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DISTRIBUTION OF CHEMICAL ELEMENTS IN ATTIC DUST IN THE VICINITY OF A FERRONICKEL SMELTER PLANT

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ABSTRACT

Urban pollution with trace element occurs mainly in industrial regions and within centres of large settlements where industry, traffic and municipal wastes are the most important sources of trace elements. The results of a first systematic study of spatial distribution of different trace elements in surface soil over the Kavadarci region, Re-public of Macedonia, known for its ferronickel mine and metallurgical activities, show some areas with critically high content of some elements. The purpose of this study was to establish contents and distribution of trace elements in attic dust in Kavadarci, and to define them according to geological and anthropogenic influences. Attic dust samples were collected in the rural area. A total of 46 elements (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) were determined by mass spectrometry with in-ductively coupled plasma (ICP-MS). Samples of attic dust were collected from October to December 2008 at 31 sites of Kavadarci and its environs. A total of 46 elements were determined. The continuous probability distribution and enrichment ratio for the attic dust samples were studied. It was found that the content for Co, Cr, Mo and Ni in attic dust samples collected around a ferronickel smelter plant are separated by significantly higher values with those from the rest of the samples of the investigated region.

KEYWORDS: trace elements, ICP-MS, air pollution, attic dust, Kavadarci, Macedonia

1. INTRODUCTION

The abundance of heavy metals in the air has been in-creased dramatically by the accelerated rate of extraction of minerals and fossil fuels and by highly technological industrial processes. The problems of the degradation of the ecosystems due to pollution became increasingly acute.

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Rapid increases of trace metal concentrations in the en-vironment are commonly coupled with the development of exploitative technologies. Significant influences for this appearance have been mining works, factories, smelter plants and many other technological industrial processes, because of the

direct metal exposition to the atmosphere. Mines produce large amounts of waste because the used ore and concentrates are only a small fraction of the total volume of the mined material [1, 2]. This kind of sudden change ex-poses the biosphere to a risk of destabilisation, since or-ganisms that developed under conditions with low concen-trations of metal present have not developed biochemical pathways capable of detoxifying the metal when it is pre-sent at high concentrations. As result of these processes in the atmosphere permanently introduce dust [3, 4]. Continuous monitoring of the content of heavy metals and other toxic components contained in dust is possible through implementation of monitoring by using samples of dust from attic beams [5, 6].

The term dust usually comprises street dust and house dust [7-11]. However, other types have also been studied in the past. A particular type of house dust – the attic dust is studied in this work. It represents dust deposited in the attics abandoned by inhabitants, so that tenant influence is minimised. The attic dust is derived predominantly from external sources such as aerosol deposits and as a result of soil dusting, and less from household activities [12]. The attic dust as sampling material has the advantage that its composition remains constant, i.e. chemically unchanged with time. Investigations of attic dust chemistry therefore reveal the average historical state of the atmosphere [12-14].

The Republic of Macedonia, as a result of anthropogenic activities is affected by the problem of atmospheric pollution with heavy metals. The significant emission sources that contribute to atmospheric pollution with heavy metals for the territory of Republic of Macedonia appear to be all mines and drainage systems, and smelter plants [15-22]. The subject of this study is to present the results of distribution of trace elements in attic dust samples as reflection of lithology and anthropogenic influence in the Kavadarci region, known for its ferronickel industrial activity in the recent past. It is found that the most important sources of trace metals deposition are ferrous and non-ferrous smelters including the area of Kavadarci and its surroundings [16, 17]. There were a limited number of investigations of soil, vegetables and fruits produced in this region but they were mainly concerned with contamination by nickel, iron, cobalt and chromium [23]. Other elements were not determined, though it is known that the minerals of many other heavy metals (As, Cd, Cu, Sb, Se, etc.) are present in iron-nickel ores used for the production of nickel in the smelter plants [24-30]. For this reason, the goal of this work was to determine the contents of distribution of trace elements in attic dust samples in Kavadarci and its environs, and to assess the size of the area eventually affected by the ferronickel smelter plant situated near the town.

2. MATERIALS AND METHODS

2.1. Study area

The study area (Figs. 1 and 2) is located in the south-central part of Macedonia with an approximate area of about 360 km^2. The study area is located in the south-central part of the country with a size of 18 km (W–E) x 20 km (S–N) (Figs. 1 and 2), which is limited with coordinates (Gauss Krueger zone 7) 7574000 (W) – 7592000 (E) and 4582000 (S) – 4602000 (N). Town Kavadarci is located in Tikveš valley (Figs. 1 and 2). It is the main vine production region in Macedonia. The municipality of Kavadarci (38,741 inhabitants; 992.44 km^2) is made 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 the east and south side of the valley with a height difference approximately between 300 and 770 m.

