UNIVERZITET U ZENICI
METALURŠKI INSTITUT
"Kemal Kapetanović"
ZENICA

ZAVOD ZA ZAŠTITU I EKOLOGIJU
Laboratorij za mjerenje zagađenosti okoline

INSTITUTE FOR ENVIRONMENTAL PROTECTION AND ECOLOGY
Laboratory measurements of environmental pollution

ELABORAT BR. 01/14-EKO

O REZULTATIMA ISTRAŽIVANJA BIO-REMEDIJACIJA TLA UPOTREBOM ALGINSKOG PREPARATA

STUDY NO. 01/14-EKO
Research into BIO-soil remediation USING AN ALGAL PREPARATION (Biocomplex)

Zenica, januar 2014. Godine
Zenica, January 2014.

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UVOD

Na osnovu interne narudžbenice br.03/2013-I od 09.10.2013.godine – Poslovi direktora Metalurškog instituta "Kemal Kapetanović" izvršili smo realizaciju projekta "Istraživanje mogućnosti bioremedijacije tla upotrebom alginskog preparata". Priprema uzoraka tla rađene su u prostorijama Zavoda za zaštitu i ekologiju, a hemijske analize tla i procijednih voda su izvršene prije i poslije tretmana sa alginskim preparatom u Hemijskom-keramičkom laboratoriju Metalurškog instituta.

INTRODUCTION

Based on internal purchase orders br.03/2013-I of 09.10.2013.godine - Jobs Director Metallurgical Institute "Kemal" We conducted our project "Exploring the possibilities of bioremediation of soil using an algal preparation." Preparation of soil samples were prepared at the Institute for Environmental Protection and Ecology, a chemical analysis of soil and leachate were performed before and after treatment with the algal composition in chemical and ceramic laboratory at the Metallurgical Institute.

1. ZNAČAJ I CILJ ISTRAŽIVANJA

Opravdanost ovog projekta ogleda se u sve većoj potrebi za remedijacijom tla: stare benzinske pumpe, divlje deponije, razna odlagališta otpada i slično. Zbog toga je neophodno da se primjene jedan ili više postupaka za uklanjanje toksičnih materija iz tla. Među raspoloživim opcijama za prečišćavanje zagađenog tla je bioremedijacija koja je najbolja zato što najmanje remeti životnu sredinu i sa ekonomske tačke gledišta - manje košta.

1 SIGNIFICANCE AND OBJECTIVE

Justification of the project is reflected in the increasing need for soil remediation in old gas stations, illegal dumps, various landfills and the like. It is therefore necessary to apply one or more operations for removing toxic matter from the soil. Among the available options for the treatment of contaminated soil is bioremediation, which is the best because it is the least disruptive to the environment and also from an economic point of view - less cost.

Bioremedijacija je zelena tehnologija kojom se zagađujuće supstance biološkim putem transformišu u do manje toksičnih ili netoksičnih jedinjenja ili se potpuno razgrađuju do ugljen-dioksida i vode. Prednosti bioremedijacije su: tehnologija bez generisanja novog otpada, sve pomoćne supstance su biorazgradljive ii inertne, bezopasan za osoblje koje ga izvodi, efikasan i relativno brz postupak i jeftina tehnologija.

Bioremediation is a green technology whereby pollutants, through several biological procedures, either transform contaminants into less toxic or non-toxic compounds or completely degrade them to carbon dioxide and water. The advantages of bioremediation are; it is a technology which does not generate new waste, all extracted substances are biodegradable or inert, it is harmless to those conducting the procedure, it is efficient, relatively quick and comparatively inexpensive.

Da bi se povećala brzina biološke razgradnje bioremedijacijom se optimizuju uslovi za rast mikroorganizama prisutnih u zemljištu, kao i poboljšanje kapaciteta njihovog enzimskog metabolizma, dodavanjem hranljivih supstanci, u ovom slučaju to je alginski preparat.

Alginski preparat je napravljen od smeđe morske alge (Ascophylum nodosum), koji raste u čistim i hladnim vodama duž obale Islanda. Sadrži bogate sastojke: 70 mikroelemenata, poliuronske sastojke identične smeđim humunskim kiselinama, vitamina, aminokiselina i alginskih kiselina.

In order to increase the rate of biodegradation of bioremediation, conditions are optimised for the growth of micro-organisms present in the soil, as well as improving the capacity of their enzyme metabolism, by adding nutrient substances, in this case, the composition of alginic acid (An insoluble colloidal acid in the form of a carboxylated polysaccharide that is abundant in the cell walls of brown algae).

The Algal product is made from brown seaweed (*Ascophylum nodosum*), which grows in the clean, cold waters along the coast of Iceland. It contains rich ingredients: 70 micronutrients, polyuronic ingredients identical to brown humic acids, vitamins, amino acids and alginic acid.

100% su prirodnog porijekla, te potpuno neškodljivi za ljude, životinje, biljke i okolinu. Proces prirodne remedijacije koje vrše prisutni mikroorganizmi u tlu traje jako dugo (godinama, decenijama), jer je potrebna velika količina enzima za razgradnju lanaca ugljikovodonika.

They are of 100% natural origin and completely harmless to humans, animals, plants and the environment. Natural remediation process carried out by micro-organisms present in the soil takes a long time (years, decades), because it requires a large amount of enzymes for the degradation of hydrocarbon chains

Dodavanjem ovog alginskog preparata u tla, mikroorganizmi iz tla stiču uslove za brže konzumiranje ugljikovodonika, što ubrzava proces razgradnje.

Adding this algal preparation of soil micro-organisms in the soil creates the ideal conditions for faster consumption of hydrocarbons, which speeds up the process of decomposition.

Cilj ovog rada bi bila primjena alginskog preparata u bioremedijaciji tla i da se utvrdi njegova djelotvornost na smanjenje udjela teških metala i drugih štetnih materija.
Istraživanjem su obuhvaćeni praćenje sljedećih elementi u tlu i procijednim vodama: Nitrogen(N), Kalijum (K), Fosfor (P) , Željezo (Fe), Mangan (Mn), Cink (Zn), Nikal (Ni), Olovo (Pb), Vanadij (V), Molibden (Mo)i Kadmij (Cd), kao i ukupna ulja i masti i pH.

The aim of this study was to use of the algal composition on the bioremediation of soil and to determine its effectiveness on the reduction of heavy metals and other harmful substances. The study included monitoring the following elements in soil and leachate: Nitrogen (N), potassium (K), phosphorus (P), iron (Fe), manganese (Mn), zinc (Zn), nickel (Ni), lead (Pb), Vanadium (V), molybdenum (Mo), and Cadmium (Cd), as well as total hydrocarbons, and pH.

2. METOD RADA

2.1. Terenska istraživanja

Terenski radovi izvršeni su oktobru mjesecu 2013. godine.
Uzeta su ukupno 4 uzorka tla sa četiri lokacije (tri uzorka koji su uzeti sa kontaminiranih lokaliteta -Tetovo i Kanal koji je u blizini postrojenja Željezare, deponija Siđe) i (Mošćanica - jedan uzorak koji je zdravi uzorak tla i koji je upotrebljen u pripremi svakog kontaminiranog uzorka tla). Takođe, je uzet uzorak industrijskog ulja sa benzinskih pumpi, koji je sastavni dio četvrtog uzorka tla. Uzorci su uzeti u površinskom sloju (0-25 cm) uz upotrebu odgovarajućeg pribora. Uzorci tla su pakovani u plastične vreće. Nakon uzimanja uzorci su odmah dopremljeni u laboratoriju radi daljeg postupka.
Uzorkovanje je vršeno u skladu sa Pravilnikom o utvrđivanju dozvoljenih količina štetnih i opasnih materija u zemljištu i metode njihovog ispitivanja (''Službene novine Federacije BiH'', broj. 52/09).

2 METHOD

2.1. Field research

Field works were carried out during October, 2013.
A total of four soil samples from four locations were taken (three samples taken from contaminated sites **Tetovo** and **Kanal**, which is close to the town's steel plants, landfills at **Siđe**) and Mošćanica – (this sample being the healthy soil sample and which was used in the preparation of each contaminated soil sample). Also, a sample taken from an industrial oil with gas stations, which is part of the fourth soil sample. Samples were taken in the surface layer (0-25 cm) using the appropriate equipment. Soil samples were packed in plastic bags. After taking the samples, they were immediately brought to the laboratory to go through further procedures.

Sampling was conducted in accordance with the Regulations on determining allowable quantities of hazardous materials in the soil and methods of investigation (" Official Gazette of the Federation BiH", no. 52/09).

2.2. Laboratorijska istraživanja

2.2.1. Priprema uzoraka tla

Priprema uzoraka tla je obuhvatalo pravljenje smjese tla, njeno održavanje i tretiranje tla alginskim preparatom određeni period-šest sedmica.
U prostorijama laboratorije je urađeno sljedeće:

- izmiješano je 10 kg tla (1.uzorak-Tetovo, 2 uzorak-Siđe, 3 uzorak-Kanal i 4 uzorak - Industrijski mulj-industrijsko ulje sa benzinskih pumpi sa tlom Siđe) sa 3 kg svježe zdrave zemlje (Mošćanica) i sa alginskim preparatom,
- dobivena smjesa je ravnomjerno raspoređena u tepsiji koja je prekrivena najlonom i izložena sunčevoj svjetlosti na otvorenom prostoru,
- osigurana je vlažnost smjese povremenim prskanjem vodom,
- sedmično prevrtanje smjesu da gornji sloj bude na dnu i da donji dođe na vrh,
- prskanje smjese alginskim preparatom svakih sedam dana,
- svaka tri dana prevrnuti smjesu da gornji sloj bude na dnu i da donji dođe na vrh i dnevno prskati vodom

U saksijama na tretirano zemljište je zasađeno nekoliko biljki: pšenica, ukrasna žara, begonija.

2.2 . laboratory studies

2.2.1 . Preparation of soil samples

Preparation of soil samples included the creation of a mixture of soil, its maintenance and treatment of the soil algal composition a certain period of six weeks.
In the laboratory premises is done as follows:

- mixed soil is 10 kg (Sample 1 - Tetovo , Sample 2 - Siđe, Sample 3 - Kanal and sample 4 - Industrial sludge - industrial oil with gas stations around Siđe) with 3 kg of fresh healthy country soild (Mošćanica) and the algal preparations (Biocomplex)
- The resulting mixture is evenly distributed in a pan which is covered with a plastic sheet and exposed to sunlight outdoors ,
- humidity is preserveded in the mixture by the occasional splash of water ,
- tilling is used to put the upper layer of the mixture on the bottom and bring the bottom layer to the top ,
- the algal composition is sprayed every seven days ,
- every three days tilling is repeated and sprayed with water daily

A few plants; wheat, decorative coleus and begonias were put into pots together with the treated soil.

Za eksperiment sa procijednim vodama je urađeno sljedeće:

- u 2 plastične boce koje su postavljeni na stolice je stavljena drenaža-kamenje i 1 kg tla Siđe,
- iznad boca sa tlom, postavljene su boce sa alginskim preparatom i običnom vodom,
- u jednu bocu sa zemljom kapao je alginski preparat, a u drugu obična voda,
- alginski preparat i obična voda prolazeći kroz zemlju su se skupljali u obliku procijednih voda (10 l) u postavljene kante ispod boca sa zemljom.

Eksperimenti su postavljeni 28.10. 2013. godine i sa zemljištem je trajao šest sedmica,a sa procijednim vodama deset dana. Brzina kapanja je bila oko 1 l na dan, s tim da je površina zemlje u boci bila pod tekućinom.

Slike tretiranog tla i procijednih voda su prikazane u prilogu Elaborata.

Experimenting with leachate was conducted as follows (see attached phots):

- two plastic bottles are placed on a chair is placed drainage stones and 1 kg of soil from Siđe,
- the upper bottle is filled with the algal composition Biocomplex and plain water,
- in a bottle with soil cap is alginic preparation, and other ordinary water,
- alginic preparation Biocomplex and plain water passing through the ground were gathered in the form of leachate (10 l) in buckets placed under the bottle to the ground.

Experiments were conducted on 28th October 2013 and the soil lasted six weeks, with ten days for leachate. Dosage rate of water w/ Biocomplex was about 1 liter per day, ensuring that the surface of the soil in the bottle was under the liquid.

Pictures of the treated soil and leachate are shown in Appendix Study.

2.2.2. Hemijske analize tla i procijednih voda

Hemijske analize su urađene u Hemijsko-keramičkom laboratoriju Metalurškog instituta "Kemal Kapetanović"
Određivanje sadržaja teških metala i drugih elemenata u tlu je izvršeno je postupku atomske adsorpcijske spektrofotometrije prema standardu JUS H.Z1.111; JUS B.H8.320; JUS B.H8.353 JUS H.Z1.150 PERKIN ELMER Analytical Methods for Atomic Absorption Spectrometry.
Određivanje sadržaja teških metala i drugih elemenata u procijednim vodama je izvršeno je postupku atomske adsorpcijske spektrofotometrije prema standardu JUS H.Z1.111; JUS B.H8.320; JUS B.H8.353 JUS H.Z1.150; MERCK The Testing of Water; PERKIN ELMER Analytical Methods for Atomic Absorption Spectrometry.
Izvještaji o analizama zemljišta i procijednih voda su date u prilogu.

2.2.2. Chemical analyzes of soil and leachate

Chemical analyzes have been made in the chemical laboratory of the ceramic Metallurgical Institute "Kemal".
Determination of heavy metals and other elements in the soil is made via procedures for atomic adsorption spectrophotometry according to JUS H.Z1.111; JUS B.H8.320; JUS JUS B.H8.353 H.Z1.150 Perkin Elmer Analytical Methods for Atomic absorption Spectrometry.
Determination of heavy metals and other elements in the leachate is made via procedures for atomic adsorption spectrophotometry according to JUS H.Z1.111; JUS B.H8.320; JUS JUS B.H8.353 H.Z1.150; MERCK The Testing of Water, Perkin Elmer Analytical Methods for Atomic Absorption Spectrometry.
Report on the analysis of soil and leachate are given in the appendix.

3. KONTAMINACIJA TLA TEŠKIM METALIMA

U svijetu se danas, zahvaljujući industrijskom razvoju, u životnu sredinu raznim putevima ispušta velika količina štetnih materija među kojima veliki udio imaju i teški metali.
Znatan dio teških metala dospijeva u tlo primjenom hemijskih sredstava u industrijskim i poljoprivrednim procesima. To su najčešće: olovo (Pb), živa (Hg), nikl (Ni), arsen (As) i bakar (Cu). Izvori unošenja teških metala u zemljište mogu da budu i neka mineralna đubriva i pesticidi. Mnogi teški metali unose se sredstvima za zaštitu biljaka, a gradsko smeće (komunalni otpad) se sve više pominje kao potencijalni izvor ovih elemenata.
Teški metali se odlikuju različitim hemijskim, fizičkim i fiziološkim dejstvom. Neki od njih su neophodni za žive organizme, a to su: cink, željezo, molibden, mangan, kobalt i selen. Toksični metali se ubrajaju u veoma opasne zagađivače i predstavljaju veliku opasnost za sve žive organizme počev od ljudi i životinja. Poznato je da teški metali, kao karakteristični polutanti, u svom geobiociklusu, odnosno atmosferskim depozicijama, dospjevaju u zemljište u kojem se mogu zadržati u površinskom (oraničnom) sloju i veoma se teško iznose iz tla. U tlu se mogu akumulirati u velikim količinama i mogu uzrokovati višestruke ekološke posljedice, zbog čega se i smatraju vodećim zagađivačima okoline.

3 CONTAMINATION OF SOIL HEAVY METALS

In the world today, thanks to industrial development, the environment, and various road transports, large amounts of pollutants are emitted, including a large proportion of heavy metals.
A significant portion of heavy metals is also due to soil application of chemicals in industrial and agricultural processes . These are the most common : lead (Pb) , mercury (Hg) , nickel (Ni) , arsenic (As) and copper (Cu). Sources introducing heavy metals in the soil may also be some fertilisers and pesticides. Many heavy metals enter via waste treatment practices, and urban garbage (waste) are increasingly mentioned as a potential source of these elements.
Heavy metals are characterised by different chemical, physical, and physiological effects. Some of them are essential for the living organisms, such as; zinc, iron, molybdenum, manganese, cobalt and selenium. Toxic metals are among the most dangerous pollutants and pose a great threat to all living organisms ranging from humans and animals. It is well known that heavy metals, as well as typical environmental pollutants, atmospheric and soil, remain in the soil surface (plowing) layer, and these are very difficult to remove. The soil can accumulate in large amounts and can cause multiple environmental consequences, which are regarded as major environmental hazards.

3.1. Rastvor tla

Rastvor tla (zemljišni rastvor) predstavlja najpokretljiviji i veoma aktivni dio tla. U njemu se vrše procesi razgradnje i sinteze organskih materija, minerala gline i obrazovanja organo-mineralnih jedinjenja. U isto vrijeme rastvor zemljišta predstavlja i izvor hranjivih materija za biljke.

Padavine ne dospijevaju u zemljište kao čista voda, već kao rastvor različitih gasova, soli i drugih materija koje voda rastvara prolazeći kroz atmosferu. U dodiru padavina sa čvrstom i gasovitom fazom zemljišta, zemljište se još više obogaćuje sa rastvorenim materijama, pa stoga u zemljištu nikad nemamo čistu vodu, već rastvore različitih koncentracija i sastava. Najvažniji elementi zemljišnog rastvora su nitrogen, fosfor, kalijum, kalcijum, magnezijum i natrijum koji su bitni pokazatelji i za interpretaciju sadržaja i dinamike teških metala u zemljištu:

3.1. soil solution

Topsoil and water (soil solution) are the most mobile and very active part of the soil. You can perform the processes of degradation and synthesis of organic matter, clay minerals and remediation of organo-mineral compounds by treating top soil. At the same time presenting a solution for the land and the source of nutrients for crop plants.

