Macedonian Journal of Ecology and Environment
Vol. XIV (1, 2)
p. 47 - 57
Skopje (2012)
ISSN 1857 - 8330
UDC: 502.3:504.5]:546.4/.8(497.714)
Original scientific paper

Monitoring of air pollution with heavy metals in the vicinity of a ferronickel smelter plant by deposited dust

Мониторинг на загадувањето на воздухот со тешки метали во близина на топилница за феро-никел со седиментна прашина

Katerina Bačeva[1], Trajče Stafilov[1*] and Robert Šajn[2]

[1]*Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia*

[2]*Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia*

Comprehensive monitoring was applied to assess environmental pollution in the vicinity of a ferronickel smelter plant in Kavadarci (Republic of Macedonia) and its environs. The total dust deposition is a very useful method to follow the increased presence of some chemical elements in the atmosphere as a result of anthropogenic activities. The data from such surveys allow for assessing both spatial and temporal trends in heavy metal deposition and an examination of the areas with higher deposition of heavy metals. In order to determine the daily amounts of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations in the area. The total quantity of deposited dust was monitored monthly for a period of one year. In total 18 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, Zn) were determined by two complementary analytical techniques: atomic emission spectrometry with inductively coupled plasma (AES-ICP) and electrotermal atomic absorption spectrometry (ETAAS). Based on the comparison of distribution patterns of elements determined in attic and deposited dust, one anthropogenic geohemical association (Co-Cr-Fe-Ni) was detected in the investigated region which is a result of the activities of a ferronickel metallurgical plant.

Keywords: Heavy metals, air pollution, deposited dust, nickel, Kavadarci

Со цел да се утврди загадувањето на животната средина во близина на топилницата за феро-никел во Кавадарци (Република Македонија) како и неговата околина, беше извршен сеопфатен мониторинг. Утврдувањето на вкупната седиментна прашина е многу корисен механизам за следење на антропогените елементи присутни во атмосферата. Податоците од вакви истражувања овозможуваат добивање на просторни и временски трендови на депозицијата на тешките метали и утврдување на области со поголемо загадување. Со цел да се утврди дневната количина на прашина во воздухот, примероци на вкупна седиментна прашина беа собрани на три локации во овој регион. Вкупното количество на седиментна прашина беше испитувана месечно, во период од една година. Вкупно беа анализирани 18 елементи (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V и Zn) со две комплементарни аналитички техники: атомска емисиона спектрометрија со индуктивно спрегната плазма (AES-ICP) и електротегмичка атомска апсорпциона спектометрија (ETAAS). Врз основа на просторната дистрибуција на испитуваните елементи во примероците од поткровна и седиментна прашина утврдена е една антропогена геохемиска асоцијација (Co-Cr-Fe-Ni). Исто така, утврдено е

---

* *trajcest@pmf.ukim.mk*

дека оваа антропогена асоцијација е резултат на активностите на металуршкиот комплекс за производство на фероникел во овој регион.

Клучни зборови: Тешки метали, загадување на воздухот, седиментна прашина, никел, Кавадарци

Introduction

The abundance of heavy metals in atmosphere has been increased dramatically by the accelerated rate of highly technological industrial processes. Mine and flotation activities lead to large amounts of waste material (Salomons, 1995; Dudka and Adriano, 1997). The most serious consequence in atmospheric terms is acid deposition, which occurs when emissions from the combustion of fossil fuels and other industrial processes undergo complex chemical reactions in the atmosphere and fall to the earth as wet or dry deposition (Sengupta, 1993; Repley et al., 1996).

The problem of the degradation of the ecosystems due to pollution has become increasingly acute. 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 the risk of destabilisation, as organisms that developed under conditions with low concentrations of metals have not developed biochemical pathways capable of detoxifying the metal when it is present at high concentrations.

Heavy metals in the atmosphere originate mainly from metal refining, fossil fuel combustion, vehicle exhaust and other human activities and stay in the atmosphere until they are removed by a variety of cleansing processes. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility and reactivity, especially under low pH conditions (Hou et al., 2005). Quantification of heavy metals is necessary, given the important biogeochemical role of some trace metals, either as nutrients (Cu, Zn) or as toxic elements (Pb, Cd, Tl) in ecosystems (Avila & Rodrigo, 2004; Hršak et al., 2003; IPCS, 1996). Dust is a generic term used to describe fine particles that are suspended in the atmosphere. 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 (Brown et al., 2006).

