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CHEMICAL CHARACTERIZATION OF WET DEPOSITIONS IN URBAN AND RURAL AREA

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Abstract

The aim of this study was to determine the chemical composition of wet depositions in two locations from urban and rural area near Bucharest from January to May 2017. For all the samples, pH, conductivity, anions, cations and heavy metals were determined. For anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Ca^{2+}, K^+, Mg^{2+}, Na^{2+}) determination an ion chromatographic method was used. Heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) were determined using AAS with flame and graphite chamber. Results showed the presence of the interested compounds in wet depositions samples with SO_4^{2-} and Ca^{2+} as the dominant anion and cation. Heavy metals concentration followed the trend: Zn > Mn > Cu > Pb > Ni > Cr > Co. Analysing the results obtained the potential sources of ambient air pollution were also suggested.

Keywords: *atmospheric deposition, heavy metals, wet depositions*

Introduction

According to EU Directive (Directive 2004/107/EC), transposed in our country through Law 104/2011, the atmospheric deposition (total or bulk deposition) are referred as being the total mass of pollutants which is transferred from the atmosphere to different surfaces (e.g. soil, vegetation, water, buildings, etc.) in a given area within a given period of time. Pollutants are removed from atmosphere either by precipitation (rain, snow, graupel and hail) in the form of wet deposition either as a result of complex atmospheric processes (turbulent diffusion, sedimentation, inertial forces, electrical migration) known as dry deposition. (Amodio et al. 2014). The characterization of the chemical composition of atmospheric deposits is relevant for the assessment of ambient air quality, providing information on the nature of atmospheric pollutants (natural or anthropic), regional and long-distance transport and impact on ecosystems. Wet deposition can include a wide variety of natural and anthropogenic pollutants, including inorganic elements and compounds (e.g., cations, anions, mercury and other metals) and also organic compounds (e.g., pesticides and herbicides). Different techniques can be used to determine these elements (Petrescu et al. 2016, Vasile et al. 2017, Tudorache et al. 2017, Vasile et al. 2016, Marin et al. 2017, Calinescu et al. 2016). There are countless studies around the world on the composition of wet atmospheric depositions (Deboudt et al. 2004, Agnieszka & Borowski 2015, Xing et al. 2017, Tiwari et al. 2016).

Acid rain is defined to have a pH of less than 5.61. Decreasing of pH values in rainwater is the result of major inorganic acids such as: sulfuric, nitric and organic acids, including carboxylic acids, carbonic acids, acetic acid, formic acid, etc.; resulting from homogeneous and heterogeneous complex reactions in the atmosphere

(Sillapapiromsuk & Chantara 2010). This shows that the wind-carried dust and soil play important roles in the chemistry of wet deposition.
The present study aimed to determine the chemical composition of wet depositions in two locations from urban and rural area near Bucharest from January to May 2017. For all the samples, pH, electrical conductivity, anions, cations and heavy metals were determined. For anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Ca^{2+}, K^+, Mg^{2+}, Na^{2+}) an ion chromatographic method was used. Heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) were determined using AAS with flame and graphite chamber.

Experimental

Sampling sites and sample collection

The wet deposition samples were collected for a period of five months from January to May 2017 from two sites as indicated in Fig. 1.

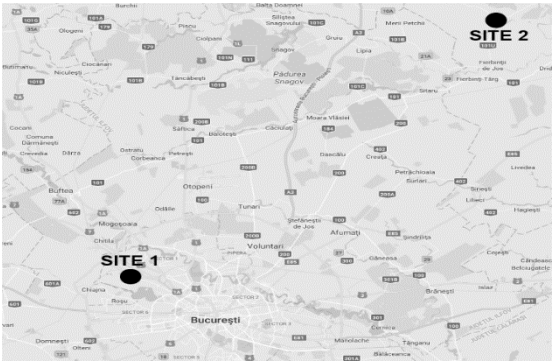

Figure 1. The sampling sites used in wet deposition, were: Site 1- Giulești (44°28'22.5"N 26°00'41.5"E) and Site 2 – Maia (44°44'14"N 26°23'58"E)

