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DETERMINATION OF HEAVY METALS ON THE EARTH'S SURFACE IN SEVERAL INDUSTRIAL REGIONS IN NORTH MACEDONIA BY THE AAS METHOD

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Abstract

Heavy metals are potential poisons to human life and the environment. Their toxicity depends on their chemical form in the soil. Heavy metals have received special attention around the world as a result of their toxic effects even at very low concentrations. Our study aimed to determine the concentration of Pb, Cr, Cd, Ni, Cu, and Fe metals on the earth's surface by the atomic absorption spectroscopy method in the industrial zone of Jegunovce, Teteks and Osllomej, Republic of North Macedonia. So three locations were analyzed: Location 1 (Jugohrom) in this location 4 points were analyzed and were marked with numbers from 1-4, Location 2 (Teteks) in this location were also analyzed 4 points and were marked with numbers from 5- 8 and Location 3 (Oslomej) in this location are analyzed 5 points and are marked with numbers from 9-13. In location number 1 the concentration of heavy metals that turned out to be above the maximum allowed amount are chromium and cadmium:
The amount of Cr in point 1 is (6 mg / kg), point 2 (11.56 mg / kg), point 3 (40.1 mg / kg) and point 4 (10.53 mg / kg) and the amount allowed according to WHO of chromium in the soil is from 0.01-0.1 mg / kg. The amount of Cd that has exceeded the allowed level was in point 2 (3.19 mg/kg) and point 3 (3.88 mg/kg) and according to EU directives, the amount of cadmium allowed in the ground varies from 1 to 3 mg/kg.
In location number 2 the concentration of heavy metals that turned out to be above the maximum allowed amount is Lead, Nickel, Chromium, and Cadmium. The amount of Pb that exceeded the allowed level was in point 8 (381.6mg/kg) while the allowable value according to EU directives is from 50-300 mg/kg. The amount of Ni above the allowed level has reached point 5 (383.1 mg/kg). Chromium has risen above the level at all points of this location, at point 5 (42.37 mg / kg), at point 6 (44.15 mg / kg), at point 7 (56.5 mg / kg) and at point 8 (24.72 mg / kg). Cadmium above the allowable level was detected at point 7 (3.75 mg/kg) and point 8 (3.36 mg/kg).

Keywords: soil pollution, heavy metals, Jugohrom, Teteks, Osllomej, atomic absorption spectroscopy.

1. Introduction

Soil, a major part of our world's ecosystem, is home to a large number of organisms, but at the same time, it is probably the most endangered component of our environment, open to influence from a variety of different pollutants arising from human activities (industrial, agricultural, etc.) (Bradl, 2005).
Also, there can occur natural emissions of heavy metals such emissions include volcanic eruption, sea salt, sprays, forest fires, rock weathering, biogenic sources, and wind-borne soil particles (Herawati et al, 2000).
The relationship between soil pollution and the world population has become an inarguable directly proportional relationship as it can be seen that the amount of potentially toxic substances released into the environment is increasing with the alarming growth in the global population. This issue has led to pollution is a significant problem facing the environment (Masindi et al, 2018).

The use of toxic materials by the transport industry can also result in soil contamination. Leaking out of oil or fuel from cars, trucks, buses, and motorcycles enter the soil since they are washed on the roadsides.
Accumulation of heavy metal compounds around the roadways is dependent on several factors including:

- Average daily traffic (ADT) or traffic volume
- Distance from the road
- Depth of the soil profile
- Prevailing wind speed and direction
- Length of exposure time or age of the road
- Type of driving, whether freeway or city and
- Vehicle age and speed.

Several other factors also affect the heavy metal contents of soil and plants along roads:

- The method of soil engineering applied during the road construction,
- The use of metal-containing pesticides to protect roadside grasses and trees, and
- The presence of local industries that discharge metals into the air as fumes or dust (Athanasopoulou et al, 2016).

