

GEOKEMIJSKI ATLAS SISKA

GEOCHEMICAL ATLAS OF SISAK

Ajka Šorša
Josip Halamić



Sisak – Zagreb, 2014.

Ajka Šorša • Josip Halamić

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GEOCHEMICAL ATLAS OF SISAK

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PREDGOVOR

Kao i u svijetu u Republici Hrvatskoj kontinuirano se povećava broj stanovnika u gradovima. Prema zadnjem popisu iz 2011. godine u manjim ili većim urbanim područjima naše zemlje živjelo je 70,39 % stanovništva. Koncentracija stanovništva u tim sredinama znatno povećava i antropogeni unos kemijskih elemenata u urbana tla (industrija, promet, kućanstva). Pošto se relativno velike površine koriste u rekreacijske svrhe (igrališta, šetnice, rekreacijski centri, parkovi i dr.) i za socijalne potrebe stanovništva (dječja igrališta, školska igrališta) te za uzgoj povrtlarskih i voćarskih kultura (mali vrtovi i voćnjaci), posebice u rubnim dijelovima, povećana je i opasnost po zdravlje urbanog stanovništva.

Grad Sisak ima dugu urbanu tradiciju od preko 2 000 godina, od keltske Segestice, preko rimske Siscie do jednog od najjačih industrijskih gradova u bivšoj SFRJ. U njemu su bile smještene kovnice novca za Rimsko carstvo, a tijekom cijelog svog postojanja bio je i važno prometno čvorište. Dugotrajna naseljenost, industrija i promet ostavili su značajne geokemijske tragove u sisačkom tlu. Tlo je u sebi, od rimskog doba pa sve do danas, zadržavalo i akumuliralo brojne kemijske elemente, od kojih i one koji su potencijalno štetni za ljudsko zdravlje.

Sisak i njegova ruralna okolica je prvi grad u Republici Hrvatskoj na čijem teritoriju je napravljeno sustavno urbano geokemijsko kartiranje. Jedan od rezultata tog istraživanja je i Geokemijski atlas Siska koji je djelo zajedničkog rada i suradnje znanstvenika Hrvatskog geološkog instituta, Gradske uprave i stanovnika Siska te Geokemijske ekspertne grupe EuroGeoSurveys-a (EuroGeoSurveys Expert Group). Ovaj atlas prikazuje sadržaj i prostornu raspodjelu koncentracija 44 kemijska elementa u tlima grada Siska i vjerujemo da će pomoći gradskoj upravi i prostornim planerima kod planiranja upotrebe i namjene zemljišta u gradu Sisku i njegovoj okolici.

Autori

FOREWORD

As well as the rest of the world the Republic of Croatia is faced with continuously increasing number of the population living in the cities. According to the last 2011 census results, 70.39% of the entire population of our country inhabits the minor or major urban areas. The population concentration in these surroundings considerably increases the anthropogenic input of chemical elements into the urban soils (industry, traffic, households). Since the relatively large areas are used for recreational purposes (playgrounds, walkways, recreational centers, parks, and other) and for social needs of citizens (children and school playgrounds) as well as for small farming of agricultural products (small gardens and orchards), particularly in the outskirts, the health risks for urban population have also increased.

The city of Sisak has a long tradition of over 2,000 years, extending from Celtic Segestica, through Roman Siscia to the one of the strongest industrial cities in former Yugoslavia. It was known for its mints which manufactured coins for the whole Roman Empire, and during its long existence it also served as a traffic junction. The long lasting colonization, industry and traffic left considerable geochemical traces in the Siscian soil. From the Roman times until recent this soil preserved and accumulated numerous chemical elements of which some are potentially harmful to the human health.

Sisak and its rural surroundings is the first city in the Republic of Croatia whose territory underwent a systemic urban geochemical mapping. One of the results of this investigation is the Geochemical Atlas of Sisak representing the accomplishment of mutual work and cooperation of the scientists from the Croatian Geological Survey, City Government and citizens of the city of Sisak, as well as the EuroGeoSurveys Geochemical Expert Group. This Atlas represents the content and spatial distribution of 44 chemical elements in the soils of the Sisak city. We believe that it will help the City Government and spatial planners in the land use planing in Sisak and its surroundings.

Authors

RIJEČ RECENZENTA

Od trenutka kad je, nakon dugog razdoblja priprema, terenskih radova i obrade podataka, konačno 2009. godine objavljen Geokemijski atlas Republike Hrvatske postalo je jasno da je poznavanje prostorne rapodjele kemijskih elemenata u površinskom dijelu tla postalo izuzetno važno ponajprije u urbanim područjima, gdje se brojni zdravstveni problemi koje trpe njihovi stanovnici sve više povezuju s povišenim koncentracijama potencijalno toksičnih elemenata u okolišu, ne samo u tlu, nego i u vodi i u zraku. Kao sudionik u projektu geokemijske karte u Hrvatskom geološkom institutu od samih njenih začetaka dalekih osamdesetih godina prošlog stoljeća, neobično mi je drago da je spomenuti Atlas postao osnova u svakom imalo ozbiljnom pristupu istraživanju geokemije okoliša bez koje nije moguće zamisliti buduće projekte. Bilo je samo pitanje trenutka kad će se spoznaje koje su stekli njegovi autori svojim predanim radom primijeniti u rješavanju nekog konkretnog i zahtjevnog problema kao što je procjena potencijalne toksičnosti kemijskih elemenata okoliša u nekoj od velikih gradskih sredina u Republici Hrvatskoj.

Kad je prije pet godina Hrvatski geološki institut predložio da grad Sisak sudjeluje u Pan-Europskom znanstveo istraživačkom projektu „Urban Geochemistry in Europe (URGE) – Soil, children, health", čiji je cilj bio procjena kvalitete urbanog tla jedinstveim metodama geokemijskog kartiranja na razini EU, bio je otvoren put potpuno novim saznanjima o geokemijskom tragu koje su industrija (željezara, rafinerija, kemijska industrija) i prometa, ali i takvi antropologeni čimbenici kao što su talionice rude i kovnice novca još iz predrimskog (Kelti) i rimskog doba, ostavili u tlu ovog grada i njegove okolice. Budući da sam i sam geolog kojem je istraživanje geokemije okoliša profesija već dugi niz godina, bilo mi je veliko zadovoljstvo vidjeti konačno dovršenje ovog istraživačkog projekta koji je doveo do objavljivanja „Geokemijskog atlasa Siska", čiji su autori dr.sc. Ajka Šorša i prof.dr.sc. Josip Halamić. Zahvaljujući suvremenoj metodologiji istraživanja, kao i statističkoj i GIS obradi podataka izrađene su 44 geokemijske karte s prikazom prostorne raspodjele elemenata u tlu grada Siska i njegove uže okolice, koje su svojom kvalitetom bez sumnje na najvišoj razini znanosti i struke u tom području geologije. Naglasio bih da ova publikacija nije samo značajna kao izuzetno koristan pri-

REVIEWER'S WORD

Since the moment when, after the long-lasting preparation period, field works and data processing, the Geochemical Atlas of the Republic of Croatia had been finally published in 2009 it was clear that insight into the spatial distribution of chemical elements in the topsoil has become extremely important, especially in urban areas where numerous health problem suffered by their residents are being more and more associated with increased concentrations of potentially toxic elements in the environment, not only in soil but also in water and air. As a member of the project team working on the Geochemical Map of Croatia in the Croatian Geological Survey since the very inception of the project in the bygone 80s of the last century I am tremendously proud that the Atlas has become the foundation in every seriously designed approach to investigation in environmental geochemistry indispensable in any future projects. It was only the question of time when insights gained by their authors through their devoted work will be applied in solution of some demanding problem such as assessment of the potential toxicity of chemical elements in one of the great urban centers in the Republic of Croatia.

When five years ago the Croatian Geological Survey has proposed the city of Sisak for participation in the Pan-European research project „Urban Geochemistry in Europe (URGE) – Soil, children, health" which aimed at assessment of the quality of urban soil by uniform methods of geochemical mapping at the EU level, the road was open for completely new insights into the geochemical trace which industry (iron foundry, oil refinery, chemical industry) and traffic but also the other anthropogenic factors such as ore smelters and coin mints from the pre-Roman (Celts) and Roman times left in the soil of this town and its surroundings. To a geologist such as me who has been dealing with problems of environmental geology for years now, it was a great pleasure to see the final realization of this research project which led to publishing of the Geochemical Atlas of the City of Sisak. The authors of the Atlas are dr.sc. Ajka Šorša i prof.dr.sc. Josip Halamić. Thanks to most recent methodology of research, including the statistical and GIS data processing, 44 geochemical maps showing the spatial distribution of chemical elements in the soil of the city of Sisak and its surroundin-

ručnik koji će biti na raspolaganju stručnjacima raznih profila, poglavito ekolozima, biolozima, zdravstvenim radnicima i mnogim drugima, nego predstavlja i vrijedan znanstveni rad prezentiran na europskoj razini. Ono što je, čini mi se, ipak u ovom trenutku najbitnije jest koliko je ovakvo djelo potrebno donosiocima strateških političkih i gospodarskih odluka, ponaprije na lokalnoj, odnosno urbanoj razini, ali i šire, jer ne treba zaboraviti što grad Sisak znači na gospodarstvenoj karti Republike Hrvatske. Svaka od prikazanih geokemijskih karata u ovom Atlasu ispisuje dugu i bogatu povijest grada, ali u svakoj od njih odražava se i njegova budućnost.

Dr.sc. Zoran Peh, znanstveni savjetnik

gs were constructed which, doubtless, seize the highest level of scientific and professional work in this field of geology. I would emphasize that this publication is not only significant as extraordinarily useful handbook available to experts of various profiles, especially environmental scientists, biologists, health professionals and many others but it also represents invaluable scientific work at the European level. In this moment it seems to me that the paramount value of this Atlas is the fact that it will be particularly required by decision makers both in economy and politics, particularly at local, that is, urban level, and then in the broader context because, it must be remembered what the city of Sisak signifies on the economy map of the Republic of Croatia. Each and every presented geochemical map in this Atlas tells a story of the long and rich city history. However, in each end every one of them its future is reflected as well.

Dr.sc. Zoran Peh, scientific advisor

1. UVOD

Grad je heterogena i kompleksna urbana cjelina koju su razvili ljudi u potrebi za zaštitom, proizvodnjom, suradnjom, trgovinom, itd. Na početku 20. stoljeća oko 15 % ljudi je živjelo u gradovima, a današnja predviđanja ukazuju da će 2050. godine gradska populacija biti dva puta brojnija od ruralne. Taj porast će konzumirati važne resurse tla u gradskim područjima pri čemu će jedan dio biti potpuno uništen izgradnjom objekata i prometnica, a drugi dio će najvjerojatnije kroz kontaminaciju i kompakciju izgubiti svoju multifunkcionalnost. Urbane sredine u Europi se općenito povećavaju pa kvaliteta okoliša u njima postaje u 21. stoljeću vrlo važan problem kao posljedica razgradnje i oslobađanja mnogih otrovnih kemijskih elemenata i sastojaka posebice kroz industrijske procese, počevši od industrijske revolucije naovamo, s naglim povećanjem nakon Drugog svjetskog rata te kao posljedica modernog stila života. Industrijska postrojenja su bila i još su uvijek u mnogim europskim gradovima smještena unutar urbanih sredina. U slučaju da su ona izmještena, unutar urbanih sredina ostaju ipak tzv. „smeđe površine“ (*brown fields*) koje predstavljaju problem za okoliš i čovjekovo zdravlje. U usporedbi s atmosferom i vodnim tijelima, mnoga kemijska zagađivala nisu rastopljena u tlu, nego se akumuliraju tijekom vremena. U mnogim slučajevima tlo djeluje kao sakupljač, gdje se, kako organske tako i anorganske tvari, adsorbiraju na koloide u tlu (humusnu tvar, minerale glina, na željezne i manganske okside). Često se otrovne supstance u tlu preoblikuju u druge, stabilnije i netopive forme. Osim sastava tla, tipovi supstanci koje se akumuliraju u tlu, ovise o pH-vrijednostima, redox uvjetima i mikroorganizmima. Karakteristika urbanih sredina je široka distribucija pepela i građevinskih materijala s neutralnim do bazičnim pH-vrijednostima. Takvi uvjeti povećavaju mobilizaciju mnogih supstanci u urbanim tlima. Ako se uvjeti u tlu mijenjaju, onda se te supstance remobiliziraju i mogu ući u sustav površinskih ili u sustav podzemnih voda.

Zbog heterogenosti i kontinuiranih promjena urbanih sredina, vrlo je važno razumijeti distribuciju kemijskih elemenata u raznovrsnim okolišnim sredinama (tlo, atmosfera, cestovna prašina, kućna prašina, tavanska prašina, voda), kao i metode za razlikovanje geokemijskih anomalija uzrokovanih ljudskom djelatnošću koje

1. INTRODUCTION

The city is a heterogeneous and complex whole developed by people with purpose of protection, economy, cooperation, market, etc. In the beginning of the 20th century about 15 % of people in the world lived in the cities while the recent forecasts suggest that the city population in 2050 will be two times greater than the rural one. That increase will consume the important soil resources in the city areas causing that a part of it will be irretrievably destroyed by building of objects and traffic lines while another part will most probably lose its function due to contamination and compaction. The urban areas in Europe are generally increasing in size so that the quality of their environment will become a highly important issue in the 21st century as a result of degradation and liberation of many toxic chemical elements and compounds particularly through industrial processes ever since the industrial revolution, with abrupt growth after the WWII, as well as a result of the modern life style. Industrial plants in many European cities have always been located within the urban centers. Even in the case of their relocation the so-called „brown fields“ within the urban centers remain representing the problem to environment and human health. In comparison to atmosphere and water bodies many chemical pollutants are not dissolved in soil but accumulate during the time. In many cases the soil functions as collector so that both organic and inorganic substances adsorb onto colloids in the soil (such as humus, clay minerals, ferric and manganese oxides). Often the toxic substances in soil reshape into other, more stabile and indissoluble forms. Besides the soil composition, the type of substances accumulating in the soil depend on pH values, redox conditions and microorganisms. The characteristics of urban environments are a wide dispersion of ashes and building materials with neutral to basic pH values. These conditions increase mobilization of many substances in urban soils. If soil conditions change these substances are remobilized and so can enter the composition of surface or underground waters.

Due to heterogeneity and continuous changes of urban environments it is highly important to understand the distribution of chemical elements in various environments (soil, atmosphere, road dust, home dust, attic dust, water) as well as the methods for screening of the geochemical anomalies caused by the human activity

se onda definiraju kao područja sa sadržajem kemijskih elemanata iznad vrijednosti pozadinskog šuma. Promjenjivi karakter prirodnog pozadinskog šuma kemijskih elemenata važan je koncept koji treba biti razumljiv, kako političkim strukturama, tako i prostornim planerima. To znači da povišene koncentracije nekog elementa u jednoj okolišnoj sredini mogu biti posljedica geokemijske anomalije, dok u drugoj, to može biti samo dio geokemijskog pozadinskog šuma. Zato je potrebno geokemijskim kartama urbanih sredina prikazati prostornu raspodjelu kemijskih elemenata i spojeva te omogućiti stvarno prepoznavanje kontaminiranih područja.

Od kada se mnogi zdravstveni problemi povezuju sa stanjem u urbanom okolišu stanovnici gradova imaju pravo znati, ne samo na kakvoj zemlji su izgrađene njihove kuće i stanovi, nego i na čemu su izgrađene škole, parkovi, igrališta, rekreacijski centri i radni prostori (Sl. 1.1.).

which are then defined as areas with concentration of chemical elements above the geochemical background. The variable character of the natural geochemical background is an important concept which ought to be comprehensible both to political structures and physical planners. It simply means that higher concentrations of certain chemical element in some type of environment can reveal the geochemical anomaly while in other it may represent the geochemical background. This is why the geochemical maps of urban environments must display the spatial distribution of chemical elements and compounds and enable the authentic recognition of the contaminated areas.

Ever since many health problems are being associated with conditions prevailing in the urban environments the city inhabitants have the right to know not only the quality of terrain on which their houses and homes are built but also what is the ground of their schools, parks, recreation centers and working areas (Fig. 1.1.).



Slika 1.1. *Naselje Kanak između Rafinerije nafte i Željezare Sisak (Foto: J. Halamić).*

Figure 1.1. *The Kanak settlement situated between petroleum refinery and steelworks Sisak (Photo: J. Halamić).*

2. PROJEKT URGE

Pan-Europski projekt „Urban Geochemistry in Europe (URGE) – Soil, children, health“ izvodi se radi procjene kvalitete urbanog tla geokemijskim kartiranjem. Projekt koordinira Geokemijska ekspertna grupa EuroGeoSurveysa (EGS GEG – www.eurogeosurveys.org), a istraživanja u Republici Hrvatskoj izvodi Hrvatski geološki institut u okviru nacionalnog projekta „Osnovna geokemijska karta Republike Hrvatske“. EGS GEG je pokrenula 2008. godine taj znanstveno-istraživački projekt s ciljem da se jedinstvenim metodama geokemijski kartiraju europski gradovi. U tu svrhu su na europskoj razini napravljene jedinstvene upute za izvođenje tog projekta. Norveška geološka služba (NGU) preuzela je koordinaciju projekta s obvezom plaćanja troškova kemijskih analiza uzoraka, dok su pojedine nacionalne geološke službe trebale financirati troškove terenskog rada i pripreme uzoraka za kemijske analize.

Nakon stručnog usuglašavanja i pripreme kandidature s Upravnim odjelom za zaštitu okoliša, ruralni razvoj i poljoprivredu Grada Siska, znanstvenici Hrvatskog geološkog instituta su na sastanku EGS GEG u Briselu u proljeće 2009. godine, predložili Sisak za sudjelovanje u projektu. Dana 22. 07. 2009. godine gradonačelnik grada Siska gospodin Dinko Pintarić poslao je Pismo namjere Grada Siska za sudjelovanje u projektu.

U projektu za sada sudjeluje 12 europskih gradova: Accero-Magliano – Italija, Ajka – Mađarska, Aschersleben – Njemačka, Atena – Grčka, Dublin – Irska, Hämänlinna – Finska, Idrija – Slovenija, Karlstad – Švedska, Kristiansand – Norveška, Prag – Češka i Sisak – Hrvatska.

U ljetu 2010. godine, neposredno prije planiranog početka terenskih radova, Norveška geološka služba odustala je od financiranja kemijskih analiza. Hrvatski geološki institut je tada ipak odlučio nastaviti s projektom i sam snositi kompletne troškove terenskih radova, analitike i prezentiranja rezultata. URGE projekt je na europskoj razini također nastavljen, ali sporijim tempom od planiranog, a neki gradovi morali su odustati. Do kraja 2012. godine uzorkovanje je završeno u sljedećim gradovima: Dublinu, Idriji, Hämeenlinni, Karlstadtu, Kristiansandu, Accero-Maglianu, Ajki, Acherslebenu i Sisku. Radi okolišne katastrofe (izlijevanja crvenog mulja u okoliš) u Mađarskoj je, prvotno predloženi grad Miskolc, zamijenjen gradom Ajka.

2. THE URGE PROJECT

Pan-European project „Urban Geochemistry in Europe (URGE) – Soil, children, health“ is carried out with purpose of assessing the quality of the urban soil using the geochemical mapping. The project is coordinated by the EuroGeoSurveys (EGS GEG – www.eurogeosurveys.org) Geochemical Expert Group while the research work in Croatia is performed by Croatian Geological Survey as a part of the national project “The Basic Geochemical Map of Croatia). This scientific research project has been launched in 2008 by the EGS GEG with purpose of the geochemical mapping of European cities by the uniform methods. The unique guidelines necessary for the project implementation have been made on the European level. The Norway Geological Survey (NGU) accepted the coordination of the project together with obligation to pay the price of the chemical analyses of the samples while the individual geological surveys had to finance the costs of the filed work and sample preparation prior to analysis.

After the expert agreeing and preparation of candidacy with the Directorial Board for Environmental Protection, Rural Development and Agriculture of the City of Sisak the scientists from the Croatian Geological Survey proposed at the EGS GEG meeting in Brussels held in spring 2009 the City of Sisak as the party in the project. On July 27th 2009 the Mayor of Sisak, Mr. Dinko Pintarić sent a Notice of Decision applying the City of Sisak for the participation in the project.

Until now the project is participated by 12 European cities including: Accero-Magliano – Italy, Ajka – Hungary, Aschersleben – Germany, Athens – Greece, Dublin – Ireland, Hämeenlinna – Finland, Idrija – Slovenia, Karlstad – Sweden, Kristiansand – Norway, Prague – Czech Republic, and Sisak – Croatia.

In the summer 2010 immediately before the planned beginning of the field work Norway Geological Survey gave up from funding the chemical analyses. In spite of this Croatian Geological Survey decided to continue with participation in the project and defray the complete expenses of the field works, analytics and presentation of results alone. The Project URGE was also continued at the European level but with slower tempo than it had been planned before while some cities had leave the project. Until the end of 2012 the sampling

Projekt URGE će u gradu Sisku opravdati financijska ulaganja kako u znanstvenom tako i u javnom interesu. S obzirom na dugu povijest Siska i njegovu industriju koja uključuje i poznate onečišćivače okoliša, ovaj projekt predstavlja početak sustavnog ispitivanja urbanog tla u samom gradu te poljoprivrednog zemljišta u okolici grada. Predstavljanjem rezultata u ovom geokemijskom atlasu bit će sustavno i kvalitetno obrađen anorganski sastav tla te identificirani mogući onečišćivači. Projekt bi trebalo nastaviti analizom organskih onečišćivala, istraživanjem interakcije anorganskih i organskih spojeva te njihovog utjecaja preko flore i faune na čovjeka i okoliš općenito.

was carried out in the following cities: Dublin, Idrija, Hämeenlinna, Karlstadt, Kristiansand, Accero-Magliano, Ajka, Achersleben and Sisak. Due to the environmental disaster (outflow of the red mud in the environment) in Hungary the preliminary selected city of Miskolc was replaced by Ajka.

The URGE Project Sisak will warrant the financial investments both in scientific and public interest. With regards to the long history of the Sisak city and its industry which includes the famous pollutants of the environment this project represents the beginning of the systematic investigation of urban soil in the city itself as well as agricultural soil in its surroundings. By presentation of the results in this geochemical atlas there will be elaborated systematically and in high quality the inorganic soil composition and identified the potential pollutants. The project should be continued with analysis of organic pollutants and investigation of interaction between inorganic and organic compounds as well as their impact via flora and fauna on people and environment in general.

3. KRATKI POVIJESNI PREGLED RAZVOJA PODRUČJA GRADA SISKA

Sisak je jedan od rijetkih hrvatskih gradova koji se može pohvaliti s poviješću dužom od 2 500 godina. Tako dugo povijesno razdoblje ostavilo je i geokemijski trag u tlu tog područja (talionice rude, kovnice novca, rimska vodovodna mreža, crna metalurgija, rafinerija nafte, kemijska industrija, promet i dr.). U tom pogledu ćemo u ovom kratkom povijesnom pregledu razvoja sisačke urbane cjeline dati naglasak samo na one događaje koji su po našem sudu ostavili jači geokemijski trag na okoliš te regije. O detaljnim povijesnim događanjima u toj regiji postoji bogata literatura od koje ćemo spomenuti samo neke radove (SLUKAN ALTIĆ, 2004; LOLIĆ, 2006).

Najstariji ostaci starijeg željeznog doba pronađeni su u koritu rijeke Kupe u blizini novog mosta i datiraju od kraja 6. do početka 4. stoljeća prije Krista (LOLIĆ, 2006).

Kelti su u 4. st. pr. Kr. utemeljili naselje Segestiku (*Segestica*), a ostaci iz tog perioda nađeni su uz desnu obalu rijeke Kupe na području današnjeg naselja Pogorelec (Sl. 3.1.).

U 1. st. pr. Kr. Rimljani su uspjeli zavladati sisačkim područjem, a naselje su nazvali Siscija (*Siscia*) (Sl. 3.1.). Siscija je utemeljena na lijevoj obali Kupe, u području današnje jezgre grada Siska, a građena je od kamenja nepravilnog oblika povezanog vapnom i pečenom ciglom (SLUKAN ALTIĆ, 2004). Na obali Kupe od 2. do 4. stoljeća nalazilo se i veliko gradsko kupalište. Osim toga, izgrađeni su silosi, svetišta i drugi objekti. Površina grada je tada bila oko 40 hektara. Siscija je postala najjače vojno uporište u Panoniji zbog značajne uloge doline rijeke Save kao prometnog pravca prema istoku. Siscija postaje i važno čvorište puteva između Panonije i Dalmacije te Italije i istoka. U 1. stoljeću osnovana je riječna flota *Classis Flavia Pannonica*. U 3. stoljeću Siscija postaje biskupsko sjedište. Početkom 4. stoljeća u Sisku je stradao sisački biskup Kvirin koji je potom proglašen svetim. Čitav Stari Sisak (antička Siscija) bio je izgrađen na povišenom terenu između rijeke Kupe i

3. A SHORT HISTORIC OVERVIEW OF THE DEVELOPMENT OF THE SISAK CITY AREA

Sisak is one of the few Croatian cities which can boast with history longer than 2,500 years. Such a long historical period left also its geochemical mark in the soil of this area (ore foundries, coin smelters, Roman aqueducts, ferrous metallurgy, oil refinery, chemical industry, traffic and other). In this respect, we shall in this short historic overview of the development of the Sisak urban core give emphasis only on those events that, by our judgment, left the stronger geochemical traces in the environment of this region. Abundant literature exists on the detailed historic events in this area of which we will mention only a few works (SLUKAN ALTIĆ, 2004, LOLIĆ, 2006).

The oldest remnants of the Early Iron Age have been found in the bed of the Kupa River near the new bridge, which are dated from the end of 6th and beginning of the 4th century BC (LOLIĆ, 2006).

During the 4th and BC the Celts had founded the settlement of Segestica. The remnants from that period were found on the right bank of the Kupa River, on the territory of the recent settlement of Pogorelec (Fig. 3.1.).

In the 1st BC the Romans successfully began their rule over the Sisak area and named settlement as Siscia (Fig. 3.1.). Siscia was founded on the left bank of the Kupa River, in the area of the recent urban core of the Sisak city. It was built of irregular blocks fit together with mortar and baked bricks (SLUKAN ALTIĆ, 2004). Between the 2nd and 4th centuries the banks of the Kupa River accommodated a big bathing-place. Besides, barns, sanctuaries and other objects were also built. The city occupied the area of 40 hectares. Siscia turned into the strongest military stronghold in Pannonia because in those times the Sava River valley played a significant role as a traffic route towards the east. Siscia becomes an important road junction connecting Pannonia and Dalmatia, Roman Empire and the East. The 1st century AD saw the establishment of the first inland waterway fleet *Classis Flavia Pannonica*. In the 3rd century AD Siscia becomes the bishop's seat. In the beginning of

potoka Šulec i Svibovica, a omeđen koritom sisačkog potoka. Potok je plavio okolicu i izazivao dizanje podzemnih voda te će on biti zasut 1876. godine (LOLIĆ, 2006).

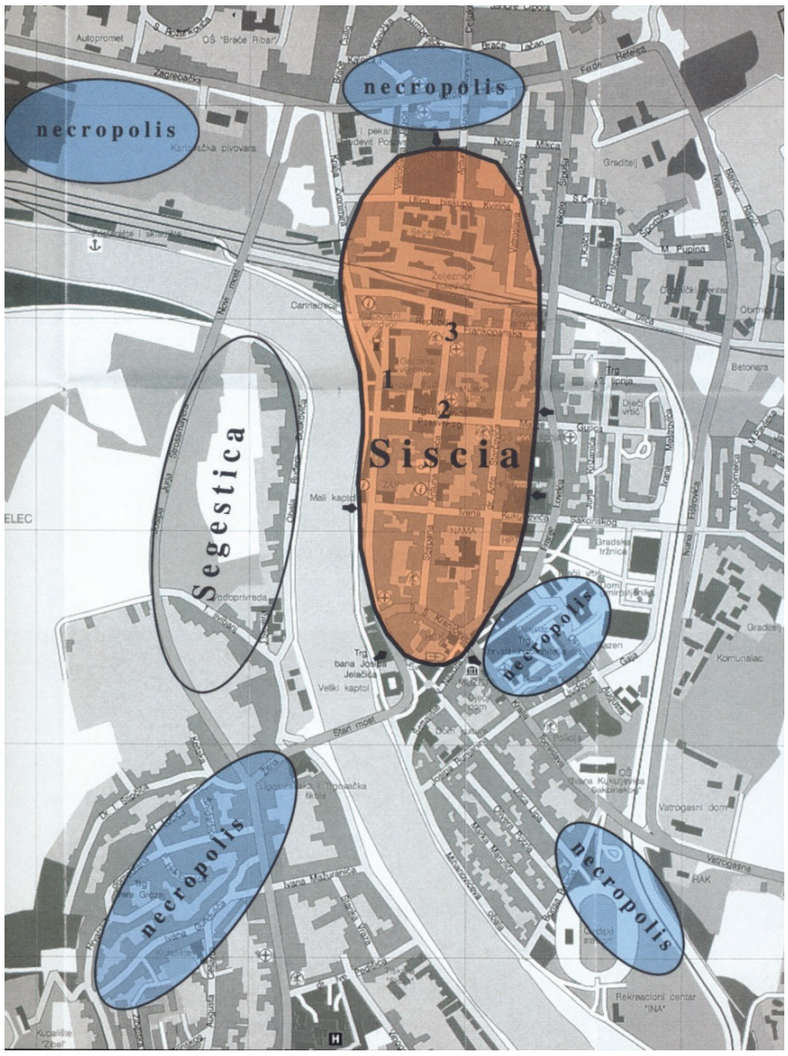
Hrvati se u Panoniju naseljavaju tijekom 7. i 8. stoljeća. U 9. stoljeću Sisak se nalazio u Panonskoj Hrvatskoj koja je bila u sastavu franačke države. U stoljećima koja slijede on sve više gubi na geostrateškom značaju. Tijekom tog razdoblja u sisačkoj regiji razvija se poljoprivreda, dok je prometna važnost bila u drugom planu (SLUKAN ALTIĆ, 2004).

Zbog opasnosti od prodora Turaka, Sisak se u 16. stoljeću počinje utvrđivati. Najznačajnija utvrda je sisački kaštel izgrađen 1544. godine na ušću rijeke Kupe u Savu. Tijekom vremena, ušće se na rijeci Savi pomaknulo preko jednog kilometra nizvodno. Do pomicanja ušća rijeke Kupe došlo je zbog izdizanja kupske terase u prostoru samog ušća što je rezultiralo i produžavanjem savskog meandra ispred ušća i njegovo pomicanje na jugoistok (SLUKAN ALTIĆ, 2004) (Sl. 3.2.)

the 4th century AD in Siscia died the Siscian bishop Quirinus who was later proclaimed Saint Quirinus of Siscia and the martyr. Entire Old Sisak (ancient Siscia) was built on the higher ground between the Kupa River and streams of Šulec and Svibovica and confined by the bed of the bed of the Sisak stream. The stream had flooded the surroundings causing the raise of the underground waters so that it was buried in the year 1876 (LOLIĆ, 2006).

The Croats settle Pannonia during the 7th and 8th centuries. In the 9th century the Sisak city was situated in the Pannonian Croatia which was the part of the Frankish state. In the forthcoming centuries the city gradually loses its geostrategic significance. During that period in the Sisak region agriculture begins to develop while the traffic becomes less important (SLUKAN ALTIĆ, 2004).

Because of the risk involving the Turk invasion Sisak began with of fortification in the 16th century. The most important fort was the Sisak castle built 1544 at the



Slika 3.1. *Rekonstrukcija antičke Siscije (1 – terme, 2 – forum, 3 – bazilika, strelicama su označene lokacije gradskih vrata); prema SLUKAN ALTIĆ, 2004.*

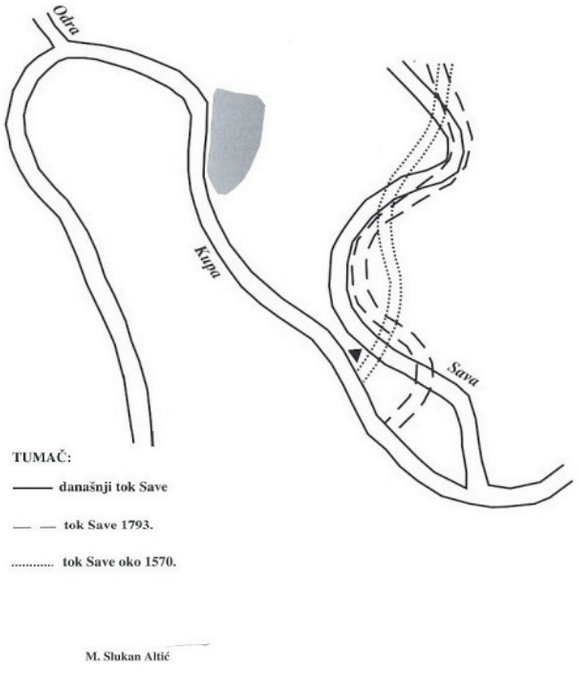
Figure 3.1. *Reconstruction of antique Siscia (1 – thermae, 2 – forum, 3 – basilica, the arrows mark the locations of the gates of the city); after SLUKAN ALTIĆ, 2004*

U 18. stoljeću Sisak opet postaje važno prometno čvorište. Prijevoz žita iz Slavonije, Vojvodine i Banata odvijao se rijekama Dunavom i Savom do Siska, gdje je ono pretovarano u manje brodove te se dalje prevozilo Kupom do Karlovca. Iz Karlovca se transport odvijao Karolinskom i Lujzijanskom cestom do luka Rijeke i Bakra na Jadranu. U tu svrhu je u Sisku izgrađen žitni magazin na desnoj obali Kupe.