The first site, Giulesti (44°28'22.5"N 26°00'41.5"E), is located on the outskirts of Bucharest; a landfill is situated at approximate 2,25 km from the site, in Rudeni, Chiajna witch could represent a potential source of pollution. In general, the area is characterized by small constructions (1 or 2 floors), low traffic and little industry.
The second site, Maia (44°44'14"N 26°23'58"E), is a commune located in Ialomița County, Romania. The main activity carried out in this area is predominantly agricultural.
Both areas are located on the south-east of Romania, with an excessive continental climate, where there is an influence from the air masses from east-continental, west-oceanic and south-mediterranean. This type of climate is characterized by pronounced contrasts from winter to summer, with high temperature differences (above 50°C). The average temperatures are between 10 and 11°C, the warmest month being July (above 30°C) and the coldest being January (-3°C). In winter, the dominate winds come from North and North-East. The precipitations have a continental character, with differences from year to year, the average quantity being 400 – 600 mm/year. For wet atmospheric deposition sampling we used bulk collector, exposed only during precipitation events in order to avoid the collection of dry atmospheric deposits. The methodology for sampling and analysis of the chemical composition of wet

atmospheric depositions was in line with the requirements of the Romanian standard SR EN 15841:2010 and are harmonized with the guidelines from EMEP (EMEP 1996) and WMO/GAW (WMO 2004). The type of collector used is shown in Fig. 2.

Figure 2. Sample collector

Wet depositions were sampled in open areas with no trees or buildings; and, in order to avoid contamination of ground samples during rain episodes, the collector height was at least 1.5 m above the ground. Field blank samples were also determined.

Chemical analysis

After sampling, the samples were labelled and transported to INCD ECOIND Air Pollution Control Laboratory to determine their chemical composition. pH and specific conductivity were immediately determined by using the Seven_Excellence multimeter, Mettler Toledo, equipped with the electrode In Lab^{TM}Expert Pro-ISM and In Lab^{TM} 741-ISM, Seven Compact^{TM} conductivity Sensor. The samples were filtered with 0.45 μm acetate cellulose membranes and stored at 4°C for the determination of anions, cations and heavy metals. For the determination of major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, K^+, Mg^{2+} and Na^+) we used an ion chromatography system model Dionex ICS-5000+ Integrade Reagent Free, equipped with a conductivity detector and Anion Self-Regenerating Suppresor (Dionex AERS 5000 2mm). For anion separation, we used IonPac AS 18 analytical column with electrolytically regenerated suppressor model Dionex AERS 500 2 mm and 20mM potassium hydroxide for elution; IonPac-CS12A column with electrolytically regenerated suppressor model Dionex CERS 500 2 mm and 10mM methyl sulfonic acid for elution were used for determination of cations. Heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) in wet precipitation samples and digested solutions were determined by an atomic absorption spectrophotometer (Varian 280FS equipped with GTA 120) according to the standard SR EN 15841:2010. National and international legislation does not provide limits on wet deposition quality.

Results and Discussion

Relationship between pH and precipitation amount and relationship between conductivity and precipitation amount are shown in Fig. 3 and 4.

