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Atmospheric Deposition of Copper and Zinc in Maramures County (Romania)

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Abstract: The need to reduce pollution to levels that minimize adverse effects on human health involve the monitoring of air quality, including dry depositions and their metal content. The analysis of these parameters aims to investigate the air quality in Maramures County (with nonferrous mining activities) and in the Romanian - Ukraine transboundary area. The paper presents the experimental results obtained for dry atmospheric deposition of copper and zinc using flame atomic absorption spectrometry (FAAS). The samples were collected from four location/cities of Maramures County (Baia Mare, Sighetu Marmatiei, Viseu de Sus and Borsa) during May-October 2014. The highest average values of copper concentration in the dry depositions were found in Baia Mare (199.88 μg/g), that is the most important industrial centre in Maramures County, followed by Borsa (111.49 μg/g), that used to be a nonferrous mining centre. In Viseu de Sus and Sighetu Marmatiei the average concentrations of copper in the dry depositions were lower: 75.63 μg/g and 64.26 μg/g, respectively. Zn average concentrations in dry depositions were 6.4-12 times higher than Cu concentrations. In Viseu de Sus and Borsa relative high values of Pearson correlation coefficients between the logarithm of Cu and Zn content in the dry deposition were found (0.702 and 0.737, respectively) estimating that both pollutants in the ambient air have the same sources, probably the re-suspension of the dust from the tailing ponds. This study is implemented within the frame of ENPI Cross-border Cooperation Programme Hungary-Slovakia-Romania-Ukraine 2007-2013, in the project *Clean Air Management in the Romania-Ukraine Transboundary Area – (CLAMROUA),* financed by the European Union.

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Introduction

The atmosphere is a large and unpredictable vector for the pollutants propagation, with both direct and indirect impact on people and also on all the environmental components (air, water and soil)[1-3]. Consequently, the prevention of the atmospheric pollution must be a local, national and international issue of major interest.

When evaluating the pollution of the environment with heavy metals, discussion on the metals in dust deposits have to be included. Dust is a main carrier of heavy metals in the atmosphere and a source of their presence in the soil and surface water. Dry depositions are generally influenced by the climate conditions and also by the dust and air pollution sources.

Maramures County, located in the north-western part of Romania is facing an historical pollution with heavy metals, due to the non-ferrous mining and metallurgical activities that have polluted the environment for many years.

Over the last 15 years, atmospheric emissions of dust in Maramures County significantly decreased. According to the Maramures Environmental Protection Agency reports[4], total emissions of heavy metals in 2001, 2008 and 2013 were: 25.0; 2.13 and 2.05 tons. This trend is a result of the closure of many industrial facilities or the decrease of their production, as well as the implementation in industry and transport activities of a lot of measures to protect the environment.

The European Directive on ambient air quality and cleaner air for Europe (2008/50/EC) addresses particular attention to sensitive populations and the environment as a whole and is calling to improve the monitoring

and assessment of air quality including the deposition of pollutants and to provide information to the public.

Exposure to individual metallic elements can affect humans in various ways. Prolonged exposure to Zn can cause arteriosclerosis, hypertension and heart disease, while copper can cause nasal septum perforation, pulmonary granuloma, pulmonary interstitial fibrosis and lung cancer[5-7].

This study is developed within a cross-border cooperation project dedicated to improve the air quality in Romania-Ukraine transboundary area. Several sampling devices and laboratory equipment were purchased with European funds in order to increase the quality of the data as public information. The project is co-financed by the Hungary-Slovakia-Romania-Ukraine ENPI Cross-border Cooperation Programme 2007-2013. The aim of the project is to develop and intensify the cooperation in environmental protection issues between Ivano-Frankivsk Region in Ukraine and Maramures County in Romania.

The present paper deals with the investigation of dry deposition levels in some urban sites located in Maramures County during May-October 2014. The content of Cu and Zn in dry depositions was determined and the variability of the data and possible relationship between the variables (Cu and Zn content in the dry deposition) in the investigated area were studied.

Experimental

Maramures County is located in the north-western part of Romania at the border with Ukraine. The non-ferrous mining and metallurgical industries in our county have polluted the environment for many of years by the emission of gases (especially sulphur dioxide) and dust, containing heavy metals as copper and zinc[8-13]. The mines were closed on January 2007, but their waste facilities (tailing ponds and dams) still have a negative

impact on the environment. No closure or remediation works were done on these facilities.

