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BIOMONITORING OF NICKEL AIR POLLUTION NEAR THE CITY OF KAVADARCI, REPUBLIC OF MACEDONIA

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ABSTRACT

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Air pollution with nickel was investigated in the vicinity of the ferronickel smelter plant near the city of Kavadarci, Republic of Macedonia. In this work the moss biomonitoring technique and atomic emission spectrometry with inductively coupled plasma was applied. The purpose of the study was to establish range of air pollution with nickel which could be expected due to the pollution from the ferronickel plant. For this purpose, 35 moss samples were collected together with 19 soil samples taken from the same localities as a topsoil (0-5 cm) and subsoil (20-30 cm). The analyses of moss and soil samples were performed using atomic emission spectrometry with inductively coupled plasma. The obtained results show that there is evidently higher content of nickel in moss samples collected in the vicinity of the ferronickel smelter plant. The median value of Ni in moss samples from the whole region (31.0 mg kg^{-1}) is much higher that the median for Macedonia (2.4 mg kg^{-1}). This fact confirms the influence of the air pollution with dust from the ferronickel plant in the larger region of city of Kavadarci.

Key words: Air pollution, nickel, moss, soil, Kavadarci, Macedonia

ИЗВОД

Бачева, К., Стафилов, Т., Шајн, Р. (2009). Биомониторинг на загадувањето на воздухот со никел во околината на Кавадарци, Република Македонија. Екол. Зашт. Живот. Сред., Том, 12, Бр. 1-2, 57-69, Скопје

Испитувано е загадувањето на воздухот со никел во околината на топилницата за фероникел близу Кавадарци, Република Македонија. Во студијата применети се техниките со биомониторинг со мовови и атомската емисиона спектрометрија со индуктивно спрегната плазма. Целта на испитувањето е да се утврди областа на загадувањето на воздухот со никел кое може да се очекува како резултат од работењето на топилницата. За таа цел земени се 35 примероци од мов како и 19 примероци почва од истите локации и тоа како површински почви (0-5 cm) и подповршински почви (20-30 cm). Земените примероци од мов и почви беа анализирани со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма. Добиените резултати покажуваат значително повисоки вредности за содржините на никел во примероците од мов земени од околината на топилницата за фероникел. Вредностите на медијаната за Ni во примероците мов од целата испитувана област на Кавадарци и неговата околина (31,0 mg kg^{-1}) е многукратно повисока од онаа за Македонија (2,4 mg kg^{-1}). Ова го потврдува фактот за влијанието на работата на топилницата врз загадувањето на воздухот во поширокиот регион на Кавадарци.

Клучни зборови: Загадување на воздухот, никел, мов, почва, Кавадарци, Република Македонија

Introduction

The data from moss surveys allow examination of both spatial and temporal trends in heavy metal deposition and identification of areas where there is high deposition of heavy metals from long-range transport and local sources. In the Republic of Macedonia the first systematic study of atmospheric pollution from heavy metals and other toxic elements based on moss analysis was undertaken in the framework of Macedonian-Russian collaboration in order to assess the general situation regarding heavy metal pollution and to jointly report these results to the European Atlas of Heavy Metal Atmospheric Deposition issues by UNECE ICP Vegetation (Barandovski 2006, 2008).

The presence of heavy metals in air in Macedonia had been previously studied only for some particular locations (Veles and Skopje), using atomic absorption spectrometry (AAS) for determination of a limited number of elements (Mulev et al. 1993; Kadifkova Panovska et al. 1996; Stafilov and Jordanovska 1997; Kulevanova et al. 1998; Stafilov et al. 2003). In 2002 moss samples were collected for the first time over the entire territory of Macedonia and subsequently analyzed by multi-element instrumental epithermal neutron activation analysis (Barandovski et al. 2006, 2008; Barandovski 2009), previously successfully used in similar studies in different Balkan countries (Stamenov et al. 2002; Cucu-Man et al. 2004; Frontasyeva et al. 2004). The obtained results from this study show that most important pollution sources are related to smelters near the cities of Veles and Kavadarci along the valley of the river Vardar extending from Skopje to Veles and continuing southeastwards toward Demir Kapija.

Therefore, the purpose of this study was to establish contents and distribution of nickel by using biomonitoring moss technique in the city of Kavadarci and its environs, and to define the extent of the air pollution with nickel.

For the comparison of the results from moss survey with the geology of the region, and to check if the pollution of the air with nickel is connected with the air particles from the surrounding soils, 19 soil samples were taken from the same localities were moss samples were collected, as a topsoil (0-5 cm) and subsoil (20-30 cm).

There were several investigations of soil, vegetables and fruits produced in this region but they were mainly concerned with contamination by nickel, iron, cobalt and chromium (Boev et al. 2005). Other elements were not determined though it is known that the minerals of many other heavy metals are present in iron-nickel ores used for the production of nickel in the smelter plants (Maksimović 1982; Stafilov et al. 1982; WBG 2006; Filipovski 2003; Everhart et al. 2006; Micro et al. 2006). Additional reason for the comparison of data from moss and soil analysis from this region are the results obtained from the first systematic study of spatial distribution of different elements in surface soil and subsoil over of the Kavadarci region, showing that the important source of trace metals deposition in the close surrounding is the ferronickel smelter (Stafilov et al. 2008).

Study area

Town Kavadarci is located in Tikveš valley about 100 km south from the capital Skopje (Fig.1). It is main vine production region in Macedonia. The municipality of Kavadarci (38,741 inhabitants; 992.44 km^2) includes of the town of Kavadarci (28,000 inhabitants) and 39 settlements. The urban area is located on 200-300 m altitude, surrounded with hills from east and south sides of the valley with height difference approximately between 300 and 770 m. The west side of the valley is surrounded by the hills Ljubaš, Dabov Vrv and the Klepa Mountain. The east side of the valley is surrounded by the mountain of Serta and the south with upland Vitačevo and the Kožuf Mountain.

