

ACCUMULATION OF SPECIFIC POLLUTANTS IN VARIOUS MEDIA IN THE AREA AFFECTED BY A PETROCHEMICAL CENTER

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The results on monitoring of oil pollution around the town of Ploiesti (South Romania), known for its petrochemical and chemical industry complexes and crude oil activity, are reported. The distribution of heavy metals, rare earth and other microelements along the wind rose profile (the oil complex – 20 km distance) was examined through the analysis of soil samples. Mosses were chosen as biomonitors of local atmospheric pollution with heavy metals and other toxic elements. The trace element content of vegetation growing near the territory of the plant was compared with that of the background one. The contamination of the river flowing in the vicinity of the plant was examined. Comparison of the spatial trends of different pollutants shows the influence of the same atmospheric transport phases on the uptake of trace elements by vegetation. A comparative evaluation of the results was carried out to indicate to what extent the amount of pollutants in the atmosphere or the amount deposited in the soil or transported by sediments contributes to pollution of the local ecosystem in the vicinity of a petrochemical center.

Key words: trace elements, air pollution, biomonitors, petrochemical center

1. INTRODUCTION

The persistent trace pollutants emitted by petrochemical centers have become of growing concern since they may constitute a health risk. The pollution around an important petrochemical center is characterized by (1) the emission of specific pollutants (i.e. As, Hg, Ni, Pb, Sb, Se and V) and organical compounds into the air, (2) the contamination of soil, plants and ground water caused by storage of industrial residua in the vicinity of the industrial objective and (3) the overflow of tailing discharges in the neighboring running waters. The air toxics accumulate in the biosphere [1]. The emissions from oil industry can affect the humans directly, through inhalation exposure, as well as indirectly, through food. The short-term exposure consists mainly of allergic effects, while the long-term exposure can result in respiratory effects, such as asthma and an increased risk of chronic respiratory infections. Nickel and lead and their compounds have an increased risk of lung and nasal cancers from exposure to nickel refinery dusts, being classified by EPA as human carcinogens [2].

The analysis of trace elements in natural organisms has been shown to be a suitable method for atmospheric pollution monitoring [3-5]. The relevant information is obtained from changes in the behaviour of the biomonitor or from the contents of chemical substances accumulated in the monitor tissues [6].

The distribution of heavy metals, rare earth and other microelements along the wind rose profile (the oil complex – 20 km distance) was examined through the

analysis of soil samples. Moss-biomonitoring technique was applied around the Ploiesti petrochemical center to provide important information on local industry emissions. The trace element content of *Populus nigra* leaves growing near the territory of the plant was compared with that of the background one. The contamination of the river flowing in the vicinity of the plant was investigated through the analysis of river sediments. This study was accomplished as part of the project “ The assessment of environmental pollution around a petroleum center using epithermal neutron activation analysis ”.

Sampling was performed in the summer of 2000 year. The samples were analyzed for up to 37 elements by epithermal neutron activation analysis. In completion, other 4 elements, namely Cd, Cu, Hg and Pb were determined by flame atomic absorption spectrometry. The geographical distribution of air toxic concentrations in mosses was presented in the form of isodepositions maps.

The objectives of this study are: (1) To determine the concentration levels of specific pollutants in soil samples, *Populus nigra* leaves and river sediments, (2) to identify and characterize the geographical concentration patterns of air toxics in *Hypnum cupressiforme* on the local scale and (3) to compare the amount of pollutants in the atmosphere with that deposited in the soil and transported by sediments to evaluate the pollution degree of the local ecosystem in the vicinity of a petrochemical center.

2. EXPERIMENTAL

2.1. Investigation area and sampling

Ploiesti is a town with several refineries, petrochemical factories, steel and chemical plants (with a different profile than the petrochemical one). It is situated in the central part of the Romanian Plain. There are about 248688 inhabitants (at 1 July 2001). The climate is moderated temperate continental, the annual average temperature is 10 °C, the annual average precipitation's is 550 mm and the dominant wind direction is from the east to west. The climate and the (black) soil support the agriculture in the surrounding regions.

The experimental material included:

- 15 surface soil samples representing a 20 km length of wind rose profile,
- 8 moss samples of *Hypnum cupressiforme* species collected in 8 cells, respectively, of a local grid network of 16 x 16 km²,
- 2 *Populus nigra* leave samples, from which one was from a tree situated closely of the Vega refinery and the other represented a control sample and
- 2 bottom sediment samples originated in Teleajen river, collected symmetrically, upstream and downstream respectively, at a distance of 5 km far from the Ploiesti city.

