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FACULTY OF GEOGRAPHY AND GEOLOGY

FIELD OF REASEARCH – ENVIRONMENTAL SCIENCE

DOCTORAL SCHOOL OF CHEMISTRY, LIFE AND EARTH SCIENCES

Modern study methods for traces of mercury and other metals in the environment

Abstract of the doctoral thesis

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2015

Content

Mercury is a metal classified by the United Nations as one of the pollutants that needs increased attention by worldwide Governments in order to protect the populations from its toxic effects. The ecosystem's balance and human health are directly threatened through industrial emissions and indirectly by consuming contaminated food due to the presence of the metal in agricultural soils or fishery products.

The aim of the scientific research is to obtain information regarding the presence and concentration of mercury and other trace metals in various environmental samples using modern analytical methods.

The objectives of the research are:

- To present an overview about the historical research regarding mercury presence in the environment using scientific literature;
- To identify the analytical methods used to study mercury and other metals presence in the environment, to present the characteristics of the methods and the equipment used for research;
- To collect data about mercury and other metals concentration in different types of samples using atomic absorption spectrometry and inductively coupled plasma mass spectrometry;
- To assess the ecological and human health risk caused by mercury using the results obtained during reaserch.

KEY WORDS: mercury, trace elements, bioaccumulation, AAS, CV-AAS, FAAS, ICP-MS, soil samples, vegetation samples, street dust, PM_{10}, Iași, Huelva, ecological risk, health risk.

The research thesis is divided in two parts: a first part dedicated to the scientific literature and a second part that contains the original results of the thesis. In the first part of the thesis it is presented the history of mercury research in the environment, the international context of mercury research as an environmental pollutant, uses in industry, emission sources, regional and global estimations, mercury cycle in nature and its toxicity.

Since the 19th century, with the development of the analytical methods, it became known that in the environment exist very small amounts of elements and in order for them to be described, the term „trace elements“was attributed. IUPAC defines a „trace elements” as „any element from a sample that has an average concentration of less than 100 parts/million atoms or less that 10 µg/g”.

Mercury is a ubiquitous pollutant, and the enrichment of the biosphere with this metal is mostly a result of anthropogenic activities. Comparisons between actual measurements of mercury to historical records of mercury in lake sediments and peat deposits has indicated a concentration of mercury that has grown by a factor of 2-5 since the early industrial period.

Mercury enters in the environment from natural sources (volcanic eruption, wild fires, geothermal activity, erosion of rocks by wind and water) and anthropogenic sources (power-plants, cement industry, waste incineration, industrial processes of obtaining non-ferrous metals, artisanal gold mining).

Acknowledged as a global pollutant, United Nations for Environmental Program has developed a special chapter for mercury issue by creating a Global Partnership for governments, industry NGO's and research centers in order to act quickly in this issue. In October 2013, in Kumamoto was adopted Minamata Convention on mercury, after 5 years since the negotiations were launched in for a legal instrument on mercury.

The bacteria that is involved in the process of methylation that produces CH_3Hg^+ adds the methyl group (CH_3) to the mercury ion (Hg^{2+}) through a series of reactions that are not completely known. In water, CH_3Hg^+ goes from the base of the food chain and biomagnifies when small organisms are consumed by the large ones: microorganisms » phytoplankton » small fish and shellfish » big fish and birds » marine mammals » human.

PART II
METHODS AND RESULTS

Atomic Absorption Spectrometry

Mercury is the only metallic element with a vapor pressure of 1.6 µbar at 20ºC. This corresponds to an approximate concentration of 14 mg/m^3 elementary mercury in vapor phase. Its determination through atomic absorption spectroscopy is therefore possible without thermal atomization (CV-AAS). In this case, mercury must be reduced to the elementary state from its compounds and transferred in vapor phase using a gas flux, in a procedure called **cold vapor technique.** This unique property has led to attempts of mercury determination since the beginnings of the elemental analysis methods.

Mercury is known in analytical chemistry for its so-called "memory effect". More precisely, it contaminates components of the detection devices by accumulation on their surface, anytime when its detection is carried out.