The Republic of Macedonia, as a result of anthropogenetic activities is affected by the problem of atmospheric pollution with heavy metals. Significant emission sources that contribute to atmospheric pollution with heavy metals in the territory of the Republic of Macedonia appear to be mines and smelters near the cities of Veles, Kavadarci, Radoviš and Tetovo (Barandovski et al., 2006, 2008; Stafilov et al., 2003, 2008, 2010; Balabanova et al., 2009; 2010a, 2010b; Serafimovski et al., 2010). In the south-central part of the country, the appearance of some metals (Co, Cr, Fe and Ni) in the air is related to the presence of a ferronickel smelter plant near the city of Kavadarci, Fig 1 (Barandovski et al., 2006; 2008; Stafilov et al., 2008, 2010; Bačeva et al., 2009; 2011). This smelter

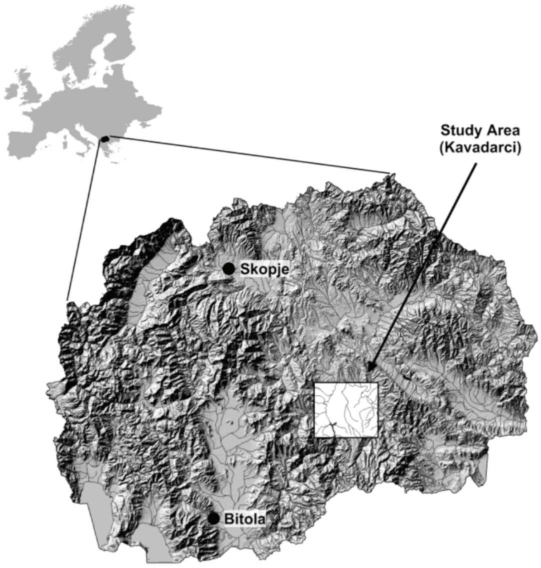

Fig. 1. The investigated region of Kavadarci and its environs

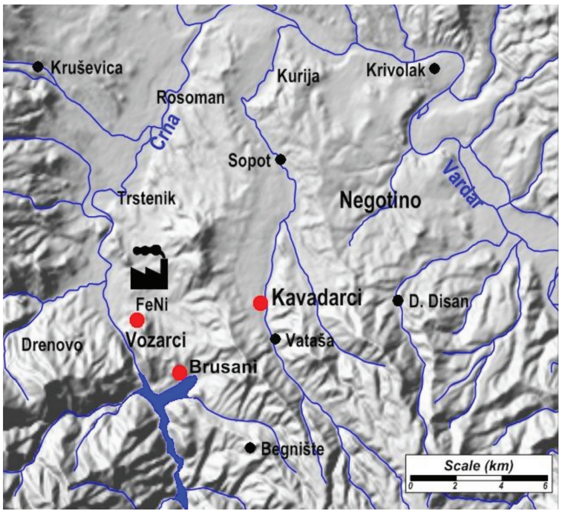

Fig. 2. Location of sampling points

plant uses nickel ore from the Ržanovo mine, about 30 km south of the plant. This smelter plant uses nickel ore from the Ržanovo mine, about 30 km south of the plant. In the last four-five years, in addition to ore from the Ržanovo mine, ore mainly from the Gebe nickel mine in Indonesia, rich in nickel (2-2.5%), has been used. It is well-known that nickel ores contain cobalt as well (0.05% on average for Ržanovo ore). It is well known that the nickel ores contain cobalt as well (0.05% on in average for Ržanovo ore) (Maksimović, 1982; Boev & Jankovic, 1996). Therefore, the dust from this plant has a similar content to the ore used as a raw material, including some the heavy metals such as nickel, cobalt and chromium. For that reason, the goal of this work was to determine the total deposition (deposited dust) from the atmosphere in Kavadarci and its surroundings.

Atmospheric total deposition (deposited dust) is very useful method for monitoring the fate of anthropogenic elements introduced into the atmosphere (Tsitouridou and Anatolaki et al., 2007; Čačkovič et al., 2009). Fine powder with a high content of heavy metals is generated as a result of emissions from the processing of ores and metallurgical processes and is distributed as a result of the wind. Many investigations have focused on the chemical composition and the content of toxic substances in deposited matter (Morselli et al., 2003; Avila & Rodrigo, 2004; Polkowska et al., 2005; Vike, 2005; Franzaring et al., 2006).

In order to determine the daily amount of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations in the area (Fig. 2). The total quantity of the deposited dust was monitored monthly for a period of one year.

Study area

The study area is large 18 (W-E) × 20 (S-N) km (Fig. 1 and 2) and is located in the south-central part of Macedonia, which is limited by the coordinates (Gauss Krueger zone 7) 7574000 (W) – 7592000 (E) and 4582000 (S) – 4602000 (N), comprising a total of 300 km^2 for the study area (Fig. 1). The town of Kavadarci is located in the Tikveš valley about 100 km south of the capital Skopje (Fig. 1). It is a region with extensive agriculture. The municipality of Kavadarci (38,741 inhabitants; 992.44 km^2) is composed of the town of Kavadarci (28,000 inhabitants) and 39 smaller settlements. The urban area is located at an altitude of 200-300 m, surrounded by hills on the eastern and southern sides of the valley with a height difference of approximately 300 to 770 m. The west side of the valley is surrounded by the hills Ljubaš and Dabov Vrv and Klepa Mountain. The eastern side of the valley is surrounded by the mountains of Serta and in the south by the Vitačevo plateau and Kožuf Mountain.