Izgradnja Vojnog Siska počinje u 18. stoljeću. Pod kraj tog stoljeća Sisak je podijeljen na Vojni i Civilni, a granica između ta dva dijela bila je rijeka Kupa. Vojni Sisak izgrađen je na izdignutoj terasi desne obale Kupe.

Uz kapelu sv. Kvirina, krajem 18. st. bilo je gradsko groblje. Kapela je srušena, a groblje prekopano 1974. godine. Danas je na toj lokaciji Dječji vrtić.

Gradski mjernik Ivan Fistrović izradio je 1822. godine urbanistički plan Siska koji je realiziran 1829. godine i u sklopu kojeg je napravljena nova parcelacija grada. Načinjen je novi plan ulica, zone grada i prenamjena zemljišta. Ulice su bile položene pravilno, 4 uzdužne i 4 poprečne. Fistrovićev plan ulica se prilično poklapa s planom ulica antičke Siscije. Takav sustav je opstao i do danas, s izuzetkom sjevernog dijela grada koji je izmijenjen gradnjom željezničkog kolodvora i industrijskog kompleksa u njegovom zaleđu.



Slika 3.2. *Pomicanje ušća rijeke Kupe u Savu; prema SLUKAN ALTIĆ, 2004.*

Figure 3.2. *Advance of the mouth of the Kupa towards the Sava River; after SLUKAN ALTIĆ, 2004*

confluence of the Kupa with the Sava River. During time the Kupa mouth in the Sava River advanced about a kilometer downstream. This movement of the Kupa mouth was brought about by the uplift of the Kupa terrace within the range of the mouth itself which resulted with prolongation of the Sava meander in front of the mouth and its movement towards the southwest (SLUKAN ALTIĆ, 2004) (Fig. 3.2.)

In the 18th century Sisak is again the significant traffic junction. The transport of wheat from Slavonia, Vojvodina and Banat used the rivers, namely the Dunav and Sava Rivers to Sisak and, after reloading; it was further transported by smaller ships by the Kupa River upstream to Karlovac. From Karlovac the transport further ran by the Karolina (Luisiana) road towards the ports of Rijeka and Bakar at the Adriatic Sea. To this purpose the wheat storehouse was built in Sisak on the right bank of the Kupa River.

Building of the Military Sisak commences in the 18th century. To the end of that century Sisak is divided into the Military and Civil parts of the city and the borderline between them was the Kupa River. The Military Sisak is built on the uplifted terrace of the Kupa River on its right bank.

Besides the chapel of Saint Quirinus (the chapel was in that par where recently is situated the kindergarten "Sisak Stari") there was towards the end of the 18th century built the city cemetery. The chapel is leveled and the graveyard bulldozed in 1974.

In the year 1822 the city geometer Mr. Ivan Fistrović worked out the town-planning scheme which was realized in 1829 and included the new land subdivision. It contained the new street plan, city zones, and reallocation. Streets were laid in the straight line, four longitudinal and four transversal. Fistrović's street plan fit into the street plan of the ancient Siscia pretty well. This system remained until today with exception of the north part of the town which is altered by the construction of the railway station and industrial complex in its hinterland.

Sisak started to develop quickly and in 1838 it turned into a big market. The railway road Zidani Most – Zagreb - Sisak was constructed in 1862 which enabled the stronger development of industry. During the whole 19th century the city is under construction and expanding. The bridge across the Kupa was built in 1862. In the beginning of the 19th century the river navigation was intensified after the invention of steam engine. The first steamboat sailed into Sisak in 1838. Besides the market and traffic the 19th century was also characterized by development of crafts.

Sisak se ubrzano počeo razvijati, pa 1838. godine postaje veliko trgovište. Pruga Zidani Most-Zagreb-Sisak izgrađena je 1862. godine čime je omogućen snažniji razvoj industrije. Zbog pruge sjeverni dio Siska postaje industrijski dio. Tijekom cijelog 19. stoljeća grad se izgrađuje i širi. Most preko Kupe izgrađen je 1862. godine. Početkom 19. stoljeća izumom parnog stroja ojačala je i riječna plovidba. Prvi parobrod uplovio je u Sisak 1838. godine. U 19. stoljeću se osim trgovine i prometa razvija i obrtništvo.

Vojni Sisak je početkom 19. stoljeća bio iste veličine kao i Civilni ili Stari Sisak, da bi sredinom stoljeća počeo polako zaostajati u razvoju. Taj dio Siska razvija se bez urbanističkog plana.

Sustavna regulacija rijeka Kupe i Save počela je tek sredinom 19. stoljeća, pa je 1868. godine izgrađen nasip duž desne obale Save, od Drenovog Boka do Galdova, a 1859. godine presječeni su meandri kod Topolovca i Prelošćice. Godine 1868. počeli su radovi i na regulaciji Kupe (Sl. 3.3.). Katastrofalna poplava 1934. godine potaknula je 1935. godine izgradnju kvalitetnih nasipa na Savi, Kupi i Odri. Godine 1934. završena su dva mosta, novi zidani most preko Kupe i novi most preko Odre.

Novo groblje kod crkvice sv. Marije (Viktorovac) formirano je na mjestu starog groblja i na njemu se građani Siska pokapaju od 1897. godine. Staro groblje kod crkve sv. Križa je sredinom 19. stoljeća stavljeno izvan funkcije, a gradska groblja su kod sv. Kvirina, kod kapele sv. Marije i kod kapele sv. Petke (OBRADOVIĆ, 1996).

Krajem 19. i početkom 20. stoljeća zatrpana je jama Kontroba (južni dio današnje ulice Franje Lovrića) na kojoj je bilo sajmište. Početkom 20. stoljeća uređuje se park-šuma Viktorovac.

Najveći broj tvrtki bio je smješten uz željezničku prugu (današnja sjeverna industrijska zona). Druga zona bila je duž grabe Kontroba (današnje ulice I. Meštrovića, J. Engela, kralja Tomislava i J. Runjanina). Treća industrijska zona izgrađena je na desnoj obali Kupe u naselju Caprag. U tom području je 1921. godine Anglo-jugoslavensko petrolejsko dioničko društvo izgradilo 4 skladišta za benzin i petrolej što se smatra začetkom Rafinerije nafte Sisak. U tridesetim godinama prošlog stoljeća područje Capraga je velikim dijelom urbanizirano.

Do kraja tridesetih godina 20. stoljeća formirane su dvije industrijske zone, na sjeveru grada i duž desne kupske obale u Capragu. Godine 1939. počinje s radom talionica u Capragu, koja je preteča Željezare Sisak.

The Military Sisak was in the beginning of the 19th century the same size as the Old Sisak. Only after the middle of the century its development slowly started to lag. That part of Sisak was further developing without the town-planning scheme.

The systematic regulation of the Kupa and Sava Rivers began only by the middle of the 19th century and in the year 1868 the causeway was built along the right bank of the Sava River, from Drenovi Bok to Galdovo, while in 1859 the meanders were cut near Topolovac and Prelošćica. In the year 1868 started the engineering works involving the regulation of the Kupa River. Catastrophic flood from 1934 induced the construction of causeways of better quality the next year on the Sava, Kupa and Odra rivers.

The new cemetery by the chapel of Saint Mary (Viktorovac) was built at the place of the old one. The citizens of Sisak were being buried on the new graveyard since 1897. The old cemetery by the chapel of Saint Cross has been out of function since the middle of the 19th century while the main city graveyard is now by the chapels of Saint Quirinus, Saint Mary and Saint Petka (OBRADOVIĆ, 1996).

By the end of the 19th and in the beginning of the 20th century the Kontroba pit (southern part of the recent Franjo Lovrić street) which then accommodated the city fair was buried. In the beginning of the 20th century the Viktorovac forest park has been cultivated.

The greatest number of firms was located by the railway (recently the northern industrial zone). The second zone was situated along the Kontroba pit (recently the streets of I. Meštrović, J. Engel, king Tomislav and J. Runjanin). The third industrial zone is built on the right bank of the Kupa River in New Sisak in the Caprag settlement. In this area the Anglo-Yugoslav petroleum holding company has built four warehoused for gasoline and petroleum which is thought to be an embryo of the Sisak oil refinery. The thirties of the last century saw the urbanization of the most part of the Caprag area.

Till the end of the thirties of the 20th century the two industrial zones have been created, one in the northern part of the city, and the another along the Kupa bank in Caprag. The year 1939 was marked by the opening of the melting plant in Caprag which is a precursor of the modern steelworks in Sisak.

After the WWII the city has been intensely industrializing. In the fifties of the 20th century Sisak becomes one of the most powerful industrial cities of the former SFRJ. Among the industries the most important were:

Nakon Drugog svjetskog rata počinje intenzivna industrijalizacija grada. U pedesetim godinama 20. stoljeća Sisak postaje jedanod najjačih industrijskih gradova tadašnje države. Istaknute industrije su bile metalurgija, naftna industrija, kemijska i prehrambena industrija te manje drvna industrija. U tom razdoblju razvija se i širi i Rafinerija nafte. Godine 1969. puštena je u rad i Termoelektrana, a 1976. godine otvorena je i Termoelektrana Sisak II. Najjače industrijsko širenje zabilježeno je u sedamdesetim godinama, a počinje stagnirati u osamdesetim.

Novi most preko rijeke Save izgrađen je 1973. godine, a povezuje industrijsku zonu s cestom prema Popovači.

U Domovinskom ratu Sisak je bio na prvoj crti bojišnice te je dosta stradao. Bombardirana su industrijska postrojenja Željezare Sisak, Rafinerije nafte Sisak, kemijske industrije, Termoelektrane i terminala Jadranskog naftovoda. Tijekom rata Rafinerija je doživjela 24 topnička napada pri čemu je izazvano 8 velikih požara (SISAČKI TJEDNIK, 1992).

Nakon Domovinskog rata Sisak počinje stagnirati, industrijski pogoni se smanjuju ili potpuno prestaju s radom.

metallurgy, oil, chemical and food industries and to a lesser extent the wood industry. In that period the refinery is developing and enlarging its capacities. In the year 1969 the thermal power plant, located near the oil refinery, was set in motion while in 1976 the thermal power plant Sisak II was also open. The most powerful industrial expanding occured in the seventies of the 20th century while in the eighties it was stagnating.

The new bridge across the Sava River was constructed in 1973 leading from the industrial zone towards Popovača.

In the Croatian War for Independence Sisak was on the first front line and it suffered considerably. The industrial plants including the steelworks, petroleum refinery, chemical industry, thermal power plant and Adriatic oil pipeline terminals were bombed. During the war the oil refinery experienced 24 bomb shelling attacks which brought about 8 great conflagrations that spread over the plant (SISAČKI TJEDNIK, 1992).

After the Croatian War for Independence Sisak experienced stagnation, industrial units began to shrink or disappeared completely.



Slika 3.3. *Sisak: Šetalište uz rijeku Kupu (Foto: Ž. Rakarić)*

Figure 3.3. *Sisak: Promenade along the Kupa River (Photo: Ž. Rakarić)*

4. PREGLED GEOMORFOLOŠKE, GEOLOŠKE I HIDROGEOLOŠKE GRAĐE

Sisak je smješten u Savskoj potolini, na aluviju rijeka Save, Kupe i Odre. Rijeke su meandrirajuće i tijekom vremena odlagale su veliku količinu klastičnog materijala na svoje poplavne ravnice. Teren je ravničarski i najveći dio urbane cjeline grada Siska nalazi se na oko 100 m nadmorske visine. Najveća visinska razlika od oko 25 m je između Kupe i Save u središnjem dijelu urbane cjeline Siska (brdo Viktorovac). Industrijska postrojenja (Rafinerije nafte i Željezare Sisak nalaze se na oko 105 m, dok su naftni terminali smješteni na oko 110 m nadmorske visine. Rijeke Kupa i Odra nalaze se na nadmorskoj visini od 97 do 99 m, a rijeka Sava od 93 do 95 m. Svaka od njih teče duboko usječenim koritom (od 3 do 5 m).

Teren šireg područja urbane cjeline Siska izgrađen je od kvartarnih i gornjo tercijarnih sedimenata. Kvartarne naslage prekrivaju 99 % terena, od čega su trećina sedimenti poplava: siltovi i pijesci koji se nalaze na sjeveru, istoku i zapadu istraživanog područja (Sl. 4.1.). U središnjem dijelu, unutar velikog meandra Kupe, nalazimo naslage prapora. Na sjeveru, na području nekadašnje Siscije, istaloženi su sedimenti terasa: siltovi, pijesci i gline. U jugoistočnom dijelu istraživanog terena nalazi se relativno mala površina barskih sedimenata (gline i glinoviti siltovi) koja se nastavlja dalje na jugoistok izvan istraživanog područja. Istočno od Siska, u naselju Topolovac, nalazimo veliku mrtvaju rijeke Save s naslagama pijesaka, siltova i glina. Sedimenti poplava, gline i siltovi, prekrivaju površinski dio urbane cjeline, mjestimično i do dubine od 13 m. Ispod tog pokrovnog sloja dolaze pijesci sa šljuncima u podlozi u vidu izduženih leća, debljine od 2,5 do 15 m. Pokrovne gline i siltovi mjestimično leže direktno na tom sloju šljunka. Ispod šljunaka na dubinama od 15 do 25 m pojavljuju se opet gline. Od juga prema sjeveru i od zapada prema istoku istanjuju površinske gline i siltovi, a dolazi do zadebljanja sloja šljunaka u podlozi (ŠIKIĆ et al., 1978).

Samo 1% istraživanog područja izgrađuju naslage pliocena (paludinske naslage) koji izdanjuju u uskom pojasu uz desnu obalu Kupe (zapadni strmac ispod brda

4. THE OVERVIES OF GEOMORPHOLOGIC, GEOLOGIC AND HYDROGEOLOGIC SETTINGS

Sisak is situated in the Sava depression, on the alluvium formed by the Sava, Kupa and Odra Rivers. The rivers are meandering and during time they deposited the great quantities of clastic material on their floodplains. The terrain is lowland so that the most part of the urban core of the Sisak is situated at about 100 m above the sea level. The greatest difference in altitude measuring about 25 m is between the Kupa and Sava Rivers in the central part of the urban core (Viktorovac hill). Industrial plants (petroleum refinery and steelworks are situated at the altitude of 105 m while the oil pipeline terminals lie at about 110 m altitude). The Kupa and Odra Rivers lie at the altitude between 97 and 99 while the Sava River flows at 93 to 95 m altitude. Each of them flows through the deeply cut riverbed (between 3 and 5 m).

The terrain surrounding the urban core is built of Quaternary and Upper Tertiary sediments and sedimentary rocks. Quaternary deposits cover 99 % of the terrain of which one third is represented by the floodplain sediments: silts and sands which occupy the area to the north, east and west of the investigated terrain (Fig. 4.1.). In the central part, inside the great meander of the Kupa River the loess deposits can be found. To the north, in the area of the former Siscia, the terrace sediments are deposited: silts, sands and clays. In the southeastern part of the investigated area there is rather small patch of land covered by swamp sediments (clays and clayey sands) spreading further to the southeast outside the investigated area. To the east of Sisak in the Topolovac settlement there is big stagnant tributary of the Sava River with deposited sands, silts and clays. The floodplain sediments, clays and silts, cover the surface area of the urban core, in some places to the depth of 13 m. Beneath this cover layer occur sands with gravels at the base, forming the elongated lenses between 2.5 and 15 m thick. The overlying clays and silts sporadically cover this gravel directly. Below the gravels, at the depth of 15 to 25 m clays occur once again. From the south to the north and from the west

Viktorovac). Manje izdanke tih stijena nalazimo i u sjeveroistočnim dijelovima naselja Kanak na strmcu prema poplavnoj ravnici rijeke Save. Sedimenti se sastoje od pijesaka, šljunaka, glina, konglomerata, pješčenjaka i ugljena (PIKIJA, 1987a; PIKIJA, 1987b).

Zbog tektonskih pokreta u kvartaru duž rasjeda pružanja *SZ-JI* dolazi do izdizanja terena na užem području grada Siska na desnoj obali Kupe (Viktorovac), što uzrokuje i njeno meandriranje oko tog izdignutog područja. Istovremeno dolazi do spuštanja područja na lijevoj obali Kupe i stvaranje terasa i poplavnih ravnica Save i Kupe. To tektonsko izdizanje omogućilo je i izdanjivanje starijih naslaga na zapadnom strmcu na Viktorovcu prema Kupi i na strmcu prema Savi između naselja Crnac i Rafinerije nafte Sisak (šljunaka, glina, konglomerata, pješčenjaka i ugljena – sredni do gornji pliocen) (Sl. 4.1.).

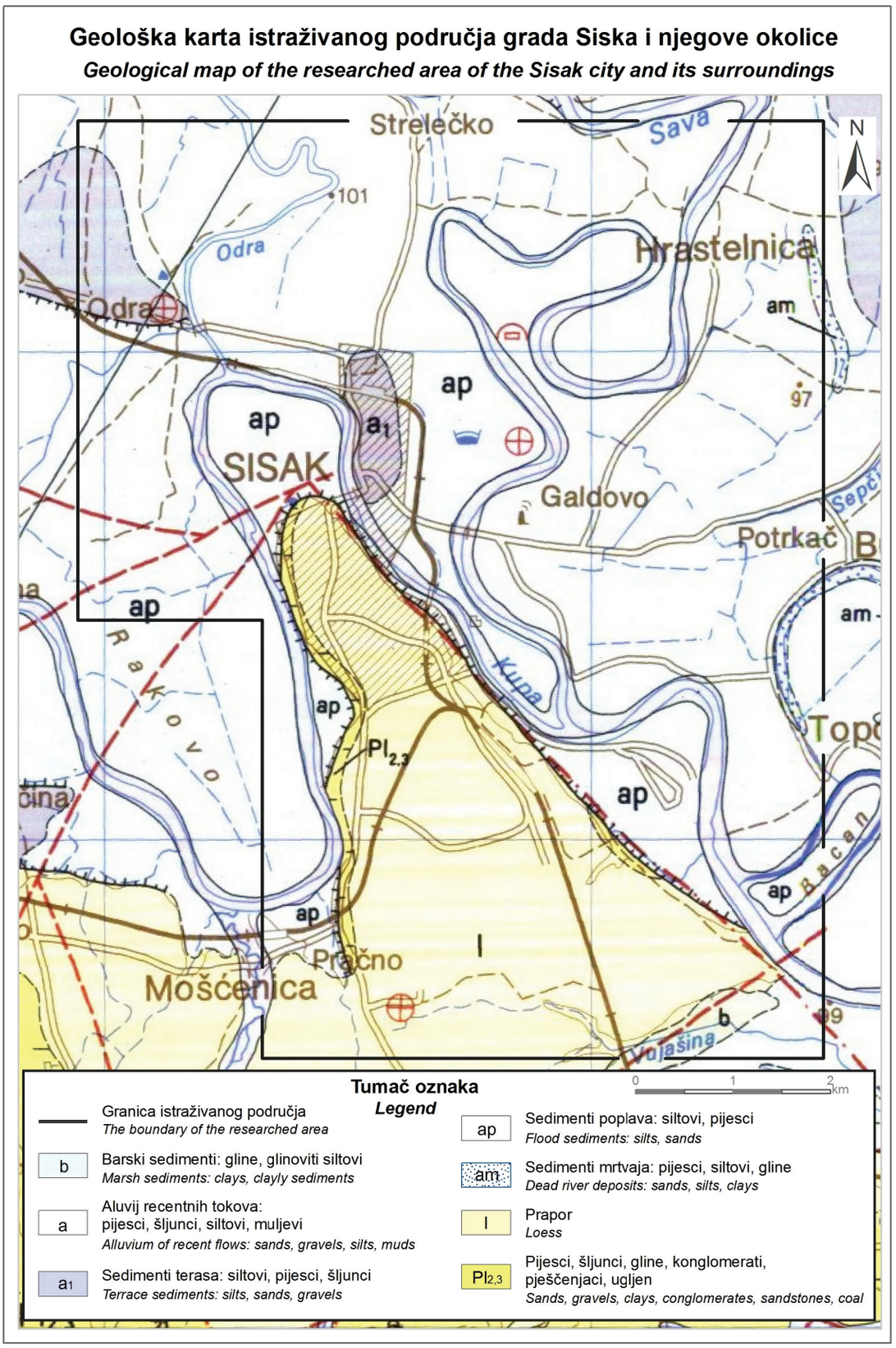
Za razvoj urbanog područja vrlo važna je bila hidrološka i hidrogeološka građa terena. Rijeke Kupa, Sava i Odra povremeno su plavile nizinsko područje Siska, tako da su se naselja razvijala na višim dijelovima reljefa. U velikom meandru Kupe dubina do razine podzemne vode u aluvijalnim naslagama je 2 m, a u nekadašnjoj Sisciji i dijelovima terena oko Save je 4 m. Na cijelom području međuzrnska vodopropusnost naslaga je dobra (ŠIKIĆ et al., 1978).

to the east the topmost layers of clays and silts are thinning while gravels in their base become thicker (ŠIKIĆ et al., 1978).

Only 1 % of the investigated area is built of the Pliocene sediments (Paludina beds) which outcrop in the narrow belt along the right bank of the Kupa River (the west steep slope beneath the Viktorovac hill). The smaller outcrops can be found also in the northeastern parts of the Kanak settlement, on the steep slope toward the Sava River floodplain. The sediments consist of sands, gravels, clays, conglomerates, sandstones and coal (PIKIJA, 1987a; PIKIJA, 1987b).

Owing to tectonic movements along the fault striking NW-SE during the Quaternary, the terrain is uplifted in the area of the Sisak city on the right bank of the Kupa River (Viktorovac) which results in the river meandering around the uplift terrain. Simultaneously, the terrain on the left bank is subsiding with formation of the river terraces and floodplains of the Sava and Kupa. Tectonic uplift resulted also in outcropping of older sediments (gravels, clays, conglomerates, sandstones and coal – Middle to Upper Pliocene) (Fig. 4.1.).

Hydrologic and hydrogeologic settings of the terrain were important for development of the urban area. The rivers Kupa, Sava and Odra occasionally flooded the lowland area so that the settlements developed in the higher parts of the relief. The depth to the underground water in alluvial sediments from the great meander of the Kupa River amounts to 2 m while in the former Siscia and parts of the terrain around the Sava River it is 4 m. In the entire area the intergranular porosity of the sediments is high (ŠIKIĆ et al., 1978).



Slika 4.1. Geološka karta istraživanog područja (PIKIJA, 1987a)

Figure 4.1. Geological map of the investigated area (PIKIJA, 1987a)

5. PEDOLOŠKE ZNAČAJKE ISTRAŽIVANOG PODRUČJA

Opis pedoloških značajki napravljen je na temelju pedološke karte koja je kompilirana iz Osnovne pedološke karte Republike Hrvatske, mjerila 1 : 50 000, list Kostajnica 1 (KALINIĆ, 1981) i list Čazma 3 (KOVAČEVIĆ et al., 1969) (HUSNJAK, 2012) (Sl. 5.1.). Na toj karti izdvojeno je 11 kartiranih jedinica tla, urbana područja i vodene površine (rijeke Kupa, Sava i Odra). U *Tablici 5.1.* naveden je popis tipova tala koji se javljaju u istraživanom području. Osnovne značajke kartiranih jedinica tla koje se odnose na matični supstrat, nagib terena, dreniranost tla, teksturnu oznaku površinskog sloja i površinu kartirane jedinice prikazane su u *Tablici 5.2.* Navedene značajke potpunije karakteriziraju pojedine sistematske i kartirane jedinice tla (HUSNJAK, 2012).

Prema klasifikaciji tla u Hrvatskoj (ŠKORIĆ et al., 1985; ŠKORIĆ, 1986) u istraživanom području se nalaze dva razdjela tla: automorfna i hidromorfna tla. Ona se razlikuju prema načinu vlaženja i sastavu vode. ***Automorfna*** tla se vlaže samo oborinama koje se ne zadržavaju dulji vremenski period u tlu. U istraživanom području nalazi se samo jedno automorfno tlo: koluvij distrični u sklopu kartirane jedinice 1 (Sl. 5.1.; Tab. 5.1. i 5.2.).

Hidromorfna tla obuhvaćaju tla s prekomjernim vlaženjem vodom i njenim duljim zadržavanjem u tlu. Za njih je karakterističan povremen ili stalan višak vode koja se zadržava u tlu. Voda može biti oborinska, slivna, poplavna i/ili podzemna. U poplavnoj ravnici Kupe i Save na istraživanom području razvile su se četiri klase hidromorfnih tala, odnosno klasa pseudoglejnih, nerazvijenih, semiglejnih i glejnih tala (Sl. 5.1.; Tab. 5.1. i 5.2.). Za hidromorfna tla u istraživanom području je karakteristično da su manje ili više zaglejena ili imaju razvijen pseudoglejni ili glejni horizont. Riječ *gley* je ruskog podrijetla i označava *blatnu masu tla*. Formira se zbog duljeg zadržavanja vode – stagniranja vode u tlu. Boja ovih tala je tamna, najčešće plavičasta ili zelenkasta s hrđastim mazotinama. Može biti i „mramorirana", hrđasta s bjeličasto-sivim pjegama.

Za tla **pseudoglejne klase** karakteristično je prekomjerno vlaženje samo površinskih dijelova tla na kojima se

5. PEDOLOGIC CHARACTERISTICS OF THE INVESTIGTED AREA

Description of pedological characteristics is made on the basis of pedological map (HUSNJAK, 2012) compiled from the Basic pedological map of the Republic of Croatia, scale 1: 50,000, sheet Kostajnica 1 (KALINIĆ, 1981) and sheet Čazma 3 (KOVAČEVIĆ et al., 1969) (Fig. 5.1.). Table 5.1. shows the list of the soil types occurring in the investigated area. The basic characteristics of the mapped units referring to parent bedrock such as slope, soil drainage, textural designation of the surface layer and size of the mapped unit, are represented in Table 5.2. The referred characteristics describe in more detail the particular systematic and mapped soil (HUSNJAK, 2012).

According to the classification of soils in Croatia (ŠKORIĆ et al., 1985; ŠKORIĆ, 1986) the investigated area is occupied by two soil divisions: automorphic and hydromorphic soils. These types are distinguished by the mode of moistening and the water composition. ***Automorphic*** soils can be moistened only by precipitation which does not remain in the soil for a longer period. In the investigated area there is only one type of automorphic soil: dystric colluvium as a part of the mapped unit 1. (Fig. 5.1., Tab. 5.1. and 5.2.).

Another division is represented by ***hydromorphic*** soils which include those with excessive moisture that remains in the soil for a longer period. These soils are characteristic for either intermittent or constant surplus of water which remains in the soil. Water can originate from precipitation, overland flow, flood and/or underground flow. The floodplains of the Kupa and Sava Rivers include four classes of hydromorphic soils – pseudogley, undeveloped soil, semigley and gley. (Fig. 5.1., Tab. 5.1. and 5.2.). It is characteristic that hydromorphic soils in the investigated area are more or less gleyed or they contain a developed pseudogley or gley horizon. The word *gley* comes from Russian and denotes a dirty *mess of soil*. It is being formed due to prolonged retention – stagnation of water in soil. The color of these soils is dark, most often bluish or greenish with rusty streaks. It may be also "marbled", rusty with white-grayish dots.

dulje ili kraće zadržava oborinska voda. Pseudoglejna tla se nalaze na jugu istraživanog područja u sklopu kartiranih jedinica 1 i 2. Klasa: **nerazvijena hidromorfna tla** su recentni riječni, jezerski i morski nanosi. Jedini tip tla koji pripada ovoj klasi su aluvijalna tla. **Aluvijalna** tla se formiraju na poplavnoj ravnici donosom i taloženjem zaobljenih i sortiranih čestica. U Sisku su se razvila uz rijeke Kupu i Savu u sklopu kartiranih jedinica: 3, 4, 5 i 6 (Sl. 5.1.; Tab. 5.2.).

Semiglejna tla su s donje strane zaglejena podzemnom vodom, obično na dubini većoj od 1m. To su tla riječnih dolina. U istraživanom području ih ima sjeverno i istočno od velikog meandra rijeke Save na kartiranoj jedinici 6.

U **glejnim tlima** voda se zadržava u gornjem dijelu profila tla, do dubine od 1 m. Na pedološkoj karti istraživanog područja u sklopu kartiranih jedinica 7, 8, 9, 10 i 11 (Sl. 5.1.; Tab. 5.1. i 5.2.) imamo dva tipa glejnih tala: **močvarno glejno i pseudoglej-glej**. Na pedološkoj karti se nalaze svi podtipovi močvarno glejnog tla: epiglejna, hipoglejna i amfiglejna tla. Ona se razlikuju po mjestu oglejavanja. **Epiglejna** tla oglejavaju djelovanjem površinskih voda do 1 m dubine. **Hipoglejna** tla oglejavaju samo odozdo djelovanjem podzemne vode. **Amfiglejna** tla oglejavaju, kako odozgo poplavnom vodom, tako i odozdo podzemnom vodom, dok u sredini imaju slabije oglejen sloj. Za tip tla **pseudoglej-glej** karakteristično je vlaženje soluma pseudoglej-glejno, odnosno u dijelu profila do 0,8 m prisutno je pseudoglejno vlaženje površinskim vodama, a ispod toga hipoglejno vlaženje podzemnom vodom.

Tablica 5.1. Popis tipova tala koji su razvijeni u istraživanom području

Odjel	Klasa	Tip
Automorfna tla	*Nerazvijena tla*	*Koluvij*
Hidromorfna tla	*Pseudoglejna tla*	*Pseudoglej*
	Nerazvijena tla	*Aluvijalno tlo*
	Semiglejna tla	*Semiglej*
	Glejna tla	*Močvarno glejno*
		Pseudoglej-glej

U okviru izrade Osnovne pedološke karte Republike Hrvatske mjerila 1 : 50 000 urbana područja nisu kartirana. Na temelju terenskih istraživanja, a uvažavajući postojeću klasifikaciju tla, u nekartiranom urbanom dijelu istraživanog područja dominiraju **tehnogena** tla (ŠKORIĆ et al., 1985; ŠKORIĆ, 1986) formirana odlaganjem tehnogenih materijala: cigle, betona, asfalta, komada željeza i drugog otpada.

U upotrebi je i termin ***urbana tla*** koji se odnosi na sva tla u urbanim područjima. Urbano tlo je nastalo proce-

The soils from the **pseudogley class** are characteristic for their excessive wetting affecting only the surface parts of the soils with shorter or longer retention of precipitation. Pseudogley soils are found to the south of the investigated area forming a part of the mapped units 1 and 2 (Fig. 5.1.; Tab. 5.1. and 5.2.). The class: **undeveloped hydromorphic soils** are the recent riverine, lake and marine deposits. A single soil type which belongs to this group is alluvial soils. **Alluvial** soils are formed on the floodplains as a result of transport and input of the rounded and sorted particles. In Sisak area they have evolved along the Kupa and Sava Rivers as a part of the mapped units 3, 4, 5 and 6 (Fig. 5.1.; Tab. 5.2.).

Semigley soils are the soils gleyed from below by the underground water, usually at the depth greater than 1 m. They are represented by the soils of the river plains. In the investigated area they occur to the north of the great meander of the Sava River occupying the mapped unit 6.

In the **gley soils** water is retained in the upper portion of the profile, to the depth of 1 m. On the pedological map of the investigated area two types of gley soils appear as a part of the mapped units 7, 8, 9, 10 and 11 (Fig. 5.1.; Tab. 5.1. and 5.2.): **marsh gley and pseudogley**. On the pedologic map there exist all subtypes of marsh gley soils: epigley, hipogley and amphigley soils. They differ according to the place of gleying. **Epigley** soils are forming as a result of activity of surface waters down to the depth of 1 m. **Hipogley** soils are forming only from below by the underground water activity. **Amphigley** soils are forming both from above due to the flooding water and as well as from below by the underground water. For the **pseudogley-gley** type of soil is typical by wetting of the solum pseudogley-gley. Otherwise said, in the part of the profile down to the 0.8 m depth there exists the pseudogley wetting due to the surface waters while beneath this depth the wetting is due to underground water.