The RA-915M Spectrometer is a portable device used for mercury determination from gaseous, liquid and solid samples whose working principle relies on the absorption of the 254 nm mercury resonance line making use of the background correction through the Zeeman effect. The device contains a cell which is crossed by the mercury vapors towards the detector, which provides instantaneous readings (at every 3 seconds) and can display an average of them. Its sensitivity is 2 ng/m^3 - 20 $\mu g/m^3$. It has been used to analyze atmospheric mercury vapors but also in the laboratory in combination with the pyrolytic annexes for the determination of mercury traces in samples of soil, vegetation and street from the city of Iași. The concentration of mercury vapors has been monitored at a fixed point near the industrial area of the city of Iași for a period of 8 months. Various parameters like air humidity and temperature and absolute pressure, solar radiation, wind velocity and amount of rain fall have been recorded for the same period. The data obtained indicate a pattern for the behavior of mercury in the atmosphere can be correlated mainly to the wind velocity and intensity of the solar radiation and then to other climatic parameters (absolute pressure, temperature, humidity) and pollutants.

Analysis of the mercury traces in soil samples. Soil and vegetation samples (53 of each type) have been collected in order to outline possible correlations between the amount of mercury in the soil and that found in plants which grew on that soil. Most of the samples have been sampled from areas near roads, categorized as traffic (36%), cross-roads (16%), gas stations (7%) and bus stations (7%) but also from industrial areas (14%) and from the waste deposits of Țuțora (6%) and Tomești (14%). Although the measured values exceed the normal thresholds recommended by authorities, these cannot be considered dangerous. They also indicate that road transport contributes to the atmospheric pollution with a significant amount of emissions which contains mercury, among other components. The smallest mercury concentration value of 8 ng/g, was recorded in the Ciurea area (traffic category) while the highest value of 433 ng/g was found in a sample sampled from the waste deposit of Tomești. Overall, the highest mercury concentration was found in samples originating from cross-roads and and from the waste deposit of Tomești (over 100 ng/g). Values of 50 – 100 ng/g were recorded in industrial areas, in cross-roads and near the new waste deposit of Țuțora. Values below 50 ng/g were recorded in the categories of traffic, gas stations and bus stations. There is no clear separation of areas which hold a higher concentration of mercury but the waste deposit of Tomești sticks out easily with high values.

Analysis of the mercury traces in vegetation samples. Tree leaves are known as a sink for atmospheric mercury, behaving as an intermediate deposit within the bio-geo-chemical transfer of mercury between the atmosphere, lithosphere and aquatic surface. The highest value of 31.3 ng/g Hg was obtained for the *Malus communis* species and the smallest one of 0.7 ng/g Hg for the *Amaranthus retroflexus* species. Differentiations of mercury concentrations in plants exist for the same collection point due to the fact that leaves are sampled from various species, according to possibilities. In addition, the research also sought differences between plant species in what concerns their capacity to store mercury. The highest concentrations were found in tree leaves while the smallest concentrations were found in the leaves of annual plants. Tree species like *Juglans regia*, *Quercus robur* and *Tilia tomentosa* shown some of the highest mercury concentrations of all samples analyzed in the present study. According to the location typology, the highest values of mercury concentration in vegetation samples have been recorded in the traffic category, cross-roads and industry. These differences are due to the type of vegetation sampled considering that in these regions they came from trees. These category shows the highest concentrations, possible due to height when compared with annual shorter plants; this fact enables an easier exchange of mercury vapors with the atmosphere. Average values in vegetation samples were found as 12.5 ng/g for intersections, 9.9 ng/g in industry, 9.3 ng/g in traffic, 7.9 ng/g in bus stations, 6.0 ng/g at the waste deposit of Țuțora, 5.2 ng/g at the waste deposit of Tomești and 4.8 ng/g at gas-stations.