Samples of deposited dust were collected in the period from January-December 2009.

Geological description

The geological description of the investigated area is presented in the Geochemical Atlas of Kavadarci and its Environs (Stafilov et al., 2008; 2010). The oldest formations are in the NW-SE direction 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 narrow belts along ruptures inside the Vardar zone. The uppermost part in the SW of the study zone is covered with marbles and dolomites, probably from the Devonian ages. Over the Paleozoic formations are developed Mesozoic (Mz) formations, mainly from the Late Cretaceous ages. Paleozoic and Mesozoic rocks cover approximately 39 km^2 in the SW part of the investigated area (Stafilov et al., 2008; 2010).

Complexes of Tertiary and Quaternary sediments cover most of the study area. The Upper Eocene ($^4E_3$) flysch sediments and yellow sandstones developed along the Vardar, Crna Reka and Luda Mara valleys and the marginal part of the Tikveš basin. Those sediments with a depth of up to 3500 m cover approximately 34 km^2 mainly in the N part of the investigated area. Pliocene sediments fill the Tikveš basin, limited by the Vardar to the north and Paleozoic-Mesozoic formations in the NW-SE direction. This sequence is represented mainly with by sandy series. Pliocene (Pl) sediments cover the largest part (about 182 km^2) of the central part of the investigated area. SE of Kavadarci, Quaternary (Q) pyroclastic vulcanites are found. They are represented by tuffs, breccias and agglomerates and cover approximately 25 km^2 (Stafilov et al., 2008; 2010).

Materials and methods

Sampling and sample preparation

Monthly samples of deposited dust were collected in Kavadarci and its environs for one year (January 2009 to December 2009) at three monitoring sites (Fig. 2): the village of Vozarci, the village of Brušani and the town of Kavadarci. The monitoring locality of Vozarci was chosen because this village is very close to the smelter plant, while the sites near the village of Brusani for follows the dominant NE wind direction (Lazarevski, 1993). The location in the town of Kavadarci was chosen to monitor the situation in the largest settlement in the vicinity of the smelter. Samples of total deposited matter (wet and dry deposition) were collected using dust deposition gauges. This method measures the dust deposition rate and involves the passive deposition and capture of dust within a funnel and a plastic container. Data are usually collected over monthly periods and the results are expressed as mg m^{-2} d^{-1} (i.e. the mass of dust deposited per m^2 per day). This method enables a determination of the relative "dustiness" of sampling locations.

The deposit gauge was comprised of a 28±1 cm diameter funnel inserted into a plastic container (at least 5-10 litres in size) through a rubber stopper (Holden, 2006), standing approximately 2 m tall with a canister to hold the plastic container and 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. An aliquot of each sample was evaporated near to dryness and then 3-5 mL of nitric acid, *p.a.* (MERCK, Germany), was added and samples were collected in 25 mL volumetric flasks.

Instrumentation

The investigated elements were analysed by the application of atomic emission spectrometry with inductively coupled plasma (AES-ICP) and electrothermal atomic absorption spectrometry (ETAAS). The following elements were analyzed: Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. The heavy metal 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). For AES-ICP instrument calibration and quantitative determination of each element in the deposited matter, a commercial standard mix solution (11355-ICP Multi Element Standard IV, Merck) was used. The correlation coefficient of the 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 limit of detection for the method was calculated based on the average measurement of the blank sample (γ ± 3δ). For all laboratory samples and standard solutions, treated ultrapure water was used. The optimal instrumental parameters for both techniques are given in Tables 1 and 2.

Table 1. Instrumentation and operating conditions for the ICP-AES 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

The QC of ICP-AES determination was performed by the standard addition method, and it was found that the recovery for the investigated elements ranged between 97.5 and 100.8%. The same method was applied for the determination of some trace elements in the reference standard materials JSAC 0401 (soil) and SARM 3 (rock), yielding values very close to certified values.

Results and discusion

The obtained statistical data for the content of elements, median values and ranges for the deposited dust samples studied in this research at three sampling sites (Fig. 2) for the entire measuring period (January-December-2009) are presented in Tables 3 and 4. Significant differences (p=0.05, ANOVA) in the annual averages of all measured pollutants were found among the sampling sites. For each observation, there were a few variables: sample identification number, locality, geographical coordinates, sample type and concentration level for 18 elements.

