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COPPER IN SURFACE SOIL OF VELES REGION, MACEDONIA

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A b s t r a c t: For the first time a systematic study of copper distribution in surface soil over of the Veles region, known for its lead and zinc industrial activity, was undertaken. A total of 201 soil samples were collected according to a dense net (0.5 km) in urban and less dense net (1 km) in rural areas. Copper was determined by flame atomic absorption spectrometry (FAAS) using microwave digestion technique with two different types of solvents: aqua regia (HCl and HNO_3) and the mixture of strong acids (HNO_3, HCl, and HF). So far the same soil samples were subjected to reactor non-destructive multi-element instrumental neutron activation analysis (INAA), it served as a reference analytical technique for bulk copper determination. The results obtained by two methods of FAAS and INAA are discussed. **GIS** technology was applied to reveal the areas most affected by copper contamination. It was found that the content of copper in soil samples around the lead and zinc smelter plant is the highest and reaches 1800 mg/kg. Copper content in surface soil all around the town of Veles exceeds maximum permissible level for urban surface soil. Elevated copper content in some rural areas of the Veles region most likely could be explained through using copper containing fungicides for agricultural needs.

Key words: soil; copper; contamination; Veles; Macedonia; microwave digestion; FAAS; INAA

INTRODUCTION

Urban pollution with heavy metals has recently become a subject of many studies (De Miguel et al., 1997; Czarnowska, 1999; Ilyin, 1997; Monaci and Bargagli, 1997; Pietuchova et al.; 1996; Birke and Rauch, 1999; Šajn et al., 1998) including several wide-spread metals such as Ba, Cd, Pb, Cu, Zn, Cr, etc. The regional contamination of soil occurs mainly in industrial regions and within centers of large settlements where factories, motor vehicles and municipal wastes are the most important sources of trace metals (A. Kabata-Pendias, H. Pendias, 2001). Because of heterogeneity and ceaseless changing of urban areas, it is necessary first to understand the natural distribution and the methods for distinguishing man-made anomalies in nature. The natural background itself is variable, which means that higher concentrations of some elements can be normal for one region but anomalous for the other. However, there are cases when the industrial enterprises, especially metallurgical plants, situated near cities can increase the pollution.

There were several investigations of soil, vegetables and fruits produced in the region of Veles but they were mainly concerned with contamination by lead, zinc and cadmium (Stafilov et al., 1994; Jordanovska and Stafilov, 1996; Stafilov and Jordanovska, 1997; Filipovski, 2003). Copper was not determined though it is known that copper minerals are present in lead and zinc ore and concentrates used for the production of Pb and Zn in the smelter plants (World Bank Group, 1998; Manahan, 2000). Copper is an essential micronutrient required in the growth of both plants and animals. Very high concentrations of copper can be toxic causing adverse effects such as injury to red blood cells, injury to lungs, as well as damage to liver and pancreatic functions (Casarett & Doull's Toxicology, 1995). For this reason the goal of this work was to determine the content of copper in the soil from the town of Veles and its surroundings and to assess the size of the area affected by the lead and zinc smelter plant situated near the town.

For the determination of copper, two different analytical techniques were applied: flame atomic absorption spectrometry (FAAS) in the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University in Skopje, and instrumental neutron activation analysis (INAA) at the IBR–2 reactor, FLNP JINR in Dubna, Russia.

EXPERIMENTAL

Study area

The study area is characterized by the biggest pollutant of the town of Veles and the wider region – the Veles lead and zinc smelter established in 1973 located on the River Vardar. The emission of lead and zinc dust that literally covers bigger parts of the town would have been significantly less if the dominant directions of the local winds were considered in the selection of the location. Veles has a specific geographical position. It lies between two major hills, and below the town is the river bed of the Vardar. As a raw material concentrate of ore with a very high content (from 25–50%) of Pb and Zn is used (mainly containing minerals galena, PbS, and sphalerite, ZnS).

Sample collection

Samples of natural surface soil in the town of Veles and surrounding region were collected according to the European guidelines for soil pollution studies (Theocharopoulos, et al., 2001).

The surroundings were sampled on a 1x1 km grid; the town on a 500×500 m; and in the polluted areas on a 250×250 m grid. A total of 201 samples were collected over the area of 33 sq. km (Fig. 1); about 20 samples of this number were collected in the direct vicinity of the plant.

Soil was sampled from the topsoils (0–5 cm). The possible organic horizon was excluded. A sample represents the composite of material collected in the sample point and in four points on 10 m around it towards N, E, S, and W.