Table 5.1. List of soil types developed in the investigated area.

Division	Class	Type
Automorphic soils	Undeveloped soils	Colluvium
Hydromorphic soils	Pseudogley soils	Pseudogley
	Undeveloped soils	Alluvial soil
	Semigley soils	Semigley
	Gley soils	Marsh gley
		Pseudogley-gley

The urban areas have not been mapped as a part of the Basic Pedological Map of the Republic of Croatia, scale 1:50,000. Based on the field investigations and accep-

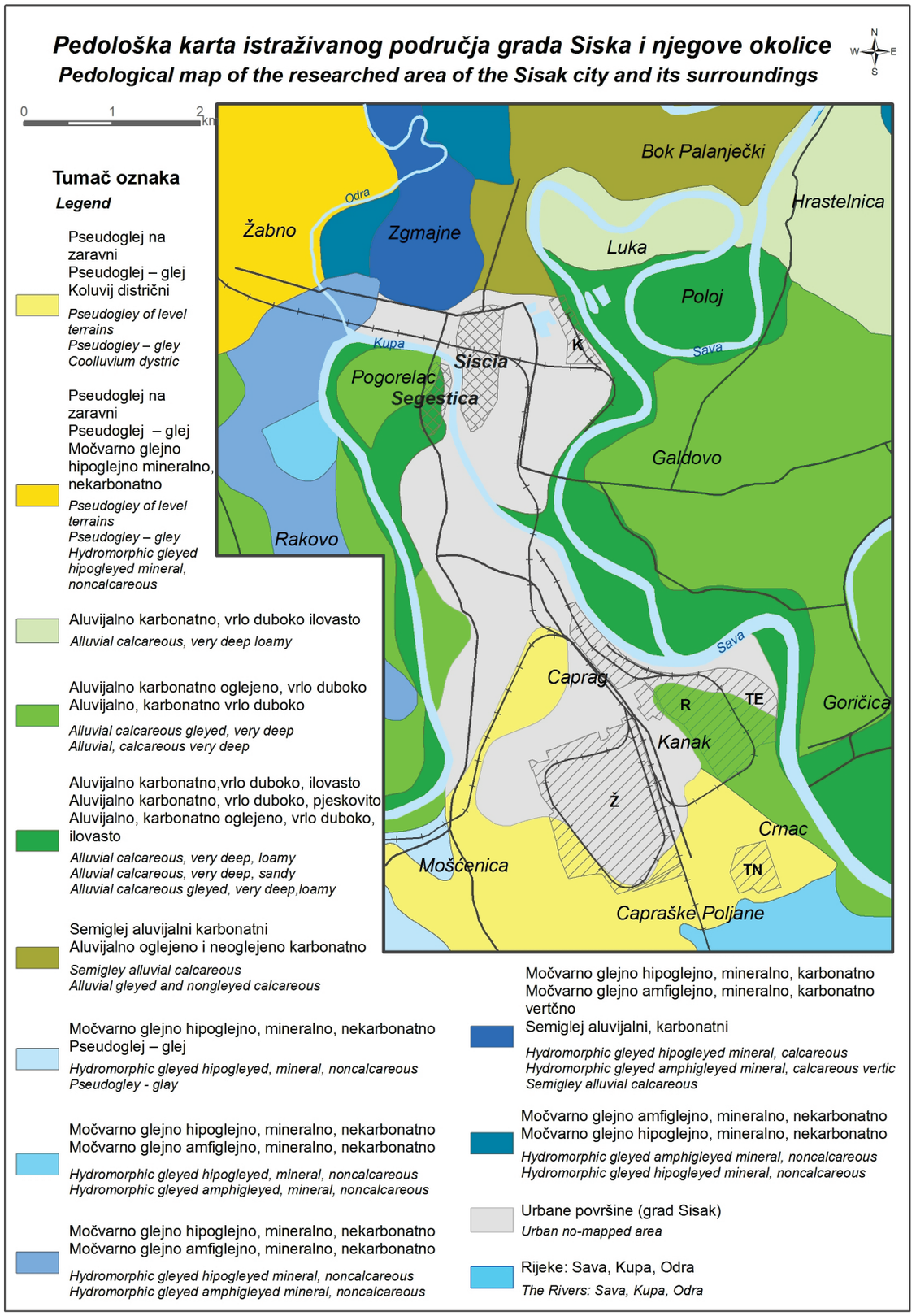
sima urbanizacije: miješanjem, iskapanjem, zapunjavanjem, onečišćenjem i pedogenezom (CRAUL, 1992; WONG et al., 2006; LEHMANN & STAHR, 2007; POUYAT, 2010). Urbana tla u Sisku su formirana u gradskom i industrijskom području. Na temelju terenskih zapažanja može se zaključiti da se uglavnom nalaze na nekartiranom području pedološke karte (Sl. 5.1., Tab. 5.2.). S obzirom na dugu urbanu povijest Siska od preko 2 000 godina, tla su u nekim dijelovima grada formirana pretežito djelovanjem čovjeka. Ona sadržavaju puno naveženog šljunka i pijeska te raznog građevinskog i drugog otpada. Za njih je karakterističan i povišen sadržaj potencijalno toksičnih elemenata (PTE-a).

ting the existent soil classification, in the unmapped urban part of the investigated area the **technogenic** soils are dominant (ŠKORIĆ et al., 1985; ŠKORIĆ, 1986). Technogenic soils are forming by deposition of technogenic material: bricks, concrete, asphalt, pieces of iron and other waste.

The term, ***urban soils***, is also in use which relates to all soils found in urban areas. Urban soil originated in the processes of urbanization: by mixing, digging, burying, contamination and pedogenesis (CRAUL, 1992; WONG et al. 2006; LEHMANN & STAHR, 2007; POUYAT, 2010). Urban soils in Sisak are formed in city and industrial area. A conclusion can be drawn based on the field observations that they can be found mostly in the unmapped area of the pedological map (Fig. 5.1., Tab. 5.2.). With regards to the long urban history of Sisak going beyond 2,000 years the soils in some other parts of the town have been formed predominantly by the human activity. They contain a great quantity of dumped gravel and sand as well as different building and other waste disposal. Owing to this they are characterized by increased content of potentially toxic elements (PTEs).

Tablica 5.2. Osnovne značajke kartiranih jedinica tla u istraživanom području
Table 5.2. The basic characteristics of the mapped soil units in the investigated area.

Kartirana jedinica tla Mapped soil unit			Dominantne značajke kartiranih jedinica tla Dominant characteristics of mapped soil units				Površina u ha Size in ha
Br.	Naziv Designation	% zastupljenosti Presence %	Matični supstrat Parent bedrock	Nagib % Slope %	Dreniranost Drainage	Tekstura površinskog sloja tla Texture of the surface soil layer	
1	Pseudoglej na zaravni; Pseudogley of level terrains Pseudoglej – glej; Pseudogley – gley Koluvij distrični; Colluvium dystric	50 40 10	Pleistocenske ilovače; Pleistocene loams	0 – 3	Umjereno dobra do nepotpuna; Moderate to incomplete	Ilovasta; Loamy	653,6
2	Pseudoglej na zaravni; Pseudogley of level terrains Pseudoglej – glej; Pseudogley – gley Močvarno glejno hipoglejno mineralno, nekarbonatno; Hydromorphic gleyed, hipogleyed, mineral, non-calcareous	60 20 20	Pleistocenske i holocenske ilovače; Pleistocene and Holocene loams	0 – 3	Umjereno dobra do nepotpuna: Moderate to incomplete	Ilovasta; Loamy	370,6
3	Aluvijalno karbonatno, vrlo duboko ilovasto; Alluvial, calcareous, very deep loamy	100	Holocenske ilovače; Holocene loams	0 – 3	Dobra; Good	Ilovasta; Loamy	456,1
4	Aluvijalno karbonatno oglejeno, vrlo duboko; Alluvial calcareous gleyed, very deep Aluvijalno, karbonatno vrlo duboko; Alluvial calcareous, very deep	80 20	Holocenske ilovače i gline; Holocene loams and clays	0 – 3	Umjereno dobra do dobra; Moderately good to good	Ilovasta do glinasto ilovasta; Loamy to clayey loamy	1 456,0
5	Aluvijalno karbonatno,vrlo duboko, ilovasto; Alluvial calcareous, very deep, loamy Aluvijalno karbonatno,vrlo duboko, pjeskovito; Alluvial calcareous, very deep, sandy Aluvijalno, karbonatno oglejeno, vrlo duboko, ilovasto; Alluvial calcareous, gleyed, very deep, loamy	60 10 30	Holocenske ilovače i pijesci; Holocene loams and sands	0 – 3	Dobra do ponešto ekscesivna; Good to somewhat excessive	Praškasto ilovasta; Silty loamy	815,3
6	Semiglej aluvijalni karbonatni; Semigley alluvial calcareous Aluvijalno oglejeno i neoglejeno karbonatno; Alluvial gleyed and non-gleyed calcareous	60 40	Holocenske ilovače; Holocene loams	0 – 3	Dobra do nepotpuna; Good to incomplete	Glinasto ilovasta; Clayey loamy	379,2
7	Močvarno glejno hipoglejno mineralno nekarbonatno; Hydromorphic gley, hipogleyed, mineral, non-calcareous Pseudoglej – glej; Pseudogley – gley	60 40	Pleistocenske i holocenske ilovače; Pleistocene and Holocene loams	0 – 3	Nepotpuna; Incomplete	Glinasto ilovasta; Clayey loamy	58,7
8	Močvarno glejno hipoglejno mineralno nekarbonatno; Hydromorphic gleyed, hipogleyed, mineral, non-calcareous Močvarno glejno amfiglejno mineralno nekarbonatno; Hydromorphic gleyed, amphgleyed, mineral, non-calcareous	70 30	Holocenske ilovača i gline; Holocene loams and clays	0 – 3	Nepotpuna do umjereno dobra; Incomplete to moderately good	Glinasto ilovasta; Clayey loamy	174,7
9	Močvarno glejno hipoglejno mineralno nekarbonatno; Hydromorphic gleyed, hipogleyed, mineral, non-calcareous Močvarno glejno amfiglejno mineralno nekarbonatno; Hydromorphic gleyed, amphigleyed, mineral, non-calcareous	50 50	Holocenske ilovače; Holocene loams	0 – 3	Nepotpuna do umjereno dobra; Incomplete to moderately good	Ilovasta i glinasto ilovasta; Clayey to clayey loamy	296,9
10	Močvarno glejno hipoglejno mineralno karbonatna; Hydromorphic gleyed, hipogleyed, mineral, calcareous Močvarno glejno amfiglejno mineralno, karbonatno vertčno; Hydromorphic gleyed, amphigleyed, mineral, calcareous, vertic Semiglej aluvijalni karbonatni; Semigley alluvial calcareous	50 30 20	Holocenske ilovače i gline; Holocene loams and clays	0 – 3	Nepotpuna do slaba; Incomplete to poor	Ilovasta i glinasta; Clayey to loamy	208,5
11	Močvarno glejno amfiglejno mineralno, nekarbonatno; Hydromorphic gleyed, amphigleyed, mineral, non-calcareous Močvarno glejno hipoglejno mineralno nekarbonatno; Hydromorphic gleyed, hipogleyed, mineral, non-calcareous	60 40	Holocenske gline i ilovače; Holocene loams and clays	0 – 3	Nepotpuna do umjereno dobra; Incomplete to moderately good	Ilovasta i glinasto ilovasta; Clayey to clayey loamy	122,4
12	Vodene površine; Water surfaces						339,1
13	Urbane površine (grad Sisak); Urban no-mapped area (city of Sisak)						1 187,6



Slika 5.1. Pedološka karta istraživanog područja (HUSNJAK, 2013)

Figure 5.1. Pedological map of the investigated area (HUSNJAK, 2013)

6. URBANA GEOKEMIJA

U drugoj polovici prošlog stoljeća dolazi do značajnog širenja gradova potaknutog intenzivnim razvojem industrije i promjenom načina života. Prema podacima Ujedinjenih naroda (2011), 1950. godine u gradovima je živjela trećina svjetske populacije, a već 2010. godine polovina. Statistike procjenjuju da će do 2050. godine dvije trećine svjetskog stanovništva živjeti u urbanim područjima (UNITED NATIONS, 2011).

U Republici Hrvatskoj postoji duga tradicija urbanog razvoja. Slično svjetskom trendu, i u Hrvatskoj do znatnijeg povećanja gradova dolazi tek u pedesetim godinama prošlog stoljeća što je povezano s pojačanim razvojem industrijske proizvodnje. Udio gradske populacije u Hrvatskoj 1953. godine bio je 24,2 % (BERTIĆ, 1972). Prema popisu stanovništva iz 2001. godine u gradovima je živjelo 57,3 % populacije (DEFILIPPIS, 2005). Trend povećanja gradova se nastavio, pa je prema popisu iz 2011. godine udio gradskog stanovništva bio 70,39 %. Podatakje dobiven na temelju broja stanovnika u svih 127 gradova Republike Hrvatske (MARKEŠIĆ et al., 2012).

Grad Sisak je započeo svoj urbani razvoj u doba Rimljana, prije više od 2 000 godina. Njegov razvoj tijekom srednjeg vijeka stagnira. U 19. stoljeću razvojem obrta i prvih industrijskih postrojenja ponovno počinje urbanizacija grada koja u pedesetim godinama prošlog stoljeća doživljava veliki skok. Širenje grada se nastavlja sve do osamdesetih godina prošlog stoljeća kad počinje opadanje industrijske aktivnosti. Danas Sisak s okolicom ima 48 632 stanovnika, a uže gradsko područje 33 681 stanovnika (Državni zavod za statistiku, 2011).

Povećanje gradova i broja stanovnika u njima neminovno povećava antropogene utjecaje u gradskim područjima. Suvremeni način života proizvodi značajnu količinu onečišćujućih tvari. Moderno stanovanje uključuje korištenje grijanja, hlađenja, troše se velike količine vode za piće, ispušta se puno otpadnih voda, intenzivno se upotrebljavaju električni kućanski aparati, nakuplja se kućni otpad i slično. Osim mjesta za stanovanje, u gradovima su smještena i brojna mjesta gdje ljudi rade. Takva mjesta uglavnom imaju i veći antropogeni utjecaj na okoliš nego područja za stanovanje. U uredima, trgovačkim centrima, infrastrukturnim i ostalim objektima producira se raznovrsni otpad.

6. URBAN GEOCHEMISTRY

In the second half of the last century the cities all over the world began their considerable expansion induced by intense development of industry and changing lifestyle. In accordance with data published by UN (2011), in the year 1950 about one third of the world population lived in the cities while in 2010 this number increased to one half. Statistical estimation shows that until 2050 the urban areas will inhabit the two thirds of the world (UNITED NATIONS, 2011).

In the Republic of Croatia there is a long tradition of the urban development. Similar to the world trend the cities in Croatia started their considerable development only in the middle of the last century. This development is associated with stronger increase of industrial production. The lot of city population in Croatia was 24.2 % in the year 1953 (BERTIĆ, 1972). According to the census carried out in 2001 the cities inhabited 57.3 % of the total population (DEFILIPPIS, 2005). The trend of city expansion continued and according to census from 2011 the portion of the city population increased to 70.39 %. This information is based on the number of inhabitants in all 127 cities in Croatia (MARKEŠIĆ et al., 2012).

The city of Sisak commenced its urban development in the Roman period 2,000 years ago. Its growth stagnated during the middle Ages. In the 19th century owing to the expansion of crafts and the first industrial plants the urbanization started again and about 1950 experienced a great leap forward. The city expansion continued until the eighties of the last century when industry started to shrink. Recently, Sisak and its surroundings are inhabited by 48,632 people while in the city area in the strict sense lives 33,681 people (DZS, 2011).

The expansion of cities and the number of their inhabitants unavoidably increases the anthropogenic influences in urban areas. The modern way of life produces considerable quantities of pollution substances. The modern lodging includes the use of heating and cooling, consumption of large quantities of drinking water, delivering of huge emissions of wastewater effluents, intense use of domestic appliances, and accumulation of domestic waste, and other things. In addition to the living places, the cities accommodate a number of pla-

Velika tvornička postrojenja, prijevoz motornim vozilima, tramvajima i vlakovima svakodnevno emitiraju manje ili veće količine ispušnih plinova i otpadnih voda. Uređivanje gradskih površina kao što je „prekapanje" gradskih parkova i vrtova, njihova gnojidba i upotreba pesticida, povećavaju količinu potencijalno štetnih tvari u tlu. Takav intenzivan antropogeni utjecaj narušava prirodnu ravnotežu te se u tlu akumuliraju teški metali i organski onečišćivači.

U osamdesetim godinama prošlog stoljeća povećala se svijest o povezanosti onečišćenja okoliša i ljudskog zdravlja. To je dovelo do intenziviranja geokemijskih istraživanja u gradovima, posebno urbanog tla. Postoji više definicija urbanog tla, ali sve uvažavaju da je urbano tlo ono tlo koje se nalazi u urbanim područjima. Unutar okolišne geokemije razvijena je nova znanstvena disciplina, urbana geokemija. Urbana geokemija proučava urbani ekosustav u urbanim područjima. Ona različitim metodologijama utvrđuje sadržaj potencijalno onečišćujućih tvari u tlu. Metodama urbanog geokemijskog kartiranja određuje se prostorna raspodjela anorganskih i organskih tvari u tlu, njihove geokemijske značajke, a detektiraju se i potencijalno onečišćena područja. Takva istraživanja doprinose otkrivanju točaka onečišćenja u gradovima te njihov monitoring i/ili sanaciju.

Na sadržaj potencijalno toksičnih elemenata u gradovima utječe prirodni sastav tla i antropogeni utjecaji na to tlo. Da bi se dobile informacije o prirodnom (geogenom i pedogenom) sadržaju tvari u tlu, geokemijska istraživanja se provode, osim u gradovima, i u njihovoj neposrednoj ruralnoj i prirodnoj okolici. Usporedbom dobivenih geokemijskih podataka u gradu i njegovoj okolici može se procijeniti koliki je antropogeni utjecaj na njihov sastav u urbanom području. Zato je urbano geokemijsko istraživanje u području Siska napravljeno i u gradu, i u njegovoj ruralnoj okolici.

Dobiveni rezultati urbanih geokemijskih istraživanja koriste se i u legislativi za propisivanje zakonskih graničnih vrijednosti onečišćenja tla s pojedinim onečišćujućim supstancama. Te granične vrijednosti se često propisuju i na temelju upotrebe zemljišta u gradovima. Onečišćivala u urbanom tlu mogu doći u kontakt s ljudima na više načina. Ljudi ih mogu udisati, mogu ih uzeti oralno putem hrane i pića ili mogu dospjeti u ljudski organizam dermalnim kontaktom. S obzirom na to, različita je opasnost za ljude u različitim urbanim okolišima. U Republici Hrvatskoj su u sklopu projekta *„Izrada Programa trajnog motrenja tala Hrvatske"* s pilot projektom predložene i granične vrijednosti za 13 potencijalno toksičnih elemenata i njihovih supstanci čija

ces where people work. These sites often exert the greater anthropogenic influence on their environment with respect to the places for living. Offices, shopping centers, infrastructure and other objects produce various wastes. The great industrial plants, transportation by motor vehicles, streetcars and trains produce greater or lesser emissions of gases and wastewater effluents. The arrangement of urban surfaces such as "digging" of the city parks and gardens, their fertilization and use of pesticides increase the quantity of potentially toxic substances in the soil. Such an intense anthropogenic impact disturbs the natural balance causing the accumulation of heavy metals and organic pollutants in the soil.

During the eighties of the last century the consciousness concerning interrelation of environment pollution and human health has increased. This fact stimulated the more intense geochemical investigations in the cities, the urban soils in particular. There are several definitions of the urban soil but they all take into consideration that the urban soil is a kind of soil located in the urban areas. Inside the field of environmental geochemistry it has been developed a new scientific discipline called urban geochemistry. It is engaged in studying the ecosystem in urban areas. Using different methodologies it determines the content of potentially polluting substances in soil. By the methods of urban geochemical mapping the spatial distribution of inorganic and organic substances in the soil can be defined and potentially polluted areas detected. These investigations contribute to detection of contaminated sites in the cities and to their monitoring and/or recovery.

The content of potentially toxic elements can be affected by both the natural soil composition and anthropogenic impact. In order to obtain information on natural (geogenic and pedogenetic) content of substances in the soil geochemical research is performed not only in the cities but also in their immediate rural and natural surroundings. By comparison of the obtained geochemical results in the city and its surroundings it is possible to assess the anthropogenic impact on the soil composition in the urban area. This is why the urban geochemical investigation in the area of Sisak is conducted both in the city itself and in its rural surroundings.

The results obtained by the urban geochemical investigations are also utilized in the legislation concerning the prescription of the legal limit values of the soil pollution by the particular pollution substances. These limit values are often prescribed with regards to the land use in the cities. Pollutants in the urban soil may come in contact with people in various manners. Peo-

koncentracija ovisi o načinu korištenja zemljišta (MESIĆ et al., 2008).

Grad Sisak je posebno zanimljiv za urbano geokemijsko istraživanje. U njemu se prepliću različiti prirodni i antropogeni utjecaji na tlo. Potencijalni izvori onečišćenja tla u Sisku su raznoliki. Dugotrajna naseljenost područja, donos različitog materijala i taloženje PTE-a Kupom, Savom i Odrom, veliko prometno čvorište i razvijena industrija doprinijele su njihovoj akumulaciji u tlima grada Siska, dok je u njegovoj okolici intenzivna poljoprivredna proizvodnja.

6.1. Potencijalno toksični elementi (PTE)

Elementi u tlu mogu imati geogeno, pedogeno i antropogeno podrijetlo. Geogeni elementi potječu iz matičnog supstrata. Pedogeno podrijetlo imaju geogeni elementi izmijenjeni pedogenetskim procesima, a antropogeni elementi su dospjeli u tlo kao posljedica ljudskih aktivnosti (KABATA-PENDIAS & MUKHERJEE, 2007).

Uobičajeni naziv za elemente koji su geogenog i/ili antropogenog podrijetla, a u povećanoj koncentraciji mogu biti opasni i toksični za ekoksustav je: „teški metali" (engl. *heavy metals*). Naziv „teški metali" ima različito značenje i definicije u različitim znanstvenim disciplinama (Sl. 6.1.). Također, prilikom donošenja zakonskih propisa za zaštitu okoliša ili znanstvenih istraživanja izdvajani su različiti potencijalno štetni elementi i spojevi i klasificirani kao „teški metali". Zbog svega navedenog, izbjegava se korištenje termina „teški metali" u okolišnoj geokemiji. Primjereniji nazivi su: potencijalno toksične tvari ili potencijalno štetne (škodljive, opasne) tvari ili ako se radi samo o elementima, umjesto termina tvar (substanca) koristiti termin element.

Potencijalno toksični elementi mogu se definirati kao kemijski elementi koji mogu biti opasni za ljude, floru i/ili faunu ovisno o njihovoj koncentraciji, biodostupnosti i bioakumulaciji. U kemijske elemente koji su potencijalno toksični, kao i za teške metale, različiti autori i zakonski propisi ubrajaju različite elemente. Kao najčešći anorganski onečišćivači navode se: As, Pb, Zn, Ni, Hg, Cu, Cd, Cr i platinska grupa elemenata. Prema Programu trajnog motrenja tala Hrvatske izdvojeno je 13 PTE-a i predložene su granične vrijednosti za njih. To su: Cd i njegovi spojevi, Cu i njegovi spojevi, Ni i njegovi spojevi, Pb i njegovi spojevi, Zn i njegovi spojevi, Cr, ukupni Cr, Hg i njezini spojevi, Co i njegovi spojevi, Mo i njegovi spojevi, As i njegovi spojevi, Ba i njegovi spojevi, V i njegovi spojevi i Tl i njegovi spojevi (MESIĆ et al., 2008).

ple can inhale them, take them orally by the food and drink or they can invade the human organism by dermal contact. With regard to what is said before the danger to the people in the different urban environments may vary. Within the project "Implementation of the Program of the permanent monitoring of the Croatian soils with a pilot project" were suggested the limit values for 13 potentially toxic elements and their substances the concentration of which depends on the land use (MESIĆ et al., 2008).

The city of Sisak is of particular interest for the urban geochemical investigation. Various natural and anthropogenic influences on the soil combine in the city area. The potential sources of the soil pollution in Sisak are diverse. The long-termed settlement of the area, input of various material and PTEs by the Kupa, Sava and Odra Rivers and its deposition, the big traffic junction and grown up industry all contributed to their accumulation in the soils of the Sisak city while in its surroundings flourish the intense agricultural production.

6.1 Potentially toxic elements (PTEs)

Elements in the soil can be of geogenic, pedogenetic and anthropogenic origin. Geogenic elements originate from the parent bedrock. Pedogenetic origin is characteristic for geogenic elements altered by the pedogenetic processes while the anthropogenic elements appeared in the soil as a result of the human activities (KABATA-PENDIAS & MUKHERJEE, 2007).

The ordinary name given to the elements of geogenic and/or anthropogenic origin which in the elevated concentrations can be dangerous and toxic for the ecosystem is "heavy metals". The term "heavy metals" is loaded with different meanings and definitions in various scientific disciplines. Also, enactment of the laws of environmental protection or scientific investigations included various potentially harmful elements and compounds that were classified as "heavy metals". Owing to all what is said above the use of the term "heavy metals" is avoided in environmental geochemistry. The more appropriate terms are: potentially toxic substances or potentially harmful (detrimental, dangerous) substances or, if only elements are in question, the term substance is replaced by the word element.

Potentially toxic elements can be defined as chemical elements which can be dangerous for people, flora and/or fauna depending on their concentration, bioavailability and bioaccumulation. Various elements are included in the list of potentially toxic elements and "heavy metals" by various authors and regulations. As

6.2. Zakonski propisi za granične vrijednosti sadržaja potencijalno toksičnih elemenata u tlu

6.2.1. Zakonski propisi u EU – primjer Nizozemske i Njemačke

U zemljama Europske unije zakonski propisi nisu jedinstveni. Pojedine zemlje samostalno su razvile svoje metode zaštite tla i definiranja graničnih vrijednosti sadržaja PTE-a i ostalih supstanci u tlu. Propisane su različite granične vrijednosti, a i način propisivanja bio je različit. Navodimo primjer Nizozemske i Njemačke. U Nizozemskoj granične vrijednosti ne ovise o upotrebi zemljišta, dok je to u njemačkim propisima od presudne važnosti.

U nizozemskom Cirkularu optimalnih i intervencijskih vrijednosti za remedijaciju tla (DUTCH GOVERNMENT, 2000; NEW DUTCH LIST, 2009) razlikuju se intervencijska vrijednost (engl. *intervention value*), indkativna razina (engl. *indicative level*) i optimalna (dopuštena) vrijednost (engl. *target value*). Remedijacijska **intervencijska** vrijednost za tlo/sediment je koncentracija koja ozbiljno ugrožava ljude, floru i faunu. Tlo je onečišćeno kada je koncentracija onečišćujućih tvari u tlu/sedimentu viša od intervencijske vrijednosti. **Indikativne** razine onečišćenja određuju se za tvari za koje nema standardiziranih mjerenja i analiza ili gdje ne postoji dovoljno podataka za određivanje toksičnosti navedenih tvari, a time i nemogućnosti postavljanja pouzdanih intervencijskih vrijednosti. **Optimalna** vrijednost je vrijednost za relativno nezagađena tla. Ona označava razinu kvalitete tla. Tu razinu treba postići ako se vrši remedijacija tla tj. potpuni oporavak funkcije tla za ljude, biljke i životinje. Smatra se da u relativno nezagađenim dijelovima Nizozemske uglavnom treba biti optimalna vrijednost za tlo.

Njemačka regulatorna politika definira načine (engl. *pathway*) na koji onečišćivala mogu dospjeti do čovjeka (BBodSchV, 1999). Razlikuje se izravan kontakt tlo-čovjek, transfer onečišćivala iz poljoprivrednog zemljišta posredno preko biljaka do čovjeka i transfer iz pašnjaka preko biljaka (životinja) do čovjeka. Također se razlikuju tri vrste vrijednosti: granične vrijednosti (engl. *trigger*), provedbene (engl. *action*) i preventivne (engl. *precautionary*). Navedene vrijednosti se propisuju ovisno o upotrebi zemljišta i vrsti onečišćujuće tvari. **Granične vrijednosti** su koncentracije onečišćivala u tlu za koje je potrebno poduzeti naknadna istraživanja tla da bi se ustanovilo jesu li štetne. **Provedbene vrijednosti** ned-

the most frequent inorganic pollutants the following elements can be listed: As, Pb, Zn, Ni, Hg, Cu, Cd, Cr and platinum group of elements. In accordance with the Program of permanent monitoring of soils in Croatia the 13 PTEs are selected together with their pertinent limit values. These are: Cd and its compounds, Cu and its compounds, Ni and its compounds, Pb and its compounds, Zn and its compounds, Cr, total Cr, Hg and its compounds, Co and its compounds, Mo and its compounds, As and its compounds, Ba and its compounds, V and its compounds and Tl and its compounds (MESIĆ et al., 2008).

6.2 Regulations on limit values for the content of potentially toxic elements in the soil

6.2.1. Regulations in EU – examples of the Netherlands and Germany

In the EU countries the regulations are not uniform. Individual countries developed independently their own methods of soil protection and definition of the limit values of PTEs and other substances in the soil. Different limit values have been prescribed as well as the process of their definition. We refer to the examples of the Netherlands and Germany. In the Netherlands the limit values are independent of the land use while in the German regulation the land use is of crucial importance.

In the Dutch Circular of target and intervention values for the soil remediation (DUTCH GOVERNMENT, 2000; NEW DUTCH LIST, 2009) there is the difference between the *intervention value*, *indicative level* and *target value*. Remediation **intervention** value for the soil/sediment is the concentration which seriously threatens the people, flora and fauna. The soil is contaminated when the concentration of pollutants in the soil/sediment is higher than the intervention value. **Indicative** levels for contamination are defined for the substances lacking the standardized measuring and analyses, or where insufficient data exist for determination of the toxicity of the mentioned substances followed by impossibility of setting the reliable intervention values. **Target** value refers to relative uncontaminated soils. It designates the level of the soil quality. That level must be achieved if the remediation of soil should be undertaken, that is, its total recovery with regards to its function for people, plants and animals. It is assumed that in the relatively uncontaminated parts of the Nether-

vojbeno upućuju na prisutnost škodljivih tvari u tlu. Treba poduzeti daljnja istraživanja i eventualnu remedijaciju. **Preventivne vrijednosti** su propisane kao mjera opreza. Ako postoji mogućnost štetnih promjena u tlu, koje mogu dugoročno ugroziti njegovu upotrebu, treba ga istražiti. Za poljoprivredno zemljište, vrtove (povrtnjake) i travnate površine uzima se u obzir kontakt tlo–biljka.

6.2.2. Zakonski propisi u Republici Hrvatskoj

U Republici Hrvatskoj propisane su samo granične vrijednosti za 7 teških metala u poljoprivrednom zemljištu (Narodne novine 9, 2014) (Tab. 6.1.). Primjena pravilnika za poljoprivredno zemljište neadekvatna je za ostale načine korištenja tla. Na temelju zakona iz nekoliko europskih zemalja (Njemačka, Švicarska, Slovenija, Italija i Slovačka) izrađen je *„Prijedlog graničnih vrijedosti onečišćujućih tvari u tlu prema različitim načinima korištenja tla“* (Tab. 6.2.) (MESIĆ et al., 2008).

Tablica 6.1. *Granične vrijednosti onečišćenja poljoprivrednih zemljišta s PTE-ima.*

Table 6.1. The trigger values of contamination in the agricultural soils by PTEs.

Element	Pjeskovito tlo (*Sandy soil*)	Praškasto – ilovasto tlo (*Silty–loamy soil*)	Glinasto tlo (*Clayey soil*)
	mg/kg		
Cd	0,0 – 0,5	0,5 – 1,0	1,0 – 2,0
Cr	0,0 – 40,0	40,0 – 80,0	80,0 – 120,0
Cu	0,0 – 60,0	60,0 – 90,0	90,0 – 120,0
Hg	0,0 – 0,5	0,5 – 1,0	1,0 – 1,5
Ni	0,0 – 30,0	30,0 – 50,0	50,0 – 75,0
Pb	0,0 – 50,0	50,0 – 100,0	100,0 – 150,0
Zn	0,0 – 60,0	60,0 – 150,0	150,0 – 200,0

U *Tablici* 6.3. prikazane su usporedne granične vrijednosti za onečišćenje tla s teškim metalima u Hrvatskoj, Nizozemskoj i Njemačkoj.

lands the limit values in the soils must generally tend towards the target value.

