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Professional paper

CONCENTRATION OF SOME HEAVY METALS ON THE SOIL IN THE TEPP OSLOMEJ, KICHEVO VALLEY, NORTH MACEDONIA

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Abstract

The aim of this study was to investigate the distribution of some heavy metals in soil focusing on the identification of natural, industrial and anthropogenic element sources of pollution of the TEPP Oslomej (coal mine), in the Kichevo area, Macedonia. During the period of April 2012,2013 to May 2014, field and analytical studies of 12 sites (localities) in the region of Kichevo valleywere made at three different distances (three zone) from the source of pollution, the Thermal Power Plant(TPP) Oslomej. In April 2012,the localities and researchpoints at different distances from the source of pollution (TEPP-Oslomej) were determined. Research study includes determination of concentration of seven heavy metals: Ni, Cu, Zn, Fe, Mn, Cd and Pb in the soil samples. The content of the available heavy metals in the soils was carried out with DTPA-diethylenetriamine pentaacetic acid (DTPA diethylenetriamine pentaacetic acid) method (Lindsay and Norvell 1978; Page 1982).
The content of heavy metals in the resulting solutions is determined by atomic absorption spectroscopy with Agilent 55A.
According to the obtained graphs or by visual analysis, it was noticed that in most of the heavy metals (total and available forms) there is a reduction of the content from the first (closest) to the second zone. For some of the elements, higher concentrations were found in the third zone due to the natural geological composition and the reduced influence of TEPP Oslomej.
Heavy metals Pb and Cd are included in the group of toxic elements if they are introduced into the body in high concentrations or through products with higher values for the MDC.
Chemical analyzes were conducted at Laboratory for Plant Ecology at the Institute of Biology, Faculty of Natural Sciences and Mathematics, Skopje using Atomic Absorption Spectroscopy (**AAS**) – flame and graphite furnace.

Keywords: Heavy metals, soils, concentration, coal mine, TEPP Oslomej

1. Introduction

The development of technology and industry in the world and in our country has a great impact on environmental pollution. Today, as a result of modern civilization, the world is facing a serious problem of pollution with various contaminating and harmful substances including heavy metals.
- Pollution is especially present in the vicinity of: power plants, mines, alongside roads, soil fed with fertilizers and pesticides, etc.
- The presence of elements in the soil is as a result of various sources. However, the presence and distribution of lithogenic elements in the soil layers is variable due to the evolution of pedogenetic processes [1].

- In the Kichevo region there are several industries, including TEPP Oslomej that affect environmental pollution of soil, water, air and crops in this region by emitting harmful pollutants in the mentioned environments. In addition to the emission of polluting gases, heavy metals are also emitted which stratify and enter the composition of surface soil and in depth soil. This is also the main problem of pollution in Kichevo municipality. A significant part of the energy capacity in the Republic of North Macedonia consists of coal power plants, such as the coal power plant REK Bitola and TEPP Oslomej - Kichevo, as well as the mineral and electrical power plant REK Berovo. There are about 20 coal mines in the territory of the Republic of North Macedonia and the total geological reserves are estimated at about 2.5 billion tons. Of all these coal deposits, especially important for the economic development and electricity of our country, are the basins of Pelagonia and Kichevo. TEPP Oslomej is located in the western part of the Republic of North Macedonia, in the territory of the municipality of Kichevo (more precisely in the Kichevo Valley) near the lignite (coal) mine (figures 1 and 2). The coal extracted in the TEPP Oslomej mines is typical lignite and is characterized by high presence of moisture, medium ash presence and low sulfur presence [2].

Figure 1. TEPP Oslomej satellite image

Figure 2. Part of the mine TEPP Oslomej–west

The purpose of this study was to investigate the spread of some heavy metals in the soil in the region around TEPP Oslomej as a contaminated region.
For that purpose, using the sampling range of 1x1 km in the first zone and 2x2km in the second zone and the third zone, a total of 24 soil samples were collected from 12 locations (soil surface layer and soil deep layer) on four sides (north, east, south, west) at three different distances from the source of pollution. 7 heavy elements were analyzedin total.
Research region: TEPP Oslomej open coal mine is located in the north of Kichevo Valley, 9 km away from the city of Kichevo. It contains a plant complex and two open pit mines for coal mining, west and east. The research is extendedin a diameter of 0-8km on all three sides from the TEPP Oslomej pollution source.

