Wet deposition analysis using UV-VIS spectrometry in Maramures county (Romania)

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Abstract. The paper Wet Deposition Analysis Using UV-VIS Spectrometry in Maramures County presents the experimental results obtained for wet deposition using Perkin Elmer Lamba 25 UV-VIS spectrometer. Four parameters were analysed: chloride, sulphate, nitrate anions and ammonium cation. The samples were collected from four location of Maramures County (Baia Mare, Sighet, Viseu and Borsa) during May-September 2014. The analysis of these parameters aims to investigate the air quality in Maramures County and in the Romanian-Ukraine transboundary area. The level of the wet deposition expressed in liter/square meter (L/mp) was different in the studied areas. The highest average level of wet deposition was in Borsa (52.03±23.64) followed by Baia Mare (43.95±23.33). The values of the wet deposition pH, considering all the sampling locations, ranged between 4.813 and 7.45. In the rain samples collected in Baia Mare area were found the highest average values of the concentrations of SO_4^{2-} (1.569±0.693) and NO_3^- (1.603±0.917) and also of ammonium cation (0.676±0.193) due to industrial influence while in Sighetu Marmatiei was found the highest average value for Cl^- (1.187±1.072).
Key Words: wet deposition, precipitation, air quality, spectrometry.

Introduction. Improving air quality is a great concern for the entire European community. The need to reduce pollution to levels that minimize adverse effects on human health, paying special attention to sensitive populations and the environment as a whole, involve the monitoring of air quality, including wet depositions.

Air quality is defined by the quality of falling dust and rainfall (wet and dry depositions). Nonferous metallurgical plants operating in Baia Mare area since the mid-19th century have caused acid rain for long periods, with serious effects on soil, vegetation, wildlife and human health and also falling dust with a huge content of heavy metals.

Deposition can include a wide variety of natural and anthropogenic pollutants, including inorganic elements and compounds (e.g., nitrogen, sulfur, basic cations, mercury and other metals) and organic compounds (e.g., pesticides and herbicides). Once deposited, pollutants can have a variety of ecosystem effects. Nitrogen and sulfur compounds, for example, can result in acidification of freshwaters, loss of aquatic species, eutrophication of estuarine and near-coastal waterways, soil nutrient and base cation leaching, and vegetation changes.

Environmental Protection Agency Maramures as applicant and the Technical University of Cluj Napoca - Centre of North University of Baia Mare as partner, is developing a project programme named Clean Air Management in the Romania-Ukraine Transboundary Area – (CLAMROUA). The goal of this article is to present the main indicators of wet depositions in four sampling locations in Maramures County.

Material and Method

Sampling location. The sampling locations were chosen considering the alignement Sighet-Viseu-Borsa in the border region and also Baia Mare as the most important city in the county and an important industrial centre. Sighetu Marmatiei is located near the Romanian-Ukrainian border, being an industrial wood processing center. Borsa is considered to be a reference area, rich in forests untouched by anthropic pollution.

The representative sampling urban locations are: Baia Mare (Colonia Topitorilor street, pressure node SGA), Sighetu Marmatiei (town water treatment), Viseu (private

location), Borsa (touristic complex). The locations were chosen according to air quality monitoring methodology (Figure 1).

Figure 1. Sampling network of wet deposition (the urban centres are marked with red circles) (http://pe-harta.ro/maramures/).

The monitoring sampling program was performed from May 2014 to September 2014, twice a month. The Monitoring program is performed using equipments and working protocols according to sampling guides.

Automatic precipitation samplers and analyser Eigenbrodt – Germany, RS 1 model are placed in Sighet, Viseu and Borsa. The device is equipped with a sensitive rain sensor, which ensures the opening of the collecting device it starts raining. When it stops raining, the collection funnel of the device is closed. In Baia Mare an automatic collector NSA 181/KE, type is placed.

Sampling program. Samples were collected over a period of 5 months, from May 2014 to September 2014. The wet and dry deposition collector is located in Sighetu Marmatiei, Viseu and Borsa. The sampes were brought into the laboratory the day they were collected and here the volume of each rain sample was determined. The analyses were performed immediately after the reception of the samples by the laboratory within no more than 1-2 days. The wet deposition samples were analysed using Perkin Elmer Lambda 25 UV-VIS spectrometer and the following indicators were studied: chloride, sulphate, nitrate, ammonium. The pH of the samples was determined by potentiometric methods, using the WTW Inolab 7110 pH meter and the conductivity was measured using a WTW Inolab 740 conductometer.

