CONTRIBUTIONS TO THE STUDY OF ENVIRONMENTAL POLLUTION WITH HEAVY METALS

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ABSTRACT: *The estimation of the pollution level and of the dangers presented by this phenomenon, implies some analyses in which the concentrations of heavy pollutant metals should be determined in samples of dusts from the air, samples of soil and plants. The analytical techniques used must have low detection limits, the lowest matrix effects possible and they must allow the determination, as precise as possible, of the major components as well as of the minor ones and in traces [6,7]. The methods that respond to these requirements are from the category of atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). The area in which the researches were done is characterized by the existence of some industrial units of extraction of some ores which contain as major components Pb, Cu, Zn and as minor components or in traces Cr, Mn, Ni, Co, Ag, Au, Al, Fe.*

The presence of these metals in the air, water and soil has negative effects on human health, plants and animals. This study analyzes these aspects in a zone of Romania strongly polluted with heavy metals.

Keywords: *heavy metals, AAS, ICP-AES, speciation,*

1. INTRODUCTION

The air, the water, the soil and the plants can be polluted with heavy metals proceeded from different natural or artificial sources. If the natural sources have a small contribution, the artificial ones bounded from different human activities, contribute in a decisive way to the pollution of the environment. The artificial polluting sources with heavy metals are: the burning stationary focus for the urban residues, the metallurgical industry the materials for construction industry, the mines and the plants for the enrichment of the nonferrous ores in useful components.

The distribution and the mobility of the heavy metals are determined by the environment in which they are emitted and by the type of combinations in which they are found.

Thus the heavy metals (Pb, Cu, Zn, Al, Fe) emitted in the atmosphere as dusts in suspension or sedimentation dusts will be unequal dispersed around the source with the contribution of local meteorological factors and of the chemical form in which the metal is found.

2. METHOD AND MATERIALS

2.1. Local polluting sources

Among the typical polluting sources the ones which have harmful emission are the two metallurgical plants from the point of view of polluting with dusts which contain heavy metals in different concentrations, the main polluting source is considered to be the metallurgical plant for the obtaining of Pb situated at NE in a district of the town.

Using technologies with low transforming efficiency after processing 150 tones mining concentrates, this plant is polluting the atmosphere with 65 kg Pb, 0.3 kg Cd and 0.8 kg As during one hour. Compared to these quantities, the other polluting sources, such as automobiles, burning of gas at each stop, the ores enrichment plants, the ores extracting mines, waste dumps, although they have a great contribution to the pollution of the area it is much smaller than that of the main polluting source, the estimation of the exact quantity being hard to make.

2.2. The collecting of samples

The sample collecting system depends on the nature of the environment from which they are collected. Mainly, the placement of the sample collecting points must regard the data obtained after the analysis of the samples which must offer an exact image on the concentrations of the pollutants in the area, meaning that the error in estimating the concentrations in places from where samples weren’t collected should be minimal and the results of the analysis should offer the possibility to estimate the contribution of the individual sources to the global field of the concentrations.

The samples were collected by sedimentation in cylindrical vases with 25 cm diameter, put on 1.5 m high supports, placed on distances from highways or building sites, in order to avoid the samples becoming impure.

2.3 The preparing of the samples

After being collected, the samples were dried at 120^{o}C and calcified at 500^{o}C, and then submitted to disintegration under pressure in a CEM MDS 2000 microwave. A mixture of Merck acids formed of 5 cm^3 fluorhydric acid, 8 cm^3 chlorhydric acid and 8 cm^3 nitric acid was used. The parameters programmed for the microwave are: 10 minutes time, 50% power and 120 psi pressure. After the total solubilisation, the solutions were passed in quoted balloons of 50 cm^3 and brought to this volume with bi-distilled water. The obtained solutions were submitted for analysis to determine the concentrations of heavy metals, the analysis being made with a BAIRD ICP 2070 spectrometer, which was calibrated with a standard Merck solution. The spectrometer operated at a power of 900 W, a flux of the cooling gas of 9 l $Ar^{\cdot} min^{-1}$ and an auxiliary flux of 1,5 l $Ar^{\cdot} min^{-1}$. The passing of samples in solution can also be done by other methods, and their selection is done regarding the nature of samples, their content and the nature of elements which are to be determined [3,4,8].

3. RESULTS AND DISCUSSION

For the analysis of the sedimentable powder samples, the BAIRD ICP 2070 spectrometer was used.

Before starting the experimental determination it's necessary to carry out the wavelength calibration at which we make the metal determinations, with the BAIRD ICP 2070 spectrometer.