From literature, pollution is defined as the introduction by man, directly or indirectly, of substances or energy into the environment resulting in such deleterious effects as harm to living resources, hazards to human health, etc (Masindi et al, 2018).
There are different types of pollutants, namely inorganic, organic and biological.
Inorganic pollutants are usually substances of mineral origin, with metals, salts, and minerals being examples (Wong, 2012).
Inorganic substances enter the environment through different anthropogenic activities such as mine drainage, smelting, metallurgical and chemical processes, as well as natural processes. These pollutants are toxic due to their accumulation in the food chains (Salomons et al, 1995).
Organic pollution can be briefly defined as biodegradable contaminants in an environment. Some of the common organic pollutants which have been noted to be of special concern are human waste, food waste, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), pesticides, petroleum, and organochlorine pesticides (OCPs) (El-Shahawi et al, 2010).
Biological pollutants are described as pollutants that exist as a result of humanity's actions and impact on the quality of the aquatic and terrestrial environment. This type of pollutants includes bacteria, viruses, molds, mildew, animal dander, cat saliva, house dust, mites, cockroaches, and pollen (Elliott, 2003).
Metals serve as "technological nutrients" without which modern society can't function (Rauch et al, 2009).
Metals exist either as separate entities or in combination with other soil components. These components may include exchangeable ions sorbed on the surface of inorganic solids, non-exchangeable ions, insoluble inorganic metal compounds such as carbonates and phosphates, soluble metal compounds, or free metal ions in the soil solution, a metal complex of organic materials, and metals attached to silicate minerals (Marques et al, 2009).
Heavy metals (HM) exist naturally in the environment, with changes in their concentration (Seiler et al, 1994). Heavy metals can be found in the form of hydroxides, oxides, sulfides, sulfates, phosphates, silicates, and organic compounds (Herawati. et al, 2000).
Toxic heavy metals entering the ecosystem can lead to accumulation, bioaccumulation, and biomagnification (Chandrappa et al, 2006).

Heavy metals are elements that exhibit metallic properties such as ductility, malleability, conductivity, cation stability, and ligand specificity. They are characterized by relatively high density and high relative atomic weight with an atomic number greater than 20 (Raskin et al, 1994).

Heavy metals affect the number, diversity, and activities of soil microorganisms. The toxicity of these metals on microorganisms depends on many factors such as soil temperature, pH, clay minerals, organic matter, inorganic anions and cations, and chemical forms of the metal (Chibuike et al, 2014).

There are around 35 metals that pose a concern as a result of our exposure to them in our jobs and living places. 23 of those metals are heavy metals like antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, iron, lead, etc. (Seiler et al, 1994).

The most common heavy or toxic metals are mercury, nickel, lead, arsenic, cadmium, aluminum, platinum, and copper (the metal form, not the ionic form required by the body) (Maxhuni, 2016). Some of them for example cadmium, lead, and nickel is easily volatilized and normally present in the atmosphere, especially near urban areas and roadways (Lagwerff et al, 1970).

Heavy metal content in nature increases in both the soil and atmosphere. In a study of heavy metal contamination of leaf surface, metal accumulation can occur in several ways, such as foliar retention, foliar absorption, and uptake from the soil (Ali F.A., 1984).

Leaves collected only a portion of the total fallout (1/6 of the total Pb and 1/12 of the total Zn). Washing of elm tree leaves with deionized water removed between 30 and 85 % of the total lead from the leaves, 45 % of total Zn, and 28 % of total Cd (Little, 1973).

The pollutants are transported to different distances, depending on the geographic area, its geology, meteorological factors (wind, rain, fog, thermal inversions), and trophic or feeding level.

The large concentrations of heavy metals in soil inhibit microbial activity by:

- altering enzyme conformations;
- blocking essential functional groups (sulfhydryl, amine, hydroxyl, carboxyl, imidazolyl);
- displacing other essential metal ions (deficiency effects) (Simeonov et al, 2006).

To cause any effect in a living organism, heavy metals have to come into contact with this organism (Bradl, 2005). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. They may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture, manufacturing, pharmaceutical, industrial or residential settings. Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children. Natural and human activities are contaminating the environment and its resources, they are discharging more than what the environment can handle (Herawati et al, 2000 and He et al, 2005).

Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations (Pulles et al, 2012).

Children are much more vulnerable than adults to heavy metals exposure because of their more rapid growth rate and metabolism (Siemonov et al, 2006). The metals accumulate in the cells and tissues, interrupt cellular function, damage DNA, and slowly destroy people’s health if they are not removed from the body.

Although HM exposure has immediate effects at the molecular and cellular levels, they may extend to higher levels of biological organization, like the genetic structure and diversity of the exposed populations (Bickham et al, 2000).

Chronic exposures at low doses are one of the factors implicated in changes in the genetic pool of the populations, especially if chemical agents are capable of inducing DNA damage, such as HM.

