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Research Article

Impact of Industrial Complex "Ferronickel" in Pollution with Heavy Metals in Soil, Surface and Ground Water of this Location

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ABSTRACT

Contamination of soil, surface and groundwater considerably decreases environmental quality and directly affects the human health. To investigate and assess the effects seen in the land and water around the Ferronickel industrial complex in Kosovo, we analyzed the concentration of heavy metals in agricultural soil; these included As, Cd, Cr, Co, Fe, Mn, Ni, Pb dhe Zn whereas in surface and groundwater elements, the following were measured: As, Cr, Fe, Mn, Ni, and Zn. The soil samples were treated according to the 3052 method in the presence of HCl and HNO_3, and for water treatments we used the 3015A method. The presence of heavy metals in our samples was analyzed using the inductively coupled plasma-atomic emission spectrometry (ICP-OES). The results in this study indicate that heavy metals are quite dispersed in the surrounding areas of Ferronickel complex in Mitrovica, Kosovo in both soil and water and should be continuously monitored so as to reduce the risks posed to the health.

Keywords: Contamination, heavy metals, water, soil, industrial complex.

INTRODUCTION

Metals constitute one of the major groups of genotoxic environmental pollutants possessing serious threats to humans, as well as the environmental well-being [4]. The contamination of surface water with high level of toxic metals is a matter of serious concern today[1-3]. To have general knowledge of heavy metal pollution emission, one should go through several processes, including air, water and soil[6]. Geosphere or land is part of the planet Earth, on which people live and from which they derive most of their food. Plants take iron in the form of Fe^{2+}, Fe^{3+}. Competition to connect with iron show copper, cobalt, nickel, zinc, chromium and manganese while at high pH inhibit Ca^{2+} and phosphate ions 5. Soil quality is one of the most important factors in sustaining the global biosphere[8]. It was said that the earth has almost unlimited buffer capacity despite human activities, but today geosphere is known to be more delicate all through different human activities. Nickel content especially in the autumn season may come as a result of geological layers by rainfall during laundering more than by human activity[7]. The territory of Kosovo in the mineralogical context is rich in beneficial minerals.[10] Within the country, as a result of various geological processes, significant deposits are formed in metallic, non-metallic, lead-zinc, iron, nickel, magnesite, bauxite etc., which occupy an important place in the economy of Kosovo[9].

Researches looking to deposit Ni-silicate in Gllavica have continued for years, where the existence of nickel ore in Kosovo was confirmed in 1958 by a team from the University of Belgrade; this also marks the same year that Ni-silicate ore was discovered in the area[10]. Junk material in various forms coupling the concentration of heavy metals is growing only because the heavy metals in the soil with complex additional material and half time degradation in much longer than when they are free and in a soluble form[11]. Analysis of the first on the ground, resulting in concentration of Ni, about 0.5%, while in September 1960, Magnesite mine worker Goles, paving the pit, on the eastern side of the deposit Gllavica, has achieved in the area contact with Ni-silicate ores in depth 4.5 m[12]. Analyses of this mineral showed good results composition of Nickel-about 2.1% and these data gave hope to the existence of minerals areas for further research Nickel, in this region. The possibility of their penetration to surface and underground waters and through then to the chain of food is very evidentual[13].

MATERIALS AND METHODS

The investigation areas included surface water (river Drenica), ground water of wells (W_1, W_2, W_3) and land in industrial complex surroundings of New Coo Ferronickel. Sampling was done in the period October 2013. The sampling points of surface water, groundwater and soil were chosen in a way that samples would represent the average quality and diluting ability of the receiving environment. Water samples were taken in plastic containers of 1 L and soil samples were taken in plastic bags of 3kg in chosen sampling points. The technique used for determining the concentration of different elements in analyzed samples was ICP-OES. Analyzed samples of soil were taken in three 3-sampling points, which are taken in different layers of soil, 5, 25 and 50 cm soil depth, which were taken in; Soil-S_1, in the neighborhood, land planted with vegetables, S_2-Wasteland in Dobroshevc village, at the bridge over the river Drenica; S_3-Loam in Qikatova neighborhood Xhemaj, all of these sampling points around Drenica River. Surface water samples were taken at three sampling points: M_1-Ws, in the discharge tube, Ferronickel neighborhood; M_2-