2. Materials and methods

Chemical analysis was performed at the Plant Ecology Laboratory at the Institute of Biology, Faculty of Natural Sciences and Mathematical at Skopje University using Atomic Absorption Spectroscopy (AAS), flame and graphite furnace.

All samples were from the soil and were dried.

0.5 g samples were measured at analytical equilibrium (0.0001 g) and transferred to a digestion flask.

8 ml HNO_3 and 4 ml H_2O_2 (1 ml at 1-hour intervals) were immediately added. The samples were dissolved at 140˚C for 24 hours.

All heavy metals analyzed were determined by atomic absorption spectrometry (AAS) in the Agilent 55A apparatus.

The concentration of heavy metals was calculated and corrected by subtracting the deviations.

a. collection and preparation of soil samples

In order to obtain a complete picture of the presence of heavy metals on the earth's surface, it was first necessary to divide the predetermined localities into three zones with different distances from TEPPOslomej (source of pollution):

- First zone (A): distance from 0-1km (north, south, east. west);
- Second zone (B): distance of 3-5km (north, south, east, west);
- Third zone (A): distance from 6 - 8 (10) km (north, south, east, west);

b. the material is collected from different soils

The following tasks have been performed for the collection of soil samples and the further processing of the material for the analysis of heavy metal presence:

From the localities previously defined by the Kichevo valley region, soil samples were collected from the TEPP Oslomej area. Soil samples were collected from 12 pre-defined localities, once in 2012 and once in 2013. During the collection of samples, protocols for standard collection of contaminated soils were followed and were described according to [3]. The collected soil samples were collected from the surface layer at a depth of 5-10 cm. During the soil collection, the organic layers present in the soil (roots, underground stalks, etc.) were carefully removed. These collected samples were processed according to standard rules and methods, which contain cleaning, drying, and crushing of the material. They were placed in a paper bag weighing 1 kg, in which are written the main data and characteristics such as: name of the locality, place of collection, altitude, distance from TEPP Oslomej (source of pollution), area, orientation and direction, living community, land mass, name and surname of the person who collected the material, as well as the date. Samples of processed materials (soils) were used for combustion and analysis of heavy metals (Cu, Zn, Fe, Ni, Mn, Cd, and Pb). Chemical analyzes were conducted at Laboratory for Plant Ecology at the Institute of Biology, Faculty of Natural Sciences and Mathematics, Skopje using Atomic Absorption Spectroscopy (AAS) – flame and graphite furnace.

c. designation and preparation of solutions from soil samples contains:
• Drying of materials in the dryer (105ºC) to absolute dry mass;
• Measurement of materials on analytical scales (1 g),
• Preparations for combustion mixtures such as: HNO_3: $HClO_4$: H_2SO_4 (10:2:1, v/v/v), (Allen et al., 1989),
• Burning of dry soil materials with combustion mixture in Kjeldahl apparatus (100 ml) placed in sand tubs (160ºC) in 24-hour duration;
• After combustion, the composition of the burnt material (1-2 ml) was dissolved in hot distilled water, filtered and collected in gourds (25 ml) with the addition of distilled water and;
• The obtained solutions were stored in the refrigerator (4ºC) before being used for heavy metal composition analysis;
• The presence of heavy metals in preparatory solutions from soils was determined by treatment with Absorbent Atomic Spectrometry (AAS), with the help of absorbent atomic spectrometer.

d. Determining the available composition of heavy metals

The composition of heavy metals present in soils was carried out with diethylentriaminepentaacetic acid (DTPA), by the method (Lindsay and Norwell 1978; Page 1982). In plastic bottles (up to 100 ml) weighing 10 gr. dry airy soil and add 20 ml of the reagent prepared in DTPA (pH = 7.2-7.3). Mix with a mixer for 2 hours. After that the solutions are filtered. Whatman 42 (slow filtration ashless) filter paper is used for filtering. The filtrate is poured into plastic flasks and stored in the refrigerator. The obtained volume of the filter is different which is related to the properties of the soil. The presence of heavy metals in the obtained solutions is determined by absorption atomic spectroscopy.