Rain precipitation is not deliverd to land as clean water, but as a solution of various gases, salts and other substances that water dissolves passing through the atmosphere. In contact with the solid precipitation and gaseous phase of soil, the soil is more enriched with dissolved substances, so the soil never receives clean water, but solutions of different concentrations and composition. The most important elements of the soil solution are nitrogen, phosphorus, potassium, calcium, magnesium and sodium, which are important indicators as these interpret the content and dynamics of heavy metals in soil:

3.1.1. Nitrogen(N)

Nitrogen je bitan elemenat za biljni rast, jer je sastojak svih proteina. S obzirom da su mnoga tla siromašna nitrogenom onda se on dodaje kao đubrivo. Najvažniji oblici nitrogena su nitrati (NO_3) i nitrogenovi oksidi (N_2O, NO).

3.1.1. Nitrogen (N)

Nitrogen is an important element for plant growth, as a constituent of all proteins. Many soils are nitrogen-poor and it is added as fertilizer. The most important forms of nitrogen as nitrate (NO3) and nitrogen oxides (N2O, NO).

3.1.2. Kalijum (K)

Sadržaj ukupnog kalijuma u zemljištu je od 0,05% u pjeskovitim tlima, do 4% u teškim glinovitim tlima. U zemljištu se nalazi u slijedećem obliku:
-u rastvoru zemljišta,
-adsorbovan na koloidnoj čestici zemljišta.

3.1.2. Potassium (K)

Total potassium content in the soil was 0.05% in sandy soils, and 4% in heavy clay soils. The content is located in the following form:
-in the soil solution,
-adsorbed on colloidal particles of soil.

3.1.3. Fosfor (P)

Oblici fosfora u tlu zavisi od pH zemljišta. Faktori koji utiču na pristupačnost faktora su:
pH zemljišta, visoki sadržaj fosfora, sadržaj vlage u zemljištu i sadržaj organske materije.

3.1.3. Phosphorus (P)

The forms of phosphorus in the soil depends on the soil pH. Factors affecting formation are: The pH of soil, a high phosphorus content, the moisture content of the soil and organic matter content.

3.2.Teški metali (opšta saznanja)

Teški metali predstavljaju prirodne sastojke tla, a potiču iz prirodnih i antropogenih izvora. Prirodni izvor metala je matični supstrat iz kojeg se metali oslobađaju raspadanjem stijena. Antropogeni izvori su: sagorijevanje fosilnih goriva, industrijska postrojenja, ekstrakcija rude, motorna vozila, deponije industrijskog i komunalnog otpada, đubriva i atmosferski talozi. Antropogeni izvori su postali značajni zagađivači tla i mogu ga kontaminirati metalima na više načina:

- emisijama prašine koja sadrži metale i koji se raznose putem atmosfere i talože na površinu tla,
- preko efluenata u slučaju izlivanja vodotoka,
- putem deponija industrijskog i komunalnog otpada,
- korištenjem mineralnih i organskih đubriva,
- korištenjem pesticida.

Unos teških metala, kao što su olovo, bakar, kadmij može biti potencijalno toksičan, te je neophodan redovan monitoring i praćenje faktora koji taj unos određuju. Unos teških metala nije uvijek posljedica aktivnosti čovjeka, već je uzrokom procesa adsorpcije koji se dešavaju usljed prisustva prirodnih sastojaka zemljišta.
Teški metali iz atmosfere suhom depozicijom ili u obliku padavina dospijevaju i talože se na zemljištu kao i na dnu vodenih površina kao teško rastvorljivi karbonati, sulfati ili sulfidi, pa kad se adsorpcijski kapacitet sedimenata iscrpi, raste koncentracija metalnih jona u vodi. Ako rijeke i jezera sadrže značajnije koncentracije ove vrste polutanata oni mogu dosta doprinijeti kontaminaciji obradivih površina plavljenjem tla.
Kritične koncentracije metala u poljoprivrednom tlu su često posljedica primjene agrotehničkih mjera kao što su navodnjavanje industrijskim i komunalnim vodama, upotreba različitih vrsta pesticida, mineralnih gnojiva, mulja, otpadnih voda koje se primjenjuju kao organsko đubrivo.

3.2.Heavy metals (general knowledge)

Heavy metals are natural constituents of the soil, and from natural and man-made sources. Natural sources of metals is the parent rock from which the metals are released by dissolution of rock. Anthropogenic sources are combustion of fossil fuels, industrial plants, extraction of minerals, motor vehicles, disposal of industrial and municipal wastes, fertilisers and atmospheric deposits . Anthropogenic sources have become significant pollutants of soil and can be contaminated metals in several ways :

- emission of dust containing metals, which is blown through the atmosphere and deposited on the surface of the soil ,
- via effluent water stream in case of spills ,
- through landfills and industrial waste ,
- use of mineral and organic fertilizers ,
- use of pesticides .

This entry of heavy metals such as lead, copper, cadmium can be potentially toxic, and regular monitoring is required, as well as monitoring of the factors that determine the input. Intake of heavy metals is not always the result of human activities, but the cause of the adsorption process occurring due to the presence of natural ingredients soil.
Heavy metals either from dry atmospheric deposition or in the form of precipitation and are not very soluble and consist of carbonates, sulfates or sulfides, so that when the adsorbent capacity of the sediment is exhausted, these concentrate the metal ions in the water. If rivers and lakes contain significant concentrations of these types of pollutants, they may well contribute to the contamination of farmland soil flooding.
Critical metal concentrations in agricultural soils are often the result of agricultural practices such as irrigation and industrial wastewater treatment depositing different types of pesticides, fertilisers, sludge, and waste used as organic fertilizer.

3.2.1 Uticaj pH tla na sadržaj teških metala

Kisela sredina uzrokuje pojavu jonskih oblika metala u zemljištu, koji su pokretni i dostupni biljkama. To znači da u kiselim zemljištima postoji mogućnost kontaminacije biljaka teškim metalima. Kod neutralne ili blago alkalne pH vrijednosti tla, teški metali prelaze u hidrokside (npr. Zn(OH)+ ili Cu(OH)+ da bi sa povećanjem pH vrijednosti prešli u nerastvorljive hidrokside i okside. Znači da se teški metali imobiliziraju u alkalnoj sredini (reakcija tla je odnos H+ + OH- jona; pH je negativni logaritam koncentracije H+ jona u gram ekvivalentima na litru otopine). Također, ako je povišen sadržaj karbonata u tlu, teški metali se inaktiviraju tj. prelaze u oblik teško pristupačan biljci.

3.2.1 Influence of soil pH on heavy metal content

The acidic environment causes ionic forms of metals in the soil, which are mobile and available to plants. This means that in acid soils there is a greater possibility of contamination of plants by heavy metals. At neutral or slightly alkaline pH value of the soil, heavy metal hydroxides in the cross (e.g., Zn (OH) +, or Cu (OH) + in order with an increase in the pH value into the insoluble hydroxides and oxides. Means to immobilize the heavy metals in an alkaline medium (soil reaction the ratio of H + + OH-ions, the pH is the negative logarithm of the concentration of H + ions in gram equivalents per liter of solution). Also, if the carbonate content in soil is high, heavy metal is inactivated, ie. taking the form of solids which aren't as accessible to plants.

3.2.2. Željezo (Fe)

Biljke usvajaju željezo u obliku Fe^{2+}, Fe^{3+} i u obliku kelata. Usvajanje je povezano s redukcijom pa kod nedostatka željeza u tlu biljke izlučuju iz korijena fenole i reducirajuće agense. Kompeticiju kod usvajanja željeza pokazuju bakar, kobalt, nikal, cink, krom i mangan, a kod viših vrijednosti pH smetaju Ca^{2+} i fosfati. Važno je napomenuti da nitratna ishrana smanjuje, a amonijačna povećava usvajanje željeza. Sadržaj željeza u tlu iznosi u prosjeku 3,2% i varira u granicama 0,01-22 % (Kastori, 1998), odnosno 1-10 % (Sarić, 1991) ili u granicama 5.000 - 50.000 mg/kg zrakosuhog tla (Ivetić et al., 1991). Skoro svo željezo vezano je u anorganskim (netopivim) spojevima, a potječe od različitih minerala kao što su silikati i alumosilikati, zatim oksidi i hidroksidi. Dio željeza se pojavljuje i u koloidnom obliku [$Fe(OH_3)$], a u veoma malim količinama i u aktivnim spojevima pretežno u obliku soli različitih kiselina. Njegova mobilnost ovisi o reakciji tla i ona raste sa smanjenjem vrijednosti pH tla. Tako se nedostatak aktivnog željeza može opaziti na karbonatnim tlima (pojava hloroze), dok se toksično djelovanje može zapaziti samo na kiselim zemljištima.

3.2.2 . Iron (Fe)

Plants acquire iron as Fe_2+, Fe_3+ in the form of chelates. Absorption is connected to the reduction and in iron deficiency in the soil from the roots of the plants expressing phenols and reducing agents. Competing with the adoption of the iron are copper, cobalt, nickel, zinc, chromium and manganese, and at higher pH values interfering Ca_2^+ and phosphate. It is important to note that reduced nitrate and ammonia increase absorption of iron. The content of iron in the soil amounts to an average of 3.2 %, and varies in the range from 0.01 to 22% (Kastori , 1998), or 1-10 % (Sarić , 1991), or in the range 5000-50000 mg / kg of soil zrakosuhog (Ivetić et al., 1991). Almost all of the iron in relation to the inorganic (insoluble) compounds, and originating from various minerals such as silicates and aluminosilicates, then oxides and hydroxides. Part of the iron occurs in colloidal form [$Fe(OH_3)$], and in very

small quantities and mainly active compounds in the form of salts of different acids. Its mobility is dependent on the response of the ground and it increases with decreasing pH value of the soil. Thus, the active iron deficiency can be observed in calcareous soils (occurrence of chlorosis), and the toxic effects can be observed only in acidic soils.

3.2.3. Mangan (Mn)

Mangan u pedosferi uglavnom potiče iz matičnog supstrata, od primarnih minerala (augit) i sekundarnih (pirolusit MnC"2, manganit Mn_2O_3" H_2O), zatim od fosfata i karbonata mangana itd. Osim iz prirodnih izvora (minerala), mangan u tlo dospijeva i unošenjem kroz đubriva kao $MnSO_4$.
Mangan u pedosferi uglavnom potiče iz matičnog supstrata, od primarnih minerala (augit) i sekundarnih (pirolusit MnC"2, manganit Mn_2O_3" H_2O), zatim od fosfata i karbonata mangana itd. Osim iz prirodnih izvora (minerala), mangan u tlo dospijeva i unošenjem kroz đubriva kao $MnSO_4$.

Ukupan sadržaj Mn u tlu je 200-3000 ppm od čega je biljkama raspoloživo 0.1-1.0%. U neutralnoj i alkalnoj sredini pristupačnost mangana je smanjena, a raspoloživost raste povećanjem kiselosti i redukcije do Mn^{2+}. Reducirani Mn biljke lako usvajaju te se označava se kao aktivan oblik, dok su više oksidirani oblici inaktivni. Oranični sloj ga sadrži više o odnosu na podoranične slojeve, isto tako više ga je na težim i karbonatnim, a manje na lakim i pjeskovitim tlima.

3.2.3 . Manganese (Mn)

Manganese in the pedosphere is mainly derived from a parent material of the primary mineral (augite) and secondary (pirolusit MnCl"2, manganite Mn2O3"H_2O), followed by phosphate and manganese carbonate and so on. Apart from natural resources (minerals), manganese in the soil enters via the fertilizer as $MnSO_4$.

The total content of Mn in soil is 200-3000 ppm of which is available to plants at a rate of 0.1-1.0 %. In neutral and alkaline soils manganese accessibility is reduced, and the growing availability of acidification and reduction to Mn_2+ . Mn - reduced plant and can easily absorb in the active form, and the oxidized forms of the inactive form. Upper layers contain more than the subarable layers, also it is more difficult and more calcareous on light and sandy soils.

3.2.4. Cink (Zn)

Cink (Zn) u tlo dolazi raspadanjem minerala biolita amfibola, piroksena i dr. ili antropogenim putem. U prirodnom tlu ga uglavnom ima od 10 do 300 mg/kg tla. U zemljišnom rastvoru (mobilan) se nalazi u obliku rastvorljivih soli ZnCl2, ZnSO4, Zn(NO3)2 i dr. Njegova mobilnost u direktnoj je zavisnosti od reakcije tla. U kiseloj sredini ispod pH 5,5 je mobilan, a u alkalnoj npr. (krečnim tlima) njegova mobilnost naglo opada usljed taloženja u obliku hidroksida ili Ca-acetata. Dakle, u alkalnoj sredini dolazi do adsorpcije Zn-a na karbonate Ca i Mg. Općenito, može se redi da je sadržaj Zn-a u tlu promjenjiv i da prvenstveno zavisi od matičnog supstrata, pH, sadržaja organske mase u tlu, CaCO3, teksturnog sastava i dr. Akumulira se u životinjama, ali ne i u biljkama.

3.2.4. Zinc (Zn)

Zinc (Zn) in the soil comes from the biological decay of minerals amphibole, pyroxene and others or by human activities. In natural soil it is generally from 10 to 300 mg / kg of soil. In the soil solution (mobile) it is in the form of soluble salts $ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$ and others. Its mobility is directly dependent on the response of the soil. In an acidic environment at pH below 5.5 it is mobile, for example. In alkaline soils (w/ lime) its mobility rapidly decreases due to precipitation in the form of hydroxide or Ca-acetate. Hence, in an alkaline medium leads to adsorption of the Zn-and Mg and Ca carbonates. Generally, it can be said that the content of Zn in the soil and its variability is primarily dependent on the master substrate, pH, content of organic matter in the soil, $CaCO_3$, textures and other factors. Zinc accumulates in animals, but not in plants.

3.2.5. Nikal (Ni)

Nikl je dosta rasprostranjen u mineralnoj i organskoj formi u tlu. U tlima nastalim na eruptivnim sedimentima ima ga do 50 mg/kg tla, a u tlima nastalim na serpentinu čak i do 600 mg/kg tla. Kao i kod ostalih elemenata, i na njegov sadržaj i mobilnost u tlu utiče reakcija tla, organska materija i glina. Količine mobilnog nikla nisu direktno toksične za biljke ako u tlu ima dosta kalcija koje umanjuje toksično djelovanje većih količina nikla.

3.2.5. Nickel (Ni)

Nickel is quite prevalent in the mineral and organic forms within soil. The soils formed on volcanic sediments have it up to 50 mg / kg soil, and soil formed on serpentine up to 600 mg / kg soil. As with other elements, and the content and mobility in soils is affected by soil reaction, organic matter and clay. The amounts of nickel are directly toxic to plants if the soil has a lot of calcium, which reduces the toxic effects of large amounts of nickel.

3.2.6. Olovo (Pb)

Olovo je teški metal i glavni kemijski polutant okoliša, porijeklom mu je prvenstveno od prometnih sredstava jer je još uvijek sastavni dio goriva.
Općenito se može reći da je prirodni sadržaj olova (Pb) u tlu uglavnom vezan za matični supstrat. Nalazi se u kiselim serijama magmatskih stijena i argilitičnim sedimentima u kojima je uobičajena koncentracija od 10-40 mg/kg, ali se javlja i u ultrabazičnim i krečnjačkim stijenama u nešto manjoj koncentraciji. Uglavnom se nalazi kao Pb+2, iako ga ima i u oksidacionom stanju kao Pb+4. Olovo se u tlu "udružuje" sa mineralima gline (naročito ilitom), zatim Mn-oksidima, Fe i Al hidroksidima i naročito sa organskom materijom zbog

čega je povišena koncentracija olova uglavnom blizu površine tla.

Olovo u tlo, osim prirodnim putem, može doći i antropogenim uticajem. Olovo kao polutant uglavnom dolazi iz raznih industrijskih postrojenja, u mineralnim oblicima (PbS, PbO, PbSO4 i dr., i u izduvnim gasovima automobila u obliku haloidnih soli (PbBr, PbBrCl, Pb(OH)Br, (PbO)2PbBr).

Inače, akumulacija olova u površinskom sloju tla utiče na biološku aktivnost tla (povećana koncentracija olova u tlu smanjuje enzimsku aktivnost mikroorganizama), a kao posljedica toga može biti nepotpuno razlaganje organske materije. Olovo kod čovjeka uzrokuje anemiju, razne digestivne poremećaje, utiče na centralni nervni sistem, izaziva kardiovaskularna oboljenja i dr.

3.2.6 . Lead (Pb)

Lead is a heavy metal and a major chemical environmental pollutant originating primarily from its means of transportation because it is still an integral part of transportation fuels.
In general it can be said that the natural content of lead (Pb) in the soil is mainly related to the parent rock. Located in acidic igneous rock series and argilitičnim sediments in which the usual concentration of 10-40 mg / kg, it also occurs in limestone and ultrabasic rocks in a lesser concentration. It generally occurs as Pb_{+2}, although in its oxidation state +4 as Pb. Lead in the ground "joins" the clay minerals (especially illite), then the oxides of Mn, Fe and Al hydroxides, and in particular the organic matter for which the concentration is increased generally near the lead surface.

Lead in the soil, except naturally, can come froms anthropogenic influences. Lead as a pollutant comes mostly from various industrial plants in mineral forms (PbS, PbO, $PbSO_4$ and others), and from car exhaust in the form haloidnih salt (PbBr, PbBrCl, Pb (OH) Br(PBO) 2PbBr).

