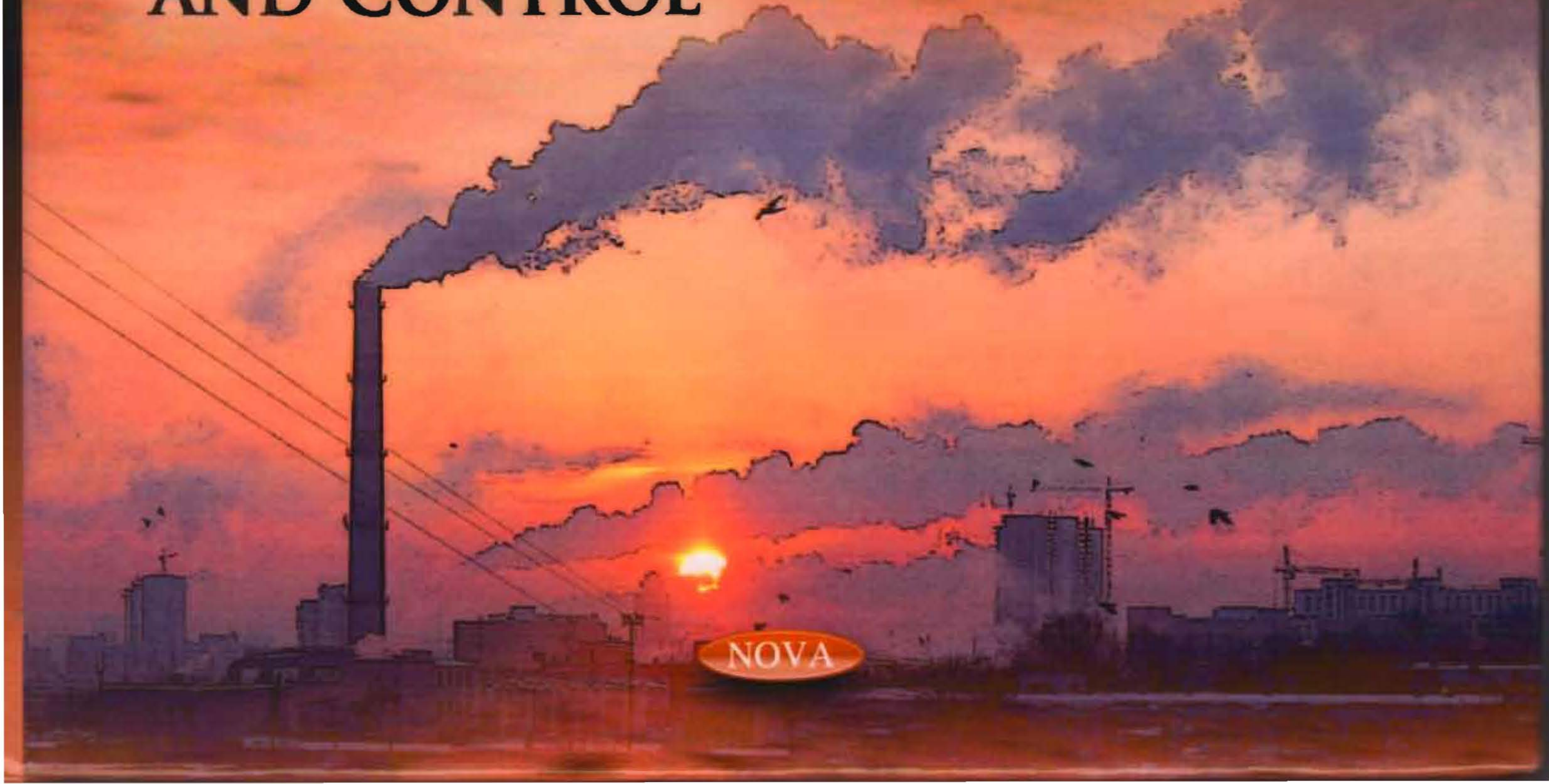
Environmental Health - Physical, Chemical and Biological Factors

LAURENT B. WOUTERS
MICHEL PAUWELS
EDITORS

DUST

SOURCES, ENVIRONMENTAL CONCERNS AND CONTROL



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SOURCES, ENVIRONMENTAL CONCERNS AND CONTROL

LAURENT B. WOUTERS
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Chapter 2

DISTRIBUTION OF HEAVY METALS IN ATTIC AND DEPOSITED DUST IN THE VICINITY OF COPPER ORE PROCESSING AND FERRONICKEL SMELTER PLANTS IN THE REPUBLIC OF MACEDONIA

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ABSTRACT

A comprehensive monitoring was applied to assess the environmental pollution in the Republic of Macedonia. Large amounts of fine dust are generated during blasts and excavations of mining minerals and from highly technological industrial processes, whereas they are distributed in the air by the winds. For that issue characterization of heavy metals content in attic dust and total deposited matter was performed. The significant emission sources that contribute to atmospheric pollution with heavy metals on the territory of the Republic of Macedonia appear to be all mines and smelter plants. In one of the region three collection stations were placed for monthly monitoring of heavy metals content in total deposited dust is near a copper mine in the Radoviš region and the second location is in the vicinity of the smelter plant known for its ferronickel industrial activity in the Kavadarci region. In both locations two most affected villages and the nearest town was monitor within one year. Characterisation of contents showed higher content of heavy metals in deposited dust, which is due to distribution of fine particles from mine and smelter plant respectively, in air and their deposition in settlements in the close vicinity.

Attic dust samples were also used in order to determine and monitor long-term air pollution with heavy metals around the copper mine and the ferronickel smelter plant.

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The total contents of about 20-40 elements were analysed by inductively coupled plasma - mass spectrometry (ICP-MS), inductively coupled plasma - atomic emission spectrometry (ICP-AES) and electrothermal atomic absorption spectrometry (ETAAS). Basic statistical methods and multivariate exploratory (factor and cluster analysis) techniques were applied for data processing. The results of the study of spatial distribution of different trace elements over these regions show some areas with critically high content of some elements. It was found that high contents of those anthropogenic elements are deposited in the close vicinity of the mine and the smelter plant.

Keywords: Air pollution, monitoring, heavy metals, attic dust, total deposited matter, copper mine, ferronickel smelter plant, Republic of Macedonia

1. INTRODUCTION

Heavy metals is the term applied to a large group of trace elements which are both industrially and biologically important. 'Heavy metals' is the most widely recognized and used term for a large group of elements with an atomic density greater than 6 g cm^{-3} (Chittum, 1964). But these elements in high contents are toxic for living organisms. Although not completely satisfactory from a chemical point of view, the term "heavy metals" is often used when speaking about the phenomenon of pollution and toxicity.

Emissions of heavy metals into the environment happen through several processes. The emission of heavy metals into the atmosphere is one of the greatest threats to human health. People are directly exposed to the effects of heavy metals through inhalation of airborne micro particles from atmospheric dust (Jarup, 2003). Atmospheric particles affect to the human health when they enter the respiratory system. Depth of penetration and deposition of particles depends on the size of particle, the defense capabilities of the respiratory tract and the respiratory pattern (Godish, 2004). Exposure to heavy metals is possible if there is a coexistence of heavy metals and people. Exposure is usually defined as a function of the pollutant content and time, i.e., that it is "an appearance achieved by direct contact between humans and the environment with the pollutant content in a given interval of time" (Clarke, 1998; Järup, 2003). The health effects of heavy metals distributed with air-dust depend on their mass concentration and where they are deposited in the respiratory tract. The most exposed group in the population to air particles are children, because the particles penetrate deeper in their lungs as compared to adults because children they breathe deeper and faster, they spend more time outdoor and they are more active. The polluted air slows down the development of pulmonary functions in children (Gauderman et al., 2000; Gauderman et al., 2004). Senior citizens, especially those with a weakened cardiovascular and respiratory system are a high risk group too. Another risk group is patients with chronic pulmonary emphysema, asthma or cardiovascular diseases (Vallero, 2008).

Air pollution with heavy metals is a global process that affects every part of the globe. The contribution of the human factor to this phenomenon is very broad and complex, which leads to feedback processes. Rapid increases of heavy metal concentrations in the atmosphere and environment are commonly coupled to the development of exploitative technologies. This kind of sudden change exposes the biosphere to a risk of destabilization, to organisms that developed under conditions whit low concentrations of metal, present have not developed biochemical pathways capable of detoxifying the metal when it is present at high concentrations. Although the human impact on the biosphere dates back to the Neolithic period, the problems of degradation of ecosystems due to the pollution became increasingly acute during the last decades of the 20th century (Barbante et al., 2004). Atmospheric deposition of heavy metals is the main subject of many studies and usually occurs in industrialized areas, in places where exploitation and processing of natural resources (oil, ore, etc.) are performed, in areas with large population centers where traffic and municipal waste are the main sources of metals, etc. (Athar et al., 1995).

Heavy metals in the atmosphere originated mainly from dust dispersion from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities and stay in the atmosphere until they are removed by a variety of cleansing processes.

Particular emphasis is given on ore deposits, mining, and smelter plants as significant anthropogenic sources of dust. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility's and reactivity's; especially under low-pH condition (Hršak et al., 2003; Avila and Rodrigo, 2004; Hou et al., 2005). They can be carried to places far away from the sources by wind, depending upon whether they are in gaseous form or as particulates. Metallic pollutants are ultimately washed out of the air by rain and deposited on the land.

1.1. Atmospheric Dust

Dust is a generic term used to describe fine particles that are suspended in the atmosphere. Atmospheric particles (alternatively referred to as particulate matter - PM) are tiny particles of solids or liquids suspended in air. These particles vary in size and density. They originate as a result of processes on the surface of the earth and in the atmosphere. They may be either emitted directly into the atmosphere or formed there by chemical reactions (Finlayson-Pitts and Pitts, 2000). Particles may be emitted naturally or have an anthropogenic origin. Therefore, some naturally occurring particulates originate from volcanoes, dust storms, forest and grassland fires, living vegetation and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power and smelter plants, mining, ore processing and various industrial processes also generate significant amounts of aerosols.

The main problem of pollution represents anthropogenic sources; however, natural pollution is not negligible. According to the origin and specific characteristics particles differ in size, mass, density, morphology, chemical composition and have various chemical and physical properties (Godish, 2004; Baron and Willeke, 2005).

According to their properties particles settle out from the atmosphere in matter of minutes if they are small and dense or remains suspended for days, even weeks (depend on weather conditions).

Atmospheric dust particles can be primary or secondary according to their origin and formation process. Primary particles in the air are the result of direct emissions in the atmosphere from different natural or anthropogenic sources. However, secondary particles occur in air as a result of different chemical reactions among particles, gases, H_2O and vapor (Godish, 2004). Emission of primary particles can occur from stationary sources (such as factories, power plants etc.) or from moving vehicle (mobile sources). Also non-point or areas sources are known when the sources represent larger areas (construction sites, large open stockpiles, open-pit mining) (Pacyna et al., 2007).

Therefore dust particles suspended in the atmosphere contain hundreds of different chemical compound due to large number of sources of primary particles, formation of secondary particles in air by atmospheric chemistry, growth of atmospheric particles and sorption of gas phase substances (Godish, 2004).

Chemical composition of particles in air differs and is dependent on origin, production processes and atmospheric history of individual particle. However, the chemical composition of particles is very important and highly variable. The chemical composition of tropospheric particles includes inorganic ions, different metals, elemental carbon, organic compounds and crustal (carbonates and compounds of alkali and rare earth elementals) substances (Vallero, 2008). Therefore wind-blown mineral dust tends to be made of mineral oxides and other material blown from the Earth's crust.

1.2. Dust Deposition

Atmospheric dust (large or coarse particles) has traditionally been considered mainly as a cause of nuisance or of health effects due to secondary pathways following its deposition to the ground. Dust deposition is therefore measured using simple passive devices (dry, wet, sticky sampling devices). However, these methods have some deficiencies due to the aerodynamic characteristics of the sampling gauge.

Wind induced flows around the gauge either prevent the entry of particles into the gauge opening or removes them (after deposition) due to a wind generated circulation inside the gauge (Hall et al., 1993). Due to exposure to various disturbances such measurement are less reliable. The strong dependency of gauge performance on wind speed and particle size leads to unrepresentative sampling results (Hall et al., 1993).

Never the less with some improvements of the measuring device results are indicative and therefore useful. The results of such measurement are expressed in g m^{-2} (or mg m^{-2}) in the unit of time; times of collection are usually different (Čačković et al., 2009). Basic principle of such measurements is gravitational force which is proportional to particle mass and gravitational acceleration and force particle to settle. Deposition is the process by which aerosol particles collect or deposit themselves on solid surfaces and thus decreasing the concentration in the air.

The rate of deposition or the deposition velocity is faster for particles of a large size. Very large particles will settle out quickly through sedimentation (settling) or impaction processes, while Brownian diffusion has the greatest influence on small particles.

According to the process of deposition two different types of deposition exist - dry and wet. Dry deposition is caused by gravitational sedimentation, interception, impaction, diffusion or Brownian motion, turbulence and other processes, such as thermophoresis, diffusiophoresis and electrophoresis.

Wet deposition includes some atmospheric phenomena which scavenge aerosol particles - rain, snow, fog, cloud, dew formation and washout the atmosphere (Godish, 2004; Vallero, 2008). The amount of dust released to atmosphere increases with increasing wind speed, with the handling of powdery materials in the open etc. A similar situation occurs with dust carried away from stockpiles.

1.3. Heavy Metals (Dust) Emission

There are many sources and release mechanisms for dust into the environment. It should be emphasized that mining activities, ore processing and processing of waste are potential emitters of heavy metals in air.

As more important are mining activities on surface excavation of ore due to the large number of direct polluting factors that are difficult to control and manage (Pacyna et al., 2001; Pacyna et al., 2007).

Special emphasis is given to the organization of the pit (road movement of dampers carrying ore waste), waste management (ore and flotation tailings) as well as the frequency of explosions for excavation of mining minerals (Sengupta, 1993). The main sources for releasing the pollutants are the extraction, concentration and separation of waste in the open. The level of the environmental pollution will depend on proper control of anthropogenic activities in the mentioned processes (Repley et al., 1996).

Fine dust generated during blasts and excavation of mining minerals is distributed in air by the winds. Rains also contribute to the erosion processes of opencast surfaces and ore tailings. This effect is known as "natural rinsing" (Dudka et al 1997; Cortes-Maramba et al. 2006). Such erosion processes contribute to the increasing content of metals in air and soil. The increased content of heavy metals in the surface layers of soil are carried by the winds in the atmosphere as fine dust (Agarval, 2009). Environmental concerns also include depositional soil contamination, waste/slag dumps and process chemical pollution. This pollution can also contribute to surface and groundwater pollution. Slag's, dust and fumes are common products in almost all extractive metallurgical operations. Dust and fumes may contain toxic metals in fine particle size and as such are a potential environmental and health hazard.

Such anthropogenic activities of using of natural resources and their processing through appropriate technological processes and waste management are a global problem of environmental pollution. Some of the activities that generate dust with high heavy metals content and disperse it in air include (in no particular order of importance):

- movement of waste to and from the facilities;
- storage of waste (under certain conditions) on the facility;
- the handling and processing of the waste materials (e.g. shredding of green waste, turning of windrows and daily cover);
- wind scouring of waste surfaces.

Vehicles driven on the facility can also have a significant impact through the:

- resuspension of deposited particulates on roadways and hard-standing;
- transport of larger particles on vehicle bodies.

External factors influence the degree to which the release and dispersion take place. Meteorological conditions are important, specially the amount of rain and strength of wind. Facilities that process wastes inside buildings are typically affected less by meteorological conditions than wastes processed in the open air.