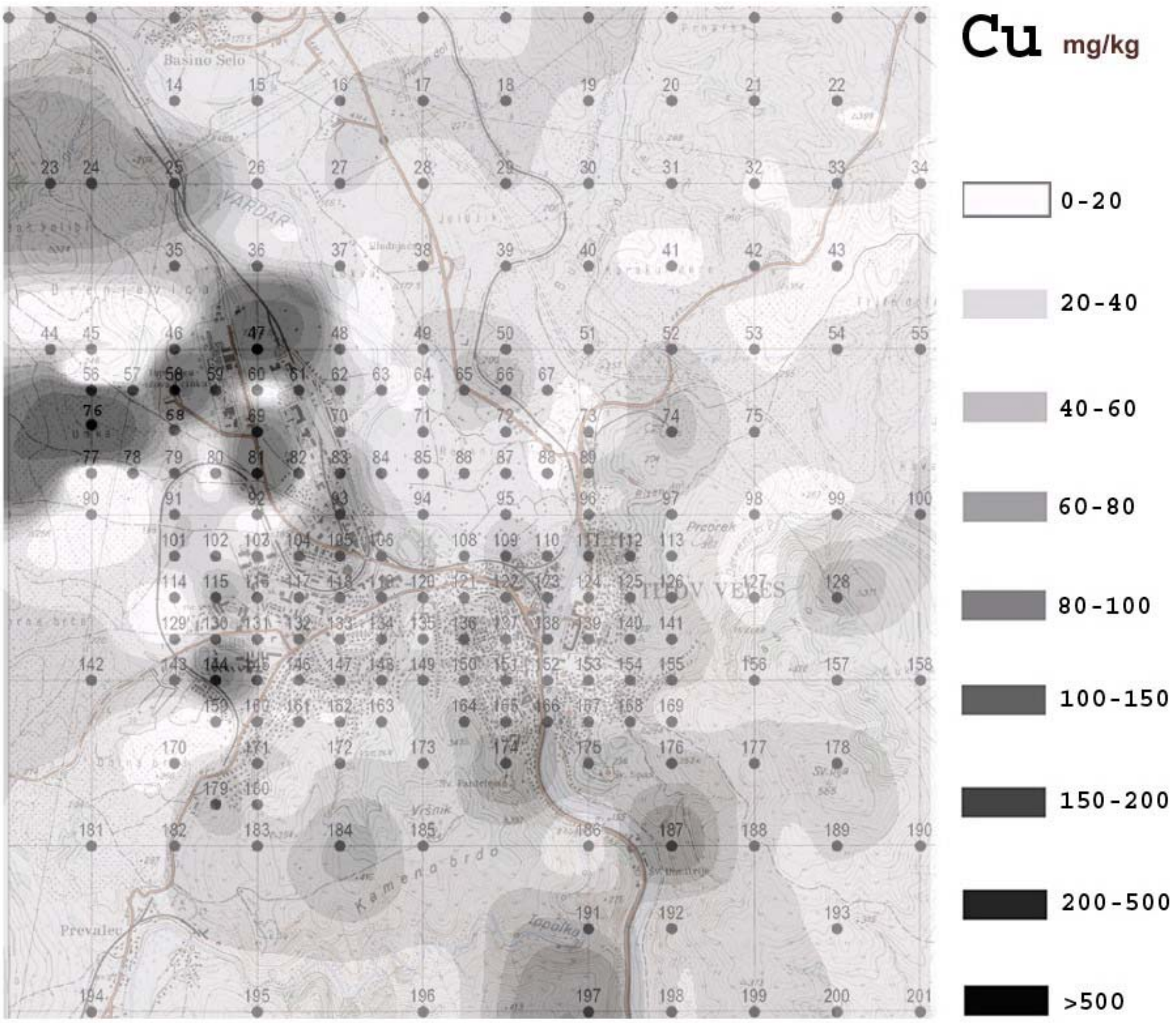

Fig. 1. Distribution map for copper in the Veles region

To provide sample representativity the mass of such composite sample was about 1 kg.

Soil samples were air dried indoors at the room temperature for about two weeks. Then they were gently crushed, cleaned from extraneous material and sifted through a plastic sieve with 2 mm meshes. The sifted mass was quartered and milled in agate mill to an analytical grain size below 0.1 mm (Šajn, 1998).

Sample preparation for the analysis

AAS. Microwave digestion. An Ethos Touch Control pressurized microwave digestion device (Milestone, Italy) with a rotor for 12 Teflon digestion vessels was used. The vessels are equipped with a pressure release system to prevent explosions. A specially designed vessel, which allows a temperature sensor and a pressure sensor to be connected and the progress of the digestion to be monitored, is substituted for one of the 12 vessels.

For AAS soil samples were dissolved by using the microwave digestion system. Soil sample of 0.25 g by weight was placed into PFA vessel and 4.5 ml HCl and 1.5 ml HNO_3 were added for the Method 1. For the Method 2, 4 ml HNO_3, 2.5 ml HCl and 1 ml HF were added to the sample of the same weight. The vessels were closed and placed into a rotor segment, then tightened using a torque wrench and then the segment was inserted into a microwave cavity connecting the temperature and pressure sensors. The conditions for these two programs are given in Table 1.