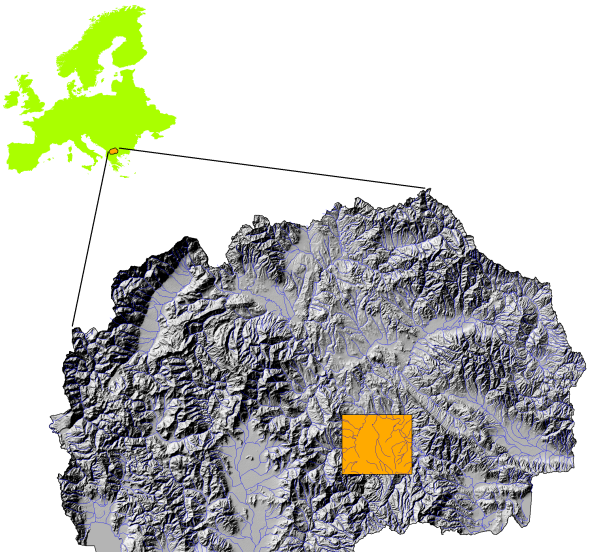


FIGURE 1 - The investigated region of Kavadarci and its environs.

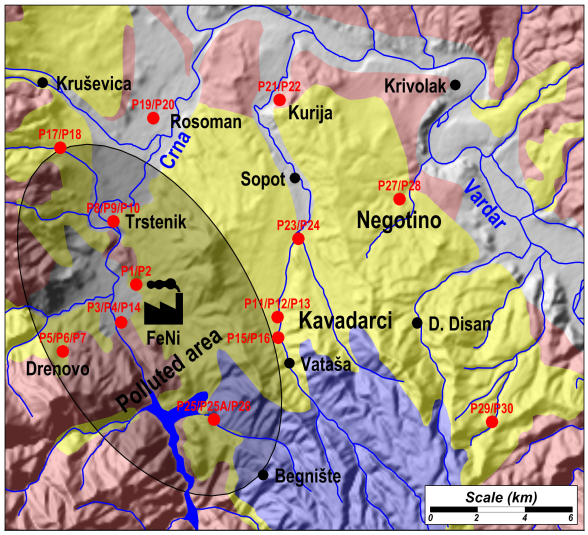
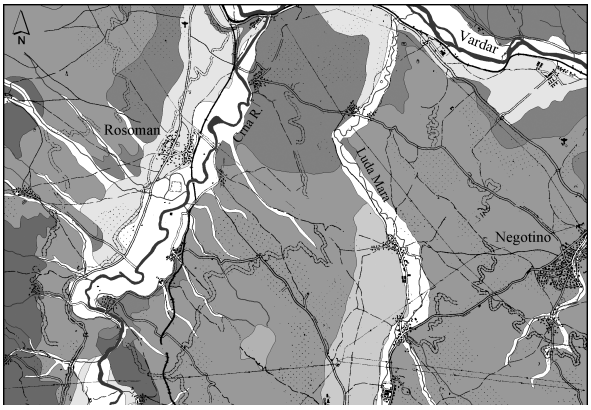


FIGURE 2 - Location of the sampling points for attic dust.

Samples of attic dust were collected in the period of October–December 2008 at 31 sites of Kavadarci and its environs. Close to each sample location an old house was chosen with intact attic carpentry. Although some of the selected houses were older than the ferronickel smelter plant, most of them were as old as the plant itself. To avoid collecting particles of tiles, wood and other construction materials, the attic dust samples were brushed from parts of wooden constructions that were not in immediate contact with roof tiles or floors [12].

2.2. Geological description

The geological description of the investigated area is presented in the Geochemical Atlas of Kavadarci and its environs [16]. It was found that the oldest formations have direction 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 amphibolechlorite schists with marbes and phylite layers (Fig. 3). 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 Cretaceous ages. Paleozoic and Mesozoic rocks cover approximately 39 km^2 in the SW and W part of the investigated area. 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 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 the Kavadarci are found the Quaternary (Q) pyroclastic vulcanites represented with tuffs, breccias and agglomerates, which cover approximately 25 km^2.



