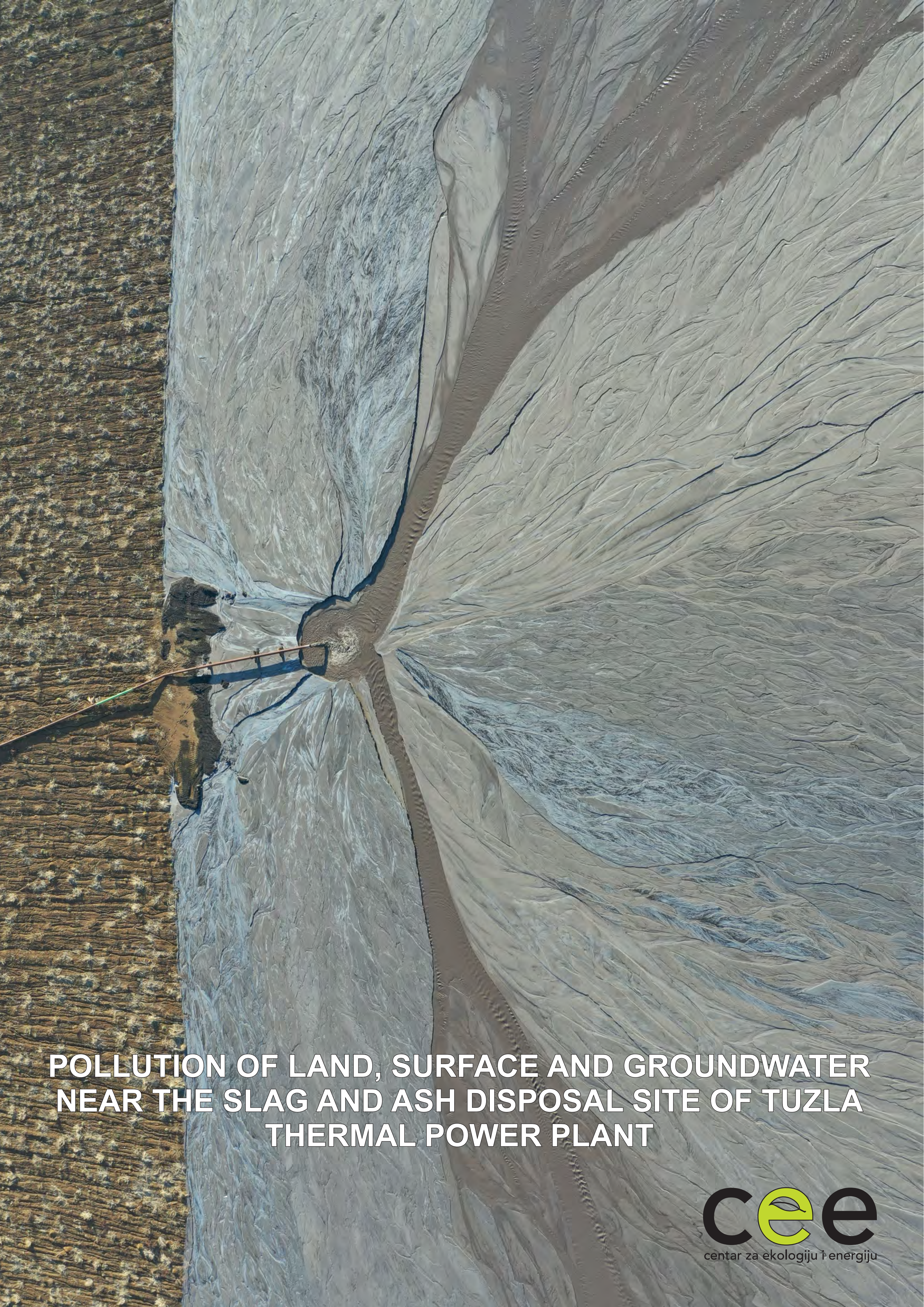

# POLLUTION OF LAND, SURFACE AND GROUNDWATER NEAR THE SLAG AND ASH DISPOSAL SITE OF TUZLA THERMAL POWER PLANT

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CEE Bankwatch Network

EUROPE BEYOND COAL

**PUBLISHER:**

**Centre for ecology and energy**
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**Print:**
OFF-SET Tuzla

This publication was produced as part of the campaign
Stop Dirty Energy – The Future is Renewable

## GLOSSARY

**Symbol Description**

CL…………………..Contamination level

$C_n$…………………...Concentration of examined metals in the sample

$C_{ref}$…………………Concentration of the examined element in the control sample

$C_{m\ of\ sample}$…………..Concentration of metals in the examined samples

$C_{m\ of\ ref.sample}$………..Concentration of metals in the control samples

$C_{gr.value}$………………Limit values of concentration of metal in soil

EPA…………………US Environmental Protection Agency

ERI …………………Ecological risk index

HEAL ………………Health and Environment Alliance

IARC………………..International Agency for Cancer Research

*N* ……………………Number of examined elements

PCBs………………..Polychlorinated biphenyl

*SNA*………………...Sulphates, nitrates and ammonium ions

$T_i$……………………..Toxic response factor

VOC…………………Volatile organic compounds

## CONTENTS

## 1. EXECUTIVE SUMMARY

From 1 March - 31 August 2020, an analysis of water and soil samples was conducted in the area of influence of the closed slag and ash disposal sites in Tuzla, Bosnia and Herzegovina (BiH) – Plane, Divkovići I, Divkovići II, Drežnik and Jezero I – as well as wastewater samples from the active ash disposal site Jezero II. Twenty-three water samples and two soil samples were analyzed.

The results showed that the wastewater at the active Jezero II ash disposal site is alkaline toxic water with cadmium, lead, nickel and chromium values exceeding the prescribed limit values.[1] This type of wastewater cannot be discharged into surface water without treatment and must not come into contact with underground water.

The soil on the closed waste disposal sites of Plane and Drežnik, which is currently used for agriculture, contains extremely high concentrations of nickel, and high concentrations of chromium and cadmium. As a result, agriculture for human and animal consumption must be stopped and full remediation and recultivation measures implemented in accordance with the Federation of BiH legislation.[2] The measures taken so far – of covering the surface of the waste disposal sites with 20 cm of soil – are inadequate.

Considering the several decades of disposal of slag and ash within a very confined area of the western part of Tuzla, as well as the existence of the active Jezero II ash disposal site, it is shocking that no research of this type has ever been done on the wells and springs in the area.

Out of the six wells tested during the analyzed period, the water from only two of them can be considered completely safe to drink according to BiH standards. The other four have different problems, including high turbidity, uncharacteristic smell, and high concentrations of nitrates or heavy metals like iron, chromium, lead and manganese.

Since there are numerous wells and drinking water springs in the close vicinity of both the active and closed ash disposal sites, an underground water quality

[1] Uredba o uslovima ispuštanja otpadnih voda u okoliš i sisteme javne kanalizacije, *Službenim novinama Federacije BiH*, Broj 26, April 2020: 48-75.
[2] Uputstvo o obaveznoj jedinstvenoj metodologiji za izradu projekata rekultivacije, *Službenim novinama Federacije BiH*, Broj 03-3-02-221/09, November 2009.

monitoring system must be set up by the operator. Regular monitoring would secure preconditions for a timely reaction in case of worsening of spring/underground water quality.

To prevent or reduce negative impacts on the environment and human health to a minimum – especially contamination of underground water – mineral lining (i.e. bentonite clay) needs to be installed on the bottom and the sides of the ash and slag disposal site. Such mineral lining must be watertight and can be complemented and fortified by other means (i.e. geomembranes) to provide the required level of protection.

The Federation of Bosnia and Herzegovina Government needs to draft and adopt a regulation clearly prescribing compulsory measures to prevent the negative impacts of slag and ash disposal sites on the environment. This regulation must lay down clear guidelines for the establishment of regular air, soil, and underground water contamination monitoring, during the active life of ash disposal sites and after their closure.

## 2. INTRODUCTION

Solid waste that originates in the process of coal combustion in thermal power plants is called slag and ash. This waste also encompasses electro-filter ash and solid waste which is the end result of the process of desulphurisation of gases. Slag and ash contain numerous chemical elements, including toxic heavy metals, which, when exposed to rainfall and wind, can cause negative effects to humans and entire ecosystems. Generally speaking, coal combustion in thermal power plants inflicts serious damage on the environment at its initial stages through massive exploitation of coal, afterwards through emissions of gases and finally through slag disposal. These effects result in permanent changes to the environment which do not only affect individual regions, but entire ecosystems. This in turn results in global changes to the biosphere. The most significant waste flow produced by the Tuzla thermal power plant, is composed of slag and ash disposed of hydraulically at the waste disposal site Jezero II. Since slag and ash contain heavy metals, it is necessary to be familiar with their chemical composition and whether the conditions of disposal and/or disposed ash cause any transformation and availability of heavy metals. Therefore, it is necessary to determine the possible negative effects on the general population living in the vicinity of ash disposal sites. Research carried out so far at slag and ash disposal sites has indicated that heavy metals present in the disposed slag and ash can cause negative effects on different environmental elements. These effects manifest when slag and ash are in contact with water. This may result in contamination of underground water flows, springs and plants. The intensity of the transfer of toxic heavy metals from the slag and ash depends on the manner of its disposal, the type of surface under the disposal site, the vicinity of surface waters, the dynamics of underground water flows and existing anthropogenic structures in the close vicinity of the disposal sites. Bearing in mind that the existing ash disposal sites of the Tuzla power plant were established in natural valleys and in the close vicinity of urban areas without lining on the bottom and sides, there is a high risk that this will result in permanent contamination of underground water and surface soil at partially re-cultivated ash disposal sites.

