APPLYING OF MULTIVARIATE ANALYSIS TO STUDY THE CORRELATION OF MERCURY AND OTHER TRACE ELEMENTS DISTRIBUTION IN SOIL FROM A CITY FROM NW ROMANIA

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ABSTRACT

The mercury (Hg) concentrations were evaluated in soils and perennial plants from four districts of Baia Mare city, a historical mining and ore processing center from NW Romania. The results showed that in 24% of the analysed soil samples the mercury concentrations exceeded the guideline value of 1.0 mg kg^{-1}, established by the Romanian Legislation, while the median concentration was 0.70 mg kg^{-1}, bellow the guideline values, but higher than the normal values for soil and the mean or median concentration in soils from other cities all over the world. In the perennial plants, the median concentration was 0.22 mg kg^{-1}, value that exceed the maximum level of Hg (0.10 mg kg^{-1}) established by European Directive 2002/32/EC for animal feed in order to prevent its transfer and further accumulation in the higher levels of food chain. Poor correlations were found between Hg and other elements such as As, Cd, Cu, Pb and Zn known as pollutants resulted from non-ferrous smelting activities, probably due to the different physicochemical properties of Hg that lead to a different dispersion patter compared to other metals emitted by the two smelters.

INTRODUCTION

Mercury is toxic even in very low concentrations and is considered as one of the most dangerous pollutants, being included in the list of priority dangerous substances established by international environmental legislation (Leopold et al., 2010). The Hg contents in soil are generally low, ranging between 0.01 - 0.2 mg kg^{-1}, with a median of 0.05 mg kg^{-1} (Rodrigues et al., 2006). The Hg emission sources can be both natural and anthropogenic. The anthropogenic sources are estimated at approximately 6×10^6 kg year^{-1} and are represented by the production of pure mercury by industrial processes, combustion of fossil fuels, chemical industry, waste incineration and smelting and refining of non-ferrous metals (Han et al., 2006). Non-ferrous metals (Pb, Cu, Au, Ag, Zn) were extracted and processed in Baia Mare region, NW Romania since ancient times, leading to a historical pollution with Pb, Cu, Zn, Cd and As (Senila et al., 2011). The smelting of non-ferrous metals is known as a source of Hg emission, due to the presence of Hg both in minerals and in the coal used in the smelting processes (Chen et al., 2010). However, no data was found in the literature regarding Hg levels in the Baia Mare area.

The aims of this study was to apply the multivariate statistical techniques in order to study the relationships between Hg in soil and plants, and between the contents of Hg, As, Cd, Cu, Pb, Zn and the physicochemical properties of soils (pH, Total Organic Carbon (TOC)).