1.4. Monitoring of Heavy Metals (Dust) Deposition

Atmospheric deposition poses significant ecological concerns. According to the process of deposition particles can be deposited at the earth's surface in two ways, dry deposition or wet deposition, depending on the phase in which a species strikes the earth's surface and is taken up (Finlayson-Pitts and Pitts, 2000). Dry deposition is characterized by direct transfer of gas phase and particulates from air to ground, vegetation, water bodies and other Earth surfaces. This transfer can occur by sedimentation, impaction, and diffusion to surfaces or in case of plants by physiological uptake. In the absence of precipitation dry deposition plays mayor role in removing pollutants from atmosphere (Finlayson-Pitts and Pitts, 2000). Wet deposition includes rain, snow, fog, cloud, dew formation and washout the atmosphere (Godish, 2004; Vallero, 2008). Rain out therefore means process in the clouds, where the occurrence of droplets on solid particles (condensation nuclei) happened. In such way disposal of pollutants by rain, snow etc. occurs. On the other hand, wash out is the process by which pollutants are removed from the atmosphere by being absorbed in or desorbed on water droplets. If two particles in air collide they tend to adhere to each other due to their attractive surface forces.

a) An alternative approach is to use exposed attic dust, because over long periods of time atmospheric particles can accumulate, providing a record of historical local deposition. The determination of historical emissions is based on the data of heavy metals concentration in the attic dust from different measurement sites of the weight of total monthly air deposit. The main idea behind determining past emissions is that heavy metals characterization of deposited dust on a small area is multiplied by the concentration of the elements in that area, the mass of the polluter which has been transported to the place of interest by air can be determinate. Undisturbed attic dusts are potential archive for atmospherically deposited particles and have been shown to be effective across urban areas and in the vicinity of smelters, mines and other potentially emission sources. These have the additional benefit that they are protected from wash and aqueous alteration that may affect other tips of samples (monitors) over long periods of time. Atmospheric emissions attributed to the extraction stage of mining come mainly from the action of wind on disturbed land and stockpiles of ore and waste material. As a result of these processes in the atmosphere permanently introduces dust (Sengupta, 1993, Reply et al., 1996). Continuous monitoring of the content of heavy metals and other toxic components contained in dust is possible thought implementation of monitoring by using samples of dust from attic beams (Ilacqua et al., 2003, Atriola et al., 2004; Tye et al., 2006). Attic dust is derived primary from external sources through aerosol deposition and as a result of soil dusting, and less than household activities (Šajn, 2003). Usefulness of attic dust as a suitable long-term monitor for determination the status and content in air is proven by numerous studies (Citizel, 1998, 1999; Gosar and Šajn, 2001, 2003; Cyrys et al., 2003; Jefrey et al., 2005; Šajn, 2005, 2006; Žibret, 2008).
b) Deposited matter refers to any dust that falls out of suspension in the atmosphere. Solid and liquid particles or dust that falls out of suspension in the atmosphere can get into the environment and lead to its contamination. Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic

elements introduced into the atmosphere (Tsitouridou et al., 2007; Čačković et al., 2008). Fine powder with a high content of heavy metals is generated as a result of emissions from the processing of ores and metallurgical process and is distributed as a result of wearing the wind. Many investigations have focused on the chemical composition and the content of toxic substances in deposited matter (Morselli et al., 2003; Avila and Rodrigo, 2004; Polkowska et al., 2005; Vike, 2005; Franzaring et al., 2006).

1.5. Study Issue

Monitoring of air pollution has proved as a most useful technique for determining deposition of heavy metals and atmospheric pollution with it's in different geographical areas. The Republic of Macedonia does not deviate from the global framework of air pollution with heavy metals. The results obtained from previous studies on air pollution, suggest that the situation in the Republic of Macedonia is not favorable in terms of air pollution with heavy metals. The main emission sources appear to be power plants, mines, as well as flotation for lead, zinc, copper and metallurgical plants for the production of nickel, steel, lead, zinc and different ferroalloys (Barandovski et al., 2006, 2008; Stafilov et al., 2008, 2010, 2010a, 2010b).

Attic dust and total deposited mater are commonly used as monitors for these purposes. These kind of monitoring programs have been performed as part of a large number of analytical studies for a long time, but their application in recent decades has taken a swing. This is due to the fact that monitoring does not require the use of expensive technical equipment. Analytical results reflect the situation for a long period of time. The monitoring allows analysis of large areas and the types of monitors are chosen according to the analyst and type of analysis.

Within this study a total content of 23 elements was determined (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Ga, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, and Zn) in attic dust, total deposited mater taken from the copper mine and flotation near Radoviš and the deposited dust taken from the ferronickel smelter plant near Kavadarci region. Analyses were performed by the application of atomic emission spectrometry with inductively coupled plasma (ICP-AES) and electrothermal atomic absorption spectrometry (ETAAS) Tables 1 and 2. However for the Kavadarci region samples of attic dust were analysed by the application of mass spectrometry with inductively coupled plasma (ICP-MS). The investigated elements are : Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, Pb, Rb, Sb, Sm, Sr, Tb, Th, Ti, U, V, Yb, Zn and Zr. The optimal instrumental parameters for this technique are given in Table 3.

The obtained values for the content of the elements in investigated samples were statistically processed using statistical software for basic descriptive statistics and bivariate analysis, which showed the correlation of the content of chemical elements in samples; multivariate statistic method was used to reveal the associations of the chemical elements.

Distribution maps for each element have been prepared separately based on the results. Statistically processed data and distribution maps for individual elements make it possible to identify narrow areas with their higher content. With that we can determine the scope of the impact of the work of this mine on increasing the content of heavy metals in air, and the direction of their distribution in the area around the town of Radoviš and the Kavadarci region. This is important because of direct human exposure to these pollutants and adverse effects on their health.

2. STUDY AREA

Research was conducted at two locations in the Republic of Macedonia. In the eastern part of the country the appearance of some metals (Au, Mg, Al, Sc, Ti, V, Cu) in the air is related to the presence of a copper mine and flotation plant, "Bučim", near the town of Radoviš (Balabanova et al., 2009; Stafilov et al., 2010b; Balabanova et al., 2010; Balabanova et al., 2011). This was one of the investigations areas. In this area an influence from the former iron mine, Damjan, has also been determined (Serafimovski et al., 2005).

The other study area is located in the south-central part of the country, where the appearance of some metals (Co, Cr, Fe and Ni) in the air is related to a presence of the ferronickel smelter plant near the city of Kavadarci, (Barandovski et al., 2006; 2008; Stafilov et al., 2008, 2010; Bačeva et al., 2009; 2011). As a result of these anthropogenic activities, increase distribution of certain heavy metals in air and their deposition in the environs were expected.

2.1. Radoviš (Copper Mine Case Study)

The study area is located in the eastern part of the Republic of Macedonia with a surface area of 20 km (W–E) × 20 km (S–N), a total of 400 km^2, limited by the coordinates N: 41°32' – 41°44' and E: 22°15' – 22°30' (Figure 1).

The region is characterised by a moderate continental climate (Lazarevski, 1993). The altitude varies between 350 and 1000 m. The average annual temperature is around 10°C. The average annual rainfall amounts to 563 mm with large variations from year to year. The most frequent winds in the region are those from the west with a frequency of 199 ‰ and speed of 2.7 m s^{-1}, and winds from the east with a frequency of 124 ‰ and speed of 2.0 m s^{-1}.

One of the major emission sources of some metals in the eastern part of the R. Macedonia is Bučim copper mine and flotation, near the town of Radoviš. The mine and plant for the preparation of ore are in function from the late seventies of the last century. Ore excavation is from open pit and the ore tailings are stored in the open, in mine vicinity. The produced copper ore from the mine is processed in the flotation plant; after the flotation of copper minerals, the flotation tailings are separated, disposed of and deposited on a dump site in an adjacent valley near the village Topolnica.

The copper mine Bučim is located in the north-west part of the studied area. The Bučim mine territorially and administratively belongs to the municipality of Radoviš, and is located 14 km from the town. In the close vicinity of the mine there are two settlements, the villages Bučim and Topolnica. Mine activities cover 7 km^2 of total mine surfaces, 4 km^2 for the placement of ore tailings and the rest of the land belongs to the open ore pit and to the plant for ore processing. The main ore contents are: 0.3 % Cu, 0.3 g t^{-1} Au, 1 g t^{-1} Ag, 13 g t^{-1} Mo, and 1–4 % pyrite; the igneous rocks have been altered to clays and micas.

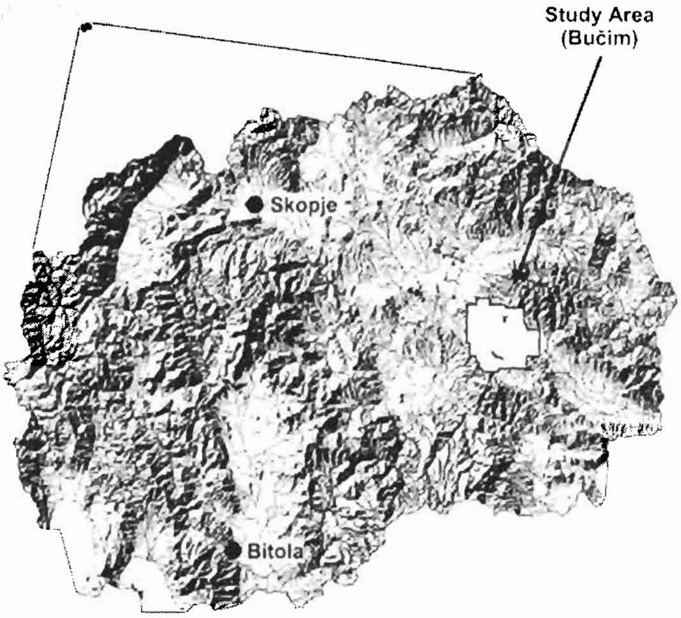

Figure 1. Location of study area of Radoviš region, Republic of Macedonia.

The important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite and hematite (Serafimovski et al., 1995; Stafilov et al., 2010b; Balabanova et al., 2011).

The "Bučim" mine and the ore processing plant have been functioning since 1979 and it is assumed that the mine has about 40 million tons of ore reserves. Ore tailings are dropped out by the dampers from the open ore pit at an open site near the mine. The ore tailings deposit occupies a surface of 0.80 km^2, located southwest of the open ore pit, near the regional road Štip-Strumica. The ore tailings deposit has about 130 million tons of ore tailings. Exposure of this great mass of ore tailings to constant air flow and wind leads to the distribution of fine dust in the air.

The flotation plant produces 4,000,000 tons of copper ore annually. In the process of flotation of copper minerals, the average annual amount of flotation tailings created is approximately 3.95 million tons. These tailings are drained and disposed of on a dump near the mine. The location of this dump is east of the flotation plant, 2.2 km to the dam.

2.1.1. Geological Description

The investigated area represents a part of the Vardar structural zone, separated from the other structural zones during the Caledonian, and subjected to strong tectonic processes, during the Herzynian orogenesis. The structural relations were further complicated by the Alpine orogenesis (Rakićević et al., 1969).

At the study area the following main geotectonic structural units have been identified: (1) the Kriva Lakavica basin (2) the Smrdeš-Gabreš syncline, (3) the Radoviš basin, (4) the Radoviš anticline divided to (4a) the Štip Block and (4b) the Bučim Block (Figure 2). The Radoviš anticline represents the eastern boundary of the Vardar zone towards the Serbian-

Macedonian mass. These two large structural units are separated by a deep NW-SE fault (Hristov et al., 1965).

The Bučim-Damjan-Borov Dol area is divided into two tectonic blocks. The Bučim tectonic block and the southern tectonic block Damjan are a part of the Vardar zone. The blocks are divided by a fault of first order in the SE direction. Despite the disposition in two different tectonic blocks, the metallogenic area is unified based on the similarities of Tertiary magmatism and the analogous ore mineralisations. The Bučim copper-porphyry deposit with additional gold mineralisation is found in the northern block (Stefanova et al., 2004).

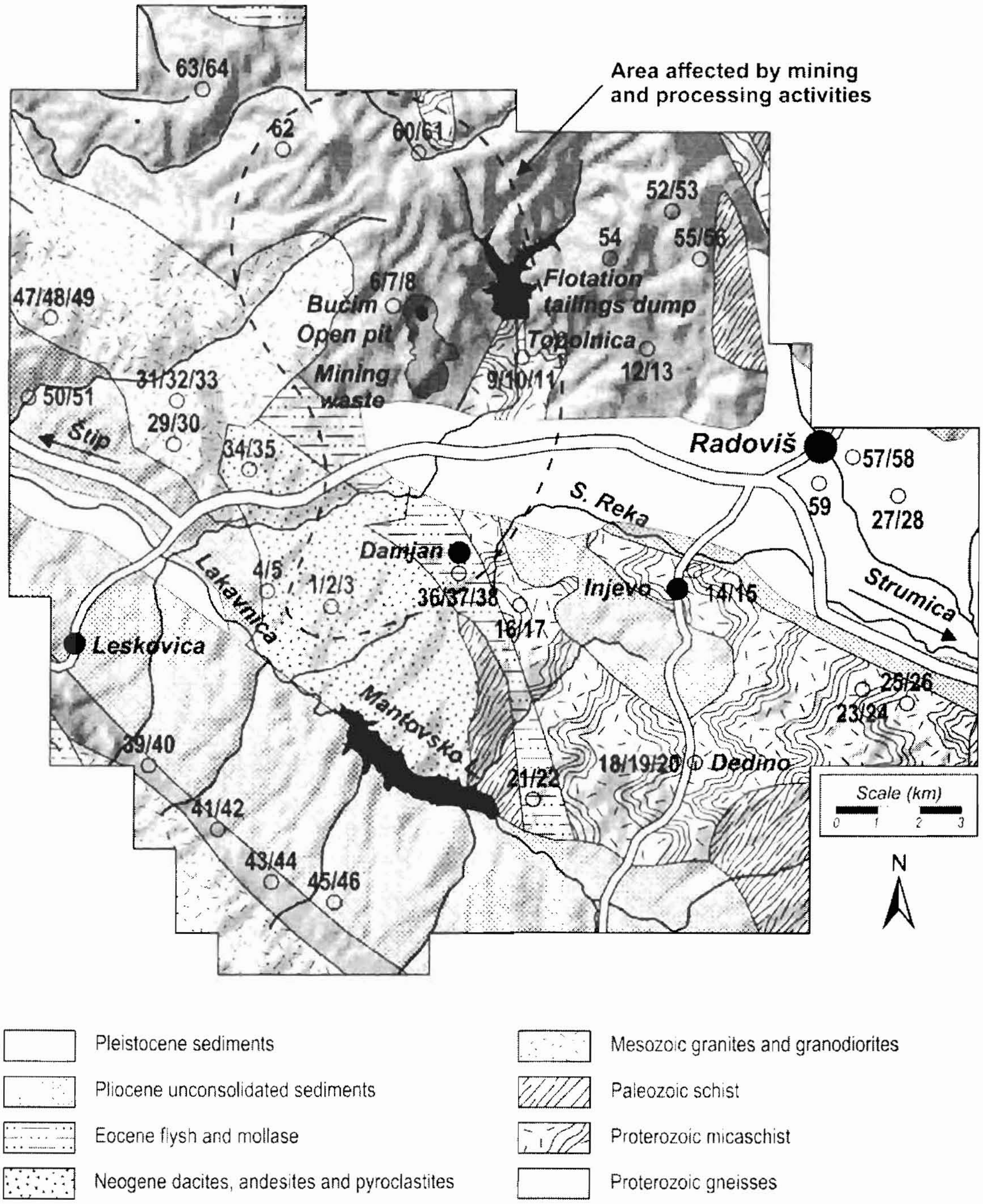

Figure 2. Attic dust sampling network and generalized geological map of Radoviš region.

2.2. Kavadarci (Ferronickel Smelter Plant Case Study)

In the south-central part of the country the appearance of some metals (Co, Cr, Fe and Ni) in the air is related to a presence of the ferronickel smelter plant near the city of Kavadarci, Figure 3 (Barandovski et al., 2006; 2008; Stafilov et al., 2008, 2010; Bačeva et al., 2009; 2011). This smelter plant uses nickel ore from Ržanovo mine, about 30 km south of the plant. In the last 4 years beside ore from Ržanovo mine, ore mainly from Gebe nickel mine, Indonezia reach in nickel (2-2.5 %), is used. It is well known that the nickel ores contain cobalt as well (in average of 0.05 % for Ržanovo ore) (Maksimović, 1982; Boev and Jankovic, 1996). Therefore, the dust from this plant has the similar content like ore used as a raw material including some of the heavy metals like nickel, cobalt and chromium. For that reason, the goal of this work was to determine the total deposition (deposited dust) in the atmosphere in Kavadarci and its surroundings.

2.2.1. Geological Description

The geological description of the investigated area is presented in the Geochemical Atlas of Kavadarci and its Environs (Figure 4) (Stafilov et al., 2008; 2010). The oldest formations have directions NW-SE and belong to the inner parts of the Vardar zone. The Lower Paleozoic (Pz) metamorphic complex is present with two series: amphibole and amphibole chlorite schist with marbles and phylite layers. Serpentinite is present in the form of the narrow belts along the ruptures inside the Vardar zone. The uttermost part in the SW of the study zone is covered with marbles and dolomites probably from Devonian ages. Over the Paleozoic are developed Mesozoic (Mz) formations, mainly form Late Cretaceous ages. Paleozoic and Mesozoic rocks cover approximately 39 km^2 in the SW part of the investigated area.