## 3. CHARACTERISTICS AND DYNAMICS OF HEAVY METALS IN COAL, SLAG AND ASH

The basic approach to management of high quantities of waste is prevention at the source and control of waste disposal. Water flows passing through waste disposal sites permanently contaminate both surface and underground waters. A very common event on slag and ash disposal sites is that the surface becomes dry, thus enabling wind to carry small solid particulate matter (PM) through the air, and consequently significantly contribute to PM air pollution. Pollution of the environment by sludge waste flows is visible through outflows of ash disposal sites (wastewater, dust, etc.). Pollutants like heavy metals (As, Cd, Cu, Cr, Ni, Pb, Hg, Tl, V, Al, Zn, etc.) are also present. It is necessary to take into account the fact that it is often claimed that waste flows are inert (for example, slag and ash from the Tuzla power plant) based only on the fact that they are classified as non-hazardous in the *Regulation on Types of Waste with lists* (FBiH Official Gazette, no. 9/05[3]). This claim is made without research on the composition of slag and ash to determine the actual level of hazard.

[3] Pravilnik o kategorijama otpada sa listama, *Službenim novinama Federacije BiH*, Broj 03-02-2-235/04, January 2005.

Industrial capacities for the production of electricity, coke, construction materials, soda, salt, detergents, artificial fertiliser, anhydrides of malefic acid, etc. have been built in the vicinity of Tuzla, Lukavac, Živinice and Banovići. The lack of a sufficient number of wastewater purification facilities has contributed to serious degradation of the quality of land, aquifers and air. Slag and ash are the most significant waste flow which occurs as a result of coal combustion. Based on research carried out so far, all elements from the periodic system of elements are present in coal[4], and therefore in slag and ash, with additional concentrations of specific elements like Boron (B), Selenium (Se), Lead (Pb) and Nickel (Ni). Based on their differing ratios contained in coal, these elements can be divided into three groups:

1. The main elements (C, H, O, N, S), present in amounts of 1,000 ppm,
2. Elements that compose the mineral parts of coal (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti) and halogen elements (F, Cl, Br, I), which are present in concentrations varying between 100 and 1,000 ppm, and
3. Trace elements (heavy metals) in concentrations less than 100 ppm.

Several existing research studies on the presence of heavy metals in coal, carried out by different authors, have concluded that the number and concentration of these heavy metals vary depending on the type of coal and process of evolution of different types of coal. Being familiar with the contents of heavy metals in coal allows us to predict their release during the combustion process. Table 3.1. lays out a comparative presentation of the average contents of chemical elements contained in the coal from the Banovići and Dubrave coal mines.

[4] Dalway J. Swaine, *Trace Elements in Coal*, London: Butterworth and Co. Ltd., 1990.

**Table 3.1.** Comparative depiction of contents of chemical elements in coal originating from different parts of the world and domestic coal used by the Tuzla coal plant[5].

| Chemical element | Global average range of concentration, mg/kg | Banovići coal mine, mg/kg | Dubrave coal mine, mg/kg |
|---|---|---|---|
| Arsenic, As | 0.5-80 | 29.9 | **141.0** |
| Copper, Cu | 0.5-50 | 25.0 | **197.0** |
| Boron, B | 5-400 | **310.0** | **347.0** |
| Beryllium, Be | 0,1-15 | - | - |
| Caesium, Cs | 0.3-5 | 3.44 | **16.6** |
| Chromium, Cr | 0.5-60 | n.d. | **1050.0** |
| Cadmium, Cd | 0.01-0.3 | 0.10 | **0.58** |
| Cobalt, Co | 0.5-50 | 12.7 | **80.4** |
| Mercury, Hg | 0.02-0.1 | - | - |
| Manganese, Mn | 5-300 | 225.0 | **1610.0** |
| Molybdenum, Mo | 0.1-10 | 1.11 | 3.67 |
| Nickel, Ni | 0.5-50 | **291.0** | **1130.0** |
| Lead, Pb | 2-80 | 7.46 | 40.2 |
| Rubidium, Rb | 2-50 | 8.82 | **75.6** |
| Selenium, Se | 0.2-4 | - | - |
| Thallium, Tl | 0.2-1 | 0.09 | 0.73 |
| Uranium, U | 0.5-10 | - | 3.53 |
| Vanadium, V | 2-100 | - | **27.5** |
| Zinc, Zn | 5-300 | 32.7 | 232.0 |
| Iron, Fe | - | 15500.0 | 93100.0 |
| Fluorine, F | 20-500 | - | - |
| Chlorine, Cl | 50-2000 | - | - |

n.d. = not detected

- = not measured

The data laid out in Table 3.1. shows that certain heavy metals in domestic coal exceed global average concentrations, following a descending sequence as follows: Mn>Ni>Cr>B>V>Cu>As>Co>Rb>Cs>Cd.

Very important data that is missing in the analysis of domestic coal is the content of mercury, which is often associated with thermal power plants. Fifty per cent of airborne mercury pollution in the USA originates in thermal power plants[6]. There is also a lack of data on fluorine and chlorine in coal, which turn into gaseous fluorides and chlorides during the combustion process and have highly damaging

[5] Walter W. Wenzel, *RECOAL - Reintegration of coal ash disposal sites and mitigation of pollution in the West Balkan area, publishable final activity report*, University of Natural Resources and Applied Life Sciences, Vienna – BOKU, 2005.
[6] United States Environmental Protection Agency, 'Cleaner Power Plants'.

effects on the environment. During the coal combustion process, heavy metals are disseminated in the following waste flows: slag and ash, airborne ash, electro filter ash, and solid particles flue gases, as indicated in Figure 3.1.

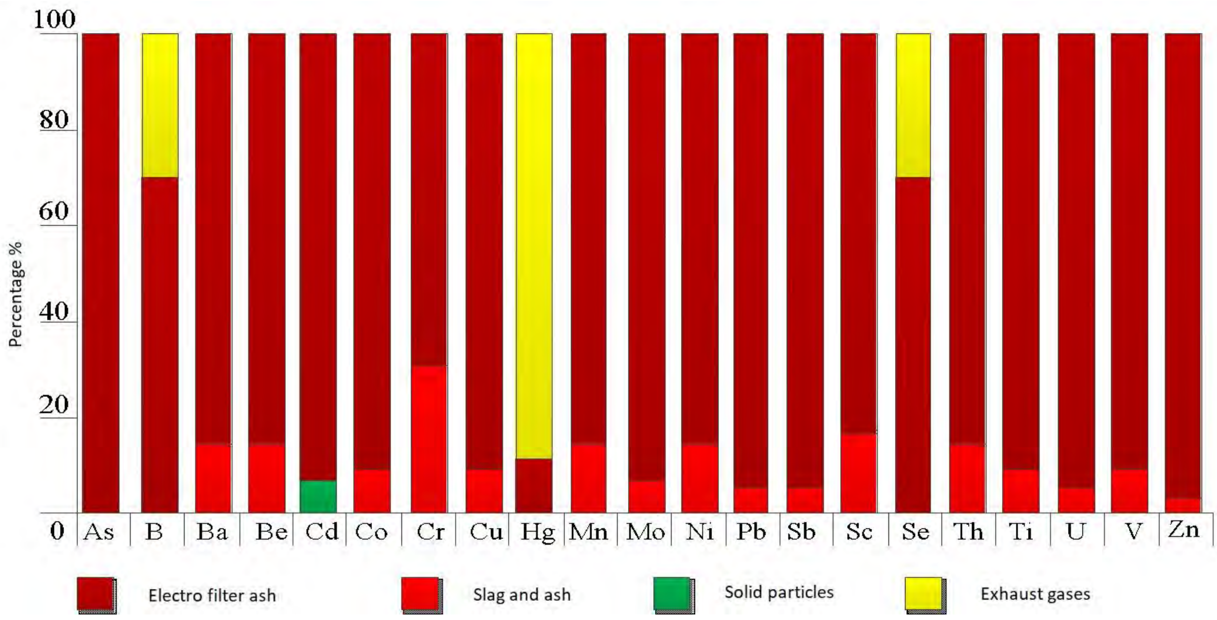


**Figure 3.1.** Distribution of some heavy metals in electro-filter ash and slag, solid particles and exhaust gases[7]

Based on research by various authors,[8,9] we can conclude that there is a trend of enriching submicronic particles with heavy metals. Some heavy metals which partially or fully evaporate during coal combustion tend to condense on submicronic particles due to their large surface area.