The study area (Figs. 1 and 2) is located in the south-central part of Macedonia with an approximate area of about 400 km^2. The investigated region is covered by a sampling grid for soil of 2 x 2 km^2; in the urbane zone and around the ferronickel smelter plant the sampling grid is denser (1 x 1 km^2). All together, in the 19 locations 38 soil samples were collected. At each sampling point were collected soil samples at two depths, top soil (0-5 cm) and subsoil (20-30 cm) soil. Within towns, we sampled urban soil such as soil in the gardens and on the grass verges. One sample represents the composite of material sampled in the sample point itself. Close to each sample location the moss samples are collected. Most of the selected moss samples were around ferronickel factory.

The geological description of the investigated area is presented in the Geochemical Atlas of Kavadarci and its Environs (Stafilov et al., 2008). It was found that the oldest formations have directions NW-SE and belong to the inner parts of the Vardar zone. The Lower Paleozoic (Pz) metamorfic complex is present with two series: amphibole and amphibolechlorite schists with marbes and phylite layers. Serpentite 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 Cretaccous ages. Paleozoic and Mesozoic rocks cover approximately 39 km^2 in the SW and W part of the investigatetd area. Complexes of Tertiary and

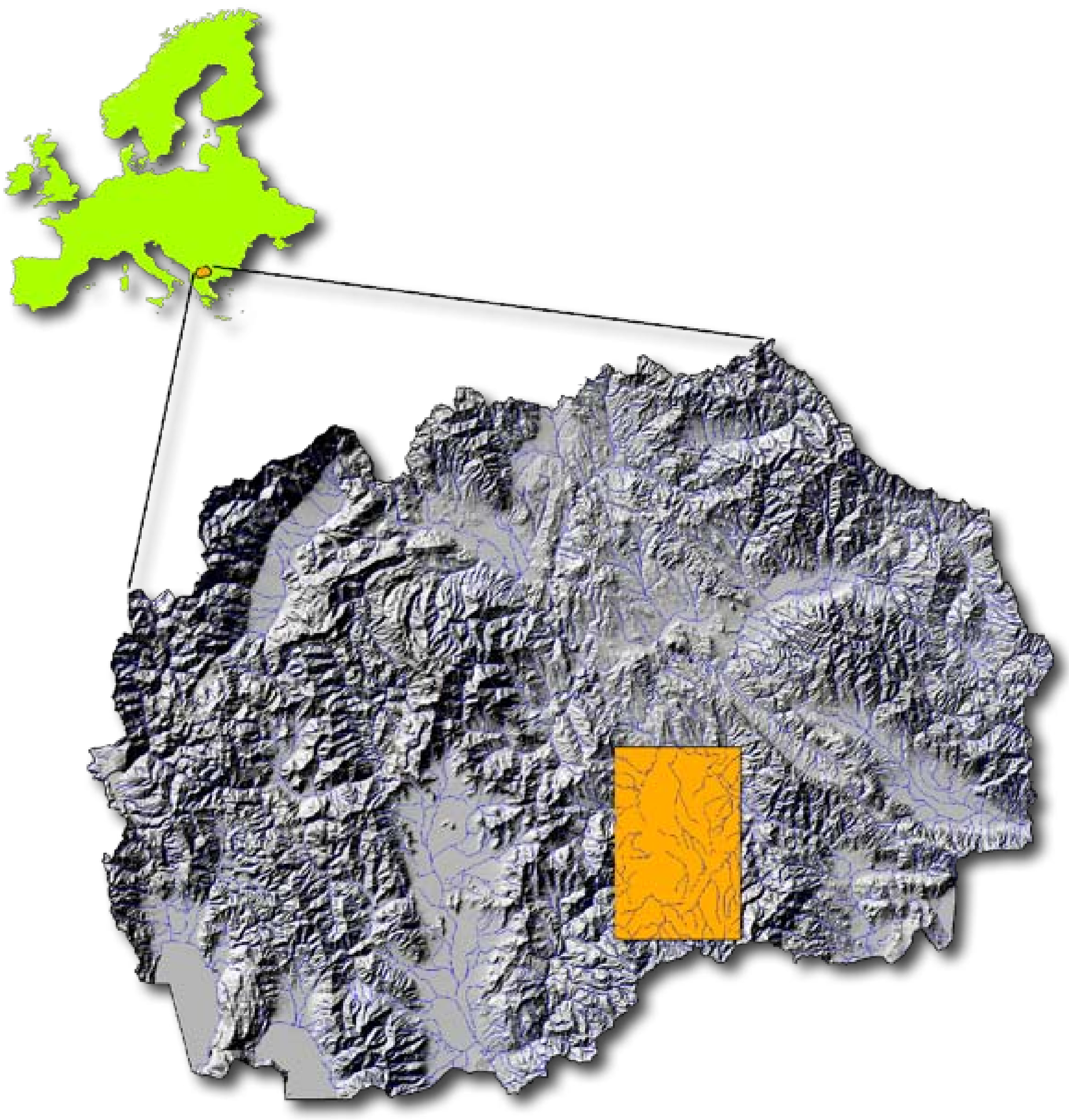


Fig. 1. The investigated region of Kavadarci and its environs
Сл. 1. Истражуваното подрачје кај Кавадарци и околината

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 sedoments 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 fomations that have directions NW-SE. This sequence is represented mainlu with sandy series. Pliocene (Pl) sediments cover the biggest part (about 182 km^2) in the central part of the investigated area. SE from the Kavadarci are found the Quaternary (Q) pyroclastic vulcanites represented with tuffs, breccias and agglomerates, whic cover approximately 25 km^2.

Materials and methods/experimental

Instrumentation

Nickel was analyzed by the application of atomic emission spectrometry with inductively coupled plasma (AES-ICP). The optimal instrumental parameters for both techniques are given in Table 1.