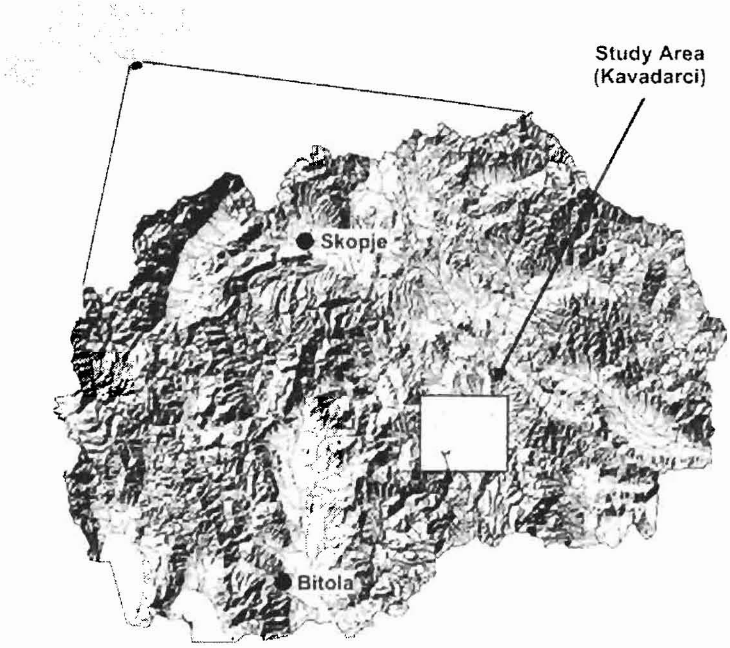

Figure 3. Location of the investigated region of Kavadarci and its environs.

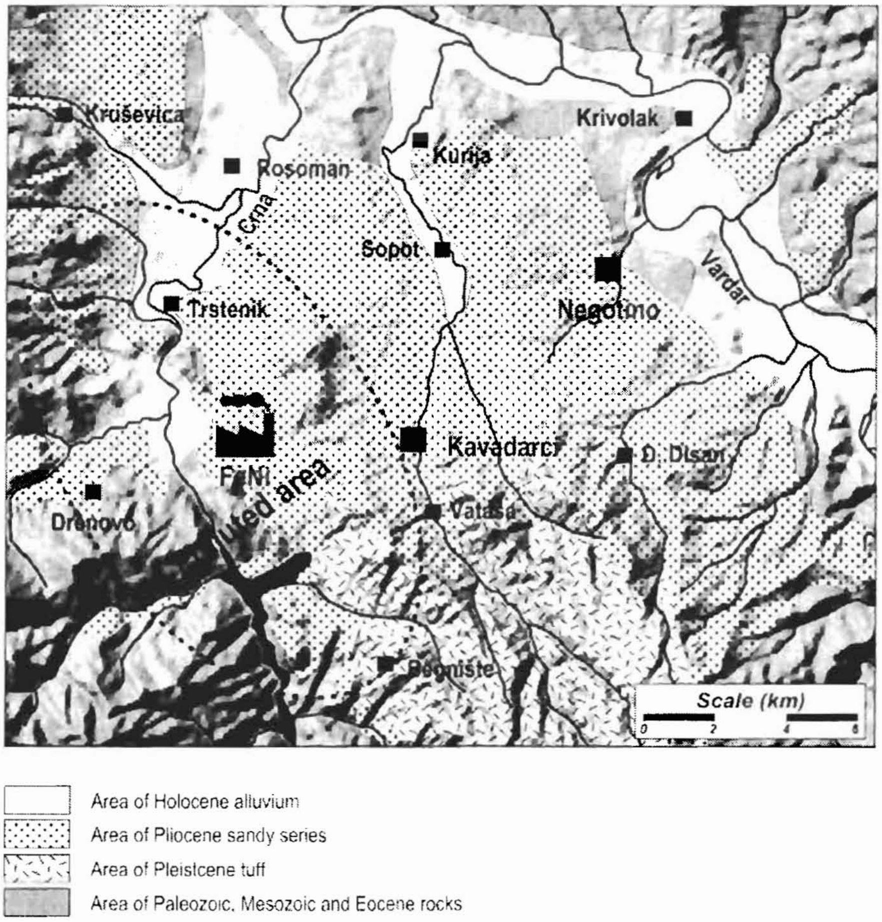

Figure 4. Generalized geological map for the Kavadarci region.

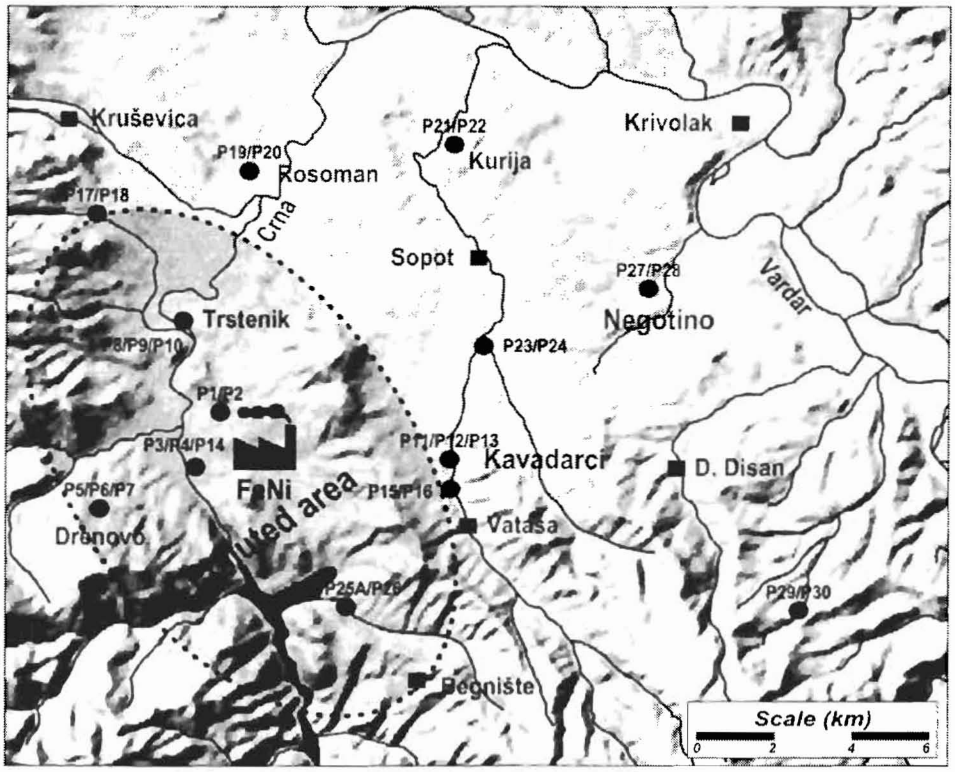

Figure 5. Attic dust sampling network map for the Kavadarci region.

Complexes of Tertiary and Quaternary sediments cover the most of the study area. The Upper Eocene ($^4E_3$) flysch sediments and yellow sandstones are developed along Vardar, Crna Reka and Luda Mara valleys and marginal part of the Tikveš basin. Those sediments with depth up to 3500 m cover approximately 34 km^2 mainly in the N part of investigation area. The Pliocene sediments fill the Tikveš basin, limited with the Vardar on the North, and Paleozoic-Mesozoic formations that have directions NW-SE. This sequence is represented mainly with sandy series. Pliocene (Pl) sediments cover the biggest part (about 182 km^2) in the central part of the investigated area. SE from Kavadarci the Quaternary (Q) pyroclastic vulcanites are found. They're represented by tuffs, breccias and agglomerates and cover approximately 25 km^2.

3. MATERIALS AND METHODS

3.1. Sampling and Sampling Preparation

Attic dust as sampling media - Samples of attic dust were examined as historical archives of smelter and mine emissions, with the aim of elucidating the pathways of pollution. Dust was collected from the attic of 29 houses in the vicinity of copper mine region (Figure 2) and 31 houses from Fe-Ni smelter plant region, built between 1920 and 1970 (Figure 5). In every settlement, attic dust was collecting from 2 or 3 houses on different sites in the setlements. The collection of attic dust samples was performed according to the adopted protocol (Šajn, 2003). Attic dust was collected with plastic brush in polyethylene bags. The surface from the attic timber was throwing across and the finest dust was collected. The size fraction of attic dust smaller than 0.125 mm was prepared by sieving. In that form samples of attic dust samples were ready for digestion. For digestion of attic dust samples, open wet digestion with mixture of acids was applied. Precisely measured mass of dust samples (0.5000 g) was placed in Teflon vessels and 5 ml concentrated nitric acid, HNO_3 was adding, until the brown vapours came out from the vessels. Nitric acid is very suitable oxidant for digestion of environmental samples. For total digestion of inorganic components was added 5-10 ml hydrofluoric acid. When the digest became clear solution, 2 ml of $HClO_4$ was added. Perchloric acid was used for total digestion of organic matter. After 15 min. cooling the vessels, 2 ml of HCl and 5 ml of H_2O were added for total dissolve of metal ions. Finally the vessels were cooled and digests quantitatively transferred to 50 ml calibrated flasks. For this study reagents with analytical grade or better: nitric acid, trace pure (Merck, Germany), hydrofluoric acid, p.a. (Merck, Germany), perchloric acid, p.a. (Merck, Germany), hydrochloric acid, p.a. (Merck, Germany), and redistilled water were used for preparation of all solutions. Standard solutions of metals were prepared by dilution of 1000 mg l^{-1} solutions (11355-ICP multi Element Standard and Merck VI-ICP multi Element Standard).

Total deposited matter as sampling media - In order to determine daily amount of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations (hot spots in the area) where were expected large amounts of deposited dust (Figures 6 and 7). The total quantity of the deposited dust was monitored monthly for a period of one year. Monthly samples of deposited dust were collected at three monitoring sites in copper mine environ from one side, and from Fe-Ni smelter plant environ from other side.

The village Vozarci, village Brušani and town Kavadarci (Figure 6) were monitoring spots around the Fe-Ni smelter plant. The town of Radoviš and the villages Bučim and Topolnica (Figure 7) were the three monitoring spots around Bučim copper mine. Samples of total deposited matter (wet and dry deposition) were collected using the dust deposition gauges. This method measures dust deposition rate and involves the passive deposition and capture of dust within a funnel and plastic container.

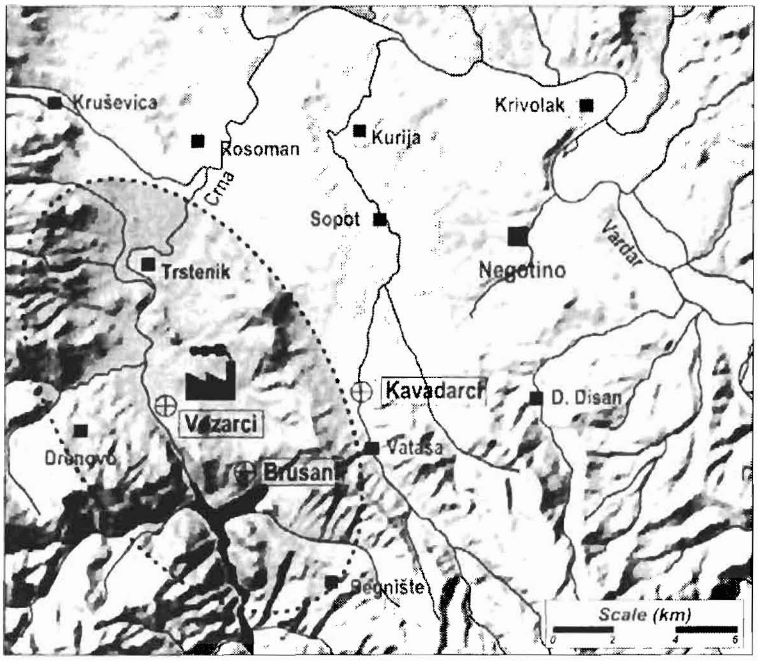

Figure 6. Location of the sampling points for deposited dust for the Kavadarci region.

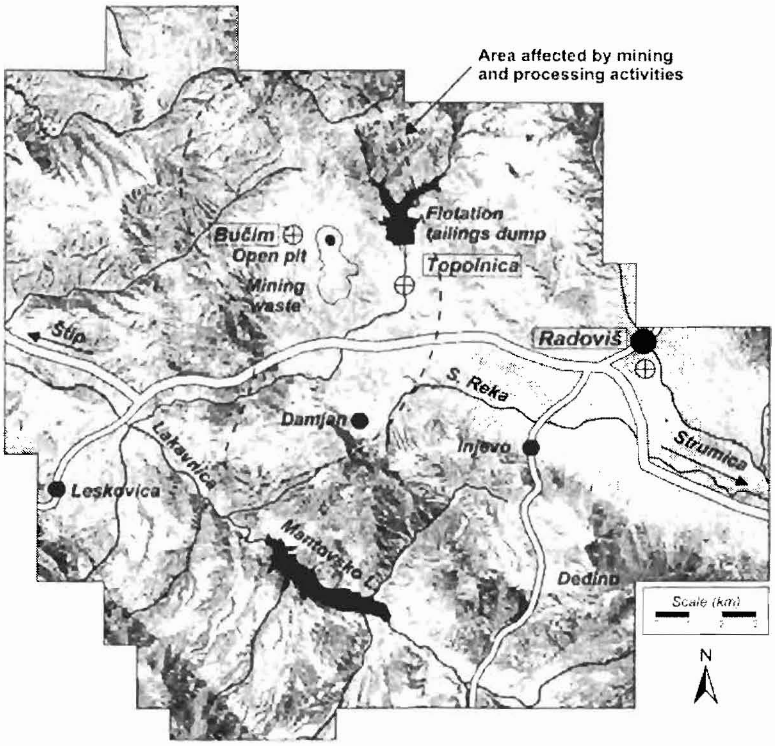

Figure 7. Location of the sampling points for deposited dust for the Radoviš region.

Data is usually collected over monthly periods and results are expressed mg m^{-2} d^{-1} (i.e. the mass of dust deposited per m^2 per day). This method enables determination of the relative 'dustiness' of sampling locations. A deposit gauge, which comprises a 28±1 cm diameter funnel inserted into a plastic container (at least 5-10 liters in size) through a rubber stopper (Holden, 2006). Stand approximately 2 m tall and a canister which holds the plastic container to protect it from sunlight. The plastic container may also collect rainwater and other material such as bugs and leaf litter, etc. This does not contaminate the sample and should not be removed in the field. After 30±2 days, any deposited matter in the funnel was washed into the plastic container using distilled water. The aliquot of each sample was evaporated near dryness and then 3-5 ml of nitric acid, *p.a.* (MERCK, Germany) was added and collected in to the 25 ml volumetric flasks.

3.2. Instrumentation

The investigated elements were analysed by the application of atomic emission spectrometry with inductively coupled plasma (AES-ICP), electrothermal atomic absorption spectrometry (ETAAS) and mass spectrometry with inductively coupled plasma (ICP-MS). The following elements were analyzed: Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, Pb, Rb, Sb, Sm, Sr, Tb, Th, Ti, U, V, Yb, Zn and Zr.

The heavy metals content was determined using ICP-AES, Varian 715-ES, for Al, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V and Zn, and ETAAS determination for As, Cd and Co (Varian SpectrAA-604Z). The optimal instrumental parameters for these techniques are given in Tables 1 and 2. For AES-ICP instrument calibration and quantitative determination of each element in deposited matter, a commercial standard mix solution (11355-ICP Multi Element Standard IV, Merck) was used. The correlation coefficient of calibration curve for each element was 0.999. In order to check for possible background contamination, blank samples were used and processed simultaneously with field samples. The method detection limit was calculated based on average measuring of the blank sample ($\gamma \pm 3\delta$). For all laboratory samples and standard solutions, treated ultra pure water was used. The QC of the applied techniques was performed by standard addition method, and it was found that the recovery for the investigated elements ranges for ICP-AES between 98.5–101.2 % and for ETAAS, between 96.9 % – 103.2 %

For ICP-MS measurements a SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer (with quadruple and single detector setup) was used (Table 3). The instrument's running parameters were checked and adjusted before every batch of measurements, using a solution with 1 $\mu g\ ml^{-1}$ In, 1 $\mu g\ ml^{-1}$ Ce, 10 $\mu g\ ml^{-1}$ Ba and 1 Th and Mg $\mu g\ ml^{-1}$. Oxide levels and double ionized levels were kept under 3%, background for both low and high mass was under 1 cps and all the other parameters were chosen considering the best signal/noise ratio. The dynamic reaction chamber (DRC) was used in RF-only mode (no gas) and its parameters optimization have been optimised elsewhere (Tănăselia et al., 2008). For sample introduction system, a classic set-up was used, consisting in a peristaltic pump, a Meinhard nebuliser and a cyclonic spray chamber, were the fine aerosols are formed that goes directly into plasma. All other reagents were supplied by Merck. 18 MΩ cm^{-1} DI water was prepared in the laboratory, using a Millipore-Milli-Q® ultrapure water purification system.