Submicronic particles exert multiple influences and are more damaging than supermicronic particles as they tend to spend more time in the atmosphere, which increases the likelihood of soil contamination. The heavy metals that do not evaporate during the combustion process are deposited in the contents of slag and ash as dissolved matter. Some of the particles are also deposited on particles of airborne ash. Other heavy metals that partially or fully evaporate pass through additional transformation in three complicated and mutually mixed processes:

[7] Jay A. Ratafia-Brown, 'Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers', *Fuel Processing Technology* 39, 1-3 (1994): 139-157.
[8] Saifi Izhar et al., 'Annual trends in occurrence of submicron particles in ambient air and health risk posed by particle bound metals', *Chemosphere* 146 (2016): 582-590.
[9] Huiming Li et al., 'Heavy metals in submicronic particulate matter (PM1) from a Chinese metropolitan city predicted by machine learning models', *Chemosphere* (2020): 261.

adsorption, condensation and chemical transformation. There are three means of dissemination of these evaporated heavy metals: steam phase, submicronic and supermicronic aerosols.

Analysis of slag and ash at Divkovići 2 (the Tuzla power plant ash disposal site), illustrated in Figure 3.2., shows that it contains over 75% compounds of silicon, aluminum and iron oxide, out of which silicon oxide makes up 49%. These components are inert to the effects of water, meaning they do not dissolve in water. Slag and ash represent an unfavourable substrate for plant growth: the presence of high concentrations of soluble salts and of carbonates in contact with water increases its pH levels to above 9, which increases the negative effects of slag on plant root systems. Slag and ash are composed of small grey or whitish particles with a surface of 2-0.06 mm. They are made of 86.56% to 96.08% fine sand-type textures. The content of dust (particles of 0.06 to 0.002 mm) and clay (particles of < 0.002 mm) is very small, varying from 1 to 4%.

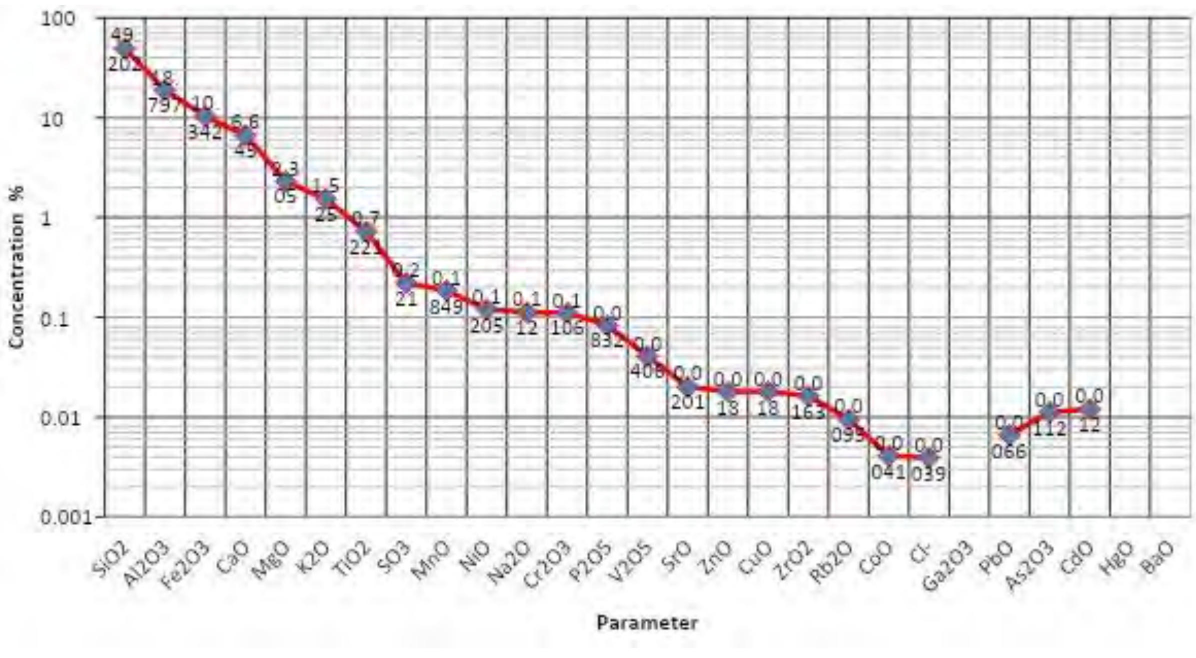


**Figure 3.2.** Chemical composition of slag and ash at Divkovići 2 - Tuzla power plant ash disposal site[10]

[10] Abdel Đozić et al., 'Fitoremedijacija: Novi pristup održive remedijacije i korištenja odlagališta šljake i pepela', *Third international conference: 'New Technologies NT-2016' Development and Application*, 2016.

Of all the aforementioned heavy metals, those that inflict the gravest impact on humans – even in small quantities – are: Arsenic (As), Chromium (Cr), Cadmium (Cd), Lead (Pb), Nickel (Ni), Mercury (Hg), Manganese (Mn) and Molybdenum (Mo). These heavy metals tend to bioaccumulate over time, when their effects are still not acute but lead to chronic, degenerative changes on important organs: the liver, bones, spleen, brain, etc.

Slag and ash disposal at the Plane and Divkovići sites started in 1964 and stopped in 2013. For the Drežnik and Jezero I sites, the overall quantities of disposed slag and ash amount to approx. 40 million $m^3$. Table 3.2. contains the basic characteristics of the slag and ash waste disposal sites associated with the Tuzla power plant.

**Table 3.2.** Characteristics of Tuzla slag and ash waste disposal sites[11]

| Waste disposal site | Plane | Drežnik | Divkovići I | Divkovići II | Jezero I |
|---|---|---|---|---|---|
| Type of surface | Open cast mine | Natural valley | Natural valley | Natural valley | Natural valley |
| Disposal start date | 1964 | 1981 | 1985 | 1985 | 1991 |
| Disposal end date | 1990 | 1991 | 1995 | 2015 | 2003 |
| Surface in hectares | 18 | 45 | 45 | 68 | 24 |
| Recultivation start date | 1991/1992 | 1993 | 2004 | - | - |
| Recultivated, hectares | 18 | 45 | 10 | - | - |
| Thickness of cover layer, in cm | 10-30 | 10-30 | 10-15 | - | - |
| Recultivated surface used for | Agriculture | Agriculture | - | - | - |

Heavy metals reach the soil in two ways, from natural (geogenous) and anthropogenic sources. Natural sources of heavy metals in the soil (besides parent rocks) are volcanic eruptions, sea aerosols and forest fires[12]. Natural or geogenous processes include the erosion of the rocky part of the lithosphere from which the

[11] Wenzel, *RECOAL - Reintegration of coal ash disposal sites and mitigation of pollution in the West Balkan area*.
[12] S. Reichman, *The responses of plants to metal toxicity. A review focusing on copper, manganese & zinc*, Prahan, Victoria: Ameef, 2002.

mineral part of the pedosphere is formed, i.e. soil. The characteristics and the chemical composition of soil are directly dependent on the chemical composition of the parent rocks, or in this case, the composition of the slag and ash. Due to their high toxicity levels, arsenic, cadmium, chromium, lead and mercury are classified as priority metals of high significance for public health. These metallic elements are considered systematically toxic matter, proven to damage multiple organs even at low levels of exposure. They are also classified as carcinogenic for humans (known or probable), according to the United States Environmental Protection Agency (EPA) and International Agency for Research on Cancer (IARC)[13].

Due to the fact that coal combustion ash is known to contain traces of various potentially toxic elements – in the case of Tuzla, Ni, Cr, As and B[14] – it must be assumed that ash disposal in such quantities represents a serious environmental problem. The main dangers arise from soil contamination, water contamination (surface and underground) and dust dispersal. All of the above represent a high risk of heavy metals entering the food chain. In addition, in the course of 2017, 3,000 $m^3$ of dangerous toxic waste classified as 17 06 05 – construction materials containing asbestos[15] – was deposed of at the Jezero II waste disposal site.

The surfaces of ash disposal sites in Tuzla is used by the local population in an uncontrolled manner. The population living in the vicinity is using plots of land on the closed sites for production of food for human and animal consumption, pasture, recreation and waste disposal. Compiling all types of land use, including unofficial usage, is of key importance for understanding environmental and human interactions.[16]

Table 3.3. contains data on the parameters related to environmental burdens for the Tuzla coal power plant during the period from 2010 to 2018.

[13] IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, *A review of human carcinogens, part C: Arsenic, metals, fibres, and dusts*, Lyon, France, 2000.
[14] Wenzel, *RECOAL - Reintegration of coal ash disposal sites and mitigation of pollution in the West Balkan area*.
[15] JP Elektroprivreda BiH, *Izvještaji o zaštiti okoliša*, 2018.
[16] RECOAL, *Handbook on treatment of coal ash disposal sites*, February 2008.