Trace analysis of mercury and other metals in street dust. One of the environmental problems affecting the city of Iași is the high amount of atmospheric dust. Road traffic is the main source of dust in the city and its contribution amounts to approximately 70% of the total. This is due to the anti-skid material used on the roads during the winter time, the poor technical state of the cars, road modernization works and lack of a ring road. A number of 36 samples of road dust have been sampled from within the industrial area of the city, where various industrial enterprises operate and there is intense road and rail traffic. Concentrations of Hg, Cd, Co, Cr, Ni, Pb, Cu, Zn, Mn and Fe were analyzed in road dust, using FAAS and CVAAS. Average values of Zn (366.52), Pb (52.96), Ni (30.68), Cu (51.41) and Hg (0.48) exceed normal values stated by the *756/1997 Act issued by the Ministry of Waters, Forests and Environment Protection for the approval of the regulation regarding the evaluation of environment pollution*, while Zn and Pb exceed the warning level for sensible soils. The highest concentration of Zn was identified at three collection near CET I and the shopping center Felicia S.C.Group Tehnoton S.A. as well as in the proximity of the water treatment station. Mercury concentration in road dust varies between 0.18 – 0.7 mg/kg, with an average of 0.48 mg/kg, distributed according to the zone specificity as: roads 0.18 – 0.68 mg/kg, parking lots 0.31 – 0.63 mg/kg and for the CET II and water treatment areas 0.48 – 0.7 mg/kg. The mercury concentration values are higher than those considered normal, but not high enough to be considered above the warning threshold.

Mass spectrometry with inductively coupled plasma

Mass spectrometry has become one of the most used techniques for identification of unknown substances and for structural studies in chemistry, environmental sciences or medicine. It is an analytical technique designed to determine the mass/charge ratio of an atom or a molecule using the motion of their ionized states in magnetic or electric fields. The samples analyzed through the ICP-MS technique were sampled in Huelva (Spain) and consisted of filters on which atmospheric dust was accumulated along the year 2014. These filters were installed at a monitoring station for urban air with industrial influences. This type of investigation is scientifically relevant due to the possibility to reveal harmful impact for human health. The dust originates from natural and anthropogenic sources which release nitrate, sulphide, and traces of metals, organic carbon and other elements of the earth curst. A number of 49 metals have been detected using the Agilent 7700 spectrometer during the year of 2014. Results which cover 15 of these samples are presented in this study. Recorded average annual values of arsenic (2.25 ng /m^3), cadmium (0.27 ng /m^3), nickel (2.18 ng /m^3) and lead (5.52 ng /m^3), do not exceed the limits imposed by European legislation.

Within the annual distribution of metals in PM_{10}, the highest occurrence rates were recorded for copper (62,49%), zinc (19,56%), lead (4,29%), manganese (4,32%) and vanadium (2,54%). The proximity of two important industrial manufacturers (Atlantic Copper and Fertiberia) is a reason for the large variety of atmosphere dusts with high content of metals.

Evaluation of the ecologic risk

The ecologic risk of mercury contamination of soil and vegetation was based on results presented in this study. Thus, measurements on the 53 samples of soil and vegetation have been taken into account, making use of the Hakanson formula. For soil, 10 samples prelevated from cross-roads and waste deposit areas indicated a moderate ecologic risk, accounting for the highest values of the mercury content, while results for the remaining samples indicate a minimum risk (Figure 21). From all vegetation samples, only one, sampled from the cross-road of Mihai Eminescu Square, can be put in the category of average risk. The remaining vegetation samples indicated a minimum ecologic risk for mercury contamination. The ecologic risk for multiple elements (*RI*) has been calculated for 36 samples of street dust. In this case an area of considerable risk was identified near the water treatment plant and near the waste deposit of Tomești. There have identified two points of moderate risk (the cross-road Felicia and Arcelor Mittal) while the remaining 33 locations have shown a minimum ecologic risk for metals included in the study.

Evaluation of the risk on human health

People are exposed to the mercury content from soil through three main paths: direct ingestion of dust particles, inhalation of mercury vapors and dermal contact. Using a method recommended by US EPA, the mercury contamination risk has been assessed for children and adult population using results recorded from the 53 soil samples which have been processed. The risk to which children are exposed is higher than that for adults. More exactly the current study revealed that the risk is in average 9 times higher for ingestion, 1.7 higher for inhalation and 1.5 times higher for dermal contact. The risk of mercury inhalation is outlined as one of the most important factors, exceeding that of dermal contact. This is justified by the fact that unlike other metals, mercury releases vapors at relatively low temperatures, which makes it quickly accessible to the human respiratory system. It is therefore confirmed that mercury poses a potential risk to human health, most notably in urban areas where emissions may be high due to industrial sources or road traffic.