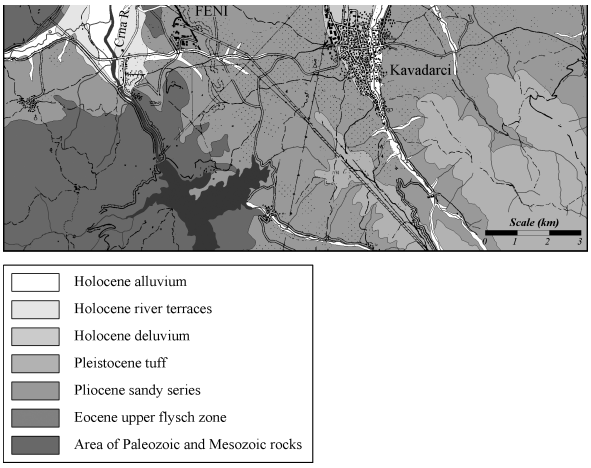


FIGURE 3 - Lithological map of the studied area

2.3. Instrumentation

The investigated elements (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) were analysed by the application of mass spectrometry with in-ductively coupled plasma (ICP-MS). The optimal instrumental parameters for these techniques are given in Table 1.

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 1). The instrument's running parameters were checked and adjusted before every batch of measurements, using a solution with 1 μg ml^{-1} In, 1 μg ml^{-1} Ce, 10 μg ml^{-1} Ba and 1 μg 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 [31]. 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 - 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

All measurements were done using the semiquantitative method (TotalQuant) supplied by Elan 3.4 software that uses a response factor calibration curve which was ob-tained by a calibration in multiple points, low, medium and high mass, for optimum set-up, using a multielement 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%.

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.

2.4. Reagents and standards

Standard solutions of metals were prepared by dilution of 1000 mg l^{-1} solutions (Merck VI ICP multi element standard). All chemical reagents used were of 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, Ger-many), and redistilled water were used for preparation of all solutions.

2.5. Sample preparation

All attic dust samples were air-dried. A fraction of attic dust smaller than 0.125 mm was prepared for the chemical analyses by sieving and the same procedure for soil sample digestion was applied.

For digestion of attic dust samples, open wet digestion with mixture of acids was applied. A precisely measured mass of dust samples (0.5000 g) was placed in Teflon vessels and 10 ml concentrated nitric acid, HNO_3 was added, 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 a 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 dissolving of metal ions. Finally the vessels were cooled and digests quantitatively transferred to 50 ml calibrated flasks.

3. RESULTS AND DISCUSSION

The descriptive statistics of analysed elements are shown in Table 2 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 [16].

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 can be seen from the data presented in Table 1, 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} (Fig. 4). Cobalt and chromium results show significantly higher contents in the samples of attic dust taken from the Kavadarci area, as well (Figs. 5 and 6). 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 elements' distribution shows an increased content in the attic dust and soil samples from the smelter plant surroundings compared to the content in the rest of the samples. Namely, the dust that comes from this plant is connected with the ferronickel ore that is being processed in this smelter plant. It contains some of the heavy metals in considerably higher numbers than their natural content in the surrounding rocks and soil.

These findings were confirmed also by the application of continuous probability distribution and enrichment ratio for the attic dust samples studied (Table 3). 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 2 and 3 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 that are 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 4–6.

Table 3 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 3 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 [32, 33] 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 presen-

TABLE 2 - 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.

TABLE 3 - 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.

ted 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. 4–6). 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 18].

Data presented in Tables 2 and 3 and in Figs. 4–6 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 [34], with the dominant winds from N and NW and SE (Figs. 4–6). 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.

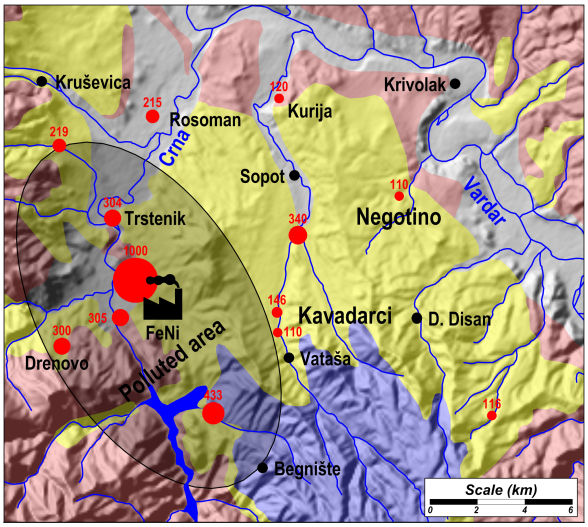


FIGURE 4 - Distribution of Ni at attic dust samples (in mg kg^{-1})