Table 1. Instrumentation and operating conditions for ICP-AES (Varian 715-ES) system

RF Generator	
Operating frequency	40.68 MHz free-running, air-cooled RF generator.
Power output of RF generator	700–1700 W in 50 W increments
Power output stability	Better than 0.1%
Introduction Area	
Sample Nebulizer	V- groove
Spray Chamber	Double-pass cyclone
Peristaltic pump	0-50 rpm
Plasma configuration	Radially viewed
Spectrometer	
Optical Arrangement	Echelle optical design
Polychromator	400 mm focal length
Echelle grating	94.74 lines/mm
Polychromator purge	0.5 L min^{-1}
Megapixel CCD detector	1.12 million pixels
Wavelength coverage	177 nm to 785 nm

Conditions for program			
RFG Power	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 l min^{-1}	Stabilization time	30 s
Auxiliary Ar flow rate	1.5 l min^{-1}	Rinse time	30 s
Nebulizer Ar flow rate	0.75 l min^{-1}	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

Element	Wavelength, nm	Element	Wavelength, nm	Element	Wavelength, nm
Al	396.152	Cu	324.754	Na	589.592
As	188.980	Fe	238.204	Ni	231.604
Ca	370.602	K	766.491	Pb	220.353
Cd	226.502	Li	670.783	Sr	407.771
Co	238.892	Mg	279.553	V	292.401
Cr	267.716	Mn	257.610	Zn	213.857

All measurements were done using the semiquantitative method (TotalQuant) supplied by Elan 3.4 software that uses a response factor calibration curve which was obtain by a calibration in multiple points, low, medium and high mass, for optimum set-up, using a multi-element Merck VI standard solution, diluted to mimic real sample composition. The drawback is that the accuracy tends to be worse than a proper quantitative method for some elements, however the main advantage is the large mass interval that can be studied (up to 65 elements per each sample during a single run), a good choice for screening type measurements that requires a large throughput of samples with many elements of interest.

For this study, a NIST 2709 and NIST 1643e certified reference materials was used to check method accuracy and for all considered elements, the difference between measured and certified values was within 15%.

Table 2. Optimal instrumental parameters for ETAAS determination by Varian SpectrAA-604Z

Parameter	As	Cd	Co
Wavelength, nm	193.7	288.8	242.5
Spectral width slit, nm	0.2	0.5	0.2
Calibration mode	Peak height		
Lamp current, mA	10.0	4.0	7.0
DRY			
Temperature, °C	120	120	120
Ramp time, s	55	55	55
Hold time, s	-	-	-
PYROLYSIS			
Temperature, °C	1400	250	400
Ramp time, s	10	5	5
Hold time, s	35	15	22
ATOMIZING			
Temperature, °C	2600	1800	2300
Ramp time, s	1	1	1
Hold time, s	2	2	2
CLEANING			
Temperature, °C	2600	1800	2650
Time, s	2	2	5
SHEATH GAS	Argon		

Table 3. Spectrometer's running parameters for ICP-MS

Parameter	Value
Plasma	
Power	1350 W
Plasma gas flow	12.00 l min^{-1}
Auxiliary gas flow	1.20 l min^{-1}
Nebuliser gas flow	1.05 l min^{-1}
Sample/Skimmer cone	Platinum
Quadrupole	
Quadruple rod offset (QRO)	0.00 V
Cell rod offset (CRO)	- 8.00 V
Cell path voltage (CPV)	- 20.00 V
Measurement mode	Peak hopping
Dwell time/ms	Varying
Integration time/ms	Varying
Reading per point	300
Reading per replicate	1
Replicate measurements	4
DRC	
Reaction Gas	None
Lens voltage	11.00 V

The theoretical limit for ICP-MS methods are in ppt (ng l^{-1}) range for the majority of the elements. Matrix effects above 1 ppb (μg l^{-1}) threshold while using TotalQuant were not observed during our study. For some elements, values between these two levels were further investigated using more complex quantitative methods.

Table 4. Lower detection limits of determinations by ETAAS and ICP-AES

Elements	Detection Limit
ETAAS	
Cd, Co	0.1 mg kg^{-1}
As	0.2 mg kg^{-1}
ICP-AES	
Ba, Mo	0.1 mg kg^{-1}
Cu, Mn	0.5 mg kg^{-1}
B, Cr, Ga, Fe, Mg, Ni, Sr, V, Zn	1 mg kg^{-1}
Al, K, Li, Pb	2 mg kg^{-1}
Ag, Na	5 mg kg^{-1}
Ca	10 mg kg^{-1}

Table 5. Lower detection limits of determinations by ICP-MS

Elements	Detection Limit
Hg	0.01 mg kg^{-1}
Ag, Bi, Cd, Ce, Co, Cs, Cu, Dy, Eu, Gd, Ge, Hf, Ho, I, Li, Mo, Nb, Ni, Pb, Rb, Sb, Sm, Tb, Th, Yb, U, Zr	0.1 mg kg^{-1}
As	0.5 mg kg^{-1}
Ba, Be, Cr, Ga, La, Mn, Sr, Zn	1 mg kg^{-1}
V, Lu	2 mg kg^{-1}
Na, Ti	0.001 %
Al, Ca, Fe, K, Mg	0.01 %

3.3. Data Processing

For the statistical analysis of data parametric and nonparametric statistical methods were used (Hollander and Wolfe, 1999). The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics. Data distribution was examined with the application of normality tests.

The application of bivariate statistics showed the correlation between the content of the investigated elements in deposited dust and attic dust samples. In order to analyse this, the linear coefficient of correlation was used, and the absolute values $r > 0.50$ indicated a good association between variables.

Multivariate statistical methods (cluster and R-mode factor analyses) were used to reveal the associations of the chemical elements. The factor analysis was performed on variables standardised to zero mean and unit standard deviation (Reimann et al., 2002; Filzmoser et al., 2005; Šajn, 2006; Žibret and Šajn, 2010). As a measure of similarity between variables, the product-moment correlation coefficient (*r*) was applied. For orthogonal rotation the varimax method was used. In the final multivariate factor solution some elements were retained. The elements with low communalities were excluded because of lack of significant associations.

The universal method kriging with linear variogram interpolation was applied for the construction of spatial distribution maps of each factor score. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100. Line and bar/colon plots were used for better visibility of elements content and trends of dust deposition through the year.

4. RESULTS AND DISCUSSION

4.1. Attic Dust as Sampling Media

4.1.1. Copper Ore Processing Case Study

For each observation there were few variables: sample identification number, locality, geographic coordinates and concentration level for total of 19 elements. Basic statistical analyses were done.

Minima and maxima mean calculation methods of median, geometrical mean, standard deviation, geometric standard deviation, skewness, kurtosis and arithmetical mean were calculated and histograms were drawn to show the distribution features. Based on the normality tests and distribution histograms of the independent variables, the normality for some elements was determined in the distribution of data.

These skewed distributions are confirmed by relatively high values of standard deviation, which is a measure of the degree of data deviation (dispersions) around the mean. On the other hand, significant differences between mean and median value were not obtained for the variables (Table 6).

On the basis of the matrix of correlation coefficients, factor analysis was done. Principal component factor analysis was used to identify and characterise element associations. From 19 analyzed variables, seven elements (Ag, Al, Ba, Fe, K, Na, and Zn), had low factor loading, or tendency to form independent factor and therefore do not belong to any factor group. But these elements generally present as naturally born in environment, so they can be considered as geogenic elements. The matrix of dominant rotated factor loadings is presented in Table 8. Tree factors were identified, two geogenic and one anthropogenic, interpreted as Factor 1, Factor 2 and Factor 3, which including 67 % of variability of treated elements.

Factor 1 (Ca, Li, Mg, Mn and Sr). These elements are naturally found in soil as macro elements (Figure 8). Contents of these elements are variable and are not related to any anthropogenic activities. Their sources are mainly natural phenomena such as rock weathering and chemical processes in soil. Occurrence of this Factor is typical for the oldest formations in the Republic of Macedonia (Proterozoic micaschist and Proterozoic gneisses).

Factor 2 (Co, Cr, Ni) presents geogenic factor (Figure 9). These determined elements are considered as 'natural' because their origin is primarily crustal, soil particles suspended and transported by wind. High factor loadings are related to some old formation as Neogene dacites, andesites and pyroclastites and Pliocene unconsolidate sediments.

Table 6. Descriptive statistics for elements content values in attic dust samples ($n=64$, values are given in mg kg^{-1})

Element	*n*	Dis.	X_a	X_g	Md	Min	Max	P_{10}	P_{90}	s	CV	A	E
Ag	64	log	0.24	0.10	0.05	0.009	1.12	1.09	13.4	0.83	17.8	0.90	-0.62
Al	64	N	11040	10292	10886	1787	21957	6407	16085	3797	34.4	0.26	0.39
As	64	log	11.3	8.34	9.58	1.16	51.6	2.13	18.8	9.29	82.2	-0.29	-1.42
Ba	64	log	4635	361	146	3.95	38676	24.2	21121	10533	227	0.43	-0.83
Ca	64	N	6049	4681	5950	342	18833	1380	10609	3624	59.9	0.79	1.30
Cd	64	log	2.02	1.97	1.98	1.09	3.11	1.39	2.64	0.46	22.8	-0.24	-0.07
Co	64	log	6.26	5.95	5.63	2.42	11.3	4.03	9.95	2.10	33.6	0.19	0.05
Cr	64	log	38.7	34.8	31.1	16.7	110	23.8	78.1	21.3	55.2	1.19	0.80
Cu	64	log	52.1	33.4	26.8	10.9	415	15.5	116	75.8	142	1.51	2.18
Li	64	log	4.82	3.98	4.10	1.20	15.9	1.61	8.72	3.09	64.1	-1.31	1.48
Fe	64	N	11966	10525	13228	1131	18350	5986	16080	4120	34.4	0.10	-0.34
K	64	N	8846	8741	8613	5560	11612	7161	10876	1362	15.4	0.02	-0.79
Mg	64	log	1321	642	715	24.6	5859	94.3	3414	1399	106	-0.43	-0.66
Mn	64	log	211	201	195	113	454	143	302	70.4	33.3	0.40	-0.17
Na	64	log	6846	5024	4784	326	28682	2348	15810	6336	92.5	-0.24	1.95
Ni	64	log	23.1	20.2	17.2	8.94	58.7	11.5	41.4	12.5	54.3	0.43	-1.11
Pb	64	log	28.8	21.4	20.4	3.12	121	7.49	53.3	23.9	83.1	-0.20	-0.07
Sr	64	log	36.1	28.4	32.1	3.64	141	10.3	60.9	25.2	69.8	-0.74	0.92
Zn	64	log	50.9	48.7	49.5	21.4	92.9	34.3	72.9	15.1	29.8	-0.20	0.11

Table 7. Matrix of correlation coefficients

Ag	1.00																		
Al	0.12	1.00																	
As	0.34	-0.11	1.00																
Ba	0.29	-0.21	**0.75**	1.00															
Ca	0.28	-0.19	-0.03	0.28	1.00														
Cd	**0.66**	0.18	-0.17	0.11	0.18	1.00													
Co	**0.67**	0.03	0.33	**0.59**	0.32	**0.76**	1.00												
Cr	**0.52**	-0.09	-0.17	0.02	0.33	**0.67**	**0.64**	1.00											
Cu	-0.01	0.28	-0.06	0.17	0.06	0.26	0.39	-0.11	1.00										
Li	**0.70**	0.09	0.57	**0.57**	0.44	0.29	**0.51**	0.31	-0.23	1.00									
Fe	**0.67**	0.29	-0.10	0.13	0.14	**0.92**	**0.77**	**0.63**	0.36	0.22	1.00								
K	0.24	0.21	-0.12	-0.44	-0.27	-0.02	-0.14	0.24	-0.41	-0.06	0.07	1.00							
Mg	0.42	-0.15	-0.20	0.05	**0.74**	0.45	0.46	**0.72**	-0.18	**0.53**	0.31	0.06	1.00						
Mn	**0.66**	-0.27	0.35	**0.60**	0.30	0.59	**0.78**	**0.57**	-0.08	**0.69**	0.49	-0.14	**0.57**	1.00					
Na	0.12	-0.21	**0.81**	**0.89**	0.09	-0.08	0.43	-0.11	0.13	**0.54**	-0.09	-0.44	-0.04	0.48	1.00				
Ni	0.36	-0.03	-0.28	-0.10	0.05	**0.74**	0.48	0.82	-0.20	0.13	**0.69**	0.12	0.46	0.48	-0.20	1.00			
Pb	0.03	**0.74**	-0.44	-0.19	0.11	0.30	0.08	0.19	0.18	0.08	0.36	0.09	0.18	-0.12	-0.27	0.23	1.00		
Sr	**0.69**	0.13	0.24	0.46	0.20	0.72	**0.70**	0.43	-0.06	**0.72**	**0.66**	-0.08	0.45	**0.83**	0.33	**0.53**	0.19	1.00	
Zn	-0.06	-0.21	0.38	0.59	0.49	-0.16	0.12	-0.18	0.20	0.34	-0.16	-0.77	0.05	0.20	**0.56**	-0.23	-0.21	0.12	1.00
	Ag	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Li	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Zn

Factor 3 (As, Cu, Pb) associates chemical elements that indicate anthropogenic influence in the studying area (Figure 10). This association of elements was expected because of the studying area geology and the open pit mining and flotation activities. The acid drainage rapidly dissolved the elements, providing increasing content in soil. The open ore pit and flotation tailings dam allows direct exposure of the finest ore particles to the atmosphere.

Corpuscle dust from the surface layer of ore body and soil is spread in the atmosphere by the winds, through which is performed atmospheric distribution of these elements in the vicinity of the mine. High loading value for this factor was attempt for Cd (0.47). That is because higher contents from this element introduces to the environment as a result of anthropogenic activity.

Table 8. Matrix of dominant rotated factor loadings (F>0.60)

	F1	F2	F3	Com
As	-0.08	-0.06	**0.78**	62
Ca	**0.80**	-0.03	-0.09	70
Cd	0.27	0.51	0.47	67
Co	0.04	**0.89**	0.09	89
Cr	-0.07	**0.90**	-0.23	89
Cu	-0.18	-0.07	**0.70**	57
Li	**0.81**	-0.18	0.04	80
Mg	**0.78**	0.21	-0.22	79
Mn	**0.76**	0.34	0.11	80
Ni	0.19	**0.85**	0.04	65
Pb	0.27	0.09	**0.70**	81
Sr	**0.72**	0.11	0.19	66
Var	31.26	19.38	16.33	66.98

F1, F2, F3-Factor loading; Var-Variance (%); Com-Communality (%).

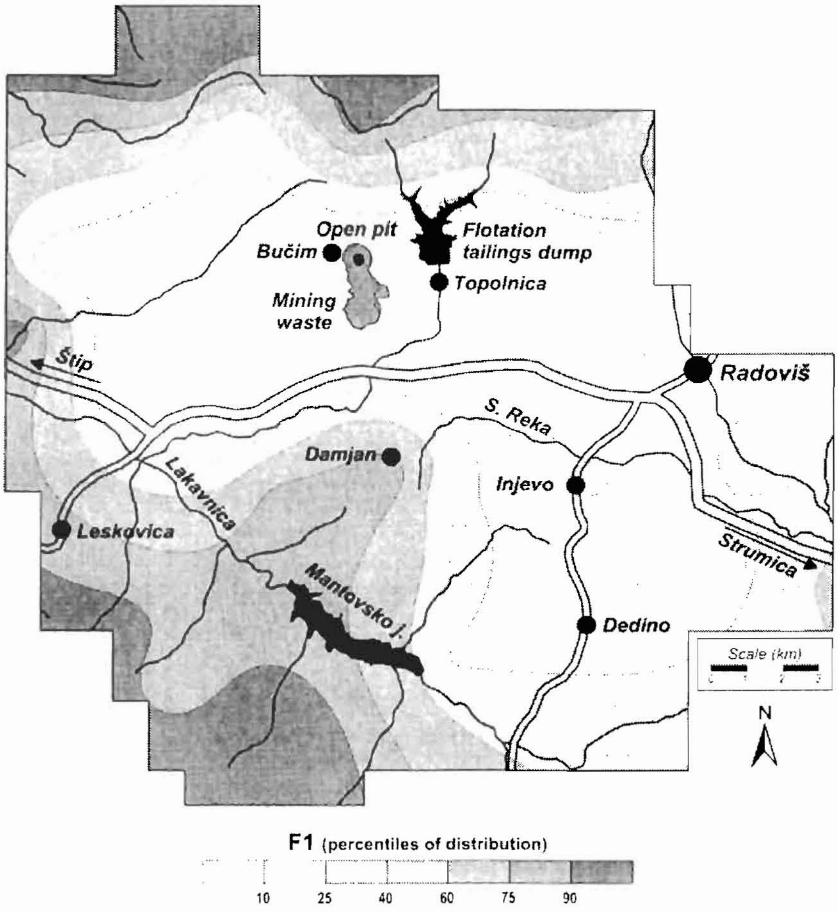

Figure 8. Spatial distribution of Factor 1 scores (Ca, Li, Mg, Mn, Sr) in attic dust samples.