Baia Mare used to be a mining and metallurgical centre and now it is still an important industrial centre in the county. The emission of gases (especially sulphur dioxide) and dust, containing heavy metals as copper and zinc[8-13] have severely polluted the environment. The copper smelter was closed in 2008 and the lead smelter used to work until 2012. As reported by Maramures Environmental Protection Agency, the air quality in Baia Mare have been significantly improving since 2012, but the soil continues to have high heavy metals contents.

Along the border of Maramures County with Ukraine, 3 collectors for falling dust were installed in the following cities: Sighetu Marmatiei, Viseu de Sus and Borsa and one collector was installed in Baia Mare, the capital city of Maramures County (marked with red circles in Figure 1). The dry depositions were monitored during May-October 2014 and the samples were collected every two weeks.

Figure 1. The studied area and sampling locations.

Borsa is a former big mining centre for non-ferrous ores, but the location of the collector is far enough from all polluting activities and

therefore it was taken as a reference sampling location. Sighetu Marmatiei and Viseu de Sus are rather known for their wood processing plants.

Figure 2. NILU SF1 Particle fallout collector.

Specific site selection criteria were followed according to the national and European recommendations: (i) locations should be generally representative of a larger area, with minimal impact of local sources; (ii) minimum 100 m from major line sources; (iii) all objects or structures have to be located at a distance from the sampling equipment of at least twice their height.

NILU SF1 Particle fallout collectors were used for collecting dry atmospheric fallout. They were fixed on steel stands that allow to adjust them to the prescribed height above ground (1.5 m), as recommended by the Romania standard for dust fall measurement (STAS 10195-75)[14].

In Borsa the collector for falling dust was installed in a forestry area with minimum impact of social and economic activities and hence it was considered as background when discussing about the amount of the dry deposition.

After collection, the dry deposition (falling dust) samples were returned to the Laboratory of Maramures Environmental Protection Agency,

weighed and prepared to be analyzed through F-AAS in order to determine heavy metals (Cu, Zn) concentrations.

The dry deposition samples were collected together with the rain water. After the water was evaporated, the dry deposit was weighed and mineralized with acidic mixture of nitric, sulphuric and perchloric acids (3:1:1). 10 mL of nitric acid 2 N were added to the mineralized sample and transferred with distilled water to volumetric flasks of 100 mL. Concentrations of Cu and Zn were measured using AAS (Perkin Elmer, AAnalyst 700), with acetylene-air flame within the range of standard solution concentrations from 0.1 to 2.0 μg/mL. When concentrations of metals in the sample solution exceeded this range, the solutions were diluted accordingly.

In order to ensure that the results of falling dust measurements were not affected by any interference, all polyethylene bottles and glassware used in chemical analyses were treated with nitric acid 20% before being rinsed several times with ultra-pure water.

For quality control, reagent blanks, replicates (N=3), Shewhart control chart and check solutions (after 10 readings) were used in the F-AAS readings to detect contamination and to assess the precision and bias of the analytical program. The recovery rates for metals in the check solutions were between 95 and 105%.

Results and Discussion

Dry deposition

The amounts of the dry deposition during the studied period are presented in Figure 3.

The dry deposition for the two weeks of exposure were expressed in g/(m^2·month) by dividing the mass of the dry deposition collected during the exposure days (14 days) and multiplying the obtained value by 30.

The maximum admissible value for the dry deposition collected during a month is 17 g/(m^2·month) in accordance with the Romanian legislation (STAS 12574-87)[15]. The values during our monitoring campaign were below the maximum admissible value in all the locations.