**Table 3.3.** Environmental parameters of Tuzla power plant for the period 2010-2018[17]

| Year | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 |
|---|---|---|---|---|---|---|---|---|---|
| Produced energy, GWh | 3,843.1 | 4,671.8 | 2,993.5 | 3,404 | 3,772 | 3,847 | 3,798 | 3,557 | 3,557 |
| Coal consumpt. Tones | 3,477,301.3 | 4,201,500 | 3,392,300 | 3,590,170 | 3,811,594 | 3,755,432 | 3,811,800 | 3,792,711 | 3,456,881 |
| Water consumpt. $m^3$ | 22,824,000 | 22,824,000 | 14,752,480 | 16,879,728 | 17,415,484 | 15,153,418 | 9,876,140 | 10,616,048 | 10,243,860 |
| Water discharged, $m^3$ | 4,870,000 | 7,130,000 | 3,721,334 | 7,666,141 | 6,948,300 | 4,028,444 | 2,056,179 | 936,288 | 1,275,269 |
| $NO_x$, t/year | 9,295 | 8,422 | 4,712 | 5,813 | 4,057 | 5,752 | 5,861 | 5,222 | 4,891 |
| $SO_2$, t/year | 57,554.7 | 54,466 | 43,728 | 53,013 | 53,156 | 61,896 | 66,431 | 57,692 | 47,499 |
| Solid particles t/year | 4,348 | 4,312 | 2,139 | 1,204 | 966 | 935 | 1,017 | 959 | 777 |
| $CO_2$, t/year | 4,128,954 | 5,077,138 | 3,708,245 | 4,016,912 | 4,461,696 | 3,759,867 | 3,941,042 | 3,564,130 | 3,054,202 |
| Slag and ash, tones | 689,463 | 639,226 | 617,833 | 1,046,324 | 639,240 | - | - | - | - |

The Tuzla power plant's impact on the environment is mirrored by the amount of water it consumes. In the period from 2010 to 2018, the plant used 140,585,158 $m^3$ of water. This is 2.1 times as much as the volume of water in the Modrac reservoir,[18] which amounts to around 66,522,627 $m^3$. Elektroprivreda BiH's data on quantities of slag and ash produced in the period from 2015 to 2018 are indicated as cumulative for the Tuzla and Kakanj power plants and therefore we cannot determine the exact quantity of slag and ash deposited at the waste disposal site Jezero II. With regard to discharged water, the data does not specify which type of wastewater is being measured – technological, communal or contaminated rainfall. The difference between water consumed and discharged is also not defined, and it is to be assumed that part of it evaporates through the cooling towers, while part of it is used for hydraulic transport of slag and ash.

The water used for hydraulic transport of ash together with precipitation water that penetrates into the ash disposal site could become a source of contamination of underground and drinking water in the long run, since the deposited ash represents a

[17] JP Elektroprivreda BiH, *Izvještaji o zaštiti okoliša*.
[18] Tarik Kupusovic et al., 'Akumulacija Modrac I njeno funkcioniranje tijekom poplave u svibnju 2014. godine', *Hrvatske vode* 23, 91 (January 2015):19-28.

hydro-geological collector of intergranular porosity. Due to the depth of deposited ash, multiple underground water reservoirs could be formed on different levels of the ash disposal site. The contaminated water from these reservoirs will mix with natural flows of underground waters and ultimately end up in local springs (well water or natural surface springs).

During the process of water transfer and/or its temporary retention in the body of the ash disposal site, decomposition of heavy metals ions could occur over longer time intervals. A decrease in the redox potential of the body of the ash disposal site (due to absence of oxygen) can result in the process of decomposition and discharge of redox-sensitive elements, like arsenic[19]. Image 3.1. illustrates a microscopic image of slag and ash particles. The slag particle is curved, with numerous craters on its surface, while particles of ash are spherical (visible in the upper part of the photo) and attached to the surface of the slag particle.

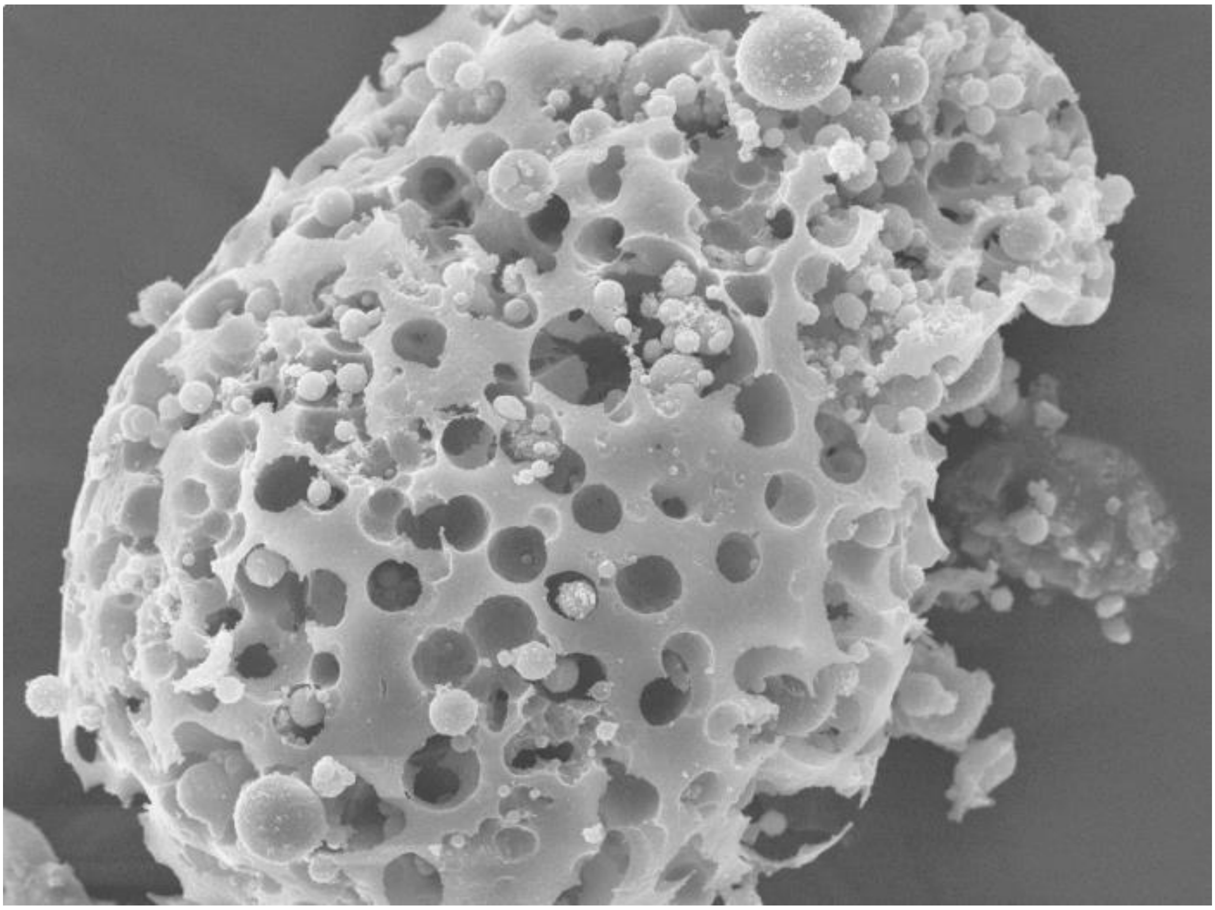

**Image 3.1.** Particles of slag and ash[20]

[19] RECOAL, *Handbook on treatment of coal ash disposal sites*.
[20] SEMTech Solutions, 'Coal ash'.

# 4. METHODOLOGY, OUTCOMES AND DISCUSSION

## 4.1. Methodology

We conducted an analysis of water and soil samples in the area of influence of the closed slag and ash disposal sites – Plane, Divkovići I, Divkovići II, Drežnik and Jezero I, as well as samples of waste water from the active ash disposal site Jezero II. In the period from 1 March 2020 to 31 August 2020, 23 samples of water and two samples of soil were analyzed. Average samples of water and soil were taken as composite (by homogenisation of individual samples). Sampling of soil was carried out in accordance with the Guideline on Procedures, Activities and Conditions for Execution of Control of Soil Fertility (Official Gazette FBiH, number 72/09[21]). The soil samples were taken from a depth of 0-25 cm.

Drinking water, regardless of its origin (well or surface spring) is exposed to various forms of contamination from point and nonpoint sources that are very hard to monitor and make estimations of regarding the type and concentration of polluting substances.

The quality of water was determined by its chemical, physical and biological parameters, which must be balanced and below the allowed limit values. The quality of drinking water is measured by whether it is safe to use as drinking water. There are different methods to determine the quality of water, the first being analysis and comparison to limit values, and the second being analysis of pollution index calculations.

The contents of heavy metals in the soil samples from closed waste disposal sites were determined with the atom absorption method AAS (extraction in aqua regia) and in accordance with the following standards: BAS ISO 11466:2000 and BAS ISO 11047:2000. Ash, as one of the main constituents of waste materials, performs with very high adsorptive characteristics of water without significant changes in its volume (it does not inflate). This means that the total of absorbed and chemically-bound water can reach a mass equal to that of the ash.

[21] Uputstvo o postupku, radnjama i uslovima za vrsenje kontrole plodnosti zemljista, *Službene novine Federacije BiH*, Broj 03-3-02-201/09, October 2009.