Reagents and standards

Stock solution of nickel with a concentration of 1000 mg L^{-1} (Solutions Plus Inc.) serves for further dilutions. All chemicals used were of analytical grade: hydrofluoric acid, p.a. (Fluka, Germany); per-

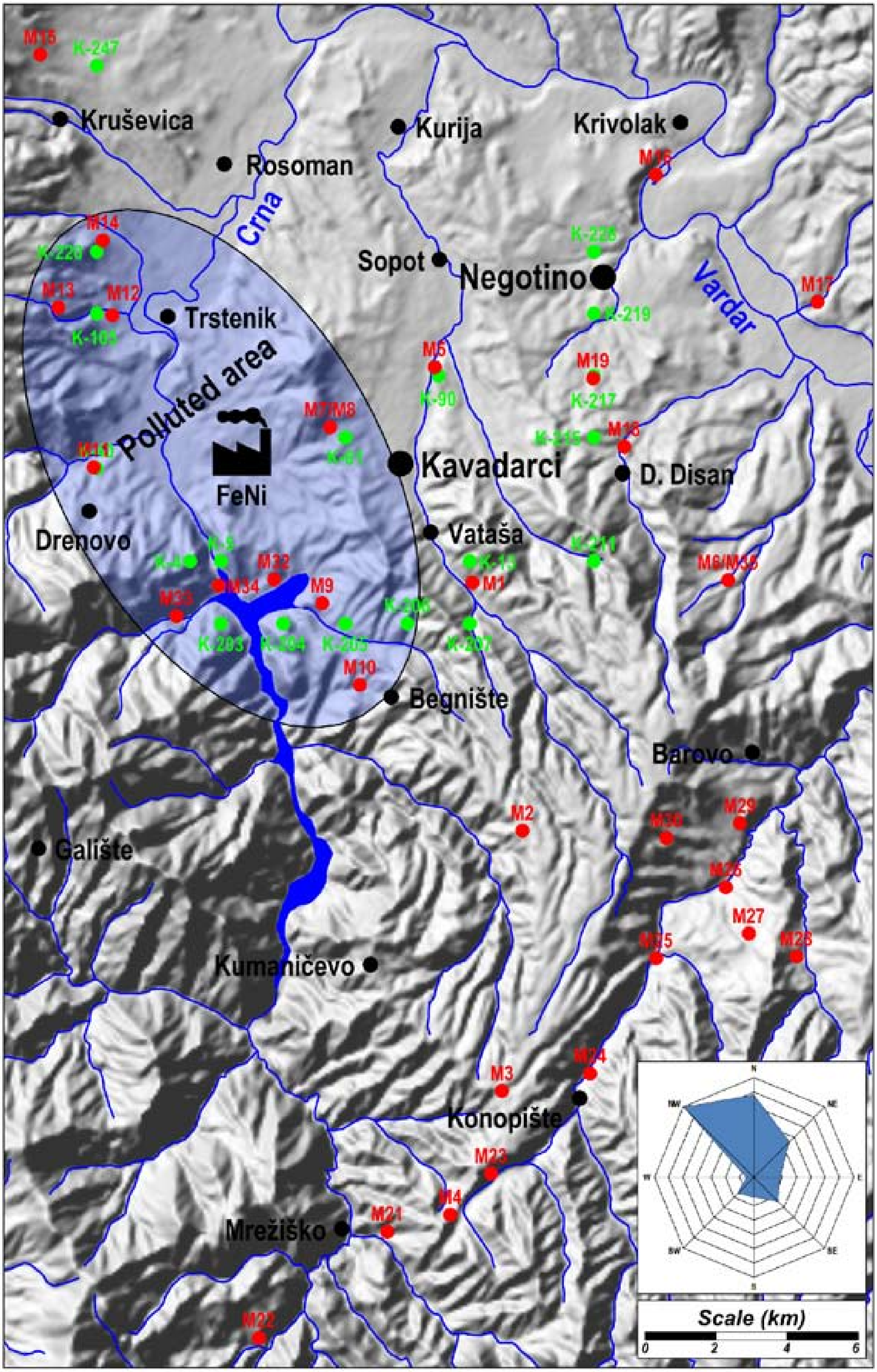


Fig. 2. Location of the sampling points for moss and soil samples

Сл. 2. Локации на точките каде беа земани проби од мовови и почви

Tab 1. Instrumentation and operating conditions for ICP-AES system
Таб. 1. Инструменти и оперативни параметри на ICP-AES системот

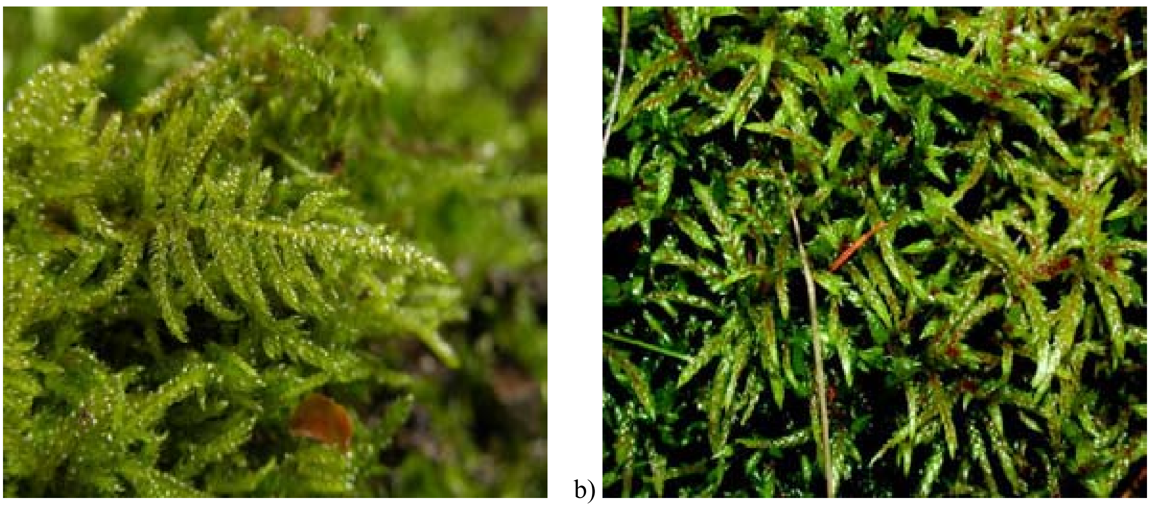
RF Generator			
Operating frequency	40.68 MHz free-running, air-cooled RF generator.		
Power output of RF generator	700–1700 W in 50 W increments		
Power output stability	Better than 0.1%		
Introduction Area			
Sample Nebulizer	V- groove		
Spray Chamber	Double-pass cyclone		
Peristaltic pump	0-50 rpm		
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		
Wavelength for Ni measurement	231.604 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