3. Results and discussion

Heavy metal presence in soil substrates in TEPP Oslomej area

In Tab. 1. the results for the total and available concentration of heavy metals investigated in the soils at the selected sites in TEPPOslomej area are presented. The results obtained did not show any significant correlation between the available and total concentrations of heavy metals investigated in the soil.

Table 1. Total (T) and available (E) concentrations of heavy metals investigated in soils at selected sites in the TEPP Oslomej area.

Locality	Distance (km)	Orientation	Ni		Cu		Zn		Fe		Mn		Pb		Cd	
			T	E	T	E	T	E	T	E	T	E	T	E	T	E
Zhubrino-north -AN	0,5	N	4,6	0,32	4,2	1,54	11,3	0,55	4726,9	63,5	72,2	17,1	17,6	0,58	0,17	0,03
Gorica -BN	3	N	10,3	1,03	7,7	1,57	24,1	0,67	8780,7	43,5	142,0	29,3	19,8	1,43	0,05	0,05
Ramnishte-CN	6,75	N	8,9	0,52	5,5	0,93	19,2	0,82	4691,6	43,0	105,9	50,9	18,1	2,06	0,05	0,05
Repetitor AW-	0,5	W	8,7	0,21	5,1	0,78	17,0	0,40	9399,0	31,6	171,3	17,7	17,3	0,45	0,05	0,02
vill.Drogomisht -BW	2,5	W	15,5	0,44	23,7	1,44	37,0	0,33	7590,7	33,5	110,8	38,2	16,8	2,33	0,05	0,02

vill. Zajaz -CW	6	W	19,1	1,00	13,3	1,34	39,9	1,03	6315,6	30,8	102,7	53,5	16,9	0,98	0,10	0,06
Osllomej-AS	0,4	S	16,1	0,30	20,1	1,18	32,7	0,49	9455,2	26,1	160,7	9,4	39,2	0,22	0,12	0,03
Cervica-BS	2,5	S	9,5	0,15	5,1	0,53	15,6	0,18	4792,3	19,6	111,4	56,8	17,4	0,45	0,05	0,01
Krushino-CS	7,25	S	34,2	1,04	21,5	1,17	43,2	1,79	4085,9	37,7	101,3	11,1	17,2	1,18	0,07	0,02
Zhubrino-west-AE	0,5	E	9,3	0,41	10,1	1,70	25,6	1,46	9376,4	31,2	177,4	43,2	19,3	0,59	0,05	0,04
Zadel. Sërbica-BE	2,5	E	3,3	0,53	3,0	0,94	10,1	0,72	3690,7	49,1	54,5	24,7	16,8	1,35	0,07	0,03
Novo Selo-CE	6	E	3,7	1,03	3,3	3,16	12,2	3,25	3492,3	159,9	67,6	33,4	15,5	0,82	0,05	0,06

Statistical analysis of the dependence of the heavy metal presence in the soil, distant from TEPP Oslomej showed that there is a significant correlation (significant correlation) in cases with total Fe, Mn, Pb and Cd presence. In all cases, as expected, there is a negative correlation, i.e. the concentration of heavy metals decreases with increasing distance from TEPP Oslomej (Tab. 1b). No statistically significant correlations were found in any of the available heavy metal forms.

Table.1b. Statistical analysis of the dependence on the presence of heavy metals in the soil distant from TEPP Oslomej

	r	F	p	n
Ni			n.s.	12
Zn			n.s.	12
Cu			n.s.	12
Fe	0,63	6,57	0,0282	12
Mn	0,64	6,93	0,0251	12
Pb	0,61	5,90	0,0355	12
Cd	0,61	5,39	0,0454	11

