



**PRESENCE OF HEAVY METALS IN THE SURFACE
AND INDUSTRIAL WASTEWATER
IN THE AREA OF THE MUNICIPALITY OF LUKAVAC**

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The presence of heavy metals in surface
and industrial wastewater in the area of the
municipality of Lukavac



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Water is essential for sustaining life, therefore sufficient quantities of this natural resource must be provided and easily accessible to all. At the same time, unsanitary water for drinking and/or hygiene purposes represents a significant health risk for the general population. Comparing the established water quality in the watercourses of the Tuzla basin based on published research with the prescribed categories, it follows that almost all watercourses are in a worse condition than prescribed by law. The majority of surface water-watercourses are still polluted or are considered "dead" watercourses, there are also no visible changes in further prevention of watercourse pollution, at the same time the need for water is growing and in the coming period it will be especially pronounced due to the planning of the construction of completely environmentally unacceptable thermal energy plants or the expansion of existing industrial capacities.

The causes of reduced water quality can be divided into natural (caused by the geological base) and anthropogenic (caused by human activity). Anthropogenic sources are the causes of inorganic and microbiological and organic groundwater pollution, such as agriculture and forestry (due to the extensive use of pesticides and animal husbandry), various industrial branches (chemical, metal, electricity production, food, coal mining, meat), all the mentioned industrial activities in the catchment area of the Spreja River and Lake Modrac emit waste water without appropriate treatment. In addition to industrial wastewater, municipal wastewater is an additional burden. In the catchment area of the Spreja River, only the urban area of Živinica has a partially solved system for the purification of this type of wastewater, the existing plant lacks a plant for the treatment of sludge created in the biological process of wastewater purification. A special category of waste water that has a distinct negative impact on the water ecosystem is landfill leachate from numerous illegal municipal waste disposal sites, also landfills that meet the minimum requirements for municipal waste disposal do not have their leachate treatment resolved. Waste water from agricultural areas belongs to the category of water with a high content of nutrients, especially phosphorus, which is responsible for the accelerated eutrophication (uncontrolled algae growth) of Lake Modrac.

Heavy metals belong to a group of pollutants that, once introduced into the environment, do not break down and in the long term, depending on the chemical state of the recipient, have a negative impact on aquatic flora and fauna. Some of them, such as iron, zinc, nickel, manganese, molybdenum, chromium, copper and cobalt are essential for the proper functioning of the body, so their lack can be harmful to the body, just like their high concentration in the body. Non-essential elements include mercury, lead, cadmium, arsenic, nickel and tin and they have no known function in the body and can be harmful to human health, and their harmful effects depend on the amount (dose), oxidation state and chemical form. Heavy metals are found in the Earth's atmosphere, hydrosphere, biosphere and lithosphere, they do not decompose but circulate in nature in different oxidation and chemical forms. Emissions from anthropogenic sources increase naturally occurring levels of heavy metals in the environment. Water and air currents transport them to great distances from the source of pollution, so they get into the soil and

plants, and through the food chain into animals and ultimately into humans. Of the 113 known elements, 17 are non-metals and 7 are semi-metals. Often some are associated with acutely toxic (arsenic, barium, chromium, mercury, nickel, lead and tin), carcinogenic (arsenic, cobalt, chromium, nickel, platinum), immunogenic (gold, cobalt, chromium, nickel, platinum), teratogenic (mercury), spermiotoxic (cadmium, mercury, nickel, lead, thallium), nephrotoxic (cadmium, uranium), neurotoxic (aluminum, mercury, magnesium, manganese, lead, potassium, thallium), genotoxic (cobalt, chromium) and allergenic (chromium, nickel, platinum, palladium) 1. Of all heavy metals, even in small quantities, **the following have the greatest negative impact on the human body: arsenic, cadmium, lead, nickel, mercury, manganese and molybdenum.** The aforementioned heavy metals show a tendency to bioaccumulate over time, when their effect is not acute, but leads to chronic, degenerative changes in certain vital organs: liver, bones, spleen, brain, etc.

According to sources dating from the Austrian period, the Spreya River was one of the richest rivers in terms of the number and type of ichthyofauna. However, its intense pollution began in the mid-1950s and early 1960s, where the aforementioned watercourse was used in the area of the Tuzla basin to supply technological water for industrial capacities and the recipient of total industrial and municipal wastewater. and uneven distribution of water), there was excessive and uncontrolled water pollution in open watercourses and a very pronounced deficit in water for the needs of the population and the economy. Lake Modrac is the largest artificial reservoir in the territory of Bosnia and Herzegovina and the most important water resource of the Tuzla Canton, water from the above reservoirs is used as technological and drinking water. Since the creation of the reservoir, there has been a problem of its pollution due to the constant deposition of sediment brought into the lake by the rivers Spreya and Turia.

The aim of this document is to inform the wider social community about the presence of heavy metals in surface and industrial wastewater in the area of the Lukavac municipality and their possible negative impact on the health of the general population with special reference to the urban area of Lukavac. Public participation is a difficult and long-term process, but it pays off in the long run because the public bears responsibility for decisions, accepts them more easily, there is less dissatisfaction, and mutual benefit. Every individual has the right to a healthy environment, and has the responsibility, personal and social, to protect and improve the state of the environment for the benefit of current and future generations. Only joint actions at local, national, regional and global levels can ensure sustainable development and thus a healthier environment.

¹ [http://whqlibdoc.who.int/publications/2006/9241572345_eng.pdf.](http://whqlibdoc.who.int/publications/2006/9241572345_eng.pdf)

1. BASIC CHARACTERISTICS OF THE SPREĀA RIVER AND LAKE MODRAC

With a length of 147.3 km and a catchment area of 1,932 km², the SpreĀa is the largest tributary of the Bosna River. Geographically, the SpreĀa river basin is part of the wider Bosna river basin, which together with the Una, Vrbas and Drina basins forms the Sava river basin. The SpreĀe basin, as the most important water resource in the Tuzla Canton, includes 12 municipalities (8 of which are in the Tuzla Canton), 483,425 inhabitants live and work there (10% of the FBiH territory and 24% of the FBiH population), and it also includes the largest part of the most populous canton in Federation of Bosnia and Herzegovina - Tuzla Canton.

Only in the basin of the Modrac reservoir, which is part of the SpreĀa basin, about 130,000 inhabitants live in 110 settlements (about 25,000 inhabitants directly next to the reservoir).

Speaking of water quality, about 2/3 of all surface waters in Bosnia and Herzegovina are polluted above the permitted levels, and research conducted by the federal Ministry of Agriculture, Water Management and Forestry in the past few years indicates that, in such an environment, "the river Bosnia the most polluted river in Bosnia and Herzegovina", and "its most polluted tributaries are Miljacka and SpreĀa with Jal". The severe chemical and microbiological pollution of SpreĀa, its tributaries and the Modrac reservoir as one of the largest BiH reservoirs was also confirmed by analyzes carried out by the Sava River Water Area Agency.

Decades of aggressive industrialization and neglect have severely degraded the diversity of plant and animal species of the river and its riparian areas. The development of industry, as well as infrastructural interventions on the riverbeds, "take away" from nature the areas where plant and animal communities have developed and established for centuries, and thus seriously disrupt the complex mutual relations and interdependence of species. Recent research shows that the number of fish and plant species in the SpreĀa River is significantly lower than in less polluted similar rivers (up to 30%), and in one part of its course, the SpreĀa River is an absolutely dead river, without any plant or animal life. The quality of fish caught by local fishermen, which is a source of food, is questionable given the real possibility that such fish is contaminated with heavy metals and persistent organic pollutants from wastewater.