Analysis of wet deposition indicators. The analysis methods used for the above mentioned indicators comply with the national and international standard (EMEP guide). The main analysed indicators were: pH, conductivity, chlorides, sulphates, ammonium. This indicators were selected according to the particular economical activity of the region such us animal breeding; the urban traffic was also taken into account.

Chlorides in wet depositions were analysed based on the dark red iron thiocyanate complex, in the presence of mercury thiocyanate. The absorbance of complex is measured at 460 nm, and the method can be used in the range of 0.05 to 5 mg/L Cl^- (EMEP Guide).

The sulphates were measured by turbidimetric method, when sulphate ions were converted into a barium sulphate suspension under controlled conditions. The resulting turbidity was measured by spectrometer compared to a calibration curve prepared based on standard solution. The range of sulphate concentration is 1-40 mg/L (Method EPA 375.4 Sulfate).

Nitrates were measured by spectrometric method using sulfosalicylic acid, applicable in the range of 0.2-5 mg/L, which can be extended by dilution of the samples (SR EN ISO 7890-3:2000).

Ammonium was measured using spectrometric method based on the formation of yellow oxiamidomercuric iodide complex using Nessler reagent in the range of 0.05-1 mg/L.

Results and Discussion. During May–September 2014, 32 samples of rain water (wet deposition) were collected from the four sampling points and the main chemical indicators (pH, conductivity and the main chemical pollutants: chloride, sulphate and nitrate anions and also ammonium cation) were analysed. The wet deposition levels were measured and recorded for each interval of sampling and location (Figure 2).

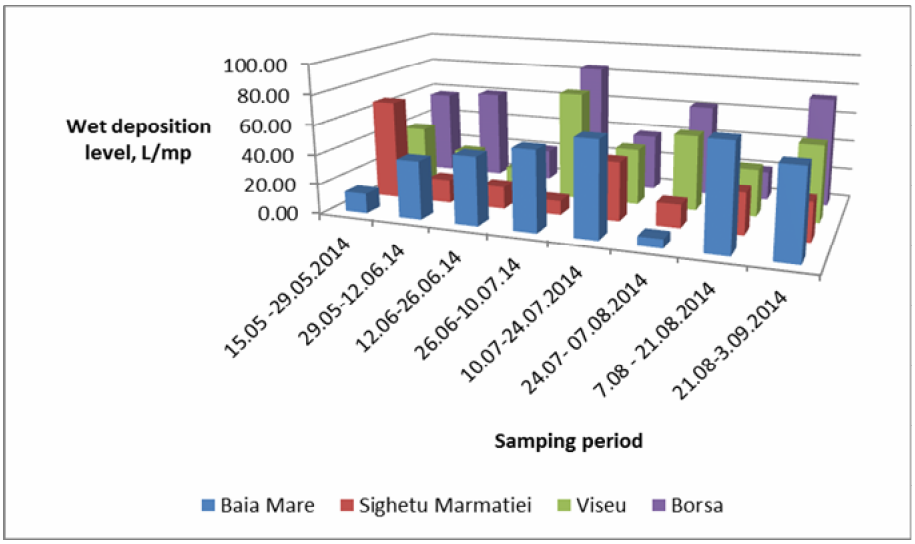

Figure 2. Wet deposition level during May-September in the sampling locations.

The level of the wet deposition expressed in liter/square meter (L/mp) was different in the studied areas and also from one sampling period to another. The highest average level of wet deposition was in Borsa (52.03±23.64) followed by Baia Mare (43.95±23.33), Viseu (41.22±17.48) and Sighetu Marmatiei (27.07±18.73).

pH and conductivity of wet depositions. The average values, the median and standard deviation of the pH and of the conductivity of wet deposition for the 4 studied locations were calculated using Excel application (Table 1).

Table 1

Statistics for pH and conductivity of wet deposition in the sampling locations: Baia Mare (BM), Sighetu Marmatiei (S), Viseu (V) and Borsa (B)

Indicator/ sampling location	*pH*				*Conductivity, µS cm^{-1}*			
	BM	*S*	*V*	*B*	*BM*	*S*	*V*	*B*
Number of sampling	8	8	8	8	8	8	8	8
Average value	5.922	6.578	6.339	6.492	15.013	21.925	11.913	11.675
Median value	6.087	6.610	6.416	6.456	13.25	10.50	10.9	10.0
Standard deviation	0.694	0.567	0.355	0.433	5.623	29.919	4.519	5.673
Minimum	4.813	5.558	5.665	6.061	8.2	8.9	6.9	6.2
Maximum	6.785	7.45	6.765	7.406	23.7	95.4	19.1	24.500

The values of the wet deposition pH, considering all the sampling locations, ranged between 4.813 and 7.45 (Table 1). The pH of wet deposition in a clean atmosphere has a value around 5.6 due to the dissolution of carbon dioxide (Al-Kashman 2009). The most acid value of wet deposition were recorded in Baia Mare area where 25 % of the samples

were in the acid range above 5.6. In the other sampling areas the average values of pH were similar.

