



AIR QUALITY AND CHARACTERISTIC SIZE DISTRIBUTION OF ATMOSPHERIC PARTICLES IN MITROVICA - KOSOVA

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SYNOPSIS

The Trepça industrial and mining area includes about 40 mines and various milling, flotation and smelting plant. The principal mining plant is the Zveçan smelter located to the town of Mitrovica. In the period 1930-1950, 825000 t Pb, 566000 t Zn, 1022 t Ag and a similar quantity of Bi were produced. At this time about 20000 miners worked there. In the 1982 a reserves of 50 Mt of ore, with a grade of 5-7% Pb and 4% Zn was estimated. The ore treatment and smelting created huge quantities of mine wastes accumulated in time in imposing dumps close to the Zveçan plant. The activity of the Zveçan smelter was stopped in August 2000 because of the very dangerous emissions in the atmosphere.

Sampling operations occurred in different campaigns carried out in 2004/2005 and 2006/2007. The first sampling campaign was accomplished in Jun 2004. The systematic sampling was based upon a predetermined geometric pattern consisting of a sampling grid constituted by square meshes. The grid spacing, that is the distance between two adjacent nodes along the x and y directions, was fixed at 1 km. The average sampling density was 4 samples / km².

INTRODUCTION

A team of researches of the Department of Environmental Sciences, University of Prishtina, went to Mitrovica in April 2001-2005 to monitor the environmental conditions of the territories of Mitrovica. In order to assess the environmental status, many samples of natural waters, soil, atmospheric particulate matter, cultivated and spontaneous plant species, little invertebrates, etc. were collected. Thousands of chemical analyses were accomplished and the data was properly processed and interpreted, enabling an overall environmental picture of the country and identification of some rather critical situations.

As a matter of facts most industrial activities in Kosovo were performed paying no attention to the possible effects of the emissions on the environment. This has led to severe environmental damages and, in some cases, serious health hazards for the resident population.

Sampling operations occurred in 3 different campaigns carried out in 2002 and 2003. The first sampling campaign was accomplished in June 2002. Soil samples (topsoil) were collected for a first evaluation of the overall environmental situation. The second campaign occurred in November 2002. The bulk of topsoil samples were collected in the whole study area together with associated cultivated plants.

The third and final campaign was performed between February and March 2003. Drill holes, at a depth of 1.5 m, were executed at selected sites in order to obtain a continuous sampling along the soil profile.

On the whole the following samples were collected:

- 452 topsoil samples (fig. 1);
- 70 soil cores collected at 22 selected sites (fig. 2);
- 120 samples of edible plant species among the most commonly cultivated and eaten by local population.

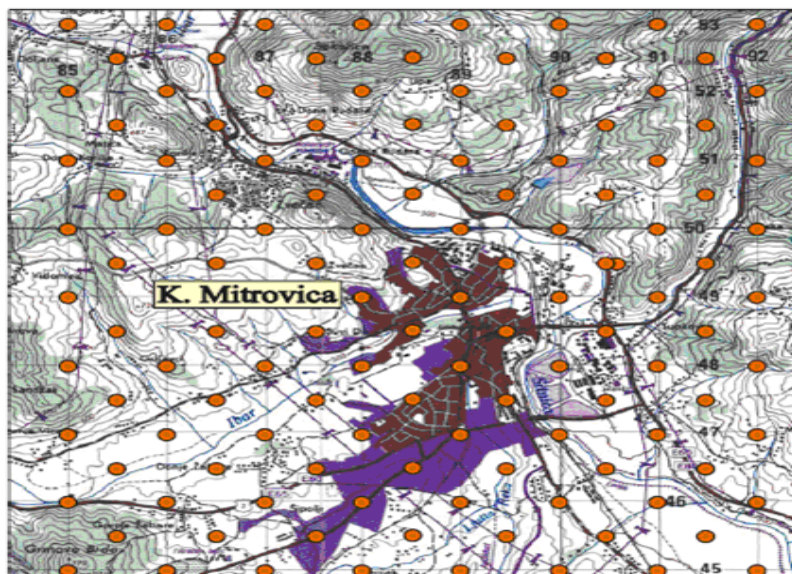


Fig. 1. Sampling grid in Mitrovica

Sampling operations and laboratory treatment of samples were carried out according to the standard procedures defined by the IGCP (International Geological Correlation Program) 259 e 360 (Darnley et al., 1995) and suggested by the FOREGS (Forum of European Geological Surveys; Salminen et al., 1998)

The topsoil samples were collected according to a systematic sampling strategy. The systematic strategy is a popular sampling scheme and is considered the most effective in studying spatially distributed variables (regionalized variables), such as the content of trace elements in soils (Olea, 1984).