Another very important aspect of the current situation is the existing organization of water management in Bosnia and Herzegovina, where one of the key problems is that a unified management system for river basins, including the SpreĀa river basin, has not yet been established. So today we have a situation where parts of the watershed around the source and mouth are under the administrative administration of the Republika Srpska, the next part of the watershed (up to the mouth of the Jala) is managed by the Tuzla Canton, the dam on the reservoir is managed by JP SpreĀa, and in the remaining part, the right bank is managed by the Federation of BiH, and the left again Serbian republic. In such a situation, it is difficult to expect effective coordination of activities, both in the direction of infrastructure development and in relation to the improvement of water quality.

The Modrac reservoir was formed in 1964 with the construction of a dam in the Modrac strait, Lukavac municipality. It is formed by the rivers SpreĀa and Turija, with their tributaries. The area of the watershed up to the profile of the dam is 1,189 km², of which 832 km² belong to the SpreĀa river basin, 240 km² to Turia and 117 km² to the immediate watershed of the reservoir.

For the designed condition, it is planned that the "Modrac" reservoir provides an average of 2.30 m³/sec of water for the needs of the population and the technological needs of economic capacities, and 4.70 m³/sec as a water management minimum in the river Spreža, downstream.

At the present time, the purpose of the reservoir, according to the order of priority established by the Law on the Protection of the "Modrac" Reservoir ("Official Gazette of the Tuzla Canton", number:

15/06), are: - provision of water for the needs of the population, - provision of water for the needs of industry, - provision of the biological minimum for the Spreže watercourse, downstream of the dam, - flood protection of the area downstream of the dam, - production of electricity at small hydroelectric plants, - development of tourism, recreation and water sports, in accordance with the aforeme

For the height of normal retardation 200.00 mn mass basic morphometric characteristics reservoirs (projected state) amounted to: - surface

area 17.10 km²

- total volume 98x10⁶ m³

- usable volume 86x10⁶ m³

- average depth 5.70 m - max.

width 1,600 m - max.

length 10,700 m - length of

coast 33,250 m

According to the measurements made in 2002, the morphometric characteristics of the reservoir have changed, and some of them amount to: - total

volume 85x10⁶ m³

- usable volume 64x10⁶ m³ .

Of the total area of the reservoir, at an elevation of 200.00 m above sea level (projected state), 63.70% (10.89 km²) is located in the territory of the municipality of Lukavac, 34.90% (5.97 km²) in the territory of the municipality of Živinice and 1.40% (0.24 km²) in the territory of Tuzla municipality. In the period of exploitation of over 46 years, about 15 million m³ were brought into the reservoir sediment (estimate), which mostly originates from wet separations and surface mines: "Kreka" Mine in Tuzla, "Banovići" Brown Coal Mine and "Jurjevik" Brown Coal Mine in Jurjevik. By the Water Classification Ordinance, the Spreža River reaches its confluence with the reservoir Modrac, all other watercourses in the basin of the reservoir and the Modrac reservoir itself are classified in the II category-water class.), and exceeded concentrations of nitrogen and phosphorus compounds, iron, manganese, and other heavy metals (Pb, Zn, Cr, Cu, Al) were determined. Based on the biological research of the waters of the Modrac reservoir, which were carried out in the past few years, it can be concluded that in the last 40 years, the reservoir has changed its trophic level and degraded that quality parameter to the limit of eutrophic waters.

2. SOURCES OF POLLUTION

The state of the environment in the area of Tuzla Canton is a direct reflection of industrial activities, the most significant waste stream in the salt factory "SOLANA" dd Tuzla is waste sludge, which is produced in the amount of about 2 t/day or about 1000 t/year. The aforementioned waste stream is discharged into the Jala river without prior treatment. In the production process of Na_2CO_3 , NaOH and NaHCO_3 in "SISECAM SODA" doo Lukavac, about 100,000 t/year is produced. of the liquid waste stream, which is deposited in the "bielo more" settling tanks, and the overflow is discharged into the river Spreya without treatment. Also, slag and ash in the amount of about 80,000 t/year. which is generated in the operation of the power plant is disposed of at the "Black Sea" landfill within the factory area. The process of burning coal in the thermal power plant "Tuzla" is accompanied by the formation of slag and ash on an annual level, which is disposed of, from 1,700,000 m³ to 2,000,000 m³. So far, about 40,000,000 m³ of slag and ash have been deposited in landfills, and overflow and leachate from the landfills are discharged into the Jala River without any treatment, which further pollutes this watercourse. Also, with the emission of waste water from the coal separation process from the "Banovići" and "Yurjevik" mines, the watercourses are enriched with suspended coal particles, which results in the intensive filling of Lake Modrac with sediment, the high content of nutrients such as phosphorus, potassium and nitrogen affects its eutrophication and impairs the lake's ecosystem.

2.1. Production of soda ash

Basic raw materials used in the production of soda ash (light soda Na_2CO_3 and heavy NaOH) and baking soda (technical, additives-food and feed grade sodium hydrogencarbonate NaHCO_3) in the Sisecam Soda Lukavac doo factory is: salt water, limestone, coal, coke, ammonia, electrolytic alkali, hydrochloric acid and fuel oil. The technological process of production belongs entirely to the field of inorganic technology, and the consumption of raw materials depends on the production capacity. The production of soda and baking soda is characterized by significant consumption of industrial and drinking water. Industrial water is provided from the lake Modrac reservoir and is used as: cooling water, for steam production, for hydraulic transport of slag and ash, for the preparation of milk of lime, for the chemical preparation of water for the needs of car washes and service workshops. Drinking water is used for the needs of restaurants and bathrooms.

The production of soda ash, heavy and food soda is carried out in the following plants: lime kiln plant, thermal power plant plant, soda plant for the production of raw bicarbonate, plant for the production of soda ash - light, plant for the production of soda ash - heavy, plant for the production of bicarbonate soda (additive feed and food grade), settling tanks "Bijelo more" for sludge waste from the soda production process, settling tanks "Crno more" for sludge waste from thermal power plants. From the Modrac reservoir, water is delivered to the pump station facility through a \varnothing 1000 mm pipeline and then through \varnothing 700 mm and \varnothing 500 mm pipelines through a free fall to the filter station with a capacity of 1440 m³/h. Sand filters 8 pcs are used for purification. Purified water is transported to consumers using pumps (2 units). In the technological process, water is used for the production of technological steam in the thermal power plant as well as for the preparation of milk of lime, waste sludge flows are generated during desilting of the apparatus, during descaling and transport of electrofilter ash, for which water used for gas purification from lime kilns (scrubbers and curtains) is used, created the waste stream is deposited in the "Black Sea" settling grounds. Wastewater generated in

the following production units: ammonia distillation, salt water preparation and boiler water preparation. Waste water from the ammonia distillation process is produced during its regeneration and contains 10% calcium chloride solution, followed by suspended particles of lime, gypsum, sand and calcium carbonate. From the salt water preparation plant, sludge is formed due to the deposition of calcium and magnesium salts, lime-soda is extracted from the brine, where it is converted into hard-to-dissolve salts. Preparation of water for the production of technological steam occurs by desilting the reactor, washing filters from the regeneration process of ion exchangers. The waste muddy flows are led to the waste water collector and then by means of pumps, through the pipeline to the "Bijelo more" settling tanks, the settling tanks can be seen as lagoons in which, due to the large surface area, the process of settling of the suspended particles takes place. The clear part is discharged into the river Spreya through the drainage system via the collection collector. A measuring device for continuous waste water monitoring is installed on this collector, which monitors: pH, flow and temperature.