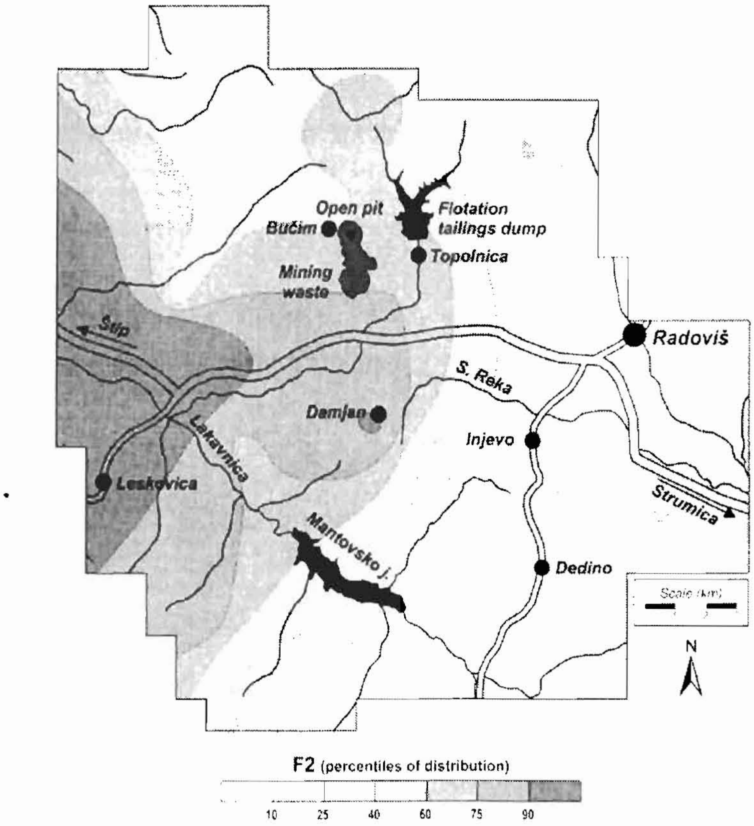

Figure 9. Spatial distribution of Factor 2 scores (Co, Cr, Ni) in attic dust samples.

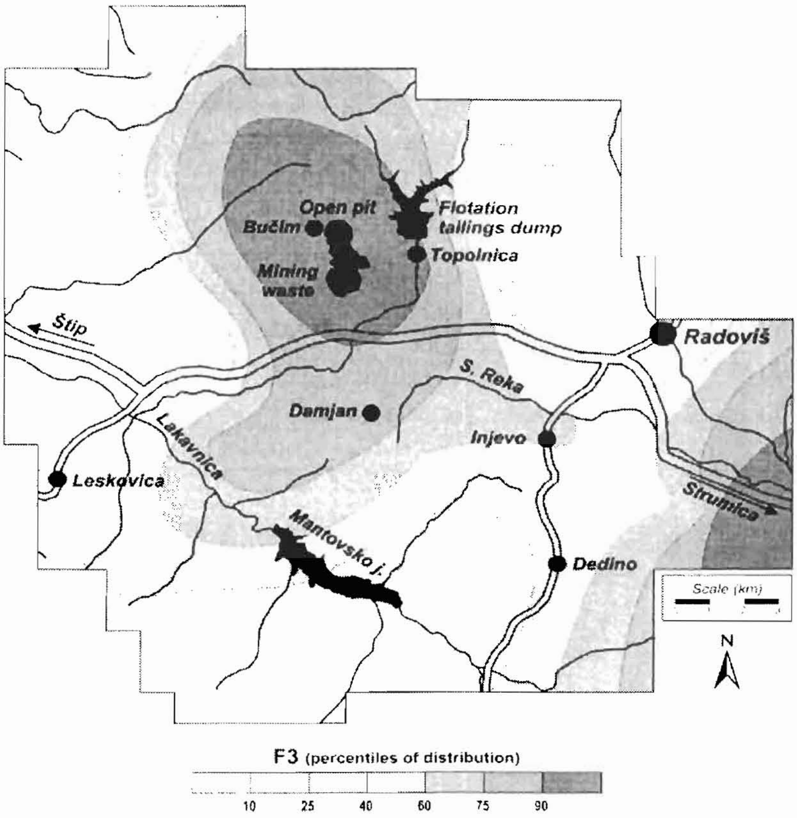

Figure 10. Spatial distribution of Factor 3 scores (As, Cd, Cu, Pb) in attic dust samples.

Urban elements and those related with mine activities, in dust are associated with fine particles, which are preferentially mobilized by wind and trapped in attics, and because old attics have had the longest time to collect this material (Miguel, et al. 1999).

4.1.2. Ferronickel Smelter Plant Case

The descriptive statistics of analysed elements are shown in Table 9 along with the results of 46 chemical elements (Ag, As, Al, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, K, Mg, Na, Ti, Dy, Eu, Ga, Gd, Ge, Hf, Hg, Ho, I, La, Li, Lu, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Sm, Sr, Tb, Th, U, V, Yb, Zn and Zr) in 31 samples of attic dust. Values of Al, Ca, Fe, K, Mg, Na and Ti are given in % and remaining elements in mg kg^{-1}.

The distributions of most of the elements in attic dust samples are closely dependent on the lithogenesis and are slightly affected by anthropogenic activities. Thus, the highest contents for Ba, La, Th and U were found in areas of the Pleistocene tuff, Holocene alluvium (W of the town of Kavadarci) and Holocene alluvium of the river Luda Mara, and their lowest values in areas of the Eocene upper flysch zone and Paleozoic and Mesozoic rocks (Stafilov et al., 2008).

Anthropogenic distribution represents the pollution when trace elements are introduced into the environment through human activities. In the case of anthropogenically produced trace elements, they concentrations can increase several times compared to the background that consists of minor elemental fluctuations. The ferronickel smelter plant uses ore that contains between 1 % and 2.5 % Ni, about 0.05 % Co, 1-3 % Cr etc. Therefore, we expect these elements to have significantly higher contents in samples of attic dust compared to the other elements.

As it can be seen from the data presented in Table 9, the median value of nickel in samples of attic dust taken from the Kavadarci area is 220 mg kg^{-1}. However, the range of values shows a high content of nickel in the samples taken from the vicinity of the ferronickel smelter plant ranges from 89 to 1200 mg kg^{-1} (Figure 11). Cobalt and chromium results show significantly higher contents in the samples of attic dust taken from the Kavadarci area, as well (Figs. 12 and 13). The median value for Co in attic dust samples taken from the studied area is 17 mg kg^{-1} (ranges from 10 to 52 mg kg^{-1}), and the median value for Cr is 140 mg kg^{-1} (ranges from 72 to 510 mg kg^{-1}). For the remaining elements there are no such significant distortions in the distribution of values.

These findings were confirmed also by the application of continuous probability distribution and enrichment ratio for the attic dust samples studied (Table 10). According to the sampling locations, attic dust samples from the polluted areas around the ferronickel smelter plant (14 samples) are compared with corresponding data with the rest of the samples of the investigated region (unpolluted area, 17 samples).

Based on the values of the data in Tables 9-10 it can be seen that the averages for samples that are around ferronickel smelter plant (polluted area) for Co, Cr, Mo and Ni are separated by significantly higher contents of these elements, in the values for averages in the rest (unpolluted area) of the samples of the investigated region.

Samples around the ferronickel smelter plant are characterised with the highest contents of those elements. Thus, the average value for the content of nickel in attic dust samples from the polluted area is 354 mg kg^{-1} and from the unpolluted area is 156 mg kg^{-1}, having an enrichment ratio of 2.27. Distribution maps for Ni, Co and Cr are presented in Figures 11–13.

Table 9. Descriptive statistic of chemical analyses of attic dust samples from Kavadarci area (*n* = 31, 46 elements) Average values of Al, Ca, Fe, K, Mg, Na and Ti are in %, remaining elements in mg kg^{-1}

Element	N	Dis	X, Xg	Md	P_{10}	P_{90}	Min	Max	A	E
Al	31	Log	2.5	2.6	1.4	3.5	0.58	7.5	-1.25	3.23
Ca	31	N	2.9	3.0	1.8	3.5	1.2	3.8	-0.99	0.64
Fe	31	N	3.7	3.5	2.4	4.9	0.53	6.5	0.43	1.79
K	31	Log	1.3	1.3	1.1	1.5	0.83	2.0	-0.39	1.88
Mg	31	N	0.44	0.45	0.17	0.74	0.10	0.83	0.13	-1.25
Na	31	N	0.84	0.84	0.41	1.3	0.20	1.9	0.62	1.61
Ti	31	N	0.38	0.38	0.32	0.46	0.019	0.58	-1.59	6.63
Ag	31	Log	2.7	2.3	1.4	6.7	1.1	9.0	0.62	-0.85
As	31	Log	18	16	11	31	4.7	190	1.68	4.56
Ba	31	Log	320	350	210	460	36	1800	-1.16	7.81
Be	31	Log	2.4	2.5	1.7	3.3	1.3	5.6	0.31	1.47
Bi	31	N	3.7	3.4	1.8	5.7	0.77	7.6	0.39	-0.28
Cd	31	Log	8.6	8.2	6.1	14	3.8	16	-0.14	0.10
Ce	31	N	38	39	17	54	3.8	99	0.96	4.15
Co	31	Log	18	17	13	29	10	52	1.05	1.18
Cr	31	Log	140	140	81	290	72	510	0.85	0.37
Cs	31	Log	1.4	1.4	0.71	2.9	0.35	5.5	-0.01	0.06
Cu	31	N	50	52	40	64	32	66	-0.09	-0.68
Dy	31	N	2.3	2.5	0.32	3.4	0.15	5.5	0.02	1.06
Eu	31	N	0.90	0.90	0.30	1.2	0.15	1.7	0.03	1.28
Ga	31	N	15	15	12	18	0.69	32	0.81	7.46
Gd	31	N	3.4	3.6	0.55	4.6	0.23	8.4	0.24	2.25
Ge	31	N	0.96	1.0	0.28	1.7	0.010	2.2	0.30	-0.95
Hf	31	N	1.0	0.89	0.47	1.8	0.030	2.4	0.74	-0.07
Hg	31	Log	0.093	0.18	0.005	0.60	0.005	4.6	-0.38	-1.17
Ho	31	N	0.44	0.45	0.090	0.66	0.030	1.0	-0.03	0.91
I	31	N	0.47	0.40	0.13	1.1	0.020	1.2	0.98	0.44
La	31	N	17	17	3.6	25	0.90	49	1.07	4.59
Li	31	N	16	17	12	21	12	22	0.32	-0.91
Lu	31	N	0.15	0.15	0.040	0.23	0.010	0.34	0.25	0.35
Mn	31	N	510	500	450	650	410	680	0.93	0.19
Mo	31	Log	3.0	4.0	0.99	6.5	0.23	21	-0.79	0.96
Nb	31	N	14	14	9.3	18	0.17	27	0.11	4.01
Ni	31	Log	230	220	110	560	89	1200	0.63	-0.22
Pb	31	Log	180	180	110	310	66	390	-0.33	0.11
Rb	31	N	56	52	34	81	11	130	1.11	3.29
Sb	31	Log	2.4	2.3	1.6	4.1	1.0	5.2	-0.04	-0.37
Sm	31	N	3.1	3.2	0.61	4.2	0.13	7.0	-0.09	1.41
Sr	31	N	170	160	110	210	51	230	-0.68	0.64
Tb	31	N	0.45	0.46	0.080	0.65	0.020	1.1	0.16	1.66
Th	31	Log	5.3	7.0	0.79	17	0.26	25	-1.05	0.81
U	31	Log	3.4	3.4	2.2	8.6	0.54	12	-0.44	3.16
V	31	N	110	100	63	170	9.8	200	0.16	-0.14
Yb	31	N	1.0	1.1	0.20	1.4	0.040	2.5	0.12	1.55
Zn	31	Log	350	350	260	510	230	600	0.24	-0.57
Zr	31	N	46	40	15	70	0.47	160	1.78	4.14

Data round at two digits; Dis. – distribution (Log - lognormal); X – mean; Xg – geometric mean; Md – median; P_{10} and P_{90} – percentile; Min - minimum; Max – maximum; A – skewness; E – kurtosis.

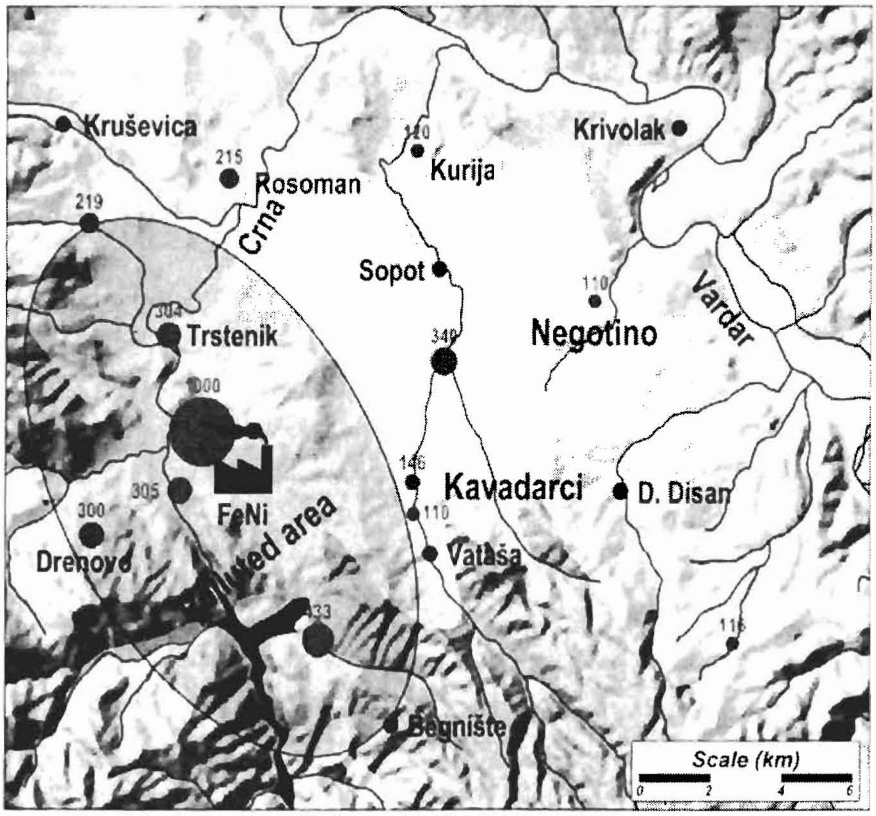

Figure 11. Distribution of Ni in attic dust samples (in mg kg^{-1}).

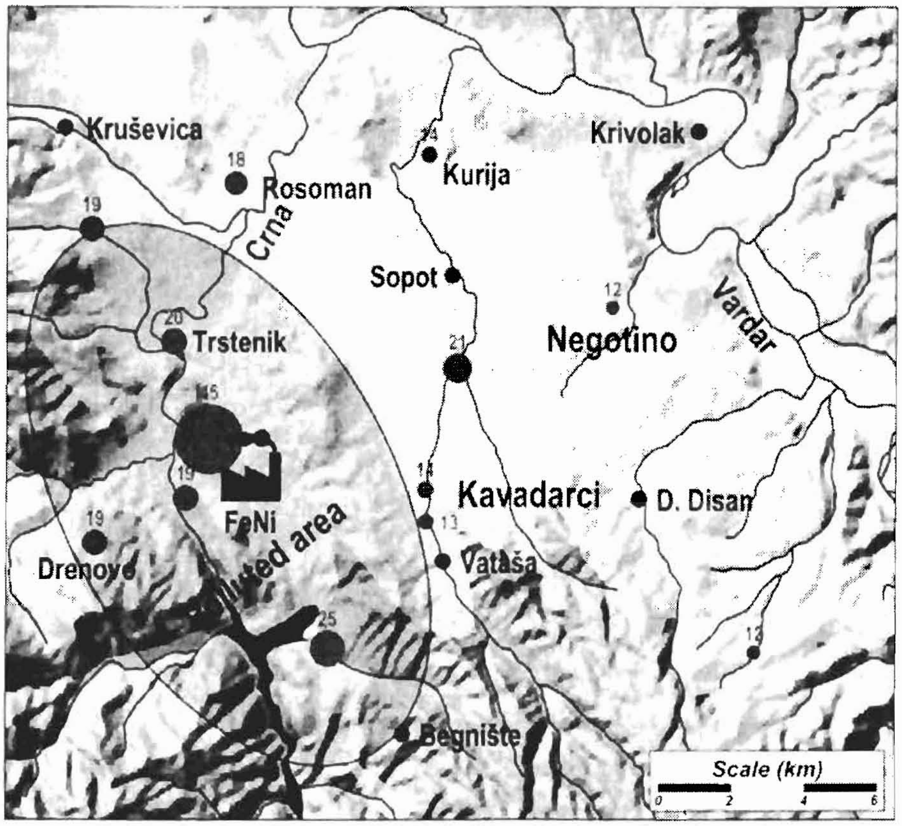

Figure 12. Distribution of Co in attic dust samples (in mg kg^{-1}).

