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A HEAVY METAL ATMOSPHERIC DEPOSITION STUDY AROUND THE LEAD AND COPPER-ZINC SMELTERS IN BAIA MARE, ROMANIA, EMPLOYING THE MOSS BIOMONITORING TECHNIQUE, **ENAA** AND **FAAS**

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Introduction

Heavy metals is one of the most dangerous groups of anthropogenic environmental pollutants due to their toxicity and persistence in the environment. Evaluation of the levels of heavy metal deposition is consequently of vital importance.

Systematical surveys of the atmospheric deposition of metals are performed in several European countries every 5 years [1, 2, 3, 4] by means of the moss biomonitoring technique. It has been established that bryophytes are among the most effective types of organisms for biomonitoring due to a number of their biological features, widespread occurrence, and tendency to accumulate and retain pollutants [5]. In comparison with higher plants bryophytes lack an advanced root system. This inhibits significant absorption of pollutants from the substrate and consequently their uptake results mainly from the ambient atmosphere. Moss surveys have several advantages over conventional deposition monitoring based on precipitation monitoring: the sampling is simple and the chemical analyses are much easier due to higher concentrations and strongly reduced contamination problems [6].

The most severe effects of air pollutants are likely to occur in the near vicinity of strong pollution sources [7]. Such a situation is illustrated by the town of Baia Mare in the north-western part of Romania, where polymetallic sulphides are extracted from deposits located in areas near the town and processed by two non-ferrous metallurgical factories in the town. Mining activities in Baia Mare are more than five centuries old and non-ferrous metallurgical industry has already existed for 150 years. The emissions from these metallurgical factories, reaching high intensity during the last decades (more than 30 tons of dust are emitted to the air each year, including more than 7 tons of lead) has caused severe environmental pollution with heavy metals [8, 9]. However, there is a lack of information about the real level of heavy metal pollution in this region. The primary purpose of this paper is to characterize qualitatively and quantitatively the regional atmospheric deposition of heavy metals and to indicate the extent of the areas polluted by these sources.

Materials and methods

The methods used in this study are based on the Scandinavian recommendations [1], but adapted to the local environmental conditions as described below.

The studied area

Baia Mare is a district town with a population of 150 000. The town is situated in the valley of Sasar river and is bordered by mountains to the east, north, and west. The prevailing wind direction is from east-north-east, following the direction of the river. The most polluting plants are located upstream the town, so the dust is spread to the town.

Sampling and sample preparation

Three species of moss samples (*Pleurozium schreberi*, *Pseudoscleropodium purum* and *Rhytidiadelphus squarrosus*) were collected on 28 sites located 2 to 17 km from the center of the town (Fig.1). This selection of species was made necessary because no single species was present at all collection sites. Sampling was performed in 2000 during the period July - September. Sampling points were chosen at least 100 m from main roads, villages and industries and at least 50 m from smaller roads and houses. On each site, 5-10 samples were collected within a 50 × 50 m area. As far as possible the samples were taken from small forest clearings and always located away from the nearest trees, so as not to be directly exposed to throughfall precipitation. Sampling and sample handling was performed using polyethene gloves and samples were stored in paper bags. In the laboratory, the samples were carefully cleaned from all dead material and attached litter, and only the green and green-brown shoots from the three latest years are analyzed, after 24 hours drying at 40 °C. Samples were not subjected to washing.

For ENAA, moss samples of about 300 mg were packed in aluminum cups for long-term irradiation. For short-term irradiation samples of about 300 mg were heat-sealed in polyethene foil.

For FAAS, weighted samples of about 1g were digested overnight in a mixture of 20 mL concentrated HNO_3 and 1 mL HCl in Erlenmeyer flasks, on a hot plate after evaporation to dryness, 1 mL distilled water was added and the solution again heated to dryness, then a mixture of 1 mL concentrated HNO_3 and 5 mL distilled water was added and boiled for a short time. After filtration the solution was diluted with distilled water to 25 mL. For some elements further dilution was necessary to achieve optimal concentration levels for analysis.