chloric acid, p.a. (Alkaloid, Macedonia); hydrochloric acid, p.a. (MERCK, Germany); hydrogen peroxide, p.a. (MERCK, Germany) and nitric acid, p.a. (MERCK, Germany).

All vessels used were pre-cleaned by leaching for 24 h each in proportion of 1 part HNO_3 and 3 parts HCl, followed by rinsing with doubly distilled water.

Sampling

Samples of the two moss species (Fig. 3), *Hylocomium splendens* (Hedw.) (32 samples) and Pleurozium *schreberi* (Brid.) (3 samples) were collected at 35 localities evenly distributed over the country during the period September–October, 2008.



a) b)

Fig. 3. Moss species used in the present study **a**) *Hylocomium splendens* (Hedw.); and b) *Pleurozium schreberi* (Brid.)
Сл. 3. Видови мов кои беа анализирани а) *Hylocomium splendens* (Hedw.); и b) *Pleurozium schreberi* (Brid.)

The sampling was carried out in accordance with the strategy of the European moss survey programme (Rühling and Steinnes 1998). Samples were collected at least 300 m from main roads, at least 100 m from local roads and at least 200 m from villages, in forest glades or on open heath to reduce throughfall effects from the forest canopy. In order to make the moss samples representative for a reasonably large area, each sample was composed of five to ten subsamples collected within an area of 50 × 50 m. Collected material was stored in paper bags. A separate set of disposable polyethylene gloves was used for collection of each sample. *Hylocomium splendens* (Hedw.) - was the dominant moss type (with 32 moss species of *Hylocomium splendens* (Hedw.) and 3 moss species of *Pleurozium schreberi* (Brid.)). Interspecies comparison (possible in a limited number of cases) did not reseal great difference in the elemental concentrations. It was mostly within the error estimations.

Sample preparation

Moss samples (0.5 g) were placed in a Teflon digestion vessels, 5 mL concentrated nitric acid and 2 mL H_2O_2 (30 %, m/V) were added, and the vessels were capped closed, tightened and placed in the rotor of the Mars microwave digestion (CEM, USA). The digestion was carried out with the following digestion program: (1) temperature 180 ˚C, 10 min ramp time, 1400 W; (2) temperature 180 ˚C, 5 min hold time, 1400 W. Finally, the vessels were cooled, carefully opened, and digests were quantitatively transferred to 25 mL calibrated flasks.

All soil samples were air-dried. All the material was spread, in a layer not thicker then 15 mm, on a tray which does not absorb any moisture from the soil and which does not cause contamination. It is essential that direct sunlight be avoided. If the soil samples have dried into clods, crushing is necessary. Before crushing, remove stones, fragments of glass and rubbish, which are larger than 2 mm by sieving and hand picking. Take care to minimize the amount of fine material adhering to the separated stones. After drying soil samples are milled in agate mill and pulverized.

Procedure for digestion of soil samples

Weigh precisely 0.500 g of the milled soil sample and placed in a Teflon digestion vessel and add 10 mL of nitric acid. Place the dish on the asbestos net plate at ring at 100 ˚C and evaporate until approximately 1 mL of nitric acid remains. Note that several successive additions of nitric acid may be necessary until the emission of nitrous vapors ceases to remove all organic matter. After the last addition of nitric acid, remove the dish from the hot plate and cool to room temperature before undertaking the digestion.

After cooling add 10 mL hydrofluoric acid and 3 mL of perchloric acid to the pretreated portion. Heat this mixture on the hot plate until the dense fumes of perchloric acid and silicon tetrafluoride cease. Do not allow the mixture to evaporate to complete dryness. Remove the vessel from the hot plate allow cooling, adding 2 mL of hydrochloric acid or 2 mL of nitric acid and approximately 5 mL of water to dissolve the residue. Transfer this solution quantitatively to the 50 mL volumetric flask, fill to the mark and mix well.

Sensitivity, accuracy and precision of analysis

Precision was controlled by relative differences between pairs of analytical determinations of the same sample. Precision was considered good (Miesch 1976).

Results and discussion

The obtained results for the content of nickel in 35 moss samples and 38 soil samples with 19 topsoil and 19 subsoil (with the lithology and the cone of the sample locality) are given in Tables 2 and 3.

Data from the descriptive statistic of chemical analyses of moss, topsoil and subsoil samples from Kavadarci area are given in Table 4; the averages and enrichment ratios of Ni (mg/kg) in different groups of moss samples according to basic lithological units in Table 5; while the averages and enrichment ratios of Ni (mg/kg) in different groups of moss, topsoil and subsoil samples according to sampling locations in Table 6.