The German regulatory politics defines the *pathways* by which the contaminants can reach the people (BBodSchV, 1999). There is the difference between the direct contact soil/human, the transfer of contaminants from the agricultural soil indirectly through plants to the people and the transfer from pastures through the plants (animals) to the people. Also, there are three types of values: *trigger*, *action* and *precautionary* values. These three are regulated depending on the land use and sort of the contaminating substance. **Trigger values** are concentrations of contaminants in the soil for which require additional investigations of soils in order to determine their harmful influences. **Indicative values** are prescribed as precautionary measures. If there is any possibility of harmful changes in the soil that may for a long time threaten its use, it must be explored. For the agricultural soil, gardens (vegetable gardens) and grasslands the contact soil-plant is being taken into account.

6.2.2. Regulations in Croatia

In Croatia only the trigger values for 7 heavy metals have been prescribed in the agricultural soil (NN9, 2014) (Tab. 6.1.). Appliance of the rules regulating the agricultural soil is inappropriate for other modes of land use. Based on the regulations from the several European countries (Germany, Switzerland, Slovenia, Italia and Slovakia) it is compiled the “Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use” (MESIĆ et al., 2008) (Tab. 6.2.).

The Table 6.3. contains the comparative trigger values for the contamination of soils by the heavy metals in Croatia, Netherlands and Germany.



Slika 6.1. *Park skulptura pored Željezare Sisak.*
Figure 6.1. *Sculpture park next to the steelworks Sisak.*

Tablica 6.2. *Prijedlog graničnih vrijednosti PTE-a u područjima prema načinu korištenja zemljišta*
Tablica 6.2. *Recommendation for the trigger values of PTEs in areas according to the various modes of land use*

Metali ekstrahirani u zlatotopci *(Metals extracted in aqua regia)*	Tla za poljoprivrednu proizvodnju *(Soils for agricultural production)*	Dječja igrališta *(Kindergartens)*	Područja za stanovanje *(Residential areas)*	Parkovi i rekreacijska područja *(Parks and recreational areas)*	Područja za industrijske i komercijalne svrhe *(Areas for industrial and commercial purposes)*
	mg/kg suhog tla *(mg/kg of dry soil)*				
Arsen i njegovi spojevi *(Arsenic and its compounds)*	20	20	30	50	100
Barij i njegovi spojevi *(Barium and its compounds)*	100	100	200	300	500
Kadmij i njegovi spojevi *(Cadmium and its compounds)*	2	5	10	10	50
Kobalt i njegovi spojevi *(Cobalt and its compounds)*	50	50	75	250	500
Krom, ukupni *(Chromium, total)*	100	100	200	500	750
Bakar i njegovi spojevi *(Copper and its compounds)*	60	60	100	300	500
Živa i njezini spojevi *(Mercury and its compounds)*	2	5	10	30	50
Molibden i njegovi spojevi *(Molybdenum and its compounds)*	10	10	40	250	500
Nikal i njegovi spojevi *(Nickel and its compounds)*	50	50	70	200	500
Olovo i njegovi spojevi *(Lead and its compounds)*	100	100	100	500	1 000
Talij i njegovi spojevi *(Thallium and its compounds)*	1	1	2	5	20
Vanadij i njegovi spojevi *(Vanadium and its compounds)*	50	50	100	200	400
Cink i njegovi spojevi *(Zinc and its compounds)*	200	200	300	700	1 200

Tablica 6.3. *Granične vrijednosti za sadržaj PTE-a u tlima u Hrvatskoj, Nizozemskoj i Njemačkoj*

Table 6.3. *Trigger values for the PTEs content in the soils of Croatia, the Netherlands and Germany*

Metali i elementi u tragovima (*Metals and trace elements*)	Hrvatska (*Croatia*)					Nizozemska (Netherlands)		Njemačka (*Germany*)						
								Direktan kontakt tlo – čovjek (*Direct contact soil – people*)				Kontakt tlo – biljka (*Contact soil – plant*)		
	Tlo za poljoprivrednu proizvodnju (*Soil for agricultural production*)	Dječja igrališta (*Kindergartens*)	Područja za stanovanje (*Residential areas*)	Parkovi i rekreacijska područja (*Parks and recreational areas*)	Područja za industrijske i komercijalne svrhe (*Areas for industrial and commercial purposes*)	Dopuštena vrijednost (Target value)	Intervencijska vrijednost (Intervention value)	Dječja igrališta (*Kindergartens*)	Područja za stanovanje (*Residential areas*)	Parkovi i rekreacijska područja (*Parks and recreational areas*)	Područja za industrijske i komercijalne svrhe (*Areas for industrial and commercial purposes*)	Poljoprivredno zemljište, vrtovi *Agricultural soil, gardens*		Pašnjak (*Pasture*)
								Granična vrijednost (*Trigger value*)				Granična vrijednost (*Trigger value*)	Provedbena vrijednost (*Action value*)	Provedbena vrijednost (*Action value*)
					mg/kg		mg/kg							mg/kg
As	20	20	30	50	100	29,0	55	25	50	125	140	[3,4]200,0	–	50
Ag	–	–	–	–	–	–	[1]15	–	–	–	–	–	–	–
Ba	100	100	200	300	500	160,0	625	–	–	–	–	–	–	–
Be	–	–	–	–	–	1,1	[1]30	–	–	–	–	–	–	–
Cd	2	5	10	10	50	0,8	12	[2]10	[2]20	50	60	–	[6]0,04/0,10	20
Co	50	50	75	250	500	9,0	240	–	–	–	–	–	–	–
*Cr	100	100	200	500	750	100,0	380	200	400	1 000	1 000	–	–	–
Cu	60	60	100	300	500	36,0	190	–	–	–	–	–	–	[7]1 300
Hg	2	5	10	30	50	0,3	10	10	20	50	80	[3]5,0	–	2
Mo	10	10	40	250	500	3,0	200	–	–	–	–	–	–	–
Ni	50	50	70	200	500	35,0	210	70	140	350	900	–	–	1 900
Pb	100	100	100	500	1 000	85,0	530	200	400	1 000	2 000	[5]0,1	–	1 200
Sb	–	–	–	–	–	3,0	15	–	–	–	–	–	–	–
Se	–	–	–	–	–	0,7	[1]100	–	–	–	–	–	–	–
Sn	–	–	–	–	–	–	[1]900	–	–	–	–	–	–	–
Te	–	–	–	–	–	–	[1]600	–	–	–	–	–	–	–
Tl	1	1	2	5	20	1,0	[1]15	–	–	–	–	[5]0,1	–	15
V	50	50	100	200	400	42,0	[1]250	–	–	–	–	–	–	–
Zn	200	200	300	700	1 200	140,0	720	–	–	–	–	–	–	–

*Cr, ukupni krom; Cr, total chromium

[1] indikativni nivo za ozbiljnu kontaminaciju; indicative level for the contaminated soil;

[2] u dvorištima i vrtovima gdje se igraju djeca i uzgaja hrana, granična vrijednost za kadmij je 2,0 mg/kg; [2] in courts and gardens where children play and food is cultivated the trigger value for cadmium is 2.0 mg/kg;

[3]ekstrakcijska metoda je zlatotopka; extraction method: aqua regia;

[4]ako je tlo osiromašeno granična vrijednost za arsen može se smanjiti na 50 mg/kg; if soil is depleted the limit value for arsenic may be reduced to 50 mg/kg;

[5]ekstrakcijska metoda je amonium-nitrat; extraction method: ammonium-nitrate;

[6]na područjima gdje se uzgaja pšenica i druge kulture sklone akumuliranju kadmija provedbena vrijijednost iznosi 0,04 mg/kg, inače iznosi 0,1 mg/kg; in areas where wheat is cultivated together with other cultures prone to accumulation of cadmium the action value is 0.04 mg/kg, otherwise 0.1 mg/kg;

[7]ako pašnjak služi za ispašu ovaca provedbena vrijednost za bakar iznosi 200 mg/kg; if pasture is aimed for ship the action value for copper is 200 mg/kg.

7. METODOLOGIJA ISTRAŽIVANJA

7.1. Terenska istraživanja

Terenski radovi u Sisku obavljeni su tijekom ljeta i jeseni 2010. godine. Tlo je uzorkovano, a uzorci su analizirani prema URGE uputama EuroGeoSurvays Geokemijske ekspertne skupine (OTTESEN, 2008). Planiranje terenskih radova napravljeno je na topografskoj podlozi mjerila 1 : 25 000 i ortofoto snimkama područja u mjerilu 1 : 5 000. Područje južno od Siska je minirano pa su u Hrvatskom centru za razminiranje (HCR, 2010) nabavljene i karte minski sumnjivog područja. Osim topografske podloge, za planiranje terena korištene su pedološka i geološka karta.

Za uzorkovanje odabrana je pravilna kvadratna mreža. Veličina kvadrata je 0,5 x 0,5 km u urbanom području i 1 x 1 km u ruralnoj okolici. Lokacija uzorkovanja bila je u središtu kvadrata ili ako to nije bilo moguće, uzorak je uzet što je bilo najbliže moguće središtu. Uzimani su kompozitni uzorci koji su se sastojali od 5 poduzoraka. Četiri poduzorka uzeta su na vrhovima kvadrata 2 x 2 m i jedan u sredini. Dubina uzorkovanja iznosila je 0 – 10 cm. „0“ je bila na površini nakon micanja biljnog pokrova, odnosno trave, lišća i sl. Koordinate lokacije uzorkovanja očitane su GPS-om ili u gradskom području s ortofoto karte u Gauss-Krügerovoj projekciji u 5-toj zoni. Ukupna površina istraživanog terena je 65,18 km^2 i na njoj su uzeta 144 uzorka.

7.1.1. Kontrola kvalitete uzorkovanja

Da bi se osigurala pouzdanost geokemijskih podataka provodi se kontrola kvalitete uzorkovanja uzimanjem terenskih duplikata uzoraka. Terenski duplikati se koriste za procjenu varijacija analitičkih rezultata uzoraka uzetih na istom mjestu odnosno u neposrednoj blizini. Uzorak i njegov duplikat služe i za predviđanje hoće li analitički rezultati biti isti ako se drugi put uzorkuje na istom mjestu. Procjena varijabilnosti rezultata na terenu je posebno važna za monitoring tla (REIMANN et al., 2008). Zato se prilikom uzorkovanja treba uzeti 5 – 10 % duplih terenskih uzoraka. Dupli uzorci trebaju biti raspršeni na cijelo istraživano područje tj. ne smiju biti uzeti po redu i biti grupirani samo u jednom dijelu

7. METHODOLOGY OF INVESTIGATION

7.1 Field research

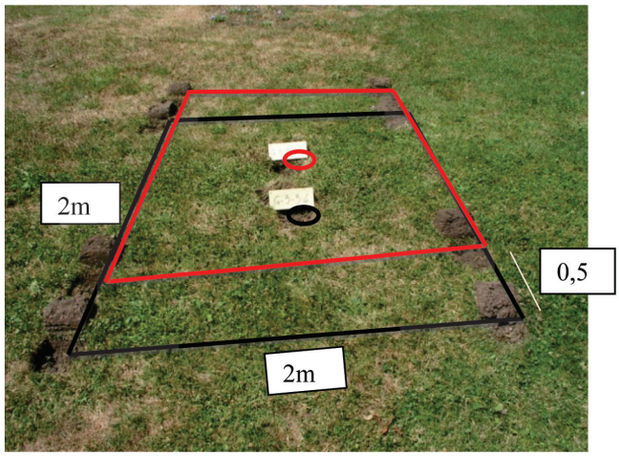
The field research in Sisak was carried out during the summer and autumn of 2010. The soil was sampled and samples were analyzed according to URGE instructions of EuroGeoSurvays Geochemical Expert Group (OTTESEN, 2008). The planning of the field works was carried out on the topographic maps, scale 1: 25,000 and ortophoto maps of the investigated area, scale 1: 5,000. The area to the south of Sisak is a mined terrain so that the Croatian Mine Action Center (HCR, 2010) was asked for and kindly supplied the maps of the mine suspect areas. Additionally to the topographic base the pedological and geological maps were also utilizes in the planning.

The regular square grid was selected for sampling. The grid size was 0.5 x 0.5 km in the urban area and 1 x 1 km in the rural surroundings. The sampling location was placed in the center of the grid or, if not feasible, as close to the center as possible. The samples were composite, consisting of 5 subsamples. The four subsamples were taken in the corners of the grid of 2 x 2 km size and one in the center. The sampling depth was 0 - 10 cm. “0” was on the surface after removing of the litter, that is, grass, fallen leaves and others. Coordinates of the sampling locations were recorded by GPS or, in the city area, from the ortophoto map based on the Gauss-Krüger coordinate system in the 5th zone. The total surface area of the investigated terrain was 65.18 km^2 which included 144 samples.

7.1.1. Sampling quality control

The quality control is being carried out during the sampling process in order to ensure the reliability of geochemical data. It is achieved by taking the field sample duplicates. The field duplicates are used for assessment of variations in samples collected from the same site or in the immediate vicinity. The sample and its duplicate serve also in forecasting the uniformity of analytical results if the sampling procedure will be carried again on the same site. Assessment of variability of the results from the field work is particularly important for the

terena. Tijekom uzorkovanja u Sisku, na svakom dvadesetom mjestu uzorkovanja, uzet je i terenski duplikat uzorka. Sveukupno je uzeto 7 terenskih duplikata. Terenski duplikati uzoraka uzimani su na istom mjestu i na isti način kao kompozitni uzorci samo su mjesta uzorkovanja translatirana u odnosu na originalni uzorak za 0,5 m (Sl. 7.1.).



Slika 7.1. Shema uzimanja jednog kompozitnog uzorka (crno) i njegovog duplikata (crveno).

Figure 7.1. The sampling scheme of collecting a composite sample (black) and its duplicate (red).

7.2. Laboratorijska ispitivanja

Krajem 2010. i tijekom 2011. godine u laboratoriju Hrvatskog Geološkog Instituta uzorci tla pripremljeni su za kemijske analize. Uzorci su osušeni na sobnoj temperaturi, usitnjeni i prosijani na frakciju < 2 mm. Nakon usitnjavanja i homogeniziranja u ahatnom mlinu odvagano je 5 grama uzorka za kemijske analize.

Kemijske analize napravljene su **inducirano spregnutom plazmom – masenom spektrometrijom (ICP MS)** (*engl. Inductively Coupled Plasma Mass Spectroscopy*). ICP MS je analitička metoda koja kombinira inducirano spregnutu plazmu i maseni spektrometar. Plazma je struja atoma argona zagrijana na temperaturi od oko 8 000 °C. Otopina uzorka tla se kao aerosol dispergira u „plamen“ argonske plazme. Uzorak disocira u ione čija masa se mjeri u masenom spektrometru. Ova analitička tehnika može determinirati veliki broj elemenata s jako niskom granicom detekcije, jer joj je osjetljivost jako visoka. Donja granica detekcije je najniža koncentracija nekog elementa koja se može izmjeriti određenom metodom.

monitoring of the soil (REIMANN et al., 2008). To this purpose 5 - 10 % duplicates ought to be collected in the field during sampling. The duplicates must be scattered over the entire investigated area, that is, they must not be collected in a sequence or be grouped only in a particular corner of the investigated area. During sampling in Sisak, at each twentieth sampling site the duplicate sample was also collected. In total, 7 field duplicates were collected. They were taken on the same site and in the same way as the composite samples; only the sampling sites have been translated 0.5 m with regard to the original sample (Fig. 7.1.).

7.2 Laboratory research

By the end of the year 2010 and during 2011 in the laboratory of HGI-CGS the soil samples were prepared for the chemical analyses. The samples were dried at the room temperature, powdered and sieved to the < 2 mm. After sieving and homogenizing in the agate mortar 5 grams of the sample were pondered for the chemical analyses.

Chemical analyses were performed by *Inductively Coupled Plasma Mass Spectroscopy*. ICP MS is an analytical method combining inductively coupled plasma and mass spectrometer. Plasma is the stream of argon atoms heated at the temperature of about 8,000 °C. Dissolved soil sample is dispersed in the form of aerosol into the "flame" of argon plasma. The sample is dissociated into ions whose mass is measured in the mass spectrometer. This analytical technique can determine the great number of elements with low detecting limits owing to its high sensitivity. The lower detection limit is the lowest concentration of an element that can be measured by the selected method.

The bulk of the sample weighing 0,5 g (< 2 mm) is digested in the 90 ml of aqua regia, then heated and boiled for one hour in the hot bath (95 °C). *Aqua regia* is the mixture of concentrated nitrate acid (HNO_3) and hydrochloric acid (HCl) in the ratio of 1:3. It has a strongly oxidizing effect dissolving the metals. After the cooling, up to 300 ml of 5 % HCl is added up to the solution. Solution is analyzed by the Perkin Elmer Elan 6000/9000 Inductively Coupled Plasma Emission Mass Spectrometer-u (ICP-MS) for the set of 53 chemical elements in the ACME Analytical Laboratories, Vancouver (Canada).

7.2.1 Quality control of the laboratory analyses

The quality of the measured data, that is, precision and accuracy of the employed analytical (*Quality Control; abbr. QC*) (REIMANN et al., 2008) is determined by

0,5 g uzorka (< 2mm) razoreno je u 90 ml zlatotopke i izluživano jedan sat u vrućoj (95 °C) vodenoj kupelji. Zlatotopka (engl. *aqua regia*) je smjesa koncentrirane dušične (HNO_3) i kloridne (HCl) kiseline u omjeru 1:3. Ima jako oksidirajuće djelovanje i otapa metale. Nakon hlađenja, otopina je nadopunjena do 300 ml s 5 % HCl-a. Otopina je analizirana na Perkin Elmer Elan 6000/9000 Inductively Coupeld Plasma Emission Mass Spectrometeru (ICP-MS) na set od 53 kemijska elementa u ACME Analytical Laboratories, Vancouver (Kanada).

7.2.1. Kontrola kvalitete laboratorijskih ispitivanja

Kvaliteta mjerenih podataka tj. preciznost i točnost korištene analitičke tehnike (engl. *Quality Control; abbr. QC*) (REIMANN et al., 2008) određuje se ponavljanjem laboratorijskih uzoraka i međunarodnih standarda u setu uzoraka pripremljenih za kemijske analize. **Preciznost** je „blizina" rezultata dobivenih ponavljanjem kemijske analize istog uzorka. Ona pokazuje raširenost ili varijabilnost ponovljenih mjerenja istog uzorka tj. koliko je precizno određena koncentracija nekog elementa u uzorku. Preciznost nije povezana s „istinitom", tj. pravom koncentracijom elementa u uzorku nego s distribucijom nasumične pogreške. Preciznost je u direktnoj relaciji sa standardnom devijacijom. Niska standardna devijacija upućuje na visoku preciznost. Ona se obično povezuje s mean-om i izračunava kao koeficijent varijacije – C.V. u postocima. Za izračun preciznosti u uzorcima iz Siska umetnuto je 18 ponovljenih laboratorijskih uzoraka (Tab. 7.1.).

Točnost (engl. *Accuracy*) je odstupanje mjerenih podataka uzorka od mjerenih vrijednosti međunarodnog geokemijskog standarda (engl. *Standard Reference Material – SRM*). S točnošću se utvrđuje prisutnost eventualne sistematske pogreške. Analitički rezultati mogu biti točni, no to ne znači da su istiniti. Za određivanje točnosti u set uzoraka dodano je 27 uzorka geokemijskih standarda: STD DS7 (7 uzoraka), STD OREAS45PA (8 uzoraka), STD DS8 (8 uzoraka) i SO-2 (4 uzorka) (Tab. 7.2.).

the reruns of the laboratory samples and international standards in the set of samples prepared for the chemical analysis. **Precision** is the "closeness" of results obtained by the rerun of the chemical analysis of the same sample. It shows the scatter or variability of the repeated measurements of the same sample, that is, how much precisely is determined the concentration of certain element in the sample. Precision is not related with "true", or real, concentration of an element in the sample but with distribution of the random error. It is in direct relation with standard deviation. The low standard deviation points at high precision. It is usually associated with mean and is calculated as a coefficient of variation – CV displayed in percentages. In order to compute the precision fir the samples from Sisak 18 reruns of laboratory samples are (Tab. 7.1.).

Accuracy is deviation of the measured data from the measured values of the *Standard Reference Material - SRM*. Accuracy defines the presence possible systematic error. Analytical results can be accurate but it does not mean that they are real. In order to determine the accuracy the set of samples is provided with 27 samples of geochemical standards: STD DS7 (7 samples), STD OREAS45PA (8 samples), STD DS8 (8 samples) and SO-2 (4 samples) (Tab. 7.2.).

Tablica 7.1. *Preciznost analiza; broj ponovljenih uzoraka 18 (12,5% populacije).*

Table 7.1. *Precision of analyses; number of reruns is 18 (12.5% population).*

Element	*C.V. (%)	Element	C.V. (%)	Element	C.V. (%)	Element	C.V. (%)
Ag	7	Cr	5	Mn	6	Se	31
Al	12	Cs	11	Mo	6	Sn	14
As	5	Cu	2	Na	17	Sr	6
Au	41	Fe	4	Nb	8	Th	7
Ba	9	Ga	6	Ni	3	Ti	8
Be	19	Hg	15	P	4	Tl	7
Bi	6	In	33	Pb	5	U	5
Ca	6	K	6	Rb	9	V	4
Cd	7	La	5	S	3	Y	3
Ce	5	Li	6	Sb	18	Zn	4
Co	5	Mg	4	Sc	8	Zr	4

*C.V. koeficijent varijacije (engl. *coefficient of variation*)

Tablica 7.2. Točnost kemijskih analiza na temelju geokemijskih standarda: STD DS7, STD OREAS45PA, STD DS8 i SO-2.
Table 7.2. Accuracy of chemical analyses based on the geochemical standards: STD DS7, STD OREAS45PA, STD DS8 and SO-2

	STD DS7			STD OREAS45PA			STD DS8			SO-2		
Element	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)
Ag	890,00	953,00	**107,1**	300,00	311,00	**103,7**	1 690,00	1 769,00	**104,7**	n.a.	n.a.	**n.a.**
Al	0,96	1,06	**110,5**	3,34	3,57	**106,9**	0,93	0,92	**98,9**	8,07	2,40	**29,7**
As	48,20	50,20	**104,2**	4,20	4,00	**95,2**	26,00	25,00	**96,2**	n.a.	n.a.	**n.a.**
Au	70,00	58,00	**83,0**	43,00	46,30	**107,7**	107,00	106,90	**99,9**	n.a.	n.a.	**n.a.**
Ba	410,00	424,00	**103,4**	187,00	178,00	**95,2**	279,00	296,10	**106,1**	n.a.	n.a.	**n.a.**
Be	1,60	1,60	**100,0**	0,60	0,50	**83,3**	5,20	5,20	**100,0**	n.a.	n.a.	**n.a.**
Bi	4,51	4,65	**103,1**	0,18	0,18	**100,1**	6,67	6,74	**101,1**	n.a.	n.a.	**n.a.**
Ca	0,93	0,97	**104,3**	0,24	0,23	**95,8**	0,70	0,72	**102,9**	1,96	0,39	**19,9**
Cd	6,38	6,47	**101,4**	0,09	0,09	**100,0**	2,38	2,46	**103,4**	n.a.	n.a.	**n.a.**
Ce	36,00	40,00	**111,1**	34,00	36,10	**106,2**	29,8	29,20	**97,9**	n.a.	n.a.	**n.a.**
Co	9,70	9,50	**97,9**	104,00	106,30	**102,2**	7,50	7,70	**102,7**	n.a.	n.a.	**n.a.**
Cr	179,00	189,00	**105,6**	873,00	830,30	**95,1**	115,00	118,30	**102,8**	16,00	6,30	**39,4**
Cs	6,36	6,58	**103,5**	1,00	1,14	**114,0**	2,48	2,55	**102,8**	n.a.	n.a.	**n.a.**
Cu	109,00	108,00	**99,3**	600,00	613,06	**102,2**	110,00	111,00	**100,9**	7,00	3,96	**56,6**
Fe	2,39	2,40	**100,4**	16,56	16,94	**102,3**	2,46	2,49	**101,2**	5,56	3,11	**55,9**
Ga	4,60	5,00	**108,7**	16,80	16,70	**99,4**	4,70	4,80	**102,1**	n.a.	n.a.	**n.a.**
Hf	0,11	0,12	**109,1**	0,51	0,51	**100,0**	0,08	0,08	**100,0**	n.a.	n.a.	**n.a.**
Hg	200,00	221,00	**110,5**	30,00	27,00	**90,0**	192,00	202,00	**105,2**	82,00	77,00	**93,9**
In	1,57	1,57	**100,0**	0,09	0,09	**100,0**	2,19	2,26	**103,2**	n.a.	n.a.	**n.a.**
K	0,44	0,47	**106,8**	0,07	0,07	**100,1**	0,41	0,42	**102,4**	2,45	0,05	**2,1**
La	11,70	13,80	**117,9**	16,20	16,30	**100,6**	14,60	15,60	**106,8**	n.a.	n.a.	**n.a.**
Li	29,30	28,60	**97,6**	5,80	6,30	**108,6**	26,30	27,00	**102,7**	n.a.	n.a.	**n.a.**
Mg	1,05	1,06	**100,9**	0,10	0,10	**100,0**	0,60	0,61	**101,7**	0,54	0,10	**18,5**
Mn	627,00	621,00	**99,0**	1 130,00	1 109,00	**98,1**	615,00	614,00	**99,8**	72,00	154,00	**213,9**
Mo	20,50	21,20	**103,0**	0,90	0,96	**106,7**	13,44	14,10	**104,9**	n.a.	n.a.	**n.a.**
Na	0,09	0,10	**107,9**	0,01	0,01	**90,9**	0,09	0,09	**97,7**	n.a.	n.a.	**n.a.**
Nb	0,71	0,47	**66,2**	0,21	0,22	**104,8**	1,10	1,15	**104,5**	n.a.	n.a.	**n.a.**
Ni	56,00	55,00	**98,4**	281,00	305,20	**108,6**	38,10	38,70	**101,6**	n.a.	n.a.	**n.a.**

Tablica 7.2. *Točnost kemijskih analiza na temelju geokemijskih standarda: STD DS7, STD OREAS45PA, STD DS8 i SO-2 (nastavak).*

Table 7.2. *Accuracy of chemical analyses based on the geochemical standards: STD DS7, STD OREAS45PA, STD DS8 and SO-2 (continuation).*

	STD DS7			STD OREAS45PA			STD DS8			SO-2		
Element	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)	Koncentracija (*Concentration*)	Izmjerena koncentracija (*Measured concentration*)	Točnost (*Accuracy*) (%)
P	0,08	0,08	**96,3**	0,03	0,03	**100,0**	0,08	0,08	**101,3**	n.a.	n.a.	**n.a.**
Pb	70,60	69,20	**98,1**	19,00	18,86	**99,3**	123,00	128,12	**104,2**	21	5,40	**25,7**
Rb	35,80	36,40	**101,7**	8,90	9,30	**104,5**	39,00	38,90	**99,7**	n.a.	n.a.	**n.a.**
S	0,19	0,20	**105,3**	0,03	< 0,02	**0,0**	0,17	0,17	**100,0**	n.a.	n.a.	**n.a.**
Sb	4,60	4,60	**98,9**	0,13	0,14	**107,7**	4,80	4,79	**99,8**	n.a.	n.a.	**n.a.**
Sc	2,50	2,70	**108,0**	43,00	45,20	**105,1**	2,30	2,30	**100,0**	n.a.	n.a.	**n.a.**
Se	3,50	3,20	**91,4**	0,50	0,50	**100,0**	5,20	5,40	**103,8**	n.a.	n.a.	**n.a.**
Sn	4,61	4,91	**106,3**	1,60	1,60	**100,0**	6,70	6,90	**102,9**	n.a.	n.a.	**n.a.**
Sr	68,70	75,20	**109,5**	14,00	13,60	**97,1**	67,70	65,50	**96,8**	340,00	8,90	**2,6**
Th	4,40	4,70	**106,8**	6,00	6,80	**113,3**	6,90	6,80	**98,6**	n.a.	n.a.	**n.a.**
Ti	0,12	0,13	**101,6**	0,12	0,14	**113,7**	0,11	0,12	**104,4**	0,86	0,05	**5,3**
Tl	4,19	4,12	**98,3**	0,07	0,09	**128,6**	5,40	5,53	**102,4**	n.a.	n.a.	**n.a.**
U	4,90	4,90	**100,0**	1,30	1,20	**92,3**	2,80	2,80	**100,0**	n.a.	n.a.	**n.a.**
V	84,00	82,00	**97,6**	221,00	222,00	**100,5**	41,00	41,00	**100,0**	64,00	40,00	**62,5**
Y	5,18	6,21	**119,9**	6,30	8,68	**137,8**	6,10	6,20	**101,6**	n.a.	n.a.	**n.a.**
Zn	411,00	394,00	**95,9**	119,00	115,40	**96,9**	312,00	311,30	**99,8**	124,00	58,50	**47,2**
Zr	5,40	5,60	**103,7**	20,50	21,30	**103,9**	2,10	2,10	**100,0**	n.a.	n.a.	**n.a.**

8. STATISTIČKA OBRADA PODATAKA

Statistička obrada podataka napravljena je u IBM® SPSS® programu i StatSoft. Inc.© STATISTICI 7.1.

Geokemijski podaci su kompleksni zbog utjecaja različitih prirodnih i antropogenih procesa Prostorno su ovisni i uglavnom nemaju normalnu prostornu raspodjelu. Raspon njihovih vrijednosti može biti veliki, a ekstremne vrijednosti mogu jako utjecati na rezultate statističke analize. Zato je njihova statistička obrada drugačija od statističke obrade ostalih podataka. U *Tablici 8.1.* navedeni su statistički termini i njihova objašnjenja koji se spominju u atlasu.

Histogram je grafička prezentacija frekvencije distribucije izabrane varijable. Stupci su klase intervala, a njihova visina je proporcionalna frekvenciji klase.

8. STATISTICAL PROCESSING

Statistical processing is performed by IBM® SPSS® and StatSoft. Inc.© STATISTICA 7.1 programs.

Geochemical data are complex because they are subject to various natural and anthropogenic processes. They are spatially dependent and for the most part are not normally distributed. The range of their values may be great and extreme values can strongly affect the results of statistical analysis. This is why their statistical analysis is different in regard to the statistical analysis of other data. In Table 8.1. are displayed statistical terms and their explanations mentioned in the atlas.

Histogram is a graphic representation of the frequency distribution of a selected variable. The columns represent the classes of intervals while their height is proportional to the class frequency.

Tablica 8.1. Statistički termini koji su korišteni u obradi podataka

Table 8.1. Statistical terms applied in the data processing

Statistički parametar *Statistical parameter*	Definicija *Definition*
Srednja vrijednost (engl. *mean*)	Izračunata prosječna vrijednost za podatke. *The computed average value of data.*
Centralna vrijednost (engl. *median*)	Vrijednost koja se u nizu rezultata poredanih po veličini nalazi točno u sredini promatranog skupa podataka dijeleći ga na dva jednaka dijela. To je 50-ti percentil (PETZ, 1997). *The value which in array of data arranged according to their magnitude is found exactly in its middle dividing it in two equal parts. This is the 50th percentile (PETZ, 1997).*
Varijanca *Variance*	Mjera varijabilnosti rezultata. *The measure of variability of the results.*
Standardna devijacija *Standard deviation*	Drugi korijen iz varijance. Za razliku od varijance standardna devijacija se može prikazati grafički. *The square root of variance. Unlike variance the standard deviation can be displayed graphically.*
Normalna raspodjela *Normal distribution*	Simetrična distribucija rezultata mjerenja koji pokazuju tendenciju grupiranja oko jedne središnje vrijednosti i tendenciju raspršivanja oko te vrijednosti. *Symmetric distribution of the results of measuring which show the tendency of grouping around a mean and tendency of dispersion around that value.*
Asimetričnost (engl. *skewness*)	Odstupanje distribucije vrijednosti od simetrije. *Deviation of data distribution from the symmetry.*
Transformacija *Transformation*	Geokemijski podatci najčešće nemaju normalnu raspodjelu. Da bi se postigla normalna raspodjela podataka, potrebno ih je transformirati. Log-transformacijama reduciraju se visoke, a provećaju male vrijednosti podataka. Obično se podaci transformiraju prirodnim logaritmom (ln) ili na bazi 10 logaritma (log10) (REIMANN et al., 2008). *Geochemical data most often are not normally distributed. In order to assume the normal distribution they ought to be transformed. The log-transformations reduce high and increase low data values. Usually, the data are transformed by the natural logarithms (ln) or using the base of 10 (log10) (REIMANN et al., 2008).*
Percentili *Percentiles*	Vrijednosti koje dijele koncentracije određenog elementa u bazi podataka na 100 jednakih dijelova. Tako, npr. 75-ti percentil predstavlja 75% izmjerenih koncentracija nekog elementa koje se nalaze ispod te koncentracije. *The values which divide the concentrations of an element in the database in 100 equal parts. Thus, for example, the 75th percentile represents 75 % of the measured concentration of an element lower than this concentration.*

Box-and-whiskers je pravokutnik (engl. *box*) oko centralne točke (medijana) koja predstavlja izabrani raspon (25-ti i 75-ti percentil) i „brk“ (engl. *whiskers*) izvan pravokutnika koji također predstavlja selektirani raspon (minimum-maksimum) (Sl. 8.1.). Boxplot dijeli vrijednosti koncentracije elementa u 4 jednaka dijela. Medijan je predstavljen ravnom crtom unutar pravokutnika (50-ti percentil). Donja granica pravokutnika je donji kvartil (25-ti percentil), a gornji rub pravokutnika je gornji kvartil (75-ti percentil). Znači unutar pravokutnika se nalazi 50 % podataka. Ravne linije, „brkovi“ koji se crtaju na gornjem i donjem rubu pravokutnika imaju dužinu do minimuma i maksimuma koji su niži od statističkih anomalnih vrijednosti. Svi podaci koji su izvan pravokutnika i „brkova“ (box-and-whiskers-a) su anomalne i ekstremne koncentracije (Sl. 8.1.).