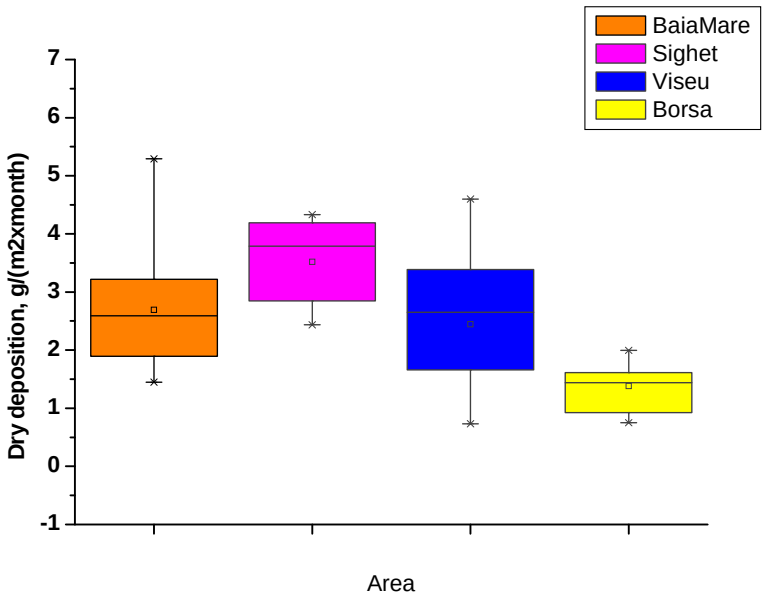

Figure 3. Box plots for dry deposition for the sampling location during May-October 2014 (sampling collection each two weeks). The central rectangle indicates the average values, the horizontal line indicates the median, and the lower and upper ends indicate 25 and 75 percentiles, respectively.

The highest average amounts of the dry depositions were collected in Sighetu Marmatiei: 3.52±0.72 g·m^{-2}·month^{-1}. Sighetu Marmatiei is an industrial centre located in a plane area. The average value for dry deposition in Baia Mare was of 2.69±1.21 g·m^{-2}·month^{-1}, lower than in Sighetu Marmatiei, but showing a higher dispersion quantified by the standard deviation. In Viseu de Sus the average dry deposition was 2.44±1.16 g·m^{-2}·month^{-1}. The lowest amounts of the dry depositions (1.38±0.45 g·m^{-2}·month^{-1}) were collected in Borsa due to the location of the sampling equipment, in a mountain site near a forest. Compared to Borsa as background (control) area, the average values for the other locations are 1.94-2.54 higher due to their past and present industrial activities, traffic

emissions, residential heating (wood and other biomass burning). On some extent, dry deposition could be a cleanliness indicator of any urban centre.

The background value for dry deposition was 100 mg m^{-2} day^{-1} in a residential rural area located in the proximity of an industrial zone, as found by Kara et al.[6] Related to this reference value, the average dry deposition amount in Borsa as background area was lower (46 mg m^{-2} day^{-1}).

Cu and Zn concentrations in dry deposition

The average values of Cu and Zn content in dry deposition for the sampling sites are presented in Table 1 while the box plot diagrams are shown in Figures 4 and 5.

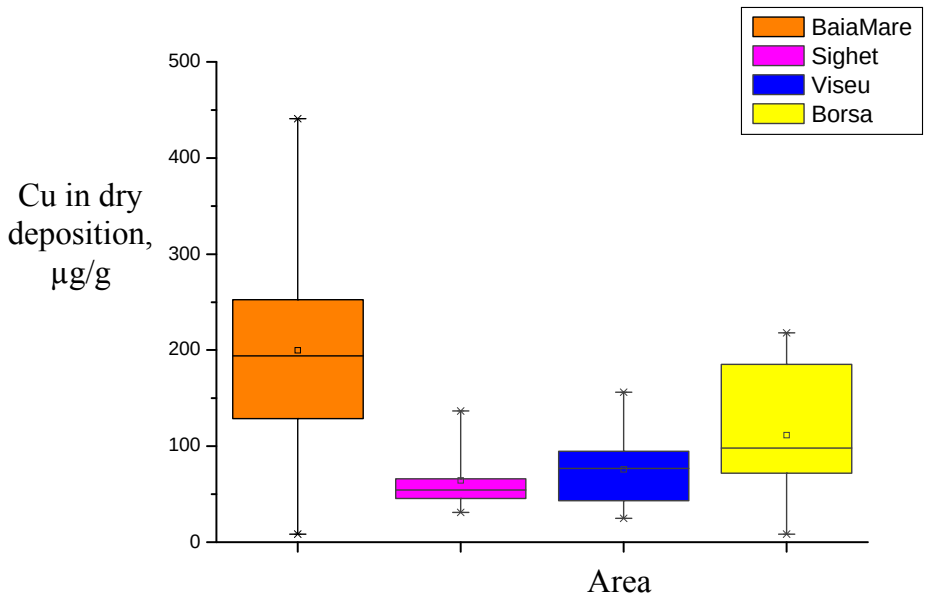

Figure 4. Box plots for Cu concentrations in dry deposition for the sampling sites during May-October 2014.

Table 1. Cu and Zn average concentrations in dry depositions and standard deviations for the studied area.