The conductivity values of wet deposition are an overall indicator referring to the inorganic pollutant loading degree of wet deposition.

Regarding the conductivity of the wet deposition samples, a relatively narrow range of values was observed (6.2-95.4 µS cm^{-1}). The highest average value of wet deposition conductivity was found in Sighetu Marmatiei (21.925 µS cm^{-1}) whilst the lowest average value was recorded in Borsa (11.675 µS cm^{-1}) close to that found in Viseu (11.913 µS cm^{-1}). In mediterranean zone , a wider range of values of rain samples conductivity was reported: 7.50–439 µS cm^{-1} (Anatolaki & Tsitouridou 2009).

High conductivity values are related to low precipitation quantities for the wet deposition collected from Baia Mare and Viseu. The values of Pearson coefficients between conductivity and precipitation quantitiy were calculated (Table 2). In Borsa, the correlation was positive indicating low level of ionic pollutants in the atmosphere.

Table 2

Pearson coefficient correlation between conductivity and wet deposition quantity (L/mp)

Location	*Baia Mare*	*Sighetu Marmatiei*	*Viseu*	*Borsa*
Pearson coefficient value	-0.902	-0.294	-0.597	0.242

Ionic composition of wet depositions. Primary statistics of data related to the major anions (chloride, sulphate and nitrate) and also of ammonium cation concentrations in the wet depositions was performed using Excel application in each of the 4 studied locations (Tables 3 and 4).

Table 3

Statistics for the chloride and sulphate concentration in wet deposition in Baia Mare (BM), Sighetu Marmatiei (S), Viseu (V) and Borsa (B), (concentrations in mg L^{-1})

Indicator concentration/ sampling location	*Cl^-*				*SO_4^{2-}*			
	BM	*S*	*V*	*B*	*BM*	*S*	*V*	*B*
Number of sampling	8	8	8	8	8	8	8	8
Average value	0.747	1.187	0.625	0.635	1.569	1.086	1.065	0.605
Median value	0.617	0.877	0.596	0.551	1.440	0.897	0.883	0.586
Standard deviation	0.249	1.072	0.441	0.453	0.693	0.803	0.424	0.328
Minimum	0.477	0.392	0.143	0.069	0.897	0.244	0.697	0.049
Maximum	1.224	3.759	1.44	1.594	3.155	2.904	1.888	1.098

In Baia Mare area, the highest concentrations of SO_4^{2-} and NO_3^- anions were found. The ammonium ion also had the highest concentration in the rain samples collected in Baia Mare, three times higher than the value obtained for the sample location in Borsa. This could be explained by the fact that Baia Mare has a population of about 140000 inhabitants, considerably larger as compared to the other towns and also the city traffic is very heavy. These features are connected to the higher concentrations of nitrates and sulphates. In the neighbourhood of Baia Mare, there are areas were zootechnics is a main activity, which accounts for the higher concentration of ammonium. On the other hand, as for the Cl^- ion, the highest concentration was found in Sighetu Marmatiei, which is possibly due to the fact that there are high salinity lakes near this town (eg. Ocna Sugatag, Costiui).

Table 4

Statistics for the nitrogen compounds (nitrate and amonium) concentration in wet deposition in Baia Mare (BM), Sighetu Marmatiei (S), Viseu (V) and Borsa (B) (concentrations in mg L^{-1})

Indicator concentration / sampling location	NO_3^-				NH_4^+			
	BM	*S*	*V*	*B*	*BM*	*S*	*V*	*B*
N	8	8	8	8	8	8	8	8
Average value	1.603	0.999	0.876	0.529	0.676	0.439	0.377	0.208
Median value	1.482	1.024	0.866	0.538	0.505	0.251	0.310	0.165
Standard deviation	0.917	0.556	0.538	0.269	0.193	0.523	0.254	0.160
Minimum	0.608	0	0	0	0.44	0.086	0.147	0
Maximum	3.575	1.79	1.863	0.815	0.998	1.685	0.934	0.504

The application of linear Regression Analysis applied to experimental data in order to find a possible dependence of pollutant ions and wet deposition level, showed an exponential dependence in the case of ammonium, in Viseu, and a logarithmic one for nitrate in the same location (Figures 3 and 4).