As it can be seen from data presented in Table 4, the average value for the content of nickel in moss samples from the investigated region is 80 mg/kg, ranges from 14 to 340 mg/kg). This value is much higher than the average of 6.6 mg/kg for the content of nickel in moss samples collected from the territory of the Republic of Macedonia, Table 5 (Barandovski et al., 2006, 2008), which show direct connection with the pollution from the ferronickel smelter plant situated near the city of Kavadarci.

Data presented in Tables 5 and 6 undoubtedly show that we can separate two populations of data which are influenced by the geological background (the differences between Pliocene (Pl) sediments and Quaternary tuff Q-tuff) (Stafilov et al., 2008), and two populations influenced by ferronickel smelter plant activities, polluted with the surface area of about 120 km^2 and unpolluted area, Fig. 4. Namely, the enrichment ratio of moss from Kavadarci area (Pleistocene sandy series vs. Pleistocene tuff) is 1.7, for samples around ferronickel plant vs. the samples from the nonpolluted area is 5.4. The values of continuous probability distribution (F) obtained by the analysis of variance for moss between

Tab. 2. The content of nickel in all investigated moss samples with the lithology and the cone of the sample locality
Таб. 2. Содржина на никел во анализираните примероци мов со литолошки карактеристики и локациите на земање проби

Sample	Lithology	Cone	Ni (mg/kg)
M1	Tuff (Q)	Surroundings	41.2
M2	Tuff (Q)	Surroundings	38.8
M3	Tuff (Q)	Surroundings	39.9
M4	Tuff (Q)	FeNi	30.3
M5	Sandy series (Pl)	Surroundings	84.6
M6/M35	Sandy series (Pl)	Surroundings	18.1
M7/M8	Sandy series (Pl)	FeNi	307.2
M9	Tuff (Q)	FeNi	221.4
M10	Tuff (Q)	FeNi	97.1
M11	Sandy series (Pl)	FeNi	190.5
M12	Sandy series (Pl)	FeNi	107.8
M13	Sandy series (Pl)	FeNi	89.1
M14	Sandy series (Pl)	Surroundings	62.2
M15	Sandy series (Pl)	Surroundings	44.1
M16	Sandy series (Pl)	Surroundings	40.6
M17	Sandy series (Pl)	Surroundings	18.8
M18	Sandy series (Pl)	Surroundings	24.0
M19	Sandy series (Pl)	Surroundings	25.1
M21	Pz-Mz rocks	Surroundings	111.6
M22	Pz-Mz rocks	Surroundings	24.8
M23	Tuff (Q)	Surroundings	19.4
M24	Tuff (Q)	Surroundings	15.6
M25	Tuff (Q)	Surroundings	19.5
M26	Sandy series (Pl)	Surroundings	14.6
M27	Tuff (Q)	Surroundings	16.2
M28	Sandy series (Pl)	Surroundings	13.8
M29	Pz-Mz rocks	Surroundings	24.3
M30	Tuff (Q)	Surroundings	16.6
M32	Sandy series (Pl)	FeNi	344.4
M33	Sandy series (Pl)	FeNi	166.2
M34	Pz-Mz rocks	FeNi	212.2

Q - Quaternary; Pl - Pliocene; Pz-Mz – Paleozoic- Mesozoic

lithological units for moss samples from Macedonia is 68.8 and for the Kavadarci area is 1.8.

Data on the presence of nickel in the soil samples (Tables 3, 4 and 6) also confirm that the main source for air pollution is dust emission from the smelter plant because the content of nickel in soil samples is relatively low (Table 4). 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 natural origin (Stafilov et al. 2008).

It can be seen also that the nickel distribution follows the wind rose (Lazarevski 1993) with the dominant winds from N and NW and SE (Figs. 4-6). The median content of Ni in moss samples from the whole region (40 mg·kg^{-1}) is much higher that the median for Macedonia (2.4 mg kg^{-1}). Even more, this enrichment factor for the moss samples collected in the near vicinity of the factory is more that 70 times higher that the median value for Macedonia (Barandovski et al., 2008).

This fact assuredly confirms the influence of the air pollution with dust from the ferronickel plant in the closest region (about 120 km^2) with the population of about 3500. Namely, this smelter plant uses the nickel ore with a content of around 1 % of Ni from the Ržanovo mine, about 30 km south of the plant. The Ržanovo ore body has the following lithological rock types: hematite, magnetite-ribe-

Tab. 3. The content of nickel in all investigated topsoil and subsoil samples with the lithology and the cone of the sample locality

Таб. 3. Содржина на никел во сите површински и потповршински почвени проби со литолошки карактеристики и локации на точките за земање проби