2.1.1. Description of the settling tank "Bijelo More"

The "Bijelo more" sedimentation basin consists of four sedimentation basins-lagoons (I, II, III and IV) with a total area of 566,000 m², namely:

- Precipitator no. And, it's currently full, it's not operational;
- Precipitator no. II and III are connected to each other, they were reinforced;
- Depository no. IV, its amplification is carried out.

The depth of sedimentation tanks without embankment is 4 m, the height of the embankment is 4 m, a total of 8 m. The sedimentation tanks have a system for removing the clarified part, which consists of overflow pipes on the surface. In order to prevent the emission of sludge in Sprey, the overflow pipes and the filling of the peripheral channels are regularly inspected. The waste sludge flow that is transported to the "Bijelo more" settling tank contains:

- dissolved substances (CaCl₂, NaCl, Na₂SO₄);
- suspended matter (CaCO₃, CaSO₄, Ca(OH)₂, SiO₂, MgCO₃, Al₂O₃ i Fe₂O₃).

2 pumps and three Ø 250 mm pipelines are used to transport the sludge waste stream to the settling basins, one of which is used for transport to the settling tank no. II, and the other two can transport the waste stream to settling tanks no. III and IV. All three pipelines extend from the collecting basin towards the Tuzla-Doboj highway, pass under the highway, after which pipeline no. 3 separates and goes to the left towards settling tank no. II, and the pipelines No. 1 and 2 go to the right parallel to the highway towards settling tanks III and IV. Precipitator no. IV has two overflows over which the clear part overflows towards the concrete sedimentation tank, in which any sediment particles remain, and then through the drainage channel to the river Spreya. Precipitator no. II and III have a common collector with three overflows, through which the clear part overflows to the concrete sedimentation tank, and then through the drainage channel to the river Spreya. The average flow at the outlet to the river Spreya is 8000 m³/day. Wastewater from the "Bijelo more" sedimentation plant is characterized by a high pH value, content of suspended substances, and a particularly high concentration of chlorides, sulfates are also present in high concentrations.

2.1.2 Description of the settling tank "Black Sea"

"Black Sea" settling tanks are used for disposal of slag and ash as well as electrofilter ash. The sludge waste stream from the thermal power plant is delivered to the settling tanks by means of Ø 150 mm pipelines by hydraulic transport. The transport of ash and slag is carried out separately, with separate pipelines and in separate settling tanks. Slag is transported to precipitator No. 1, and fly ash is transported to the other three. The condition of the clarifiers is as follows:

- precipitator no. 1, is almost completely filled;
- precipitator no. 2 filled 90%, currently not in operation, (disposable electrofilter ash);
- precipitator no. 3, volume about $V=40000$ m³, emptied and ready for disposal;
- precipitator no. 4, volume about $V=33000$ m³, emptied and currently in operation.

Each of the above-mentioned sedimentation plants has built overflow and drainage systems for draining excess water, as well as peripheral channels that drain seepage and overflow water into the Spreya River. For the hydraulic transport of fly ash and slag to the "Crno More" settling tanks, water from gas "washing" in lime kilns with a pH value of 4 to 6 is used, in this way partial neutralization of the overflow of the "Black Sea" settling tanks is carried out. The average flow at the outlet to the river Spreya (common collector) is 11400 m³/day. Waste water from the "Crno More" settling tank can have an increased pH value as well as an increased content of chloride, ammonia and total nitrogen. Overflow water with an increased pH value from the "Bijelo More" settling tank can have a negative impact on the ecosystem of the Spreya River, since significant pollution comes with the Jala River, any further pollution is unacceptable and only increases the negative impact. Wastewater with a pH value greater than 9 is toxic to all types of freshwater ichthyofauna. The increased pH value can be explained by the high carbonate content in the waste water. According to previous research, chlorides have been designated as a pollutant with a devastating effect on the environment, in lower concentrations they are necessary for all organisms, however, at high concentrations, they have a toxic effect. Chlorides are chemical indicators of pollution and are permanent components of industrial and municipal waste water, they are designated as a pollutant with a devastating impact on the environment. They are found in the form of sodium, calcium and magnesium salts, most of the mentioned salts are soluble in high concentrations, the saturation of water with sodium chloride is 360 g/kg of water (at 25 °C), which corresponds to the amount of 218 g of chloride ions per kilogram of water. In addition to industrial and municipal waste water, chlorides also reach surface and especially underground water during the use of artificial and manure, and as a result, groundwater pollution under agricultural land.

2.1.3 Alluvial sediment of Lake Modrac

The largest artificial reservoir in the territory of Bosnia and Herzegovina and the most important water resource of the Tuzla Canton and beyond is Lake Modrac. Since the creation of the reservoir, there has been a problem of very poor management of this valuable resource, namely the lake has not been cleaned of alluvial sediment, nor have the conditions been created for its protection due to the emission of waste water. Also, anthropogenic activities in its catchment area affect the reduced water flow. The river Spreya, as the main tributary of the lake, is also the recipient of water streams Litva, Oskova, Gostelja, which are recipients of waste water from mines.

"žurjevnik" and "Banovići", but also municipal wastewater from urban and rural settlements in the catchment area of Lake Modrac. It prevents after the mouth of the Oskova river to the mouth of the Modrac reservoir, it can be considered a "critical watercourse". These watercourses are excessively loaded with suspended matter as well as organic matter from sewage systems.

(Modrac Reservoir Protection Strategy, 2012). As a result of the input of alluvial sediment originating from: waste water from coal mines located in the basin of the reservoir, industrial and municipal waste water and natural phenomena (flood flows and soil erosion) there is a constant backfilling and reduction of the volume of the reservoir. What was indicated by the current hydrographic measurements on the reservoir, carried out in 1964, 1985, 2002 and 2012. According to the latest measurements, carried out during 2011/2012. year, the following data were obtained:

- The total amount of sediment deposited in the reservoir is 15,025,121 m³;
- The total volume of the reservoir is reduced by the same value (and this is mostly a reduced "useful" volume of the reservoir), which is unfavorable from the point of view of reservoir management;
- The introduced sediment is mainly deposited in the reservoir in the area of the mouth of the river Spreča, on an area of 4-5 km² or in an area of over 25% of the total volume of the reservoir;
- The height of deposited sediment, in the area of deposition, ranges from 0.5 to 2.5 m;
- It is characteristic of the introduced sediment that a part of the sediment (larger granulation) has a higher settleability, it settles in the area immediately after the mouth of the river Spreča, and one part of the sediment (smaller granulation) almost does not settle at all, it forms a muddy suspension that is moved by the movement of water and 4-5 km from the mouth of the river Spreča.

The concentration of suspended substances in the water of the river Spreča depends on the water flow and ranges from 100-400 mg/l on average, occasionally up to 1,000 mg/l. According to tests carried out in 2010, the intake of pollution from suspended matter amounted to about 100 t/day, and in earlier periods up to 400 t/day.

2.1.4 Waste stream from ammonia-phenol wastewater treatment plant

Ammonia-phenolic water appears as one of the side products during the production of coke. Her origin is twofold. A smaller part is created by a chemical reaction during the dry distillation of coal (pyrogenetic water), while the other part, a larger part, originates from the moisture contained in the coal for coking. In the vapor state, it condenses and absorbs all gaseous products that have the property of dissolving in water in proportion to their concentration and degree of solubility. The content of these ingredients in water depends on the type of coking coal, the type of coke ovens, the method of conducting the coking process and gas cooling. Water from the coking process is directed to primary precipitation and separation of tar in separators, and decantation in tanks - decanters. Such water is called "tar water". In addition, in the system of washing ammonia from coke gas with fresh water, the so-called "enriched water". All of these waters are characterized by a high content of ammonia and phenol, so they are called "ammonia" or "phenolic" waters, i.e. ammonia-phenol wastewater. In addition to ammonia and phenol, they also contain a number of other pollutants.