For statistical analysis of the data, parametric and nonparametric statistical methods were used. Minimal and maximal mean calculation methods of the median, geometrical mean, standard deviation, geometric standard deviation, skewness, kurtosis and arithmetical mean were calculated and histograms were drawn to show the distribution. Table 3 shows the basic statistics for samples of deposited dust for the period from January-December 2009. As can be seen from the obtained data presented in Table 3, the median values for the nickel in the deposited dust samples taken from the study area was 101 mg kg^{-1} and the min/max range of values showed a much higher content of this element in the samples from this area (range from 5.24 to 1289 mg kg^{-1}). Similar results were obtained for the distribution of Co and Cr; the median value and the min/max range for these elements indicate increased content of these elements. The median value for Cr in deposited dust samples taken from the study area was 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 study area was 3.91 mg kg^{-1} (range from 0.23 to 75.58 mg kg^{-1}).

The amount of total deposited dust that was spread in the air is presented in Fig. 3. From the results obtained in this investigation, it is evident that a large amount of deposited dust was recorded in the summer of 2009 when the values were close to or above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}).

The ferronickel smelter plant uses ore that contains between 1% and 2.5% Ni, about 0.05% Co and 1-3% Cr. Therefore, we expect these elements to have significantly higher contents in samples of deposited dust compared to other elements. As can be seen from the data presented in Table 4, the median value for nickel in samples of deposited dust taken from the Kavadarci area was 28 mg kg^{-1} with a range from 5.23 to 140.9 mg kg^{-1}; in Brušani village, the median value for nickel in samples of deposited dust was 196.3 mg kg^{-1} with a range from 24.7 to 290 mg kg^{-1}; for Vozarci village, the median value of nickel in deposited dust samples was 144.9 mg kg^{-1} with a range from 20.7 to 393 mg kg^{-1}. From these results,

Table 2. Optimal instrumental parameters for ETAAS determination

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	

it can be seen that the values for the content of Ni in Vozarci village, located near the ferro-nickel smelter plant (Fig. 2), had the highest content of Ni compared to the other two locations where monthly samples of deposited dust were collected from the Kavadarci area in 2009.

Figures 4-6 show the values for the content of Ni, Cr and Co in deposited dust collected at all three locations. The values obtained for the content of nickel in deposited dust collected in Vozarci village (near the ferronickel smelter) in January-March 2009 was very high (477 to 1290 mg kg^{-1}) while the content was relatively low (25 to 222 mg kg^{-1}) at the other locations with the exception of the samples collected in July (301 mg kg^{-1}) and September (428 mg kg^{-1}), as shown in Figure 4. This trend of increased nickel content in the deposited dust was followed by an increased content of chromium (Fig. 5) and cobalt (Fig. 6). The content of chromium in deposited dust collected in Vozarci village was high for the first four months of 2009 (65 to 140 mg kg^{-1}). For cobalt (Fig. 6), the highest values were obtained from the deposited dust collected in Vozarci village in January-March 2009 (28 to 76 mg kg^{-1}). This suggests that increased emission of dust from the smelter plant occurred during these months.

These elements (Co, Cr and Ni) can enter the atmosphere from refining plants. Once they are airborne, they can attach to dust in the air. Over time, the dust falls to the ground or mixes with rain or snow, where it enters the soil. Exposure to nickel in the general population takes place via the inhalation of dust or the ingestion of food and water. Inhaled nickel is absorbed by the body, depending on the solubility of nickel in the air (WHO, 1991).

The median value for Co in deposited dust samples taken from Kavadarci was 1.43 mg kg^{-1} (range from 0.23 to 7.5 mg kg^{-1}), while in Brušani village the median value was 10.8 mg kg^{-1} (range from 1.7 to 75.5 mg kg^{-1}) and for Vozarci village the median value was 3.9 mg kg^{-1} (range from 0.99 to 25 mg kg^{-1}). The median value for Cr in Kavadarci was 4.3 mg kg^{-1} (range from 0.7 to 33.5 mg kg^{-1}), while the median for Brušani village was 31.9 mg kg^{-1} (range from 1.83 to 139 mg kg^{-1}) and for Vozarci village the median was 14 mg kg^{-1} (range from 4.3 to 47 mg kg^{-1}). In Brušani village, the content of cobalt and chromium in deposited dust samples was higher compared to the content of these elements in Vozarci village and Kavadarci. From these results, it can be concluded that the dust distribution follows the dominant winds from the N, NW and SE (Lazarevski, 1993). These results indicate that the contents of these elements (Co, Cr and Ni) were significantly higher compared with the other elements that were investigated.

In terms of the nickel content in the soil in Kavadarci and its environs, it was found that the medi-

Table 3. 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.