Analysis

Neutron activation analysis

Neutron activation analyses were performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Reasearch, Dubna, Russia and Geological Institute of Russian Academy of Sciences, Moscow, Russia. Most elements were determined by ENAA with detection limits around 1 μg/g. The samples were irradiated in IBR-2 fast pulsed reactor, the flux parameters of which are shown in Table 1.

Table 1. The flux parameters of irradiation sites

Irradiation site	$\Phi_{th} \cdot 10^{12}$. n/(cm^2·s) E=0 ÷ 0.55 eV	$\Phi_{th} \cdot 10^{12}$. n/(cm^2·s) E=0.55 ÷ 10^5 eV	$\Phi_{th} \cdot 10^{12}$. n/(cm^2·s) E=10^5 ÷ 25 10^6eV
Ch1 (Cd-screened)	0.023	3.31	4.23
Ch2	1.23	2.96	4.10

Two kinds of analysis were done: long irradiation of 100 h in Ch1 were used to determine elements associated with long lived radionuclides (As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, La, Rb, Sb, Sc, Se, Sm, Th, Zn) and short irradiation of 2 min in Ch2 was used for short-lived radionuclides (Al, Ca, Cl, I, K, Na, Mg, Mn, Ti, V). The gamma-activities of samples were measured four times after decay periods of 5 min, 10 min, 5 days and 13 days, respectively. The γ-spectra of samples was recorded using a high purity Ge detector. Four elements were determined by FAAS (Kvant-2A) at Geological Institute of Russian Academy of Sciences. Lead (Pb) cannot be determined by INAA and for three other elements FAAS also chosen because the detection limits for cadmium (Cd), copper (Cu) and nickel (Ni) are better than in ENAA.

For AAS, the analytical performance was checked by the regular analyses of the reference materials IAEA-336, lichen, and IAEA-359, cabbage, issued by the International Atomic Energy Agency whereas IAEA-336, IAEA-359 and moss DK-1 (Danish moss) for NAA.

Results and Discussion

The results obtained for Pb, Cd, As and I are shown in Fig. 2 in comparison with relevant data from areas in Russia, Poland and Norway.

Strongly elevated arsenic values were found in the Baia Mare region. The mean value is comparable with concentrations from Ural Mountains, 3-4 times times higher than concentrations from other industrial areas and 7 times higher than an Norwegian background level. The As values are between 0.48 *ppm* and 7.42 *ppm*, with an avarage of 2.17 *ppm*.

The Cd mean value of 1.43 *ppm* is 2 to 5 times higher than in other European regions. The range of registered concentrations for Cd is between 0.37 *ppm* and 5.54 *ppm*.

The obtained values for Pb (mean of 46 *ppm*, range from 11 to 175 *ppm*) are also higher than in Ural Mountains and Polish Copper Basin.

The Baia Mare region is well known not only for its high heavy metal pollution but, also, for its endemic character due to iodine depletion. This fact is supported by our results. The mean iodine concentration (0.59 *ppm*) in mosses from Baia Mare is 2.5 times lower than the background level in Norway and systematically lower than mean values elsewhere in Europe.

Following the obtained data for Cu and Pb we can clearly distinguish their different emission sources. The correlation coefficient calculated for these two elements for all collected samples is very low, only 0.46, but if we divide the samples in two categories with regard to the their distribution around the polluting sources, we observe much higher correlation coefficients for each direction (Fig. 3).

A similar situation is noted for the other two pairs of elements: As–Cd and As-Pb (Fig. 4).

Providing factor analysis for part of elements determined we distinguish 4 factors. First of them represents the group of "native" elements, the second groups four of pollutant elements, the third one unifies the other two pollutants. The fourth factor distinguishes iodine (Table 2).