In any event, accumulation of lead in the surface layer of the soil affects the biological activity of the soil (lead concentration increased in the soil reduces the enzymatic activity of micro-organisms), and as a result can inhibit decomposition of organic matter. Lead causes anemia in humans, a variety of digestive disorders, affects the central nervous system, as well as cardiovascular diseases, and causes the other health hazards.

3.2.7. Vanadij (V)

Biljna tvar sadrži ultra male količine vanadija. Ovaj element je neophodan za neke mikroorganizme i alge, a kod viših biljaka vjerovatno sudjeluje kao katalizator različitih fizioloških procesa.

3.2.7. Vanadium (V)

Plant matter contains ultra small amounts of vanadium. This element is necessary for some microorganisms and algae, and in higher plants is is likely involved as a catalyst of various physiological processes.

3.2.8. Molibden (Mo)

Molibden ima ulogu specifičnog katalizatora za fiksaciju azota iz vazduha , kao od strane simbiotski, tako i nesimbiotičkih azotofiksatora .Ima izvjesnih podataka koji pokazuju da je pod uticajem molibdena fiksacija azota povećana čak na 600-700%. Dokazano je da igra ulogu u redukciji nitrata. Ovaj uticaj se objašnjava time što on ulazi u sastav enzima nitrareduktaze. U velikim koncentracijama molibden može nepovoljno da utiče na rast i razviće biljaka, a osobito nekih vrsta žita.

3.2.8. Molybdenum (Mo)

Molybdenum plays a role as a specific catalyst for the fixation of nitrogen from the air, as by symbiotic, and Nitrogen-fixing bacteria. Certain data shows that under the influence of molybdenum, nitrogen fixation increased up to 600-700%. It has been shown to play a role in the reduction of nitrate. This effect is explained by the period it enters into the composition of the enzyme nitrogen reductase. At high concentrations, molybdenum can adversely affect the growth and development of plants and in particular some types of cereals.

3.2.9. Kadmij (Cd)

Kadmij je elemenat sa vrlo toksičnim djelovanjem za biljku, životinje i čovjeka. Ima ga naročito u magmatskim i sedimentnim matičnim supstratima gdje je uglavnom vezan za cink (Zn), ali ima jak afinitet i prema sumporu (S). Cd i Zn su vrlo slični, a pored toga Cd može zamijeniti (imitirati) ponašanje i nekih drugih esencijalnih elemenata u primanju i metabolizmu. Glavni uzrok toksičnosti Cd predstavlja veliki afinitet Cd za tiolne grupe (SH) u enzimima i i drugim proteinima. Višak Cd također može poremetiti metabolizam Fe i izazvati hlorozu. U ishrani životinja i ljudi Cd je kumulativni otrov. Remeti metabolizam Ca i P, te uzrokuje bolest kostiju, ali i respiratornih organa i nervnog sistema. Cd se brzo transportira iz tla u biljku. Pristupačnost mu u najvećoj mjeri ovisi o pH, te prisustvu ostalih katjona. Ca i Zn smanjuju primanje Cd, a transport u velikoj mjeri zavisi od koncentracije u okolini. Utvrđeno je da 30-60% kadmijuma, sadržanog u biljkama dolazi direktno iz atmosfere, a 40-60% iz tla. Jedan od načina kojim on dospjeva u tlo su mineralna đubriva, koja se dobijaju razlaganjem sirovih fosfata mineralnim kiselinama. U korelaciji je sa niklom.

Rastvorljivost kadmija u tlu je u visokoj zavisnosti od pH vrijednosti tla. Tako Cd adsorbovan u tlu na pH iznad 7,5 i nije lako pokretljiv, uglavnom je kao $CdCO_3$ i $Cd_3(PO_4)_2$. Također, značajan je i koeficijent energije vezivanja kadmija adsorpcijom za organsku materiju i minerale gline u tlu. Kadmij je najpokretljiviji u kiselim tlima gdje je pH od 4,5-5,5, ali se

može desiti i da u alkalnim tlima monovalentni hidroksidi CdOH+ jona ne mogu zauzeti mjesto u kompleksima izmjene katjona, što znači da mogu biti mobilni.

Antropogenim uticajem kadmija na tlo dolazi uglavnom iz zraka, iz rudnika olova i cinka, topionica i drugih postrojenja. Kadmij se kod čovjeka akumulira u nekim tkivima, naročito u jetri i bubrezima. Višegodišnji efekti dovode do hipertenzije, raka prostate i pluća.

3.2.9 . Cadmium (Cd)

Cadmium is a highly toxic element to the action of plants, animals and humans. It is found especially in igneous and sedimentary parent material which is mainly related to zinc (Zn) , but has a strong affinity towards sulfur (S). Cd and Zn are very similar, and in addition Cd can replace (mimic) the behavior of some other essential elements in absorption and metabolism. The main cause of the toxicity of Cd is such that Cd represents a large affinity for the thiol group (SH) in the enzymes and other proteins. Excess Cd may also disrupt the metabolism of Fe and cause chlorosis. In animal and human nutrition, Cd is a cumulative poison. It disturbs the metabolism of Ca and P, and causes bone disease, respiratory tract nervous system trauma. Cd is rapidly transported out of the soil to the plant. Accessibility largely depends on pH and the presence of other cations. Ca and Zn reduce Cd absorption and transport largely depends on the concentration in the environment. It was found that 30-60% of cadmium, contained in the plants coming directly from the atmosphere, and 40-60 % of the soil. One of the ways in which it accrues to the soil is from mineral fertilizers, which are obtained by decomposing raw phosphate mineral acids in correlation with the nickel.

The solubility of cadmium in soil is highly dependent on the pH value of the soil. Thus Cd adsorbed in the ground at a pH above 7.5 is not easy to move, as is generally found as $CdCO_3$ and $Cd3(PO_4)_2$. Also significant is the coefficient of the binding energy of cadmium adsorption to organic matter and clay minerals in the soil. Cadmium is the most mobile in acidic soils with a pH of 4.5-5.5, but it can happen that in alkaline soils monovalent hydroxides CdOH + ions can not take the place within complex cation changes, which means that they can be mobile .

Anthropogenic effects of cadmium in the soil comes mainly from the air, from the lead and zinc mines, smelters and other plants. Cadmium accumulates in humans, in some tissues, particularly the liver and kidneys. Multi-year effects lead to hypertension, prostate cancer and lung cancer.

4. ZAKONSKA REGULATIVA

Za interpretaciju rezultata korišteni su granične vrijednosti prema Pravilniku o utvrđivanju dozvoljenih količina štetnih i opasnih materija u zemljištu i metode njihovog ispitivanja (''Službene novine Federacije BiH'', broj. 52/09). Prema teksturi tla, uzorci tla na datim lokalitetitima su pjeskovite teksture.

Tabela 1. Granične vrijednosti sadržaja teških metala i drugih anorganskih spojeva izraženo u mg/kg zrakosuhog tla su:

Teški metali (ukupni oblik)	Granične vrijednosti u zavisnosti od teksture tla		
	Pjeskovito tlo	Praškasto-ilovasto tlo	Glinovito tlo
Kadmij (Cd)	0,5	1	1,5
Nikal (N)i	30	40	50
Olovo (Pb)	50	80	100
Cink (Zn)	100	150	200
Molibden (Mo)	10	15	20
Vanadij (V)	30	40	50

U sljedećoj tabeli su date granične vrijednosti sadržaja nekih teških metala susjednih evropskih zamalja.

4 LEGISLATION

To interpret these results, data sets were used limit values according to the Regulations on determining allowable quantities of hazardous materials in the soil and methods of investigation (''Official Gazette of the Federation BiH'', no. 52/09). According to the texture of the soil, soil samples at the given localities are sandy texture.

Table 1 Limit values of heavy metals and other inorganic compounds expressed in mg / kg dry soil:

heavy metals (overall shape)	Limit values depending on the texture of the soil		
	Sandy soil	Silty-loam soil clay soil	Sandy soil Silty
Cadmium (Cd)	0,5	1	1,5
Nickel (N)i	30	40	50
Lead (Pb)	50	80	100
Zinc (Zn)	100	150	200
Molybdenum (Mo)	10	15	20
Vanadium(V)	30	40	50

The following table contains the limit values of some heavy metals neighboring European countries.

Tabela 2. Granične vrijednosti sadržaja teških metala u tlu (mg/kg)

Element	Švicarska	Njemačka	Austrija	Hrvatska
Kadmij (Cd)	0,8	1,5	1-3	1-2
Olovo (Pb)	50	100	100	100-150
Cink (Zn)	200	200	300	200-300
Željezo(Fe)	-	-	-	50.000

Table 2 Limit values of heavy metals in soil (mg / kg)

Element	Switzerland	Germany	Austria	Croatia
Cadmium (Cd)	0,8	1,5	1-3	1-2
Lead (Pb)	50	100	100	100-150
Zinc (Zn)	200	200	300	200-300
Iron(Fe)	-	-	-	50.000

Tabela 3. Sadržaj teških metala u uzorcima tla (mg/kg) koji su korišteni u tretiranju sa alginskim preparatom

Teški metali	Uzorak tla 1- Tetovo	Uzorak tla 2- Siđe	Uzorak tla 3-Kanal
Kadmij (Cd)	180	<1	170
Nikal (N)i	<1	200	<1
Olovo (Pb)	200	200	300
Cink (Zn)	200	200	500
Molibden (Mo)	<1	100	<1
Vanadij (V)	100	100	<1

Table 3 The contents of heavy metals in the soil samples (mg / kg) that have been used in this trial to demonstrate treatment with the algal composition Biocomplex:

Heavy Metal	Soil sample 1- Tetovo	Soil sample 2 - Siđe	Soil sample 3-Kanal
Cadmium (Cd)	180	<1	170
Nickel (N)i	<1	200	<1
Lead (Pb)	200	200	300
Zinc(Zn)	200	200	500
Molybdenum (Mo)	<1	100	<1
Vanadium (V)	100	100	<1

5. REZULTATI ISTRAŽIVANJA

5.1. Rezultati analiza tla

Tabela 4. Rezultati analize hemijskih elemenata u tlu (mg/kg) – Tetovo -prije tretmana i poslije tretmana alginskim preparatom

UZORAK TLA 1 – TETOVO		
Parametar	**Prije tretmana**	**Poslije tretmana**
pH	7,6	8,2
Ukupna ulja i masti	<1	<1
Ukupni N	840	70
K	19000	29000
P	6450	3500
Fe	40000	40000
Mn	1100	1200
Zn	200	100
Ni	<1	<0,1
Pb	200	<0,1
V	100	<0,1
Mo	<1	<0,1
Cd	180	30

Kod rezultata analize tla - Tetovo poslije tretmana očitano je povećanja vrijednosti ph, kalija, mangana, vrijednosti željeza i ukupnih ulja i masti su ostale iste, a svi ostali elementi, uključujući i teške metale su smanjeni u odnosu na uzorak koji nije tretiran alginskim preparatom.

5 RESULTS

5.1. The results of analysis of soil

Table 4 Results of the analysis of the chemical elements in the soil (mg / kg) - Tetovo- pretreatment and after treatment of the algal composition

Soil samples 1 - Tetovo		
parameter	**Before treatment**	**After treatment**
pH	7,6	8,2
The total hydrocarbons	<1	<1
Total N	840	70
K	19000	29000
P	6450	3500
Fe	40000	40000
Mn	1100	1200
Zn	200	100
Ni	<1	<0,1
Pb	200	<0,1
V	100	<0,1
Mo	<1	<0,1

Cd	180	30

Tabela 5. Rezultati analize hemijskih elemenata u tlu (mg/kg) – Siđe-prije tretmana i poslije tretmana alginskim preparatom

UZORAK TLA 2 – SIĐE		
Parametar	**Prije tretmana**	**Poslije tretmana**
pH	8,1	8,3
Ukupna ulja i masti	<1	<1
Ukupni N	210	70
K	27000	33000
P	600	1200
Fe	44000	4100
Mn	2000	1600
Zn	200	100
Ni	200	<0,1
Pb	200	0,1
V	100	<0,1
Mo	100	<0,1
Cd	<1	20

Iz tabele može se vidjeti da je na tretiranom uzorku tla Siđe došlo do povećanja vrijednosti pH, fosfora, kadmija, dok su svi ostali nabrojani elementi smanjeni.

Table 5 Results of the analysis of the chemical elements in the soil (m/kg) – Siđe -treatment before and after treatment of the algal composition

Soil samples 2 - Siđe		
parameter	**Before treatment**	**After treatment**
pH	8,1	8,3
The total hydrocarbons	<1	<1
Total N	210	70
K	27000	33000
P	600	1200
Fe	44000	4100
Mn	2000	1600
Zn	200	100
Ni	200	<0,1
Pb	200	0,1
V	100	<0,1
Mo	100	<0,1
Cd	<1	20

Tabela 6. Rezultati analize hemijskih elemenata u tlu (mg/kg) – Kanal-prije tretmana i

poslije tretmana alginskim preparatom

UZORAK TLA 3- KANAL		
Parametar	**Prije tretmana**	**Poslije tretmana**
pH	7,7	8,4
Ukupna ulja i masti	<1	<1
Ukupni N	2400	280
K	13000	13000
P	7150	1400
Fe	205000	151000
Mn	9000	5500
Zn	500	400
Ni	<1	<0,1
Pb	300	<0,1
V	20	<0,1
Mo	<1	<0,1
Cd	170	30

Kod rezultata tretiranog tla Kanal je očitano povećanje vrijednosti pH, dok su svi ostali elementi smanjeni.

Table 6 Results of the analysis of the chemical elements in the soil (mg/kg) – KANAL- prior to the treatment and after treatment of the algal composition Biocomplex:

Soil samples 3 – KANAL		
Parameter	**Before treatment**	**After treatment**
pH	7,7	8,4
The total hydrocarbons	<1	<1
Total N	2400	280
K	13000	13000
P	7150	1400
Fe	205000	151000
Mn	9000	5500
Zn	500	400
Ni	<1	<0,1
Pb	300	<0,1
V	20	<0,1
Mo	<1	<0,1
Cd	170	30

If the score of the treated soil channel is read increasing pH, while all other elements are reduced.

Tabela 7. Rezultati analize ukupnih ulja i masti u tlu (%) -Industrijski mulj - prije tretmana i poslije tremana alginskim preparatom

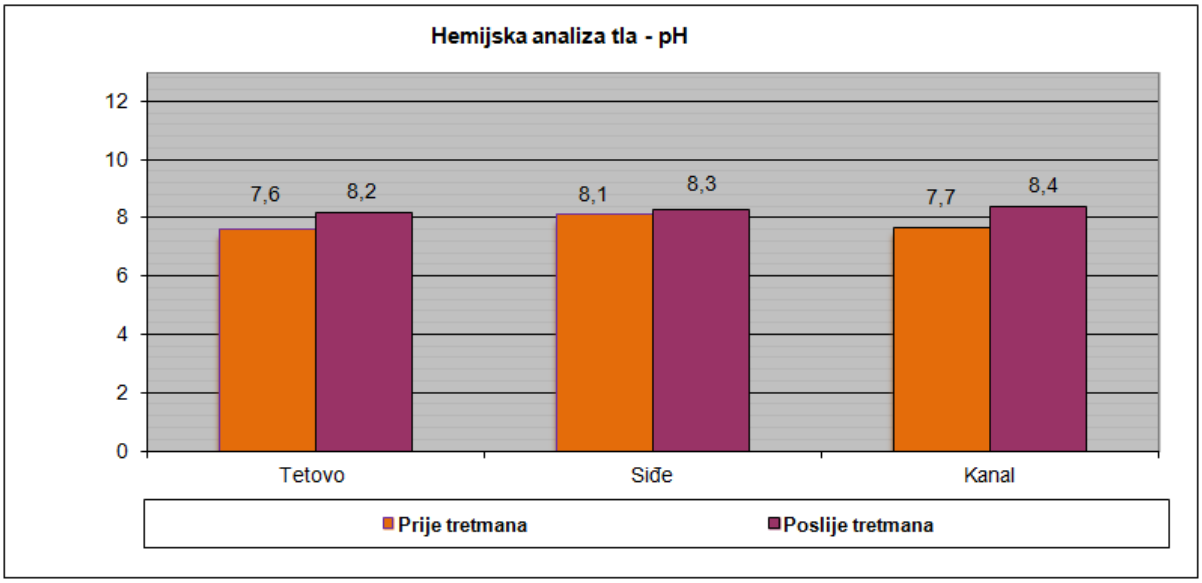
UZORAK TLA 4 - INDUSTRIJSKI MULJ		
Parametar	**Prije tretmana**	**Poslije tretmana**
Ukupna ulja i masti	>95%	1 %

Kod uzorka tla industrijskog mulja došlo je do smanjenja ukupnih ulja i masti.

Table 7 Results of the analysis of total hydrocarbons in soil (%) Industrial Sludge - before treatment, and after treatment algal composition

Soil samples 4 - INDUSTRIAL SLUDGE		
Parameter	**Before treatment**	**After treatment**
Total hydrocarbons	>95%	1 %

The industrial sludge soil sample almost totally eliminateded total hydrocarbons.