Table 4. Statistical parameters for annual values for the content of chemical elements in samples of deposited dust measured in Kavadarci and its environs

Average values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg kg^{-1}

Element/ Statistical parameters	**Sampling sites**								
	Kavadarci			**Vill. Brušani**			**Vill. Vozarci**		
	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.

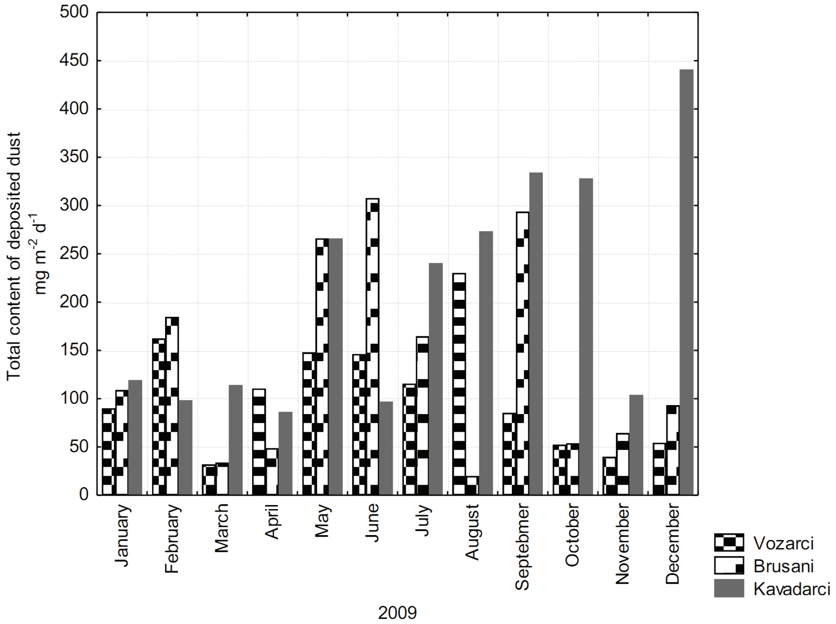

Fig. 3. The total content of deposited dust

an and average values were very similar (72 mg kg^{-1} and 74 mg kg^{-1}, respectively) and that the content of nickel in the entire investigated area ranged between 42 and 150 mg kg^{-1} (Stafilov et al., 2010). The average value for the content of nickel in moss samples from the investigated region was 80 mg kg^{-1} and ranged 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 nickel content in moss samples collected from the territory of the Republic of Macedonia (Barandovski et al., 2006, 2008), and shows a direct connection with pollution from the ferronick-

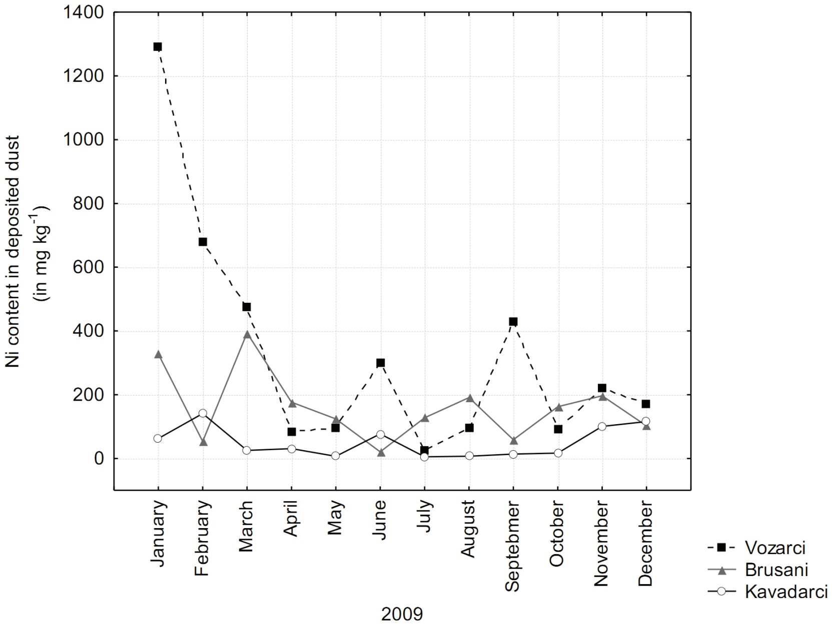

Fig. 4. Content of Ni in deposited dust (in mg kg^{-1})