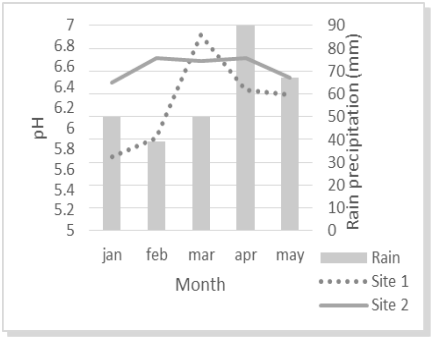

Figure 3. Variation of monthly precipitation amounts and pH mean value

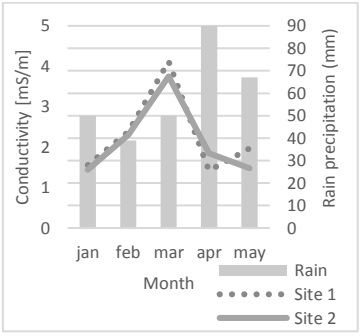

Figure 4. Variation of monthly precipitation amounts and conductivity mean value

For site 1 the mean value of the pH was 6,24 (min. pH=4,6 max. pH =7,02) and for site 2 the mean pH was 6.59 (min. pH =5,86 max. pH =7,50). The samples with pH values above 6.0 may suggest various inputs of alkaline species into precipitation (Sillapapiromsuk & Chantara 2010). Specific conductivity values varied between 1,42 and 4,12 mS/m for site 1 and were situated between 1.44-3,75 mS/m for site 2. The mean concentrations of major ions (Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^{2+}) are shown in Fig. 5 for site 1 and Fig. 6 for site 2.

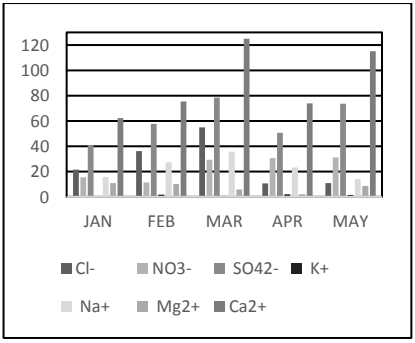

Figure 5. The monthly concentrations of ions in wet deposition samples - Site 1

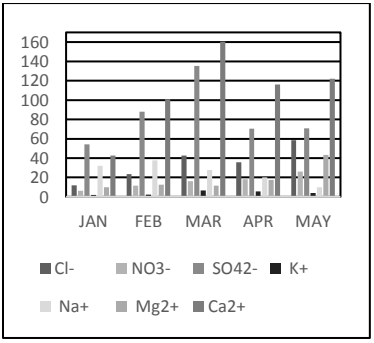

Figure 6. The monthly concentrations of ions in wet deposition samples - Site 2

The highest average fluxes found for the ions in site 1 were: $Ca^{2+} > SO_4^{2-} > Cl^- > >NO_3^- > Na^{2+} > Mg^{2+} > K^+$, and the ions in site 2 were in the order: $Ca^{2+} > SO_4^{2-} > Cl^- > Na^{2+} > Mg^{2+} > NO_3^- > K^+$.

The mean concentrations of heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) are shown in Fig. 7 for site 1 and Fig. 8 for site 2.

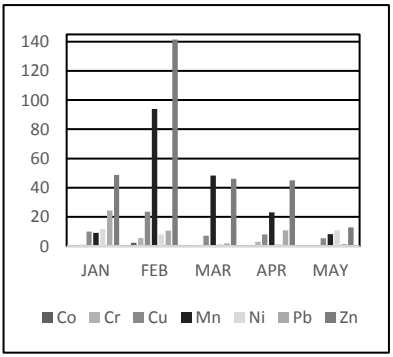

Figure 7. The monthly concentrations of heavy metals in wet deposition - Site 1

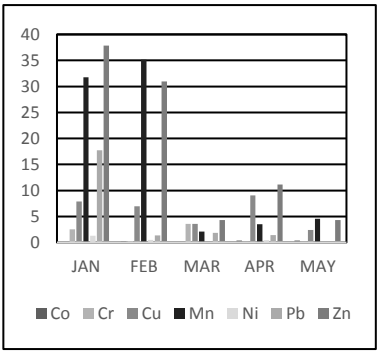

Figure 8. The monthly concentrations of heavy metals in wet deposition - Site 2

The highest average fluxes found for the ions in site 1 were in the order: Zn > Mn > Cu > Pb > Ni > Cr > Co.
The highest average fluxes found for the ions in site 2 were in the order: Zn > Mn > Cu > Pb >Cr > Ni > Co.

Statistical Analysis
In order to determine the associations among ions and heavy metals in wet deposition as well as the possible sources of pollutants, correlations are calculated and listed in Table 1 and Table 2 for site 1 and Table 3 and Table 4 for site 2. Spearman correlation coefficients (r) is a useful technique to characterize relationships among the ions present in wet deposition (Kanellopoulou 2001, Arsene et al. 2007).