Grafikon 1. Vrijednost pH tla prije tretmana i poslije tretmana alginskim preparatom

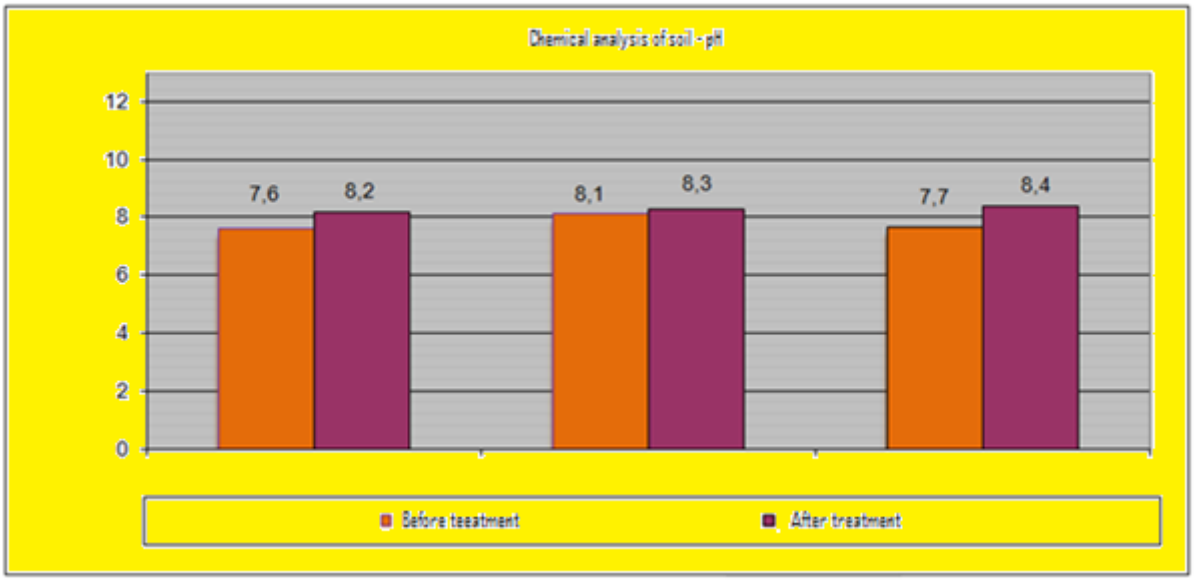
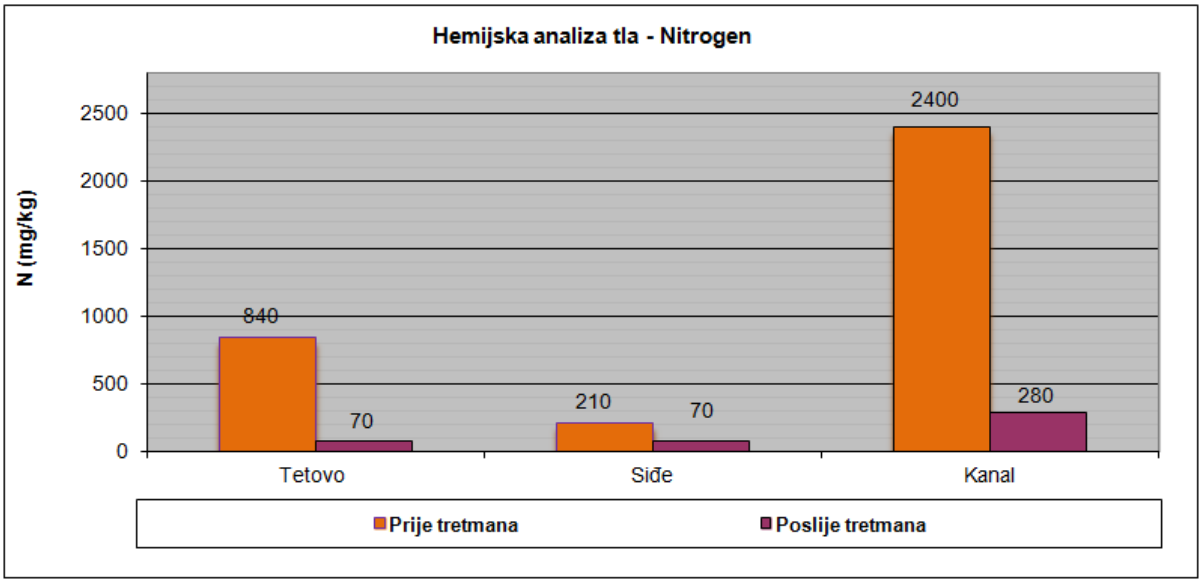


Figure 1 The pH of the soil prior to treatment and after treatment by the algal preparation



Grafikon 2. Vrijednost nitrogena u tlu prije tretmana i poslije tretmana alginskim preparatom

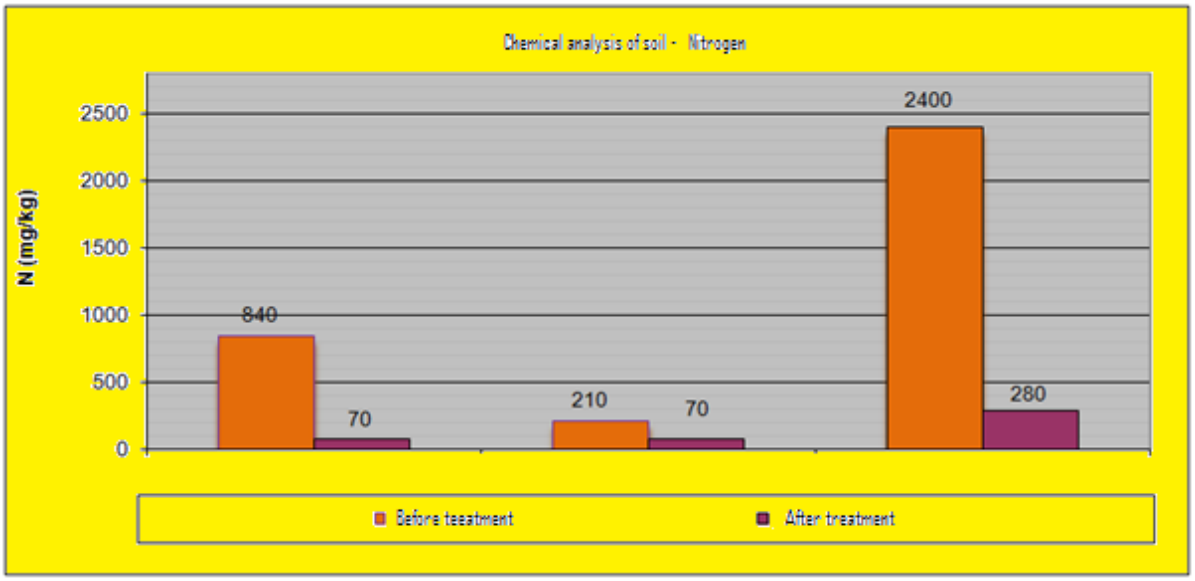
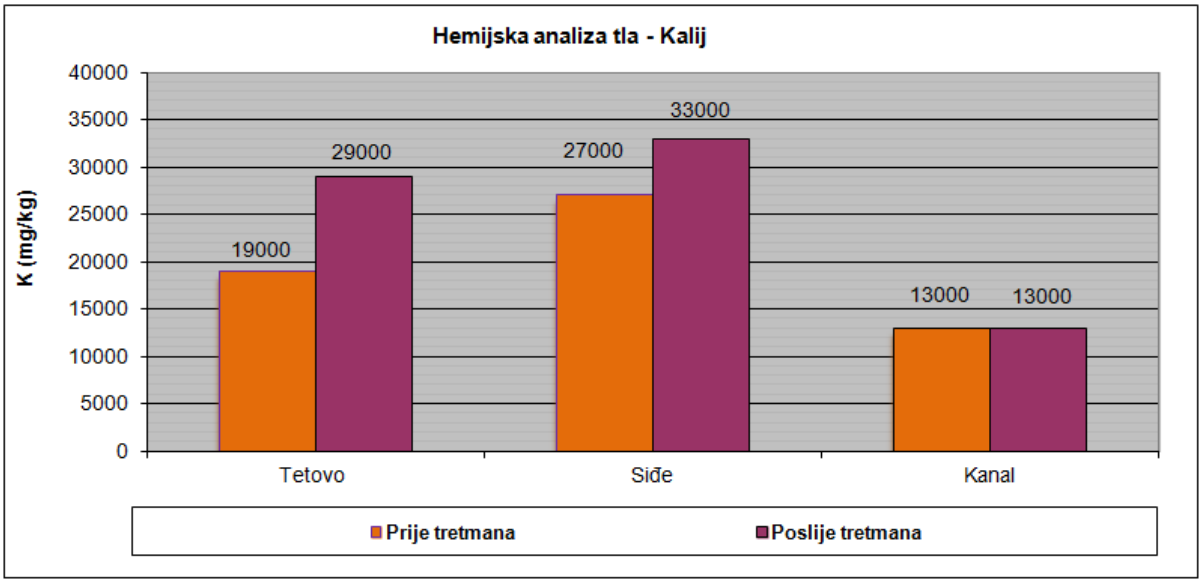


Figure 2 The value of nitrogen (N) in the soil before treatment and after treatment by the algal composition



Grafikon 3. Vrijednost kalija u tlu prije tretmana i poslije tretmana alginskim preparatom

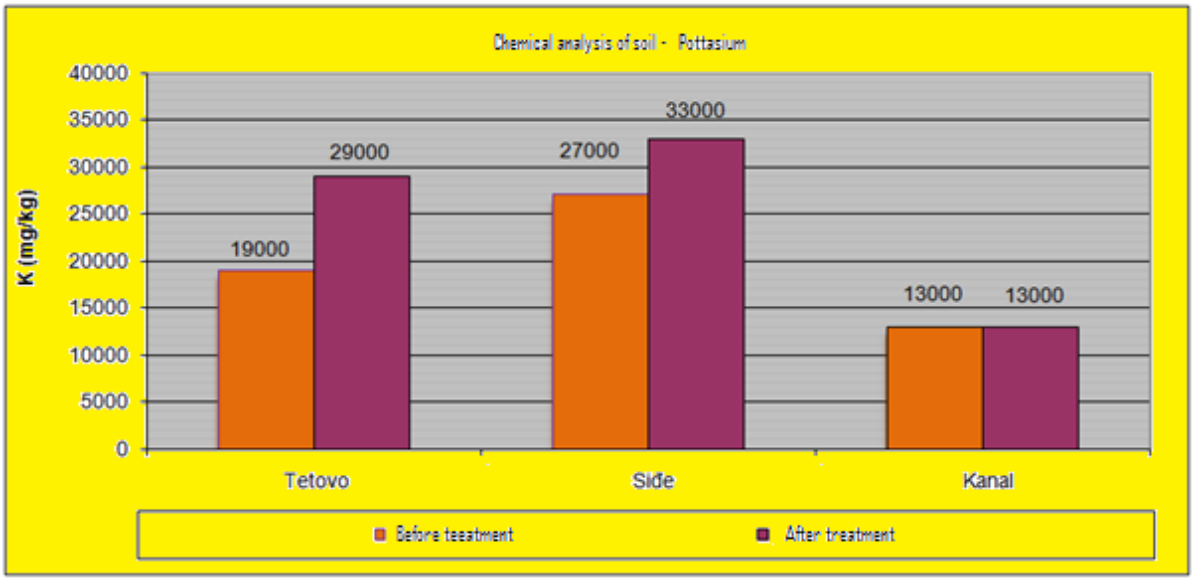
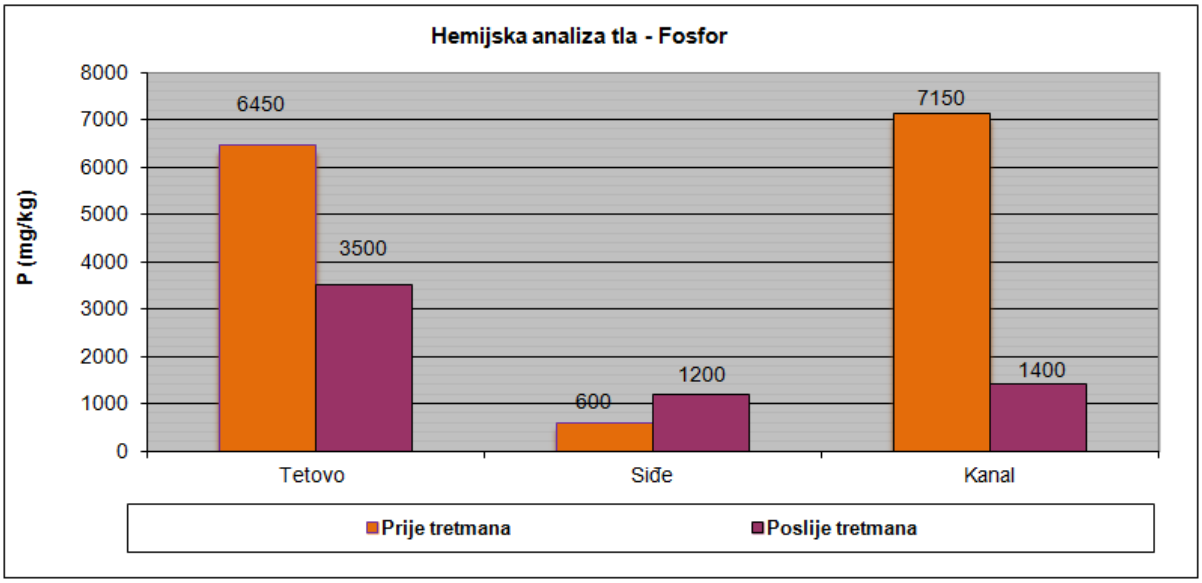


Figure 3 The value of potassium (K) in the soil before treatment and after treatment by the algal composition



Grafikon 4. Vrijednost fosfora u tlu prije tretmana i poslije tretmana alginskim preparatom

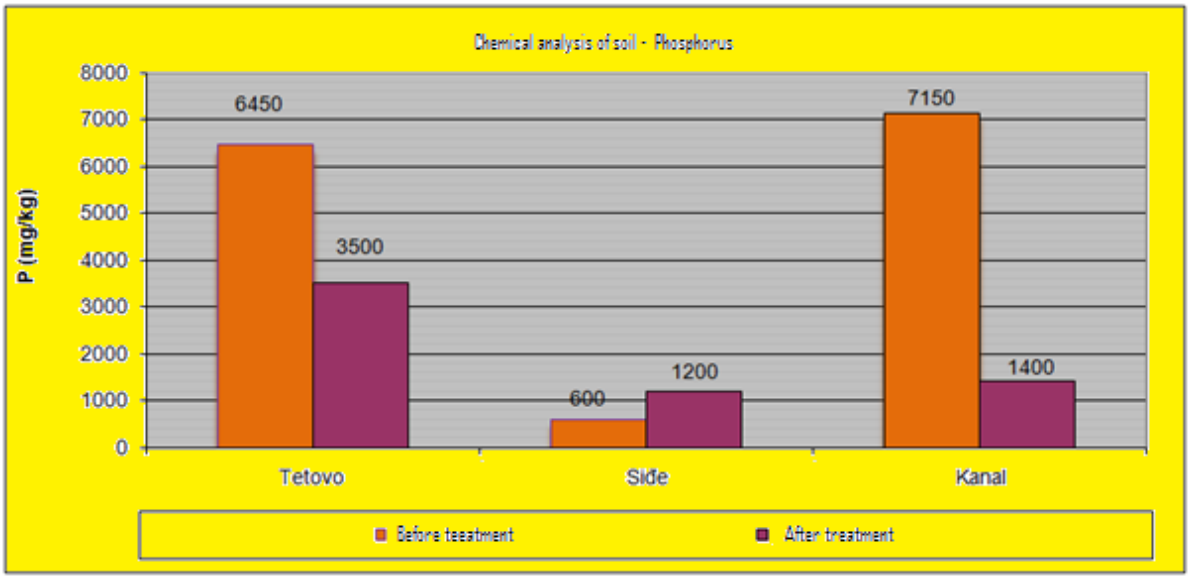
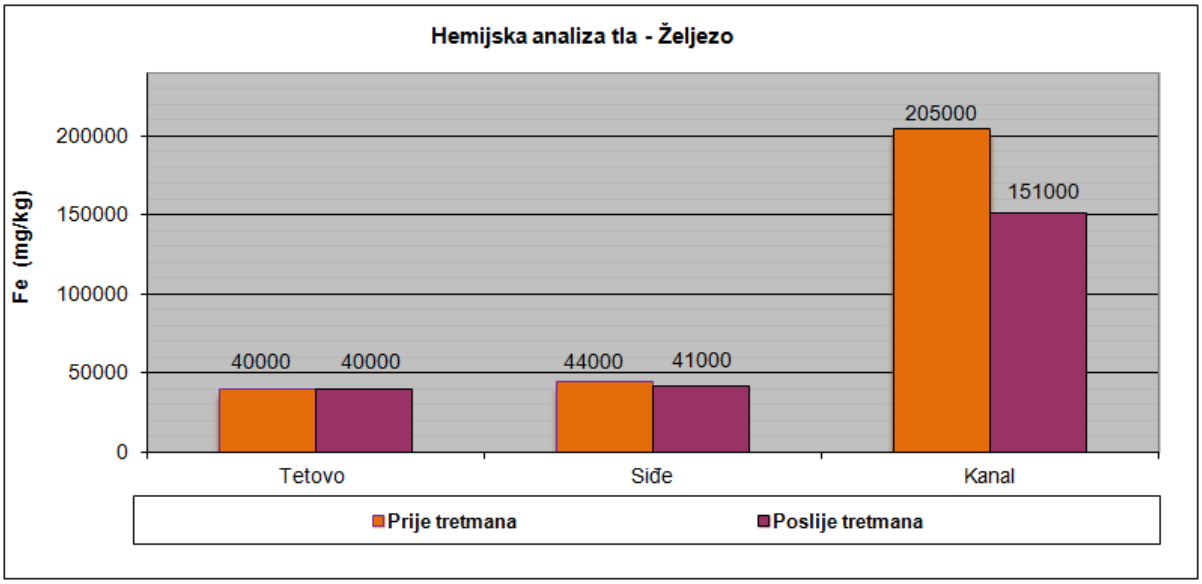