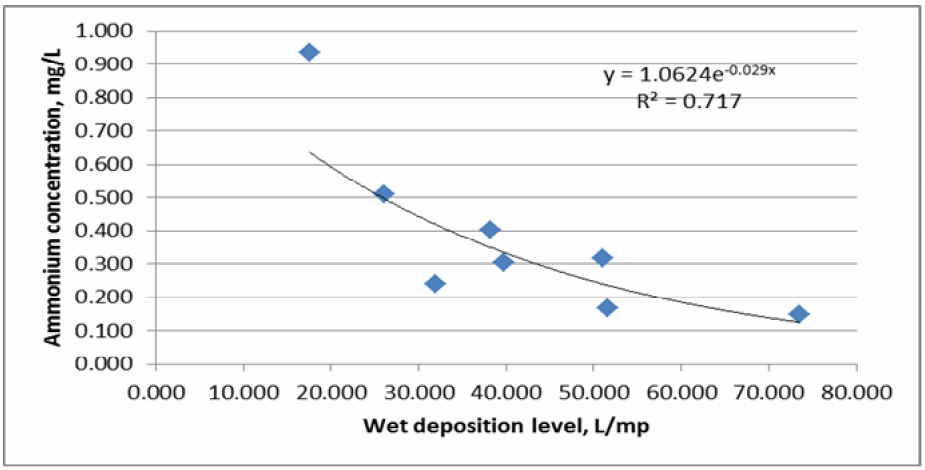

Figure 3. The relationship of ammonium concentration and wet deposition level in Viseu.

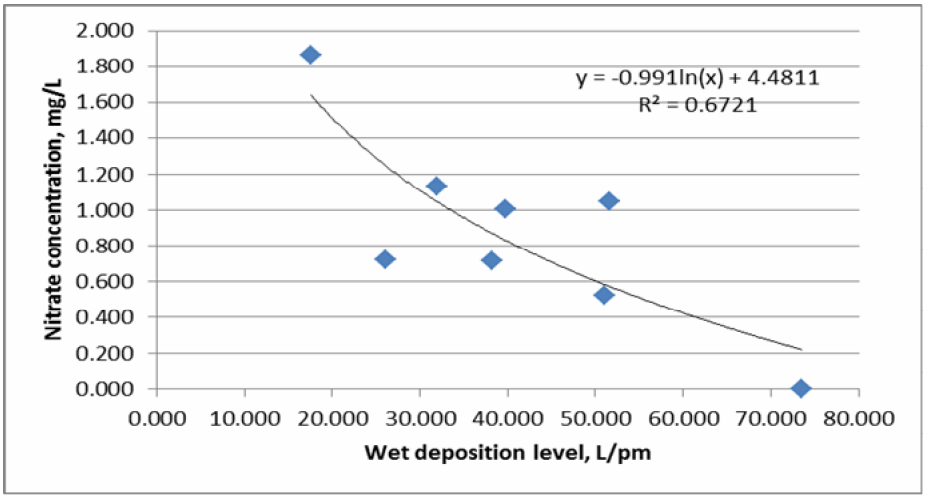

Figure 4. The relationship of nitrate concentration and wet deposition level in Viseu.

Conclusions. The level of air pollution investigated by measuring the wet deposition differs in the studied locations and also from one period of sampling to another. In Baia Mare, the highest concentration of pollutant ions was registered -nitrate, sulphate and ammonium - and also the highest frequency of an acid pH was found.

The highest pollutant concentrations were recorded in the periods with the lowest rain quantities in Baia Mare, Viseu and Sighetu Marmatiei areas. As an exception to this behaviour, Borsa stands out from the rest with its low concentrations of pollutants.

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References

Anatolaki C., Tsitouridou R., 2009 Relationship between acidity and ionic composition of wet precipitation. A two years study at an urban site, Thessaloniki, Greece. Atmospheric Research 92(1):100–113.

Al-Khashman O. A., 2009 Chemical characteristics of rainwater collected at a western site of Jordan. Atmospheric Research 91(1):53-61.

*** SR EN ISO 7890-3:2000 Water quality. Determination of nitrate content, part 3: Spectrometric method with sulfosalicilic acid [in Romanian].

*** Method EPA 375.4 Sulfate (Turbidimetric). Available at: http://www.caslab.com/EPA-Methods/PDF/EPA-Method-3754.pdf.

*** EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe. Available at: http://www.itm.su.se/reflabmatningar/dokument/EMEP_Manual.pdf.

*** http://pe-harta.ro/maramures/.

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