Sample	Soil layer	Lithology	Cone	Ni (mg/kg)
K-4/1	Topsoil	Pz-Mz rocks	FeNi	769.9
K-4/2	Subsoil	Pz-Mz rocks	FeNi	821.9
K-5/1	Topsoil	Pz-Mz rocks	FeNi	83.5
K-5/2	Subsoil	Pz-Mz rocks	FeNi	79.9
K-13/1	Topsoil	Tuff (Q)	Surroundings	28.9
K-13/2	Subsoil	Tuff (Q)	Surroundings	61.1
K-40/1	Topsoil	Sandy series (Pl)	FeNi	73.6
K-40/2	Subsoil	Sandy series (Pl)	FeNi	70
K-61/1	Topsoil	Sandy series (Pl)	FeNi	74.7
K-61/2	Subsoil	Sandy series (Pl)	FeNi	74.1
K-90/1	Topsoil	Sandy series (Pl)	Surroundings	70.6
K-90/2	Subsoil	Sandy series (Pl)	Surroundings	79.7
K-105/1	Topsoil	Pz-Mz rocks	FeNi	262.8
K-105/2	Subsoil	Pz-Mz rocks	FeNi	235.7
K-203/1	Topsoil	Pz-Mz rocks	FeNi	43.9
K-203/2	Subsoil	Pz-Mz rocks	FeNi	36.1
K-204/1	Topsoil	Pz-Mz rocks	FeNi	112.9
K-204/2	Subsoil	Pz-Mz rocks	FeNi	98.4
K-205/1	Topsoil	Sandy series (Pl)	FeNi	62.2
K-205/2	Subsoil	Sandy series (Pl)	FeNi	61.2
K-206/1	Topsoil	Sandy series (Pl)	FeNi	39.7
K-206/2	Subsoil	Sandy series (Pl)	FeNi	34.5
K-207/1	Topsoil	Sandy series (Pl)	Surroundings	73
K-207/2	Subsoil	Sandy series (Pl)	Surroundings	75
K-211/1	Topsoil	Tuff (Q)	Surroundings	15.2
K-211/2	Subsoil	Tuff (Q)	Surroundings	13
K-215/1	Topsoil	Sandy series (Pl)	Surroundings	80.1
K-215/2	Subsoil	Sandy series (Pl)	Surroundings	57.1
K-217/1	Topsoil	Sandy series (Pl)	Surroundings	47
K-217/2	Subsoil	Sandy series (Pl)	Surroundings	46.5
K-219/1	Topsoil	Sandy series (Pl)	Surroundings	50.1
K-219/2	Subsoil	Sandy series (Pl)	Surroundings	53.6
K-220/1	Topsoil	Pz-Mz rocks	FeNi	73.9
K-220/2	Subsoil	Pz-Mz rocks	FeNi	76.5
K-228/1	Topsoil	Sandy series (Pl)	Surroundings	62
K-228/2	Subsoil	Sandy series (Pl)	Surroundings	61.7
K-247/1	Topsoil	Sandy series (Pl)	Surroundings	103.4
K-247/2	Subsoil	Sandy series (Pl)	Surroundings	106.7

Q - Quaternary; Pl - Pliocene; Pz-Mz – Paleozoic- Mesozoic

cite schists, dolomite-talc schists, talc schists and serpentine (Maksimović 1982; Boev and Jankovic 1996). In the last 4 years beside ore from Ržanovo mine, ore mainly from Gebe nickel mine, Indonezia (saprolite-limonite type) reach in nickel (2-2.5 %), is used. Therefore, the dust from this plant has the same content as the ore used as a raw material.

Tab. 4. Descriptive statistic of chemical analyses of moss, topsoil and subsoil samples from Kavadarci area; n = 31 (moss), n=19 (topsoil, subsoil).

Таб 4. Дескриптивни статистички параметри на хемиските анализи на мов, површински и длабински почвени проби од кавадаречко; n=31 (мовови), n=19 (површински и потповршински почвени проби).

	Material	Dis.	X	s	Xg	sg	Md	Min	Max	A	E
Ni	Moss	Log	80	89	48	2.7	40	14	340	0.55	-1.00
Ni	Topsoil	Log	110	170	73	2.3	73	15	770	1.20	3.71
Ni	Subsoil	Log	110	180	72	2.3	70	13	820	1.17	4.53

Dis. – distribution (Log - lognormal); X – mean; Xg – geometric mean; s – standard deviation; sg – geometric standard deviation; Md – median; Min - minimum; Max – maximum; A – skewness; E – kurtosis. Data round at two digits.

Dis. - дистрибуција (Log - lognormal); X –средна вредност; Xg – геометриска средна вредност; s -стандардна девијација; sg – геометриска стандардна девијација; Md - медијана; min- минимум; max- максимум; A - асиметричност; E - кутоза.

Tab. 5. Averages and enrichment ratios of Ni (mg·kg^{-1}) in different groups of moss samples according to basic lithological units. Data sources: Macedonian – Moss (Barandovski, 2009); Kavadarci – Topsoil (Stafilov et al., 2008, 2010).

Таб 5. Просечни вредности и индекс на збогатување со Ni (mg·kg^{-1}) во различни групи од анализираните примероци од мовови според основните литолошки единици. Изворни на податоците: мовови од Македонија (Barandovski 2009); површински почви од кавадаречко (Stafilov et al. 2008, 2010)..

	Macedonia – Moss				Kavadarci – Moss			
	Average	Pl-S	ER (I)	F	Pl-S	Q-T	ER (II)	F
n	72	13			16	11		
Ni	6.6	20	3.0	<u>68.8</u>	57	34	1.7	1.8

n – number of samples; Pl-S – Pliocene sandy series; Q-T – Pleistocene tuff; ER (I) – enrichment ratio – Macedonia (Pleistocene sandy series vs. Macedonian average); ER (II) – enrichment ratio of moss - Kavadarci area (Pleistocene sandy series vs. Pleistocene tuff); F – continuous probability distribution (analysis of variance) for moss between lithological units, significant values (p=0.05) are underlined.

n-број на проби; Pl-S - Плиоценска песоклива серија; Q-T - Плеистоценски туф; ER (I) - индекс на збогатување - Македонија (Плеистоценска песоклива серија / македонски просек); ER (II) - индекс на збогатување кај мововите - кавадаречко (Плеистоценска песоклива серија / Плеистоценски туф); F - непрекината веројатна дистрибуција (анализа на варијанса) за мововите помеѓу литолошките единици; статистички значајните вредности (p=0,05) се подвлечени.

Tab. 6. Averages and enrichment ratios of Ni (mg·kg^{-1}) in different groups of moss, topsoil and subsoil samples according to sampling locations. Data sources: Kavadarci – Topsoil (Stafilov et al., 2008, 2010).

Таб 6. Просечни вредности и индекс на збогатување со Ni (mg·kg^{-1}) во различни групи од анализираните примероци од мовови, површински и потповршински почви според локациите на земање проби. Извори на податоците: површински почви од кавадаречко (Stafilov et al. 2008, 2010).