Figure 4 Phosphorus (P) in the soil before treatment and after treatment by the algal composition



Grafikon 5. Vrijednost željeza u tlu prije tretmana i poslije tretmana alginskim preparatom

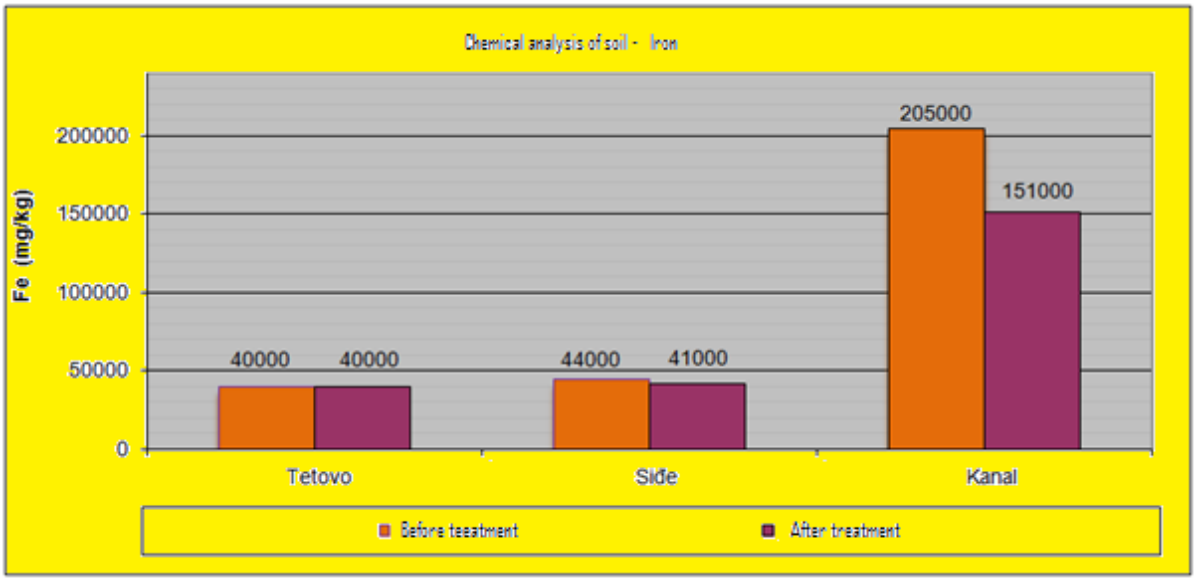
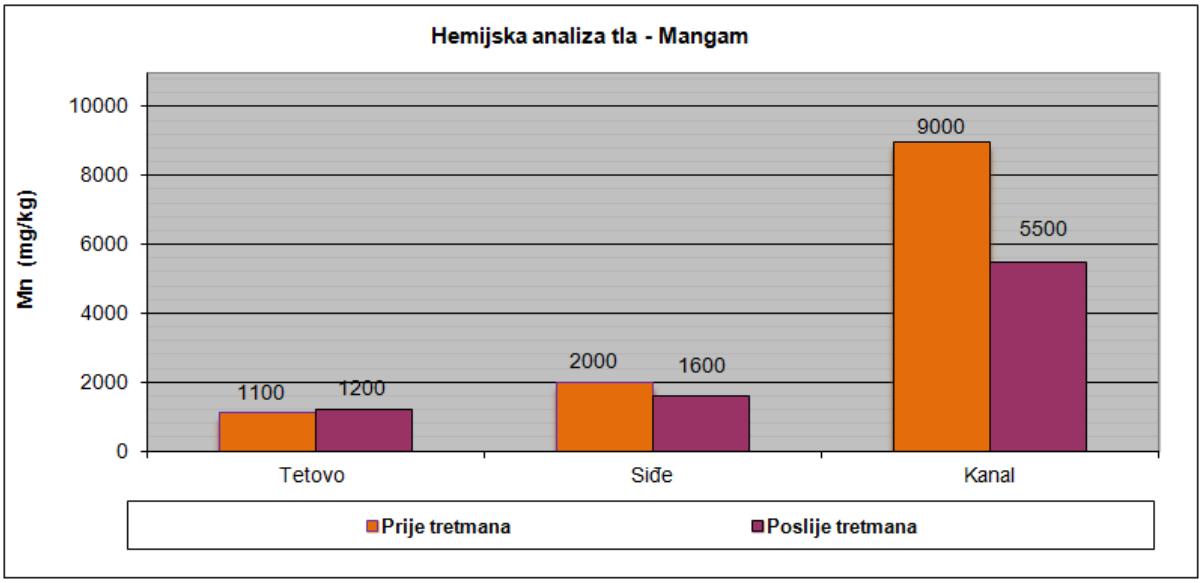


Figure 5 The value of iron (Fe) in the soil before treatment and after treatment by the algal composition



Grafikon 6. Vrijednost mangana u tlu prije tretmana i poslije tretmana alginskim preparatom

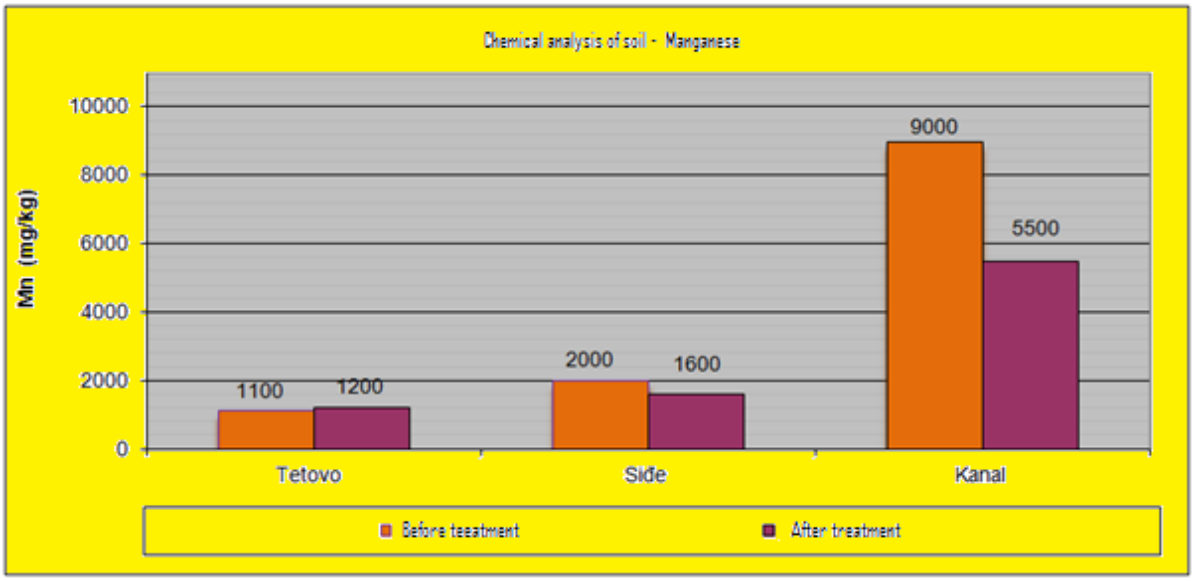
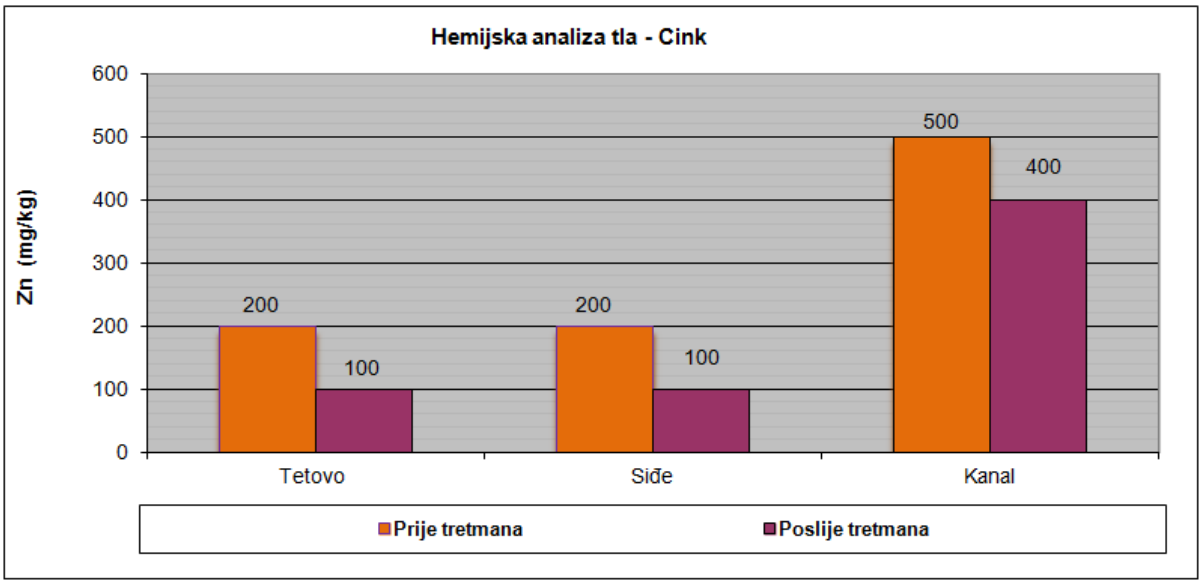


Figure 6 The value of manganese in the soil before treatment and after treatment by the algal composition



Grafikon 7. Vrijednost cinka u tlu prije tretmana i poslije tretmana alginskim preparatom

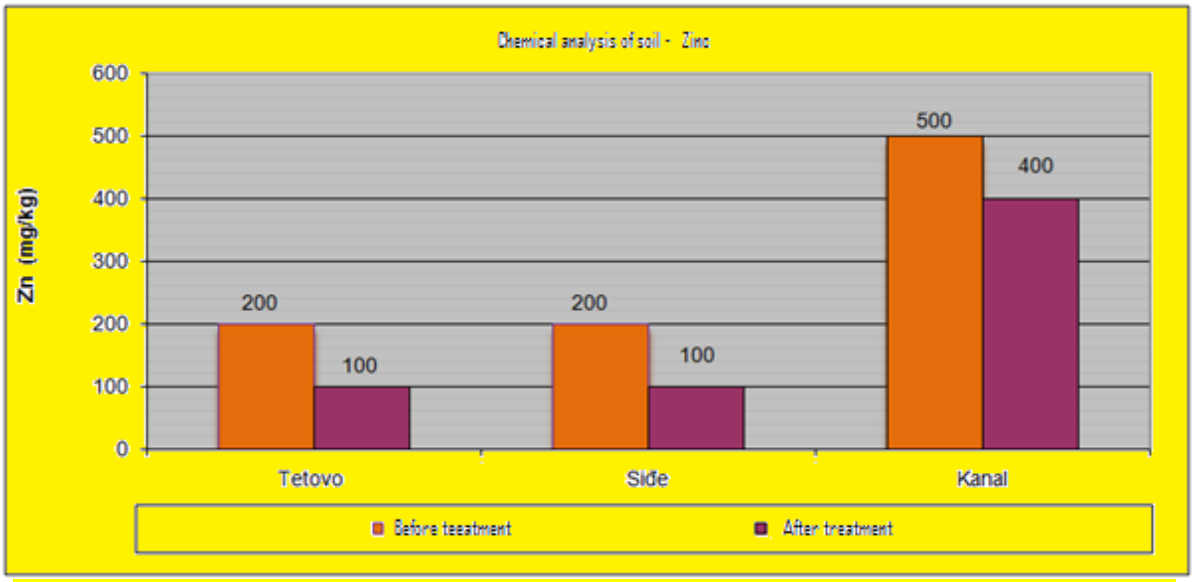
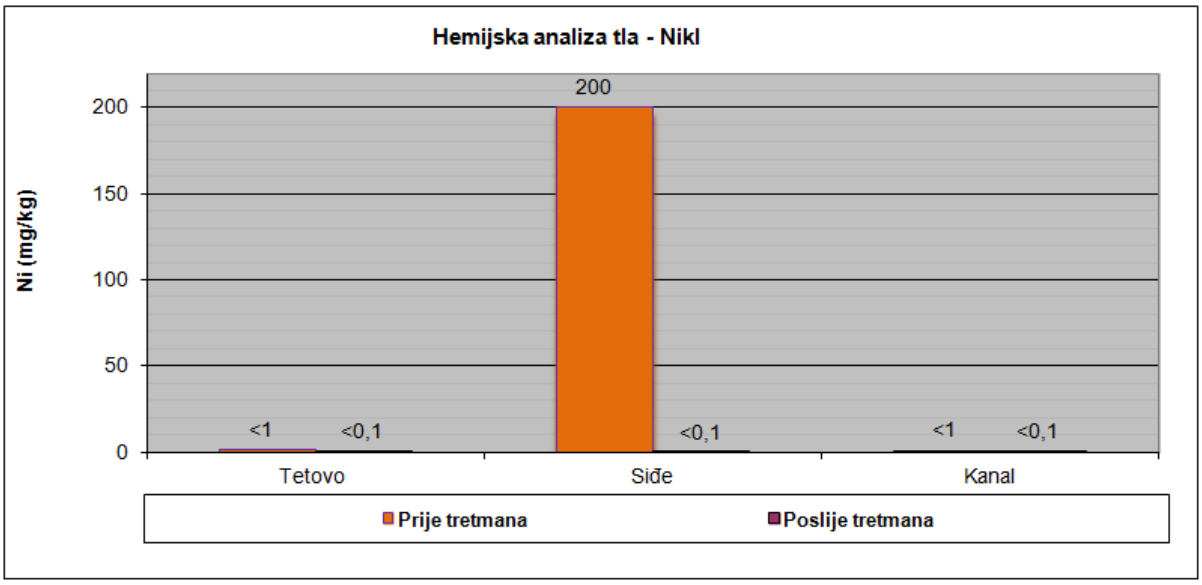


Figure 7 The value of zinc in the soil before treatment and after treatment by the algal composition



Grafikon 8. Vrijednost nikla u tlu prije tretmana i poslije tretmana alginskim preparatom

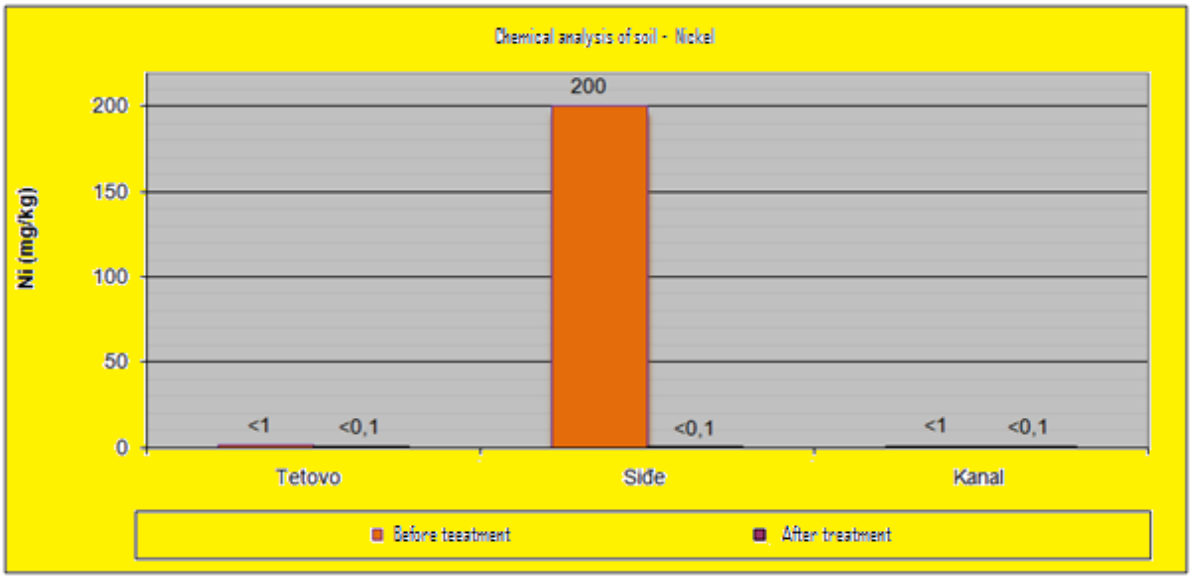
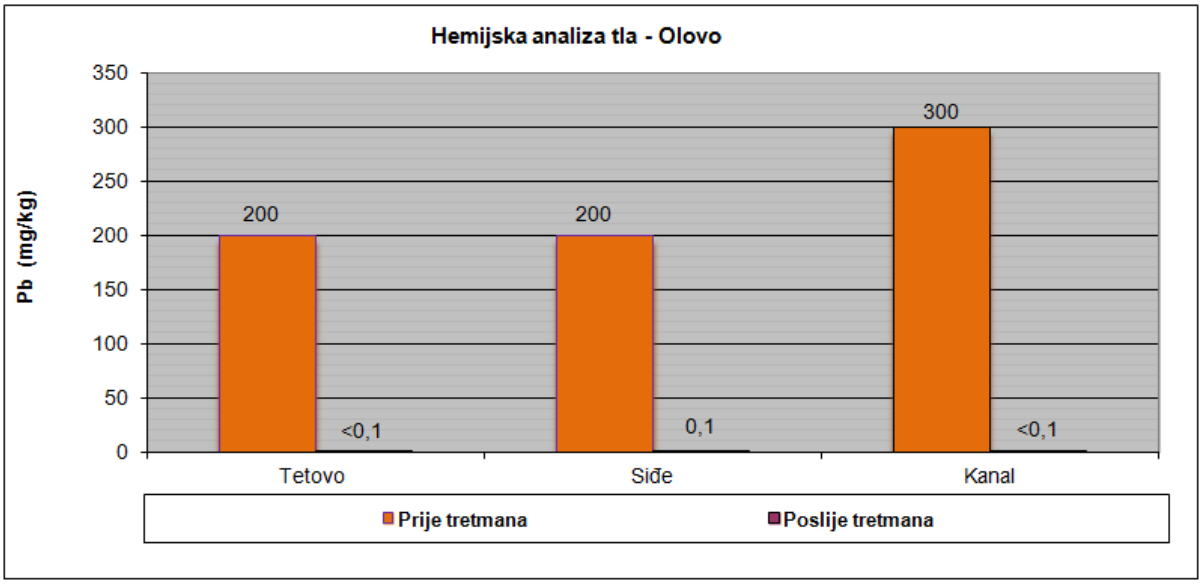