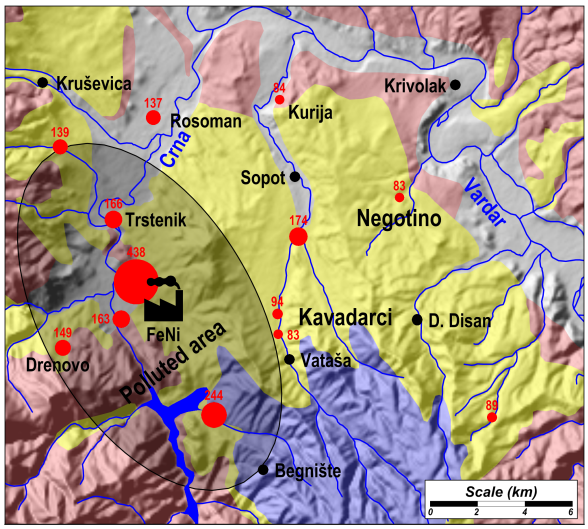


FIGURE 5 - Distribution of Cr at attic dust samples (in mg kg^{-1})

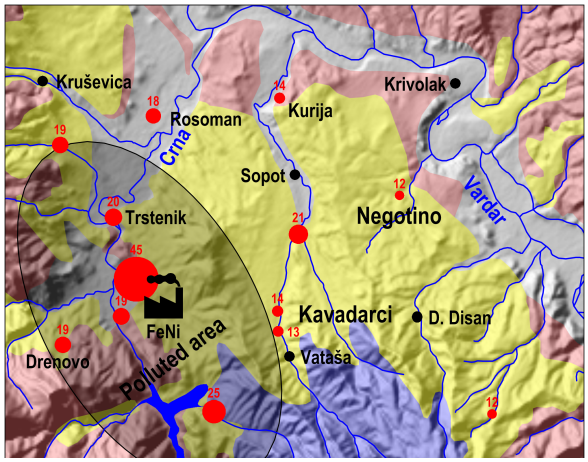


FIGURE 6 - Distribution of Co at attic dust samples (in mg kg^{-1})

4. CONCLUSIONS

Distribution of 46 elements (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) in attic dust samples was investigated in the vicinity of the ferronickel smelter plant near the city of Kavadarci, Republic of Macedonia. The activities carried out in ferronickel ore processing and smelter plant lead to increased content of certain heavy metals (Co, Cr, Mo and Ni) in the atmosphere, which was determined through the conducted monitoring with attic dust samples. These findings were confirmed by the application of continuous probability distribution and enrichment ratio for the attic dust samples studied. It was found that the content for Co, Cr, Mo and Ni in attic dust samples collected around ferronickel smelter plant (polluted area) are separated by significantly higher values than those from the rest of the samples of the investigated region. Samples that are around the ferronickel smelter plant are characterized 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.

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MIXING CHARACTERISTICS AND TRANSPORT FLUX RATIO OF POLLUTANTS IN BRAIDED RIVERS

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ABSTRACT

It is well-known that the mechanism of the pollutant transport in braided rivers is not quite clear at the present time compared with straight and meandering rivers. Therefore, in this paper, a physical model of a typical braided river with a braid bar between two anabranches was set up to explore the pollutant mixing characteristics. Different tracer release locations were adopted at the left bank, 1/3 width, centerline and 2/3 width of the straight flume before branching reach. 100 experimental runs including four tracer release locations, five upstream flow-rates, and five width ratios of two anabranches, were conducted. The cross-sectional velocities and concentration distributions at the bifurcation, two anabranches and confluence in the braided river were measured and analyzed. The transport processes and mixing characteristics of pollutants in the braided river were obtained. The tracer release location and width ratio are the main influence factors in the tracer transport process. For the centerline discharge, as the width ratio of anabranch 1 to both anabranches changed from 0.5 to 0.33, the section concentration distributions in both anabranches changed from symmetry to asymmetry, and the ratio of tracer into anabranch 2 increased obviously. For left bank discharge with different width ratios, tracer flowed along the left bank and almost transported into the anabranch 1.