The systematic approach was chosen as it does not need a preliminary geochemical knowledge of the area. Besides, it is quite easy to implement and is not affected by executor decisions.

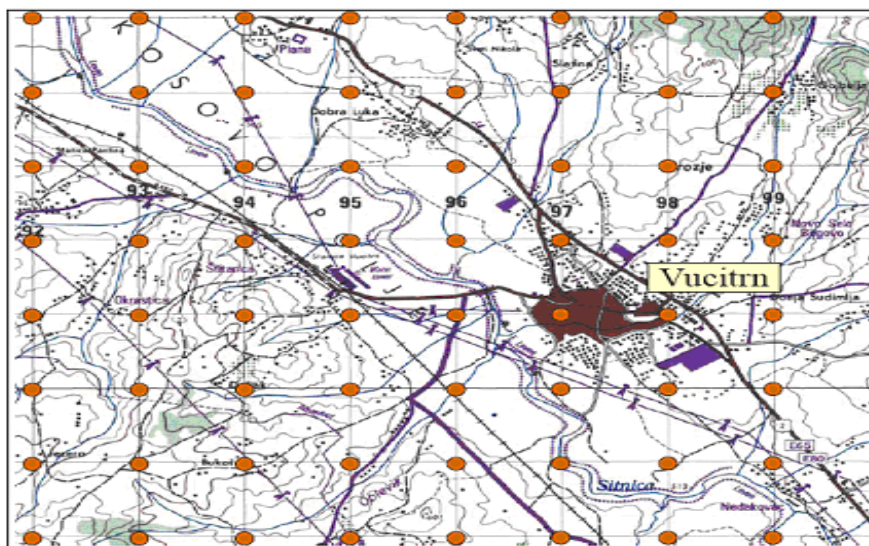


Fig. 2.Part of study area soil sampling

This sampling scheme allowed achieving analytical results of statistical significance and realizing geochemical maps.

The systematic sampling was based upon a predetermined geometric pattern consisting of a sampling grid constituted by square meshes. In this grid the sampling sites coincided with the nodes of the grid (fig. 2). The grid spacing, that is the distance between two adjacent nodes along the x and y directions, was fixed at 1 km.

MATERIALS AND TREATMENT OF SAMPLES IN LABORATORY

Soil samples were dried at constant temperature (40°C) in a ventilated oven. Then the dried samples were manually sieved using a metal-free 2 mm sieve.

The soil fraction < 2 mm was homogenized by quartering and an aliquot of 100 g. was powdered in an agate mortar using mechanical pulverizes.

TECHNIQUES OF SAMPLE DIGESTION

About 0.15 g of powdered soil sample was digested with 2 ml HNO₃, 2 ml HCl, 1 ml HF and 1 ml HClO₄, for 30 minutes in Teflon bombs employing the microwave lab station ETHOS 900 of Milestone. The solution was properly filtered and then analyzed by ICP-MS.

To accomplish the analyses for arsenic, chlorine-free chemical reagents were used. An acid mixture consisting of 2 ml HNO₃, 2 ml HF and 1 ml H₂O₂ (30%) was utilized.

The solutions were filtered and diluted with ultrapure water to a final volume of 100 ml ultrapure grade reagents (Baker and Merck) were used.

ANALYTICAL METHODS

In this study various analytical methods and instruments were employed such as: X-Ray Fluorescence Spectroscopy (XRF), Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Raman Spectrometry, (RS). Here briefly we will deal with the main methods utilized for chemical analysis: XRF and ICP-MS.

The analyses of major (Al₂O₃, CaO, Fe₂O₃ (tot), K₂O, MgO, Na₂O and SiO₂), minor (MnO, P₂O₅, TiO₂) and trace elements (Co, Cr, Cu, Ni, Pb e Zn) in soil samples were performed by XRF using a Philips Mag'X spectrometer. The ICP-MS (Elan 6100 spectrometer of the Perkin Elmer-Sciex) was employed to determine the content of As, Cd, Sb in soil samples and Cr, Co, Ni, Cu, Zn, As, Cd, Sb e Pb in plant samples.

The quality of XRF analyses was checked by the following certified reference materials: BR, DR-N, GH, produced by CNRS (Centre National de la Recherche Scientifique, Notre Dame des Pauvres, France), DTS-1 produced by USGS (United States Geological Survey, Denver, Colorado), NIM-L and GBW 07603 produced by IGGE (Institute of Geophysical and Geochemical Exploration of Langfang, China) and NIST 2709 produced by the National Institute of Standards and Technology (Gaithersburg, Maryland).

The confidence level of the analyses was 68 %.