Figure 8 The value of nickel in the soil before treatment and after treatment of the algal composition



Grafikon 9. Vrijednost olova u tlu prije tretmana i poslije tretmana alginskim preparatom

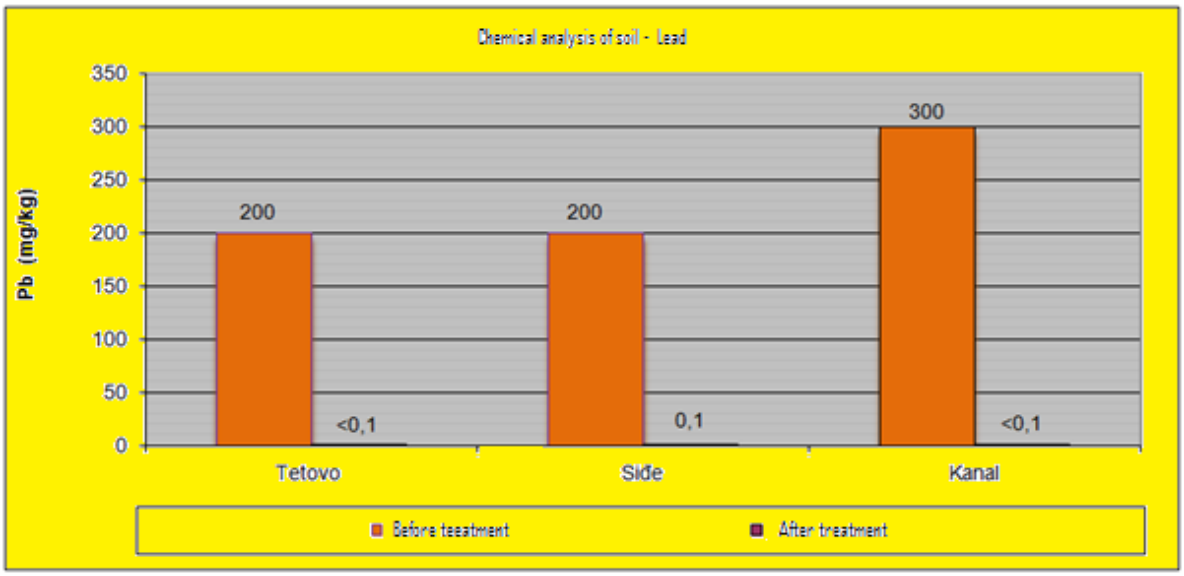
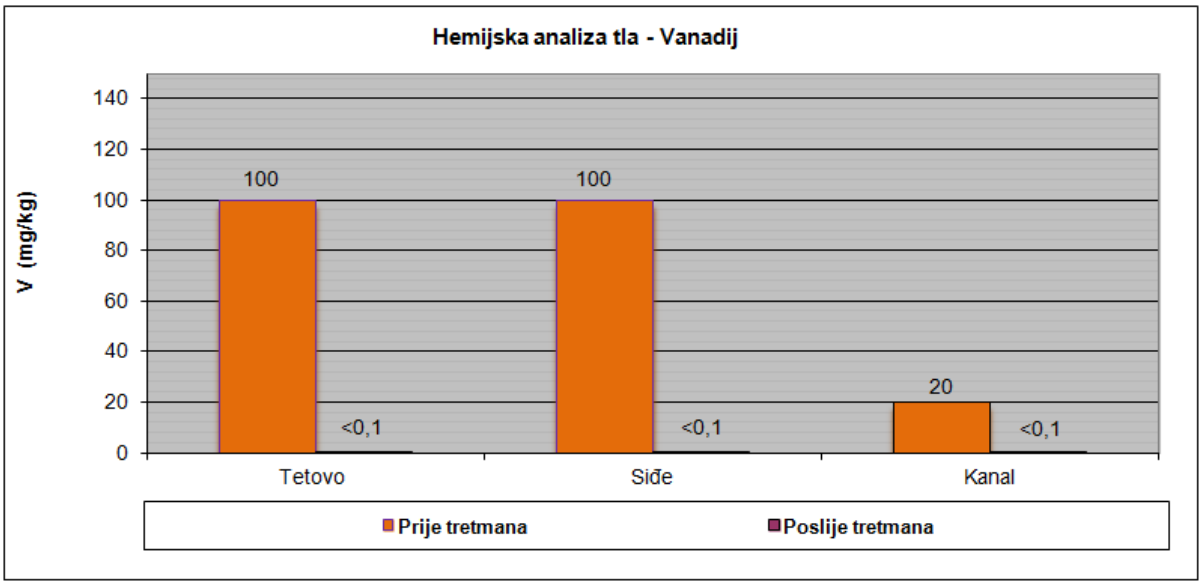


Figure 9 Value of lead in the soil before treatment and after treatment by the algal composition



Grafikon 10. Vrijednost vanadija u tlu prije tretmana i poslije tretmana alginskim preparatom

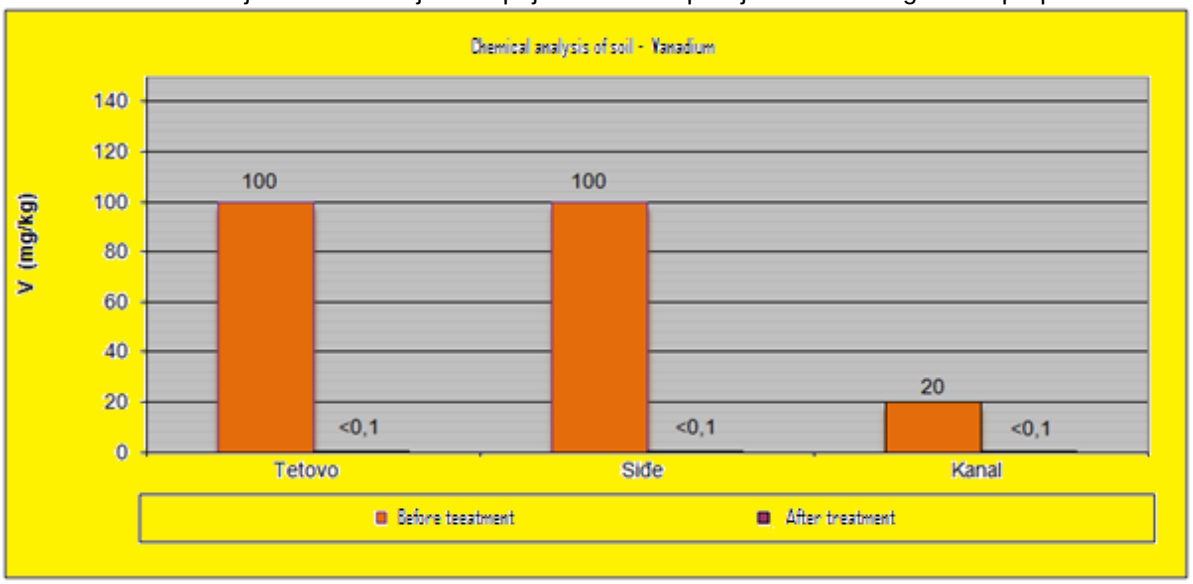
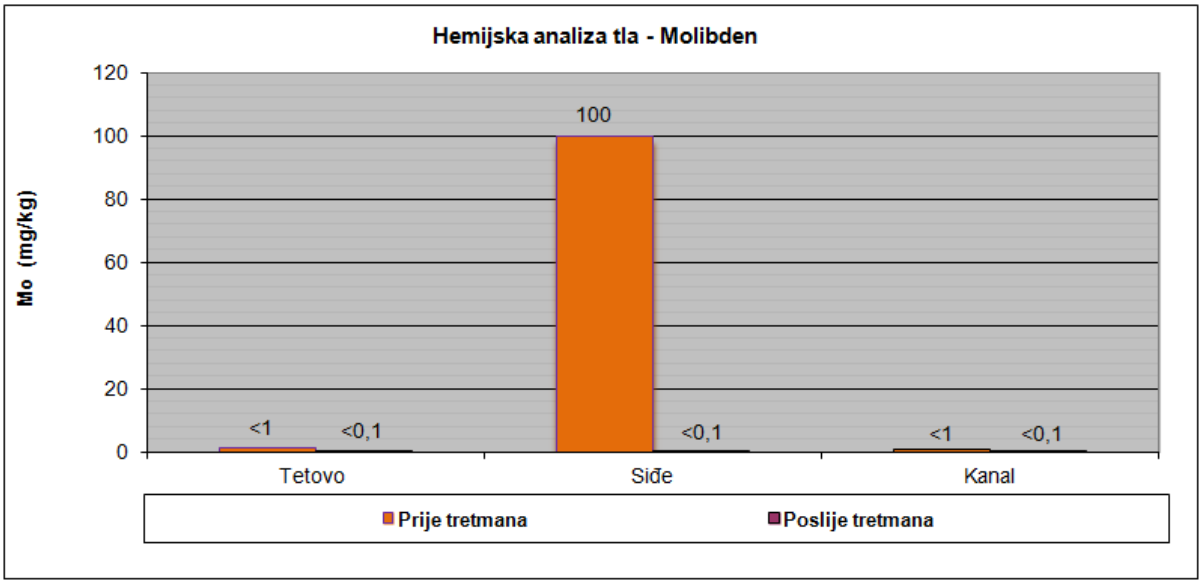


Figure 10 The value of vanadium in the soil before treatment and after treatment by the algal composition



Grafikon 11. Vrijednost molibdena u tlu prije tretmana i poslije tretmana alginskim preparatom

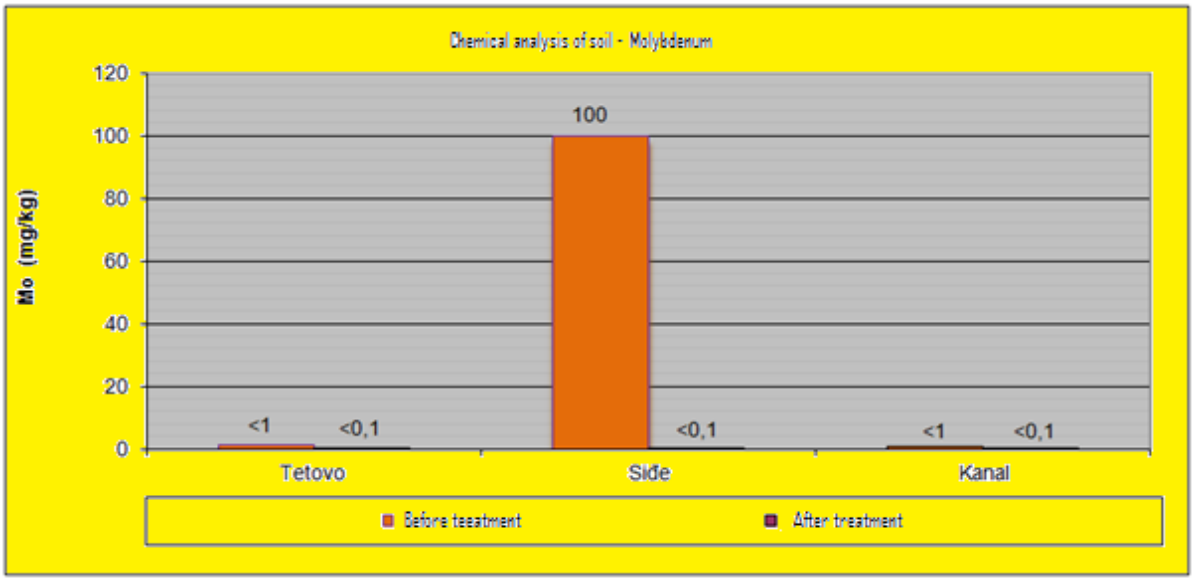
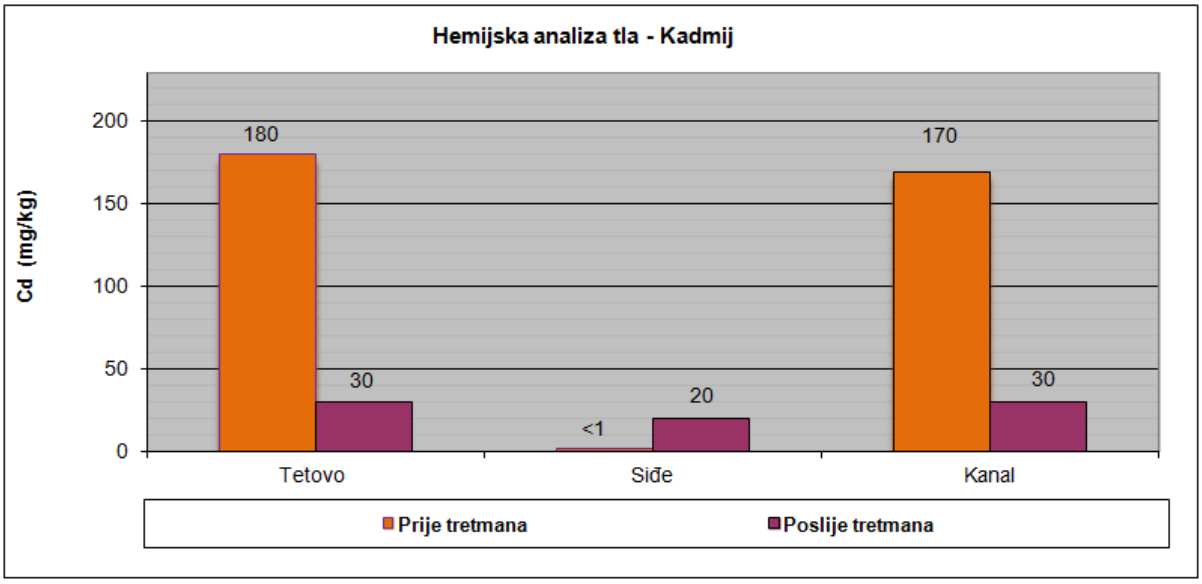


Figure 11 Value of molybdenum in the soil before treatment and after treatment by the algal composition



Grafikon 12. Vrijednost kadmija u tlu prije tretmana i poslije tretmana alginskim preparatom

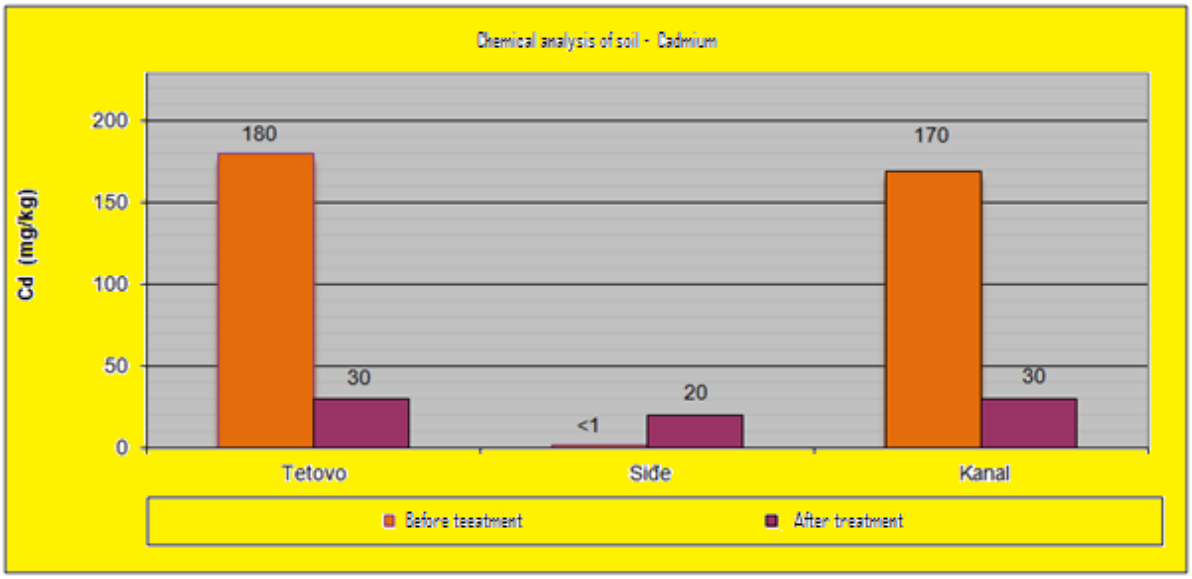


Figure12 Value of cadmium in the soil before treatment and after treatment by the algal composition

5.2. Rezultati analiza tla sa procijednim vodama

Tabela 8. Rezultati analize hemijskih elemenata u tlu (mg/kg) – Siđe-prije tretmana, tretirano alginskim preparatom i sa vodom

Parametar	A. Tlo-Siđe prije tretmana	B. Tretirano tlo-Siđe sa rastvorom algi	C. Tlo-Siđe sa vodom
pH	8,1	8,5	7,7
Ukupna ulja i masti	<1	<1	<1
Ukupni N	210	140	140
K	27000	8000	1200
P	600	1700	1600
Fe	44000	17000	36000
Mn	2000	700	1800
Zn	200	100	100
Ni	200	<0,1	<0,1
Pb	200	200	300
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,1	<0,1

U uzorcima B. i C.(osim olova koji je povećan) došlo je do smanjenja koncentracije teških metala u odnosu na uzorak tla A.
U uzorku B. su smanjene koncentracije teških metala u odnosu na uzorke A. i C. ili su iste u odnosu na uzorak C., ali je došlo do povećanje pH vrijednosti, kalija i fosfora.