Due to high levels of calcium oxides, slag and ash have a high pH reaction which spans from 8.18 to 8.86. It can be assumed that pH values rise with depth, while the surface layer values are somewhat lower due to the influence of rainfall and consequential leaching. As the ash disposal sites represent a kind of hydrological collector, mostly of precipitation water, we can conclude that long-term, leached water from the waste disposal site with very high pH values will emerge, which has very negative effects on the environment.

To better understand the toxic influence of the disposed of slag and ash, Table 4.1. contains the limit values of heavy metals in their total forms, which are determined by the above mentioned FBiH Regulation (*Guideline on Procedures, Activities and Conditions for Execution of Control of Soil Fertility (Official Gazette FBiH, number 72/09*)). The values in Table 4.1. relate to soil with acidic and carbonate reactions, with the values increased by 25% for carbonate soil in relation to acidic soil. Regarding inorganic compounds, the limit value for sulphur is 300 mg/kg for sandy soil, 400 mg/kg for dust-loam soil and 350 mg/kg for clay soil.

**Table 4.1.** Limit values of heavy metals in total forms for acidic and carbonate soils

| Heavy metal | Limit values, mg/kg | | | | | |
|---|---|---|---|---|---|---|
| | Sand soil | | Sand-loam soil | | Clay soil | |
| | Acidic | Carbonate | Acidic | Carbonate | Acidic | Carbonate |
| Arsenic, As | 10 | 12.5 | 15 | 18.75 | 20 | 25 |
| Cadmium, Cd | 0.5 | 0.625 | 1 | 1.25 | 1.5 | 1.875 |
| Copper, Cu | 50 | 62.5 | 65 | 81.25 | 80 | 100 |
| Barium, Ba | 60 | 75 | 80 | 100 | 100 | 125 |
| Boron B | 30 | 37.5 | 40 | 50 | 50 | 62.5 |
| Chromium, Cr | 50 | 62.5 | 80 | 100 | 100 | 125 |
| Cobalt, Co | 30 | 37.5 | 45 | 56.25 | 60 | 75 |
| Molybdenum, Mo | 10 | 12.5 | 15 | 18.75 | 20 | 25 |
| Nickel, Ni | 30 | 37.5 | 40 | 50 | 50 | 62.5 |
| Lead, Pb | 50 | 62.5 | 80 | 100 | 100 | 125 |
| Thallium, Tl | 0.5 | 0.625 | 1 | 1.25 | 1 | 1.25 |
| Vanadium, V | 30 | 37.5 | 40 | 50 | 50 | 62.5 |
| Zinc, Zn | 100 | 125 | 150 | 187.5 | 200 | 250 |
| Mercury, Hg | 0.5 | 0.625 | 1 | 1.25 | 1.5 | 1.87 |

Limit values set in the *Guideline on Procedures, Activities and Conditions for Execution of Control of Soil Fertility (Official Gazette FBiH, number 72/09*[22])

[22] Uputstvo o postupku, radnjama i uslovima za vrsenje kontrole plodnosti zemljista, *Službene novine Federacije BiH.*

Different methods of calculating the degree of contamination are used to determine the degree of soil contamination with heavy metals. To calculate soil contamination levels we used: contamination level (CL) and the ecological risk index (ERI).

For soil that is used for agriculture, it is necessary to determine the contamination level (CL) in order to categorize the pollution present in the soil. The contamination level is calculated by the following formula[23]:

$$CL(\%) = \left(\frac{C_{m.of\ sample}}{C_{limit\ value}}\right) x100$$

$C_{m.of\ sample}$ is the concentration of metals in the analyzed sample, (mg/kg), and $C_{limit\ value}$ is the limit value of metal concentration in soil (mg/kg). Based on the contamination level, agricultural land is classified into five classes, listed in Table 4.2.

**Table 4.2.** Agricultural soil classification[24]

| Class | Class definition |
|---|---|
| I | CL<25%, pure soil, suitable for agriculture |
| II | CL=25-50%, soil with higher contamination, plant cultivation with the necessary protection from heavy metal imissions |
| III | CL=50-100%, highly contaminated soil, plant cultivation with enhanced protection from heavy metal imissions |
| IV | CL=100-200%, contaminated soil, not suitable for plant cultivation, remediation necessary |
| V | CL>220%, extremely contaminated soil, plant cultivation for human and animal consumption prohibited, full measures of remediation and recultivation required |

[23] Zvjezdana Stančić et al., 'Sposobnost akumulacije teskih metala kod razlicitih samoniklih biljnih vrsta', *Inzenjerstvo okolisa* 2, 1 (2015): 7-28.
[24] Ibid.

The ecological risk index is used to determine the synergetic influences of heavy metals in slag and ash at disposal sites[25]. It is defined as:

$$IER = \sum_{i=1}^{n} \left(T_i \frac{C_{m.of\ sample}}{C_m ref.sample}\right)$$

Where $C_{m.of\ sample}$ represents concentration of metals in the examined sample (mg/kg), $C_m ref.sample$ is the concentration of metals in a control sample (mg/kg), and $T_i$ is the factor of toxic response (As=10, Hg=40, Cd=30, Cu=Pb=Ni=5, Cr=2 and Zn=1). The limit values for the analyzed heavy metals were taken as a reference sample. Based on the ecological risk index, the soil is classified according to the criteria outlined in Table 4.3.

**Table 4.3.** Ecological risk index categories

| Value | Description |
|---|---|
| ERI < 150 | Low ecological risk |
| 150 < ERI < 300 | Moderate ecological risk |
| 300 < ERI < 600 | Significant ecological risk |
| ERI > 600 | High ecological risk |

## 4.2. Results of the wastewater quality analysis

Sampling and analysis of wastewater was carried out in order to determine the heavy metal content and general quality of wastewater at the active Jezero II ash disposal site and at the main wastewater collector for the Tuzla power plant. The results of the analysis are presented in Table 4.4. Images 4.1. and 4.2. show the wastewater sampling locations at Jezero II and their coordinates. Image 4.3. shows the wastewater sampling locations. The coordinates for location E2 are 44.530168, 18.621266 and for location E3 are 44.518810, 18.599027.

[25] Lars Håkanson, 'An ecological risk index for aquatic pollution control, a sedimentological approach', *Water Research* 14, 8 (1980): 975-1001.

**Table 4.4.** Wastewater analysis results

| Parameter | Unit | Sample 1 | Sample 2 | Discharge E2 | Discharge E3 | Emission limit value |
|---|---|---|---|---|---|---|
| Temperature | °C | 21.3 | 21.1 | 22.9 | 18.5 | 30 |
| pH value | - | 13.49 | 13.45 | 7.34 | 2.38 | 6.5 – 9.0 |
| Electrical conductivity | µS/cm | 8470 | 9030 | 804 | 665 | - |
| Colour | Pt/Co scale | 28.5 | 29.1 | 20.1 | 14 | - |
| Smell | - | noticeable | noticeable | no | no | - |
| Total suspended matter | mg/l | 30 | 14 | 1 | 23 | 35 |
| Chemical absorption of oxygen | $mgO_2/l$ | 20.1 | 20.3 | 5 | 29.6 | 125 |
| Biological absorption of oxygen | $mgO_2/l$ | 4 | 5 | 1 | 18 | 25 |
| Dissolved oxygen content | $mgO_2/l$ | 6.93 | 6.79 | 7.36 | 2.4 | - |
| Ammoniacal nitrogen | mgN/l | 0.445 | 0.625 | 0.18 | 0.55 | 10 |
| Total nitrogen | mgN/l | 4.7 | 6.1 | 1.3 | 1.3 | 15 |
| Total phosphorus | mgP/l | 0.03 | 0.03 | 0.03 | 0.03 | 2.0 |
| Sediment matter by Imhoff method | ml/l | 0.1 | 0.1 | <0.1 | 0.3 | 0.5 |
| Toxicity test (48LC50) | % | 5.23 | 5.18 | 79 | 3.20 | >50* |
| Volatile lipophile matter (total of oils and grease) | mg/l | 3.4 | 3.3 | 1.94 | 1.56 | 20 |
| Sulphates | mg/l | 454.2 | 448.9 | 294.7 | 144 | 2000 |
| Cadmium | mg/l | 0.0328 | 0.0456 | 0.0070 | 0.000282 | 0.005 |
| Zinc | mg/l | 0.0805 | 0.0813 | 0.0575 | 0.4437 | 2.0 |
| Lead | mg/l | 0.4154 | 0.5526 | 0.1309 | 0.00279 | 0.02 |
| Nickel | mg/l | 0.1486 | 0.1966 | 0.1750 | <0.1 | 0.05 |
| Arsenic | mg/l | 0.0098 | 0.0362 | 0.00114 | 0.0045 | 0.05 |
| Copper | mg/l | 0.0028 | 0.0039 | 0.00056 | 0.248 | 0.05 |
| Chrome | mg/l | 0.0839 | 0.0832 | 0.00422 | 0.01448 | 0.05 |
| Manganese | mg/l | - | 0.013 | 0.016 | 0.287 | 1.0 |

*The determined toxicity test values indicate what % of toxicity in samples is enough to cause >50% of test organisms to die.