Presence of heavy metals in the soil

The highest average value for Ni presence in soil substrates is observed in localityKrushino (CS), (34.2 mg • kg-1, followed by: Zajas (CW), (19.1 mg • kg-1), vill. Oslomej-South (AS), (16.1 mg • kg-1), Strogomishte (BW) (15.5 mg • kg-1), Gorica (BN) (10.3 mg • kg-1), Cervica (BS) (9.5 mg • kg-1), Zhubrino-East (AE) (9.3 mg •) kg-1), Ramnishte (CN) (8.9 mg • kg-1), Oslomej-west, Repetitor (AW) (8.7 mg • kg-1¬) The lowest Ni presence was found in the soils of Novo Selo (CE) (3.7 mg • kg-1) and Zadel-Srbica (BE) (3.3 mg • kg-1). However, the values obtained for Ni presence were lower than the values recorded for Ni presence in the soils of the region of Kichevo Valley, [3]. These authors found maximum values of 56 mg • kg-1, minimum values of 5.5 mg • kg-1, while the mean values for Ni presence in the soils of the study region were 21 mg • kg-1. It is important to note that the average value for Ni presence in surface soils in Europe is 18 mg • kg-1 [3].

According to the results for the Cu presence in the soils from the researched places in the area around the TEPP Oslomej, the high presence of this element is recorded in the localities Drogomisht (BW) (23.7 mg • kg-1), Krushina (CS) (21.5 mg • kg-1), Oslomej-South (AS) (20.1 mg • kg-1¬) and Zajas (CW) (13.3 mg • kg-1). Lower values for Cu presence were observed in the soils of Novo Selo (CE) (3.3 mg • kg-1) and Zadel (EU) (3.0 mg • kg-1). The values obtained for the Cu presence in the soil were lower compared to the results for the Cu presence of the soils in the Kichevo Valley.,[3]. In the research region, these authors found maximum values of 53 mg • kg-1, and minimum values of 5.4 mg • kg-1, while the mean values for the Cu presence were 21 mg • kg-1. The average value of Cu presence in surface soils in Europe is 13 mg • kg-1.

With high values of Zn presence in the soil around TEPPOslomej were recorded in the localities: Krushino (CS) (43.2 mg • kg-1), Zajas (CW) (39.9 mg • kg-1), Drogomisht (BW) (37.0 mg • kg-1), Oslomej-south (AS) (32.7 mg • kg-1), Zhubrino-North (AN) (25.6 mg • kg-1) and Gorica (BN) (24.1 mg • kg-1). Minimum values for Zn presence were found in Novo Selo (CE) (12.2 mg • kg-1) and Zadel-Srbica (EU) (10.1 mg • kg-1). The values obtained from this study on the Zn presence in the soils of TEPP Oslomejarea were significantly lower than the results for this metallic presence from soil samples collected from the Kichevo region., [3]. According to these authors, the maximum value for Zn presence was 1700 mg • kg-1, the minimum value was 11.0 mg • kg-1, while the average value was 150 mg • kg-1. The relatively high Zn presence (1136 mg • kg-1) has been recorded in soils from settlements near a copper mine in Korea., [1]. The average value for Zn presence in surface soils in Europe is 52 mg • kg-1.

Regarding the presence of Mn, the minimum values for the presence of this metal were determined in localities Zadel-Srbica (EU) (54.5 mg • kg-1), while maximum values are taken in the locality Zhubrino-North (AN) (177.4 mg • kg-1) and locality Oslomej-Repetitor (AW) (171.3 mg • kg-1).

Regarding Fe, high values of this metal have been recorded in the soils collected from the localities: Oslomej-South (AS) (9455.2 mg • kg-1), Oslomej-Repetitor (AW) (9399.0 mg • kg-1) and Zhubrino-North (AW) (9376.4 mg • kg-1). On the other hand, the lowest Fe presence was obtained in soil samples collected from Zadel-Srbica (EU) (3690.7 mg • kg-1) and Novo Selo (CE) (3492.3 mg • kg-1).

According to the results obtained, the Pb presence in the lands of the area around TEPP Oslomej was above the maximum values per locality Oslomej-South (AS) (39.2 mg • kg-1) up to the minimum values observed for locality Novo Selo (CE) (15.5 mg • kg-1). However, the results for Pb presence in the soils of TEPPOslomejarea are significantly lower than those of Kick et al. (1980) [5]. According to this author, the tolerable Pb presence in soil is about 100 mg • kg-1.