In general, there are four mechanisms by which HM exerts its effects on the genetic diversity of exposed populations:

1. Some HM are genotoxic, mutagenic, and alter DNA repair processes, increasing the mutational load of the individuals;
2. HM exposure favors the presence of tolerant genotypes and the elimination of intolerant ones, changing the genetic composition of the exposed population;
3. HM may cause bottlenecks and
4. Alter migration patterns, increasing or decreasing genetic flow between population

Exposed populations to HM pollution may have two types of responses to genetic diversity levels:

a) Increase in genetic diversity levels as a consequence of induced mutations by genotoxins or
b) Decrease in genetic diversity levels as a result of bottlenecks (Sanches et al, 2018).

The Republic of Macedonia was involved in the UNECE ICP Vegetation – Heavy Metals in European Mosses, for the first time in 2002 (survey 2000/2001) and again in 2005 and 2010 when atmospheric deposition of trace elements was studied over the entire territory of the country using samples of terrestrial mosses Hypnum cupressiforme and Homalothecium lutescens. The results from all three studies show that the regions near the towns of Skopje, Veles, Tetovo, Radoviš, and Kavadarci were found as most affected by pollution, even the median elemental contents in the mosses in 2010 for Cd, Cr, Cu, Ni, Pb, and Zn were slightly lower than the previous surveys (Stafilov, 2014).

The purpose of this paper is to show the pollution of the soil with these heavy metals, taking into consideration that this region is generally considered a place of high pollution with heavy metals based on some scientific works in our country in the last ten years.

2. Material and method

2.1. The study area: The study is the city of Tetovo and Kicevo, more accurately we have studied two key points in Tetovo near two old factories. One of them is the suburbs of Jegunovce, in this place is located the Jugohrom factory, which least years was in big public pressure for setting filters because from many analysis of air quality in this region according to their conclusion this factory was the main factor for enormous pollution of air in the city of Tetovo. The second point in Tetovo is next to Teteks factory, which has been the textile factory, where now inside the factory are some small landfills.
Related to the study point in Kicevo, more precisely Osllomej we have studied the pollution of the soil in this region because of the presence of the Osllomoj factory which is a thermal power station for electricity production.

2.2. Soil samples: Soil samples were collected from 13 points in three different locations mentioned above. The coordinates of the samples are shown in Table 1.

Table 1. Sample coordinates

Sample number-Location	North	East
1-Jugohrom	$42^{\circ}\,4'\,23''$	$21^{\circ}\,6'\,14''$
2	$42^{\circ}\,4'\,31''$	$21^{\circ}\,7'\,19''$
3	$42^{\circ}\,4'\,26''$	$21^{\circ}\,6'\,4''$
4	$42^{\circ}\,4'\,20''$	$21^{\circ}\,6'\,57''$
5-Teteks	$41^{\circ}\,59'\,38''$	$20^{\circ}\,58'\,17''$
6	$41^{\circ}\,59'\,37''$	$20^{\circ}\,58'\,19''$
7	$41^{\circ}\,59'\,37''$	$20^{\circ}\,58'\,13''$
8	$41^{\circ}\,59'\,41''$	$20^{\circ}\,58'\,17''$
9- Osllomej	$41^{\circ}\,35'\,39''$	$21^{\circ}\,1'\,3''$
10	$41^{\circ}\,34'\,54''$	$21^{\circ}\,0'\,19''$
11	$41^{\circ}\,34'\,54''$	$21^{\circ}\,0'\,23''$

12	$41^{\circ}\,34'\,22''$	$21^{\circ}\,0'\,13''$
13	$41^{\circ}\,34'\,30''$	$21^{\circ}\,0'\,8''$

2.3. Apparatus and reagents: The concentration of heavy metals was determined with the atomic absorption spectroscopy method, using Nov AA400 Analytic Jena Spectrometer.
Reagents needed to carry out the experimental part are: 35% HCl, 65% HNO_3, 30% H_2O_2, distilled water, and twice distilled water.

2.4. Sample collection: A total of four samples were analyzed, where 5 samples were taken for each point for a more comprehensive result. Samples of one point were in distance between themselves about one meter, one sample was taken in the center, and four in the corner. All the samples were taken in-depth 5 cm and for each sample, we collected around 0.5 kg of soil. After collection samples were placed in plastic bags. After that, we sent the samples to the laboratory for the experimental part.

2.5. The treatment of soil samples: Soil samples are cleaned from foreign materials and they have drained in the air at a temperature of 25-35 ℃ for seven days. Closely 1 gram from each sample was settled in glass for digestion, there was added 20 ml (5ml HNO_3 *and* 15ml HCl). Firstly, the samples were left to stay quiet for 72 hours at room temperature, then they were heated until to 150 ℃ for one hour, and after that the temperature was increased to 250 ℃ for two hours. After cooling the glasses, the digested material was carried out quantitatively in a volumetric vessel of 50ml, and the rest of the container was filled with redistilled water up to the mark.