After that, we analyze each sample to determine the content in heavy metals.

For the concentration determination of the following metals Pb, Cu, Zn, Fe, Al, from sedimentable powders, the measurement was accomplished at the wavelengths showed in table 1 [1,2,5].

Table 1. The wavelengths used in the experimental determinations

No.	Element	Wavelength (nm)
1	Pb	220.35
2	Cu	324.75
3	Zn	213.86
4	Fe	238.20
5	Al	396.15

The concentrations of the metals in the analyzed samples are showed in table 2. The data from table 2 show maximum concentrations for Fe, Cu, Zn in sample 2 from 1.5 Km W far from the main polluting source. Pb achieves the maximum concentration in sample 1 at 0.5 Km W, and Al achieves the maximum in sample 9 at 30 km W.

Table 2. Variation with the distance of the concentration

No	Element	0,5 km	1,5 km	2 km	2,5 km	3,5 km	4 km	6 km	10 km	30 km	60 km
		Concentration (ppm)									
1	Fe	48123	57634	54885	55312	53130	50463	46801	40912	28211	23969
2	Pb	55121	27232	30121	35242	25213	30145	23120	17125	10523	7114
3	Al	10130	7254	5410	7541	10235	15540	30211	28541	50514	29213
4	Cu	9126	15233	12720	9345	8586	6125	4250	3252	2131	1872
5	Zn	6261	8542	7231	5810	5452	5100	4521	3501	2160	1641

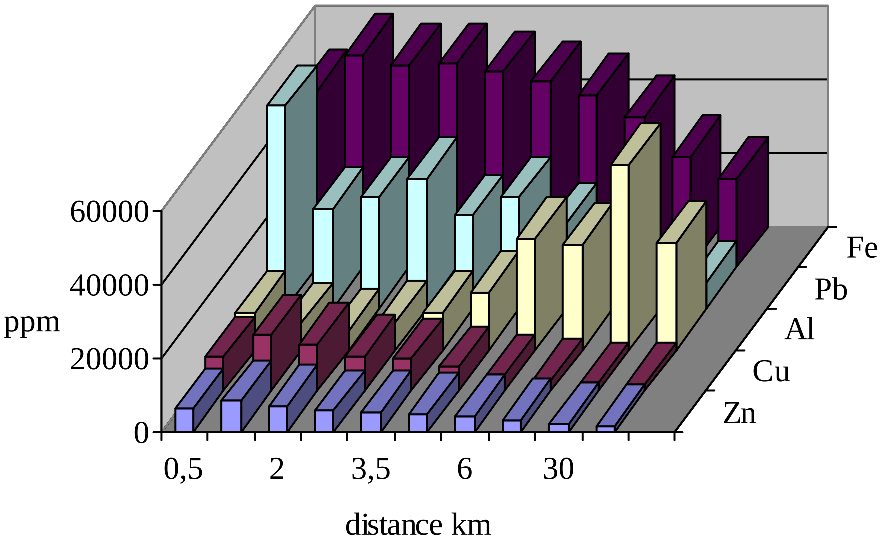


Fig.1 Variation with the distance of the concentration

Although it is hard to establish exact rules valid in heavy metals distribution in atmosphere, yet it is certain that Pb achieves the highest level of concentration at the closest point to the polluting source, while Cu, Zn and Fe at 1.5 Km from the source. That distribution could be explained regarding the local meteorological parameters and chemical combinations in which the analysed metals are found. The wind direction that appears with the highest frequency is ENE, with a frequency of 15%, followed by the directions NE, W, SW. The main speeds of the wind are situated at values below 4m/s and in about 70% of the cases it is below 2m/s. At 100-200m altitude the E, SE, W directions prevail at 500m, SE and W and above 500m the SE and W directions.

The fog appearance creates unfavorable conditions for pollutants diffusion. Clear days make possible picking up the pollutants at heights and spreading them on an area with larger radius; instead, on cloudy days, the cloud ceiling prevents the pollutants from lifting at heights, the dispersion is limited and the local concentrations grow up. The rains, which appear in almost half of the days in a year, can decrease the concentrations of the pollutants from the air by washing, but this way a big pollution of the soil occurs.

The local meteorological factors that were analyzed do not create conditions to make favorable the quick dispersion of the pollutants, so that high concentrations appear on a small area around the pollution source, mainly in points situated in the most frequent directions of the wind.