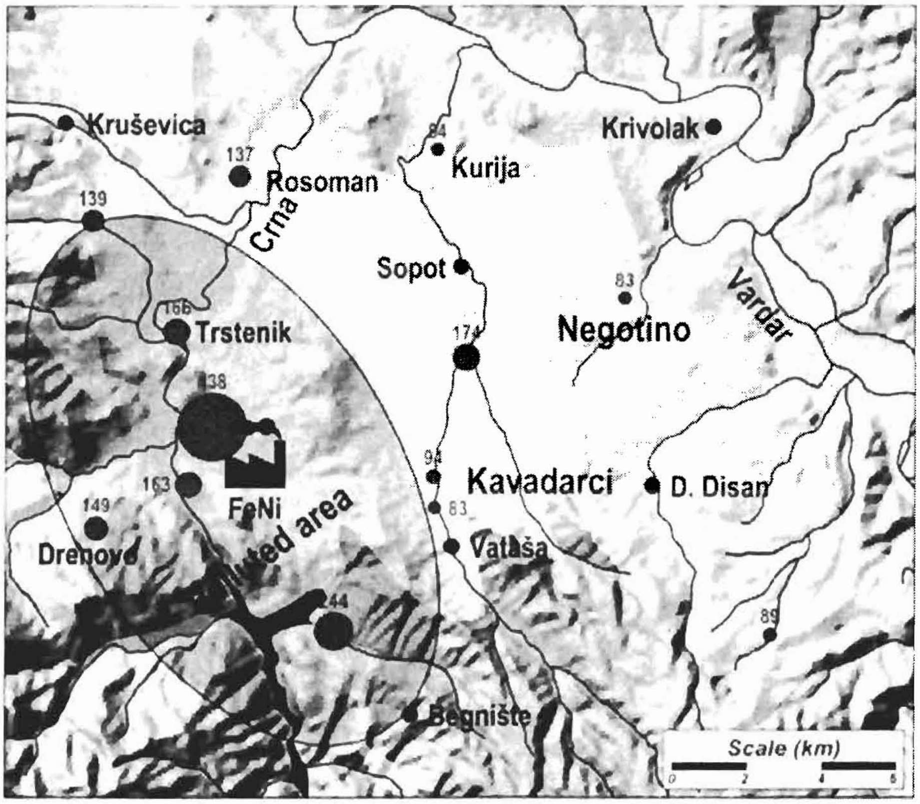

Figure 13. Distribution of Cr in attic dust samples (in mg kg^{-1}).

Table 10 also presents the values of the continuous probability distribution – F, which is acquired by a running variation analysis on the attic dust samples between two variables (samples in the vicinity of the smelter plant and samples from the rest of the investigated area). This data confirms that in this area an anthropogenic group consisting of the elements Co, Cr, Mo and Ni distinguishes itself.

From the results shown in Table 10 it is clear that the values for the continuous probability distribution – F, for Co, Cr, Mo and Ni in the attic dust samples originating from the vicinity of the smelter plant and the ones from the remainder of the investigated area are significantly higher compared to the F values of the rest of the elements. Namely, if these values are compared with the tabular critical value for F, which for the corresponding number of samples and freedom degrees is 2.32 (Miller and Miller 1993) it is clearly noted that the values for some of these elements are remarkably high (17.90 for nickel, 18.67 for chrome, 12.86 for cobalt and 5.15 for molybdenum).

The presented data makes it clear that the source of some of the heavy metals in the air in the investigated region is the dust that comes from this smelter plant (Figs. 11-13). Moreover, the content of these elements is considerably higher in the attic dust collected from this region than their natural content in the surrounding rocks and soil (Stafilov et al., 2010).

Data presented in Tables 9 and 10 and in Figs. 11–13 undoubtedly show that we can separate two populations that are influenced by activities of the ferronickel smelter plant, polluted area, which spreads about 120 km^2, and the unpolluted area. Distribution of these elements follows the wind direction (Lazarevski 1993), with the dominant winds from N and NW and SE (Figures 11–13). This fact assuredly confirms the influence of the air pollution with dust from the ferronickel plant in the closest region with the population of about 3500.

Table 10. Averages and enrichment ratios of 46 chemical elements in attic dust samples according to the sampling locations. Values of Al, Ca, Fe, K, Mg, Na and Ti are in %, remaining elements in mg kg^{-1}

No	Element	Average for Kavadarci region	Samples around the FeNi smelter	Samples from the rest of the region	ER (Feni/Rest)	F (around Feni smelter)
1	Al	2.5	2.0	2.9	0.69	4.71
2	Ca	2.9	3.0	2.8	1.09	1.05
3	Fe	3.7	3.8	3.5	1.10	0.59
4	K	1.3	1.3	1.3	1.03	0.23
5	Mg	0.44	0.44	0.44	1.00	0.00
6	Na	0.84	0.83	0.85	0.98	0.02
7	Ti	0.38	0.38	0.38	1.00	0.00
8	Ag	2.7	2.4	2.9	0.85	0.52
9	As	18	18	17	1.08	0.08
10	Ba	320	297	342	0.87	0.45
11	Be	2.4	2.4	2.5	0.96	0.11
12	Bi	3.7	4.5	3.2	1.41	5.18
13	Cd	8.6	7.9	9.2	0.86	1.77
14	Ce	38	32	43	0.74	3.48
15	**Co**	18	**22**	**15**	**1.50**	**12.86**
16	**Cr**	140	**193**	**105**	**1.84**	**18.67**
17	Cs	1.4	1.2	1.5	0.81	0.90
18	Cu	50	48	52	0.92	1.52
19	Dy	2.3	2.0	2.7	0.73	3.10
20	Dy	0.90	2.0	2.7	0.73	3.10
21	Eu	15	0.80	0.98	0.81	2.16
22	Ga	3.4	15	15	1.00	0.00
23	Gd	0.96	3.1	3.6	0.86	0.71
24	Hf	1.0	0.91	1.1	0.80	1.19
25	Hg	0.093	0.076	0.11	0.69	0.24
26	Ho	0.44	0.41	0.47	0.86	0.69
27	I	0.47	0.43	0.50	0.86	0.35
28	La	17	16	18	0.90	0.28
29	Li	16	17	15	1.12	2.88
30	Lu	0.15	0.13	0.16	0.82	1.10
31	Mn	510	522	508	1.03	0.25
32	**Mo**	3.0	**4.4**	**2.1**	**2.07**	**5.15**
33	Nb	14	14	13	1.02	0.04
34	**Ni**	230	**354**	**156**	**2.27**	**17.90**
35	Pb	180	167	182	0.92	0.30
36	Rb	56	59	54	1.08	0.32
37	Sb	2.4	2.5	2.4	1.07	0.23
38	Sm	3.1	2.8	3.2	0.87	0.64
39	Sr	170	155	173	0.90	1.48
40	Tb	0.45	0.41	0.49	0.83	1.06
41	Th	5.3	4.4	6.1	0.72	0.63
42	U	3.4	3.7	3.3	1.12	0.29
43	V	110	112	110	1.02	0.02
44	Yb	1.0	0.93	1.1	0.85	0.73
45	Zn	350	337	368	0.92	0.87
46	Zr	46	40	51	0.78	0.75

n – number of samples; FeNi – Area around ferronickel smelter (polluted area); Rest – unpolluted area; F – continuous probability distribution (analysis of variance) for attic dust between polluted area and unpolluted area, significant values ($p=0.05$) are underlined; ER – enrichment ratios of attic dust - Kavadarci area (polluted area vs. unpolluted area). Average values of Al, Ca, Fe, K, Mg, Na and Ti are in %, remaining elements in mg kg^{-1}. Data round at two digits.

4.2. Total Deposited Dust as Sampling Media

4.2.1. Copper Mining and Ore Processing Case

The obtained values for 17 elements content were proceed using descriptive statistics (Table 11). As it can be seen, median values for the copper in deposited dust samples taken from the studied area is 158 mg kg^{-1} and the min/max range of values shows much higher content of this element in the samples from this area (ranges from 52 to 1182 mg kg^{-1}). Similar results were obtained for the distribution of Fe, Pb and Zn thereby the median value and the min/max range for these elements indicate increase content of these elements.

Table 11. Descriptive statistics of measurements (N=36, 18 elements) Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1}

Element	N	X	Xg	med	min	max	P_{10}	P_{90}	s	A	E
Al (%)	36	0.2	0.16	0,17	0.02	0.57	0.07	0.3	0.13	1.51	2.16
Ca (%)	36	6.20	4.01	4.17	0.52	21.9	1.01	14.6	5.65	1.30	1.19
Fe (%)	36	0.32	0.26	0.27	0.05	1.00	0.14	0.66	0.20	1.59	2.77
K (%)	36	1.21	0.84	0.77	0.12	6.21	0.28	2.20	1.23	2.62	7.14
Mg (%)	36	0.48	0.44	0.44	0.15	1.36	0.24	0.81	0.24	1.56	3.71
Na (%)	36	0.51	0.35	0.35	0.06	2.42	0.08	1.06	0.48	2.06	5.71
B	36	443	195	188	8.91	3085	38.3	1427	654	2.52	7.02
Cr	36	8.61	6.60	6.69	0.96	41.2	3.17	17.8	7.36	2.75	10.4
Cu	36	310	210	158	52.5	1182	84.1	861	313	1.70	1.95
Li	36	3.70	1.99	2.06	0.27	60.3	0.95	3.83	9.77	5.89	35.1
Mn	36	183	162	151	50.8	459	95.7	362	98.9	1.37	1.53
Mo	36	4.25	2.73	3.59	0.50	15.7	0.50	9.57	3.70	1.37	1.91
Ni	36	21.7	13.5	12.9	1.78	148	5.39	35.3	28.8	3.24	11.5
Pb	36	49.3	35.1	28.6	7.19	189	14.6	122	47.3	1.83	2.61
Sr	36	212	128	132	16.9	887	34.0	572	223	1.59	1.79
V	36	9.35	8.01	7.24	2.31	27.1	4.34	16.8	5.47	1.27	1.76
Zn	36	259	176	149	38.9	1045	72.7	665	275	2.04	3.29

The amount of total deposited dust that is spread in the air is presented in Figure 14. From the results obtained in this investigation it is evident that large amounts of deposited dust were recorded in the close vicinity of the mine (villages Bučim and Topolnica). In some period of the year the values are much above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}).

The first months of the year (January to February), mining activities were placed on hold due to the decline in the price of copper. Such suspension of mining activities for a short period indicates the impact of mining on the amount of fine dust spread in the air. Maximum value for the total deposited dust (815 mg mg m^{-2} d^{-1}) was obtained in August in the Bučim village. This is the highest value for the amount of total deposited dust compared to the other two places.

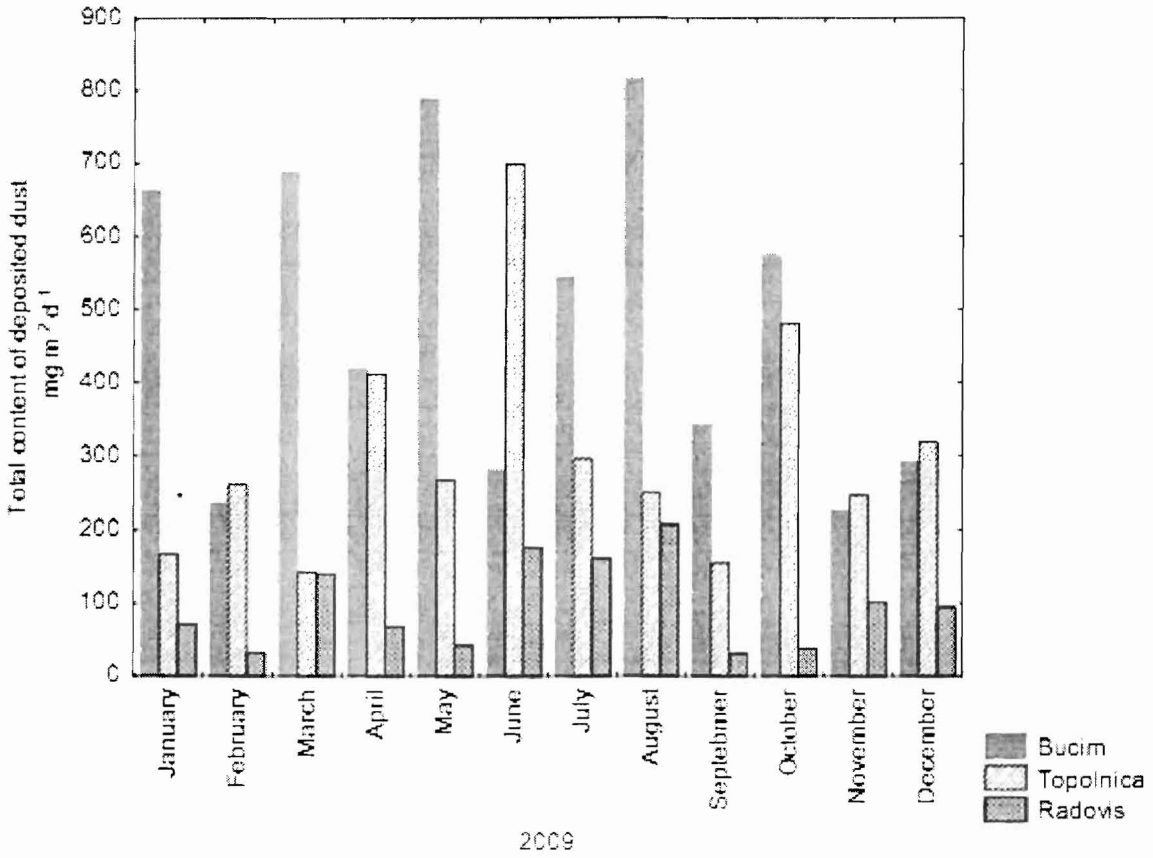

Figure 14. The total content of deposited dust.

The annual average for the total deposited dust in the vicinity of the Bučim village is 489 mg mg m^{-2} d^{-1}, for Topolnica the 309 mg mg m^{-2} d^{-1} and accounted for Radoviš is 97 mg mg m^{-2} d^{-1}. These values indicate that in the vicinity of the Bučim village the population is exposed to high amounts of dust in the air.

A lower value was obtained for the amount of the total deposited dust in village Topolnica environ, while for Radoviš was obtained a much lower value (Figure 14). The town of Radoviš was not affected by the dust deposition from the mine activities. Bučim village is exposed to large amounts of dust almost through the whole year.

Because of high ore content of Cu (0.3 %) and large amount of copper in flotation tailing (Serafimovski et al., 2005) was expected this element to have significantly higher content in samples of deposited dust compared to the other elements.

As it can be seen from the data presented in Table 12. the median values for Cu in samples of deposited dust taken from the Radoviš area is 396 mg kg^{-1} and the ranges (from 94.8 to 1171 mg kg^{-1}) for the Topolnica village the median values in samples of deposited dust is 150 mg kg^{-1} with ranges (from 52.5 to 1183 mg kg^{-1}) and for the Bučim village the median values in deposited dust samples is 145 mg kg^{-1} and the ranges (from 85.3 to 317 mg kg^{-1}).

From these results can be seen that the maximum value for the content of Cu was obtained from Topolnica village (settlement near by the flotation tailings landfill). In the town of Radoviš was not found deposited dust above the maximum permitted amount of dust powder, but high content of Cu content was worrying.