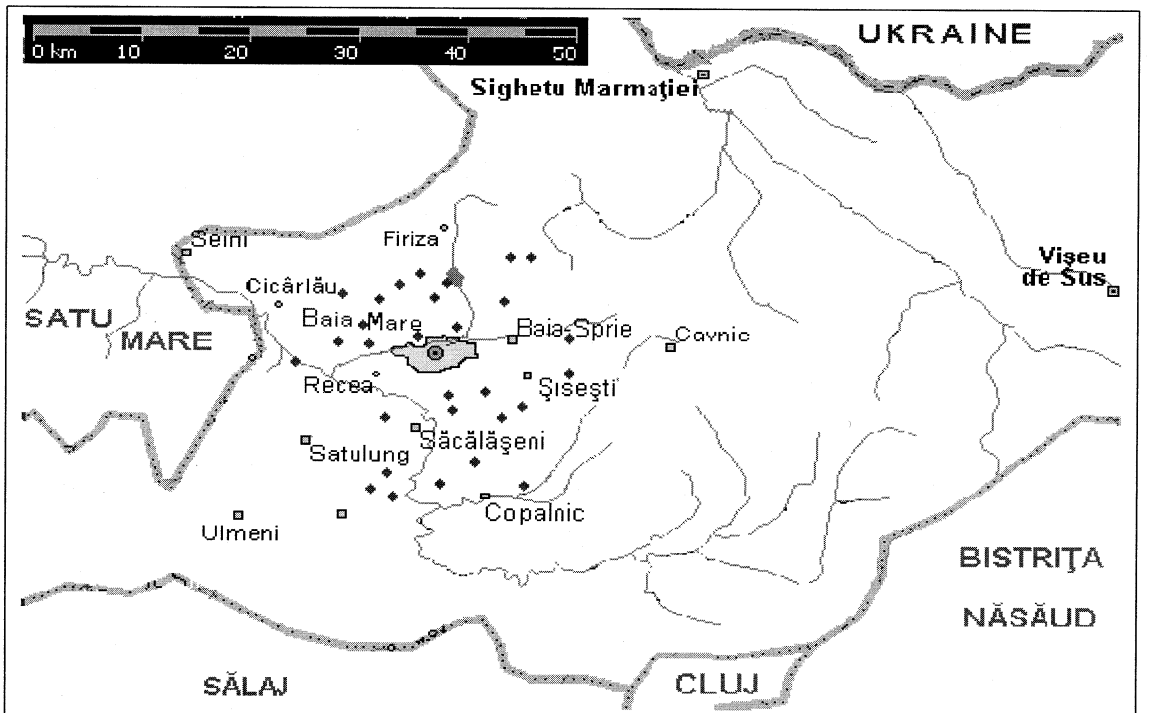

Figure 1. Sampling map

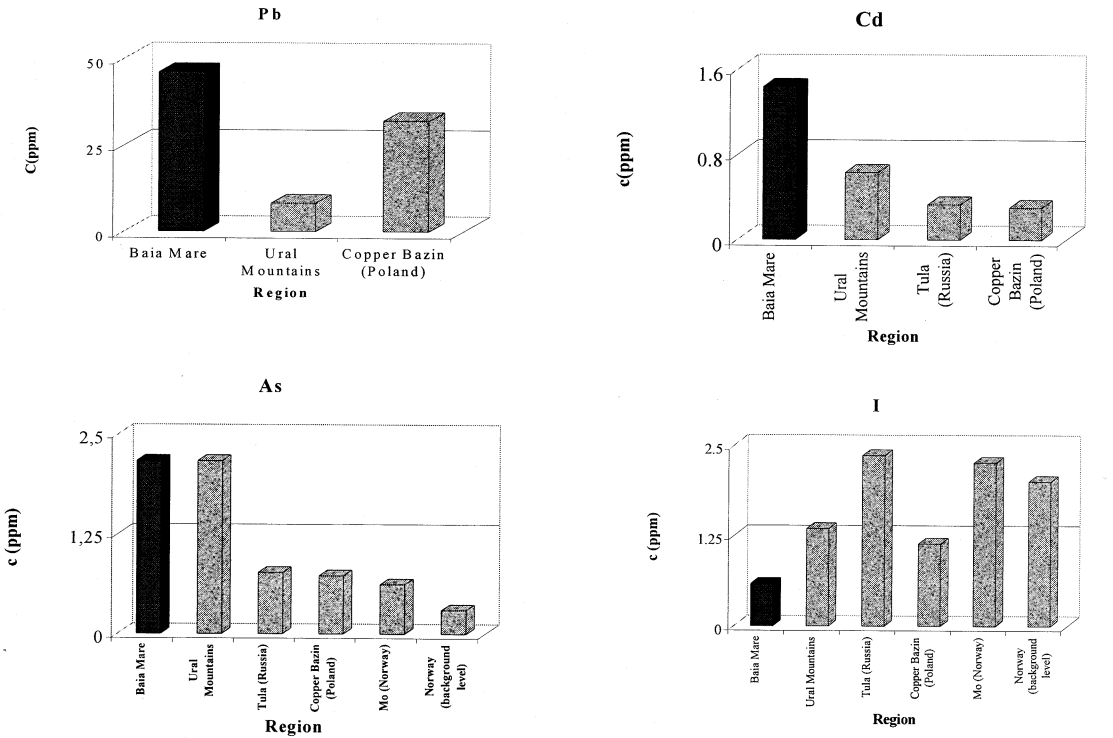

Figure 2. Baia Mare *versus* other European regions

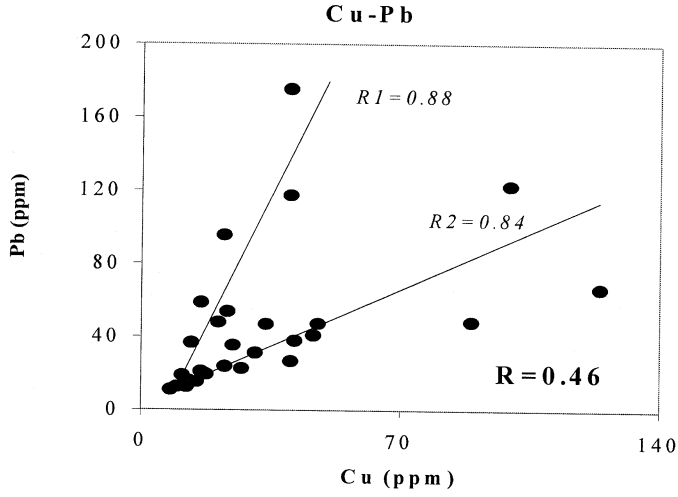

Figure 3. Correlation graphic Cu *versus* Pb

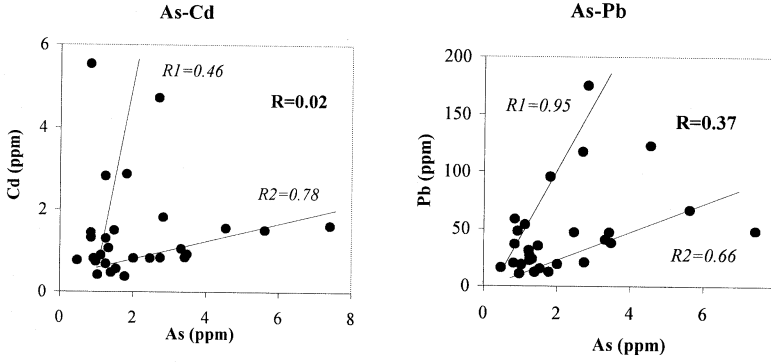

Figure 4. Correlation graphics As *versus* Cd and As *versus* Pb

Table 2 Rotated Component Matrix

Component	1	2	3	4
Na	**0.87**	-0.21	0.13	0.18
Mg	**0.92**	0.07	-0.01	0.01
Sc	**0.91**	0.00	-0.02	0.25
Ca	**0.71**	0.29	0.02	-0.29
Cu	-0.07	**0.90**	-0.02	0.00
Zn	0.38	0.01	**0.74**	0.44
As	0.18	**0.90**	-0.11	0.19
Cd	-0.09	0.07	**0.92**	0.01
Sb	0.04	**0.91**	0.16	0.07
I	0.08	0.12	0.10	**0.87**
Pb	-0.05	**0.67**	0.49	-0.20
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.				
Rotation converged in 5 iterations.				