5.2. The results of analysis of soil leachate

Table 8 Results of the analysis of the chemical elements in the soil (mg / kg) – Siđe – treated with the algal composition Biocomplex, and treated with plain water:

Parameter	A. Siđe - prior to treatment	B. Siđe – Treated with solution of algae	C. Siđe – Treated with water
pH	8,1	8,5	7,7
The total hydrocarbons	<1	<1	<1
Total N	210	140	140
K	27000	8000	1200
P	600	1700	1600
Fe	44000	17000	36000
Mn	2000	700	1800
Zn	200	100	100
Ni	200	<0,1	<0,1
Pb	200	200	300
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,1	<0,1

Tabela 9. Rezultati analize hemijskih elemenata u tlu (mg/kg) –Siđe-prije tretmana, tretirano sa alginskim preparatom i procijednih voda (mg/l) kroz tretirano tlo

Parametar	A.Uzorak tla-Siđe prije tretmana	B.Tretirano tlo-Siđe sa rastvorom algi	Procijedne vode kroz tretirano tlo -Siđe sa rastvorom algi
pH	8,1	8,5	7,5
Ukupna ulja i masti	<1	<1	<1
Ukupni N	210	140	254,9
K	27000	8000	124
P	600	1700	2,2
Fe	44000	17000	10,3
Mn	2000	700	0,2
Zn	200	100	0,4
Ni	200	<0,1	<0,1
Pb	200	200	<0,1
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,1	<0,1
Suhi ostatak	-	-	7295

Analize procijednih voda koje su prošle kroz tlo tretirano alginskim preparatom je zapaženo da su povećane su koncentracije nitrogena, a iste su vrijednosti nikla, vanadij, molibden, kadmija, a smanjene su vrijednosti kalija, fosfora, željeza, mangana, cinka, olovo, ph u odnosu na tretirano tlo kroz koje je prošla procijedna voda.

Table 9 Results of the analysis of the chemical elements in the soil (mg / kg) before treatment-Siđe, treated the algal composition Biocomplex and leachate (mg / l) levels through the treated soil, also containing the algae composition Biocomplex.

Parameter	A.Siđe – Soil sample before treatment	B.Siđe – Treated with a solution of algae	Siđe - Leachate through the treated soil - with a solution of algae
pH	8,1	8,5	7,5
The total hydrocarbons	<1	<1	<1
Total N	210	140	254,9
K	27000	8000	124
P	600	1700	2,2
Fe	44000	17000	10,3
Mn	2000	700	0,2
Zn	200	100	0,4
Ni	200	<0,1	<0,1
Pb	200	200	<0,1
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,1	<0,1
Dried Residue	-	-	7295

Tabela 10. Rezultati analize hemijskih elemenata u tlu (mg/kg) –Siđe-prije tretmana, tretirano sa vodom i procijednih voda (mg/l) kroz tlo sa vodom

Parametar	A. Tlo-Siđe prije tretmana	C. Tlo-Siđe sa vodom	Procijedne vode kroz tlo - Siđe sa vodom
pH	8,1	7,7	7,7
Ukupna ulja i masti	<1	<1	<1
Ukupni N	210	140	4,2
K	27000	1200	27,0
P	600	1600	1,0
Fe	44000	36000	0,1
Mn	2000	1800	<0,1
Zn	200	100	0,1
Ni	200	<0,1	<0,1
Pb	200	300	<0,1
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,1	<0,01
Suhi ostatak	-		402

Procijedne vode koje su prošle kroz tlo sa običnom vodom zapaženo je da su iste vrijednosti nikla, vanadija, molibdena, a smanjeni su svi ostali elementi u odnosu na tlo sa vodom kroz koje je prošla procijedna voda.

Table 10 Results of the analysis of the chemical elements in the soil (mg / kg) before treatment Siđe-, was treated with water and the leachate (mg / l) of water through the soil

Parameter	A.Siđe Soil before treatment	C. Siđe - Treated with water	Siđe - Leachate through the soil with water
pH	8,1-	7,7	7,7
The total hydrocarbons	<1	<1	<1
Total N	210	140	4,2
K	27000	1200	27,0
P	600	1600	1,0
Fe	44000	36000	0,1
Mn	2000	1800	<0,1
Zn	200	100	0,1
Ni	200	<0,1	<0,1
Pb	200	300	<0,1
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,1	<0,01
Dried Residue	-		402

Leachate that passed through the soil with plain water was observed to have the same values of nickel, vanadium, molybdenum, and reduced all other elements in relation to the ground water that has passed through the leachate water.

Tabela 11. Rezultati analize hemijskih elemenata u tlu (mg/kg) –Siđe-prije tretmana, i procijednih voda (mg/l) kroz tlo tretirano sa alginskim preparatom i procijednih voda kroz tlo sa vodom

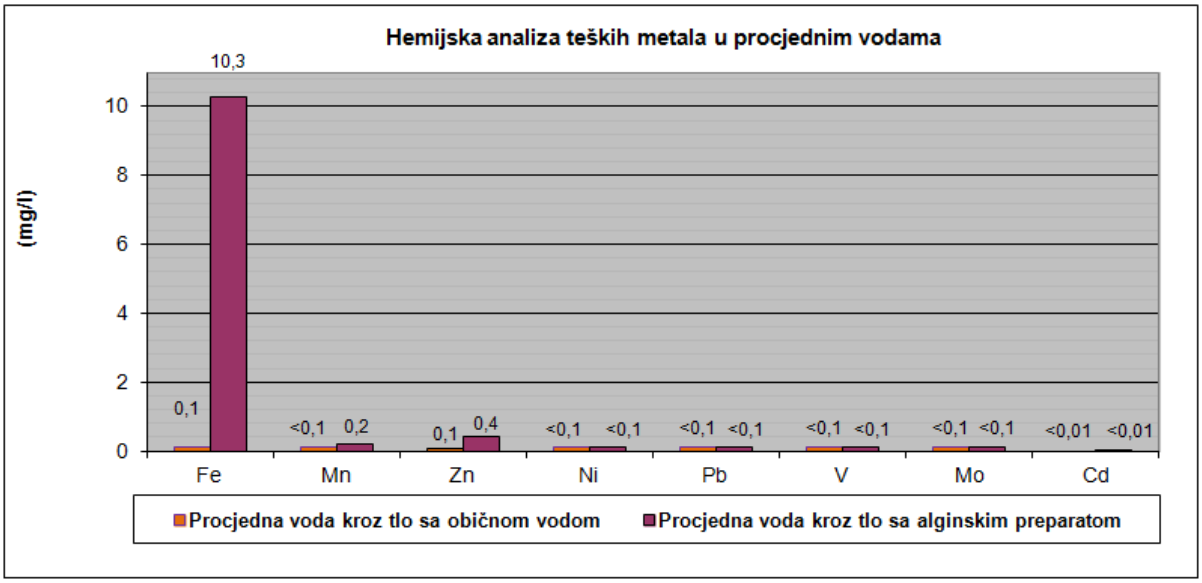
Parametar	A.Uzorak tla-Siđe prije tretmana	Procijedne vode kroz tretirano tlo -Siđe sa rastvorom algi	Procijedne vode kroz tlo -Siđe sa vodom
pH	8,1	7,5	7,7
Ukupna ulja i masti	<1	<1	<1
Ukupni N	210	254,9	4,2
K	27000	124	27,0
P	600	2,2	1,0
Fe	44000	10,3	0,1
Mn	2000	0,2	<0,1
Zn	200	0,4	0,1
Ni	200	<0,1	<0,1
Pb	200	<0,1	<0,1
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,01	<0,01
Suhi ostatak	-	7295	402

U procijednim vodama koje su prošle kroz zemljište koje je tretirano algama su povećane koncentracije nitrogena, kalija, fosfora, željeza, mangana, cinka, a ostali teški metali su isti kao i procijednoj vodi koja je prošla kroz tlo sa običnom vodom.

Table 11 Results of the analysis of the chemical elements in the soil (mg / kg) before treatment Siđe-, and leachate (mg/l) through the soil treated with the algal composition, and leachate through the soil with water

Parameter	A.Siđe - Soil samples before treatment	Siđe - Leachate through the treated soil with a solution of the algae	Siđe - Leachate through the soil with water
pH	8,1	7,5	7,7
The total hydrocarbons	<1	<1	<1
Total N	210	254,9	4,2
K	27000	124	27,0
P	600	2,2	1,0
Fe	44000	10,3	0,1
Mn	2000	0,2	<0,1
Zn	200	0,4	0,1
Ni	200	<0,1	<0,1
Pb	200	<0,1	<0,1
V	100	<0,1	<0,1
Mo	100	<0,1	<0,1
Cd	<1	<0,01	<0,01
Dried Residue	-	7295	402

The leachate that passed through the land is treated algae has increased concentrations of nitrogen, potassium, phosphorus, iron, manganese, zinc and other heavy metals are the same as leachate water that has passed through the soil with plain water.



Grafikon 13. Hemijska analiza teških metala u procijednim vodama

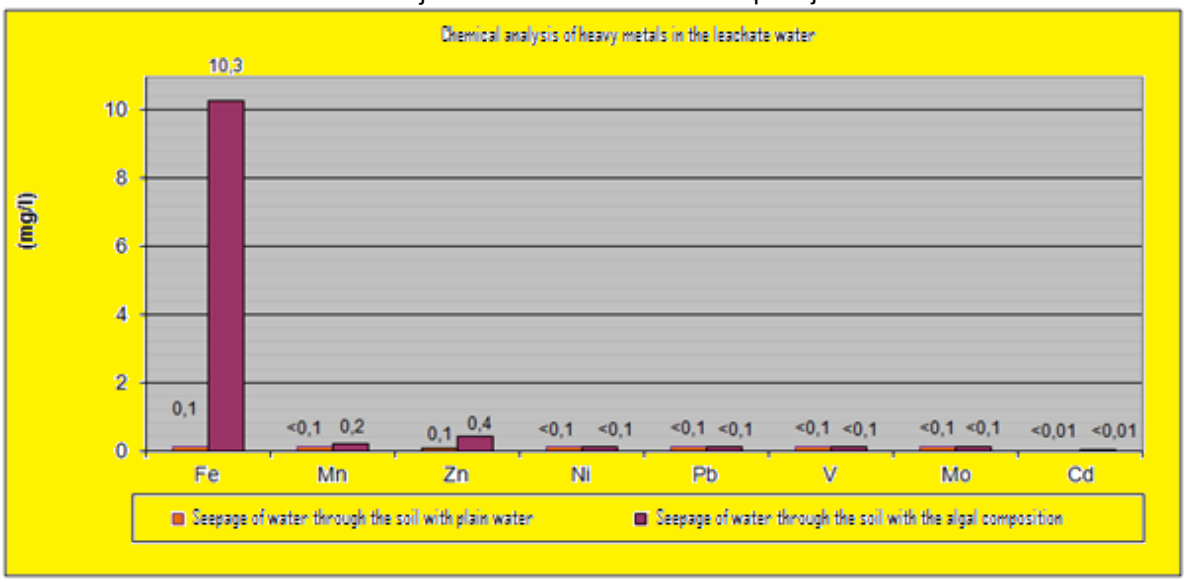
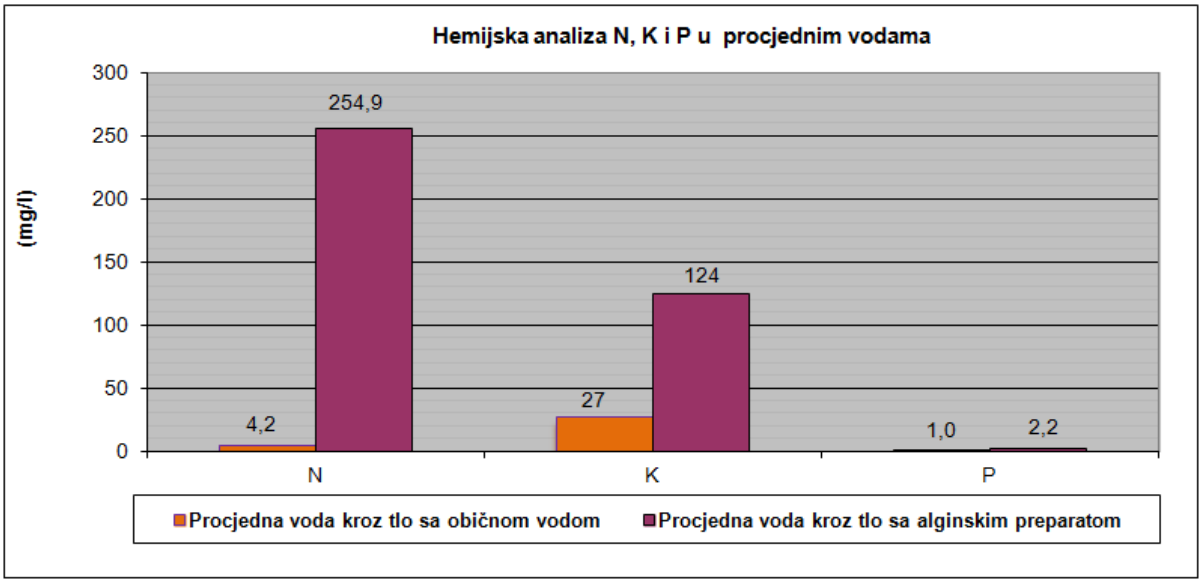


Figure 13 Chemical analysis of heavy metals in the leachate



Grafikon 14. Hemijska analiza N, K i P u procijednim vodama

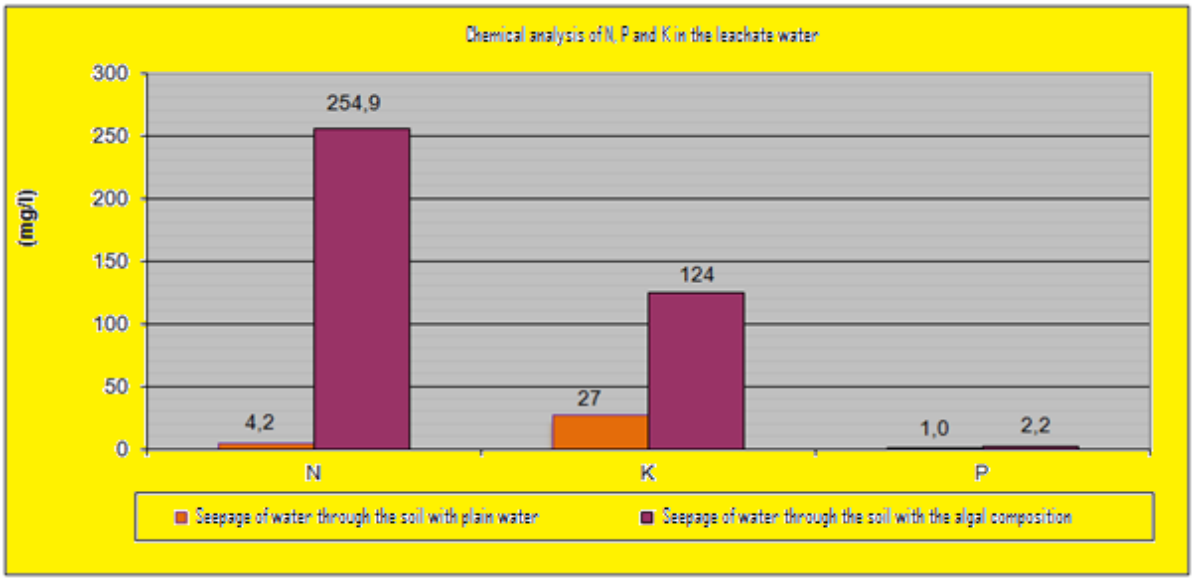
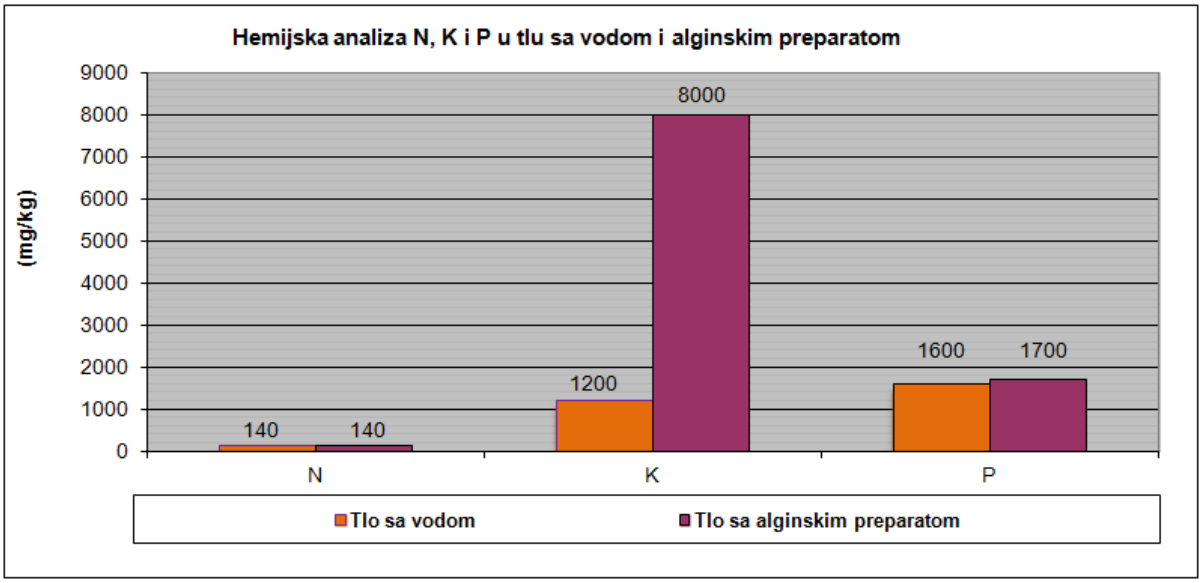