2.6. Quality control of the analysis: Quality control for determination with AAS is based on the standard addition method.

2.7. Statistical Analysis: The processing of experimental results is realized through the computer program EXCEL.

3. Results and discussion

The concentration of heavy metals expressed in mg/kg for soil samples analyzed in the territory of the municipality of Tetova, mainly in the vicinity of the Jugohrom factory, is presented in Table 2.

Table 2. The concentration of metals (in mg/kg of dry weight) in soil samples in the analyzed industrial regions.

Sample/point	Pb	Ni	Cu	Cr	Cd	Fe
1-J	21.23	21.47	22.19	6	2.42	-
2	60.8	30.93	66.45	11.56	3.19	-
3	17.53	17.72	44.63	40.1	3.88	-
4	22.53	44.65	66.7	10.53	3	-
5-T	62.260	383.1	76.4	42.370	2.76	-
6	23.080	59.650	52.2	44.150	0.360	-
7	11.70	39.640	48.695	56.500	3.750	-
8	381.6	33.3	83.9	24.720	3.360	-
9-Os	16.29	28.06	23.65	-	-	2276.00
10	21.91	18.69	24.20	-	-	2204.5
11	24.935	28.63	30.11	-	-	2301.00

12	28.43	24.189	33.14	-	-	2290
13	20.695	30.22	43.52	-	-	2096.5

In table 3 are shown the maximum, minimum, median, and average for all soil samples analyzed**.**

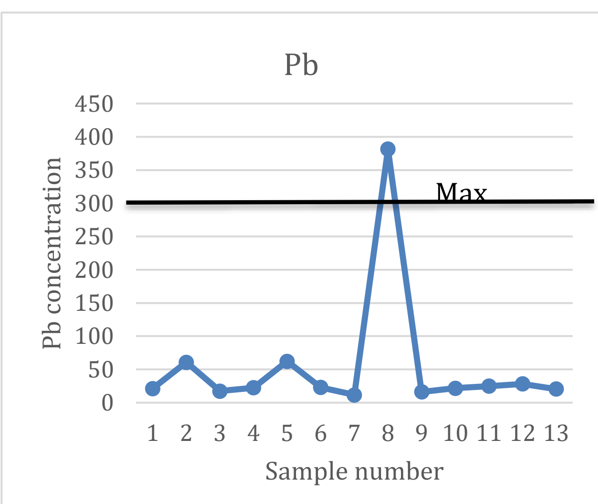
Table 3. Statistical data of the studied points

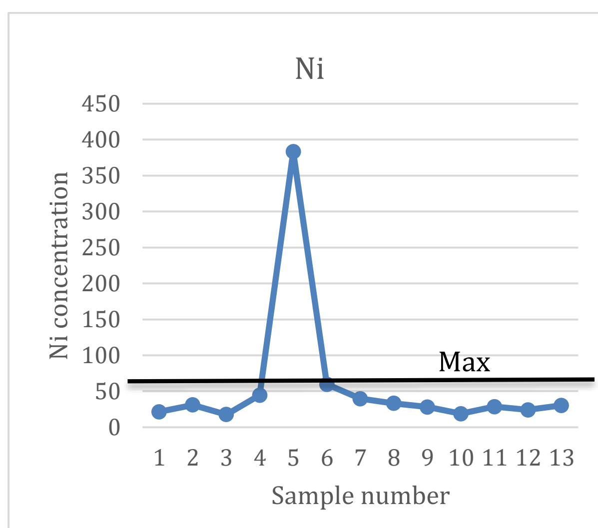
	Location	**Pb**	**Ni**	**Cu**	**Cr**	**Cd**	**Fe**
	Jugohrom	30.5225	28.6925	49.9925	17.0475	3.1225	-
	Teteks	119.66	128.9225	65.29875	41.935	2.5575	-
Average	Osllomej	22.452	25.9578	30.924	-	-	2233.6
	Jugohrom	60.8	44.65	66.7	40.1	3.88	-
	Teteks	381.6	383.1	83.9	56.5	3.75	-
Maximum	Osllomej	28.43	30.22	43.52	-	-	2301
	Jugohrom	17.53	17.72	22.19	6	2.42	-
Minimum	Teteks	11.7	33.3	48.695	24.72	0.36	-
	Osllomej	16.29	18.69	23.65	-	-	2096.5
	Jugohrom	21.88	26.2	55.54	11.045	3.095	-
	Teteks	42.67	49.645	64.3	43.26	3.06	-
Median	Osllomej	21.91	28.06	30.11	-	-	2276