Table 12. Statistical parameters for annual values for the content of chemical elements in samples of deposited dust measured in Radoviš and is environs Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1}

Element	N	Sampling site					
		Vill. Bučim		Vill. Topolnica		Radoviš	
		Md	**Range**	**Md**	**Range**	**Md**	**Range**
Al %	12	0.13	0.02-0.19	0.15	0.07-0.58	0.25	0.16-0.56
Ca %	12	9.12	1.74-2.19	1.32	0.53-4.74	7.25	1.56-20.9
Fe %	12	0.23	0.05-0.34	0.27	0.10-1.02	0.36	0.14-0.77
K %	12	0.76	0.12-4.71	0.86	0.28-6.21	0.69	0.23-2.12
Mg %	12	0.43	0.15-0.84	0.34	0.21-0.84	0.48	0.19-1.36
Na %	12	0.16	0.06-0.92	0.31	0.08-0.87	0.77	0.24-2.41
B	12 •	203	8.91-1427	93.4	34.7-305	454	101-3085
Cr	12	4.22	0.96-7.78	6.32	1.74-20.1	12.6	6.42-41.2
Cu	**12**	**145**	**85.3-317**	**150**	**52.5-1183**	**396**	**94.8-1171**
Li	12	1.17	0.27-2.11	2.13	1.20-5.16	2.79	0.95-60.3
Mn	12	128	50.8-459	148	69.8-411	197	98.4-419
Mo	12	3.53	0.50-6.91	2.51	0.50-12.3	4.18	0.50-15.7
Ni	12	6.94	2.81-14.1	13.5	6.49-27.8	26.9	1.79-148
Pb	12	25.7	12.1-56.6	26.8	7.20-184	69.5	20.1-189
Sr	12	303	70.7-888	46.4	16.9-269	170	34.1-572
V	12	5.49	2.31-8.23	8.63	4.34-27.1	13.1	5.23-18.5
Zn	12	217	92.5-1045	89.0	38.9-240	176	86.6-665

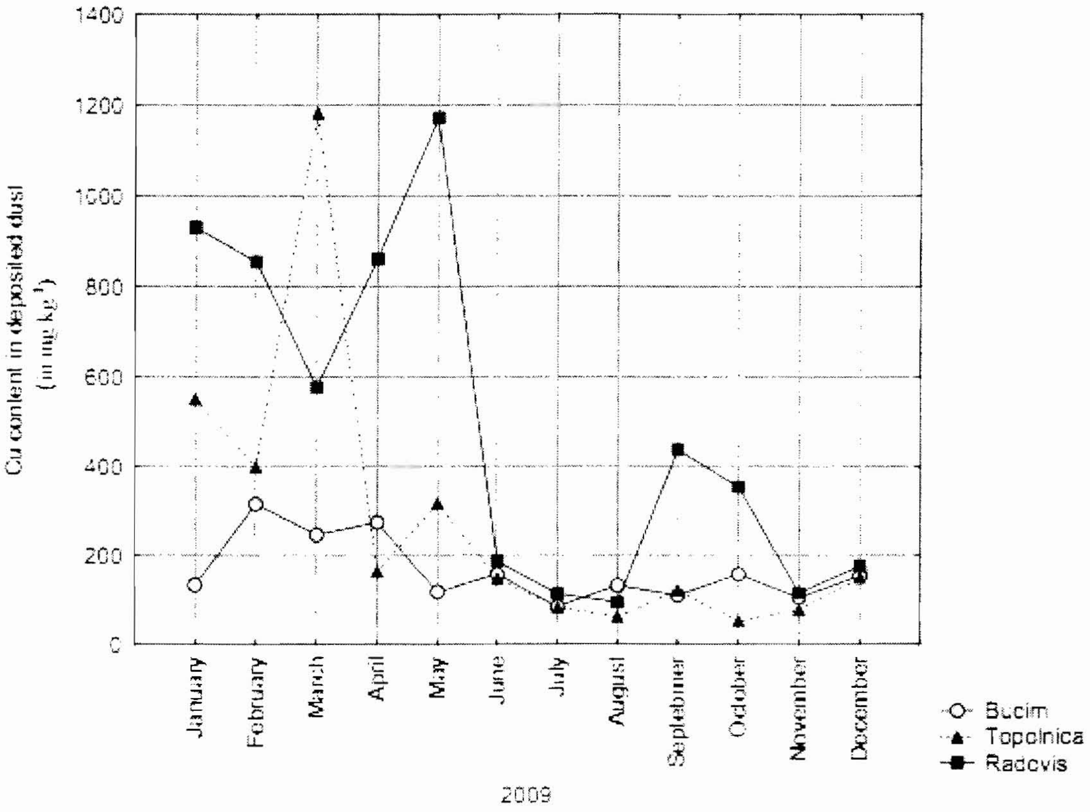

Figure 15. Trends of copper content in deposited dust through the whole year.

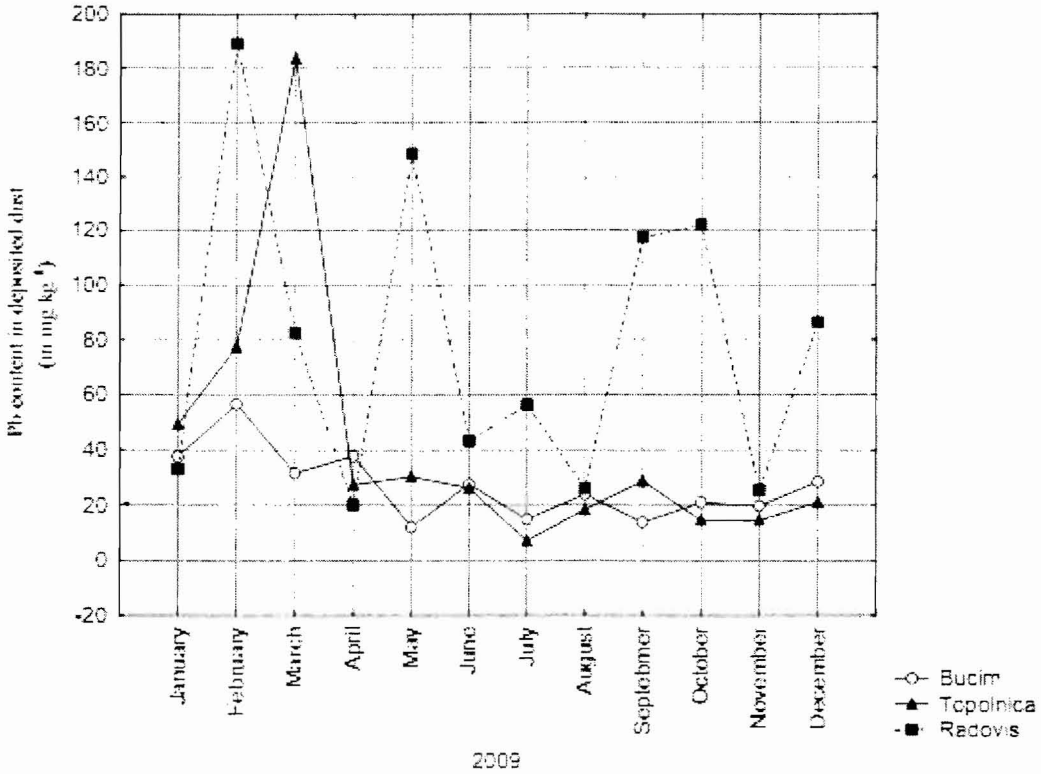

Figure 16. Trends of lead content in deposited dust through the whole year.

Similar results were obtained for the content of Pb, where clearly is visible that the Bucim village was not affected from high content of lead in the deposited dust from air. Maximum value was obtained from the town of Radoviš (189 mg kg^{-1} in February) and varies during the whole year. Despite the large amounts of total deposited dust from Bučim village, there were not found high values for the lead contend. Maximum value (183 mg kg^{-1}) for the lead content in deposited dust from the Topolnica village was obtained in March, when starts' decreasing of lead content and the trend is retained until the end of the year.

The ultimate effect is that despite large amounts of deposited dust, population in Bučim village is not affected with high content of anthropogenic introduced metals (Cu and Pb) due to copper mining works. Unexpectedly the town of Radoviš, despite little amounts of deposited dust, was affected by large content of Cu and Pb. This suggests that there is Cu and Pb distribution on large distance from mine, which was not concluded with the historical monitoring using attic dust samples.

4.2.2. Ferro-Nickel Smelter Plant Case

For each observation there were few variables: sample identification number, locality, geographic coordinates, sample type and concentration level for 18 elements. For statistical analysis of data was used parametric and nonparametric statistic. Minima and maxima mean calculation methods of median, geometrical mean, standard deviation, geometric standard deviation, skewness, kurtosis and arithmetical mean were calculated and histograms were drawn to show the distribution features. Table 13 shows the basic statistics for samples of deposited dust for the period from (January-December-2009). As it can be seen from the obtained data presented in Table 13, the median values for the nickel in deposited dust samples taken from the studied area is 101 mg kg^{-1} and the min/max range of values shows much higher content of this element in the samples from this area (ranges from 5.24 to 1289 mg kg^{-1}). Similar results are obtained for the distribution of Co and Cr, thereby the median value and the min/max range for these elements indicate increase content of these elements. The median value for Cr in deposited dust samples taken from the studied area is 11.96 mg kg^{-1} (ranges from 0.73 to 139 mg kg^{-1}), and for Co the median value in deposited dust samples taken from the studied area is 3.91 mg kg^{-1} (ranges from 0.23 to 75.58 mg kg^{-1}).

The amount of total deposited dust that is spread in the air is presented in Figure 17. From the results obtained in this investigation it is evident that a large amount of deposited dust were recorded in summer in 2009 when the values are close to or above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}).

Table 13. Descriptive statistics of measurements (N=36, 18 elements) Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1}

Elements	N	X	Xg	Md.	Min.	Max.	P_{10}	P_{90}	s	A	E
Al %	36	0.13	0.10	0.12	0.01	0.41	0.03	0.27	0.09	1.23	1.86
Ca %	36	6.24	5.23	6.06	1.17	14.09	1.85	11.23	3.33	0.37	-0.53
Fe %	36	0.26	0.13	0.16	0.01	1.42	0.02	0.59	0.33	2.24	5.19
K %	36	2.09	1.28	1.23	0.32	15.69	0.49	2.88	3.23	3.52	12.34
Mg %	36	0.74	0.62	0.60	0.19	1.96	0.31	1.55	0.48	1.06	0.05
Na %	36	0.74	0.54	0.59	0.07	2.04	0.18	1.66	0.56	0.92	-0.23
As mg kg^{-1}	36	10.55	6.47	7.98	0.24	39.19	0.45	21.45	8.33	1.28	2.55
Cd mg kg^{-1}	36	0.93	0.63	0.79	0.10	4.94	0.20	1.55	0.97	2.69	8.46
Co mg kg^{-1}	36	9.80	3.92	3.91	0.23	75.58	0.31	25.18	15.57	3.05	10.14
Cr mg kg^{-1}	36	24.02	11.93	11.96	0.73	139	2.13	47.11	31.97	2.64	7.48
Cu mg kg^{-1}	36	227	115	82.1	17.2	1093	23.0	703	270	1.63	2.11
Li mg kg^{-1}	36	6.47	3.16	2.54	0.37	42.21	1.09	20.17	9.92	2.71	7.18
Mn mg kg^{-1}	36	180	110	114	11.48	795	26.81	513	188	1.76	2.77
Ni mg kg^{-1}	36	180	89.38	101	5.24	1289	13.62	428	243	3.15	12.31
Pb mg kg^{-1}	36	354	127	121	6.66	2306	14.20	1079	525	2.40	6.03
Sr mg kg^{-1}	36	160	135	144	31.21	325	47.59	287	84.9	0.30	-0.88
V mg kg^{-1}	36	16.01	6.60	7.14	0.81	136	0.81	41.75	26.52	3.30	12.43
Zn mg kg^{-1}	36	754	282	227	59.88	7346	61.77	1392	1550	3.31	10.86

N-number of samples; X – mean; Xg – geometric mean; Md – median; Min - minimum; Max – maximum; P_{10} - 10 percentile; P_{90} - 90 percentile; s – standard deviation; A – skewness; E – kurtosis. Data round at two digits.

The ferronickel smelter plant uses ore that contains between 1 % and 2.5 % Ni, about 0.05 % Co, 1-3 % Cr etc. Therefore, we expect these elements to have significantly higher contents in samples of deposited dust compared to the other elements. As it can be seen from the data presented in Table 14, the median values for nickel in samples of deposited dust taken from the Kavadarci area is 28 mg kg^{-1} and the ranges (from 5.23 to 140.9 mg kg^{-1}) for the Brušani village the median values in samples of deposited dust is 196.3 mg kg^{-1} with ranges (from 24.7 to 290 mg kg^{-1}) and for the Vozarci village the median values in deposited dust samples is 144.9 mg kg^{-1} and the ranges (from 20.7 to 393 mg kg^{-1}). From this results can be seen that the values for the content of Ni in Vozarci village which is near the ferro-nickel smelter plant (Figure 18), has the highest content of Ni compared with the other two locations where are collected monthly samples of deposited dust from the Kavadarci area in 2009.

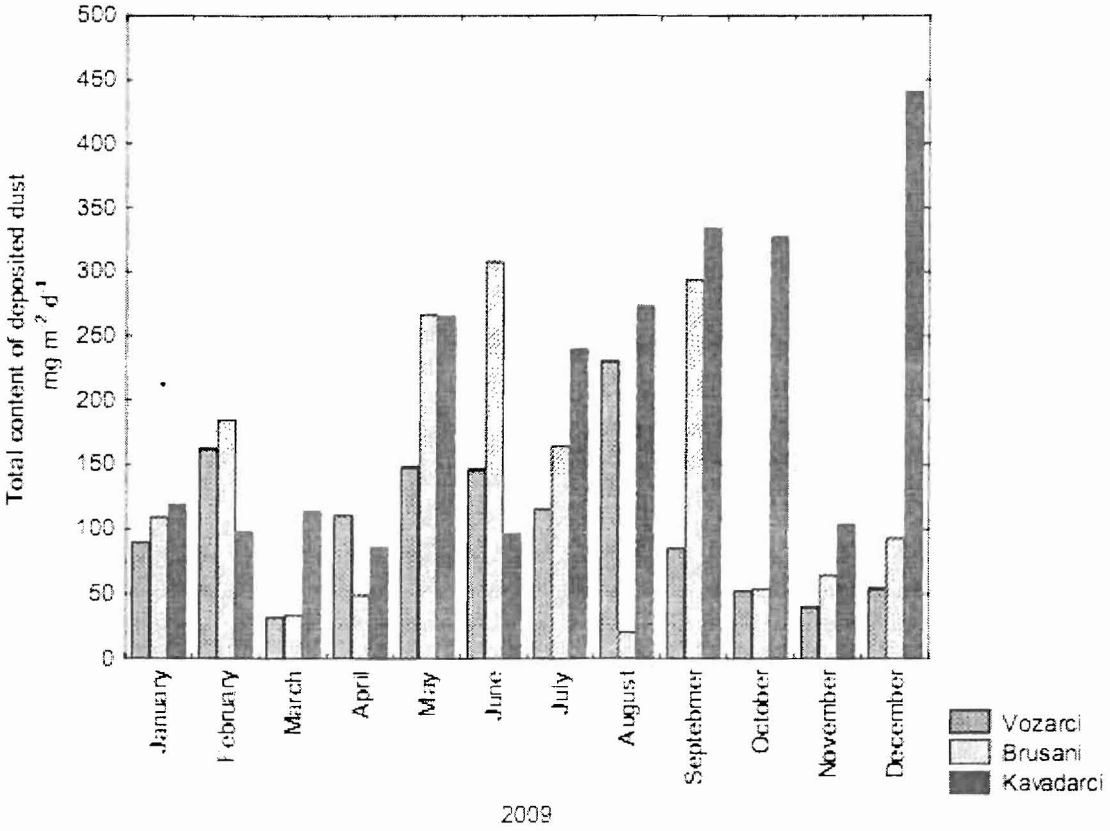

Figure 17. The total content of deposited dust.

Figures 18–20 has shown the values for the content of Ni, Cr and Co in deposited dust collected at all three locations. The obtained values for the content of nickel in deposited dust collected in the Vozarci village (near ferro-nickel smelter) in January-March 2009 is very high (477 to 1290 mg kg^{-1}) while the remainder content is relatively low (25 to 222 mg kg^{-1}) with the exception of the samples collected in July (301 mg kg^{-1}) and September (428 mg kg^{1}), Figure 18.

This trend of increased content of nickel in the deposited dust is followed by increased content of chromium (Figure 19) and cobalt (Figure 20). The content of chromium in deposited dust collected in the Vozarci village is high for the first four months of January-April 2009 (65 to 140 mg kg^{-1}) and for the cobalt (Figure 20). The obtained values in deposited dust collected in the Vozarci village in January-March 2009 (28 to 76 mg kg^{-1}). This suggests that in these months had increased emission of dust from the smelter plant. These elements (Co, Cr and Ni) can enter the atmosphere from refining plants. Once it is airborne, they can attaches to dust in the air.

Over time, the dust falls to the ground or mixes with rain or snow, where it enters the soil. The exposure to nickel for the general population takes place via inhalation of dust, ingestion of food and water. Inhaled nickel is absorbed by the body depending on the solubility of the nickel compound in the air.

The median value for Co in deposited dust samples taken from the Kavadarci is 1.43 mg kg^{-1} (ranges from 0.23 to 7.5 mg kg^{-1}), for the Brušani village the median values is 10.8 mg kg^{-1} and the ranges (from 1.7 to 75.5 mg kg^{-1}) and for the Vozarci village the median values is 3.9 mg kg^{-1} and the ranges (from 0.99 to 25 mg kg^{-1}). The median value for Cr for Kavadarci is 4.3 mg kg^{-1} with ranges (from 0.7 to 33.5 mg kg^{-1}), the median for Brušani village is 31.9 mg kg^{-1} with ranges (from 1.83 to 139 mg kg^{-1}) and for Vozarci village the median is 14 mg kg^{-1} and ranges (from 4.3 to 47 mg kg^{-1}).