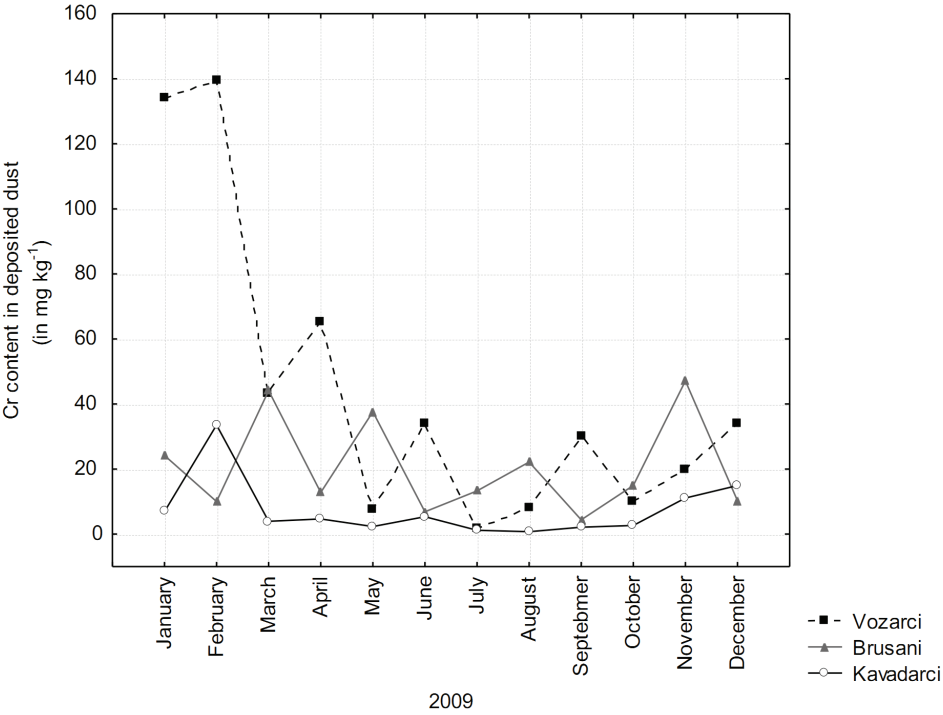

Fig. 5. Content of Cr in deposited dust (in mg kg^{-1})

el smelter plant situated near the city of Kavadarci. Data on the presence of nickel in soil samples also confirm that the main source of air pollution is dust emission from the smelter plant, because the content of nickel in soil samples was relatively low. Moreover, it was found that the nickel contents in the subsoil and topsoil were almost the same, which shows that the nickel in soil is of natural origin (Stafilov et al., 2008). Critically high concentrations of Ni and Cr were found in both the topsoil and subsoil and at sampling points from the SW, W and NW parts of the investigated region. The highest concentrations of Cr and Ni were found at sampling points near the village Debrište, SE of the village Vozarci and W of the hydropower plant at Tikveš (Stafilov et al., 2010).

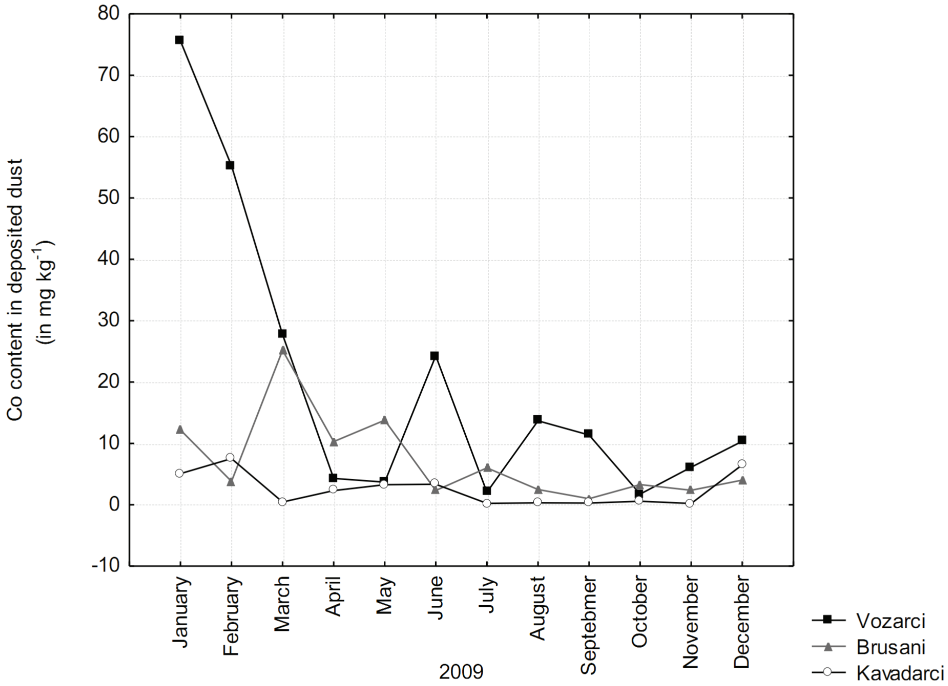

Fig. 6. Content of Co in deposited dust (in mg kg^{-1})

Our previous investigation on the distribution of Ni, Co and Cr in attic dust showed increased content in samples from the smelter plant surroundings compared to the content in the rest of the samples from the same region (Bačeva et al., 2011). Samples of attic dust were collected during the same period at 31 sites in Kavadarci and its environs.