	Kavadarci – Moss				Kavadarci – Topsoil				Kavadarci – Topsoil			
	FeNi	Rest	ER	F	FeNi	Rest	ER	F	FeNi	Rest	ER	F
n	10	21			10	9			10	9		
Ni	150	28	5.4	<u>45.70</u>	98	52	1.9	3.30	93	54	1.7	2.07

n – number of samples; FeNi – Area around ferronickel smelter (polluted area); Rest – Nonpolluted area; F – continuous probability distribution (analysis of variance) for moss, topsoil and subsoil between polluted area and nonpolluted area, significant values (p=0.05) are underlined; ER – enrichment ratios of moss, topsoil and subsoil – Kavadarci area (polluted area vs. nonpolluted area).

n-број на проби; FeNi - подрачје околу топилницата за фероникел (загадено подрачје); Rest - незагадено подрачје; F - непрекината веројатна дистрибуција (анализа на варијанса) за мововите, површинските и потповршинските почви помеѓу загаденото и незагаденото подрачје; статистички значајните вредности (p=0,05) се подвлечени; ER - индекс на збогатување кај мововите, површинските и потповршинските почви - кавадаречко (загадено/незагадено подрачје).

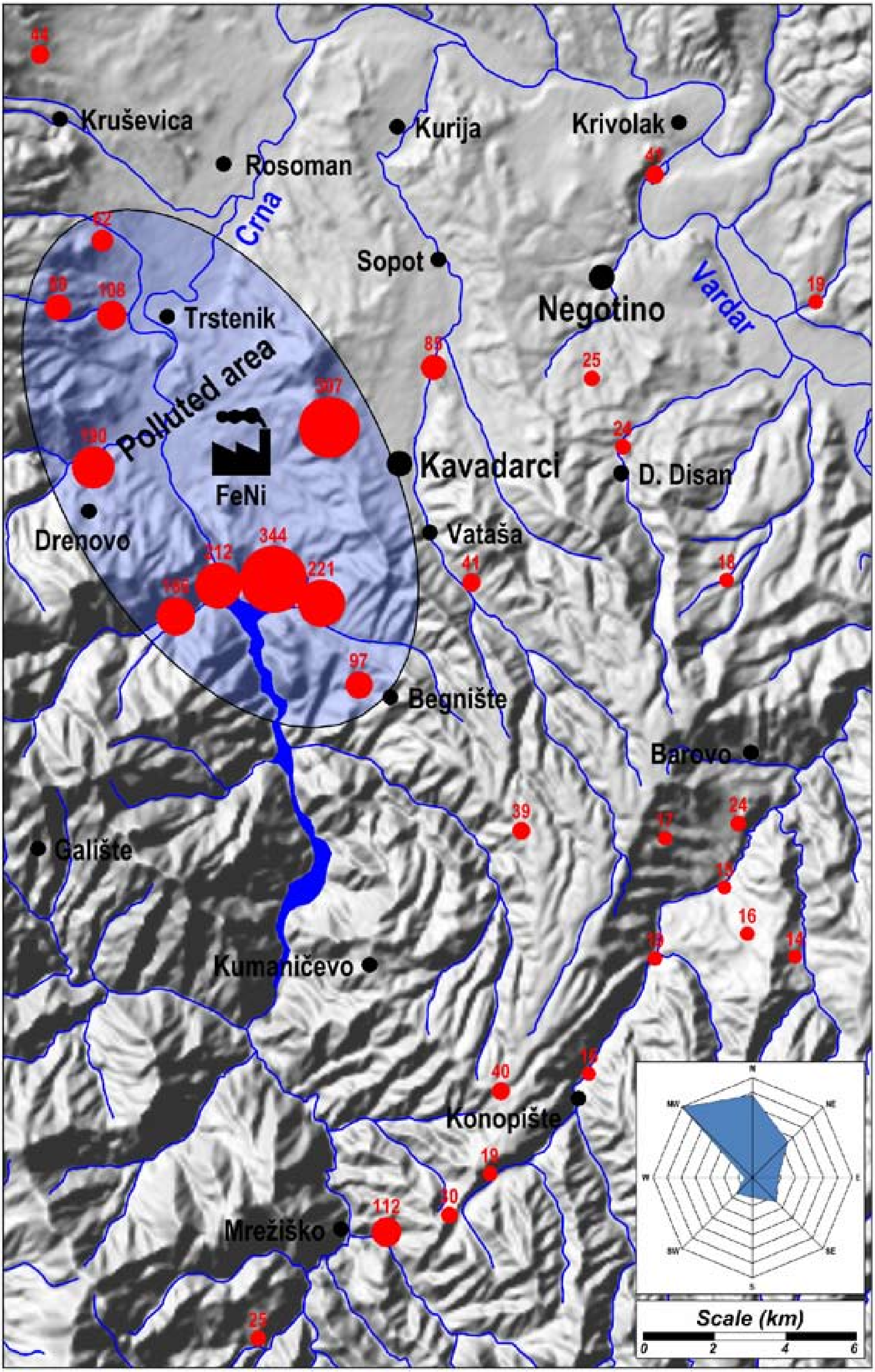


Fig. 4. Distribution of Ni in moss samples
Сл. 4. Дистрибуција на Ni во примероците мов