Area	Cu (µg/g)	Zn (µg/g)
Baia Mare	199.88±115.00	1282.98±686.44
Sighetu Marmatiei	64.27±33.77	655.73±139.64
Viseu de Sus	75.63±38.77	760.37±310.32
Borsa	111.49±66.05	1343.97±974.33

The highest average concentration of Cu in the dry depositions was obtained in Baia Mare (about 200 µg/g) followed by Borsa, Viseu de Sus and Sighetu Marmatiei, while the highest concentration of Zn was found in Borsa (1343.97 µg/g) followed by Baia Mare (1282.98 µg/g), Viseu de Sus and Sighetu Marmatiei.

Borsa used to be a mining centre for non-ferrous ores, and copper in dry deposition have anthropic sources. In Sighetu Marmatiei were found the lowest copper and zinc average concentrations in the collected dry depositions (64.27 and 655.73 µg/g).

The ratio of the average content of Zn and the average content of Cu in dry deposition was 6.42 for Baia Mare while for the other locations it varied between 10.05 and 12.05. This is explained by the historical pollution in Baia Mare where a copper smelter used to work for decades.

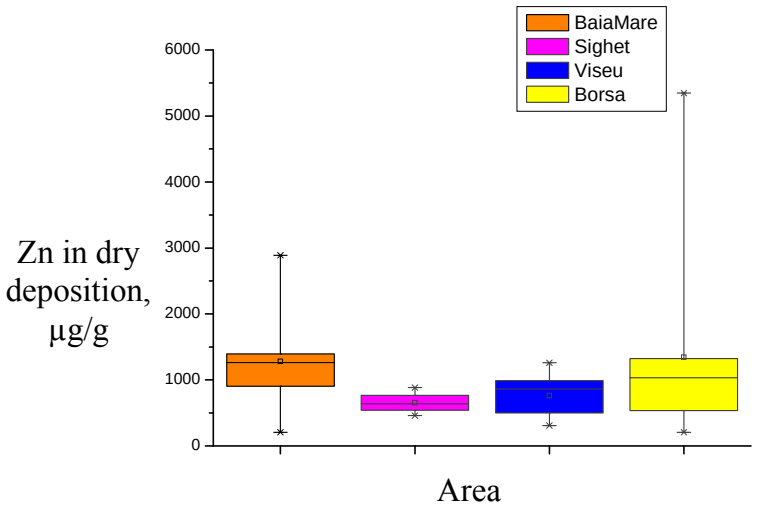

Figure 5. Box plots for Zn concentrations in dry deposition for the sampling location during May-October 2014.

The normality of data was tested by calculating the standardized skewness and standardized kurtosis using Statgraphics programme. The Zn content in dry deposition in Borsa and Baia Mare showed significant deviation from normality. In order to compare the results we calculated the logarithm of Cu and Zn content and we tested the Pearson correlation of the variables as shown in Table 2.

Table 2. Pearson correlation coefficient between the logarithm of Cu and Zn concentrations in dry depositions

Area	Pearson correlation coefficient
Baia Mare	0.042
SighetuMarmatiei	0.370
Viseu de Sus	0.702*
Borsa	0.737*

*significant correlation at P<0.05

P-value that tests the statistical significance of the estimated correlations, was below 0.05 for Cu and Zn content in dry depositions in Viseu and Borsa indicating statistically significant non-zero correlations at the 95.0% confidence level.

The Pearson correlation analysis revealed high correlation between the two metals in Borsa and Viseu de Sus, while in Baia Mare and in Sighetu Marmatiei no significant correlation were found.

The correlation between Cu and Zn in Borsa indicates that both pollutants in the ambient air have the same sources probably due to the re-suspension of the dust from the tailing ponds. The lack of correlation found in Baia Mare is probable due to a complex origin of copper: from mining, copper and lead metallurgy, traffic and other sources.

Conclusions

Dry depositions were collected each two weeks from 4 urban centres in Maramures County (Baia Mare, Sighetu Marmatiei, Viseu de Sus and Borsa) during May-October. The highest average value was obtained in Sighetu Marmatiei followed by Baia Mare, Viseu de Sus and Borsa that was considered as background area.

Cu and Zn concentrations in dry depositions were determined. The highest average value of Cu was found in Baia Mare, that used to be a centre of nonferrous mining and metallurgy, where copper and lead smelters

were working until few years ago. Zn average concentrations in dry depositions were higher than Cu average concentrations, the highest being found in Borsa and Baia Mare. The Pearson correlation analysis revealed significant correlation between the two metals in Borsa and Viseu de Sus, while in Baia Mare and Sighetu Marmatiei no significant correlation was found.

The present paper is part of a complex study on the air quality in Maramures County. Future work will investigate the seasonal variability of dry deposition and its heavy metal content.

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