Figure 14 Chemical analysis of N, P and K in the leachate



Grafikon 15. Hemijska analiza N, K i P u tlu kroz koje je prošla voda i alginskog preparata

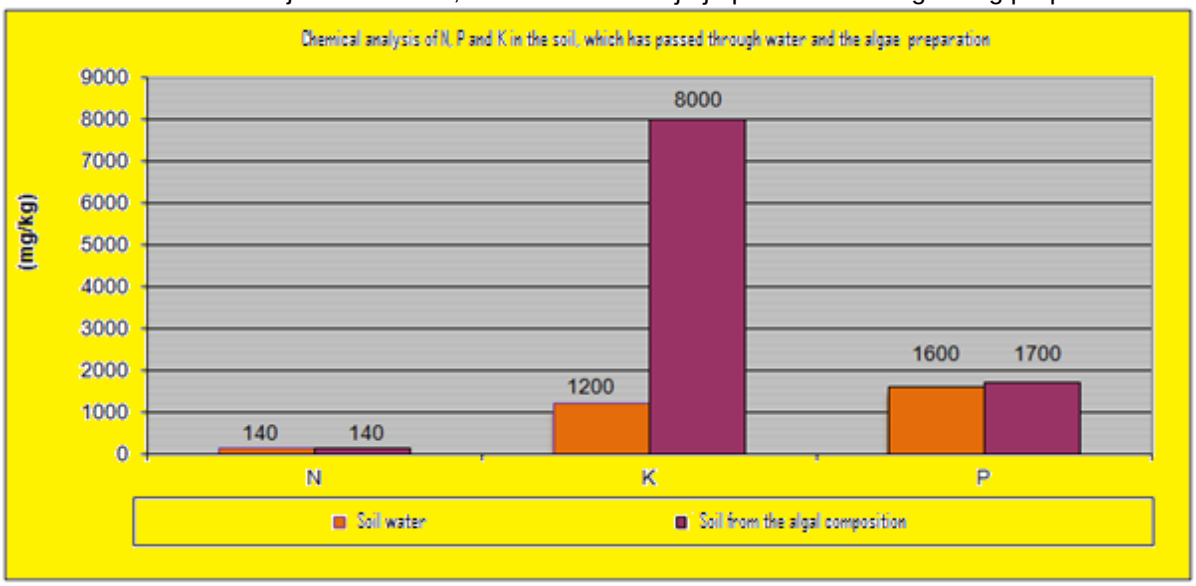
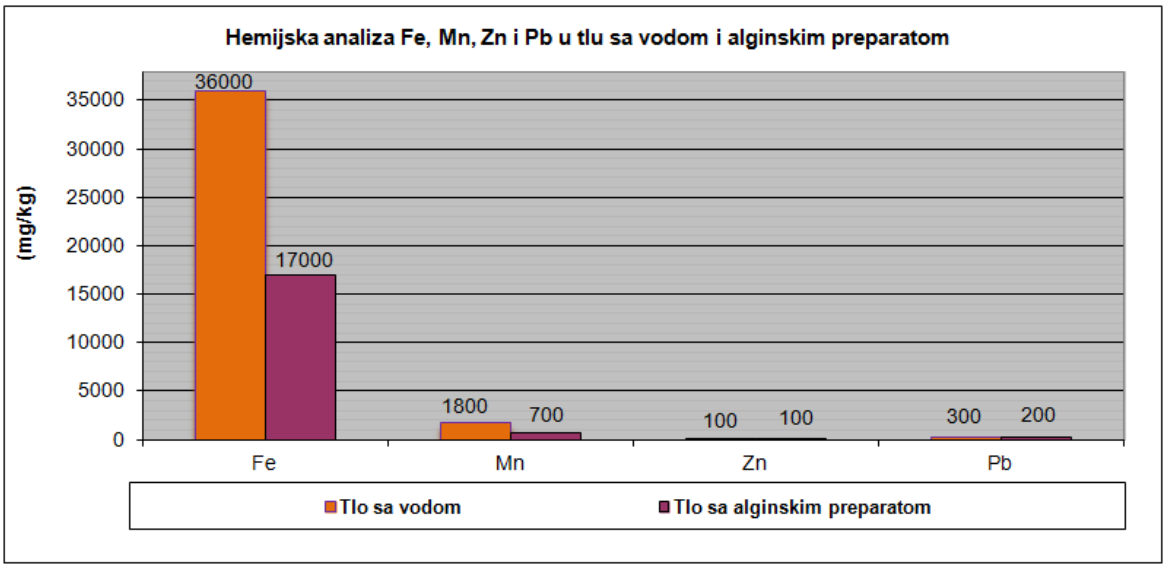


Figure 15 Chemical analysis of N, P and K in the soil, which has passed through water and the algae preparation



Grafikon 16. Hemijska analiza Fe, Mn, Zn i Pb u tlu kroz koje je prošla voda i alginskim preparatom

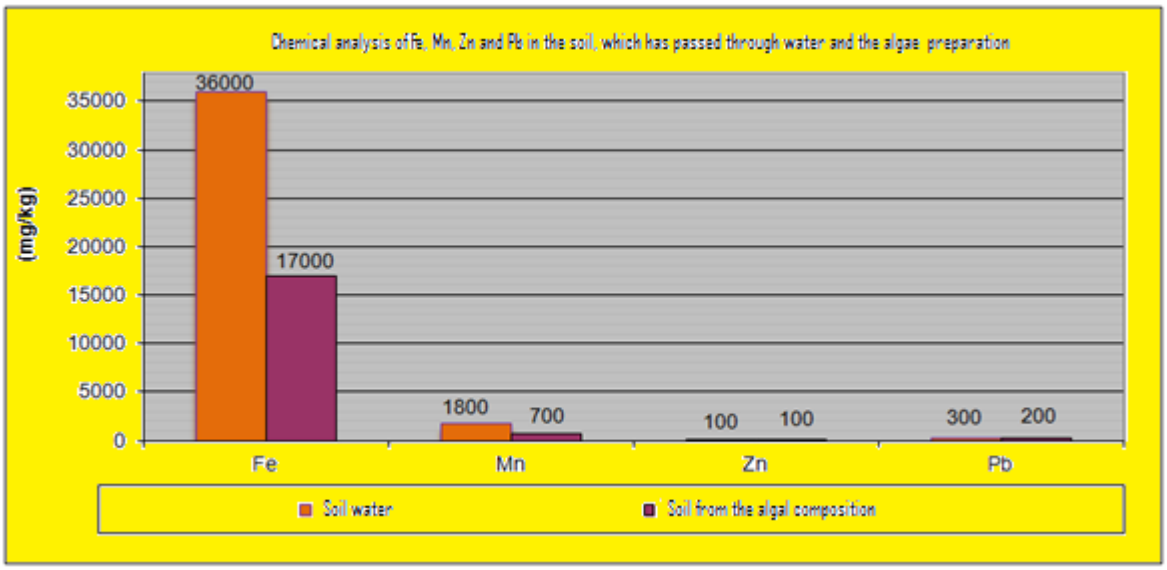
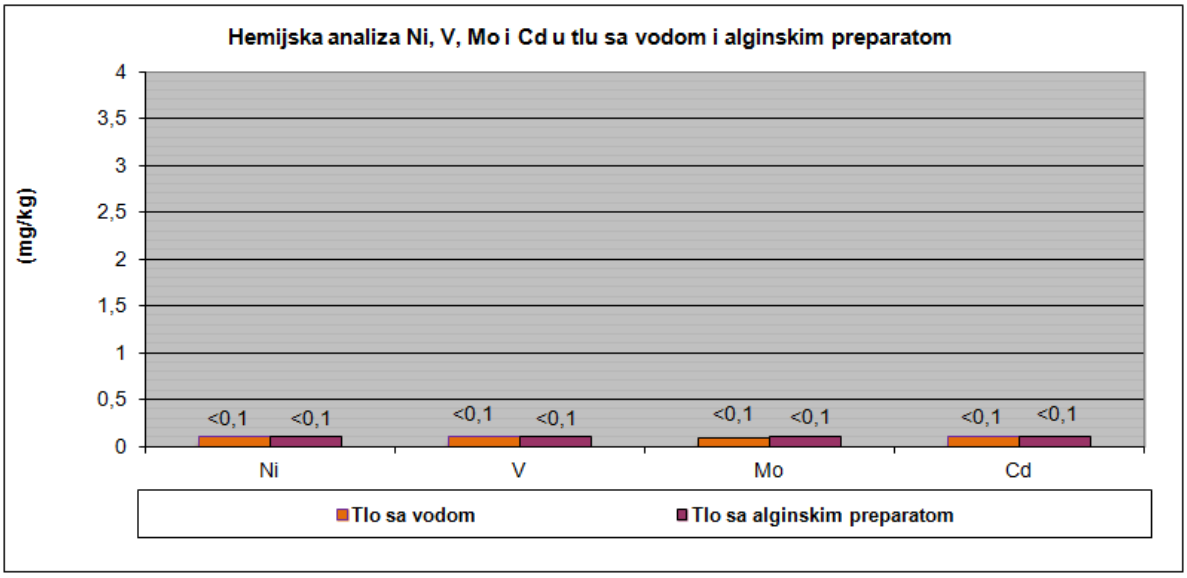


Figure 16 Chemical analysis of Fe, Mn, Zn and Pb in the soil, which has passed through water and the algae preparation



Grafikon 17. Hemijska analiza Ni, V, Mo i Cd u tlu kroz koje je prošla voda i alginskim preparatom

Figure 17 Chemical analysis of Ni, V, Mo and Cd in the soil through which has passed through water and the algae preparation

5.3. Rast biljke na tretiranom tlu

Na tretiranom tlu je zasađeno nekoliko biljaka: pšenica, ukrasna žara, begonije, paprike. Zasađene biljke bile su vitalne i usporedbi sa probom pokazivale su rast novih listova. Primjećeno je brže klijanje pšenice za razliku od probe koja je bila zasađena na običnom tlu.

5.3. The growth of plants in the Biocomplex-treated soil

The treated soil was planted a few plants: wheat, decorative coleus, begonias, peppers. Treated plants were vital compared with the control plants and showed the growth of new leaves. It was observed that the germination of wheat was more rapid, unlike the control, which was like that of wheat planted in ordinary ground.

6. PREPORUKE BUDUĆIM ISTRAŽIVANJIMA

S obzirom da se ovim elaboratom istraživao uticaj alginskog preparata na smanjivanje teških metala i ukupnih ulja i masti u tlu, a u cilju daljeg otklanjanja posljedica zagađenja tla i voda , može se preporučiti primjena ovog preparata i njegovo dalje istraživanje:

- na mjestu zagađenja, s tim da se vodi o računa o faktorima koji utiču na efikasnost bioremedijacije (vlažnost, temperatura, ph, zemljište),
- u bioremedijaciji zemljišta od organskih zagađivača nafta, naftni derivati, pesticidi, deterdženti, polimeri, fenoli, organski rastvarači), drugi teški metali (bakar, živa,), toksični elementi (arsen, cijanidi), otrovni gasovi, radionuklidi (uranijum, plutonijum),
- u bioremedijaciji zemljišta uz dodatak autohtone mikloflore mikroorganizama, koja se izoluje iz zemljišta i razmnožava u bioreaktorima,
- u prečišćavanju otpadnih voda.

Istraživanja bi mogla biti i usmjerena u pravcu objašnjenja kojim reakcijama se smanjuju koncentracije teških metala u laboratoriijskim uslovima (u ovom eksperimentu su bile upotrebljene kvadratne tepsije obložene najlonom) iz kojih matali nisu mogli "otići" nigdje, već su morali biti transformirani. Kao potvrda ovome trebalo bi dokazati i šta se dešava sa teškim metalima na otvorenom terenu tla.

6 RECOMMENDATIONS future research

Given the health effects that the algae preparations had in reducing heavy metals and total hydrocarbons in the soil, in order to further its effect on the soil and water, we recommend the application of this Biocomplex product and its further research :

- water contamination at the site, taking into account the factors that influence the effectiveness of bioremediation (humidity, temperature, pH, and soil type),
- in the bioremediation of organic soil pollutants including oil, petroleum products, pesticides, detergents, polymers, phenols, organic solvents), other heavy metals

(copper, mercury,), toxic elements (arsenic, cyanide), toxic gases, radionuclides (uranium, plutonium),

- in the bioremediation of soil with the addition microflora, indigenous microorganisms, which were isolated from soil and propagated in bioreactors,
- in wastewater treatment.

This research suggests that the treatments in these trials can reduce the concentration of heavy metals in laboratory conditions (in this experiment nylon-coated square baking pans were used) in which Metals could not "go" anywhere, but had to be transformed. Confirmation of this should prove what happens with heavy metals in the open field soil.

7. ZAKLJUČAK

Na osnovu rezultata istraživanja teških metala željezo (Fe), Mangan (Mn), Cink (Zn), Nikal (Ni), Olovo (Pb), Vanadij (V), Molibden (Mo) i Kadmij (Cd) , ph tla, ukupnih ulja i masti i ostalih elemenata, a usljed primjene alginskog preparata na 4 vrste uzorka zemljišta, kao i sastava procijednih voda može se konstatovati:

1. U ispitivanim uzorcima zemljišta (3 uzorka) došlo je **do smanjenja koncentracije nikla, olova, vanadija, molibdena, cinka, željeza, mangana i kadmija** (izuzev u uzorku Tetova koncentracija mangana i u uzorku Siđe koncentracija kadmija se povećala)
2. Povećala se Ph vrijednost zemljišta se upotrebom alginskom preparata.
3. U uzorku industrijskog mulja je došlo **do drastičnog pada ukupnih masti i ulja**.
4. Sadržaj teških metala u procijednim vodama (koje su prošle kroz tlo tretirano sa rastvorom algi i običnom vodom) je manji u odnosu na početni uzorak tla koji nije bio tretiran.
5. Biljke koje su bile sađene na tretirano zemljište bile su vitalne, pokazivale nove izbojke listova za razliku od njihovih proba. Žito je pokazalo kraće vrijeme klijavosti.

Na osnovu sadržaja koncentracija analiziranih elemenata u tlu tretiranih alginskim preparatom može se konstatovati da je to proizvod za popravljanje kvaliteta zemljišta, univerzalna hranjiva podloga za mikroorganizme tla. Naučna istraživanja su dokazala da su molekularni lanci poliuronskih kiselina iz morske alge po strukturi isti kao i u smeđim huminskim kiselinama.

7 CONCLUSION

Based on the research of heavy metals iron (Fe), manganese (Mn, zinc (Zn), nickel (Ni), lead (Pb), vanadium (V), molybdenum (Mo) and Cadmium (Cd), soil pH, total hydrocarbons and other elements, treated with the algial preparations in 4 types of soil samples, as well as on the composition of the leachate, it can be stated :

1 In the studied soil samples (3 samples the algal composition Biocomplex decreased concentrations of nickel, lead, vanadium, molybdenum, zinc, iron, manganese and cadmium (except in the sample Tetovo manganese concentration in the sample went down cadmium concentration is increased)

2 Increase the pH value of the soil using the alginic preparation.

3 In the sample of industrial sludge, there was a drastic decline in total hydrocarbons.

4 The content of heavy metals in the leachate (when treated with soil which was treated with a solution of algae and fresh water) is lower than the initial soil sample that was not treated.

5 The 5 plants that were planted in the treated soil were vital, exhibited new leaf shoots, unlike the control cultivars. Wheat grown in the treated soil showed a shorter time of germination.

Based on the content of the concentration of the analysed elements in the soil treated with the algal composition, it can be concluded that the algal preperation improves soil quality and provides universal nutrient substrate for soil microorganisms. Scientific studies have shown that the molecular polyuronic acids chains from marine algae have the same structure as in brown humic acids.

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9. PRILOZI

-Uzorak tla -Tetovo
- Uzorak tla -Siđe
- Uzorak tla -Kanal
- Uzorak tla -Industrijski mulj
- Procijedne vode
- Biljke
- Izvještaj 460/13-H o hemijskoj analizi zemljišta
- Izvještaj 466/13-H o hemijskoj analizi zemljišta
- Izvještaj 477/13-H o hemijskoj analizi zemljišta
- Izvještaj 508/13-H o hemijskoj analizi zemljišta
- Izvještaj 509/13-H o hemijskoj analizi procijednih voda
- Izvještaj 543/13-H o hemijskoj analizi zemljišta

9 ATTACHMENTS

-Soil samples Tetovo
- A sample of soil-Siđe
- A sample of soil- Kanal
- Soil samples and industrial sludge
- Leachate
- Plants
- Report 460/13-H The chemical analysis of the soil
- Report 466/13-H The chemical analysis of the soil
- Report 477/13-H The chemical analysis of the soil
- Report 508/13-H The chemical analysis of the soil
- Report of chemical analysis 509/13-H leachate
- Report 543/13-H The chemical analysis of the soil