Geokemijska raspodjela elemenata u prostoru može jako varirati zbog prirodne geogene varijacije koncentracije elemenata i/ili njihovog antropogenog unosa. **Geokemijski (prirodni, geogeni) pozadinski šum** (engl. *geochemical background*) je prirodna koncentracija elementa geogenog porijekla koja se nalazi unutar graničnih vrijednosti. G**ranična vrijednost** (engl. *threshold*) definira se kao koncentracija nekog elementa u tlu koja je iznad ili ispod vrijednosti koncentracija geokemijskog pozadinskog šuma. To su jako visoke ili niske koncentracije elemenata. **Geokemijska temeljna vrijednost** (engl. *baseline*) je koncentracija elementa/supstance u okolišu u određenom vremenskom trenutku. Ona je zbroj geogenog pozadinskog šuma i antropogenog unosa nekog elementa.

Anomalne (engl. *outliers*) **i ekstremne koncentracije** su koncentracije elementa koje značajno i vrlo značajno odstupaju od središnjih tendencija statističke raspodjele. Njihov izračun napravljen je na temelju vrijednosti percentila (REIMANN et al., 2005; TUKEY, 1977). Formula za izračun je:

$$A_k = Q_3 + h_1(Q_3 - Q_1)$$

Pri čemu su:

$A_{k\,=}$ anomalne koncentracije

Q_1 = donji kvartil (25-ti percentil),

Q_3 = gornji kvartil (75-ti percentil) i

h_1 – faktor 1,5 za anomalne vrijednosti.

Formula za izračun ekstremne vrijednosti je slična kao i za izračun anomalnih vrijednosti. U njoj se umjesto vrijednosti faktora h_1 upotrebljava faktor h_2 čija vrijednost je 3.

Donja granica detekcije (ili osjetljivosti) (*engl. detection limit, DL*) je najniža koncentracija koja se može

Box-and-whisker is a rectangle (box) around the central point (median) which represents the selected range (between 25th and 75th percentile) and “whiskers” beyond the box which also represents the selected range (minimum – maximum) (Fig. 8.1.). The boxplot divides the element concentration values in 4 equal portions. Median is represented by the straight line inside the box (50th percentile). Lower margin of the box is the lower quartile (25th percentile) while the upper margin represent the upper margin (75th percentile). It means that 50 % of all data inside the box. The length of the straight lines, or whiskers, which are drawn on the upper and lower margins of the box, reaches maximum and minimum, respectively, which are below the statistically defined anomalous values. All data falling outside the box-and-whiskers area are anomalous and extreme concentrations (Fig. 8.1.).

Geochemical distribution of elements in the space can vary considerable due to natural (geogenic) variations in their concentrations and/or their anthropogenic input. **Geochemical (natural, geogenic) background** is a natural concentration of elements of geogenic origin which varies within the range of threshold values. The **threshold value** is defined as concentration of some element in the soil which is above or below the value of geochemical background. They are represented by very high or very low concentration of an element. **Geochemical baseline** is concentration of an element/substance in the environment in a particular time period. It represents the sum of geochemical background and anthropogenic input of some element

Anomalous (outliers) and extreme concentrations are those which significantly and highly significantly deviate from the mean tendencies of the statistical distribution. Their computation is based on the percentile values (REIMANN et al., 2005; TUKEY, 1977).

They are computed from the following formula:

$$A_k = Q_3 + h_1(Q_3 - Q_1)$$

Where:

A_k = anomalous concentrations,

Q_1 = lower quartile (25th percentile),

Q_3 = upper quartile (75th percentile) and

h_1 = index 1.5 for anomalous values.

The extreme values are computed after the formula similar to that displayed above. However, instead of index h_1 the index h_2 is used having the value of 3.

Lower detection limit, LDL is the lowest concentration that can be measured by certain laboratory method

izmjeriti određenom laboratorijskom metodom (ROLLINSON, 1993). Previsoke koncentracije mogu biti nemjerljive određenom analitičkom tehnikom. Takve koncentracije su iznad gornje granice detekcije. Analitičkim podacima čija je vrijednost ispod donje granice ili iznad gornje granice detekcijskog limita su prije statističke obrade dodijeljene vrijednosti prema sljedećim pravilima:

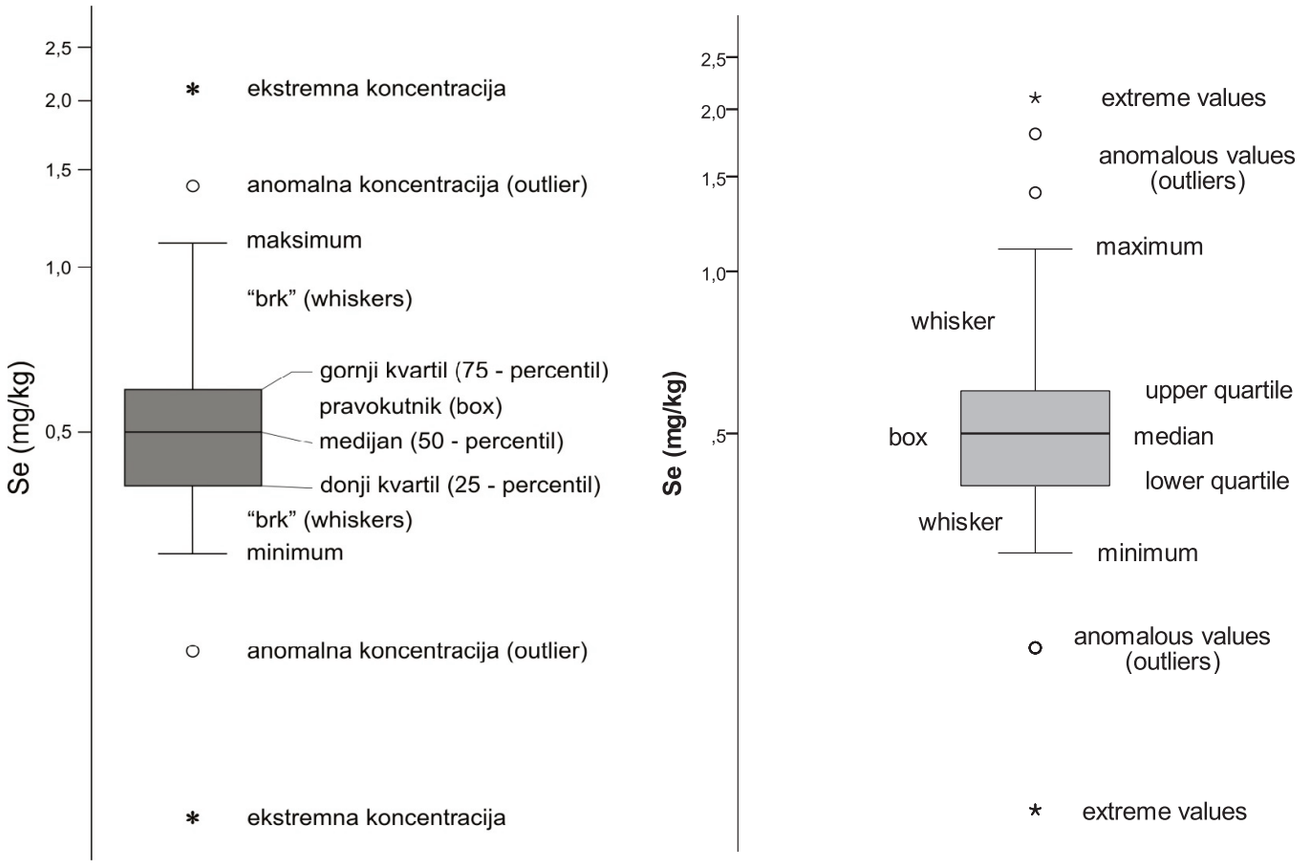
a) ako je sadržaj nekog elementa bio ispod donje granice detekcije zamijenjen je 1/2 vrijednosti donje granice detekcije;

b) ako je koncentracija elementa bila iznad gornje granice detekcije analitičke metode uvećana je za 1 mg/kg

(ROLLINSON, 1993). Concentrations that are too high can also escape the measuring by some analytical technique. Such concentrations are above the upper detection limit (UDL). Before the statistical processing the values are allocated to the analytical data below or above the detection limit according to following rules:

a) If the content of some element is below LDL it will be replaced with ½ value of LDL;

b) If concentration of an element is above UDL it will be increased by 1 mg/kg.



Slika 8.1. Box i whiskers dijagram

Figure 8.1. Box-and-whiskers plot

9. GIS OBRADA PODATAKA

Podaci prikupljeni na terenu i dobiveni rezultati laboratorijskih analiza pohranjeni su u bazu podataka. Svi podaci projekta URGE u Sisku spremljeni su u ESRI® ArcGIS™ bazu. U kreiranoj GIS bazi podataka pohranjene su koordinate lokacija uzorkovanja, okoliš, tip uzorka, razna terenska zapažanja i analitički rezultati. Iz te baze generirane su i geokemijske karte koje prikazuju raspodjelu PTE-a u uzorcima tla.

Na geokemijskim kartama urbanih područja distribucija PTE-a na mjestu uzorkovanja najčešće se prikazuje samo pojedinačnim simbolima tj. „*točkama*". Takvo točkasto prikazivanje na kartama koristi se zbog velike prostorne varijabilnosti sadržaja PTE-a u uzorcima urbanog tla (FORDYCE et al., 2005). Simboli za prikaz koncentracija najčešće su puni krugovi različite veličine ovisno o vrijednosti sadržaja kemijskog elementa na lokaciji uzorkovanja. Zbog preglednosti prikazivanja, koncentracije pojedinog elementa u uzorku se grupiraju u klase. Granice klasa su 5-ti, 10-ti, 25-ti, 50-ti, 75-ti, 90-ti i 98-i percentil. Veličina punog kruga se povećava od najniže klase, a krug je najveći u osmoj, najvišoj klasi. Da bi posebno istaknuli koncentracije iznad 98-og percentila nekog elementa u tlu, oko najvećeg punog kruga iscrtan je još jedan prazan crni krug.

Iako je točkasto prikazivanje koncentracije nekog elementa na geokemijskoj karti najpreciznije, ipak su, zbog preglednosti karte, izgenerirani i poligoni. Poligoni su generirani IDW (Inverse Distance Weighting) interpolacijskom metodom u ekstenziji programa ArcInfo®-a, Geostatistical Analyst. Da bi se izbjegle veće pogreške u izračunu je zadano da međusobni utjecaj imaju samo 4 susjedne točke i da je radijus njihovog utjecaja maksimalno 600 m. S obzirom da su lokacije uzorka međusobno udaljene oko 500 m takvim načinom izračuna osiguralo se međudjelovanje samo susjednih točaka uzorkovanja. Granice klasa poligona također su percentili. Boje za njihovo prikazivanje na geokemijskoj karti su od plave za najnižu klasu do tamnosmeđe za najvišu.

Na geokemijskim kartama su date vrijednosti za statističke parametre: minimum, maksimum, srednju vrijednost, medijan i standardnu devijaciju. Vrijednosti koncentracije pojedinog elementa transformirane su na bazi 10 logaritma (log10) (REIMANN et al., 2008) da bi se dobila normalnija raspodjela. Od log-transformiranih podataka elementa iscrtani su njihovi dijagrami: histogram i box-and-whiskers plot.

9. DATA PROCESSING IN GIS

The data collected in the field and results of laboratory analyses are stored in a data base. All data of the URGE in Sisak are stored in an ESRI® ArcGIS™ base. In this database are stored the coordinates of sampling locations, environment, sample type, various field observations, and analytical results. From this base the geochemical maps displaying the distribution of PTEs in the soil samples have been generated.

On the geochemical maps of the urban areas the concentration of PTEs at each sampling site is most often represented solely by the single symbols, or "*dots*". A dotted display on maps is utilized due to the great spatial variability of the PTEs content in the soil samples of the urban soil (FORDYCE et al., 2005). The symbols displaying the concentrations are most often full circles of different size depending on the concentrations value for an observed element at the location site. Because of perceptiveness of display the concentration of a single element in the sample are grouped in the classes. The class limits are represented 5^{th}, 10^{th}, 25^{th}, 50^{th}, 75^{th}, 90^{th} and 98^{th} percentile. The size of the full circles increases from the lowest class and the circle is the biggest in the eighth, highest class. In order to emphasize the concentrations above the 98^{th} percentile of a single element in the soil another hollow circle is drawn around the biggest full circle.

Although the dotted display of the concentration of a single element on the geochemical map is the most precise the map perceptiveness requires the generation of polygons. The polygons are generated by the IDW (Inverse Distance Weighting) interpolation method, included in the extension of the ArcInfo®, Geostatistical Analyst software. In order to avoid major mistakes only the four neighbor points with maximum 600 m of distance between them are included in calculation as those exerting the most important mutual influence. Considering that the point locations are removed 500 m from each other this mode of computation would assure the interdependence of only the neighbor sampling sites. The class limits concerning the polygons are also percentiles. The colors for their designation on the geochemical map range form blue for the lowest class to dark brown for the highest.

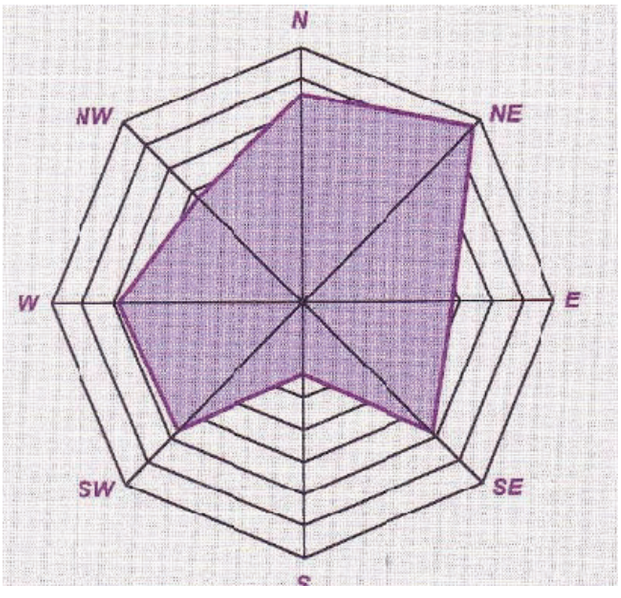
Geochemical maps also include the values of statistical parameters: minimum, maximum, mean, median and standard deviation. The concentration values for every

*

Zbog specifičnosti teksta ovog poglavlja svu korištenu literaturu za dobivanje tih podataka navest ćemo u ovom uvodnom dijelu kako bismo izbjegli nepotrebna ponavljanja literaturnih navoda u daljnjem tekstu. Korištena je je slijedeća literatura: TUĆAN (1957), TRÖGER (1969a,b), TAJDER & HERAK (1972), WEDEPOHL (1969, 1970, 1972, 1974, 1976), ROSLER & LANGE (1976), SCHROLL (1976a, b), ROSE et al. (1979), KRÖMER et al. (1981), ADRIANO (1986), THALMANN et al. (1989), FILIPOVIĆ & LIPANOVIĆ (1995a,b), BERMANEC, (1999), KABATA-PENDIAS & PENDIAS (2001), REIMANN et al. (2003), SLOVENEC & BERMANEC (2003), WMSY (2004), SALMINEN et al. (2005), SHERWOOD (2005), de VOS et al. (2006), KABATA-PENDIAS & MUKHERJEE (2007), HALAMIĆ & MIKO (2009), JOHNSON et al. (2011), ČAKŠIRAN (2011) i ŠORŠA (2014).

Smjer puhanja vjetra je važan za raspršenje elemenata i njihov transport zrakom. Prema podacima meteorološke postaje Sisak. Na *Slici.9.1.* prikazana je ruža vjetrova na području Siska.

Na *Slici. 9.2.* prikazane su lokacije uzorkovanja i legenda koja se odnosi na sve karte prostorne raspodjele elemenata. Rafinerija nafte Sisak i postrojenja Jadranskog naftovoda prikazani su kao „bijele fleke“ zbog toga što nam nije bio dopušten ulaz i uzorkovanje na njihovom području. Stoga se prilikom generiranja karata nije mogla izgenerirati i prostorna raspodjela elemenata u njima.



Slika 9.1. *Ruža vjetrova u području Siska.*

Figure 9.1. *The wind rose in the Sisak area.*

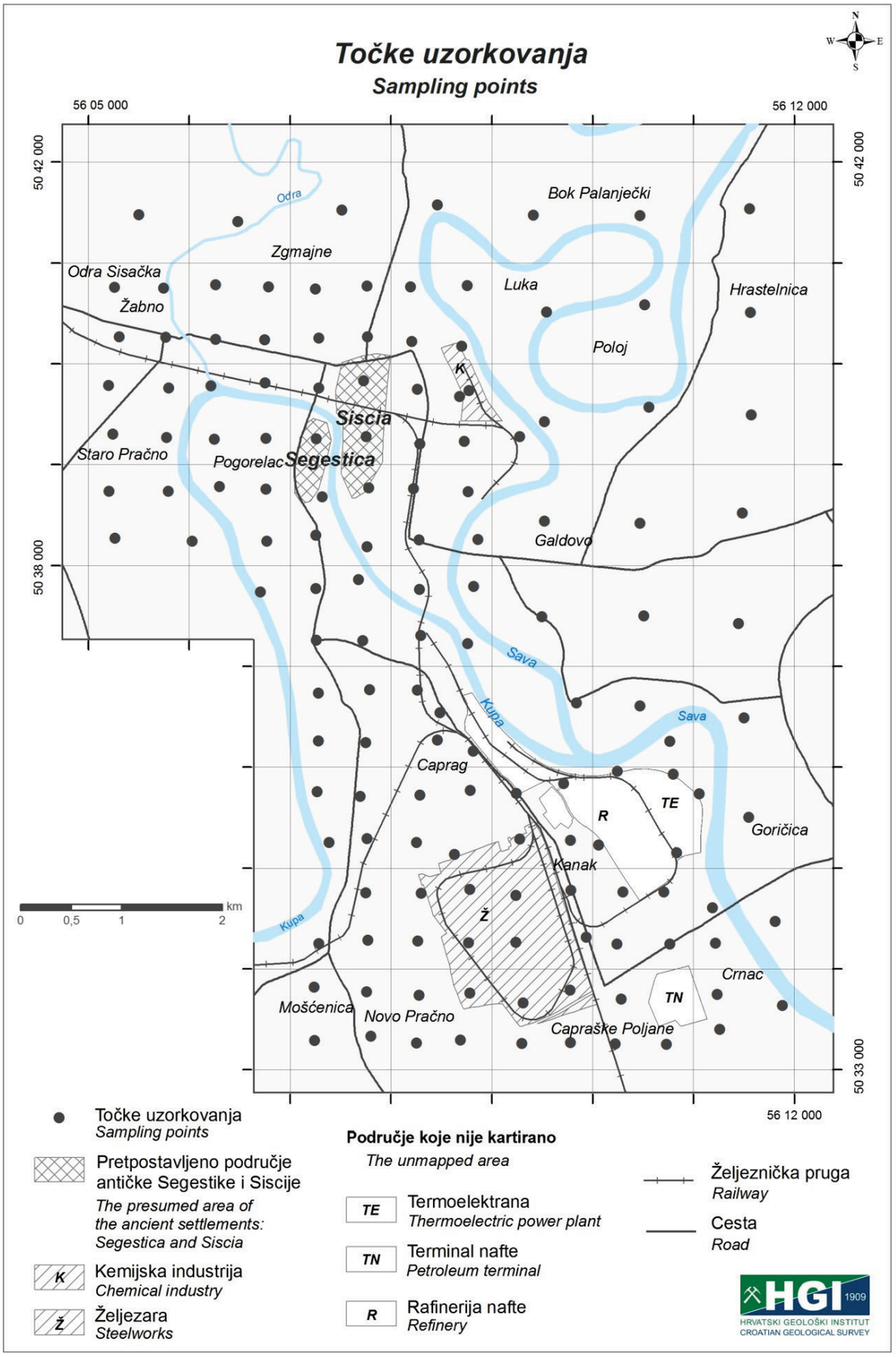
single element are transformed using the Log base 10 (log10) (REIMANN et al., 2008) in order to achieve the distribution closer to normal. The log-transformed data are used in drawing their diagrams: histogram and box-and-whiskers plot.

*

Because of specificity of this chapter all references used in collecting the desired data will be cited in this introductory part of the text in order to avoid unnecessary repetition of cited references further in the text. The following literature is cited: TUĆAN (1957), TROGER (1969a, b), TAJDER & HERAK (1972), WEDEPOHL (1969, 1970, 1972, 1974, 1976), ROSLER & LANGE (1976), SCHROLL (1976a, b), ROSE et al. (1979), KRÖMER et al. (1981), ADRIANO (1986), THALMANN et al. (1989), FILIPOVIĆ & LIPANOVIĆ (1995a,b), BERMANEC, (1999), KABATA-PENDIAS & PENDIAS (2001), REIMANN et al. (2003), SLOVENEC & BERMANEC (2003), WMSY (2004), SALMINEN et al. (2005), SHERWOOD (2005), de VOS et al. (2006), KABATA-PENDIAS & MUKHERJEE (2007), HALAMIĆ & MIKO (2009), JOHNSON et al. (2011), ČAKŠIRAN (2011) and ŠORŠA (2014).

The wind direction is very important for dispersion elements and their airborne transmission. According to data of the Sisak meteorological station the Figure 9.1. shows the rose of the winds of the Sisak area.

Figure 9.2. shows the sampling sites and explanation related to all the spatial distribution maps of elements. The Sisak oil refinery and the plants of the Adriatic pipeline are represented as the “white spots” because of the entrance to that area and sampling were forbidden. This is why the generation of maps could not include the spatial distribution of elements within them.



Slika 9.2. Lokacije točaka uzorkovanja i zajednička legenda za geokemijske karte prostorne raspodjele elemenata.

Figure 9.2. Sampling locations and common legend for geochemical maps of the spatial distribution of elements.

10. OPIS KARATA PROSTORNE RASPODJELE ELEMENATA

10. DESCRIPTION OF MAPS OF SPATIAL DISTRIBUTION OF ELEMENTS

Ag

10.1. Ag – SREBRO (atomski broj 47) SILVER (atomic number 47)

Srebro je element u tragovima s halkofilnim i siderofilnim karakteristikama. Ono je plementi metal koji je asociran s Au, Cu, Pb i Zn. Geokemijske karakteristike srebra slične su bakru.

Prosječni sadržaj u magmatskim stijenama je 0,07 mg/kg (ultrabaziti 0,06 mg/kg, bazalti 0,1 mg/kg i graniti 0,04 mg/kg). Od sedimentnih stijena šejlovi sadrže 0,11 mg/kg, pješčenjaci 0,0 x mg/kg i karbonatne stijene 0,0 x mg/kg. Sadržaj ovog elementa u tlima kreće se od 0,03 do 0,4 mg/kg. U slatkoj vodi prosječan sadržaj srebra je 0,0003 mg/L. Topivo je u kiselim vodama kao Ag^{1+} ili u formi kloridnih kompleksa.

Srebro je dobro mobilno, ali ako je pH tla > 4 onda je ono skoro imobilno. Srebro tvori teško topive halogenske spojeve. Adsorbira se na Fe-Mn okside i na organsku tvar.

Ovaj element je problematičan s aspekta toksičnosti za biljni i životinjski svijet. Jako je otrovan za niže organizme, pogotovo za one koji žive u vodi. Veći sadržaj srebra u tlima s manje organske tvari je potencijalno otrovniji za biljke od onog s većim sadržajem organske komponente.

Srebro se pridobiva prilikom taljenja Cu, Zn i Pb ruda. Ono je plemeniti metal s mnogostrukom tehničkom primjenom (baterije, novac, nakit, srebrna roba, lemljenje, katalizatori, elektronička industrija, posrebrivanje). Otkriveno je oko 4 000 godina pr.Kr. kada se koristilo u izradi nakita i kao sredstvo razmjene.U okoliš se srebro raspršuje kao industrijski otpad, prije svega preko otpadnih voda iz fotolaboratorija, muljeva iz pročistača otpadnih voda, kućnog otpada (baterije, ogledala) te raketa za suzbijanje tuče.

Silver is a trace element with chalcophile and siderophile characteristics. It is a noble metal that is associated with Au, Cu, Pb and Zn. Geochemical characteristics of Ag are similar to that of copper.

Average content in igneous rocks is 0.07 mg/kg (ultramafic rocks 0.06 mg/kg, basalts 0.1 mg/kg and granites 0.04 mg/kg). Of sedimentary rocks the shales contain 0.11 mg/kg, sandstones 0.0 mg/kg, and carbonate rocks 0.0 mg/kg. The content of this element in soil ranges from 0.03 to 0.4 mg/kg. In sweet water the average content of Ag is 0.0003 mg/L. Silver is soluble in acid waters as Ag^{1+} or in the form of chloride complexes.

Silver is well mobile but if the soil pH is > 4 it is almost immobile. Ag forms hardly soluble halogenic compounds. It adsorbs on Fe-Mn oxides and organic matter.

This element is problematic from the aspect of toxicity in the plant and animal world. It is highly toxic for lower organisms, particularly those living in water. Higher contents of Ag in soils with less organic substance are potentially more toxic for plants with respect to soil rich in organic component.

Silver is produced by the smelting of Cu, Zn and Pb ores. It is a noble metal with multiple technical usage (batteries, coins, jewelry, silver ware, soldering, catalysts, electronic industry, silvering). It is discovered about 4,000 BC since when it served as jewelry and as a means of exchange, that is, trade.

Ag is disseminated in the environment as industrial waste, especially through the waste waters from the photo laboratories, mud from the waste water cleaners, from the household wastes (dry cells, mirrors, etc.) and from the anti hail rockets.

Na temelju karte raspodjele koncentracije srebra u tlu, vidljivo je da su povišene vrijednosti isključivo vezane za nekadašnje (Kelti, Rimljani) i sadašnje urbano područje grada Siska te industrijsko područje na jugistoku. Naime, prema ruralnim dijelovima koncentracije srebra u tlima naglo padaju ispod medijana za istraživano područje.

Izmjerene koncentracije srebra u tlima grada Siska kreću se od 33 do 1 678 μg/kg s medijanom od 101,5 μg/

Based on the distribution of the silver content in the soil it is obvious that the elevated values are associated exclusively with former (Celts, Romans) and recent urban area of the city of Sisak as well as with industrial area to the southwest. Namely, toward the rural parts the concentrations of silver in the soil abruptly decline below the median values for the investigated area.

The measured concentrations of Ag in the soils of the Sisak city range between 33 and 1,678 μg/kg with me-

kg. Najveća koncentracija izmjerena je na lokaciji na Pogorelcu. Visoke i anomalne koncentracije izmjerene su i na lijevoj obali Kupe na potezu od željezničke postaje pa sve do sisačke gmajne (Zgmajna) na sjeveru. Na tim područjima nalazila su se keltska i rimska naselja Segestica i Siscija pa su visoki sadržaji ovog elementa u tlu na tom području rezultat ljudske aktivnosti toga vremena (vjerojatno talionice srebrne rude, kovnice novca i nakita). Pogledom na kartu, moglo bi se reći da raspodjela srebra u tlu na tom području ocrtava nekadašnja prapovijesna naselja (Sl. 3.1.).

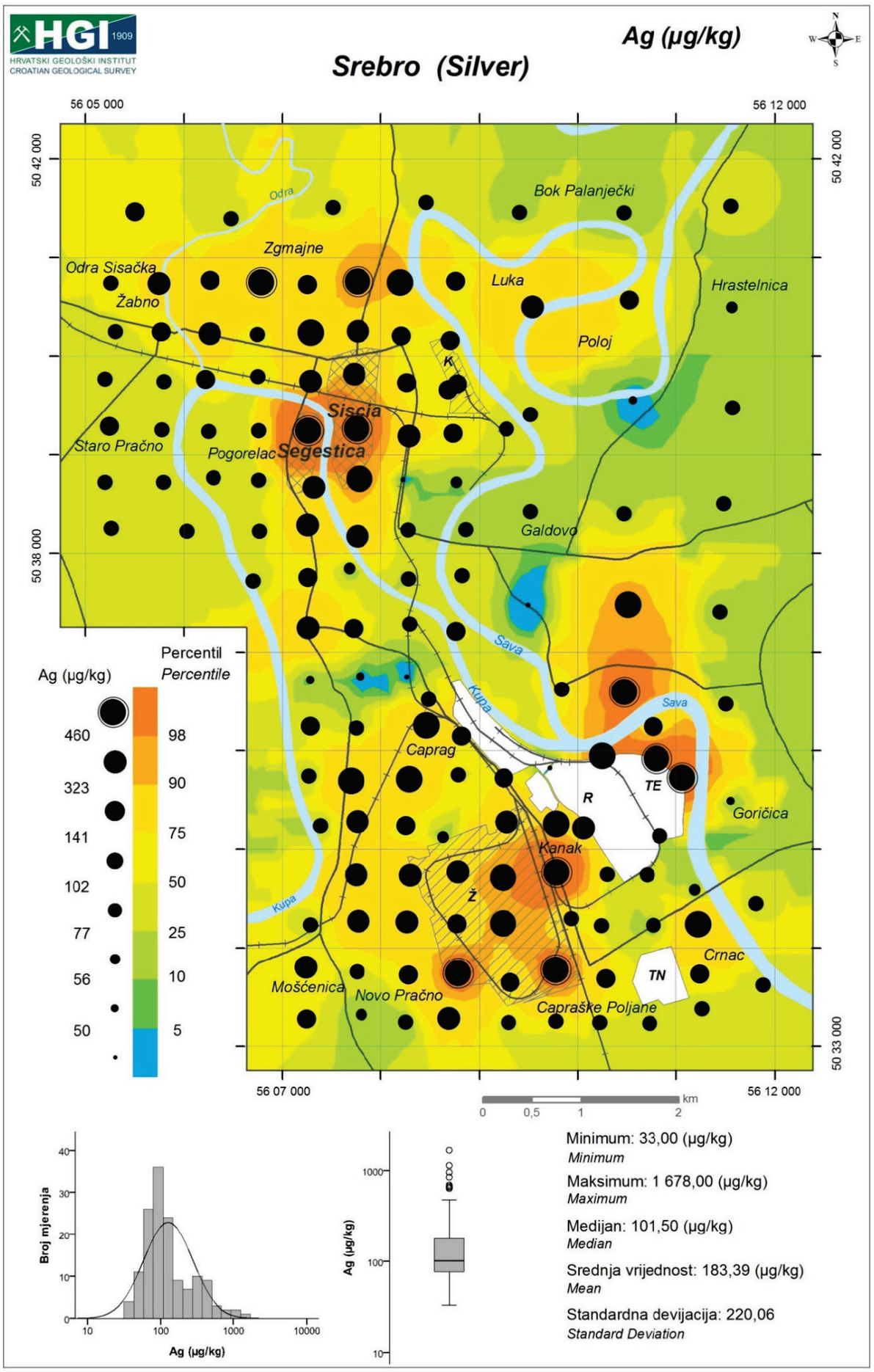
Drugo veliko područje s anomalnim koncentracijama srebra u uzorkovanom tlu je industrijska zona u jugoistočnom dijelu urbane cjeline grada Siska. Te koncentracije vezane su za željezaru, termoelektranu i rafineriju nafte . Područje Termoelektrane Sisak te neposredna lijeva obala Save, preko puta Termoelektrane, pokazuju anomalne vrijednosti srebra skoro na svim uzorkovanim lokacijama. Tako visoke koncentracije ovog elementa rezultat su sagorijevanja fosilnih goriva, prerade ugljikovodika u rafineriji te taljenja ruda i obrade željeza u željezari. Potrebno je istaknuti visoku koncentraciju srebra u naselju Kanak, koje se nalazi između Željezare Sisak i Rafinerije nafte Sisak. Osim toga, visoke koncentracije izmjerene su i u naselju Caprag, neposredno uz željezaru.