An estimation of analytical uncertainty of XRF data was performed by measuring 30 times the GSP-2 and AGV-2 standard reference material (USGS). For each element analyzed, mean and standard deviation were calculated by the replicates.

RESULTS AND DISCUSSIONS

Here we comment on the content and distribution of chemical elements of interest (Pb, Zn, Cu, As, Cd, Sb, Cr, Ni, Co) in topsoil of the study area. The comments are to be read in conjunction with the geochemical maps. The maps that appear in the text are schematic summaries of the complete geochemical maps enclosed to the present final report.

| Statistical indices | | Percentiles % | |
|------------------------|----------|-----------------|---------|
| N ^o of data | 452 | 5 ^o | 99.4 |
| | | 10 ^o | 118.8 |
| mean | 972.76 | 20 ^o | 155.1 |
| median | 294.15 | 25 ^o | 179.0 |
| | | 30 ^o | 194.2 |
| min | 49.90 | 40 ^o | 235.6 |
| max | 37122.87 | 50 ^o | 294.2 |
| stand. dev. | 2593.15 | 60 ^o | 401.9 |
| | | 70 ^o | 577.8 |
| lower quartile | 178.98 | 75 ^o | 703.6 |
| upper quartile | 703.58 | 80 ^o | 879.3 |
| | | 90 ^o | 1931.5 |
| skewness | 8.39 | 95 ^o | 3736.4 |
| kurtosis | 95.47 | 98 ^o | 8046.2 |
| | | 99 ^o | 10924.0 |
| Data in mg/kg | | | |

Table 1. Statistical indices and percentiles of lead content in topsoil.

Lead concentrations in the 452 soil samples analyzed were in the wide range 49.9 mg/kg to 37122.9 mg/kg (Table 1), with a mean of 972.8 mg/kg and a significantly lower median (294.1 mg/kg).

The frequency distribution of lead concentrations was lognormal, with accentuated positive asymmetry (skewness = 8.39) and clustering of values between 100 and 250 mg/kg (Fig. 3).

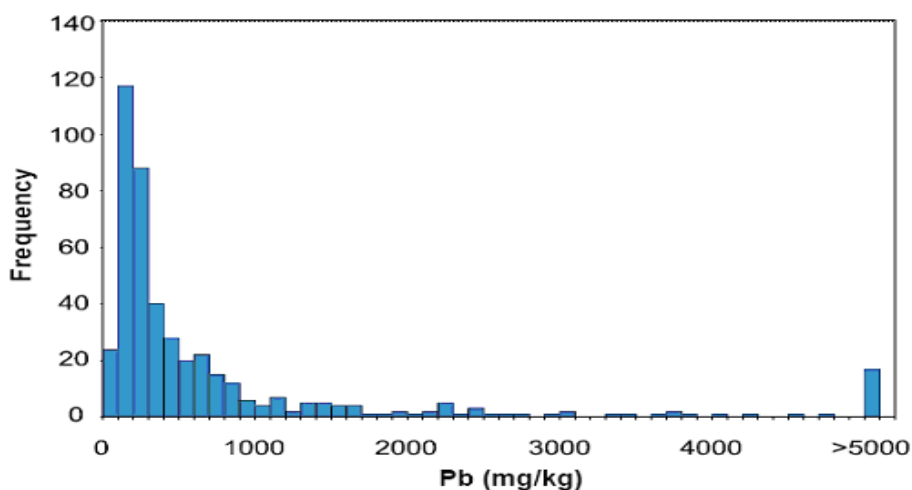


Fig. 3. Frequency distribution of lead concentrations in topsoil

The cumulative frequency distribution showed 25% of analytical values below 179.0 mg/kg (lower quartile or 25th percentile) and a similar percentage of samples above 703.6 mg/kg (upper quartile or 75th percentile).

Analysis of the series of percentiles also showed that only 5% of lead contents in soil were below 100 mg/kg (Table 1) and about 10% exceeded 2000 mg/kg.

Soil concentrations of lead showed a strong positive correlation with other trace elements, such as antimony (coefficient of correlation = 0.92) and copper (c.c.= 0.81), and to a lesser extent arsenic (c.c.= 0.70).

Descriptive statistical analysis of the analytical data suggested the median (294.1 mg/kg) to be a stable index representative of the central tendency of lead concentrations. This indicates a geochemical background of 300 mg/kg for lead in this area, a concentration far exceeding the clarke (average abundance of lead in the continental crust) of the element (12.5 mg/kg; Taylor, 1964) and the baseline level recognized for soil (17 mg/kg; Reimann e de Caritat, 1998).

Lead concentrations of topsoils sampled in the Mitrovica area were constantly above the upper limit for unpolluted soils, namely 50 mg/kg (Shacklette et al., 1971; Fergusson, 1990; Koljonen, 1992).