In Brušani village the content of cobalt and chromium in deposited dust samples is higher compared to content of these elements in village Vozarci and Kavadarci. From here it can be conclude that the dust distribution follows the wind rose (Lazarevski 1993) with the dominant winds from N and NW and SE. These results indicate that content for these elements (Co, Cr and Ni) are significantly higher, compared with the other elements that are investigated.

Table 14. Statistical parameters for annual values for the content of chemical elements in samples of deposited dust measured in Kavadarci and is environs Average values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1}

Element/	Sampling sites								
	Kavadarci			Vill. Brušani			Vill. Vozarci		
Statistical parameters	N	**Md**	**Range**	N	Md	**Range**	N	Md	**Range**
Al %	12	0.08	0.02-0.306	12	0.13	0.05-0.41	12	0.13	0.01-0.20
Ca %	12	4.71	1.17-14.09	12	6.35	1.69-11.3	12	7.14	1.22-11.8
Fe %	12	0.06	0.008-0.86	12	0.28	0.01-1.42	12	0.18	0.03-0.59
K %	12	1.27	0.43-15.68	12	0.86	0.51-2.52	12	1.33	0.32-2.88
Mg %	12	0.40	0.18-1.34	12	0.77	0.31-1.96	12	0.67	0.28-1.69
Na %	12	0.42	0.07-2.03	12	0.55	0.18-1.88	12	0.82	0.28-1.76
As mg kg^{-1}	12	2.85	0.24-25.17	12	8.97	3.55-39.2	12	14.73	7.43-21.7
Cd mg kg^{-1}	12	0.28	0.10-1.220	12	0.90	0.30-4.94	12	0.83	0.20-2.99
Co mg kg^{-1}	**12**	**1.43**	**0.23-7.51**	**12**	**10.86**	**1.74-75.5**	**12**	**3.91**	**0.99-25.18**
Cr mg kg^{-1}	**12**	**4.3**	**0.73-33.53**	**12**	**31.92**	**1.83-139**	**12**	**14.11**	**4.38-47.1**
Cu mg kg^{-1}	12	46.2	17.2-319	12	83.78	37.6-839	12	438.83	40-1093
Li mg kg^{-1}	12	1.81	0.36-10.2	12	2.45	0.86-39.8	12	5.98	1.32-42.2
Mn mg kg^{-1}	12	64.1	21.5-289	12	153.1	11.4-608	12	145.8	26.8-795
Ni mg kg^{-1}	**12**	**28.13**	**5.23-140.9**	**12**	**196.3**	**24.7-290**	**12**	**144.9**	**20.7-393**
Pb mg kg^{-1}	12	53.3	6.66-485	12	229.2	14.9-306	12	236.9	30.6-1163
Sr mg kg^{-1}	12	122.5	31.2-286	12	132.2	40.6-323	12	215.4	46.9-325
V mg kg^{-1}	12	3.6	0.81-24	12	7.14	0.81-41.7	12	9.91	0.81-135
Zn mg kg^{-1}	12	189	59.8-7346	12	235	60.3-5140	12	272.66	61.7-1113

N-number of samples; Md-median.

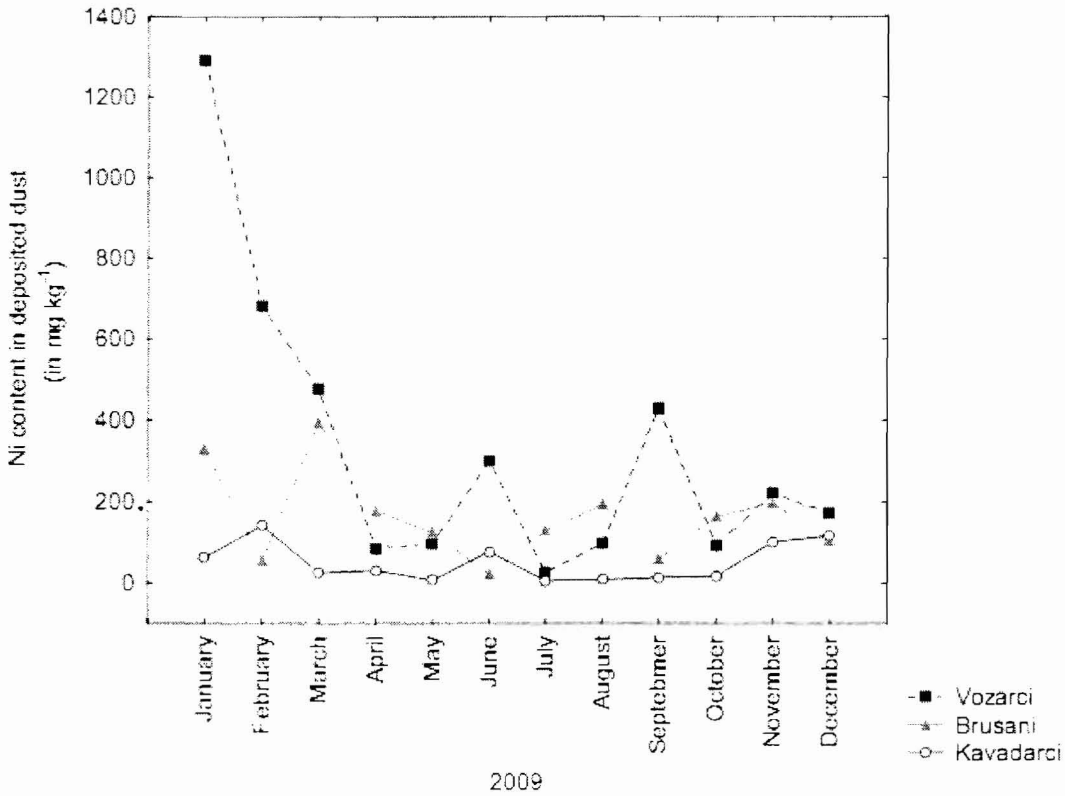

Figure 18. Trends of nickel content in deposited dust trough the whole year (in mg kg^{-1}).

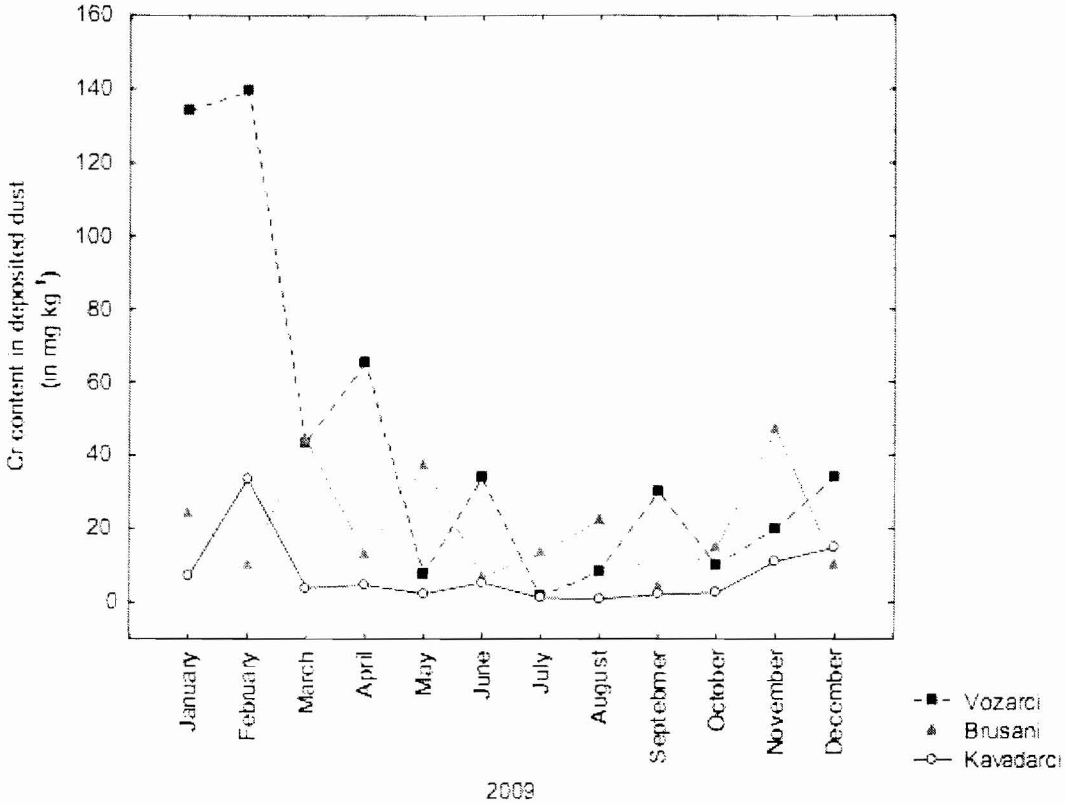

Figure 19. Trends of chrome content in deposited dust trough the whole year (in mg kg^{-1}).

Atmospheric deposition of heavy metals can pollute soils and sediments and can have severe ecological impacts such as bioaccumulation or loss of biodiversity (Mulder and Breure, 2006; Norr and Riepert, 2007; Morvan et al., 2008; Kwaterczak and Helios-Rybicka, 2009; Schröder et al., 2010). Therefore, deposition measurements are key to soil monitoring (Schröder et al., 2004) and are needed for spatial estimations of soil contamination through atmospheric deposition (Zheng et al., 2008).

The same region has been investigated for the soil pollution (Stafilov et al., 2008, 2010), and did not identify a statistical significance between the soil samples. For the nickel content in the soil in Kavadarci and its environs, it is found that the median and average values are very similar (72 mg kg^{-1} and 74 mg kg^{-1}, respectively) and that the content of nickel in the whole investigated area ranges between 42 and 150 mg kg^{-1} (Stafilov et al., 2010). Moreover, it was found that nickel content in subsoil and topsoil is almost the same, which shows that the presence of nickel in soil is from natural origin.

The average value for the content of nickel in moss samples from the investigated region is 80 mg kg^{-1}, ranges from (14 to 340 mg kg^{-1}) (Bačeva et al., 2009). This value is much higher than the average of 6.6 mg kg^{-1} for the content of nickel in moss samples collected from the territory of the Republic of Macedonia, (Barandovski et al., 2006, 2008), which show direct connection with the pollution from the ferronickel smelter plant situated near the city of Kavadarci. Therefore, main goal was to follow the influence on the elements' distribution in the air caused by the ferronickel smelter plant and its connection to the some other natural conditions' (climate conditions, lithological, dust, etc).

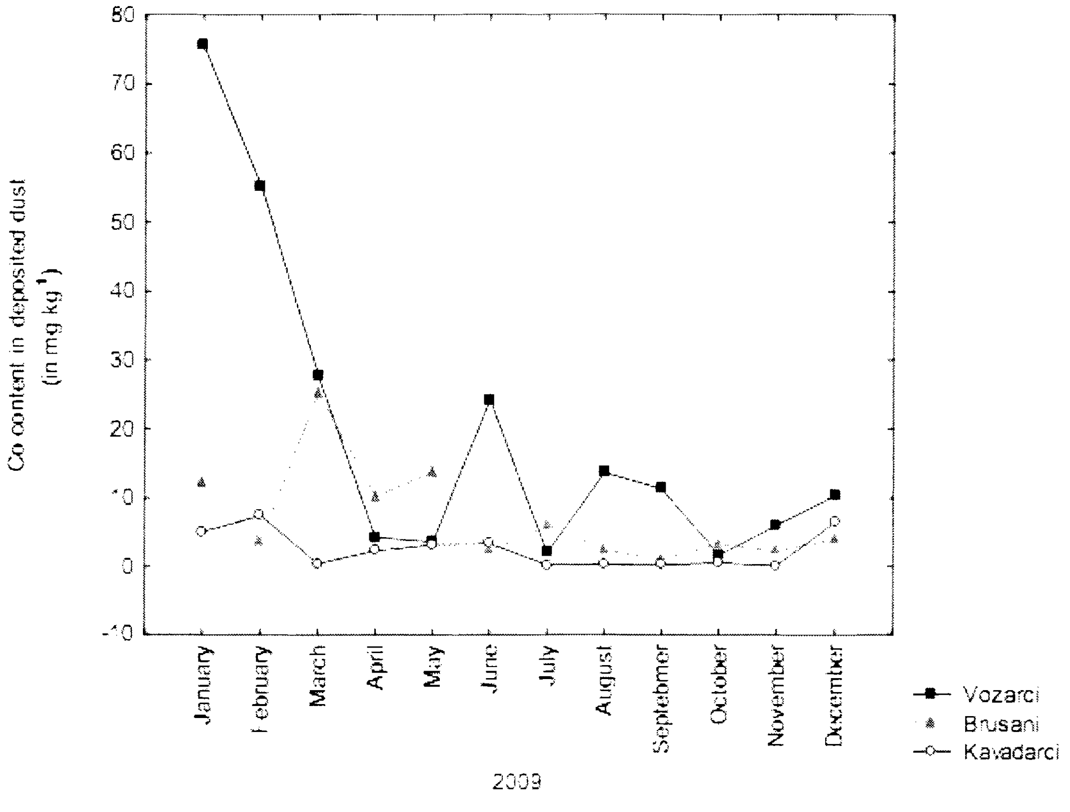

Figure 20. Trends of cobalt content in deposited dust trough the whole year (in mg kg^{-1}).

Our previous investigation on the distribution of Ni, Co and Cr, in attic dust shows an increased content in the samples from the smelter plant surroundings compared to the content in the rest of the samples of the same region (Bačeva et al., 2011). This also confirms that the dust that is discharged from this plant is connected with the ferronickel ore that is being processed in this smelter plant.

CONCLUSION

Attic and total deposited dust has proved to be very effective environmental samples for monitoring historical and present distribution of heavy metals in a potentially contaminated area. In this Chapter data about the air pollution with heavy metals in the vicinity of copper mine and ferro-nickel smelter plant are given.

The historical (long period) distribution was followed by the analysis of the content of heavy metals in attic dust collected from the houses in the investigated areas. The presence (since the operation starts) of an open copper ore pit, ore processing and flotation plant (Bučim mine, near the town of Radoviš, Republic of Macedonia) leads to increased content of copper in attic dust in its surroundings (max. content of Cu 415 mg kg^{-1}). Apart from the copper, increased content of As and Pb in attic dust (max. contents 51 mg kg^{-1} and 121 mg kg^{-1}, respectively) were also found, singled out as anthropogenic association with copper. The distribution of the anthropogenic association of elements (As, Cu and Pb) at distant regions was not determined. The distribution of the rest of the elements relies on the geology of the region. The distributions of most of the elements in ferronickel smelter plant environ in attic dust samples are closely dependent on the lithogenesis and are slightly affected by anthropogenic activities. Historical record (attic dust) of nickel distribution showed high contents deposited in Kavadarci environ (max. content 1200 mg kg^{-1}). Cobalt and chromium results show significantly higher contents in the samples of attic dust taken from the Kavadarci area, as well (max. contents 52 mg kg^{-1} and 510 mg kg^{-1}, respectively).

The distribution of dust with heavy metals was also followed by the present distribution (total deposited dust), were it assumed that anthropogenic elements although deposit in higher content at distant regions from their hot spots. In close vicinity of the copper mine environ, there was deposition of large amounts of dust, values much above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}); annual average for the total deposited dust in the vicinity of the Bučim village - 489 mg mg m^{-2} d^{-1}, for Topolnica - 309 mg mg m^{-2} d^{-1} and for Radoviš - 97 mg mg m^{-2} d^{-1}. Maximum value for the Cu content was obtained from Topolnica village (settlement near by the flotation tailings landfill). In the town of Radoviš was not found deposited dust above the maximum permitted amount of dust powder, but high content of Cu content was worrying (1171 mg kg^{-1}). The population from mentioned villages is continuously exposed to a high content of copper and lead, which has a negative effect on human health and toxic effects on the environment.

It was found that ferronickel smelter plant (the second case study) affects on the distribution of large amounts of dust in it environ trough the whole year. From the results obtained it is clear that a large amount of deposited dust were recorded in summer when the values are close to or above the maximum amount of dust powder (300 mg m^{-2} d^{-1}). The values for the content of nickel in deposited dust collected in the village Vozarci (near smelter plant) in the winter period is very high while in the remaining period of its content is relatively low (max. content 1290 mg kg^{-1}). This trend of increased content of nickel in the dust monitor is followed by the content of chromium and cobalt in deposited dust. The dust distribution followed the wind rose with the dominant winds from N and NW and SE. These results indicate that content for these elements (Co, Cr and Ni) are significantly higher, compared with the other elements that are investigated. The population of the settlements near smelter plant was affected with the high contents of these elements due to large amounts of dust distribution from ferronickel smelter plant.

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