The boxes in red show exceedances of the limit values set in the *Regulation on the conditions for discharging wastewater into the environment and public sewerage systems (Official Gazette FBiH, number 26/20).*[26]

[26] Uredba o uslovima ispuštanja otpadnih voda u okoliš i sisteme javne kanalizacije, *Službenim novinama Federacije BiH.*

**Image 4.1.** Sampling point (Sample 1) - at Jezero II (44.540470, 18.617755)

**Image 4.2.** Sampling point (Sample 2) - at Jezero II (44.538114, 18.617218)

Sample 1 represents wastewater taken from the active ash disposal site Jezero II above the upper dam. Sample 2 is also wastewater from Jezero II taken from the lower dam. Discharge E2 (Sample 3) is a concrete channel transporting water from the direction of Jezero II. Discharge E3 (Sample 4) is the main wastewater discharge from the Tuzla power plant. Below is the descending sequence for heavy metals, according to the samples:

Sample 1: Cr>As>Cu>Pb>Ni>Zn>Cd>Mn
Sample 2: Cr>As>Mn>Cu>Pb>Ni>Zn>Cd
Sample 3: Mn>Cr>As>Cu>Ni>Pb>Zn>Cd
Sample 4: Pb>Mn>Cu>Cr>As>Zn>Ni=Cd


**Image 4.3.** Layout of wastewater measuring points (▲)

The wastewater from ash and slag disposal site Jezero II can be divided into:

- Wastewater used for hydraulic transport and
- Drainage water from the ash disposal site.

Due to the size of the ash disposal site, the first type of wastewater remains at the disposal site for a certain time, during which some water evaporates and some runs gravitationally towards the lowest point of the ash disposal site, while the remainder is drained through older layers of slag and ash, where it either stops or passes through into the underground water. Drainage water from ash disposal sites represents a surplus of water which cannot be stored, but is returned to the Tuzla power plant through pipes, while some of the drainage water is occasionally discharged at point E2 by concrete channel, without treatment, into the River Jala. This discharge is especially intensive during rainfall.

The wastewater analysis results for Samples 1 and 2 (Table 4.4.) indicate very high levels of toxicity of 5.23% and 5.12%. The determined toxicity test values indicate that the 5.23% of toxicity in sample 1 and 5.12% of toxicity in sample 2 is enough to cause >50% of test organisms to die. The toxicity test represents a comprehensive evaluation of the samples, meaning that it estimates the combined influence of both analyzed substances and substances that were not analyzed but present in the samples.

The toxicity of wastewater represents an independent parameter to estimate its quality. Chemical analyses determine the composition of the wastewater (the presence of certain contaminating substances) and the concentration of contaminants, while the toxicity test indicates the negative impact of these contaminants on living organisms.

The greatest influence on the toxicity of the analyzed specimens is their extremely high pH values and significantly high concentrations of heavy metals. Earlier research executed under the RECOAL[27] project also indicated high pH levels, not only in water that is used for ash/slag transport but also in water from boreholes at the Drežnik ash landfill. The results indicated very high pH levels in waters that are used to transport the ash (12), drained water from the disposal site (10.5) and from

[27] Wenzel, *RECOAL - Reintegration of coal ash disposal sites and mitigation of pollution in the West Balkan area*.

boreholes (10). The results also indicated high levels of electrical conductivity[28]. The analyzed wastewater samples indicate high concentrations of chromium, arsenic, copper, lead and cadmium.

The process of arsenic reduction from V-valence to III-valence, which is more toxic and mobile than V-valence, happens in anaerobic conditions (without the presence of oxygen) which are present in the body of the ash disposal site. Exactly because of this characteristic, high concentrations of arsenic are possible in underground or well waters in the vicinity of active, but also closed, ash disposal sites[29]. Chromium, according to existing research, can compose up to 30% of slag and ash in the form of $Cr^{6+}$. This form of chromium is carcinogenic for humans[30]. Earlier research in Tuzla concluded that during the transport of slag and ash, chromium was present as toxic $Cr^{6+}$, which was later reduced to $Cr^{3+}$. Moreover, it is probable that chromium was present as cation $Cr^{3+}$ and adsorbed in much greater measures on alkaline ash particles, which resulted in a significant reduction of the concentration of dissolved chromium in drained waters[31].

Earlier research done through the RECOAL[32] project indicated much higher concentrations of arsenic in boreholes and water draining from the Drežnik ash disposal site, compared to the water used to transport slag and ash to the then-active Divkovići II site. Slag and ash disposal sites represent systems where different physical and chemical processes occur and where the chemical state of the elements present changes through time. Due to this, slag and ash in the long term represent a source of different pollutants dominated by heavy metals. If the bottom and sides of the ash disposal site are not properly lined and the disposal site is located on a water porous area or in the valleys of local streams (like the Banovac spring), there is a high risk of contamination of underground waters, or well and spring waters.

The negative effects on the environment do not cease with the termination of disposal of slag and ash, although the impacts of surface wastewater are reduced.

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[28] RECOAL, *Handbook on treatment of coal ash disposal sites*.
[29] Wenzel, *RECOAL - Reintegration of coal ash disposal sites and mitigation of pollution in the West Balkan area*.
[30] European Chemical Agency, 'Substance information - Chromium', last updated 26 June 2020.
[31] Alex Dellantonio et al., 'Environmental risks of farmed and barren alkaline coal ash landfills in Tuzla, Bosnia and Herzegovina', *Environmental Pollution* 153 (2008): 677-686.
[32] Wenzel, *RECOAL - Reintegration of coal ash disposal sites and mitigation of pollution in the West Balkan area*.

However, over time, due to leaching and rainfall, negative effects on underground waters may oscillate from enhanced to lowered, depending on numerous geological and physical chemical processes in the body of the ash disposal site.

The high electrical conductivity in Samples 1 and 2 results from the presence of soluble salts, i.e. the presence of high concentrations of cations and anions with prevailing $Ca^{2+}$ and $SO4^{2-}$. High pH values of wastewater of 13.49 and 13.45 should cause a reduction of heavy metal concentrations that appear in cation forms; however, the opposite happened in the analyzed samples – high concentrations of heavy metals are a result of oxidation processes due to a high content of dissolved oxygen.

The sample results from E3 measuring point (44.518810, 18.599027) are specific due to two parameters which deviate extremely from the prescribed limit values. The pH of the wastewater is 2.38, which is highly acidic and has a destructive impact on the ecosystem of the Jala River. Such high acidity influences the toxicity parameters, which are 3.20% – an extremely low (i.e. highly toxic) value. This type of wastewater cannot be allowed to flow into the River Jala without prior purification. It is not known which processes at the Tuzla power plant (or preparatory activities for the construction of Unit 7) caused the extremely low quality of wastewater at measuring point E3.

## 4.3. Quality of well and surface spring waters, results of analysis

Several decades of disposal of slag and ash within a very confined area of the western part of Tuzla, as well as the existence of the active Jezero II ash disposal site, has resulted in precisely defined negative environmental impacts. Some of these are visible, such as dust from the disposal site in dry periods, overflowing water during heavy rainfall and destruction of natural soil by the disposal of slag and ash. In order to determine less visible impacts, we analyzed well (underground) and surface spring water in the vicinity of the disposal site to examine the landfills' possible impacts on underground waters.

Table 4.5. shows the results of the analysis of underground water in urban areas near the slag and ash disposal sites. The location of sampling points is shown in Image 4.5. and in Table 4.6., the coordinates of sampling points.

**Table 4.5.** Results of quality analysis of underground water

| Parameter | Unit | Well 1 | Well 2 | Well 3 | Well 4 | Well 5 | Well 6 | Limit value |
|---|---|---|---|---|---|---|---|---|
| Colour | - | None | none | None | none | white | none | - |
| Smell | - | non characteristic | none | None | none | non characteristic | none | - |
| Taste | - | - | - | - | - | - | - | - |
| Turbidity | NTU | 1.1 | 0.77 | 1.2 | 0.5 | 17 | 0.8 | - |
| pH value | - | 6.81 | 6.92 | 6.40 | 7.09 | 6.74 | 7.09 | 6.5-9.5 |
| Consumption of $KMnO_4$ | $mgO_2/l$ | 2.0 | 1.20 | 0.40 | 1.20 | 2.00 | 3.3 | 5 |
| Electric conductivity (20 $^0$C) | μS/cm | 273 | 533 | 478 | 347 | 633 | 345 | 2500 |
| Ammoniacal nitrogen | mgN/l | 0.00 | 0.00 | 0.00 | 0.01 | 0.07 | 0.16 | 0.50 |
| Residual chloride | mg/l | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.5 |
| Chlorides | mg/l | 10.0 | 20.0 | 18.0 | 8.0 | 27.0 | 15.7 | 250 |
| Nitrite ($NO^{2-}$) | mg/l | 0.29 | 0.02 | 0.00 | 0.00 | 0.10 | 0.13 | 0.5 |
| Nitrate ($NO^{3-}$) | mg/l | 7.55 | 6.99 | 54.27 | 16.04 | 19.95 | 13.6 | 50 |
| Sulphates | mg/l | 55.45 | 83.85 | 92.22 | 39.14 | 178.97 | 39.9 | 250 |
| Iron | mg/l | 0.03 | 0.01 | 0.02 | 0.02 | 0.37 | 0.24 | 0.2 |
| Cadmium | mg/l | <0.050 | <0.050 | 0.00007 | <0.050 | <0.050 | 0.0049 | 0.005 |
| Lead | mg/l | 0.00081 | 0.00071 | 0.0020 | 0.0007 | 0.0006 | 0.0889 | 0.01 |
| Arsenic | mg/l | <0.50 | <0.50 | <0.50 | <0.50 | <0.50 | <0.50 | 0.01 |
| Chromium | mg/l | <0.50 | <0.50 | 0.0017 | 0.0011 | <0.50 | 17.51 | 0.05 |
| Manganese | mg/l | 0.027 | 0.014 | 0.01 | 0.016 | 0.061 | 0.0290 | 0.05 |