Ws, Drenica River on-line visa Poklek Old village, around 1.5km from S_1, and; S_3-Ws, visa-line with Dobroshevc village, also in river Drenica, some 2km from S_2. Also, groundwater samples were taken at three sampling points as; S_1-Gw, in Well-$_1$ in land planted with vegetables, Ferronickel neighborhood, 15m away from the discharge tube horizontally through the right side; S_2-Gw-, in Well-$_2$ at the Old Qikatova in the well for water supply for irrigation, around 2km from S_1, and; S_3-Gw, in water Well-$_3$, at the Old Qikatova, 50 m above the S_1-prong dross landfill and the waste sterility Ferronickel.

Area description

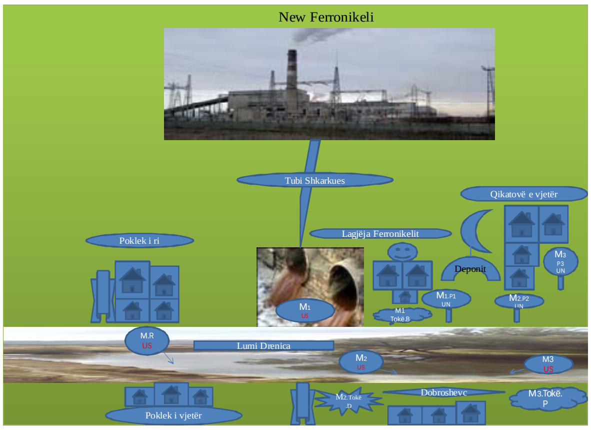

Figure 1: Study area for soil, surface water and groundwater.

In the figure below (Figure 1), the sampling points for soil, surface and groundwater near Ferronickel complex in Mitrovica, Kosovo are presented.

Sampling points are taken in the effluent intertwining, where we thought that invades pollution in water sampling points of surface, groundwater and agricultural areas, in terms of pollution Ferronickel from discharge tube and dross and sterility landfills.

Sample preparation

During water sampling we used polyethylene bottles and we stored the samples in 4°C during the laboratory transportation and we preserved the samples by adding HNO_3 up to pH = 3.5, and we treated the samples according to[14].

Soil samples were collected in plastic bags, dried and grinded and for further treatments we used[15].

Once the digestion of samples was done, we filtered the samples, leveled the samples with distillated water to 100 ml and measured the elements by using ICP-OES technique.

RESULTS AND DISCUSSION

The results of this research are presented in tabular and graphic form for concentration of heavy metals in soil, surface water and groundwater.

Table 1: Coordinates of sampling points, GPS measured, Magelan type

Sample	Coordinates X	Coordinates Y	Elevation
Surface Water - S_1-Sw-Discharge tube	492325	4719984	591 m
Surface Water - S_2-Sw	492643	4719914	579 m
Surface Water - S_3-Sw	493219	4721455	586 m
Groundwater - S_1-Gw	492363	4719999	584 m
Groundwater – S_2-Gw	493305	4721733	584 m
Groundwater – S_3-Gw	493306	4721763	580 m
Soil- S_1-Soil	492352	4719995	584 m
Soil- S_2-Soil, (Wasteland)	493216	4721456	581 m
Soil- S_3-Soil, (Loam)	493796	4721886	579 m

Table 2: Metal concentrations in soil samples, in mg/kg.

	Elements in mg/kg								
Sample	As	Cd	Cr	Co	Fe	Mn	Ni	Pb	Zn
S_1-Soil	23.56	0.079	121.250	18.857	17561.61	713.33	129.95	26.77	51.96
S_2-Soil	11.51	10.725	180.843	9.357	12096.89	806.29	167.53	85.06	86.61
S_3-Soil	20.15	0.039	179.443	33.835	14882.41	1035.97	225.18	36.43	52.71

Table 3: Metal concentrations in surface water samples, in mg/dm^3.