3. TOXICOLOGICAL PROPERTIES OF HEAVY METALS

Heavy metals are ecologically very important because they are non-degradable and do not disappear, but move through the ecosystem and have a normal biogeochemical cycle. The intensity of circulation is uneven throughout the year and depends on climatic conditions, the proximity of pollution sources and the activity of biological systems. Some of them, such as iron, manganese, copper, zinc, molybdenum, cobalt, vanadium and strontium, belong to the group of essential elements and are necessary in small quantities for numerous functions of a living organism.

At higher concentrations, they exhibit toxic effects and if they are included in the food chain, they pose a danger to the health of animals and humans. Some heavy metals, such as lead, nickel, arsenic and mercury exhibit toxic effects in case of their excess in the environment. Their anthropogenic redistribution causes increased penetration into food chains and causes various disturbances in both natural and anthropogenic ecosystems. In the rest of the text, the basic toxicological properties of arsenic, chromium, cadmium, lead and mercury are described. These heavy metals have an extremely negative effect on all components of the environment, even in very low concentrations.

Heavy metals in their ionic form can be replaced by another ion in metal-protein enzymes. The best-known example is the replacement of Zn^{2+} with Cd^{2+} , which results in enzyme inactivation and inhibition, i.e. complete blocking of important biochemical processes in the body. The most toxic ions of heavy metals (Zn^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+}) are also the most stable forms of the mentioned metals that build very stable and extremely toxic compounds with biomolecules.

3.1. Arsenic

Arsenic belongs to metalloids. It appears in the compounds As^{3+} and As^{5+} , it is most often found in the form of the trivalent oxide As_2O_3 , which is also the most toxic. In nature, it is mostly present in rocks (99%), and the rest is found in soil and water.

The average concentration of arsenic in the earth's crust is estimated at 1.5-2 mg/kg. It also enters the biosphere from anthropogenic sources, such as refineries and smelters. In nature, arsenic is mostly bound in various geological formations, from which it usually seeps into watercourses. Arsenic is very mobile in the soil, which allows it to contaminate groundwater. Soil and plants accumulate and retain it, so it is found in lower concentrations in groundwater. Arsenic is a subject of bioaccumulation, rarely of biomagnification.

Arsenic in its organic form is considered relatively non-toxic except for those synthetically created and developed as components of pesticides.

Groundwater contamination is the most important problem related to exposure to arsenic compounds. These are inorganic As species, while organic compounds are significantly less toxic or non-toxic. The toxicity of inorganic As includes skin changes (hyperkeratoses, even skin cancer), neurotoxicity and carcinogenicity, and there are indications that it could also act as a reproductive and developmental toxin and cause diabetes. Cardiovascular

arsenic toxicity is associated with hypertension and the so-called black feet disease, due to peripheral circulation disorders, as well as atherosclerosis, heart attack, stroke, etc.

3.2. Chrom

Chromium enters the environment in the form of trivalent and hexavalent chromium (Cr³⁺ and Cr⁶⁺) as a result of natural processes and anthropogenic activities. Cr³⁺ ions are much less mobile than Cr⁶⁺ ions, which have a wide range of negative effects. The carcinogenic influence of Cr⁶⁺ was first discovered at the end of the 19th century when tumors were first described in workers who worked with chromium-based pigments in Scotland. The occupational disease caused by chromium was discovered in 1936 in Germany. In this period, numerous studies were published describing the occurrence of lung cancer in workers who were in contact with chromium salts. Cr⁶⁺ reaches humans and animals only through inhalation or as a product of industrial pollution.

The average concentration of chromium in the lithosphere is about 100 mg/kg, and in the pedosphere 100-300 mg/kg. The main sources of anthropogenic chromium are metallurgical plants, production of cement, paper, combustion of fossil fuels, fertilizers and sewage sludge. The concentration of chromium in most soils is extremely low in a form accessible to plants. The amount of Cr in the soil depends on the geographical area and the degree of contamination from anthropogenic sources so that concentrations range from 1 to 1000 mg/kg with average concentrations from 14 t

3.3. Cadmium

It has no essential biological function, but has been found in more than 1,000 species of terrestrial and aquatic flora and fauna. It is the most dangerous heavy metal in the soil and environment, which is why special attention is paid to it. The natural source of cadmium is the parent substrate and most often appears in the composition of sphalerite and galena, i.e. as an admixture in sulphide ores of zinc and lead.

Anthropogenic emission of cadmium in the atmosphere occurs during the production and use of cadmium and its compounds, disposal of waste containing cadmium, burning of fossil fuels, production of cement, etc. Cadmium is present in the soil as its natural constituent and its content is 0.1-1.0 mg/kg of soil, or 1-3 mg/kg in air-dry soil. The content of cadmium in the soil is relatively low, but it has a high tendency to accumulate, especially in the surface horizon. Its mobility is high and therefore it is more accessible to plants, unlike other heavy metals in the soil. Due to anthropogenic influence, cadmium reaches the soil mainly from the air. Cadmium is absorbed in the soil from which plants take it, and thus, through the consumption of food directly or through animals, it enters the food chain.

Cadmium can replace zinc, calcium and potassium in the body and is difficult to remove. It remains in the kidneys and liver for up to 40 years and in the bones. Cadmium is primarily toxic to the liver and kidneys, then the digestive tract, and chronic intake with insufficient calcium intake or due to high intake can be incorporated into the bones and cause the so-called itai-itai, i.e. painful bone disease. The content of cadmium in the air is from 0.1 to 500 ng/m³, the retention time is 20-30 days, the concentration of cadmium in water ranges from 0.01 µg/l for unpolluted waters to 42000 µg/l for polluted waters, time retention of cadmium in lake water is from 1 to 2 years.

The sediment contains cadmium in a concentration of 0.01 $\mu\text{g/g}$ to 50,000 $\mu\text{g/g}$, the estimated retention time is $2\text{-}5 \times 10^8$ years. The mechanism of the toxic effect on organisms is reflected in the binding of cadmium to SH groups in enzymes and the replacement of zinc with cadmium in metallo enzymes. In the aquatic environment, ichthyofauna are particularly sensitive to high concentrations of cadmium, cadmium displaces Ca^{2+} and Mg^{2+} ions from the tissue in the gills (the gills are completely destroyed), this phenomenon is especially pronounced in water with a high concentration of Ca^{2+} and Mg^{2+} of the so-called "hard" waters.

At lower concentrations, Cd causes hyperactivity and muscle spasms. Acute toxicity of Cd is reflected in the disruption of calcium metabolism, which causes respiratory paralysis. Cadmium accumulates in the body in the liver, muscles, kidneys, salivary glands, testicles and pancreas. 15 to 20% of the total ingested amount is retained in the liver, and 30% in the kidneys. Smokers are especially exposed to the toxic effects of cadmium, the concentration of cadmium in tobacco is from 1 to 2 $\mu\text{g/g}$, cigarette consumers absorb from 0.1 to 0.2 μg of cadmium per cigarette.

3.4. Lead

Occurs in traces in the lithosphere and pedosphere, lead as well as cadmium is a non-essential toxic heavy metal with a pronounced negative impact on biological systems. It enters the environment mainly from anthropogenic sources such as: burning of fossil fuels, landfills and landfill fires, waste industrial sludge, lead from phosphate-based fertilizers, vehicle exhaust gases and pesticides. The participation of natural sources in environmental pollution with lead is small, its high concentrations in ecosystems are a sure sign of its anthropogenic origin. It is found in the form of its compounds: sulfate, sulfide and carbonate.