Općenito gledano, izmjerene koncentracije srebra u tlima Siska su daleko ispod toksičnih (granica toksičnosti za ljude je 60 mg/kg, a smrtonosna granica je 1 300 mg/kg – KABATA-PENDIAS & MUKHERJEE, 2007). Međutim, nema dovoljno literaturnih podataka o reakciji ljudskog organizma na dugu izloženost ovom metalu.

dian of 101.5 μg/kg. The greatest concentration of silver is measured at the location of Pogorelec. High and anomaly concentrations are registered also on the left bank of the Kupa River between the railway station and Sisak lawn (Zgmajna) to the north. These areas were occupied by the Celtic and Roman settlements of Segestica and Siscia so that the high contents of this element in soil resulted from the human activity during that period (probably foundries the silver ore, coin mints and jewelry). By reviewing the map one can tell that the distribution of silver in the soil in that area reflects the prehistoric settlements (Fig. 3.1.).

Another large area with anomalous concentrations of silver in the sampled soil is the industrial zone in the southeastern part of the urban core of the Sisak city. These concentrations are associated with steelworks, thermal power plant and oil refinery. The area of thermal power plant and immediate left bank of the Sava River across the thermal power plant show the anomalous values of Ag in almost all sampling sites. Thus the high concentrations of this element come from the combustion of fossil fuels, production of hydrocarbons in the petroleum refinery and ore smelting and iron production in the steelworks. It is necessary to emphasize the high concentration of silver in the settlement of Kanak which is placed between the steelworks and the petroleum refinery. Besides, the high concentrations are registered also in the Caprag settlement which is directly related to steelworks.

Generally, the registered concentrations of silver in the soils of the City of Sisak are far below the toxic limits (the toxicity limit for people is 60 mg/kg while the lethal dose is 1,300 mg/kg – KABATA-PENDIAS & MUKHERJEE, 2007). However, there is no sufficient published data on the reaction of the human organism on the longer exposition to this metal.


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Ag (µg/kg)
Srebro (Silver)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Sisija
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
Ag (µg/kg)
460
323
141
102
77
56
50
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
Ag (µg/kg)
Minimum: 33,00 (µg/kg)
Minimum
Maksimum: 1 678,00 (µg/kg)
Maximum
Medijan: 101,50 (µg/kg)
Median
Srednja vrijednost: 183,39 (µg/kg)
Mean
Standardna devijacija: 220,06
Standard Deviation

Al

10.2. Al – ALUMINIJ (atomski broj 13) ALUMINUM (atomic number 13)

Aluminij je litofilni makroelement, treći element po količini u sastavu Zemljine kore (iza silicija i kisika). Najčešće se javlja u obliku alumosilikata.

Srednji sadržaj u magmatskim stijenama iznosi 8,2 % (ultrabaziti 1,0; bazalti 9 % i graniti 8 %). Od sedimentnih stijena šejlovi sadrže 8 %, pješčenjaci 2,5 %, karbonati 0,4 % i evaporiti 0,003 %. U tlu je aluminij koncentriran u mineralima glina. Prosječni sadržaj mu varira od 1 do 4% što je ovisno o sastavu matičnih stijena. U lateritima je izraženo obogaćenje ovog elementa. Najveće koncentracije aluminija nalazimo u boksitu. Srednji sadržaj u slatkoj vodi je oko 0,24 mg/kg.

Mobilnost aluminija u procesu trošenja je vrlo niska i uvelike ovisi o pH vrijednostima vodenih otopina u tlu. Znatna je razlika u trošenju mafitnih i kiselih magmatskih stijena koje sadrže aluminij. K-feldspati i Na-bogati feldspati su relativno otporni na trošenje, dok se Ca-bogati feldspati i mnogi Fe-Mg-silikati puno lakše troše. Razlika u trošenju će imati važnu ulogu za koncentraciju aluminija u uzorcima tla. Osim toga, sadržaj organske komponente u tlu ima važniju ulogu za koncentraciju aluminija od granulometrijskog sastava. Adsorpcija na minerale glina u tlu nema većeg značenja.

Biološka funkcija aluminija nije potpuno definirana i on može biti obogaćen u nekim biljkama. U tlima s pH vrijednostima < 5 ovaj element u većim koncentracijama može biti otrovan za biljke. Toksičnost aluminija je složen fenomen i ovisi o tvrdoći vode, pH vrijednosti i otopljenom organskom ugljiku (SOC) u vodi. Slobodni Al^{3+} može biti umjereno otrovan za ljude i životinje. Najviše ga ima u kosi i plućima. Kisele kiše generiraju Al-hidroksid-sulfate koji se otapaju u tlima, ako pH vrijednost padne ispod 4,2. U sedamdesetim i osamdesetim godinama 20. stoljeća utvrđeno je izumiranje šuma u Europi, USA i Kanadi uslijed kiselih kiša koje su oslobađale metale u tlo, posebice aluminij. aluminij je poznati neurotoksični metal). Relativno lako se izlučuje iz organizma kroz bubrege. Aluminij ima široku primjenu u svim industrijskim sektorima kao što su metalurgija, pakiranje, transport, građevinarstvo, elektroindustrija (prijenos električne energije) i kemijska industrija. Koristi se kod proizvodnje papira, pročišćivanja vode, proizvodnji šećera, konzervaciji drva, štavljenju kože, kod proizvodnji vodootpornih tkanina, rentgenskoj industriji, proizvodnji antikorozivnih sredstava i dr.

Vraća se u okoliš u obliku raznovrsnog industrijskog i kućnog otpada (porculan, cigla, staklo, abrazivna sredstva, otpad od pakiranja i kemikalije). Jako veliki geogeni udio ovog elementa u okolišu otežava mogućnost procjene njegovog antropogenog unosa.

Aluminum is a lithophile major element, the third abundant element in the earth's crust (after silica and oxygen). Most often, it appears in the form of silicates.

The average content in then igneous rocks is 8.2 % (ultramafic rocks 1.0; basalts 9 % and granites 8 %). Among the sedimentary rocks the shales contain 8 %, sandstones 2.5 %, carbonates 0.4 % and evaporites 0.003 %. In the soil aluminum is concentrated in the clay minerals. The average content varies between 1 and 4 % which depends on the composition of parent rocks. In laterites this element is considerably enriched. The highest concentrations of aluminum are found in bauxite. The average content of sweet water is about 0.24 mg/kg.

Mobility of aluminum in the process of weathering is very low and chiefly depends on pH values of the water solutions in the soil. There is considerable difference in weathering of mafic and acid igneous rocks which contain aluminum. K-feldspars and Na-rich feldspars are relative resistant to weathering while Ca-rich feldspars and many Fe-Mg-silicates weather more easily. The difference in weathering will have an important role in concentration of aluminum in the soil samples. Besides, the content of organic component in soil is more important for the concentration of aluminum with regard to granulometric composition. Adsorption on clay minerals in soil is not of much importance.

Biological function of aluminum is not entirely defined and aluminum can be enriched in some plants. In soils with pH values < 5 this element in greater concentrations can be toxic for plants. Toxicity of aluminum is a complex phenomenon and it depends on the water hardness, pH value and soluble organic carbon (SOC) in the water. Free Al^{3+} can be moderately toxic for people and animals. The greatest quantities can be found in hair and lungs. The acid rains generate Al-hydroxides-sulfates which are dissolved

in soils if pH values fall below 4.2. During the 70's and 80's of the 20th century it was determined that the forest decline in Europe, USA and Canada was caused by acid rains which released metals, Al in particular, into the soil. Aluminum is a notoriously neurotoxic metal (it can provoke Alzheimer disease and cause the damage of neural cells). Otherwise, it is relatively easily extracted from organism through the kidneys which is why the function of these organs can provoke accumulation of Al in the brain cells and the bones.

Aluminum has a very broad industrial application. It is utilized in all industrial sectors including metallurgy, packing, transport, building, electro industry (transfer of electric energy) and chemical industry. It is used in production of paper, water purifying, sugar production, wood conservation, tanning and leather processing, production of waterproof textile, roentgen industry, production of anticorrosive agents, etc.

Aluminum returns into environment in the form of diverse industrial and household waste (porcelain, bricks, glass, abrasive materials, waste form packing, and chemicals). A considerable geogenic portion of this element in the environment makes the possibility of assessment of its anthropogenic input difficult.

Izmjerene koncentracije aluminija na istraživanom području su u rasponu od 0,44 do 4,63 % s medijanom 1,57 %. Najveća vrijednost registrirana je u krugu Željezare Sisak.

Visoke koncentracije utvrđene su u krugu željezare, na njezinom južnom rubu, oko Rafinerije nafte Sisak te u gradskom naselju Kanak. Povišene vrijednosti utvrđene su i u naselju Caprag. Sve te koncentracije posljedica su antropogenog unosa aluminija u tlo uslijed industrijske aktivnosti.

U tlima na aluviju rijeka Kupe i Odre registrirane su također visoke koncentracije aluminija, no one su ovdje geogenog podrijetla. Naime, aluvijalne naslage tih rijeka izgrađene su pretežito od sitnozrnatih klastičnih sedimenata (pijesci, siltovi, gline) koji se sastoje od kvarca, tinjaca i alkalijskih feldspata koji sadrže aluminij. Suprotno tomu, tla na aluviju poplavnih sedimenata rijeke Save imaju koncentracije aluminija manje od vrijednosti medijana. Sava velikim dijelom nosi i odlaže materijal koji je pretežito karbonatan i sadrži relativno malo mineralne komponente bogate aluminijem. Ovaj element, također, može biti pokazatelj da se na temelju geokemijskog sastava tla mogu dešifrirati matične stijene, a i izvorišna područja materijala koji izgrađuje te matične stijene (slično kao i element kalcij).

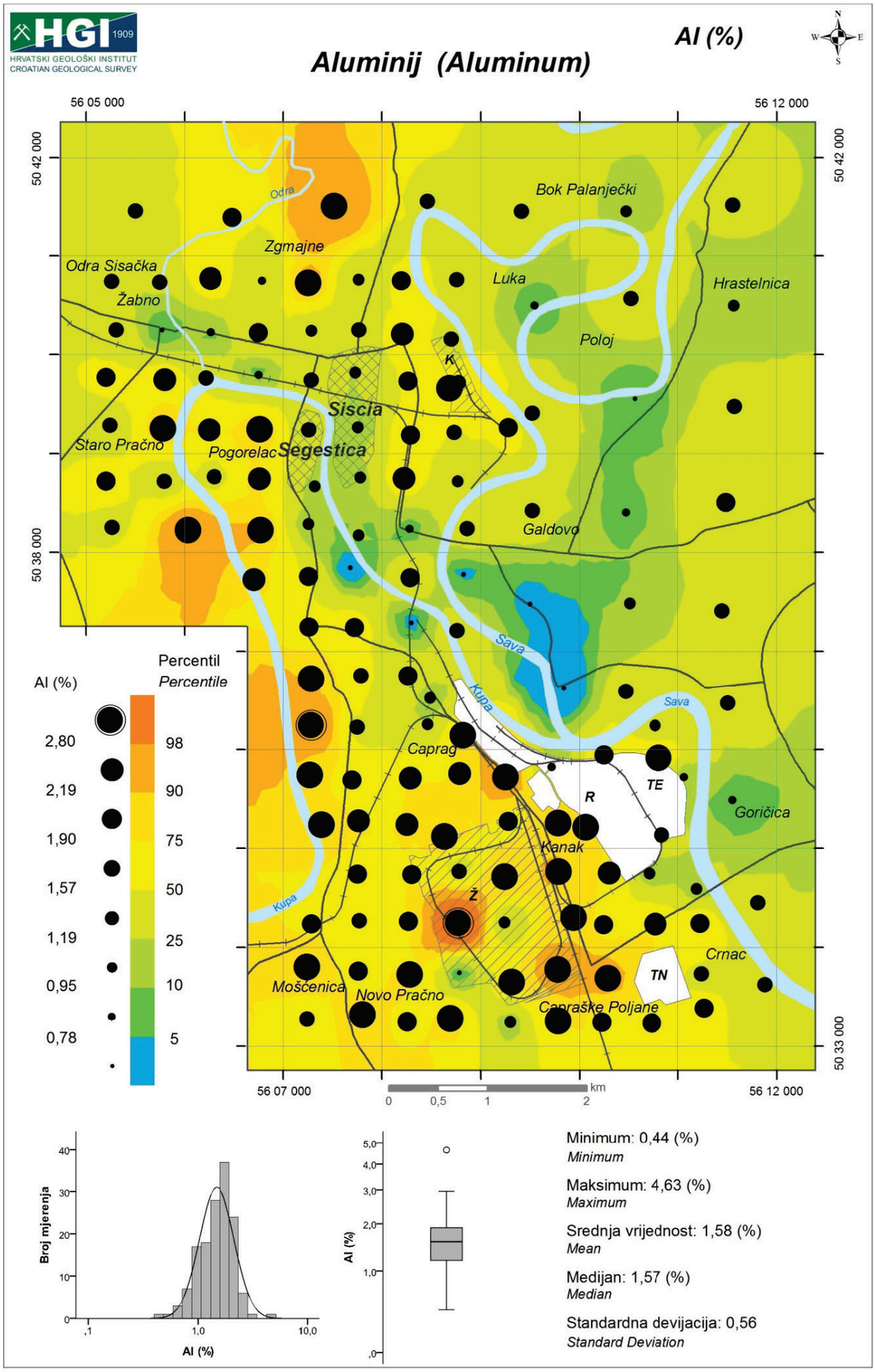
Izrazito niske vrijednosti aluminija u tlima na lijevoj i desnoj obali Kupe u blizini gradskog stadiona (nekadašnje vojarne-desna obala i stadiona Galdovo-lijeva obala) govore u prilog činjenici da je nekadašnje ušće Kupe u Savu bilo znatno uzvodnije nego što je danas (Sl. 3.2.).

Concentrations of aluminum measured in the investigated area range from 0.44 to 4.63 % with median of 1.57 %. The greatest values are registered in the circle around the Sisak steelworks.

The high concentrations are determined in the area surrounding the steelworks, on its southern rim, around the oil refinery, and in the city settlement of Kanak between the steelworks and the oil refinery. Increased values are registered also in the Caprag settlement. All these concentrations are the result of the anthropogenic input of Al into the soil owing to industrial activity.

In the soils on the alluvium of the Kupa and Sava Rivers the high concentrations of Al are also registered but in this case of geogenic origin. Namely, alluvial sediments of these rivers are built predominantly of fine-grained clastic sediments (sands, silts, clays) which consist of quartz, micas and alkali feldspars containing aluminum. On the contrary, the soils developed on alluvium of the Sava River have concentrations below median values. The material transported and deposited by the Sava River is predominantly carbonate and is poor in mineral component containing aluminum. This element can also say that based on the geochemical composition of soils one can define the parent rock materials and their source areas (similar to the element Calcium).

Distinctly low values of Al in soils on the both banks of the Kupa River close to the city stadium (a former barracks – right bank, and stadium of Galdovo – left bank) speaks in favor that the former confluence of the Kupa and Sava Rivers was placed considerably more upstream than it is now (Fig. 3.2.).


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Aluminij (Aluminum)
Al (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
Al (%)
2,80
2,19
1,90
1,57
1,19
0,95
0,78
98
90
75
50
25
10
5
Broj mjerenja
Al (%)
5,0
4,0
3,0
2,0
1,0
,0
,1
1,0
10,0
Minimum: 0,44 (%)
Minimum
Maksimum: 4,63 (%)
Maximum
Srednja vrijednost: 1,58 (%)
Mean
Medijan: 1,57 (%)
Median
Standardna devijacija: 0,56
Standard Deviation

As

10.3. As – ARSEN (atomski broj 33) ARSENIC (atomic number 33)

Arsen je halkofilni element u tragovima i nalazi se na 53. mjestu po učestalosti u Zemljinoj kori. Čest je u zajednici sa živom, antimonom i bizmutom.

Od magmatskih stijena ultrabaziti imaju srednji sadržaj od 0,5 mg/kg, bazalti 2 mg/kg, intermedijarne stijene 2,4 mg/kg i kisele stijene 1,5 mg/kg. U sedimentnim stijenama arsen je obogaćen u crnim šejlovima i ugljenu i njegov srednji sadržaj se kreće i do 13 mg/kg, a u pješčenjacima i karbonatima je 1 mg/kg. Srednji sadržaj u tlu iznosi 6 mg/kg.

Arsen je relativno mobilan. Oslobađanje arsena tijekom trošenja zahtijeva niske pH i Eh vrijednosti, jer inače As^{3+} brzo oksidira u netopivi As^{5+}. Količina organske tvari u tlu može imati značajan utjecaj na mjerene koncentracije. As^{5+} može zamijenjivati P^{5+} u fosfatima (apatit) i može biti značajno obogaćen u poljoprivrednim tlima kroz umjetna gnojiva. Oksidacijom rudnih minerala u visoko vrijedne As-spojeve, prije svega u arsenate, tvore se teško topivi spojevi sa Fe, Ni, Co, Cu, Ca i Pb.

Arsen može biti esencijalan za neke organizme, no, on je problematičan element s toksičnim osobinama. As^{3+} je otrovniji od As^{5+}. Nakuplja se u kosi i noktima,izaziva promjene na koži, plućima, bubrezima, jetri i mokraćnom mjehuru. Međutim, on pospješuje rast svinja te se radi toga dodaje njihovoj hrani. Upotreba gnojiva s farmi svinja može dovesti do obogaćenja arsenom u poljoprivrednim tlima. Otrovnost arsena poznata je od Rimljana koji su arsenolit (As_2O_3) koristili za ubojstva.

Koristi se kao komponenta legure olova (sačma), pri preradi kože i krzna, u farmaceutskoj i staklarskoj industriji, zaštiti drva, proizvodnji fotoelektričnih uređaja, Pb-kiselinskih baterija, a najviše za pesticide (danas 90 % pesticida sadrži organske spojeve arsena).

Opterećenje okoliša ovim elementom izraženo je u rudokopima, deponijima, talionicama sulfidnih ruda (bakra, cinka, olova, zlata i srebra) i metalurgiji (prašina, šljaka i dr.). Oslobađa se u zrak pri sagorijevanju ugljena te pri upotrebi pesticida u poljoprivredi, jer su As-komponente sastavni dio mnogih herbicida, insekticida i fungicida.

Arsenic is chalcophile trace element and is 53rd in abundance in the Earth's crust. It is common in associations with mercury, antimony and bismuth.

Among igneous rocks the ultramafic rocks average 0.5 mg/kg of arsenic, basalts 2 mg/kg, intermediary rocks 2.4 mg/kg and acid rocks 1,5 mg/kg. Among sedimentary rocks arsenic is enriched in black shales and coal with up to 13 mg/kg while in sandstones and carbonates its content is 1 mg/kg. The average content of arsenic in soil is 6 mg/kg.

Arsenic is relatively mobile. Its release during weathering requires the low pH and Eh values, otherwise As^{3+} quickly oxidizes into insoluble As^{5+}. The quantity of organic substance in the soil can demonstrate a considerable influence on the measured concentrations. As^{5+} can replace P^{5+} in phosphate (apatite) and can be significantly enriched in agricultural soils through chemical fertilizers. By oxidation of the ore minerals into highly valued As-compounds, notably arsenates, arsenic form the hardly soluble compounds Fe, Ni, Co, Cu, Ca and Pb.

Arsenic can be essential for some organisms. However, it is a troublesome element with toxic properties. As^{3+} is more toxic than As^{5+}. It accumulates in hair and fingernails. Besides, it causes the changes on the skin, lungs, kidneys, liver, and bladder (cancer). However, it enhances the growth of pigs which is why it is added to their diet. As a consequence, the use of the manure from the pig farms can lead to the As enrichment in agricultural soils. Toxicity of arsenic is notorious since the Roman times when (As_2O_3) was often used in murders.

It is used as a component for the lead alloys (buckshot), in lather and fur processing, in pharmaceutics, glass industry, wood protection, production of photoelectric devices, Pb-acid batteries, and notably in production of pesticides (nowadays 90 % of pesticides contain organic compounds of arsenic).

The impact on environment by this element is evident through mining, depots, foundries of sulfide ores (copper, zinc, lead and silver) and metallurgy (dust, slag, and other). It is released in the air by combustion of coal and use of pesticides in agriculture because As-components are constituent parts of many herbicides, insecticides and fungicides.

Arsen je element koji spada u grupu potencijano toksičnih elemenata. S druge strane, on nalazi vrlo široku primjenu u poljodjeljstvu kao sastavni dio većine pesticida. Zbog toga, ovom elementu treba posvetiti posebnu pažnju pri geokemijskom proučavanju okoliša. Nadalje, na sisačkom urbanom području nalazi se mnogo privatnih vrtova za uzgoj povrća i voća za osobnu upotrebu, koji su također izloženi deponiranju čestica iz zraka, posebice u blizini industrijskih pogona. Tim više, što su u nekim regijama u Hrvatskoj uočeni povišeni pa i anomalni sadržaji arsena i u podzemnim vodama (ĆAVAR et al., 2005; UJEVIĆ et al., 2010).

U uzorcima tla na urbanom području Siska izmjerene su koncentracije arsena u rasponu od 5,1 do 29,7 mg/kg. Visoke i anomalne koncentracije ovog elementa registrirane su u tlima oko većih industrijskih postrojenja kao što su rafinerija, termoelektrana, željezara i kemijska industrija. Maksimalna koncentracija arsena u tlu izmjerena je na sjevernom rubu Rafinerije nafte u blizini Termoelektrane Sisak. Visoke i anomalne koncentracije arsena u tlu na tim lokacijama posljedica su industrijske aktivnosti u gore navedenim postrojenjima (rafinerija – prerada ugljikovodika; termoelektrana – spaljivanje fosilnih goriva; željezara – topinica ruda i prerada metala te kemijska industrija – proizvodnja pesticida). Osim navedenih područja, anomalne koncentracije arsena izmjerene su u uzorcima u naselju Mošćenica, u jugozapadnom dijelu urbanog područja Siska i na ranžirnom kolodvoru između ušća Odre u Kupu i novog cestovnog mosta. Tlo na lokaciji u Mošćenici je šumsko tlo, izuzetno bogato organskom tvari koja akumulira arsen, tako da je povećan sadržaj ovog elementa dijelom geogenog, a dijelom i antropogenog podrijetla (depozicija iz zraka i akumulacija u tlu). Na dijelom antropogeno podrijetlo ukazuju i sadržaji arsena u drugim okolnim uzorcima u području Mošćenice. Anomalna koncentracija arsena u uzorku na ranžirnom kolodvoru je najvjerojatnije isključivo antropogenog podrijetla (utovar, istovar i pretovar raznovrsnih roba i materijala).

Povišeni sadržaji ovog elementa registrirani su i u dolini Kupe i Odre. Ovdje se radi o uzorcima aluvijalnog tla koje je razvijeno na poplavnim ravnicama ovih rijeka (fluvisol) i bogato je mineralima glina i organskom tvari. Obogaćenje arsenom u tim uzorcima je djelomično geogenog podrijetla. Lokacije uzorkovanja nalaze se na poljoprivrednom zemljištu pa povećana koncentracija arsena može biti rezultat gnojidbe umjetnim gnojivima i upotrebe pesticida. Navedene točke uzorkovanja smještene su u blagim geomorfološkim depresijama. U njima se dulje zadržava voda, odnos materijala je slabiji, što pogoduje nakupljanju onečišćujućih tvari.

Arsenic is an element falling into a group of potentially toxic elements. On the other side, it is widely used in agriculture as a constituent part of the most of pesticides. Owing to that arsenic deserves the special attention in the geochemical investigation of the environment. Further, in the Sisak urban area there are many private gardens where people cultivate fruits and vegetables for private use, and these are also exposed to deposition of airborne particles, particularly in the vicinity of industrial plants. All the more important, increased to anomalous contents of arsenic in underground waters are already registered in some parts of Croatia (ĆAVAR et al., 2005; UJEVIĆ et al., 2010).

The concentrations of arsenic registered in the soil samples of the urban area of Sisak range between 5.1 and 29.7 mg/kg. The high and anomalous concentrations of this element are registered in the soils around major industrial plants such as oil refinery, thermal power plant, steelworks and chemical industry. The maximum concentration of As in the soil is measured around the northern rim of the refinery, close to thermal power plant. High and anomalous concentrations of As in the soil on these locations result from industrial activity in the aforementioned plants (refinery – hydrocarbon processing; thermal power plant – combustion of fossil fuels; steelworks – ore smelting plant and metal processing; and chemical industry – production of pesticides). Save from the aforementioned areas the anomalous concentrations of arsenic are measured in the samples from the Mošćenica settlement in the southwestern part of the urban Sisak area and in the freight-yard between the confluence of the Odra and Kupa Rivers and new road bridge. The soil on the location of Mošćenica is exceptionally rich in organic matter which accumulates arsenic so that the increased content of this element is partly of geogenic, and partly of anthropogenic (airborne deposition and accumulation in soil)). The partly anthropogenic origin is indicated also by arsenic contents in other neighboring samples in the Mošćenica area. Anomalous concentration of arsenic in the sample form the freight-yard is most probably of anthropogenic origin (shipping, discharge and reloading of diverse good and materials).

Increased contents of this element are registered also in the valley of the Kupa and Odra Rivers. Here, they are found in the samples of alluvial soil which is developed on the floodplains of these rivers (Fluvisol) and thereby rich in clay minerals and organic matter. Enrichment in arsenic in these samples is partly of geogenic origin. The sampling sites are situated on the agricultural land so that the increased content of arsenic can result from fertilization by man-made fertilizers and use of pesticides. The mentioned sampling sites are located in the gentle geomorphological depressions where wa-

Na temelju novog *Pravilnika o zaštiti poljoprivrenog zemljišta od onečišćenja (Narodne novine 9, 2014)* element arsen nije uvršten kao onečišćujuća tvar, tako da u Republici Hrvatskoj nemamo zakonski propis o maksimalno dozvoljenim koncentracijama (MDK) za ovaj element u poljoprivrednim tlima. Međutim, Agencija za zaštitu okoliša je u svom *Programu trajnog motrenja tala u Republici Hrvatskoj* (MESIĆ et al., 2008) predložila granične vrijednosti onečišćujućih tvari u tlu prema različitim načinima korištenja. Za dječja igrališta MDK za arsen su 20 mg/kg, za područja za stanovanje 30 mg/kg, za parkove i rekreacijska područja 50 mg/kg i za industrijska područja su 100 mg/kg. Detaljnim uvidom u koncentracije arsena po pojedinim lokacijama u urbanom području Siska i usporedbe s predloženim graničnim koncentracijama, može se reći da čitavo izučavano područje ne pokazuje prekoračenje preporučenih koncentracija arsena u tlima.

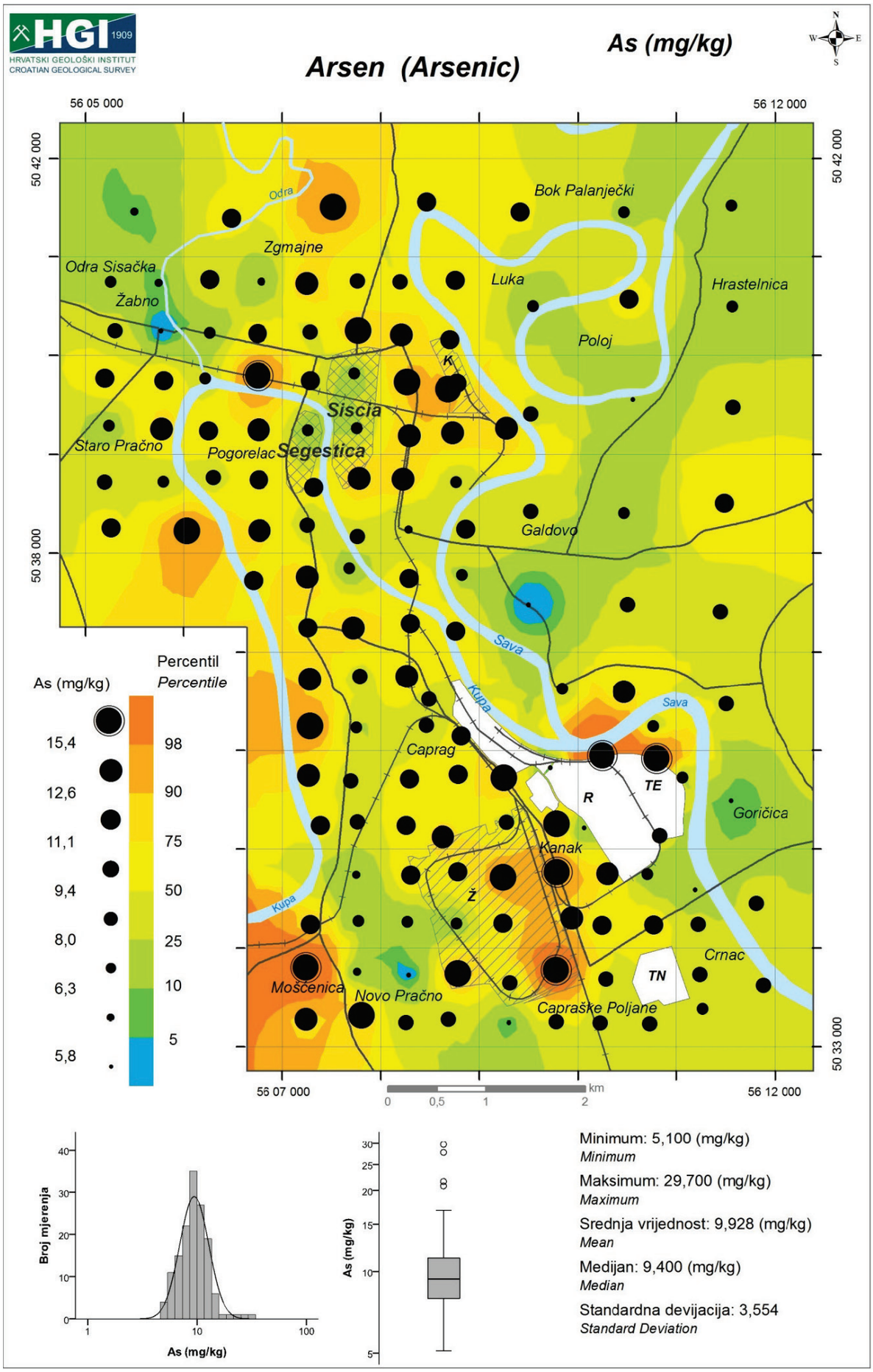
ter is longer retained so that material is removed more slowly, favoring the accumulation of contaminating substances.

Based on the new Regulations on protection of agricultural land from pollution (NN9, 2014) arsenic is not included as contaminating substance so that in Croatia no legal framework concerning the Maximum permitted concentration (MPC) in agricultural soils is yet in existence. However, Croatian Environment agency in its Program of permanent monitoring of soils in Croatia (MESIĆ et al., 2008) suggested the limit values of soil pollutants according to different modes of land use. For the kindergartens the MPC values concerning arsenic are 20 mg/kg, for residential areas 30 mg/kg, for parks and recreation areas 50 mg/kg while for industrial areas 100 mg/kg. By detailed inspection into the arsenic concentrations on particular locations in the urban core of Sisak and by their comparison with suggested limit concentrations one can say that the entire study area does not exceed the prescribed concentration of arsenic in the soil.



Slika 10.1. *Panorama prigradskog dijela Siska (Foto: Ž. Rakarić).*

Figure 10.1. *The panorama of the suburban part of Sisak (Photo: Ž. Rakarić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Arsen (Arsenic)
As (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
As (mg/kg)
15,4
12,6
11,1
9,4
8,0
6,3
5,8
98
90
75
50
25
10
5
Broj mjerenja
As (mg/kg)
Minimum: 5,100 (mg/kg)
Minimum
Maksimum: 29,700 (mg/kg)
Maximum
Srednja vrijednost: 9,928 (mg/kg)
Mean
Medijan: 9,400 (mg/kg)
Median
Standardna devijacija: 3,554
Standard Deviation

Au

10.4. Au – ZLATO (atomski broj 79) GOLD (atomic number 79)

Zlato je vrlo rijedak element u Zemljinoj kori.