Table 1

Microwave program for dissolution with aqua regia

Step	Time (min)	Temperature (°C)	Power (W)
		Method 1	
1	10	200	500
2	15	200	500
		Method 2	
1	6	160	500
2	4	210	500
3	20	210	500

Finally the vessels were cooled, carefully opened, and digests were quantitatively transferred into 50 ml calibrated flasks.

All chemical reagents used were of analytical grade. HCl, HNO_3 and HF are p.a. from Alkaloid, Skopje. Stock standard solution for Cu is from Solution Plus Inc. (USA) with a concentration of 1 mg ml^{-1}.

INAA. The same well homogenized soil material was used for don-destructive multi-element INAA. Samples of about 0.100 by weight were sealed in polyethylene bags for short time irradiation in the reactor IBR–2m FLNP JINR, Dubna.

Analysis

FAAS. Copper was determined by flame AAS using Sollar 2 by Thermo Elemental. Instrumental conditions for FAAS determination are given in Table 2.

Table 2

Instrumental parameters for copper determination by FAAS

Parameters	Cu
Wavelength	324.8 nm
Spectral slit	0.5 nm
Lamp current	5 mA
Gas mixture	Acetylene–Air
Background correction	D_2

NAA. In spite of a low detection limit for copper determination in soil (30 mg/kg) by INAA, this reference analytical technique provided data on copper from irradiation of soil samples for determination of short-lived isotopes. After a 60 second irradiation and 5 – 7 minutes delay the activity of ^{64}Cu (half-life time 5 min) was recorded by γ-spectrometry using the 1039 keV line. Further details on irradiation and counting facilities are given elsewhere (Frontasyeva and Steinnes, 1995).

Quality control

The QC of AAS determinations was performed by standard addition method and it was found that the recovery for the investigated elements ranges between 98.5 to 101.2 %.

The QC of NAA results was ensured by simultaneous analysis of the examined samples and reference materials SDM (Soil) and Sl–1 (Bottom sediments) IAEA (International Atomic Energy Agency).

Mapping

The program GRINVEIW from the geographical information system software package GIS–INTEGRO with raster and vector graphics was used to generate raster-based contour map for copper distribution over the entire sampled area.

RESULTS AND DISCUSSION

Copper is relatively abundant in the earth's crust. The amount of copper present in soil is dependent on the parent rock type, distance from natural ore bodies and/or man-made air emission sources. The primary source for the plants is from the soil, but small amounts may result from copper-based fungicides. Although copper concentrations in plants tend to increase with increasing copper concentrations in the soil, soil properties such as the acidity level and organic matter content can affect the amount of copper taken up. Acidification of the soil through the application of certain fertilizers, such as ammonium nitrate or organic materials such as peat moss and pine needles, can increase the uptake of copper into plants.

The content of copper in soil samples varied depending on the type of the soil and the geochemical characterization of the region (Kabata-Pendias and Pendias, 2001). The mean content of copper ranges from 10 – 20 mg kg^{-1} for the most of the soil samples from all over the world to 50 – 60 mg kg^{-1} for some fluvisols or ferrasols (Kabata-Pendias and Pendias, 2001). Contamination of soil by copper compounds results from utilization of copper-containing materials such as fertilizers, sprays, and agricultural or municipal wastes, as well as from industrial emissions. The most important for copper contamination of soils is its great ability of surface soils to accumulate this metal. As a consequence, the copper content in soils has already been built up to the extremely high concentration of about 3500 mg kg^{-1} Cu from industrial sources of pollution and of about 1500 mg kg^{-1} from agricultural origins of the metal (Beavington, 1975; Freedman and Hatchison, 1980; Tchuldziyan and Khinov, 1976; Barcan and Kovnatsky, 1998; Kabata-Pendias and Pendias, 2001).

Therefore, it is very important to follow the content of copper in the regions with metallurgical non–ferrous plants producing metals from sulfidic ores in addition to the content of major pollutant metals. In this work the content of copper in soil samples from the town of Veles and its neighbourhood was determined. Namely, near the town lead and zinc smelter plant is situated and the pollution from lead, zinc and cadmium has been already registered (Filipovski, 2003; Stafilov et al., 1994; Jordanovska and Stafilov, 1996; Stafilov and Jordanovska, 1997).

It was important to verify the possibility of analysis of copper in the samples by their dissolving in the microwave digestion system using two different acid mixtures: aqua regia (nitric and hydrochloric acid) and aqua regia and hydrofluoric acid. If copper is connected more with silicate minerals in the samples, higher values of copper can be expected in the sample solution obtained by dissolutions with acid mixture with HF. The obtained results show that the average content of copper obtained by HF dissolution is 64.86 mg kg^{-1}, while the average obtained by aqua regia dissolution is 61.51 mg kg^{-1} (5.16 % in general). This means that the most part of copper in the soil samples is not connected with silicates but with sulfides, sulfates or oxides (Fig 2).