The surface soil samples were collected from an area of 15 x 15 cm² on depths of about 10 cm in 1 kg of weight. In order to estimate the contamination and its transfer from the petrochemical plants, soil samples were collected according to

the wind rose direction. The first four soil samples were taken close to 4 refineries and the rest up to 15 were sampled at different distances from the town, as follows: 500m, 1 km, 2 km, 3 km, 5km, 7 km, 10 km, 12 km, 15 km, 17 km and 20 km (background zone). After discarding stones and rods the material was air-dried about a month. Each sample was carefully grounded and mixed several times in a porcelain mortar with stepwise reduction of the sample by quartering. About 30 g of soil powder was distributed in a thin layer and dried again in air for more than 2 days, and forced through a 100 μm sieve.

Leave samples were air dried for a month. About 50 g in weight were cut in small pieces and homogenized in a porcelain mortar.

The moss samples were collected and prepared for the analysis according to Scandinavian guidelines [7].

About 2 kg of bottom sediment samples were collected from the riverbank from a depth of about 5 cm after removing the top sediment cover and eliminating all plants and stones. Prior to analysis, the sediment samples were dried and carefully homogenized and sieved to obtain a fraction up to 100 μm .

The same material was subjected both to epithermal neutron activation analysis and flame atomic absorption spectrometry.

2.1. Epithermal neutron activation analysis

The vegetation samples (i.e. leaves, mosses) of 0.3 g and soil and sediments samples of 0.2 g and relevant certified reference materials were heat-sealed in polyethylene bags for short-term irradiation and packed in aluminum cups for long-term irradiation. To determine the elements, which have short half-life nuclides, samples and standards were irradiated for 3 min with thermal ($1.23 \cdot 10^{12} \text{ ncm}^{-2}\text{s}^{-1}$) and epithermal neutrons ($2.96 \text{ ncm}^{-2}\text{s}^{-1}$). Gamma-ray spectra were measured twice after 3-5 min of decay for 3 and 20 minutes, respectively. HPGe detector with a resolution of 2.5 keV for the ^{60}Co and relative efficiency of 20 % 1332 keV line was used.

The elements which have medium half-life and long half-life nuclides were determined by irradiating the samples and standards for 4-5 days in a flux of epithermal neutrons of $2.96 \text{ ncm}^{-2}\text{s}^{-1}$. After cooling for 4 to 5 days (for medium half-lives) and for 14 to 20 days (for long half-lives), the gamma-ray spectra were measured for 40-50 min and 2 h 30 min - 3 h, respectively. The gamma-ray spectra analysis was carried out using software developed in FLNP, JINR [8] and the element concentrations were determined by conventional relative standardization.

Table 1.
Detection limits obtained at the ENAA analysis of soil and vegetation samples

Soil samples				Vegetation samples			
Au	1 ppb	Sb	0.1 ppm	Au	0.1 ppb	Rb	1 ppm
Ag	2 ppm	Sc	0.1 ppm	Ag	0.2 ppm	Sb	0.005 ppm
As	1 ppm	Se	2 ppm	As	0.01 ppm	Sc	0.01 ppm
Ba	100 ppm	Sr	100 ppm	Ba	5 ppm	Se	0.1 ppm
Br	1 ppm	Ta	0.5 ppm	Br	0.01 ppm	Sr	10 ppm
Ca	0.1 %	Th	0.5 ppm	Ca	0.01 %	Ta	0.05 ppm
Co	1 ppm	U	0.1 ppm	Co	0.1 ppm	Th	0.1 ppm
Cr	1 ppm	W	1 ppm	Cr	0.3 ppm	U	0.01 ppm
Cs	0.5 ppm	Zn	20 ppm	Cs	0.05 ppm	W	0.05 ppm
Fe	0.05 %	La	0.1 ppm	Fe	0.005 %	Zn	2 ppm
Hf	0.5 ppm	Ce	1 ppm	Hf	0.05 ppm	La	0.01 ppm
Hg	0.5 ppm	Nd	3 ppm	Hg	0.05 ppm	Ce	0.1 ppm
Mo	0.5 ppm	Sm	0.1 ppm	Ir	0.1 ppb	Nd	0.3 ppm
Na	100 ppm	Eu	0.2 ppm	Mo	0.05 ppm	Eu	0.05 ppm
Ni	10 ppm	Tb	0.2 ppm	Na	1 ppm	Tb	0.1 ppm
V	1 ppm	Yb	0.1 ppm	Ni	2 ppm	Yb	0.005 ppm
Rb	20 ppm	Lu	0.1 ppm	V	0.5 ppm	Lu	0.001 ppm

Cadmium, copper, lead and mercury were determined by flame atomic absorption spectrometry (FAAS) at the Centre of Environmental Protection from “Politehnica” University. The moss samples of 0.5 g (d. w.) were digested with 6 ml concentrated nitric acid at 120 °C for 6 h. After cooling to room temperature the samples were filtered and distilled water added up to 50 ml.