Njegova prosječna koncentracija u kontinentalnoj kori je 3 μg/kg i ima ga više u magmatskim stijenama nego u sedimentima. Srednja vrijednost u magmatskim stijenama je od 0,5 do 5 μg/kg (ultrabaziti 5 μg/kg, bazalti 4 μg/kg, neutralne magmatske stijene x μg/kg i kisele magmatske stijene 4,5 μg/kg). Srednji sadržaj u šejlovima iznosi 1 μg/kg, a u pješčenjacima i karbonatima x μg/kg. Srednji sadržaj zlata u tlima je jako ovisan o matičnim stijenama i uvjetima njihovog trošenja. Prosječna vrijednost u nekim tlima varira od 1 do 1 800 μg/kg (USA, Rusija). Srednji sadržaj u slatkoj vodi je oko 0,01 μg/L.

Zlato je relativno stabilno u hipergenoj zoni, pa je stoga njegova mobilnost vrlo mala. Ne otapa se u kiselinama ni lužinama, osim u zlatotopki (HNO_3 : HCl – 1 : 3) i u cijanidnim otopinama koje sadrže kisik. Zlato može biti mobilizirano kao $Au(CN)_2$ u tlima pod vegetacijom. Osim toga, ono može, pod određenim uvjetima, tvoriti komplekse $AuCl_2^{2-}$, $AuBr_4^-$, AuI_2^-, $Au(CN)_2^-$, $Au(CNS)_4^-$ i $Au(S_2O_3)_2^{2-}$ koji su dosta mobilni. Izgleda da je zlato transportirano najčešće u formi organometalnih spojeva ili helata. Trošenjem pirita koji sadrži zlato u oksidativnim uvjetima jedan dio zlata ostaje u limonitu koji zamjenjuje pirit, a drugi se dio u otopini transportira i reprecipitira na gline i Fe hidrokside.

Zlato nije esencijalni element. Trovanje zlatom nije poznato, ali se eventualno može pojaviti kod terapija u kojima se rabi zlato u spojevima.

Svjetska proizvodnja ovog plemenitog metala bila je u 2000. godini oko 2 590 t. Najčešća metoda produkcije je amalgamacija živom što predstavlja veliki rizik za okoliš. U novije vrijeme postalo je važan sporedni produkt kod proizvodnje Cu i Pb.

Zlato ima jedinstvenu ulogu u svjetskoj ekonomiji kao protuvrijednost papirnom novcu u opticaju. Osim toga, puno se koristi za izradu nakita, kovanica, u elektronskoj industriji, informatičkoj industriji, telekomunikacijama, medicini, vojnoj i svemirskoj industriji i dr.

Gold is a very rare element in the Earth's crust.

Its average concentration in the continental crust is 3 μg/kg and it is more abundant in igneous than in sedimentary rocks. The average value in the igneous rocks varies from 0.5 to 5 μg/kg (ultramafic rocks 5 μg/kg, basalts 4 μg/kg, neutral igneous rocks x μg/kg and acid igneous rocks 4.5 μg/kg). The average value in shales amount to 1 μg/kg while in sandstones and carbonates x μg/kg. The average value of gold in soils is strongly dependent on parent rocks and conditions of their weathering. In some soils it varies from 1 to 1,800 μg/kg (USA, Russia). The average value in sweet water is about 0.01 μg/L.

Gold is relatively stabile in the hypergene zone which is why its mobility is very low. It is not soluble in acids nor alkalis, except in aqua regia (HNO_3:HCl - 1:3) and in cyanide solutions containing oxygen. Gold can be mobilized as $Au(CN)_2$ in the soils covered by vegetation. Besides, under certain conditions it may form the complexes of $AuCl_2^{2-}$, $AuBr_4^-$, AuI_2^-, $Au(CN)_2^-$, $Au(CNS)_4^-$ and $Au(S_2O_3)_2^{2-}$ which are rather mobile. It seems that Au is transported most frequently in the form of organometallic compounds or chelates. By weathering of gold-bearing pyrite under the oxidizing conditions one portion of gold remains in limonite substituting pyrite while another portion is transported in solution co-precipitating with clays and Fe-hydroxides.

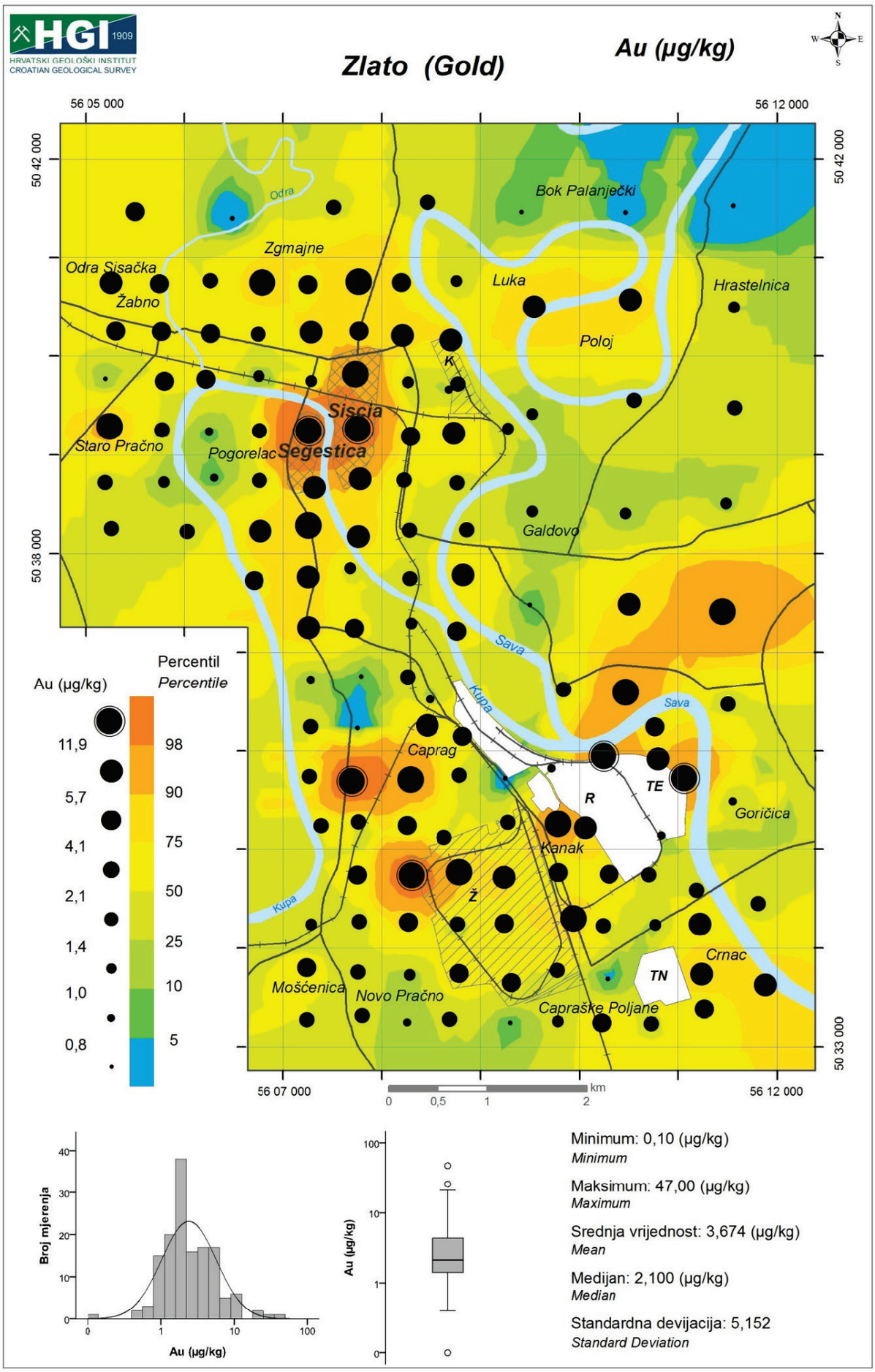
Gold is not an essential element. Poisoning with gold is not known but it may occur with therapies using gold in compounds.

The world production of this noble metal was about 2,590 t in the year 2000. The most often method of its production is amalgamation using mercury which represents a great risk to the environment. In the more recent times gold became an important byproduct in production of Cu and Pb.

Gold plays an important role in the world economy as a counter value to the paper currency. Besides, it is much used in the making of jewelry, coins, in the electric and information industry, telecommunications, medicine, military and space industry and others.

Općenito gledano, izmjerene koncentracije zlata u tlima urbanog područja Siska nisu značajne. Međutim, raspodjela tog elementa u analiziranim uzorcima daje nam neke zanimljive podatke za to područje. Izmjerene koncentracije kreću se od 0,1 do 47 μg/kg vrijednošću medijana od 2,1 μg/kg što je, u odnosu na srednji sadržaj u Zemljinoj kori, neznatno povišenje. Najveća koncentracija, kao i ekstremne vrijednosti, registrirane su na Pogorelcu, zatim u jugozapadnom dijelu istraživanog područja te na sjeverozapadnom rubu željezare. Slično kao kod srebra najveće koncentracije ovog elementa u tlu vezane su za područje koje su naseljavali Kelti i Rimljani (Pogorelec, pa na sjever prema Zgmajni). Ti povećani sadržaji zlata u tlu upućuju na antropogeni unos tijekom proteklih nekoliko tisuća godina ljudske aktivnosti. Zlato bi, zajedno sa srebrom, moglo poslužiti kao element indikator za pronalaženje dodatnih lokacija koje su nastanjivali ili Kelti ili Rimljani. Anomalne koncentracije u blizini Željezare Sisak (naselje Caprag), Rafinerije nafte Sisak i Termoelektrane Sisak (naselje Kanak te lijeva i desna obala Save – područje između Goričice i Galdova) vezane su vjerojatno za industrijsku aktivnost u tim postrojenjima. Uočljivo je i područje s vrlo niskim koncentracijama zlata u tlu, a koje se proteže od Kupe na zapadu, preko Viktorovca prema Galdovu i Hrastelnici na sjeveroistoku. Ta zona jasno razdvaja Stari Sisak od Novog, industrijskog Siska koji svaki za sebe ima drugačije podrijetlo zlata u tlu. Ostala uzorkovana područja imaju koncentracije zlata znatno ispod vrijednosti medijana.

Generally, the measured concentrations of gold in the soils of the urban area of the Sisak city are not significant. However, distribution of this element in the analyzed samples provides some interesting data for this area. The measured concentrations range from 0.1 to 47 μg/kg with median value of 2,1 μg/kg which is negligible increase with respect to the average value in the Earth's crust. The highest concentration together with extreme values is registered on Pogorelec, then in the southwestern part of the investigated area and on the northwestern rim of the steelworks. Similar to silver, the greatest concentrations of this element in the soil are associated with the area settled by Celts and Romans (Pogorelec and to the north towards lawn Zgmajna). These elevated contents of gold in soil indicate the anthropogenic ingress during the last few thousands of years owing to human activity. Gold together with silver could serve as an element-indicator for detection of additional locations that were inhabited by either Celts or Romans. Anomalous concentrations in the vicinity of steelworks (the Caprag settlement), oil refinery, and thermal power plant (the Kanak settlement together with either bank of the Sava River – area between Goričica and Galdovo) are probably associated with industrial activity in these plants. Also, it can not be overseen an interesting area with very low concentrations of gold in the soil, which extends from the Kupa River to the west, across Viktorovac toward Galdovo and Hrastelnica to the northeast. This zone clearly separates Old Sisak from new industrial Sisak which both have different origins of gold in their soils. Other sampled areas have the concentrations of gold considerably below the median values.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Zlato (Gold)
Au (µg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Sisclа
Segestica
Staro Pračno
Pogorelac
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Au (µg/kg)
Percentil
Percentile
11,9
5,7
4,1
2,1
1,4
1,0
0,8
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
Au (µg/kg)
Minimum: 0,10 (µg/kg)
Minimum
Maksimum: 47,00 (µg/kg)
Maximum
Srednja vrijednost: 3,674 (µg/kg)
Mean
Medijan: 2,100 (µg/kg)
Median
Standardna devijacija: 5,152
Standard Deviation

Ba

10.5. Ba – BARIJ (atomski broj 56) BARIUM (atomic number 56)

Barij je litofilni element u tragovima i po učestalosti u Zemljinoj kori nalazi se na 14. mjestu. U magmatskim stijenama prateći je element kalija.

Srednji sadržaj barija u ultrabazitima iznosi 5 mg/kg, u bazičnim stijenama 330 mg/kg, u intermedijarnim stijenama 650 mg/kg i kiselim stijenama 830 mg/kg. Srednja vrijednost barija u šejlovima je 100 mg/kg, pješčenjacima 35 mg/kg, a u karbonatima je u rasponu od 20 do 55 mg/kg. U ugljenu ga može biti od 75 do 330 mg/kg (u nekim lignitima i do 1 420 mg/kg). Koncentracija u tlu kreće se od 100 do 3 000 mg/kg sa srednjom vrijednošću od 500 mg/kg. Tla u blizini baritnih ležišta mogu sadržavati koncentracije i do 3,7 %. U slatkoj vodi ga ima oko 0,02 mg/L.

Barij se mobilizira tijekom trošenja i mobilan je u otopinama bez sulfata. Lako se adsorbira na okside i hidrokside mangana i željeza, organsku tvar i na minerale glina. Padajući niz vezivanja barija na minerale glina je: montmorilonit-->kaolinit-->ilit. Barij može koprecipitirati s manganom te zbog toga može biti obogaćen u manganovim prevlakama u tlu. U prisutnosti sulfatnog ili karbonatnog iona formiraju se barijevi minerali barit i viterit, čime se imobilizira barij u tlima.

Nije biološki bitan, ali može biti esencijalan za neke organizme. Umjereno je otrovan za biljke, a manje za sisavce. Kao $BaSO_4$ gotovo je neotrovan. Spojevi topivi u vodi su otrovni. Povećani sadržaj barija u organizmu smanjuje sadržaj kalija (sličan ionski radijus). Otrovnost se manifestira kroz poremećaj u probavnom i respiratornom traktu te mineralizaciju u kostima. Moguća je hipertenzija i nenormalan rad srca. Zamijećena su i njegova kancerogena svojstva. U šećeru, siru, kakau i škrobu ga ima od 1 do 6mg/kg. Najveći sadržaj registriran je u listovima crnog čaja (oko 10 mg/kg) te u brazilskom orahu. U ljudski organizam se unosi najviše preko povrća (iznad 50 %), životinjskog mesa (30 %) i napitaka (10 %).

Svjetska proizvodnja barija u 2000. godine iznosila je oko 2,9 milijuna tona.

Barit je osnova za bijele boje, služi za izradu opeka, pločica, stakla, keramike, sintetskih guma, materijala za ispunu (kaučuk, papir), za povećanje specifične težine isplake kod bušenja, u pirotehnici (zelena boja), u kemiji te kao zaštita od zračenja u medicini.

Antropogeni unos ovog elementa u okoliš slijedi kroz industrijski i kućanski otpad, kao talog iz zraka te kroz fosfatna mineralna gnojiva.

Barium is a lithophile trace element which is 14th in abundance in the Earth's crust. In igneous rocks barium is the element accompanying potassium.

The average content of barium is 5 mg/kg, u mafic rocks 330 mg/kg, in intermediary rocks 650 mg/kg and in acid rocks 830 mg/kg. The average value of barium in shales is 100 mg/kg, sandstones 35 mg/kg, while in carbonates it ranges from 20 to 55 mg/kg. In coal it can amount to 75 to 330 mg/kg (in some lignite up to 1,420 mg/kg). Concentrations in soils are between 100 and 3,000 mg/kg, averaging 500 mg/kg. The soils in the vicinity of barite deposits can contain concentrations up to 3.7 % of barium. In sweet water its concentration is about 0.02 mg/L.

Barium is mobilized during the weathering and is mobile in the sulfate-free solutions. It is easily adsorbed on the Mn and Fe oxy-hydroxides, organic matter and clay minerals. Decreasing order of barium bonding with clay minerals is: montmorillonite-->kaolinite-->illite. Barium can co-precipitate with manganese and thus it can be enriched in manganese coatings in the soil. In the presence of sulfate or carbonate ion it forms barium minerals barite and viterite which immobilize barium in soils.

It is not biologically vital but it may be essential to some organisms. It is moderately toxic for plants and less for mammalians. As $BaSO_4$ it is almost non-toxic. Compounds soluble in water are toxic. Increased content of barium in organism reduces the content of potassium (similar ionic radius). Toxicity is manifested through the disturbance in the digestive and respiratory tracts and mineralization in the bones. Hypertension and abnormal function of heart are also possible. Its carcinogenic attributes are also observed. In sugar, cheese, cacao, and starch barium is present with 1 to 6 mg/kg. The highest content is registered in the leaves of the black tea (about 10 mg/kg) and in the Brazilian nut. Input into the human organism is mostly through the vegetables (above 50 %), red meat (30 %) and juices (10 %).

The world production of barium at the level of the year 2000 was about 2.9 million tons.

Barite is a base for white colors. It serves for production of bricks, tiles, glass, ceramics, synthetic tires, filling material (Indian rubber, paper), for increasing of the specific weight of drilling mud during drilling, in pyrotechnics (green color), in chemistry, and as the protection from radiation in medicine.

Anthropogenic input of this element into environment is due to industrial and household waste, airborne precipitation and phosphate mineral fertilizers.

Raspodjela elementa barija u tlima grada Siska pokazuje jasnu podjelu istraživanog područja na dva dijela, urbani i industrijski. Visoke, anomalne i ekstremne vrijednosti ovog elementa registrirane su u uzrocima u industrijskom dijelu grada (u željezari, rafineriji, termoelektrani, te u naseljima Caprag, Kanak i Crnac). Ostali dijelovi urbanog područja pokazuju koncentracije u tlu oko srednjih vrijednosti za to područje. Prigradska i ruralna područja imaju koncentracije barija u tlu znatno ispod vrijednosti medijana.

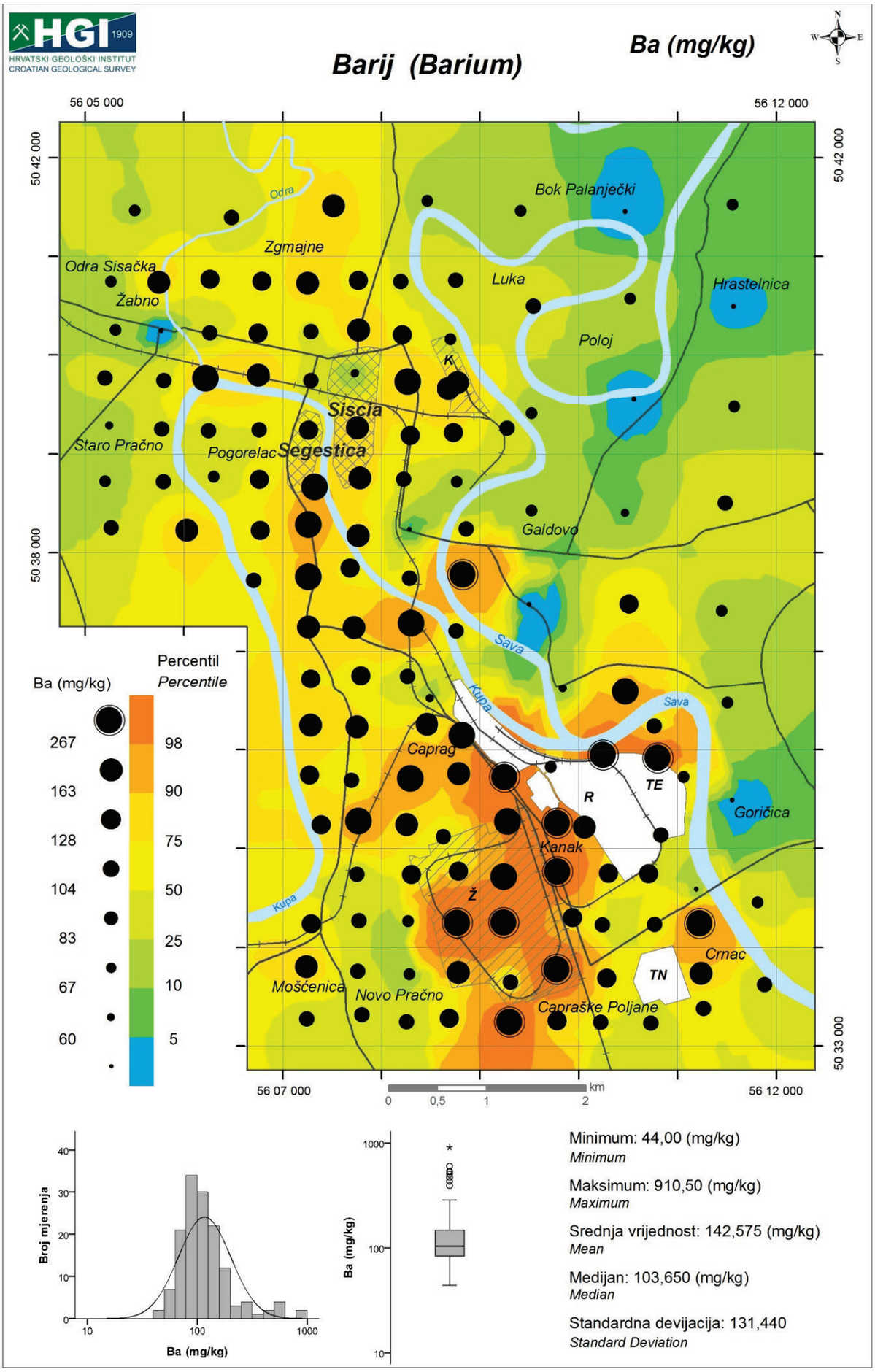
Najviša izmjerena koncentracija ovog elementa izmjerena je u uzorku u krugu Željezare Sisak, dok su anomalne vrijednosti karakteristične i za ostale uzorke u krugu Željezare, zatim za naselje Kanak te za područje u neposrednoj blizini Rafinerije Nafte Sisak i Termoelektrane Sisak. Anomalne koncentracije registrirane su i u uzorku neposredno sjeverno od naselja Crnac, kao i na rubu nogometnog igrališta Sportskog društva „Galdovo“ na lijevoj obali Save. Sve navedene anomalne koncentracije barija posljedica su industrijske proizvodnje u željezari i rafineriji te spaljivanja fosilnih goriva u termoelektrani. Anomalna koncentracija barija u Galdovu nalazi se također u blizini industrijskih postrojenja u tom dijelu grada (npr. Brodoremont i dr.).

Uže urbano područje i stari dijelovi grada imaju povišene sadržaje barija u tlu koji su posljedica antropogenog unosa putem boja, keramike, opeke i stakla. Povećane koncentracije ovog elementa u tlu uz glavne prometne pravce u gradu na nekim dijelovima mogu biti posljedica njegove upotrebe u proizvodnji automobilskih guma. Samo manji dio tih povišenih vrijednosti je geogenog podrijetla uslijed koncentriranja barija u teškoj mineralnoj frakciji u aluvijalnim sedimentima Odre i Kupe (npr. na lijevoj obali Kupe u Starom Pračnu te na lijevoj i desnoj obali Odre – Zgmajne i naselje Žabno.

Distribution of barium in the soils of the city of Sisak displays a clear division of the investigated area into two parts: urban and industrial. The high, anomalous and extreme values of this element are registered in the samples from the industrial part of the city (steelworks, oil refinery, thermal power plant, as well as in the settlements of Caprag, Kanak and Crnac). Other parts of the urban are show the concentrations around the average values for this area. Suburbia and rural areas have the concentrations of barium in the soil considerably below the median value.

The highest measured concentration of this element is found in a sample from the collected in the sphere of steelworks but anomalous values are also characteristic for other samples around the steelworks and for those in the settlements of Kanak between the steelworks and oil refinery, and for the area in the close vicinity of the refinery and thermal power plant. Anomalous concentrations are registered also in the sample right to the north of the Crnac settlement as well as on the border of the football ground of Sports Society Galdovo on the left bank of the Sava River. All aforementioned anomalous concentrations of barium in the soil are the result of industrial production in the steelworks and refinery as well as combustion of fossil fuels in the thermal power plant. Anomalous concentration of barium in Galdovo is also located near the industrial plants in this part of the city (e.g. Brodoremont and others).

The narrow urban area and old parts of the city show increased contents of barium in the soil which result from the anthropogenic input into the environment by paints, ceramics, bricks and glass. The increased concentrations of this element in the soil along the main traffic lines in the city may at some places appear as a consequence of the barium application on the production of car tires. Only a minor part of these elevated values is of geogenic origin, due to accumulation of barium in the heavy mineral fraction in the alluvial sediments of the Odra and Kupa Rivers (e.g. on the left bank of the Kupa River in Staro Pračno and on the both left and right banks of the Odra River – Žabno settlement and lawn Zgmajna).


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Barij (Barium)
Ba (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
Ba (mg/kg)
267
163
128
104
83
67
60
98
90
75
50
25
10
5
Broj mjerenja
Ba (mg/kg)
10
100
1000
40
30
20
10
0
Minimum: 44,00 (mg/kg)
Minimum
Maksimum: 910,50 (mg/kg)
Maximum
Srednja vrijednost: 142,575 (mg/kg)
Mean
Medijan: 103,650 (mg/kg)
Median
Standardna devijacija: 131,440
Standard Deviation

Be

10.6. Be – BERILIJ (atomski broj 4) BERYLLIUM (atomic number 4)

Berilij je rijedak zemnoalkalni litofilni element u tragovima. Nakuplja se u fluidnim reziduima kiselih magmi. Asociran je s Li, B, Sn, Nb, Ta, Th, U i W. Po pojavljivanju u Zemljinoj kori nalazi se na 47. mjestu. Geokemijski je sličan aluminiju i može u kristalnim rešetkama zamijenjivati Si i Al.

Raspon koncentracija berilija u Zemljinoj kori kreće se od 4 do 6 mg/kg. Magmatske stijene imaju prosječnu koncentraciju ovog elementa 2,8 mg/kg (ultrabaziti 0,x mg/kg, bazalti 1 mg/kg i graniti od 2 do 5 mg/kg – srednja vrijednost 3 mg/kg). Od sedimentnih stijena šejlovi imaju 3 mg/kg, a pješčenjaci i karbonati < 1 mg/kg. Prosječna vrijednost berilija u tlima je 6 mg/kg. Njegova koncentracija u ugljenu može varirati od 11 do 330 mg/kg, a u pepelu može dosezati i 47 mg/kg. Koncentracija Berilija u mazutu je od 0,0005 do 0,5 mg/kg. U slatkoj vodi ga prosječno ima 0,0055 mg/L. U vodi se nalazi otopljen kao Be^{2+}, $Be(OH)_2^{2+}$, BeF^{1+}, $BeOH^{1+}$ ili u vidu organokompleksa.

Be-minerali su relativno otporni na trošenje te je zbog toga mobilnost berilija niska. U oksidativnim uvjetima on koprecipitira s Fe i Al oksi-hidroksidima. Berilij se također adsorbira na površinu minerala glina (montmorilonit) te se veže na organsku tvar.

Nije esencijalni element. Jako je otrovan za sve organizme (inhaliran kao aerosol-berilioza) i kancerogen za neke životinjske vrste. Povećnim koncentracijama berilija dolazi do poremećaja Ca-metabolizma. Metal berilij i mnogi njegovi spojevi su alergeni. Neke biljke ga akumuliraju (američki orah – hickory).

Svjetska proizvodnja berilija u 2003. godini iznosila je 255 000 t.

U industriji berilij služi za izradu raznovrsnih legura. Be-oksid je vrlo važan u izradi Cu-Be legure koja se koristi u metalurškoj indistriji. Nadalje, služi u izradi atomskih reaktora, a u novije vrijeme koristi se i u raketnoj industriji.

Disperzija u okoliš je relativno mala, ali radi sve veće upotrebe berilija u raznovrsnim novim tehnologijama (gorivo za rakete, legure koje su lagane, tvrde i otporne na koroziju) te spaljivanjem ugljena i mazuta u termoelektranama znatno se povećava njegov unos u zrak i tlo.

Beryllium is rare earth alkali lithophile trace element. It is accumulated in the fluid residues of the acid magmas. As the 47th abundant element in the Earth's crust it is associated with s Li, B, Sn, Nb, Ta, Th, U and W. Geochemically, it is similar to aluminum and it can substitute Si and Al in the crystal lattices.

The range of the concentrations of Be in the Earth's crust is between 4 and 6 mg/kg. Igneous rocks contain in average 2.8 mg/kg of this element (ultramafic rocks 0.x mg/kg, basalts 1 mg/kg and granites from 2 to 5 mg/kg – the average is 3 mg/kg). Among sedimentary rocks, shales contain 3 mg/kg while sandstones and carbonates contain < 1 mg/kg. The average content of Be in the soils is 6 mg/kg. Its concentration in coal can vary from 11 to 330 mg/kg while in ash it can amount to 47 mg/kg. Concentration of Be in crude oil varies from 0.0005 to 0.5 mg/kg. U sweet water it averages 0.0055 mg/L. In the water beryllium is dissolved as Be^{2+}, $Be(OH)_2^{2+}$, BeF^{1+}, $BeOH^{1+}$, or in the form of organic complexes.

Be-minerals are relatively resistant to weathering which is why its mobility is low. In oxidizing conditions Be co-precipitates with Fe and Al oxy-hydroxides. Beryllium is also adsorbed on the surface of clay minerals (montmorillonite) and bound the organic matter.

Beryllium is not an essential element. It is highly toxic for all organisms (inhaled as aerosol-berylliosis) and carcinogenic for some animal forms. Due to elevated concentrations of beryllium Ca-metabolism can be disturbed. This metal and many of its compounds are allergenic. Some plants accumulate Be (American nut – hickory).

The world production of Be in the year 2003 was 255,000 t.

In industry beryllium serves in production of various alloys. Be-oxide is highly important in production of Cu-Be alloy which is used in metallurgy. Further, Be serves in manufacturing of atomic reactors while in the more recent times it is also utilized in the rocket industry.

Dispersion in the environment is relatively small but owing to the expanded use of Be in diverse new technologies (rocket fuel, alloys that are light, hard and resistant to corrosion) and combustion of coal and crude oil in the thermal power plants its ingress into the air and soil is considerably increased.

Po koncentracijama berilija u analiziranim uzorcima tla grada Siska jasno se odvaja industrijsko područje i dolina Kupe i Odre. Kao i za većinu drugih elemenata ruralni dijelovi imaju manje koncentracije ovog elementa u tlu nego urbani i industrijski.

Najveća koncentracija berilija u tlu registrirana je u zapadnom dijelu kruga Željezare Sisak, dok su anomalne vrijednosti (preko 1,3 mg/kg Be) izmjerene u naselju Kanak te oko postrojenja Rafinerije nafte Sisak i Termoelektrane Sisak. Anomalne koncentracije ovog elementa utvrđene su i u uzorcima tla na području gradskog vodovoda te neposredno južno od lokacije na desnoj obali Kupe. Naselja Staro Pračno i Pogorelec imaju također anomalne vrijednosti berilija u tlu kao i tla na Zelenom brijegu i Zgmajni na lijevoj obali Odre. Visoke koncentracije berilija u tlu u jugoistočnoj industrijskoj zoni i oko kemijske industrije u sjevernom dijelu grada su antropogenog podrijetla (prerada željezne rude, prerada ugljikovodika, spaljivanje fosilnih goriva te kemijska i ostale industrije), dok su anomalije uz rijeke Kupu, Odru i Mošćenicu geogenog podrijetla. Naime, u tim područjima se radi o aluvijalnim, pretežito glinovitim tlima (fluvisoli), gdje je berilij vjerojatno vezan za minerale glina.

Područje Starog Siska, zatim park-šuma zapadno od Željezare i sjeverni dio grada oko Zagrebačke ulice te naselja Galdovo i Hrastelnica kao i područje Poloja i Luke uz rijeku Savu pokazuju koncentracije berilij u tlu ispod ili daleko ispod vrijednosti medijana za istraživano područje.