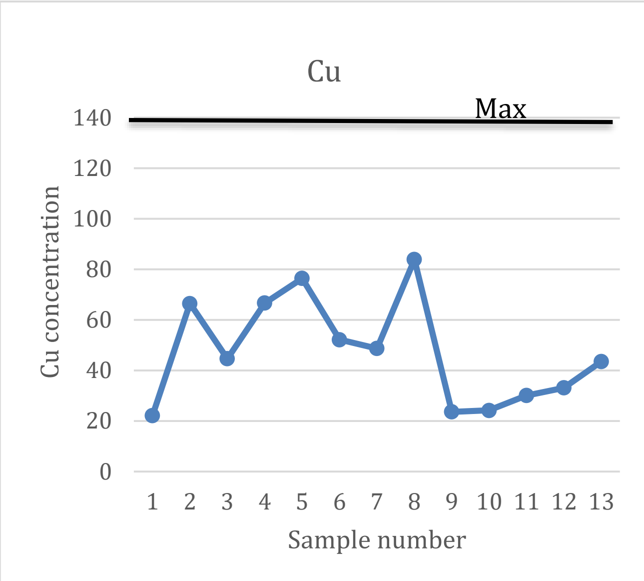
Intensity concentration of heavy metals based on their average values for soil samples in the following graphs are compared with the limit values of concentration of some heavy metals in soil according to EU directives (Council Directive 86/278/EEC, 1986).

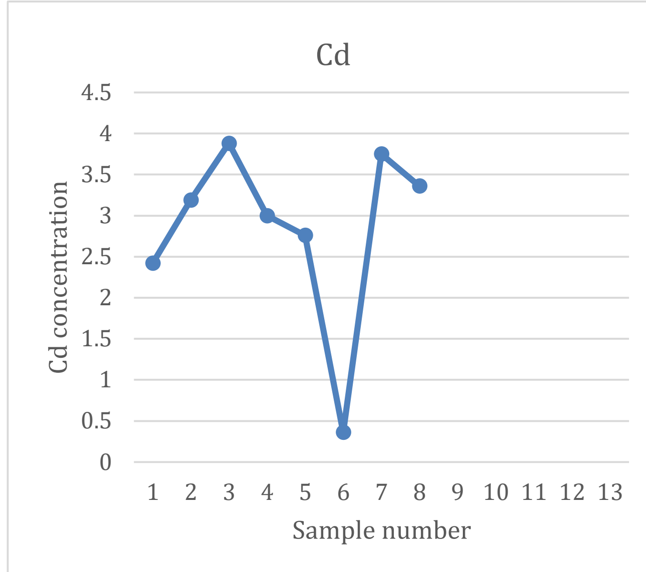
Table 4. Boundary values of concentration of some heavy metals in soils according to EU directives

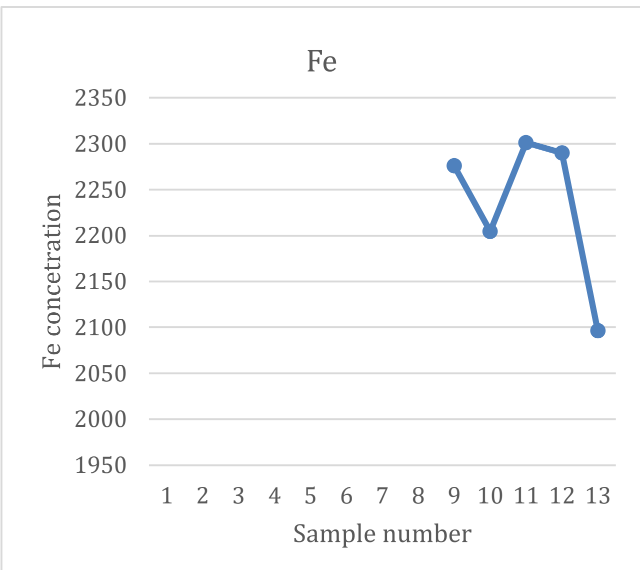
Metals	**Border values in mg/kg**
Cadmium	1 – 3
Lead	50 – 300
Copper	50 – 140
Zinc	150 – 300
Nickel	30 – 75
Chromium	-