MATERIALS and METHODS

Site Description and Sampling

The city of Baia Mare is located in Maramures County, (Northwest Romania), 228 m elevation above sea level. Together with the surrounding peri-urban regions, the city totals 235.7 km², of which 31.7 km² are agricultural fields (Levei et al., 2009). The industry developed around the city was based mainly on mining and processing of non-ferrous minerals from the epithermal Pb–Zn(–Cu–Au–Ag) ore deposits. At the end of 19th and beginning of the 20th century in the Eastern part of the city, one Cu and one Pb smelter were operating. In the summer of 2009 a total of 29 surface soil samples and perennial plants (*Agrostis, Agropirum repens, Trifolium repens, Urtica dioica*) grown on these soils were collected from 4 areas of Baia Mare. The locals use the studied plant species to feed the animals in their households. The samples were collected as follows: samples 1-8 from Ferneziu district (FE) located in the North-Eastern part of the city, in the proximity of the Pb smelter; samples 9-18 from Săsar district (SA), located in the Northern part, close to the mining area; samples 19-24 from the residential area in the Southern part of Baia Mare (BM), samples 25-29 from Tautii Magheraus (TM) in North-Western part of Baia Mare located far from all industrial activities (Fig. 1). The coordinates of the sampling points were recorded with a 310 Magellan GPS.
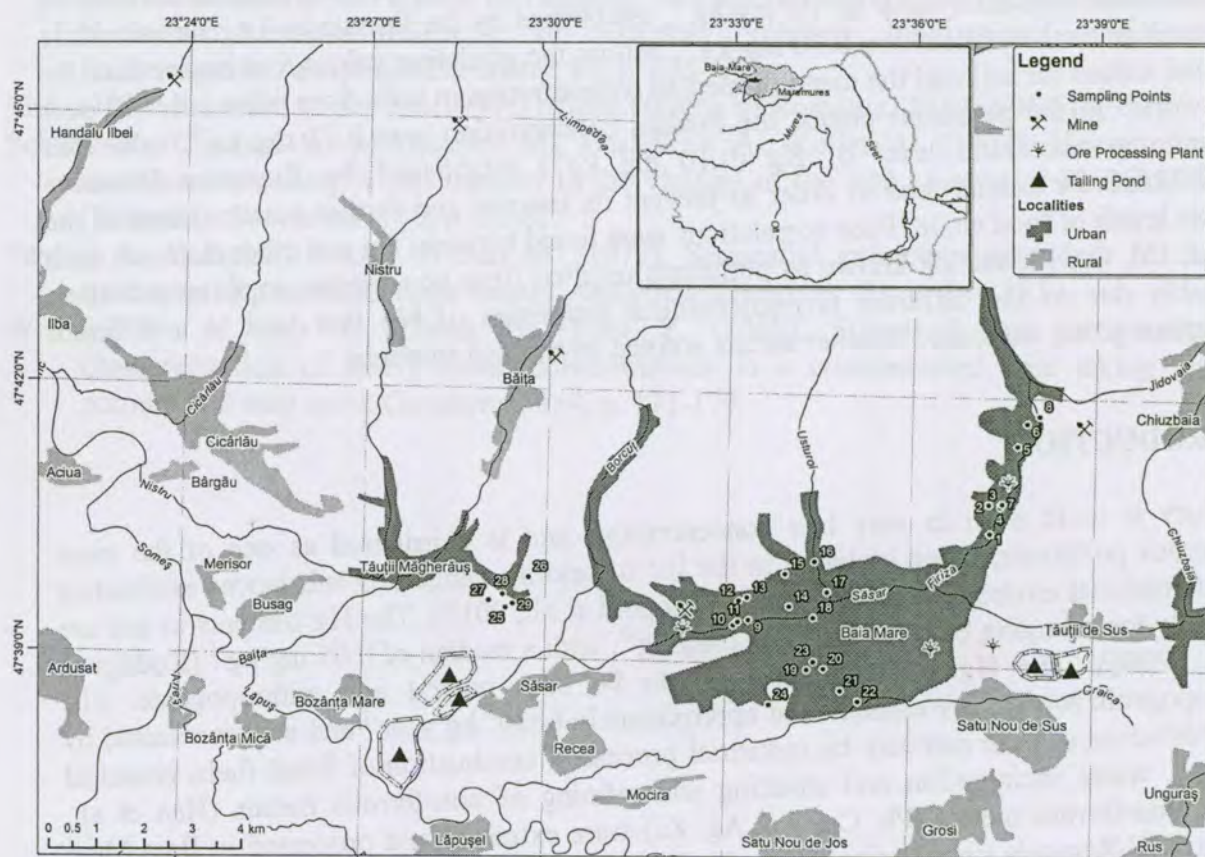
Figure 1. Sampling points and the main pollution sources from Baia Mare area

Instrumentation, Reagents, Standard Solutions and CRMs

The direct measurements of Hg from solid samples (soil and plants) were carried out by thermal decomposition cold vapor atomic absorption spectrometry (TD-CV-AAS) using an Automated Direct Hg Analyzer Hydra-C (Teledyne Instruments, Leeman Labs, USA). The As, Cd, Cu, Pb and Zn concentrations were determined by inductively coupled plasma optical

emission spectrometry (ICP-OES) using the OPTIMA 3500 DV spectrometer (Perkin-Elmer, USA), after *aqua regia* digestion. Soil pH was measured with a Consort 2000 pH-meter equipped with a pH electrode (Consort, Belgium). Total Organic Carbon (TOC) content was measured by using a multi N/C 2100S analyzer (Analytic Jena, Germany).