	Elements in mg/dm^3					
Sample	As	Cr	Fe	Mn	Ni	Zn
S_1-Sw/D.tube	0.018	0.018	0.436	0.074	0.052	0.078
S_2-Sw/D.River	0.002	0.012	0.332	0.054	0.068	0.044
S_3-Sw/D.River	0.002	0.004	0.252	0.154	0.050	0.020

Table 4: Metal concentrations in groundwater samples, in mg/dm^3

	Elements in mg/dm3					
Sample	As	Cr	Fe	Mn	Ni	Zn
S_1-Gw/Well-$_1$	0.016	0.018	0.282	0.632	0.026	0.042
S_2-Gw/Well-$_2$	0.004	0.012	0.152	0.038	0.028	0.030
S_3-Gw/Well-$_3$	0.002	0.034	0.082	0.036	0.016	0.014

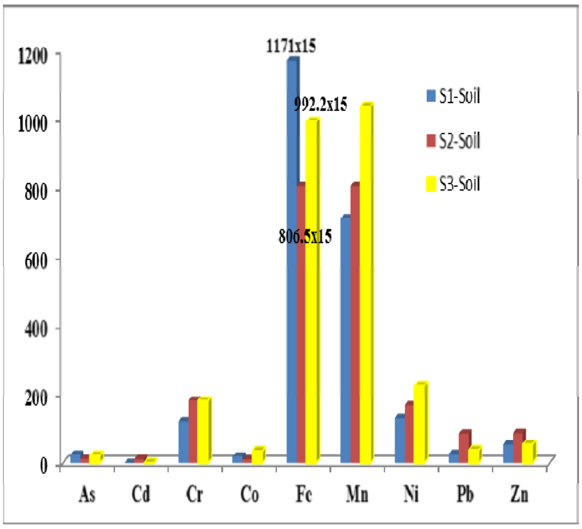

Figure 2: Distribution of metals in soil in different sampling points.

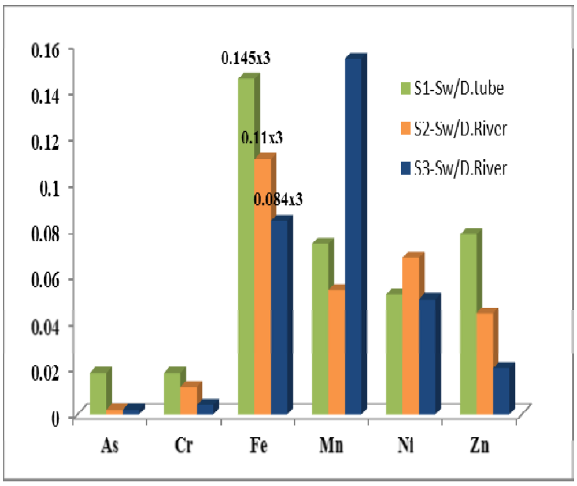

Figure 3: Distribution of metals in surface water in different sampling points.

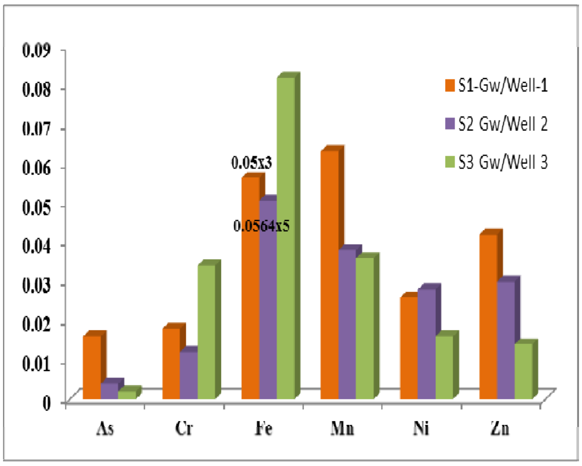

Figure 4: Distribution of metals in groundwater in different sampling points.