Table 1. Spearman correlation coefficients between ions for site 1

Ion	K^+	Na^{2+}	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
K^+	1.000						
Na^{2+}	0.100	1.000					
Mg^{2+}	-0.600	-0.300	1.000				
Ca^{2+}	0.000	0.400	-.400	1.000			
Cl^-	-0.500	**0.700**	0.300	0.500	1.000		
NO_3^-	0.200	-0.500	-0.600	0.300	-0.600	1.000	
SO_4^{2-}	000	.400	-.400	**1,000**	0.500	0.300	1.000

All values in μeq/L
A correlation was seen between SO_4^{2-} and Ca^{2+} (r=1.000) indicating they originated from similar sources. Other relatively good correlations were observed between Cl^- and Na^{2+} with correlation values of r=0.70 (marine sources).

Table 2. Spearman correlation coefficients between heavy metals for site 1

Ion	Co	Cr	Cu	Mn	Ni	Pb	Zn
Co	1.000						
Cr	0.100	1.000					
Cu	-0.600	-0.300	1.000				
Mn	0.000	0.400	-0.400	1.000			
Ni	-0.500	**0.700**	0.300	0.500	1.000		
Pb	0.200	-0.500	-0.600	0.300	-0.600	1.000	
Zn	000	0.400	-0.400	**1,000**	0.500	0.300	1.000

All values in μg/L

A correlation was seen between Zn and Mn (r=1.000), Ni and Cr (r=0,700), indicating they originated from similar sources.

Table 3. Spearman correlation coefficients between ions for site 2

Ion	K^+	Na^{2+}	Mn^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
K^+	1.000						
Na^{2+}	-0.500	1.000					
Mn^{2+}	-0.300	-0.700	1.000				
Ca^{2+}	**0.900**	-0.600	0.400	1.000			
Cl^-	**0.700**	-0.800	**0.700**	**0.900**	1.000		
NO_3^-	0.600	-0.900	**0.900**	**0.700**	**0.900**	1.000	
SO_4^{2-}	0.600	0.100	0.100	**0.700**	**0.500**	0.200	1.000

All values in μeq/L

A correlation was seen between SO_4^2 and Ca^{2+} (r=0.70) indicating they originated from similar sources. Similar, a strong correlation was seen between Ca^{2+} and K^+ (r = 0.90), suggesting the common source of these ions was a natural source (e.g. crustal origin). Other relatively good correlations were observed between Cl^- and Na^{2+}, between NO_3^- and Mg^{2+}, between NO_3^- and Ca^{2+}-, and between SO_4^{2-} and Ca^{2+}, with correlation values of r=0.80, r =0.90 and r =0.70.

Table 4. Spearman correlation coefficients (r) between heavy metals for site 2

Ion	Co	Cr	Cu	Mn	Ni	Pb	Zn
Co	1.000						
Cr	-0.872	1.000					
Cu	-0.205	-0.300	1.000				
Mn	0.051	-0.100	0.100	1.000			
Ni	-0.395	0.051	**0.667**	**0.718**	1.000		
Pb	-0.872	0.600	0.500	-0.200	0.462	1.000	
Zn	-0.205	-0.100	0.600	**0.800**	**0.975**	0.300	1.000

All values in μeq/L

A correlation was seen between Zn and Mn (r = 0,80), Zn and Ni (r = 0,975), Ni and Cu (r = 0,667), Ni and Mn (r = 0,718) indicating they originated from similar sources.

Conclusions

During the winter months, the concentrations of SO_4^{2-} were higher in the rural area due to the use of coal as a source of heating for the living quarters. There were no acid rain phenomena due to the relatively high cation content (almost double to the urban area), pH samples in the rural area being much more alkaline than the urban area. The

application of Spearman correlation coefficients analysis suggested that Ca^{2+}+ is likely to be the major neutralizing agent for SO_4^{2-}.
The samples with pH values above 6.0 may suggest various inputs of alkaline species into wet deposition. Zn and Mn were the dominant heavy metals found in the wet deposition; these may have sources in the soil resuspension and the building's rooftops in both areas.
The results presented in this paper are preliminary result in a study we intend to continue for a longer period.

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