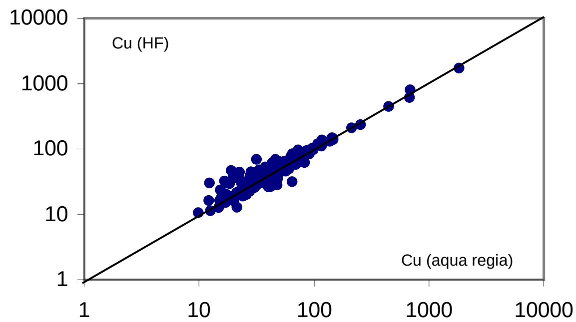

Fig. 2. Comparison of data for copper content (in mg kg^{-1}) obtained by strong acid mixture with HF and with aqua regia

However, some small portions of the sample still cannot be totally dissolved with the acid mixture even using HF. This can be proved by the comparison of the obtained data with neutron activation analysis data and those obtained by FAAS (Fig. 3). The comparison was performed for copper content determined by INAA in 36 samples. (Copper content in the rest of soil samples was at the detection limit or below it.) It can be seen that the bulk copper content determined by INAA is systematically higher than those determined by FAAS.

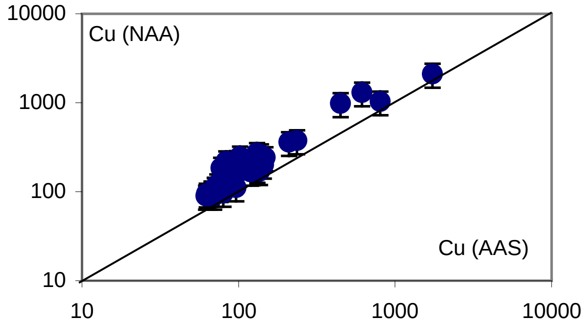

Fig. 3. Comparison of data for copper content (mg kg^{-1}) obtained by INAA *versus* FAAS with strong acids mixture

Copper average content in soil for the whole investigated region of Veles is 49 mg kg^{-1}, while the average content for the surroundings is 33 mg kg^{-1}. Range of copper concentrations is from 10 to 1800 mg/kg. For Veles town the median is 49 mg kg^{-1}, showing that soil in the surroundings of the town of Veles also characterized by relatively high copper content. This is especially important for the soils around the lead and zinc smelter plant were the content of copper in more than 20 soil samples is higher than 100 mg kg^{-1} (in some cases more than 500 mg kg^{-1}) with maximal copper content of 1800 mg/kg in sampling point. Comparing these results with the maximum permissible levels for soil in some European countries (for example, in the Netherlands were the limits is 36 mg kg^{-1}, or Germany with the limit of 50 mg kg^{-1} (Kabata-Pendias and Pendias, 2001) the soils of the large part of Veles region are contaminated with copper.

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Р е з и м е

ЗАСТАПЕНОСТ НА БАКАРОТ ВО ПОВРШИНСКИ ПОЧВИ ОД РЕГИОНОТ НА ВЕЛЕС, МАКЕДОНИЈА

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Клучни зборови: почви; бакар; загадување; Велес; Македонија; микробраново разложување; FAAS; INAA

Извршено е систематско испитување на дистрибуцијата на бакарот во површински почви во регионот на Велес, познат по металуршкиот капацитет за производство на олово и цинк. Собрани се вкупно 201 примерок почви, со густина на мрежата од 0,5 km во урбаната област и со помала густина на мрежата (од 1 km) во руралната област. Бакарот е определуван со пламена атомска апсорпциона спектрометрија (ПААС) со претходна примена на микробранова техника за разложување со две различни смеси од киселини: "царска вода" (HCl и HNO_3) и смеса од силни киселини (HNO_3, HCl и HF). Исто така, примероците од почва се и предмет на испитувања со реакторската недеструктивна мултиелементна инструментална неутронска активациона анализа (ИНАА), која служи како референтна техника за определувањето на бакар. Во трудот се дискутирани резултатите добиени со ПААС и ИНАА. Применета е технологијата GIS за утврдување на загадените области со бакар. Утврдено е дека содржината на бакар во примероците од почва во околината на топилницата за олово и цинк е највисока, достигнувајќи и до 1800 mg kg^{-1}. Содржината на бакарот во почвите околу градот ја надминува максимално дозволената вредност за урбана област (според нормите на некои европски држави). Променливите вредности за содржината на бакар во руралната област на регионот на Велес можат да се објаснат и со примената на заштитни средства во земјоделството.