Ultrapure water obtained by a Milli Q system (Millipore, France) was used for dilutions. 1000 mg L^{-1} Hg and 1000 mg L^{-1} As, Cd, Cu, Pb, Zn multielemental standard solutions (Merck, Germany) were used for calibrations. A soil certified reference material SRM 2709 San Joaquin Soil (New York, USA) and two vegetable certified reference materials NCS ZC 85006 Tomato (Beijing, China) and IAEA-359 Cabbage (Vienna, Austria) were used for the quality control of metals determination.

RESULTS AND DISCUSSIONS
Concentrations of mercury in urban soils and perennial plants in Baia Mare city
According to the Romanian legislation, the typical Hg content in soils is 0.1 mg kg^{-1}. The alert and intervention levels for Hg in soils from sensitive areas, set by the Romanian legislation, are 1.0 mg kg^{-1}dw and 2.0 mg kg^{-1}dw, respectively (MO 956, 1997). In the soils from FE district the Hg average concentration (1.09 mg kg^{-1}dw) was higher than the guideline value of 1.0 mg kg^{-1}dw. Moreover, the intervention limit of 2.0 mg kg^{-1}dw was exceeded in one sample. Hg content in plants from this area exceeds the maximum level (0.10 mg kg^{-1}) established by the European Directive 2002/32/EC (EU Directive 2002/32/EC) allowed in animal feed in order to avoid its transfer and further accumulation in the higher trophic levels of food chain. In SA, the contents of Hg in soil were more homogenously distributed than in FE with a mean (1.02 mg kg^{-1}dw) that slowly exceeded the guideline value of Hg for soil. In plants collected from this area, the Hg concentrations ranged between 0.24 – 0.72 mg kg^{-1}dw with an average concentration two times higher than in plants from FE. In the BM and TM districts, the concentrations of Hg in soils were below the alert level. In plants collected from TM, the Hg concentrations were generally below 0.10 mg kg^{-1}dw, while in those from BM and FE they were similar.

Multivariate statistics
In agreement with other studies (Esteban et al., 2008), the Pearson's correlation matrix revealed a significant positive correlation between the soil Hg and TOC contents, that can be explained by the role of soils organic carbon in Hg sorption. Significant positive correlations were found between Cu, Pb, Zn, Cd and As. Significant positive correlation between Hg and As contents was found, and can be explained by the low mobility of these elements in soils (Cabrera et al., 2008). The lack of correlation between Hg in soil and plants revealed that the accumulation of Hg in shoots is mainly determined by Hg absorption from the atmosphere, while the uptake from soil is less important. The Hg content in soils and plants did not correlate with the soil pH, suggesting that pH is not the governing parameter for the Hg transfer.

The varimax rotated factor loadings of principal components (PCs) for the soil metals contents and physicochemical properties were used. Three PC's with eigenvalues higher than 1, explains about 80% of the total variance of the system. The first component (PC1) exhibits 41% of the total variance with positive loadings on Cu, Cd, Pb, Zn and As. This factor indicates the strong association of *aqua regia* extractable Cu, Cd, Pb, Zn and As in soil, related to the pollution caused by non-ferrous mining and processing activities, and reflects the high values of these elements in the proximity of the industrial area of the city.

The second component (PC2) explaining 25% of the total variability contains the soil Hg, As, TOC and pH and reflects the different chemical and physical properties of Hg and, partially, As compared to the other metals, and their interactions with TOC.

The third component (PC3), explaining 13% of the total variability contains the Hg in plants and reflects the Hg transfer in plants by roots and leaves.

CONCLUSIONS

Our results revealed a moderate pollution with Hg in the Baia Mare urban area, with the average concentrations exceeding the typical values for urban and agricultural areas in the world. The level of Hg concentrations in perennial plants shoots exceeded the maximum Hg level allowed in animal feed. The analyses showed a high level of pollution with Pb, Cu, Zn, Cd and As, especially in areas located in the proximity of active or inactive smelting activities. Despite the fact that the average concentration of Hg in soils from the four studied areas follows the same trend as the other studied metals, the multivariate analysis revealed poor correlations between mercury and the others analysed metals. This finding can be explained by the special physicochemical properties of Hg and by the additional Hg contamination sources. Hg concentration in soil was significantly positively correlated with TOC, expressing the role of TOC on the Hg distribution in soils. No significant correlations were found between Hg in soil and plants.

ACKNOWLEDGMENTS

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