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Куликов О.А. и др. E14-2001-163
Изучение атмосферных выпадений тяжелых металлов
в районе свинцового и медно-цинкового комбинатов
в Байа-Марэ, Румыния, с использованием мхов-биомониторов, эпитеплового
нейтронного активационного анализа и метода пламенной атомной абсорбции

Для изучения атмосферных выпадений металлов вблизи свинцового и медно-цинкового комбинатов в Байа-Марэ использовались мхи *Pleurozium schreberi*, *Pseudoscleropodium purum* и *Rhytidiadelphus squarrosus*. Образцы, представляющие собой трехлетний прирост зеленой части мхов, были собраны в 28 точках пробоотбора в радиусе 2–20 км от источников загрязнения окружающей среды и проанализированы с помощью инструментального нейтронного активационного анализа с использованием эпитепловых нейтронов (ЭНАА) и метода пламенной атомной абсорбции (FAAS). В целом было определено 30 элементов, включая большинство тяжелых металлов, которые выбрасываются в атмосферу данными типами производств. Концентрации As и Cu, полученные в районе Байа-Марэ, сравнимы с аналогичными данными для Карабаша (Южный Урал) — одного из самых «грязных» регионов Европы. Отмечается высокая степень корреляции этих элементов между собой. Средние значения для цинка (136 ppm) и свинца (41 ppm) существенно превышают известные литературные данные. Самое высокое значение для свинца (175 ppm) было определено в образце, собранном в непосредственной близости от свинцового комбината. Среднее значение для сурьмы (0,56 ppm) значительно превышает фоновый уровень содержания сурьмы в норвежских мхах, но в 5 раз ниже средней концентрации сурьмы на Южном Урале. Наблюдается сильная корреляция между сурьмой и свинцом. Результаты данной работы свидетельствуют об эндемичном характере данного региона по йоду. Среднее содержание йода во мхах в районе Байа-Марэ в 2,5 раза ниже, чем в фоновом районе Норвегии, и систематически ниже среднеевропейских значений.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

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A Heavy Metal Atmospheric Deposition Study Around the Lead
and Copper-Zinc Smelters in Baia Mare, Romania, Employing
the Moss Biomonitoring Technique, ENAA and FAAS

The mosses *Pleurozium schreberi*, *Pseudoscleropodium purum* and *Rhytidiadelphus squarrosus* were used as biomonitors to study the atmospheric deposition of metals around the lead and copper-zinc smelters in Baia Mare. Samples representing the last three years' growth of moss or its green part, collected on the ground at 28 sites located 2–20 km from the source area, were analyzed by instrumental neutron activation analysis using epithermal neutrons (ENAA) and by flame atomic absorption spectrometry (FAAS). A total of 30 elements were determined, including most of the heavy metals known to be released into the air from this kind of industry. Obtained concentrations for As and Cu are comparable with those observed in Karabash, South Ural Mountains, one of the most polluted regions in Europe. Besides, these two elements correlate very well with each other. The mean values for Zn (136 ppm) and Pb (41 ppm) are substantially higher than those normally found in the literature. The highest value for Pb (175 ppm) was observed in a sample collected in the vicinity of the lead plant. The mean value for Sb (0.56 ppm) is much higher than the background level in Norway but 5 times lower than the mean Sb concentration in parts of the South Ural Mountains. A high correlation between Pb and Sb was observed. Moreover this study evidences the endemic character of the examined area due to iodine depletion. Its mean value in the moss is 2.5 times lower than the background level in Norway and systematically lower than the mean European values.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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