The highest lead concentrations were found between Mitrovica and Grabovac, where they exceeded 5000 mg/kg and reached a maximum of 37123 mg/kg.

These samples constituted 4% of the analytical data and describe an elliptical hot spot having a NNW-SSE major axis about 5.5 km long. This area surrounds the mine plants of Zvečan and falls almost entirely in the Ibar valley.

Lead concentrations between 1000 and 5000 mg/kg were recorded in topsoil from a vast portion of the study area between Mitrovica, to the south, and the Kamenica area, to the north. These anomalous levels of lead, found in about 14% of the samples analyzed, came from the final tract of the Sitnica valley, near Mitrovica, as well as from a wide portion of the Ibar valley. This anomaly is spatially and genetically related to the mine plants of Zvečan, and extends north of Zvečan in particular. This is probably due to the morphology of the Ibar and Sitnica valleys, which are somewhat different. The Ibar valley, narrow and steep-sided, could channel the Zvecan plant emissions, increasing their range of fallout. Between Mitrovica and Zvecan, the distribution pattern of lead concentrations in soil showed a different gradient on opposite sides of the Ibar valley. On the right side the anomaly extended further than on the left side, where the ridge of the Zvecan castle acts as a barrier that presumably limits atmospheric transport.

Lead concentrations in the interval 500-1000 mg/kg were recorded in 17% of soil samples. These values define anomalous areas with discontinuous distribution from Vucitrn to Sočanica. The largest anomalous areas are in the alluvial plain of the Sitnica River, between Mitrovica and Vučitrn, and the tract of the Ibar valley between Kamenica and Sočanica.

Arsenic content in topsoil's of the Mitrovica area ranged from 4.7 mg/kg to 622.6 mg/kg (Tab. 2), with mean (87.1 mg/kg) about double of median (36.8 mg/kg).

The frequency distribution of analytical data is lognormal with positive asymmetry. About 25% of the arsenic concentrations were below 20 mg/kg and a similar percentage above 95 mg/kg. A relevant part of topsoil samples (approximately 10%) had a total content of arsenic higher than 200 mg/kg, with 1% exceeded 500 mg/kg.

Table 2. Statistical indices and percentiles of arsenic content in topsoil

| <i>Statistical indices</i> | | <i>Percentiles %</i> | |
|------------------------------|--------|----------------------|--------|
| N^o of data | 96 | 5 ^o | 11.23 |
| | | 10 | 14.20 |
| mean | 87.06 | 20 | 17.57 |
| median | 36.84 | 25 | 19.72 |
| | | 30 | 22.06 |
| min | 4.72 | 40 | 30.36 |
| max | 622.56 | 50 | 36.84 |
| stand.dev | 119.37 | 60 | 51.83 |
| | | 70 | 70.43 |
| lower quartile | 19.72 | 75 | 94.42 |
| upper quartile | 94.42 | 80 | 132.46 |
| | | 90 | 218.96 |
| skewness | 2.48 | 95 | 388.73 |
| kurtosis | 6.21 | 98 | 458.47 |
| | | 99 | 506.82 |
| Data in mg/kg | | | |

CONCLUSIONS

To conclude this study, we underline the points emerging from the study and considerations arising from several years of experience in this part of the Balkans.

1. The geochemical study of the soils of the Mitrovica area revealed high and sometimes extremely high contents of toxic heavy metals over a vast area that included the Ibar and Sitnica valleys from Leposavic to Vucitrn.

2. The source of pollution was the Zvecan smelter which was allowed to function without any regard for the environmental consequences of the massive emissions.

3. The main contaminants are lead and cadmium, though significant levels of arsenic and antimony are locally present.

4. The high concentrations of toxic heavy elements recorded in soil means that contaminants are absorbed by plants. Edible parts of plants consumed by humans and animals contain variable and largely unpredictable quantities of toxic heavy elements, in relation to local physicochemical parameters and plant species.

5. Remediation is made simpler and less expensive because of the entity and type of pollution by the current depth of penetration of the contaminants, which is relatively superficial.

6. Problems not considered in this report include remediation of the industrial areas of Zvecan and Mitrovica, the mine dumps and tailings.

7. The state of the area would affect any of our nationals in the area. As long ago as spring 2001, when the possibility of pollution was realized, certain dietary items (e.g. bread) of military personnel in Kosovo were analyzed. The results were always reassuring and immediately communicated to the military command. However, since Italian personnel is working at UNMIK headquarters in Mitrovica, inside the polluted area, they should be adequately informed in order to avoid overexposure from consumption of local produce.

8. Our internal market should also be protected against arrival of products from the polluted area.

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