The boxes in red show exceedances of the limit values set in the *Ordinance on the health safety of drinking water (Official Gazette BiH 40/10)*.[33]

[33] Pravilnik o zdravstvenoj ispravnosti vode za pice, *Službeni glasnik BiH*, broj 40/10, January 2010.

Considering the fact that no similar research has previously been done on underground waters in the area in question, the results of this study are the first of their kind and could be used to determine natural concentrations of heavy metals, but only as long as they do not exceed the limit values for drinking water. Our research was done in accordance with the EU Water Framework Directive (2000/60/EC[34]) and the Directive on the Protection of Groundwater Against Pollution and Deterioration (2006/118/EC[35]) which is aimed at preserving the good chemical condition of underground water.

**Table 4.6**. Coordinates of sampling points for underground and surface water

| Well | Well 1 | Well 2 | Well 3 | Well 4 | Well 5 | Well 6 |
|---|---|---|---|---|---|---|
| Coordinates | 44°31'44.6"<br>18°36'47.6" | 44°31'41.8"<br>18°36'50.7" | 44°31'44.2"<br>18°36'57.4" | 44°31'43.7"<br>18°36'56.2" | 44°31'41.9"<br>18°36'39.7" | 44°32'36.0"<br>18°37'07.5" |

**Image 4.4.** Hydraulic transport of ash and slag from the Tuzla power plant to Jezero II ash disposal site

[34] European Commission, The EU Water Framework Directive - integrated river basin management for Europe.
[35] Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration, 12 December 2006.


**Image 4.5.** Locations of sampling points for underground water (⬇)

The average depth of the sampled wells is 6 metres. Wells no. 1-4 are situated in the Hudeč settlement, Well 5 in Bukinje, and Well 6 is nearest to the active Jezero II landfill. Well 1 cannot be used for drinking due to high levels of clouding and an uncharacteristic smell. Well 3 cannot be used for drinking due to high levels of nitrates. Well 5 cannot be used for drinking due to a colour and smell which are not characteristic for drinking water and high concentrations of iron (0.37 mg/l) and manganese (0.061 mg/l).

## 4.4. Results of soil quality analysis at the Plane and Drežnik ash disposal sites

Slag and ash disposal at the Plane and Drežnik sites ceased 20 years ago. The remedial techniques applied consisted of covering the surface layer of slag and ash with a layer of soil approximately 20 cm thick. After covering the site, the process of auto-recultivation started (wild vegetation appeared, in the form of weeds), and part of the surface was also used by the local population for agriculture (growing grain and grazing cattle). During our visits to the ash disposal sites we noticed that slag and ash were visible on horizontal surfaces, due to agricultural activities. As such activities have not been prevented, nor the recultivation of closed disposal sites fully completed, there is a high risk of heavy metals entering the food chain. The primary risk is that plants would absorb heavy metals via their roots, while the other risk is that grazing animals ingest small particles of slag and ash with the grass.

From a fertility point of view, slag and ash have a humus content which ranges from 1.14% up to 4.76%. The content of calcium carbonate is 0.3 to 3.3%. All values of physiologically active potassium ($K_2O$) are very high and range from 39.7 to 110 mg/100 g of soil.[36] The sulphur in coal and its combustion processes also influence the slag and ash pH value. Combustion of coal with a low sulphur content provides alkaline ash and vice versa.[37]

The high pH level of slag and ash reduces the mobility and accessibility of most heavy metals, except for arsenic (As), boron (B), molybdenum (Mo) and selenium (Se), which are available to plants even at high pH. At ash disposal sites in the early stages of closure, there are high concentrations of boron present, which can

[36] Enova d.o.o., *Plan rehabilitacije za zatvaranje deponije šljake i pepela 'Plane', 'Divkovići 1' i 'Divkovići 2'*, JP Elektroprivreda BiH, 2018.
[37] Dellantonio et al., 'Environmental risks of farmed and barren alkaline coal ash landfills in Tuzla, Bosnia and Herzegovina'.

have phytotoxic effects. During the field visits to the disposal sites, it was determined that such surfaces have poor vegetation (low numbers of plants) and that only weeds had developed. The soil is shallow and poor, with slag and ash visible on horizontal surfaces, as well as vertical cuts (excavations).[38] Unlike most organic pollutants that lose their toxicity over time, heavy metals cannot be dissolved or destroyed.

**Image 4.6.** Soil sampling area on Plane ash disposal site

**Image 4.7.** Agriculture crops at the soil sampling area on Plane ash disposal site

[38] Enova d.o.o., *Plan rehabilitacije za zatvaranje deponije šljake i pepela 'Plane', 'Divkovići 1' i 'Divkovići 2'*.

Image 4.6. shows the agricultural land on the Plane ash disposal site from where soil samples were taken, while Image 4.7. shows the same area during a period of intensive agricultural production.

The results of soil samples analyses, which were taken from area used for agriculture at the Plane and Drežnik ash disposal sites, are presented in Table 4.8. This table also presents the results of measurements of the soil contamination levels (CL).

**Table 4.8** Soil quality parameters at the Plane and Drežnik ash disposal sites (February 2020)

| Parameter | Unit | Plane | Drežnik | Limit value | CL %, Plane | CL %, Drežnik |
|---|---|---|---|---|---|---|
| pH ($H_2O$) | - | 8.93±0.06 | 7.90±0.13 | - | - | - |
| pH (KCl) | - | 8.36±0.06 | 6.55±0.08 | - | - | - |
| Humus | % | 0.7±0.07 | 0.9±0.011 | - | - | - |
| $CaCO_3$ | % | 2.42±0.13 | 4.63±0.24 | - | - | - |
| Total N | % | 0.035±0.00 | 0.045±0.00 | - | - | - |
| Phosphorus ($P_2O_5$) | mg/100g | 3.079±0.313 | 4.6±0.050 | - | - | - |
| Potassium ($K_2O$) | mg/100g | 21.936±2.041 | 35.1±0.050 | - | - | - |
| Chromium | mg/kg | 81.61±4.10 | 113.91±0.050 | 50 | 163.2 | 227.8 |
| Manganese | mg/kg | 720.14±36.14 | 768.92±5.72 | - | - | - |
| Cobalt | mg/kg | 23.50±1.18 | 29.93±1.50 | 30 | 78.3 | 99.6 |
| Nickel | mg/kg | 189.15±9.40 | 368.49±18.32 | 30 | 630.5 | 1228.3 |
| Cadmium | mg/kg | 1.63±0.08 | 2.01±0.10 | 0.5 | 326.0 | 402.0 |
| Lead | mg/kg | 20.48±1.03 | 22.89±1.15 | 50 | 40.6 | 45.7 |
| Zinc | mg/kg | 43.67±2.24 | 54.25±2.78 | 100 | 43.6 | 54.2 |
| Copper | mg/kg | 46.73±2.58 | 59.93±3.31 | 50 | 93.4 | 119.8 |

The boxes in red show exceedances of the limit values set in the *Guideline on Procedures, Activities and Conditions for Execution of Control of Soil Fertility (Official Gazette FBiH, number 72/09).*[39]

[39] Uputstvo o postupku, radnjama i uslovima za vrsenje kontrole plodnosti zemljista, *Službene novine Federacije BiH.*

According to the determined pH values, the soil in Plane and Drežnik is moderately to highly alkaline. This is the opposite of what would be expected by biological remediation of the soil. Low contents of humus were also spotted with lack of organic matter in the soil, which leads to reduced activities of microorganisms, which, in turn, reduces the ammonium and hydrogen sulphide, i.e. reduces the soil's oxidation, which reduces its pH value.

**Image 4.8.** Soil sampling area on Drežnik ash disposal site

**Image 4.9.** Agriculture crops at the soil sampling area on Drežnik ash disposal site

In order to calculate the ecological risk index for Plane and Drežnik, a wider variety of parameters are needed, which could not be sampled due to lab accreditation reasons. Therefore, results of earlier research are used, as presented below.