The reference materials used in analysis were the SRM L-336 lichen, Pine needles, SD-M-2/TM soil and SL-1 sediment (issued by the International Atomic Energy Agency). The detection limits obtained for vegetation and soil samples are presented in Table 1.

3. RESULTS AND DISCUSSION

3.1. Specific pollutant concentrations

To detect the spatial trends of the different atmospheric emission processes, the comparison between the results on V versus Ni in soil and sediment samples and mosses was done (Figs. [2] and [3]).

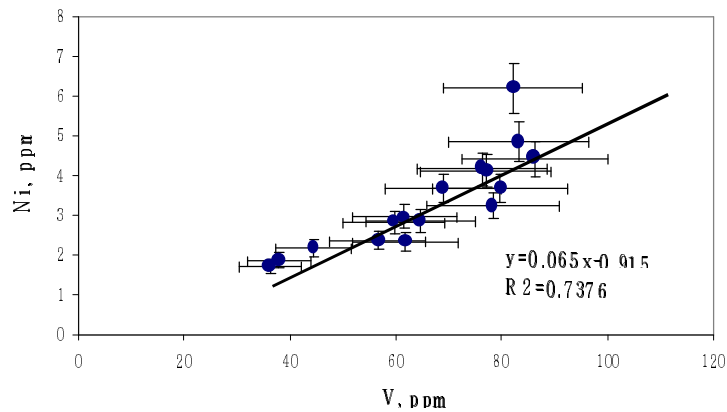


Fig.2 - Ni versus V in soil

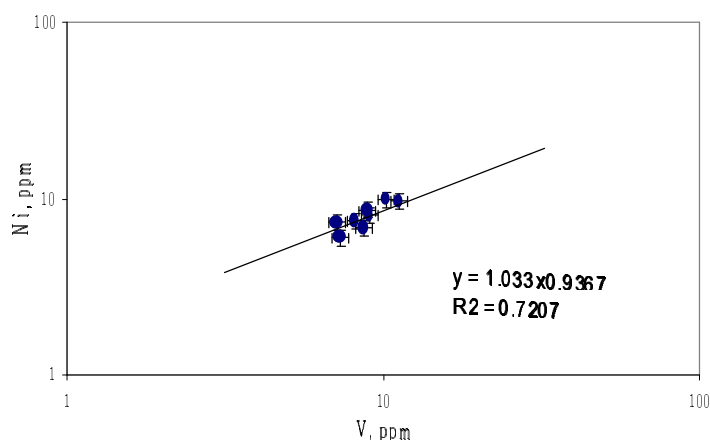


Fig. 3 - Ni versus V in mosses

The log-log diagram of Ni vs V shows the same strong correlation between the two elements in soil and river sediments and mosses. This behaviour confirms the common origin of the mentioned pollutants in petrochemical industry emissions.

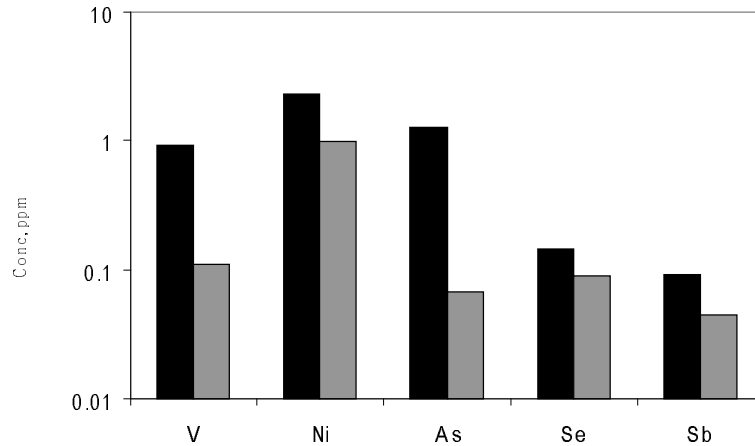


Fig. 4 - The content of specific pollutants at the oil refining plant versus background

The content of air toxics in black poplar leaves released by petrochemical industry was examined at the plant site versus a control sample (Fig. [4]). It can be seen that the V and As content exceed more than 10 times the background value. Ni, Se and Sb content in leaves exceed the background value by a factor of 2. The registered comparative levels plant/background are related with the contamination of vegetation released by oil processing.

3.2. Isodeposition maps

Fig. 5 presents the isodeposition maps for 6 trace elements specific to oil industry emissions. They show somewhat different local deposition patterns, reflecting contributions from sources other than oil burning. V and Ni show quite similar deposition profiles, oriented from NE to SV, pointing two pollution centers. They correspond to 2 significant petrochemical plants in Ploiesti, from which one is located in the northeastern part and the other in south of the town. The rest of the maps indicate at least high values at the above plant sites. As, Cd and Hg maps are quite similar each other and besides the oil burning source they are connected also with coal and oil mining. Lead presents a local distribution pattern situated south of Ploiesti, probably connected with hard oil processing.