The sterile and slag deposit from the "New Ferronickel" complex has caused tremendous damage to the surrounding land—this is best indicated by the results of the soil samples, which were collected in three sampling points, namely S1-Soil, S2- Earth-wasteland, S3-Fertile soil. A high concentration of heavy metals is noticed in the samples, such as Fe 17561.61mg/kg, Cr 180.843 mg/kg, Mn 1035.97 mg/kg, Ni 225.18 mg/kg, Pb 85.06 mg/kg, As 23.56 mg/kg, Zn 86.61mg/kg, as opposed to the concentration of elements such as Cd and Co. One can say that such a high concentration of these elements is due to the geological origin, as that geographical area sits in a mineral basin which dates back to prehistory. The agricultural lands, which are annually plowed in a layer up to 20 centimeters thick, are plowed and prepared for crops, thus leading to the exposure of the lower soil layers. This leads to the conclusion that crops have been plowed more often and this causes the contamination of the agricultural lands, on the one hand; and on the other hand, the planting seed may potentially absorb an amount of minerals during its growth. It is mostly grasslands and meadows which, according to our findings, are more contaminated by heavy metals, as opposed to fertile lands.

Table 3 shows that the concentration of heavy metals in surface waters in several sampling spots is high. However, since there are massive amounts of deposited sterile and slag—and heavy metals being regarded as some of the most hazardous no degradable pollutants—these concentrations can thus pose huge risks to the environment. The metals can move to aqueous systems in salt form in various means, and may later bond with other compounds while in ionic form. After making their way to the metabolism, they cause toxic effects and various cancers and terminal diseases. The heavy metal concentration varies among the different samples, such as $S_{1\text{-}SW}$, $S_{2\text{-}SW}$, $S_{3\text{-}SW}$; iron concentrations were particularly recorded, with 1.072 mg/dm^3, whereas the concentration of others was Ni 0.068 mg/dm^3, Zn 0.010 mg/dm^3, As 0.302 mg/dm^3, Cr 0.026 mg/dm^3 and Mn 0.154 mg/dm^3. It may be concluded that these concentrations are rather low in comparison to Fe. Table 4 shows a difference in heavy metals concentration in the sampling spots $S_{1\text{-}GW\text{-}WELL1}$, $S_{2\text{-}GW\text{-}WELL2}$ dhe $S_{3\text{-}GW\text{-}WELL3}$. The concentration of heavy metals is higher, as is the pollution, in sampling spots I, II and III where the pollution has accumulated over time due to the rainfall; this has led to these sampling spots showing higher heavy metal contamination, especially indicated by Fe 0.282 mg/dm^3, Ni 3.374 mg/dm^3, Cr 2.864 mg/dm^3, Mn 29.344 mg/dm^3 and Zn 1.582 mg/dm^3, which are regarded as high values, as opposed to As with 0.016 mg/dm^3, which is lower. This pollution might have also been triggered by another equipment of the “New Ferronickel” technology system, due to the fact that this system is rather large and provides a large ore extraction capacity; the pollution source might also be different. Therefore, the concentration of some heavy metals exceeds the tolerated upper limits; they are regarded as high when compared to the EU or WHO standards for surface and groundwater’s.

CONCLUSION

This paper shows an overview of the quality of river Drenica during the October 2013; a particular area of focus was the measurement and assessment of the heavy metal concentration in the soils and ground waters (wells), which was important given the discharge of industrial wastewaters into the river, as well as the pollution caused by the sterile and slag deposits from the “New Ferronickel” complex. This complex causes permanent damage to the Drenica river supporting indicators are the flora and fauna which once used to include several fish species which are now extinct in a range of at least ten kilometers from the point where water performs self-purification. The remaining waters from “New Ferronickel” are constantly discharged into Drenica river through surface and underground tubes without any prior treatment whatsoever. These waters, when discharged in large amounts, disturb the ecological equilibrium in the river and cause pollution of concerning degrees. According to the experimental data, it can be inferred that an important factor in polluting the Drenica river are the sterile and slag deposits, in particular in the aftermaths of atmospheric precipitation. This conclusion is confirmed by comparing the chemical quality of the Drenica river in two spots: the first in a spot away from the influences of the industrial wastewater discharged into the river through tubes and the slag and sterile deposits, and the other in a polluted spot. The experimental data shows that the polluted water has a high heavy metals concentration and such waters then flow into surface or groundwater streams. In addition, the soils in this area are also contaminated with heavy metals as a result of the deposits and other pollutants; their surface encompasses a large area. Subsequently, these have had their chemical, physical, water and biological properties changed in an area as large as 100 hectares. This location is heavily contaminated and this leads to permanent damages to this area, and in particular to the agricultural lands surrounding this deposit.

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