This also confirms that the dust that is discharged from this plant is connected to the ferronickel ore that is being processed at the smelter plant. Namely, the median value of nickel in attic dust samples taken from the entire investigated area was 220 mg kg^{-1}. However, a very high nickel content was found in attic dust samples taken from the vicinity of the ferronickel smelter plant (range from 89 to 1200 mg kg^{-1}). Thus, the average value for the content of nickel in attic dust samples from the polluted area was 354 mg kg^{-1}, while in the unpolluted area the average was 156 mg kg^{-1}, an enrichment ratio of 2.27. The cobalt and chromium results also show significantly higher contents in the samples of attic dust taken from the same investigated region. The median value for Co in attic dust samples taken from the studied area was 17 mg kg^{-1} (range from 10 to 52 mg kg^{-1}) and the median value for Cr was 140 mg kg^{-1} (range from 72 to 510 mg kg^{-1}).

From the results shown in Table 5, it is clear that the values for the continuous probability distribution – F (which is acquired by running a variation analysis on the attic dust samples) for Co, Cr and Ni in the attic dust samples originating from the vicinity of the smelter plant and those from the rest of the investigated area were significantly higher compared to the F values for the other elements. Namely, if these values are compared with the tabular critical value for F, which for the corresponding number of samples and degrees of freedom is 2.32 (Miller and Miller, 1993), it is clear that the values for some of these elements were remarkably high (17.90 for nickel, 18.67 for chromium and 12.86 for cobalt). The present data make it clear that the source of some of the heavy metals in the air in the investigated region is dust that comes from this smelter plant.

Conclusions

Monitoring samples of total dust deposition and deposited matter showed the distribution of high contents of the investigated elements at greater distances from the ferronickel smelter plant. From these results, it is clear that a large amount of deposited dust was recorded in the summer of 2009; these values were close to or above the maximum permissible amount of dust powder (300 mg m^{-2} d^{-1}). The values for the nickel content in deposited dust collected in the village of Vozarci (near the ferronickel smelter) in the winter period of 2009 was very high, while in the remaining period, this content was relatively low, with the exception of July and Septem-

Table 5. Averages and enrichment ratios of Co, Cr and Ni in attic dust samples according to the sampling locations (values are given in mg kg^{-1})

Element	Average for Kavadarci region	Samples around the FeNi smelter	Samples from the rest of the region	ER (Feni/Rest)	F (around Feni smelter)
Co	18	22	15	1.50	12.86
Cr	140	193	105	1.84	18.67
Ni	230	354	156	2.27	17.90

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).

ber. This trend of increased nickel content in dust monitoring was followed by the content of chromium and cobalt in deposited dust. This suggests that, during these months, the emission of dust from the smelter had increased.

References

Avila, A. & Rodrigo, A. (2004). Trace metal fluxes in bulk deposition, through fall and stemflow at two evergreen oak stands in NE Spain subject to different exposure to the industrial environment. *Atmospheric Environment*, **38**: 171–180.

Bačeva, K., Stafilov, T., Šajn, R. (2009). Biomonitoring of nickel air pollution near the city of Kavadarci, Republic of Macedonia. *Ecology and Protection of the Environment*, **12**: 57–69.

Bačeva, K., Stafilov, T., Šajn, R., Tănăselia, C., Ilić Popov, S. (2011). Distribution of chemical elements in attic dust in the vicinity of ferronickel smelter plant. *Fresenius Environmental Bulletin*, **20**(9): 2306-2314.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2009). Atmospheric pollution with copper around the copper mine and flotation, Bučim, Republic of Macedonia, using biomonitoring moss and lichen technique. *Geologica Macedonica*, **23**: 35–41.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2010a). Bıomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia. *Journal of Environmental Science and Health, Part A*, *Toxic/Hazardous Substance & Environmental Engineering*, **45**: 1504–1518.

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2010b). Distribution of chemical elements in attic dust as reflection of lithology and anthropogenic influence in the vicinity of copper mine and flotation. *Archives of Environmental Contamination Toxicology*, **61**: 173–184.

Barandovski, L., Cekova, M., Frontasyeva, M. V., Pavlov, S. S., Stafilov, T., Steinnes, E., Urumov, V. (2006). *Air pollution studies in Macedonia using the moss biomonitoring technique, NAA, AAS and GIS Technology*. Preprint E18-2006-160, Joint Institute for Nuclear Research, Dubna.