**Table 4.9.** Contents of heavy metals in surface layers of slag and ash at waste disposal sites of Plane and Drežnik[40]

| Parameter | | Plane | | Drežnik | | Limit value |
|---|---|---|---|---|---|---|
| | | overlay | Slag and ash | overlay | Slag and ash | |
| Arsenic | mg/kg | 24 | 61 | 23 | 69 | 10 |
| Boron | mg/kg | 67 | 187 | 66 | 116 | 30 |
| Cadmium | mg/kg | 0.2 | 0.3 | 0.3 | 0.3 | 0.5 |
| Cobalt | mg/kg | 33 | 41 | 35 | 38 | 30 |
| Chromium | mg/kg | 228 | 352 | 323 | 354 | 50 |
| Caesium | mg/kg | 5.2 | 9 | 5.4 | 9.1 | - |
| Copper | mg/kg | 49 | 100 | 46 | 81 | 50 |
| Molybdenum | mg/kg | 0.4 | 0.9 | 0.5 | 0.7 | 10 |
| Nickel | mg/kg | 368 | 682 | 418 | 597 | 30 |
| Lead | mg/kg | 22 | 17.4 | 18 | 16 | 50 |
| Selenium | mg/kg | 1.3 | 2.3 | 1.4 | 1.8 | - |
| Uranium | mg/kg | 1.3 | 2.5 | 1.0 | 2.6 | - |
| Vanadium | mg/kg | 64 | 120 | 82 | 148 | 30 |
| Zinc | mg/kg | 82 | 85 | 80 | 90 | 100 |

Table 4.8. clearly indicates that arsenic, boron, cobalt, caesium, nickel and vanadium are contained in the disposed slag and ash in concentrations which exceed the limit values. Additionally, in the cover layer, the aforementioned elements, apart from copper, exceed the limit values but are of geogenic and not anthropogenic origin. Considering the concentration of heavy metals presented in Tables 4.8. and 4.9., we have calculated the ecological risk index for Plane to be 208.0, which represents a moderate ecological risk index for a surface layer. If the deposited slag and ash reach the surface level, which is not rare, the ecological risk index for Plane amounts to 450.6, which represents a considerable ecological risk to the environment. The ecological risk index for Drežnik is 257.3 for the surface layer,

[40] Dellantonio et al., 'Environmental risks of farmed and barren alkaline coal ash landfills in Tuzla, Bosnia and Herzegovina'.

which is also a moderate value. The ecological risk index for the deposited slag and ash at Drežnik is 397.7, which represents a considerable ecological risk.

Based on the research, we can conclude that the covering layer, slag and ash are not a substrate where agriculture should be allowed. The highest degrees of contamination on both disposal sites were determined to be from nickel, cadmium and chromium. The calculated levels of contamination of the surface layers on both sites are extremely high and it is necessary to prohibit all agricultural activities, both for human and animal consumption, until full remediation and recultivation measures are implemented.

## 4.5 Health impacts of the heavy metals found at elevated levels in Tuzla

Heavy metals in soil are classified as degradable and changeable in organic and non-organic compounds and as structurally non-degradable components of soil minerals. Of the aforementioned formats of heavy metals, the highest negative impact is inflicted by changeable (bioavailable) and degradable elements which are consumable by plants. The highest negative impact on the plant and animal world is inflicted by arsenic, mercury, cadmium and lead. These heavy metals are not essential (required for living organisms), they inhibit photosynthesis, inflict negative effects on the morphological and anatomical structure of plants, accumulate in plants' roots and fruits and in this way enter our food chain.

The toxicity of chromium compounds is related to the strong oxidation characteristics of hexavalent compounds, which are gradually reduced to trivalent form after absorption in the body. Absorption happens through the gastrointestinal tract and lungs, while systematic effects are also possible via the skin. Around 60% of the absorbed dose is then excreted through urine within eight hours after absorption. Chromium compounds are irritants to the skin and mucous membranes and act as allergens to the skin and lungs. Hexavalent chromium compounds are carcinogenic (bronchogenic carcinoma). The respiratory system is the main channel for absorption of chromium. According to the IARC[41], hexavalent chromium is classified as a Group 1 carcinogenic element[42].

[41] International Agency for Research on Cancer, Homepage.
[42] International Agency for Research on Cancer, 'Chromium (VI) compounds', 2018.

Cadmium is a heavy metal with extremely negative impacts on all environmental elements, which is why it has received special attention. Cadmium is present in soil as a natural compound at around 0.1-1 mg/kg, or 1-3 mg/kg in dry soil. The amounts of cadmium in the soil are relatively small, but the element tends to accumulate, especially on the surface where it reaches high concentrations and therefore is more accessible to plants than other heavy metals found in soil. According to the IARC, cadmium is classified as a Group 1 carcinogenic substance for humans and animals[43]. Cadmium enters the human organism through the digestive and respiratory systems and skin. It is primarily toxic for the liver, kidneys and digestive tract. High intake of cadmium in an organism with insufficient calcium intake can lead to cadmium entering the bone structures. It can remain in the liver and kidneys for up to 40 years, and it also accumulates in the bones. Cadmium causes other negative effects in human bodies, such as reproductive toxicity, teratogenesis, negative effects on the liver, hematoma (negative impacts on blood), endocrine (system of glands with internal secretion) and immunity impacts.

Nickel is primarily absorbed through the respiratory system, and to a lesser extent through the digestive system. It is easily tied to plasma proteins and is quickly removed from the kidneys. In humans, the effects of nickel compounds (soluble in water) emerge after skin contact or through inhalation (which causes irritation of the respiratory system and asthma). Human exposure to inorganic nickel compounds (indissoluble in water) often happens through inhalation of smoke or dust. The acute toxicity of nickel and its compounds is low. According to the IARC, there is evidence that nickel and its compounds cause cancer of the lungs, nose cavity and paranasal sinuses[44].

Inorganic lead is classified as Group 2A carcinogenic[45], i.e. probably carcinogenic to humans. Lead that enters the human body is swiftly absorbed by the bloodstream and binds itself to erythrocytes (half-life of 20-40 days). Most long-term accumulated lead (90%) is found in bone tissue (half-life of 20-30 years). It slowly re-enters the bloodstream from bone tissue, especially during physiological or

[43] International Agency for Research on Cancer, 'Cadmium and cadmium compounds', 2018.
[44] International Agency for Research on Cancer, 'Nickel and nickel compounds (Group 1-)', Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42, 1987.
[45] Marie-Claude Rousseau et al., 'IARC carcinogen update', Environmental Health Perspectives 113, 9 (September 2005): A580–A581.

pathological processes of demineralisation of bones, such as pregnancy, breast-feeding and osteoporosis. Lead influences almost every organ in the body, including the blood and cardiovascular system, and endocrine, digestive, immune and reproductive systems. The most critical tissue that is influenced by lead is the central nervous system, especially developing brains, where lead can exert damage on the cognitive development and intellectual capabilities of children even at low exposure levels.

**Image 4.10.** Jezero II ash and slag disposal site - Tuzla thermal power plant

## 5. CONCLUSIONS AND RECOMMENDATIONS

- The wastewater at the active Jezero II ash disposal site is alkaline toxic water with values of cadmium, lead, nickel and chromium that exceed the prescribed limit values[46]. This type of wastewater cannot be discharged into surface water without treatment and must not come into contact with underground water.
- The soil on the closed ash disposal sites of Plane and Drežnik, which is currently used for agriculture, contains extremely high concentrations of nickel, and high contamination levels of chromium and cadmium. As a result of the calculated pollution levels at these sites, agriculture for human and animal consumption must be stopped and full remediation and recultivation measures implemented in accordance with existing FBiH legislation[47] and BAT standards. The measures taken so far – covering the surface of the waste disposal sites with 20 cm of soil – are inadequate.
- Considering the number of underground (well) and surface springs of drinking water in the close vicinity of both the active and closed ash disposal sites (with no hydraulic barriers installed), an underground water quality monitoring system must be instituted by the operator. Regular monitoring would secure preconditions for a timely reaction in case of worsening of spring/underground water quality.
- To prevent or reduce negative impacts on the environment and human health to a minimum – especially the reduction and prevention of contamination of underground water – mineral lining (i.e. bentonite clay) needs to be installed on the bottom and the sides of the ash and slag disposal site. Such mineral lining must be watertight to at least K ≤ 1.0 × 10-7 m/s; ground thickness ≥ 1 m. If it fails to meet these conditions, it can be complemented and fortified by other means (i.e. geomembranes) to provide the required level of protection.
- The Federation of Bosnia and Herzegovina Government needs to draft and adopt a bylaw clearly prescribing compulsory measures to prevent the negative impacts of slag and ash disposal sites on the environment. This regulation must lay down clear guidelines for the establishment of regular air, soil and underground water contamination monitoring, during the active life of ash landfills and after their closure.

[46] Uredba o uslovima ispuštanja otpadnih voda u okoliš i sisteme javne kanalizacije, *Službenim novinama Federacije BiH.*
[47] Uputstvo o obaveznoj jedinstvenoj metodologiji za izradu projekata rekultivacije, *Službenim novinama Federacije BiH.*

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This publication was produced as part of the campaign

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