The chemical combination types in which the metals are found, their solubility and molecular mass can explain the distribution of the pollutants, experimentally found. To identify the chemical combination types, speciation analyses of Pb, Cu and Zn were done. For Pb and Cu the following combinations were identified: sulphates, sulphides, oxydes and carbonates and for Zn: sulphates, oxides and carbonates, silicates and sulphides. Speciations being done on extracted and processed ore samples in the area, it was found that Pb is found in medium percentage of 88% sulphides, 9.8% oxide and carbonate and 2.2% sulphate.

Although it would be expected that after the pirometallurgical processes of ore processing, Pb to be found mostly in oxidic combinations in sedimentable powders, the following percentages were found: sulphides 47%, oxides and carbonates 18% and sulphates 35%

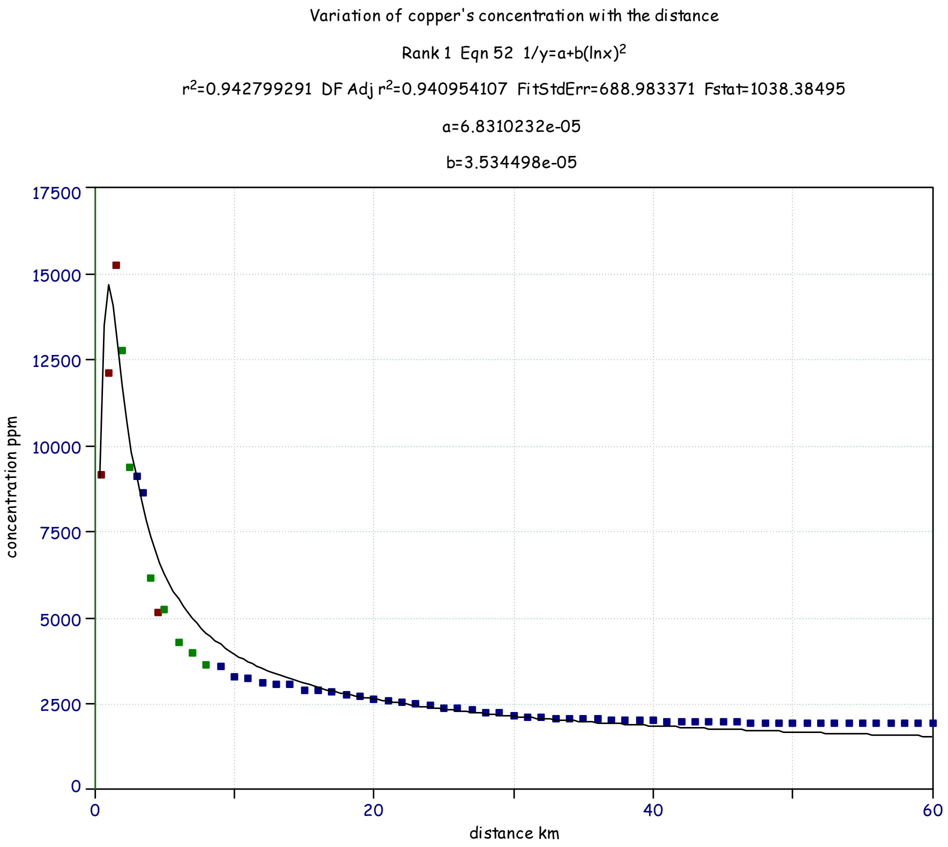
The high molecular mass and the low solubility of the combinations limit the mobility of Pb and they achieve high concentrations when it is close to the polluting source.

In ores, Cu was found as 4.48% sulphate, 0.22% oxide and carbonate, 95.2% sulphide, and in sedimentable powders it was identified as 17% sulphate, 34% oxid and carbonate, 49% sulphide. Considering the percentage over 69 of the Cu's unsoluble combinations in sedimentable dusts, we can explain their low mobility and the distribution of Cu in high quantities at distances of up to 6 km to the pollution source.

For Zn there were identified in ores 94% sulphide, 0.4% sulphate, 2.5% silicate and 3.1% oxide and carbonate and in sedimentable powders 39% sulphide, 31% sulphate, 16% silicate and 14% oxide and carbonate. The increased amount of sulphate in dusts, compared to the ores, is explained by the partial transforming of sulphide oxide under the influence of sulphuric acid drops which exist in the atmosphere in the area, strongly polluted with sulphur dioxide. This compositional structure correlated with local meteorological factors explains it.

Zn distribution is in the greatest amount when it is close to the main polluting source.

Using a graphics programme for the experimentaly obtained data, we find for example (figure 2) that the variation of the copper's concentration with the distance takes place according to the following law:



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