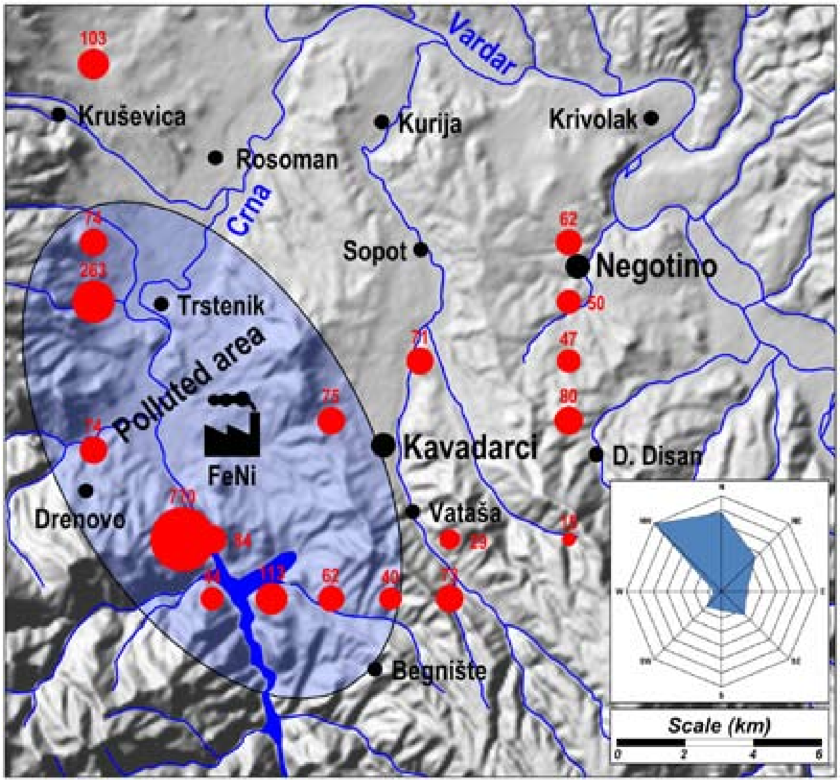


Fig. 5. Distribution of Ni in topsoil samples

Сл. 5. Дистрибуција на Ni во површинските почвени проби

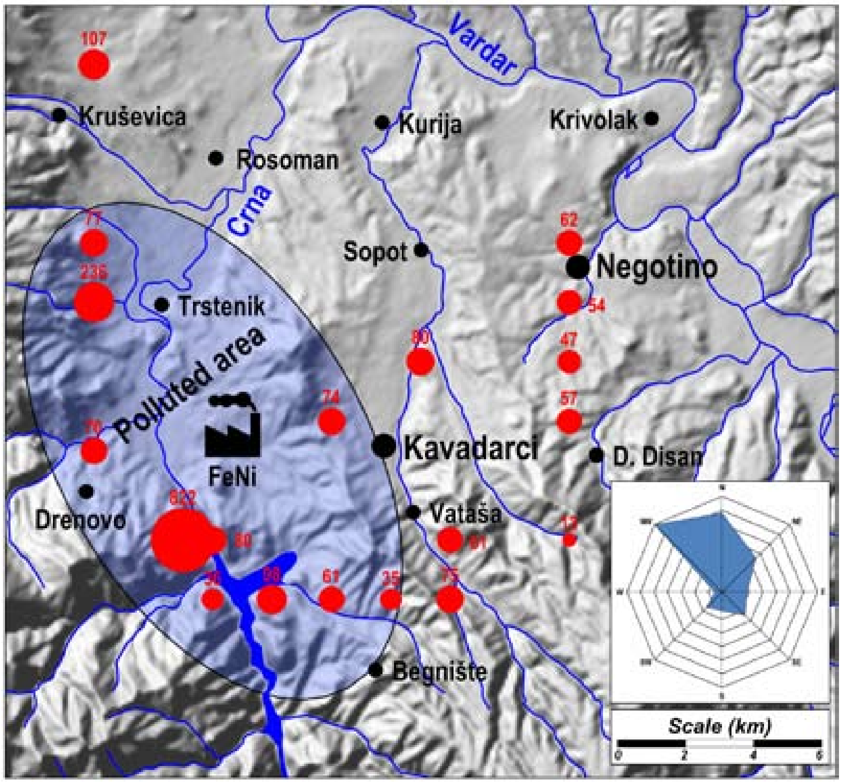


Fig. 6. Distribution of Ni in subsoil samples

Сл. 6. Дистрибуција на Ni во потповршинските почвени проби

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БИОМОНИТОРИНГ НА ЗАГАДУВАЊЕТО НА ВОЗДУХОТ СО НИКЕЛ ВО ОКОЛИНАТА НА КАВАДАРЦИ, РЕПУБЛИКА МАКЕДОНИЈА

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Резиме

Испитувано е загадувањето на воздухот со никел во околината на топилницата за фероникел близу Кавадарци, Република Македонија. Во студијата применети се техниките со биомониторинг со мовови и атомската емисиона спектрометрија со индуктивно спрегнатата плазма. Целта на испитувањето е да се утврди областа на загадувањето на воздухот со никел кое може да се очекува како резултат од работењето на топилницата. За таа цел земени се 35 примероци од мов како и 19 примероци почва од истите локации и тоа како површински почви (0-5 cm) и потповршински почви (20-30 cm). Земените примероци од мов и почви беа анализирани со примена на атомската емисиона спектрометрија со индуктивно спрегнатата плазма. Добиените резултати покажуваат значително повисоки вредности за содржините на никел во примероците од мов земени од околината на топилницата за фероникел. Вредностите на медијаната за Ni во примероците мов од целата испитувана област на Кавадарци и неговата околина (31,0 mg kg^{-1}) е многукратно повисока од онаа за Македонија (2,4 mg kg^{-1}). Ако се споредат вредностите за вредноста на медијаната за содржината на никел во моловите земени во непосредната околина на топилницата, со медијаната за содржината на никел за Македонија, фактор на зголемување надминува 70. Ова го потврдува фактот за влијанието на работата на топилницата врз загадувањето на воздухот во поширокиот регион на Кавадарци. Добиените вредности, пак, за содржината на никел во почвите земени во околината на топилницата не покажуваат некое забележително зголемување. Ова е дополнително потврдено со фактот што содржините на никел се поголеми во подповршинските почви во однос на површинските. Ова дополнително укажува на влијанието на работата на топилницата само на загадување на воздухот во неговата непосредна околина.