The lead content in the soil is on average 0.1-20 mg/kg. Lead is also introduced into terrestrial and aquatic ecosystems by atmospheric deposition on exposed surfaces. It is considered a leading pollutant of the environment and increasingly endangers the living world, especially the environment of large industrial plants, busy roads and large cities. It accumulates in the surface soil horizon and sediments where it remains bioavailable for a long time, however it does not show affinity for bioaccumulation. Due to its pronounced toxic effect, the use of lead in fishing tackle is prohibited in Great Britain due to the high mortality rate in swans caused by lead. Only minor concentrations of lead from soil are available to plants. The intensity of its adoption depends on the concentration in the soil, the pH-value of the soil, the content of organic matter, the ratio of cations and anions, as well as other environmental factors.

Humans are exposed to the toxic effects of lead by ingesting food and water contaminated with lead, but also by inhaling particulate matter containing lead, absorption through the skin is only possible for tetraethyl and tetramethyl lead. Lead is quickly absorbed into the bloodstream and binds to erythrocytes in the form of Pb^{2+} and through the blood about 90% is deposited in the bones in the form of $\text{Pb}_3(\text{PO}_4)_2$. In the case of acidosis (increased acidity), the mobility of lead from the bones in the form of Pb^{2+} can occur, which has a toxic effect, that is, a negative effect on the central nervous, circulatory and immune systems and the kidneys.

3.5. Mercury

Mercury is a liquid metal and has the ability to dissolve other metals with which it forms a chemical compound known as amalgams. It is stable in air, does not react with bases and most acids. The emission of mercury into the environment comes from two sources, natural and anthropogenic. Natural sources are volcanic eruptions, soil erosion, and anthropogenic primary combustion of fossil fuels, ore smelting and waste incinerators. Due to the use of mercury in numerous industrial branches, it is considered that its content in the biosphere has increased threefold in the last 100 years. The cycle of mercury in the environment can be divided into four interconnected parts: atmospheric, soil, aquatic and biotic. The atmosphere is dominated by the gaseous form of mercury in the form of HgO . As a result of numerous reactions due to the presence of various compounds in the atmosphere and under the influence of solar radiation, mercury from the atmosphere reaches aquatic and terrestrial systems in the form of Hg^{2+} . In the soil and water environment, mercury changes into its most toxic form, methylmercury (Hg-CH_3^+), through the process of methylation, and the above-mentioned form is also adopted by living plants through the root system. In the soil due to the action of microorganisms, mercury in the form of Hg^{2+} by reduction, it is converted into elemental, which evaporates again and returns to the atmosphere. By evaporation, elemental mercury turns into inorganic mercury that connects with water vapor, dust and wet deposition falls on the earth's surface, where it settles in the soil or in the water environment in sediment. Mercury vapors are extremely dangerous because they pass through the respiratory tract into the bloodstream and then into the brain, where they cause serious damage. IN

in the water environment, inorganic mercury partly turns into insoluble mercury sulfide (HgS), while part of the mercury turns into its most toxic methyl form (Hg-CH_3^+) with the help of methanogenic bacteria. Mercury is a heavy metal prone to bioaccumulation, once it is introduced into the body, it is permanently incorporated into the cells, and its concentration increases (biomagnifies) at each subsequent stage of the food chain. Methylmercury is particularly prone to biomagnification, the main factors that influence the increase in mercury concentration through the food chain are the very slow decomposition of Hg-CH_3^+ in the body and the biological resistance of mercury to other compounds. Fish and invertebrates are the most susceptible to adopting organic forms of mercury, the acute toxicity of mercury is directly proportional to the temperature and acidity of the water and inversely proportional to the content of dissolved oxygen and the hardness of the water. The fetal and newborn brain is most sensitive to methylmercury toxicity. Mercury exerts its toxic influence by blocking the functional thiol groups of enzymes, which causes numerous disorders. Neurotoxic disorders occur as a result of damage to the cell membrane, the mutagenic effect is associated with the inhibition of protein synthesis, that is, there is a reduction of DNA in the cell. In nature, it is not broken down by any known biological process, and because of this, entering the environment, it becomes an inseparable part of it, affecting all components of the environment negatively. Inorganic mercury is poorly absorbed (<10% of ingested mercury) through the human digestive system. Mercury vapors are absorbed in the lungs, and methylmercury is almost completely (>90%) absorbed after ingestion in the digestive tract. Taking inorganic mercury with food, its oxidized form can cause abdominal cramps, stomach ulcers and kidney dysfunction. The result of kidney dysfunction caused by oxidized mercury is the so-called proteinuria, in which the urine contains abnormal amounts of protein. Constant exposure to the influence of mercury vapor can cause various disorders of the central nervous system in people, the consequences of which can be: tremors, sleep disorders, and even memory loss, depression, delirium and hallucinations.

Consumption of fish with an increased content of methylmercury can lead to increased levels of mercury in the blood of unborn children and young children, which can damage their nervous system. Code

in adults, small amounts of mercury in the body are associated with chronic neurodegenerative diseases, such as Parkinson's disease, Alzheimer's disease, rheumatoid arthritis, etc., as well as disorders of the immune system and allergies. Therefore, the danger of mercury poisoning for humans depends on the chemical form of mercury, the amounts to which humans are exposed, the age of the person (the fetus is the most sensitive), the time of exposure, the method of exposure: inhalation, food intake, in contact with the skin, and the previous state of health of the person who is exposed.

3.6. Barium

The most important ores of barium are barite and witherite, from which barium is obtained by reduction with aluminum or silicon. It is used in the oil industry (barium sulfate, thickening of crude oil), nuclear technology, metallurgy (alloys), pyrotechnics, production of dyes, permanent magnets, plastics, glass and medicine. All barium compounds that are soluble in water or acids are strong poisons. In very small amounts, barium acts as a muscle stimulant, while in larger amounts it acts on the nervous system, causing heart irregularities, tremors, weakness, anxiety, dyspnea and paralysis. This happens because of its ability to block potassium ion channels, which are essential for the proper functioning of the nervous system. Barium sulfate can be taken orally, due to its high water insolubility and is completely eliminated from the digestive tract. Unlike other heavy metals, barium does not bioaccumulate. If dust containing barium compounds is inhaled, it can accumulate in the lungs leading to a condition known as barytosis.

3.7. Bake

Copper comes in alloys, most commonly: brass, bronze and nickel-plated silver. Copper is slowly affected by dilute hydrochloric acid or dilute sulfuric acid. It is soluble in ammonia water. Copper is a necessary (essential) element in the human body. It has the ability to slow the growth of bacteria, eg Legionella, in drinking water systems. Insufficient intake of copper in the body can lead to larger ones consequences for human health than would be the case with increased copper intake. The increased amount of copper is mainly due to its migration into beverages (including drinking water) or due to accidental or intentional increased intake of copper salts. The most common symptoms in this case are: vomiting, drowsiness, acute hemolytic anemia, kidney and liver damage, brain damage (neurotoxicity), increased blood pressure. In some cases, coma and death can occur. Chronic copper poisoning has not been reported.