It can be deduced from Fig. [5] that specific air pollutant levels released by the petrochemical industry decrease up to regional background levels within a downwind distance of about 20 km from the main polluting sources.

We are planning a further study including the isodeposition maps of human diseases and their geographical patterns according to the atmospheric pollution released by petrochemical industry.

4. CONCLUSIONS

The specific pollutants emitted by petrochemical industry are characterized by high retention capacities of the studied biomonitors. The correlation coefficient of Ni and V in moss is the same with that in soil, i.e. 0.73 ± 0.046 , indicating the same source causing the enrichment of the two elements in the analyzed media, namely the oil industry. The vegetation (poplar leaves) and soil samples present a decreasing of 44% of the specific pollutant levels along the studied profile.

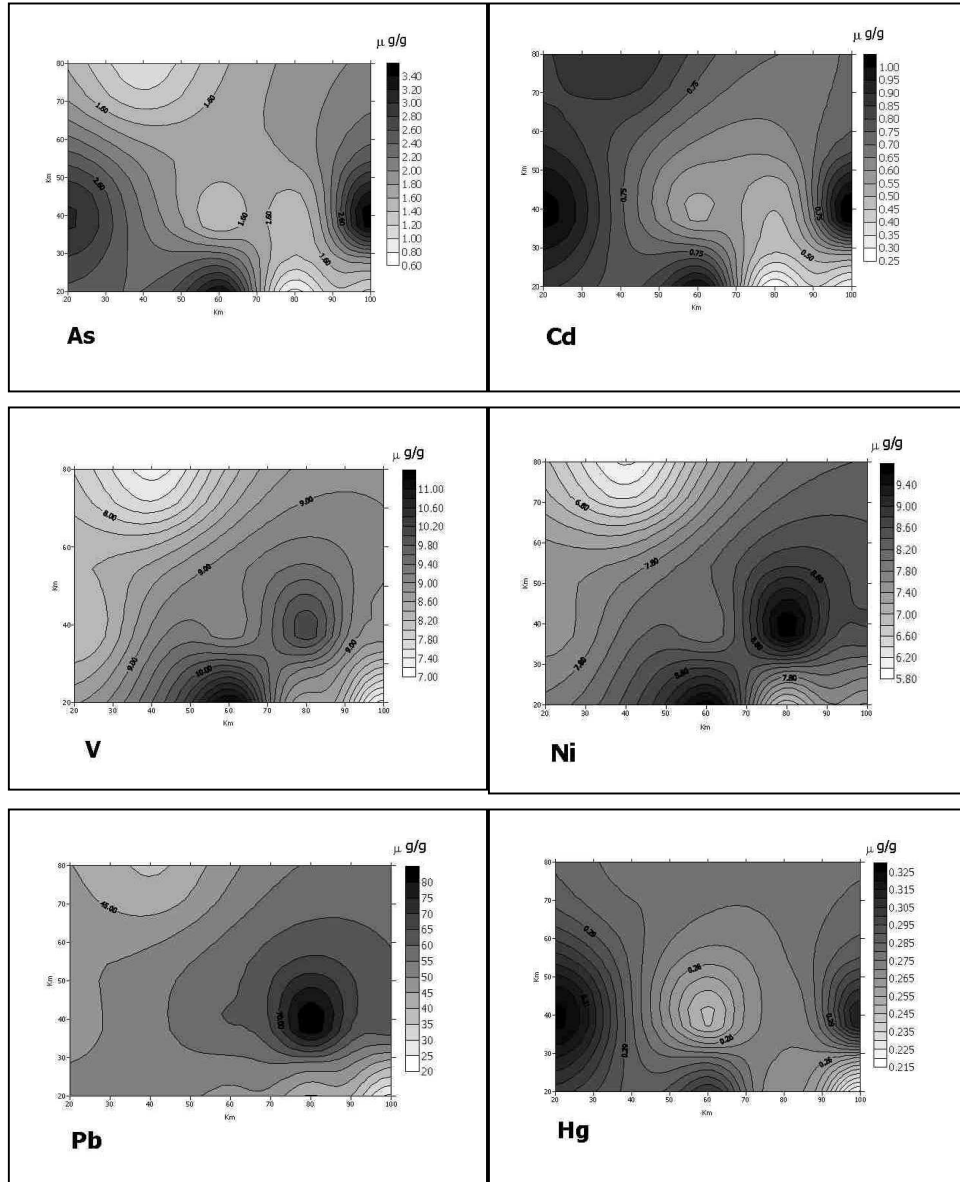


Fig. 5 - Isodeposition maps of specific pollutants in *Hypnum cupressiforme* from the Ploiesti region.

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