

15. Morselli, L., Olivieri, P., Brusori, B., Passarini, F., 2003. Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy. Environmental Pollution 124, 457-469.

16. Majestic, B.J., Schauer, J.J., Shafer, M.M., 2007. Application of synchrotron radiation for measurement of iron red-ox speciation in atmospherically processed aerosols. Atmospheric Chemistry and Physics 7, 2475-2487.

17. Shi, G., Chen, Z., Teng, J., Li, Y., 2015. Spatio-temporal variation of total mercury in precipitation in the largest industrial base in China: impacts of meteorological factors and anthropogenic activities, Tellus B: Chemical and Physical Meteorology 67:1, 25660

18. Siudek, P., Frankowski, M., Siepak, J., 2015. Trace element distribution in the snow cover from an urban area in central Poland. Environmental Monitoring and Assessment 187, 225-240.

19. Siudek, P., Kurzyca, I., Siepak, J., 2016a. Atmospheric deposition of mercury in central Poland: Sources and seasonal trends. Atmospheric Research 15, 14-22.

20. Siudek, P., Frankowski, M., Siepak, J., 2016b. Atmospheric particulate mercury at the urban and forest sites in central Poland. Environmental Science and Pollution Research 3, 2341-2352.

21. Walna, B., 2015. Human impact on atmospheric precipitation in a protected area in western Poland. Results of long-term observations: Concentrations, deposition and trends. Atmospheric Pollution Research 6, 778-787.

22. Wang, Y.M., Wang, D.Y., Meng, B., Peng, Y.L., Zhao, L., Zhu, J.S., 2012. Spatial and temporal distributions of total and methyl mercury in precipitation in core urban areas, Chongqing, China. Atmospheric Chemistry and Physics 12, 9417-9426.

23. Weerasundara, L., Amarasekara, R.W.K., Magana-Arachchi, D.N., Ziyath, Abdul, M., Karunaratne, D.G.G.P., Goonetilleke, A., Vithanage, M., 2017. Microorganisms and heavy metals associated with atmospheric deposition in a congested urban environment of a developing country: Sri Lanka. Total Science of the Total Environment, doi.org/10.1016/j.scitotenv.2017.01.121.

Highlights
1. Bulk deposition samples were analyzed for As, Zn, Ni, Pb, Cu, Cr and Cd in central Poland
2. The seasonal variability in trace elements deposition was evident
3. Zn and Cu were the most abundant elements in rainwater
4. Different factors influence TEs concentration levels in rainwater