3.8. Nickel

In world production, nickel participates with 87% in the production of alloys and 9% in the platinization process. There are at least 3,000 different alloys that contain nickel. The main use of nickel is in the production of high-quality, corrosion-resistant alloys with iron, copper, aluminum, chromium, zinc and molybdenum. Absorption of free nickel ions in the digestive tract can be 40 times higher than nickel in food bound in the form of a complex. Absorption of nickel from drinking water increases during fasting. Inorganic nickel compounds are absorbed from the digestive tract at about 10% or less. Although there are no specific estimates for nickel, it appears that soluble nickel, released from materials in contact with

with food, it is very easily absorbed, unlike nickel in food, which comes bound in complexes. Therefore, nickel-contaminated food and drinks, from materials containing it, should be reduced.

3.9. Cobalt

Cobalt is used in the production of high-strength alloys. In the glass and ceramic industry, cobalt oxide is used in small quantities to neutralize the yellow coloring due to the presence of iron in glass, enamel and clay dishes. Increased concentrations are used to obtain the blue coloring of the mentioned products. Cobalt oxide is also used in enameled coatings on steel, to improve the adhesion of the enamel to the metal. Cobalt is a relatively unreactive metal. It does not oxidize in dry and wet conditions at normal temperatures. Cobalt reacts with most acids, but is passivated in the presence of concentrated nitric acid. Cobalt is resistant to the action of alkalis, but when heated, binds to halogen elements. Cobalt is an essential element, and an amount of 5 mg of vitamin B12 is required in the body to avoid anemia. In general, cobalt has low toxicity. Gastrointestinal absorption of soluble cobalt compounds is estimated at 25%. Cobalt is used in the production of artificial fertilizers, since small amounts of cobalt in the ground can cause its deficiency in livestock (sheep, cattle).

Cobalt is also used in human medicine, in the treatment of anemias that cannot be treated with iron. Although cobalt is an essential element, cases of poisoning have also been reported. It has been observed that increased consumption of beer with a high concentration of cobalt (to prevent fermentation) affects the heart, blood pressure, causes pain in the stomach (abdomen), breathing difficulties and can even lead to death.

3.10. Aluminum

Aluminum occurs naturally in bauxite ore, and in that state in which it is naturally found is not harmful to humans. Bauxite is converted into alumina, and pure aluminum is obtained by electrolysis, which was used primarily in electronics and some other parts of industries. With the development of civilization and technological progress, it began to be excessively used for other purposes, which is why it got into the human body, where it does not belong, and thus we have been continuously poisoned by daily exposure. Aluminum is a known neurotoxin and has a harmful effect on immune system. It has become a ubiquitous metal in our everyday life, although our body does not need it biologically at all. Since we are overloaded with aluminum, the only thing we can do is reduce its harmful effects. According to the instructions of the World Health Organization (WHO), from 1993, there are no health guidelines with recommendations for drinking water. However, directive 98/83/EC, on the quality of water intended for drinking, states a standard value of 0.2 mg/L, as a compromise between the value of the practical use of aluminum salts in the treatment of drinking water and the discoloration of water in distribution. represents a danger. Aluminum is excreted by the kidneys and only a small part of aluminum is absorbed. However, soluble aluminum salts are more easily absorbed. Patients with weakened kidney function and undergoing dialysis may have increased aluminum content in the blood. The WHO has concluded that aluminum is not the cause of Alzheimer's disease.

4. RESULTS OF THE ANALYSIS OF THE CONTENT OF HEAVY METALS IN THE SEDIMENT

As part of the preparation of this document, an analysis of sediment samples of the Spreĵa River was carried out immediately before the confluence with Lake Modrac (S-1), below the dam in the settlement of Modrac (S-2) and below the industrial zone in the settlement of Puraĵiĵ (S-3). Sediment is defined as material deposited in a watercourse in the form of silt or solid sediment. Sediment consists of organic and inorganic substances, particles of sand, gravel, silt, and mud that reach the watercourse due to weathering and are transported downstream by the action of water. In the watercourse, sediments have a high ecological value because they are an integral and dynamic part of the water ecosystem, sediment is the basis for the construction and development of aquatic flora and fauna. Sediments in aquatic environments play an important role in the nutrition cycle because they represent a habitat for numerous organisms, in the sediment there is an exchange of nutrients from the water body to the sediment and vice versa, but also of pollutants. For this reason, the determination of sediment quality is of particular interest in the study of the state of watercourses and the environment as a whole. By analyzing the sediment we can get data on the pollution of the researched area at a certain time or at any time period in the past. The results of the analysis of sediment samples for the content of heavy metals are shown in table 4.1. In table 4.2. sediment quality values taken from Sediment Quality Criteria in Use Around the World² are presented. In table 4.3. comparative values of the content of heavy metals in the sediment of the river Spreĵa with the sediment of the surrounding rivers and several rivers from different parts of the world are presented.

Table 4.1. Results of analysis of sediment samples for the content of heavy metals, mg/kg

Sample mark	As	Cd	Co	Cr	Cu	Hg	Pb	Mn					Ni	V	Zn
S-1	37,8	99,5	37,2	442,1	64,8	9,2	22,4	724,6	322,5	132,4	100,2				
S-2	10,5	92,1	8,8	400,5	58,4	n.d.	25,1	992,7	279,9	100,9	87,1				
S-3	33,6	175,4	17,2	890,2	69,3	9,8	20,5	941,7	94,6	143,3	131,7				

 Toxic effect on organisms in the sediment

Table 4.2. Sediment quality values according to the guidelines specified in (*Sediment Quality Criteria in Use Around the World*), mg/kg

Extremely negative influence of heavy metals							
Sediment quality guidelines	As	Cr	Cd	Pb	Hg	In	With
TET	17	100	3	170	1	61	86
SEL3	33	110	10	250	2	75	110
Threshold value above which negative impacts occur							
Sediment quality guidelines	As	Cr	Cd	Pb	Hg	At	With
TEL4 0,6 0,6	5,9	37,3		35	0,17	18	35,7
LEL 0,2	6	26		31		30	70

TET – toxic effect threshold - limit value of toxic effect, concentrations have a toxic effect

SEL – severe effect level - concentration at which the negative effects on organisms in the sediment are strongly expressed

TEL - threshold effect level - concentration above which negative effects on organisms in the sediment are possible

LEL - least effects level - the lowest metal concentration at which a negative impact can occur on very sensitive organisms in the sediment

² <http://link.springer.com/article/10.1007/s102010200008#page-1>

³ Ontario Ministry of Environment Screening Level Guidelines, ANZECC 1997

⁴ Canadian Freshwater Sediment Guidelines. ANZECC 1997

Table 4.3. Comparison of heavy metal concentrations (mg/kg)

<i>Rijeka Cr Spreya</i>	<i>In</i>	<i>With</i>	<i>Zn</i>	<i>Reference</i>				
400.5-890.2	94.6-322.5	58.4-69.3	87.1-131.7					
<i>Danube</i>	<i>17.8-45.3</i>	<i>23.7-116.4</i>	<i>17.8-45.3</i>	<i>49.4-389.5</i>	<i>Milenkovič et al. (2005)</i>			
<i>Lianshan</i>	<i>29-106</i>	<i>114-797</i>			<i>Zheng et al. (2008)</i>			
<i>Hindon</i>	<i>42.9-250.4</i>	<i>9.4-195.1</i>	<i>3.9-85</i>	<i>Han 2.5-13</i>	<i>7.6-14</i>	<i>34.3-55</i>	<i>Kim et al.</i>	<i>Suthar et al.(2009)</i>
<i>Day</i>	<i>11.6-52.3</i>	<i>32.6-40.7</i>	<i>49.8-149.1</i>					<i>Barakat et al. (2012)</i>
<i>Own</i>	<i>45.3-186.0</i>	<i>102.0-141.9</i>	<i>32.0-47.1</i>	<i>93.1-127.2</i>				
<i>Bosnia</i>	<i>135.4-193.4</i>	<i>187.7-236.9</i>	<i>46.8-55.9</i>	<i>44.1-182.4</i>				
<i>Vrba</i>	<i>42.0-61.3</i>	<i>74.1-120.1</i>	<i>30.8-53.7</i>	<i>87.1-118.4</i>				
<i>One</i>	<i>51.9-70.5</i>	<i>74.1-110.3</i>	<i>30.0-73.6</i>	<i>88.2-123.6</i>				
<i>Drina</i>	<i>51.1-128.3</i>	<i>86.7-130.1</i>	<i>34.5-59.4</i>	<i>73.4-357.8</i>				