Barandovski, L., Cekova, M., Frontasyeva, M. V., Pavlov, S. S., Stafilov, T., Steinnes, E., Urumov, V. (2008). Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique. *Environmental Monitoring and Assessment*, **138**: 107–118.

Boev, B. & Jankovic, S. (1996). *Nickel and nickeliferrous iron deposits of the Vardar zone (SE Europe) with particular references to the Rzanovo-Studena Voda ore-bearing series*. Special issue No. 3, 103–126, Faculty of Mining and Geology, Stip.

Brown, R. J. C., Shaw, M. C., Roberts, M. R. (2006). Practical methodology for the solubility speciation analysis of ambient dust deposits for heavy metals: application to a 6 month measurement campaign. *International Journal of Environmental Analytical Chemistry*, **86**: 453–460.

Čačković, M., Kalinić, N., Vadjić, V. G., Pehnec, G. (2009). Heavy metals and acidic components in total deposited matter in Šibenik and National park Kornati, Croatia. *Archives of Environmental Contamination and Toxicology,* **56**: 12–20.

Dudka, S, & Adriano, C. D. (1997). Environmental impacts of metal ore mining and processing: A review. *Journal of Environmental Quality*, **26:** 590–602.

Franzaring, J., Hrenn, H., Schumm, C., Klumpp, A., Fangmeier, A. (2006). Environmental monitoring of fluoride emissions using precipitation, dust, plant and soil samples. *Environmental Pollution*, **144**: 158–165.

Holden, T. (2006). Air Quality - Dust Monitoring. Environmental Defender's Office Ltd (NSW).

Hou, H., Takamatsu, T., Koskiwa, M. K., Hosomi, M. (2005). Trace metal sin bulk precipitation and throughfallin a suburban area of Japan. *Atmospheric Environment*, **39**: 3583–3595.

Hršak. J., Škrbec, A., Balagovic, I., Šega, K. (2003). Thallium content in Zagreb. *Bulletin of Environmental Contamination and Toxicology*, **71**: 131–134.

IPCS (1996). *Environmental Health Criteria-182,* *Thallium*. WHO, Geneva.

Lazarevski, A. (1993). *Climate in Macedonia*. Kultura, Skopje.

Maksimović, Z. (1982). *Mineralogical Study of the Ore from Ržanovo Mine*. Faculty of Geology and Mining, Belgrade.

Miller, J. C. & Miller, J. N. (1993). *Statistics for Analytical Chemistry*. 3rd ed., Ellis Horwood PTR Prentice Hall, London.

Morselli, L., Olivieri, P., Brusori, B., Passarini, F. (2003). Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy. *Environmental Pollution*, **124**: 457–469.

Polkowska, Z., Astel, A., Walna, B., Małek, S., Mędrzycka, K., Górecki, T., Siepak, J., Namieśnik, J. (2005). Chemometric analysis of rain water and throughfall at several sites in Poland. *Atmospheric Environment*, **39**: 837–855.

Ripley, E.A, Redmann, R.E., Crowder, A.A. (1996). *Environmental effects of mining*. St. Luice Press, Delray Beach, FL, 356 pp.

Salomons, W. (1995). Environmental inpact of metals derived from mining activities: Processes, predictions, preventions. *Journal of Geochemical Exploration*, **44**: 5–23.

Sengupta, M. (1993). *Environmental impacts of mining*: *Monitoring, restoration and control*, Lewis Publishers, Boca Raton, FL.

Serafimovski, T., Stefanova, V., Volkov, A.V. (2010). Dwarf copper-gold porphyry deposits of the Buchim-Damjan-Borov Dol ore district, Republic of Macedonia. ***Geology of Ore Deposits***, **52:** 179–195.

Stafilov, T., Bojkovska, R., Hirao, M. (2003). Air pollution monitoring system in the Republic of Macedonia. *Journal of Environment and Protection Ecology*, **4**: 518–524.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski**, M. (2008).** *Geochemical atlas of Kavadarci and the environs*. Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, Skopje.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M., Lepitkova, S. (2010). Distribution of some elements in surface soil over the Kavadarci Region, Republic of Macedonia. *Environmental Earth Sciences*, **61**(7): 1515–1530.

Tsitouridou, R., Anatolaki, Ch. (2007). On the wet and dry deposition of ionic species in the vicinity of coal-fired power plants, northwestern Greece. *Atmospheric Research*, **83**: 93–105.

Vike, E. (2005).Uptake, deposition and wash off fluoride and aluminium plant foliage in the vicinity of aluminum smelter in Norway. *Water, Air and Soil Pollution*, **160:** 145–159.

WHO (1991) International Programme on Chemical Safety, Environmental Health Criteria – *Nickel*, World Health Organization: Geneva.