The Cd presence in the soils of the studied region is relatively low and the maximum values are recorded in locality Zhubrino-North (AW) 0.17 mg • kg-1, while the minimum values were observed in several localities: Gorica (BN), Ramnishte (CN), Oslomej-Repetitor (AW), Drogomisht (BW), Cervica (BS), Zhubrino-East (AE) and Novo Selo (CE) (0.05 mg • kg-1).

Stafilov et al., (2011) [3]., showed the presences of heavy metals investigated in the soils of the Kichevo Valley: Ni (21 mg • kg-1), Cu (17 mg • kg-1), Zn (150 mg • kg- 1), Fe (2.9 mg • kg-1), Mn (760 mg • kg-1), Pb (96 mg • kg-1) and Cd (0.47 mg • kg-1). According to European standards, the average values for the presence of heavy metals in surface soils are: Ni (18 mg • kg-1), Cu (13 mg • kg-1), Zn (52 mg • kg-1), Fe (3.5 mg • kg-1), Mn (650 mg • kg-1), Pb (23 mg • kg-1) and Cd (0.15 mg • kg-1). Statistical analysis, depending on the presence of heavy metals from in the soil, distant from TEPPOslomej showed that there is a significant negative correlation in cases with the total concentration of Fe, Mn, Pb and Cd (Table 1b). Yossifova et al., (2009) [8], show that the

basic constituent elements of TEPP Oslomej's lignite are C, Fe, Mg, Si, Al, K, Ca. In addition, C, Pb, Sc, S, Cr, Y, Zr, Ti, Mn, Zn, B, Ni, Co, Ba and Cu showed EDF> 2. From our data and lignite composition an explanation can be found for reduced Fe and Pb concentrations, distant from TEPP Oslomej as a source of pollution. However, in the case of Ni and Cu no statistical dependence was found, although these two elements have EDF> 2 in TEPP Oslomej lignite.
According to the graphs obtained (not shown) ie from visual analysis, it has been observed that in heaviest metals (total and available form) there is a decrease in the presence of heavy metals from the first (nearest) zone to the second zone. For some of the elements, higher concentrations were observed in the third zone due to the natural geological composition and the reduced impact of TEPPO slomej (or lack of significant impact). This indicates the need for specific research to determine the impact of TEPP Oslomej on the chemical composition of the soil in a smaller radius (up to 5 km). Heavy metals such as lead and cadmium are extremely harmful (toxic) affecting humans, plants and animals. They also have a detrimental effect on the wild fungi that are present here, where the concentration of heavy metals, especially Pb and Cd are in high values and directly affects human health [6], [7], [8].

4. Conclusions

- Statistical analysis of the dependence of the heavy metal presence in the soil around TEPP Oslomej showed that there is a significant correlation in cases with total Fe, Mn, Pb and Cd presence.
- In all cases, as expected, there is a negative relationship, i.e. the concentration of heavy metals decreases with increasing distance from TEPP Oslomej.
- From our data and the composition of lignite can be found an explanation for the decrease of Fe and Pb concentrations by leaving the TEPP Oslome as a source of pollution. However, in the case of Ni and Cu no statistical dependence was found, although these two elements have EDF> 2 in TEPP Oslomej lignite.

According to the graphs obtained from the visual analysis it is observed that in most heavy metals (total and available form) there is a decrease in the presence of heavy metals from the first zone (closest) to the second zone.

- For some of the elements, higher concentrations are observed in the third zone due to the natural geological composition and the reduced impact of TEPP Oslomej (lack of significant impact). This indicates the need to conduct specific research to determine the impact of TEPP Oslomej on the chemical composition of the soil, ie environmental pollution, but in a smaller radius (5 km).

According to the results obtained on the presence of heavy metals examined in the collected soils it can be concluded that:

- TEPP Oslomej environment is a polluted area due to increased coal use and the introduction of high-tech industrial processes;
- Environmental pollution in the vicinity of TEPP Oslomej is done through the release of heavy metals in the processing of coal in the soil and water and air, which results in the accumulation of

metals in plant organisms (low and high plants), lichens and fungus from the group of Macromycetes.

- The obtained results are also in line with the research of Yossifova et al., (2009) [2], which concludes that TEPPOslomej's environment is significantly contaminated with heavy metals.

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