On the basis of the conducted research, it can be concluded that the sediments at the measuring site S-1, S-2 and S-3 (Spreya, before the confluence with Lake Modrac, Spreya, below the dam (modrac settlement) and Spreya, below the industrial zone (Purajiv settlement) **they contain arsenic, cadmium, chromium, mercury and nickel in concentrations that are toxic to organisms in the sediment.** Also, compared to the results of research by other authors (Table 5.3), it is evident that the analyzed sediment samples from the Spreya River contain extremely high concentrations of Cr and Ni, **High concentrations of heavy metals at all measuring points is a direct consequence**

multi-decade discharge of municipal and industrial wastewater, where such concentrations have been reached that have **a toxic effect on the benthos of the Spreya River.**

A special danger to the ecosystem of Lake Modrac is the intake of sediment loaded with heavy metals, based on the research carried out as part of the preparation of this document, it can be concluded that it is necessary to undertake urgent activities related to the cleaning of alluvial sediment from Lake Modrac, considering its ecotoxicity and the reduction of the useful volume of the lake as a water object that has the role of flood protection. Figure 4.1 shows the appearance of the sediment at the measuring site S-1.



Figure 4.1. Sediment of the river Spreya immediately before its confluence with Lake Modrac

⁵ International Sava River Basin Commission (ISRBC), Sediment management in Sava river basin available online at: www.savacommission.org.


5. SOIL QUALITY IN THE FLOODING AREAS OF THE SPREË RIVER

Directly next to the river SpreËa, in the territory of the municipality of Lukavac, there are significant agricultural areas that have been used for the cultivation of various types of agricultural crops in the last few years. Contamination of the soil, a non-renewable natural resource and a basic prerequisite for sustainable agricultural production, with heavy metals today represents one of the main environmental problems, which has an extremely negative impact on the environment and humans, and for which it is still necessary to find an efficient and economical technological solution.

Land contamination with heavy metals is relatively easy to determine today, however there are differences and certain difficulties due to different types of land. The presence of a certain compound, in a certain amount, does not have to cause a disturbance in plant production in one type of land, but its presence in another type of land can reduce the quality and quantity of yield. Today, there are far more of these elements in agricultural land, even though they were not present in such a content in the parent substrate on which the land was formed. This is caused by anthropogenic sources of pollution, i.e. emissions of various types of waste streams that most often contain highly toxic pollutants. Given that the observed area was exposed to catastrophic floods in 2014, it is necessary to show the actual state of heavy metal pollution of agricultural land in flooded areas. For this purpose, we used the data of the Federal Institute for Agropedology⁶. In table 5.1. the results of the analysis of three average soil samples are shown, and Figure 6.1. positions of measuring points.

Table 5.1. Concentrations of heavy metals in the agricultural soil of the floodplains of the SpreËa River

Label sample	As	Cd	Co		Cr	With	Hg	Pb	In	Zn
Bokavici	8,24	1,14	32,33	127,00	29,67	0,21	15 28,23	181,56	54,94	
Lukavac 7.08	1.83	40,29	175,97	30.90	0.64	28.32	407.43	84.85		
Turkey 4.68	0.93	29.73	147.70	23.20	0.105	22.77	313.80	46.17		
Dobošnica 6.23	1.30	32.55	102.91	31.97	0.52	30.06	301.11	62.70		
Nine 6.59	2.10	24.07	87.40	31.67	0.94	27.87	240.70	38.00		
Narrower 5.34	1.87	28.80	109.20	35.40	0.65	25.83	277.00	36.67		
Manure 5.93	1.05	29.65	113.12	24.04	0.31	24.28	234.75	48.31		
Krtova 4,96	1,11	32,83	150,27	25,64	0,43	22,63	313,25	45,25		
Berkovica 4.62	0.93	36.43	171.70	15.07	0.05	17,33	351.80	23.17		

 Above the limit values

Based on the data presented in table 6.1. it can be concluded that the agricultural soil in the area of the Lukavac municipality in the floodplains of the river SpreËa, in all locations, is contaminated with chromium and nickel. Also, cadmium pollution was not determined only at one measuring site (PuraËiË), the soil was contaminated with mercury in the area of Lukavac, Dobošnica, Devetak and SiËje. In Figure 5.2. the layout of the agricultural soil sampling area after the floods of 2014 is shown. From picture 5.2. the alluvial sediment that covered the surface layer of the underlying agricultural soil is clearly visible.

⁶ <http://www.agropedologija.gov.ba/wp-content/uploads/2015/08/Izvjestaj-o-dodatnim-istrazivanjima-u-zagadenom-podrucju-donjeg-toka-rijeke-Sprece.pdf>

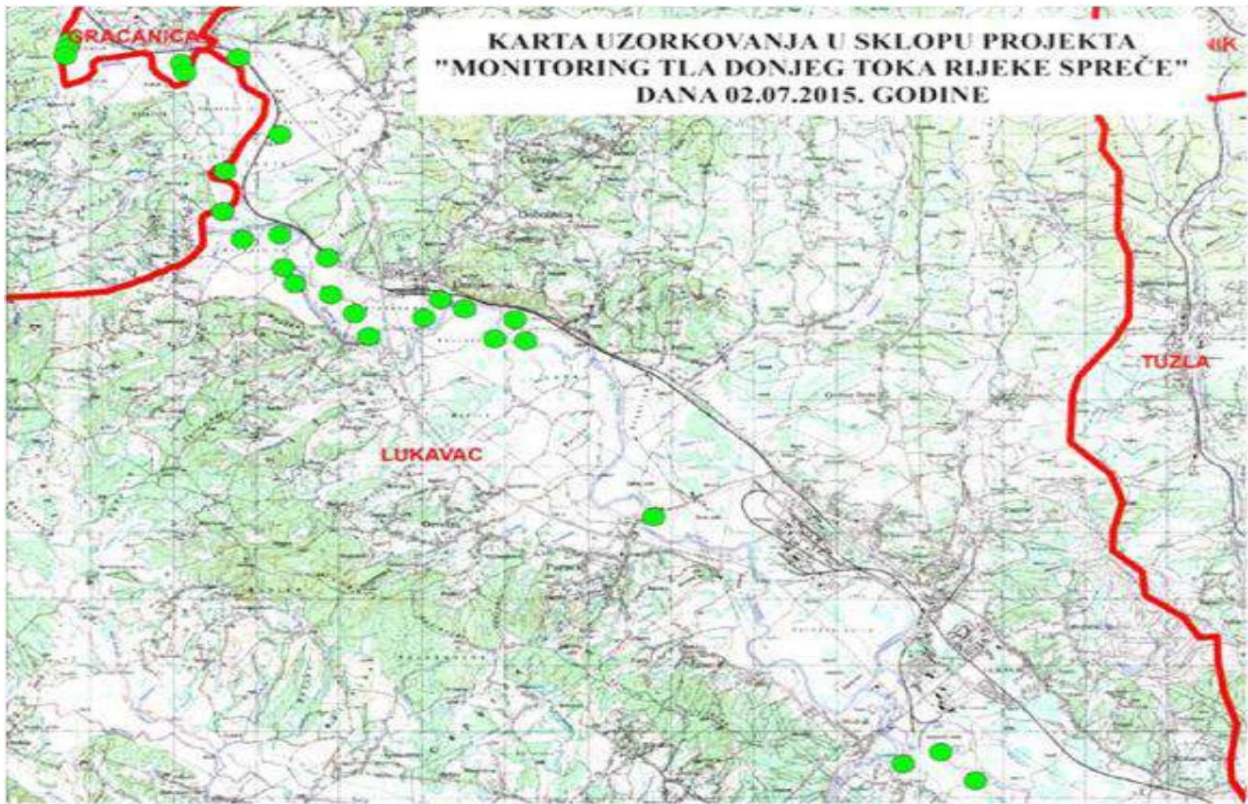


Figure 5.1. Positions of agricultural soil sampling sites⁷



Figure 5.2. Layout of the agricultural soil sampling area after the 2014 floods.