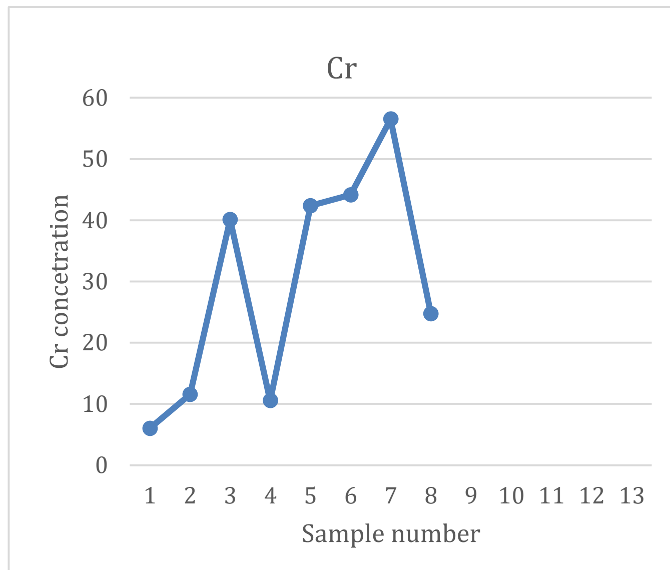












From the performed measurements of the concentration of heavy metals in the above points, we obtained the following results.

Regarding the concentration of lead, from all points analyzed only in point number 8 the amount of lead has exceeded the level, the maximum allowed amount of lead according to European conditions is 300 mg/kg and at this point number 8 the amount of lead is 381.6 mg/kg.

The concentration of Nickel has been within the allowed values except in point number 5 where its measured concentration is 383.1 mg/kg, while the allowable value is from 30-75 mg/kg.

Both Ni and Pb metals that have come out with a higher level than allowed in the above points should be noted that they are at the location of the Teteks factory.

The results of copper show that its concentrations are within the values allowed by the EU.

Regarding Chromium, the EU directives do not specify the permissible level of chromium in the soil, but from some scientific papers that will be cited in the conclusion, the permissible value of chromium in the soil according to the World Health Organization varies from 0.01- 0.1 mg/kg. From this, it can be seen that from all the analyzed points the value of chromium has come out significantly above the level allowed in the two studied locations around the factory Jugohrom and Teteks. According to this, it can be confirmed that the

concerns of the Eco Guerrilla organization in Tetovo that the Jugohrom factory is polluting the air with heavy metals were true and with this scientific work, it can be concluded that the Earth is also polluted with the chromium.
In point 2 the concentration of Cd was measured to be slightly above the allowable level which is 3.00 mg/kg, at this point it was measured to be 3.19 and in point 3 it is 3.88, so clearly above the allowed level and in point number 4 is on the border. Regarding the concentration of Fe in the soil, they are according to the expectations, considering that the soil contains high amounts of iron, its amounts have turned out to be higher than the other metals analyzed.

4. Conclusions

The concentration above the allowed level of Ni and Pb at the location of the Teteks factory is justified by the fact that in the vicinity of these points where the values of these metals have exceeded the allowed level, sewage discharges have been made from the textile factory (Ghannem Samir et al, 2016) as well the higher than the allowed level of Ni in point 5 is as a result of the fact that in the vicinity of this point there is a coal landfill which stays in the outer space for years since the closure of the factory.
According to the results (Geoffrey et al, 2020) the allowed amount of hexavalent chromium in the soil according to WHO is 0.05 to 0.1 mg/kg, in both locations analyzed at all points the amounts of Chromium have exceeded the level allowed by WHO. In terms of quantity much higher than allowed at the points studied in the vicinity of the Jugohrom factory can be explained by the production of ferrochrome from the Jugohrom electrometallurgical plant (Geoffrey et al, 2020). On the other hand, the higher than allowed quantities of chromium at the points near the location of the Teteks factory can be assumed to stem from the industrial activity that has taken place at the textile factory, and the higher quantities of Cd at points 3 (3,88 mg/kg) can be described as anthropogenic sources such as industrial activity and transport (Yuanliang et al, 2019).
On the other hand, the results of heavy metals at the points studied at the plant for the production of electricity Oslomej, show that their quantity is at the allowable level, but we can't conclude with certainty that soil was not polluted at all with these metals, because as we know from many studies that have been done in this that soil composition, pH, etc. play a very big role in retaining metals or releasing them from the soil (Andersson, 1977). In our future studies, we will analyze the composition of the soil in this region and after that, we can give a complete conclusion about the pollution of the soil in this region.

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