⁷ <http://www.agropedologija.gov.ba/wp-content/uploads/2015/08/Izvjestaj-o-dodatnim-istrazivanjima-u-polluted-area-of-the-lower-stream-of-the-Sprece-river.pdf>

6. QUALITY OF INDUSTRIAL WASTEWATER

As a result of human activity, waste materials in most cases end up in watercourses, which indirectly affect, most often negatively, the quality of freshwater ecosystems. Knowing the quality of waste water that is discharged into a natural recipient is of crucial importance for determining the state of the water ecosystem, i.e. the use of such water for irrigation, recreational purposes or as drinking water. In table 6.1. the results of the analysis of wastewater produced in Sisecam Soda Lukavac are presented. In Figure 6.1. the appearance of the Bijelo More settling tank is shown.

Table 6.1. Quality of industrial wastewater, Sisecam Soda Lukavac

Tested parameter/Measurement unit	Outlet The White Sea	Outlet Black more	Fecal sewage discharge	MDK
Protok (m3/dan)	8073	11410	45 21,1	19,9
Temperature (°C) pH	20,7	30		
	11,17 ± 0,04	8,76 ± 0,04	7,63 ± 0,03	6,5 –9,0
Buoy (Pt Co rock) 71		59	37	-
Dissolved oxygen content (mgO2/L) 1.62 ± 0.02	4.10 ± 0.06	3.31 ± 0.05	-	
HPK-Cr (mg O2/L) 90 125		107	111	
BPK5 (mg O2/L) 17 25		18	23	
Total suspended solids 62.4 ± 5.7 20.3 ± 1.9 19.3 ± 1.8 35.0 particles (mg/L)				
Electrical conductivity (µS/cm at 20 0C)	110702	2490 ± 1,9	2710 ± 25,7	
Volatile residue at 1050C (mg/L)	111004	2874	2995 870	547
Loss on ignition (mg/L)	1100	2331	143 2014	143
Ukupni alkalinity (mg CaCO3/L) m-	1180	317	0,00 300,1 ± 25,8	
alkalinity (mgCaCO3/L) p-	143	206,1 ± 17,7		
alkalinity (mgCaCO3/L)	1037			
Hloridi (mgCl- /L)	59067,2			250,0
Sulphates (mgSO4- /L)	587,5	126,4	101,1	200,0
Amonijak NH4 – N (mgN/L)	0,2	14,0	4,6	10,0
Nitrites NO2 – N (mgN/L)	0,03	0,07	0,05	0,50
Nitrati NO3 – N (mgN/L)	0,1	1,11	0,8	10,0
Ukupni nitrogen (mgN/L)	5,1	18,4	6,2	15,0
Ortho-phosphates (mgP/L)	0,04	0,8	0,8	
Total phosphorus (mgP/L)	0,05	0,9	0,9	2,0*
Toxicity test (48 LC50) Daphnia magna Straus (%)	1,5	It is not toxic	It is not toxic	> 50
Total oils and fats (mg/L)	0,0	5,3	8,6	20
Total surfactants (detergents, etc.) (mg/L)	0,0	0,2	0,2	1,0
Mineral oils (mg/L)	0,0	0,5	0,0	10,0

Based on the results shown in table 6.1. it can be concluded that the overflow from the white sea sedimentation plant contains extremely high chloride concentrations. According to previous research, chlorides have been designated as a pollutant with a devastating effect on the environment, in lower concentrations they are necessary for all organisms, however, at high concentrations, they have a toxic effect. Chlorides are chemical indicators of pollution and are permanent components of industrial and municipal waste water, they are designated as a pollutant with a devastating impact on the environment. They are found in the form of sodium, calcium and magnesium salts, most of the mentioned salts are soluble in high concentrations, the saturation of water with sodium chloride is 360 g/kg of water (at 25 °C), which corresponds to the amount of 218 g of chloride ions per kilogram of water. In addition to industrial and municipal waste water, chlorides also reach surface and especially underground water during the use of artificial and manure as a consequence of the pollution of underground water under agricultural land.



Figure 6.1. The appearance of the active settling tank white sea Sisecam Soda Lukavac

7. CONCLUSIONS

- Sediments in the Spreya River contain **arsenic, cadmium, chromium, mercury and nickel in concentrations that are toxic to organisms in the sediment**. High concentrations of the aforementioned heavy metals are the result of the discharge of untreated municipal, industrial and landfill leachate from the wider catchment area of the Spreya and Jala rivers. The extremely high content of heavy metals in the sediment at the confluence of Spreya and Lake Modrac represents a high ecological risk for the sensitive lake ecosystem,
- Values of the concentrations of heavy metals tested (As, Cd, Cr, Co, Cu, Hg, Ni, Pb and Zn) compared with the maximum allowed concentrations (MDK) for the type of soil tested. In flooded areas, **chromium and nickel** values are above MDK at the measuring points Bokaviyi, Lukavac, Purajiy, Dobošnica, Devetak, Sižje, Gnojnica, Krtova and Berkovica. The values of **cadmium** concentration are less than MDK only at one measuring point (Purajiy), while at other measuring points they are above, which represents a very high risk of transferring toxic cadmium to agricultural crops.
- Mercury at the measuring points Lukavac, Devetak, Dobošnica and Sižje is above the limit value, mercury is the only heavy metal that evaporates at room temperature, which in addition to the soil in these locations also pollutes the air. Based on the measured concentrations of heavy metals, it can be concluded that the agricultural land in the floodplains of the Spreya River in the area of the Lukavac municipality is contaminated with heavy metals and as such cannot be used for agricultural purposes.
- High concentrations of heavy metals in surface watercourses such as the Spreya River and industrial waste waters have affected that a significant part of the once fertile agricultural land has become unsuitable for growing plant crops intended for human and animal consumption. In the investigated localities, it is necessary to prohibit any agricultural activities and to carry out phytoremediation of the polluted land as soon as possible, for which it is necessary to use the following plant cultures:
 - to remove nickel and cadmium Dandelion (*Taraxacum officinale*), White clover (*Plantago lanceolata*), Fluffy honeysuckle (*Holcus lanatus*), Buckthorn (*Trifolium repens*) and Apple (*Populus nigra var. italica*),
 - to remove chromium and mercury Sunflower (*Helianthus annuus*) and Mustard (*Brassica juncea*).

By applying phytoremediation techniques and banning the use of polluted agricultural soil, the risks of heavy metals entering the food chain, groundwater pollution and negative impacts on the health of the general population of the Tuzla Canton are reduced.

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