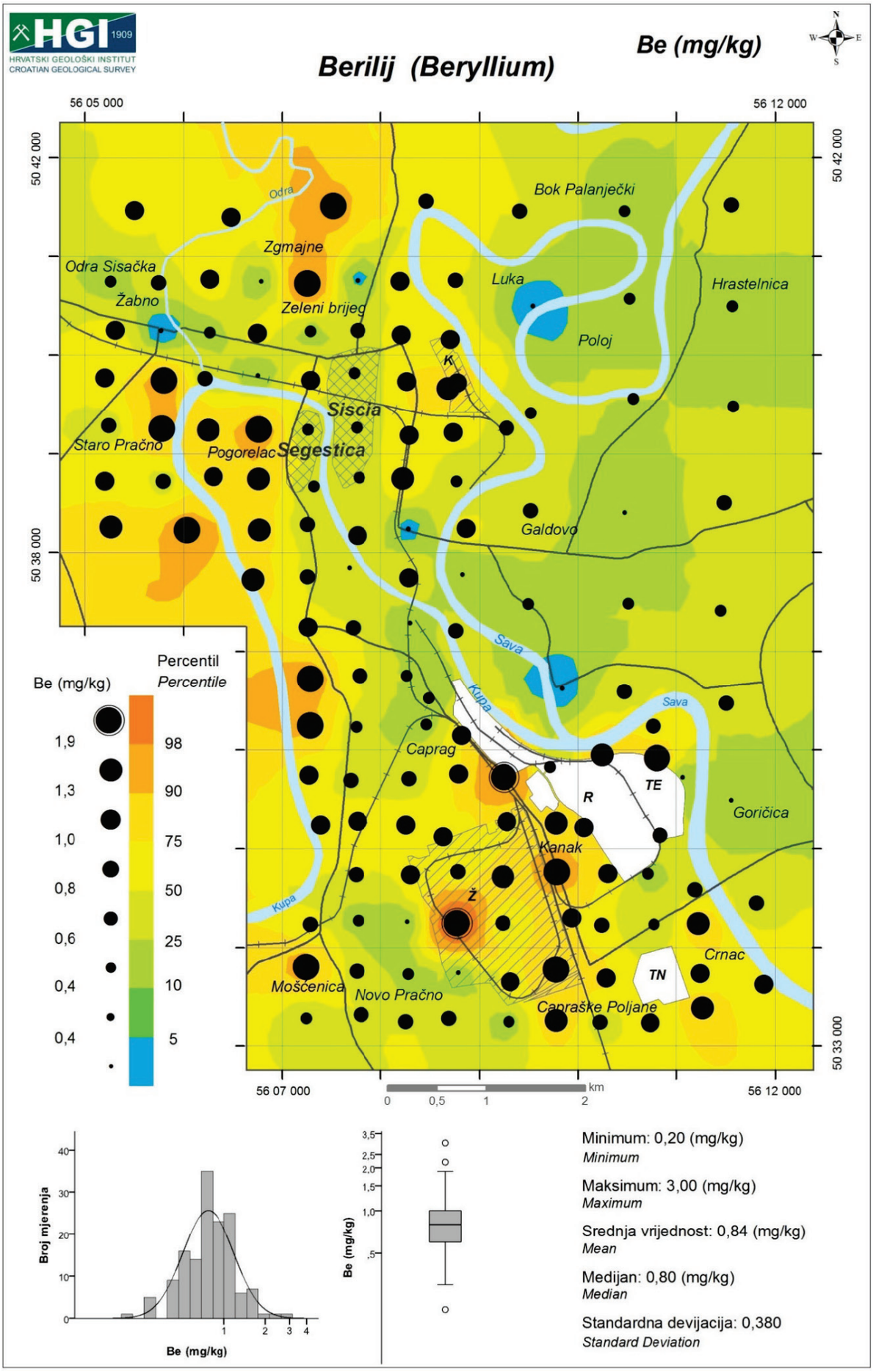
Iako koncentracije berilija na urbanom području Siska nisu visoke, zbog njegove toksičnosti treba obratiti pozornost na emisije ovog elementa u zrak, posebice u blizini industrijskih postrojenja.

Inspection into the concentrations of beryllium in the analyzed samples collected in the Sisak area shows that the clear distinction between the industrial zone and the valleys of the Kupa and Odra Rivers. Similar as in the case of the most other elements the rural parts are characterized by lower concentrations of this element in the soil compared to urban and industrial areas.

The greatest concentration of beryllium in the soil is registered in the western part of the steelworks zone while anomalous values (over 1.3 mg/kg) are measured in the Kanak settlement and around the oil refinery and the thermal power plant. Other areas with anomalous concentrations of this element are determined in the zone of the city water supply line and closely to the south of that location on the right bank of the Kupa River. The settlements of Staro Pračno and Pogorelec also show the anomalous values of beryllium as well as the soils on the Zeleni Brijeg and lawn Zgmajna on the left bank of the Odra River. High concentrations of Be in the soil in the southeastern industrial zone and around the chemical industrial plant in the northern part of the town are of anthropogenic origin (iron ore processing, hydrocarbon processing, combustion of fossil fuel, and chemical and other industries), whereas anomalies along the Kupa, Odra and Mošćenica rivers are of geogenic origin. Namely, in these areas are occupied by alluvial, predominantly clayey soils (Fluvisols) wherein beryllium is probably associated with the clay minerals.

The area of Old Sisak, the forest park to the west of steelworks, and the northern part of the city around the Zagrebačka Cesta road, as well as the settlements of Galdovo and Hrastelnica and areas of Poloj and Luka along the Sava Rivers all show the concentrations of Be in soil far below the median value for the investigated terrain.

Although the concentrations of beryllium in the urban area of Sisak are not high the toxicity of this element draws attention to its air emissions, especially in the vicinity of the industrial plants.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Berilij (Beryllium)
Be (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Zeleni brijeg
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Be (mg/kg)
Percentil
Percentile
1,9
1,3
1,0
0,8
0,6
0,4
0,4
98
90
75
50
25
10
5
Broj mjerenja
Be (mg/kg)
Minimum: 0,20 (mg/kg)
Minimum
Maksimum: 3,00 (mg/kg)
Maximum
Srednja vrijednost: 0,84 (mg/kg)
Mean
Medijan: 0,80 (mg/kg)
Median
Standardna devijacija: 0,380
Standard Deviation

Bi

10.7. Bi – BIZMUT (atomski broj 4) BISMUTH (atomic number 4)

Bizmut je rijedak element u tragovima s halkofilnim i litofilnim svojstvima i po učestalosti pojavljivanja u Zemljinoj kori zauzima 70. mjesto. Asociran je s Ag, As, Co, Pb, Sb i Zn.

Srednja vrijednost koncentracije bizmuta u Zemljinoj kori kreće se od 0,06 do 0,13 mg/kg. Prosječna koncentracija ovog elementa u ultrabazitima je 0,001 mg/kg, bazitima 0,007 mg/kg, neutralnim magmatskim stijenama 0,01 mg/kg i granitima 0,01 mg/kg. Srednja vrijednost ovog elementa u šejlovima je 0,001 mg/kg, dok za ostale sedimentne stijene nema dovoljno podataka. Prosječni sadržaj ovog elementa u tlima kreće se od 0,13 do 1,52 mg/kg (srednja vrijednost 0,2 mg/kg).

U sekundarnom okolišu bizmut je slabo mobilan. Mobilni bizmut tvori netopive soli, adsorbira se na Fe i Mn oksi-hidrokside te se veže na organsku tvar.

Ovaj element nije esencijalan. Otrovnost mu nije visoka, ali ima neke toksične efekte kod ljudi (npr. kod upotrebe kozmetike).

Svjetska godišnja produkcija bizmuta u 2003. godini iznosila je 447 000 t. Proizvodi se i kao sporedni produkt pri preradi rude olova i volframa.

Upotrebljava se za izradu lako topivih legura, izradu upaljača i raspršivača, u proizvodnji stakla i keramike, a služi i kao katalizator (u proizvodnji gumenih i akrilnih vlakana). Osim toga, služi i u drugim metalurškim industrijama, a nalazimo ga i u elektroničkim uređajima. Upotrebljava se i kao neotrovna zamjena za olovo u mnogim uređajima za obradu hrane. Dodatno, on nalazi primjenu u farmaceutskoj i kozmetičkoj industriji, zubotehnici, a u medicini već od antičkih vremena.

Značajno raspršenje bizmuta u okoliš odvija se putem pepela pri sagorijevanju ugljena i drugih fosilnih goriva. Osim toga, značajni izvori unosa ovog elementa u okoliš su mineralna gnojiva, muljevi iz pročistača otpadnih voda, a posebno fosfatni otpad. U fosfatnim mineralnim gnojivima može biti prisutan i radionuklid bizmuta Bi-214.

Bismuth is a rare trace element with chalcophile and lithophile properties which is 70th in abundance in the Earth's crust. It is associated with Ag, As, Co, Pb, Sb and Zn.

The average value of the concentrations of bismuth in the Earth's crust varies from 0.06 to 0.13 mg/kg. In ultramafic rocks the average value is 0.001 mg/kg, in basalts 0.007 mg/kg, neutral igneous rocks 0.01 mg/kg and in granites 0.01 mg/kg. In shales the average value is 0.001 mg/kg whereas for other sedimentary rocks the data are scarce. The average value of this element in soils varies between 0.13 and 1.52 mg/kg (average value is 0.2 mg/kg).

In the secondary environment Bi is poorly mobile. The mobile bismuth forms insoluble salts, adsorbs on Fe and Mn oxy-hydroxides and bounds on organic matter.

This element is not essential. Its toxicity is not high but nevertheless can have some toxic effects with people (e.g. with use of cosmetics).

The world production of bismuth in the year 2003 was 447,000 t. It is produced as a byproduct during the lad and tungsten processing.

Bismuth is utilized for production of easily melting alloys, production of lighters and diffusers, in production of glass and ceramics, and also as a catalyst (in production of rubber and acrylic fibers). Besides, it serves in other metal industries, and can be also found in many electronic devices. It is used as a non-toxic substitute for lead in many devices for food processing. Additionally, it is applicable in pharmaceutical and cosmetic industry, dental engineering while in medicine it is utilized from ancient times.

Significant dispersion of bismuth into environment is carried out by ashes from the combustion of coal and other fossil fuels. Besides, significant sources for input of this element into environment are mineral fertilizers; muds form the waste water cleaners, and particularly the phosphate waste. In the phosphate mineral fertilizers it can be present as the radionuclide Bi-214.

Ukupne mjerene koncentracije bizmuta u tlima grada Siska kreću se od 0,09 do 1,66 mg/kg vrijednošću medijana od 0,27 mg/kg. Maksimalna koncentracija ovog elementa izmjerena je na sjevernom rubu termoelektrane u blizini rafinerije. Na temelju raspodjele bizmuta u tlu na karti se može jasno odvojiti industrijski dio od ostalog urbanog odnosno ruralnog dijela.

Ekstremne i anomalne koncentracije ovog elementa zabilježene su u industrijskom dijelu u području oko Termoelektrane Sisak i Rafinerije nafte Sisak, u Željezari Sisak te u naselju Kanak. Osim toga, anomalna koncentracija ovog elementa registrirana je i u sjeverozapadnom dijelu naselja Crnac. Sve te ekstremne i anomalne koncentracije posljedica su rada industrijskih postrojenja. Dalje prema urbanim i ruralnim područjima, sadržaj ovog elementa u tlu naglo opada ispod medijana za istraživano područje. Raspršenje u okoliš se u industrijskoj zoni najvjerojatnije odvija dimom, odnosno ispušnim plinovima u zrak te naknadnim obaranjem čestica na tlo. To je jasno vidljivo po izduženom području raspodjele u smjeru *JZ-SI* što odgovara ruži vjetrova za to područje.

Povećane koncentracije u odnosu na medijan, izmjerene su i u uzorcima tla u Starom Sisku (područje rimske Siscije). Te povećane koncentracije također su antropogenog podrijetla (raspršenje u okoliš, od antičkih vremena pa do danas).

Veće koncentracije bizmuta u tlu na desnoj i lijevoj obali Kupe te na lijevoj obali Odre (Zgmajna) su geogenog podrijetla i antropogenog taloženja iz zraka. Tla na tim lokacijama spadaju u grupu aluvijalnih tala (fluvisoli) koja su bogata humusom, mineralima glina i Fe i Mn oksi-hidroksidima (radi relativno visoke razine podzemne vode) na koja se bizmut preferirano veže.

Sva ostala urbana i ruralna područja imaju koncentracije bizmuta ispod medijana za istraživano područje.

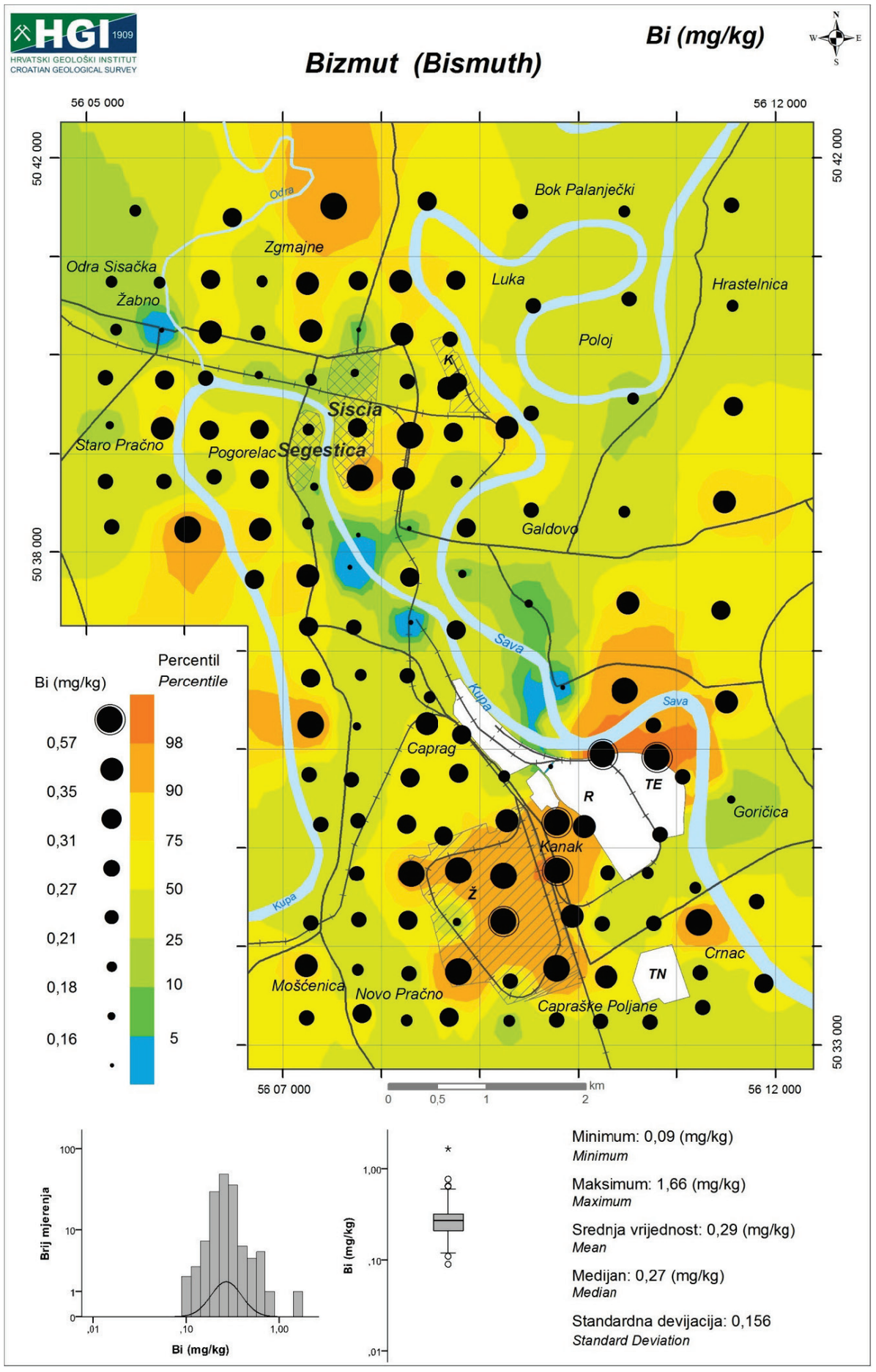
The total measured concentrations of bismuth in the soils of the Sisak city vary between 0.09 and 1.66 mg/kg with median value of 0.27 mg/kg. Maximum concentration of this element is measured on the northern rim of the thermal power plant close to oil refinery. Based on distribution of bismuth in soil on the map one can clearly separate industrial part from other urban and rural input, respectively.

Extreme and anomalous concentrations of this element are registered in the area around the thermal power plant and refinery, in the steelworks and in the Kanak settlement which is situated between the steelworks and refinery. Besides, the anomalous concentration of this element is registered also in the northwestern part of the Crnac settlement. All these extreme and anomalous concentrations result from the work of industrial plants, because the content of bismuth decreases abruptly below the median value for the investigated area away from them toward both urban and rural zones. Dispersion into the environment in the industrial zone is most probably effective through smoke, that is, gaseous emissions into the air and subsequent precipitation of particles to the land surface. This is clearly visible from the elongated area of spatial distribution in the SE-NE direction, which corresponds to the rose of winds in that area.

Increased concentrations with regard to the median value are measured in the soil samples in Old Sisak, that is, the Roman Siscia. These values are also of anthropogenic origin (dispersion into the environment from the ancient times up to the recent).

Major concentrations of bismuth in the soil on the both banks of the Kupa River and on the left bank of the Odra River (Zgmajna) are both of geogenic origin and anthropogenic precipitation form the air. The soils on these locations fall into the group of alluvial soils (Fluvisols) which are rich in humus, clay minerals, and Fe-Mn oxy-hydroxides (owing to the relative high groundwater level) on which bismuth is preferably binding.

All other urban and rural areas show the concentrations of bismuth below the median value for the investigated area.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Bizmut (Bismuth)
Bi (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Bi (mg/kg)
Percentil
Percentile
0,57
0,35
0,31
0,27
0,21
0,18
0,16
98
90
75
50
25
10
5
km
0
0,5
1
2
Brij mjerenja
Bi (mg/kg)
Minimum: 0,09 (mg/kg)
Minimum
Maksimum: 1,66 (mg/kg)
Maximum
Srednja vrijednost: 0,29 (mg/kg)
Mean
Medijan: 0,27 (mg/kg)
Median
Standardna devijacija: 0,156
Standard Deviation

Ca

10.8. Ca – KALCIJ (atomski broj 20) CALCIUM (atomic number 20)

Kalcij je glavni element, obogaćen u stijenama omotača zajedno s Al, Mg, Na i Si, a u Zemljinoj kori i karbonatima s Mg, Mn i Sr. Prema učestalosti u Zemljinoj kori nalazi se na 5. mjestu.

Srednji sadržaj u magmatskim stijenama iznosi 4,2 % (ultrabaziti < 1 %, bazalti 7,6 %, granodioriti > 2,5 % i graniti 0,5 %). Od sedimentnih stijena šejlovi imaju srednji sadržaj kalcija oko 1,6 %, pješčenjaci 3,9 %, vapnenci 30 % i dolomiti 16 %. Koncentracija kalcija u tlu znatno se razlikuje, a srednja vrijednost za najčešće tipove tla je od 0,5 do 2 %. Nekarbonatna tla opskrbljuju se kalcijem iz silikatnih minerala, uključujući feldspate, piroksene i amfibole. Prisutnost kalcija pomaže flokulaciju čestica glina u tlu.

Ovaj element je vrlo mobilan. U tlu zamjenjuje natrij kad je pH 5 – 8, a izlužuje se u kiselijim tlima. Dostupnost željeza može biti ograničena u tlima bogatim kalcijem.

Kalcij je esencijalni biogeni element za sva živa bića osim, za bakterije i gljive. Praktički je neotrovan. Služi kao element za izgradnju struktura (stijenki stanica biljaka, ljuštura, kostiju i dr.). Kalcij je važan prehrambeni sastojak za biljke i unosi se u poljoprivredno tlo preko gnojiva (kalcij je komponenta mnogih N i P gnojiva). Kalcitizacijom u nekarbonatnim poljoprivrednim tlima u humidnoj klimi smanjujemo kiselost tla. S druge strane, kalcitizacija tala bogatih organskom materijom vodi prema brzoj mineralizaciji (gubljenje organske komponente) što može dovesti do otapanja nitrata, pa je u tom slučaju treba izbjegavati. Drastična promjena pH-vrijednosti uzrokovana prekomjernom kalcitizacijom, može povećati dostupnost nekih elemenata (npr. molibdena), što onda nepovoljno utječe na zdravlje pojedinih životinja. Sumnja se da je mala koncentracija kalcija u pitkoj vodi razlog endemskih problema sa srcem.

Pečeni vapnenac i dolomit se upotrebljavju kao građevinski materijal, materijal za ispunu, gnojivo, u proizvodnji kemikalija (klorid i dr.). Proizvodnja kalcija kao metala količinski je podređena.

Dispergirani kalcij se u okolišu ne prepoznaje zbog njegova visokog udjela u geološkoj građi (vapnenci, dolomiti).

Calcium is a major element. It is enriched in the mantle rocks together with Al, Mg, Na and Si while in the Earths crust and carbonates it participates with Mg, Mn and Sr. Calcium is the 5th abundant element in the Earth's crust.

The average content in igneous rocks is 4.2 % (ultramafic rocks < 1%, basalts 7.6 %, granodiorites > 2.5% and granites 0.5 %). Among sedimentary rocks the average content of calcium in shales is about 1.6 %, sandstones 3.9 %, limestones 30 % and dolomites 16 %. Concentration of Ca in soil varies considerably while the median values for the most common soil types is from 0.5 to 2 %. Non-carbonate soils are provided with calcium from the silicate minerals including feldspars, pyroxenes and amphiboles. The presence of Ca enhances the flocculation of clay particles in the soil.

This element is highly mobile. In soil it substitutes sodium at pH 5 – 8. It is leached in the more acid soils. Availability of iron can be limited in soils enriched in calcium.

Calcium is essential biogenic element for all beings except bacteria and fungi and is practically non-toxic. It serves for building of structures (cell membranes in plants, shells, bones and others). Calcium is an important alimentary component for the plants which is finds its way into the agricultural soil through the fertilizers (Ca is a component of many N and P fertilizers). Calcitization in non-carbonate agricultural soils in the humid climates decreases the soil acidity. On the other side, calcitization of soils rich in organic matter leads to quick mineralization (loss of organic component) which can cause the solution of nitrates which is why in that case it must be avoided. Drastic change of pH value caused by excessive calcitization can increase the availability of certain elements (such as molybdenum) which then unfavorably affects the health of some animals. Doubts exist that small concentration of Ca in drinking water provoke endemic problems with heart.

The baked limestone and dolomite are utilized as the building material, filling material, fertilizer, in the production of chemicals (chlorides and others). Production of calcium as a metal is negligible.

Dispersed calcium in the environments is recognized by its high participation in the lithologic settings (limestones, dolomites).

Kalcij je jedan od glavnih elemenata i kao što je vidljivo po njegovom 5. mjestu po učestalosti u Zemljinoj kori, on je sveprisutan element u većini tipova tala i to u relativno visokim koncentracijama.

Raspon koncentracija ovog elementa u analiziranim uzorcima kreće se od 0,03 % do 17,92 % s medijanom od 3,52 %, što je u odnosu na prosječne vrijednosti u Republici Hrvatskoj (0,82 %) i u Posavini (0,83 %) (HALAMIĆ & MIKO, 2009) i do nekoliko puta više.

Maksimalna koncentracija kalcija izmjerena je na južnom rubu haldišta željezare. Nadalje, anomalna koncentracija izmjerena je u jednom uzorku, također u krugu Željezare Sisak, u njenom zapadnom dijelu, u neposrednoj blizini željezničke pruge. Podloga željezničkih tračnica izgrađena je od komada vapnenca i dolomita (tzv. šakanac) te je povećana koncentracija kalcija na tom lokalitetu u izravnoj vezi s nasipanim materijalom. Inače se vapnenac ($CaCO_3$) i dolomit ($Ca,Mg(CO_3)_2$) puno koriste u niskogradnji (za nasipanje cesta i drugih građevinskih objekata), a i sastavni su dio građevinskog pijeska, šljunka i vapna, tako da je povećana koncentracija kalcija u tlima urbanih sredina u blizini cesta i građevinskih objekata normalna pojava. Zbog toga su, u istraživanim urbanim dijelovima Siska, registrirane koncentracije kalcija iznad srednjih vrijednosti.

Međutim, analizirajući kartu raspodjele tog elementa na čitavom istraživanom terenu mogu se razlikovati dva geogeno različita područja. Jedno su tla razvijena na aluvijalnim sedimentima Kupe i Odre u zapadnom dijelu, a drugo područje čine tla na poplavnim sedimentima Save u istočnom dijelu. Tla na aluviju rijeka Kupe i Odre su siromašnija kalcijem i registrirane koncentracije su ispod medijana, dok su tla na aluviju rijeke Save obogaćena kalcijem. To je u neposrednoj zavisnosti o transportiranom materijalu tih rijeka. Naime, sedimenti Kupe i Odre se većim dijelom sastoje od siliciklastičnog materijala, dok Sava donosi većinom karbonatni materijal (vapnenac i dolomit).

Kalcij je sveprisutan element u okolišu i praktički je neotrovan pa zbog toga povećani sadržaji tog elementa u analiziranim uzorcima tla grada Siska nisu od većeg značaja za ljudsko zdravlje.

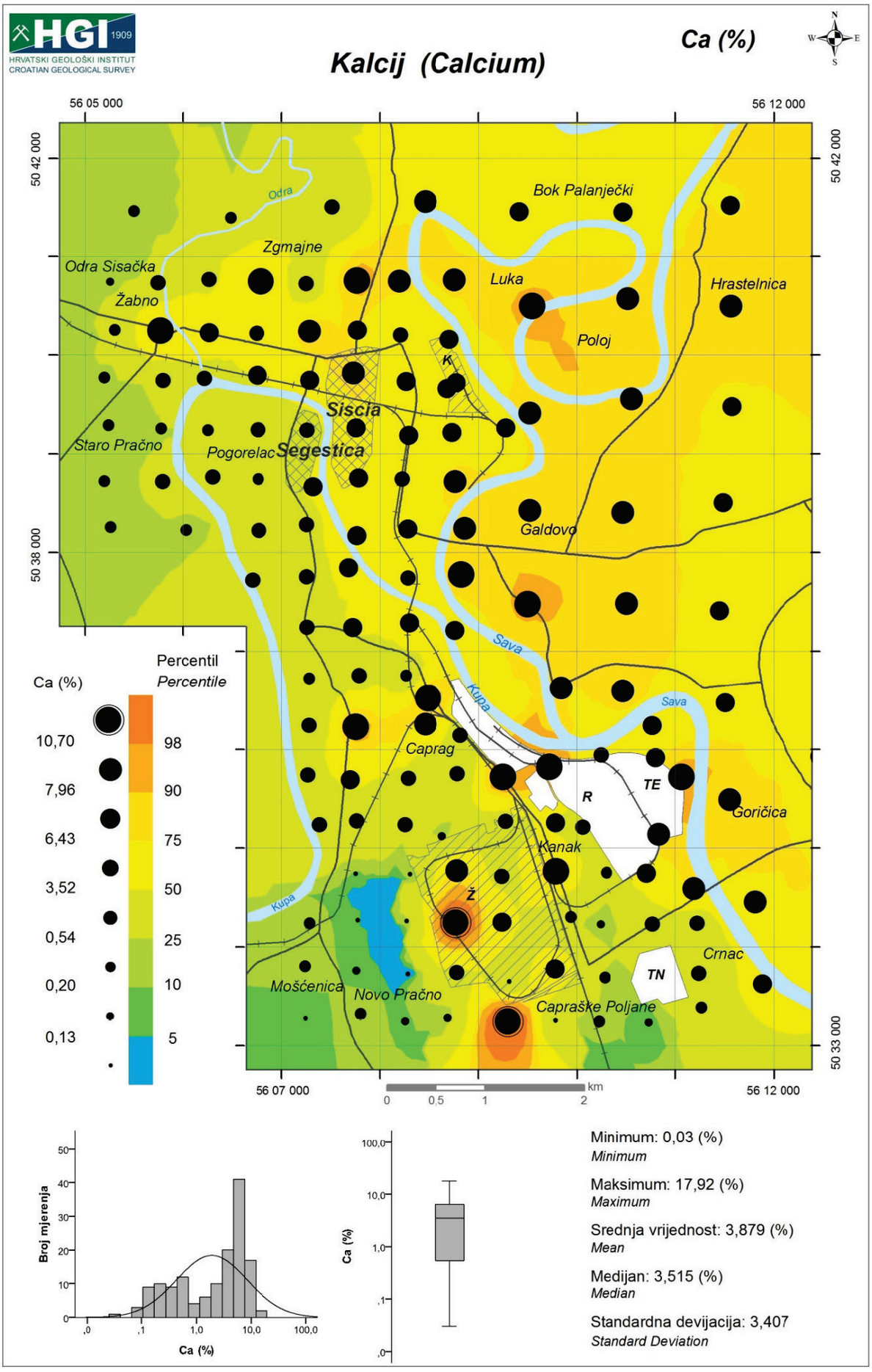
Calcium is one of the major elements which is obvious by its 5th position in abundance in the Earth's crust. Thus it is the omnipresent element in the most soil types occurring in the relative high concentrations.

The concentration range of this element in the analyzed samples is between 0.03 % and 17.92 % with median of 3.52 % which is several times more with respect to the average values in Croatia (0.82 %) and in the region of Posavina (0.83 %) (HALAMIĆ & MIKO, 2009).

Maximum concentration of calcium is measured on the southern rim of the landfill of the Sisak steelworks. Further, the anomalous concentration is measured in a single sample, also from the steelworks milieu, from its western part in the immediate vicinity of the railway. The railway base is built of the limestone and dolomite chunks (the so-called "šakanac") so that the increased content of calcium on that locality is directly related to the dumped material. Otherwise, limestone ($CaCO_3$) and dolomite ($Ca,Mg(CO_3)_2$) are abundantly applied in the civil engineering (dumping of roads and other building objects) but they are also the component parts of the building sand, gravel and lime which is why the increased calcium concentrations are the common phenomenon in the soils of urban cores in the vicinity of roads and building objects. Because of that the concentrations of calcium above the average values are registered in the investigated urban parts of the city of Sisak.

However, by analyzing the spatial distribution map of that element in the entire investigated territory one can distinguish two different areas in the geogenic sense. One is represented by the soils developed on alluvial sediments of the Kupa and Odra Rivers in the western part and the other is by soils formed on the floodplain sediments of the Sava River in the eastern part. The soils on the alluvium of the Kupa and Odra are poorer in calcium with concentration below median while those on the alluvium of the Sava are, on the contrary, enriched in calcium. This is closely dependent on the material carried by these rivers. Namely, the sediments of Kupa and Odra are for the most part composed of siliciclastic material whereas the Sava River carries mostly the carbonate material (limestone and dolomite).

Calcium is ubiquitous in the environment and practically non-toxic so that the increased quantities of this element in the analyzed samples of the city of Sisak are not of major importance for the human health.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
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Kalcij (Calcium)
Ca (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
Ca (%)
10,70
7,96
6,43
3,52
0,54
0,20
0,13
98
90
75
50
25
10
5
0
0.5
1
2
km
Broj mjerenja
Ca (%)
Minimum: 0,03 (%)
Minimum
Maksimum: 17,92 (%)
Maximum
Srednja vrijednost: 3,879 (%)
Mean
Medijan: 3,515 (%)
Median
Standardna devijacija: 3,407
Standard Deviation

Cd

10.9. Cd – KADMIJ (atomski broj 48) CADMIUM (atomic number 48)

Kadmij je rijedak halkofilni, srebrnosivi metal u tragovima i nalazi se na 65. mjestu po učestalosti u Zemljinoj kori. Po osobinama jako sliči cinku.

Srednji sadržaji u magmatskim stijenama su: ultrabaziti 0,05 mg/kg, baziti 0,19 mg/kg, intermedijarne stijene 0,13 mg/kg i kisele stijene 0,1 mg/kg. U šejlovima on iznosi 0,3 mg/kg, u pješčenjacima 0,02 mg/kg, u karbonatima 0,035 mg/kg i u glinama 0,42 mg/kg. Srednji sadržaj ovog elementa u tlima kreće se od 0,06 do 1,1 mg/kg sa srednjom vrijednošću od 0,5 mg/kg. U slatkoj vodi ga prosječno ima 0,08 μg/L.

Mobilnost ovog elementa je vrlo mala i jako ovisi o pH-vrijednosti okoliša. Postojan je na utjecaj atmosferilija. Otapa se u kiselinama, teže u neoksidirajućim, a lakše u kiselinama koje imaju oksidacijsko djelovanje. Dostupan kadmij formira helate s organskom tvari ili se apsorbira u minerale glina. Kadmij se obogaćuje u otpadnim muljevima koji se često rabe kao gnojivo u poljoprivredi.

Kadmij je esencijalan za neke životinje, ali u vrlo malim koncentracijama. Nije biogeni element. Otrovan je za ljude i životinje. Smatra se jednim od najotrovnijih ekotoksičnih metala za ljude, životinje i biljke, a unosi se inhalatorno ili putem hrane i pića. Neke biljke akumuliraju kadmij u korijenju. Tla s koncentracijama ovog elementa većim od 5 mg/kg rezultiraju manjim urodom. Pšenica, celer i mrkva akumuliraju kadmij, dok ga, primjerice, krumpir ne akumulira.

Godišnja proizvodnja ovog metala je od 1990. godine u opadanju i 2003. godine ona je iznosila

16 800 t. Kadmij se dobiva kao nusproizvod kod proizvodnje metala cinka. U današnje vrijeme se intenzivno reciklira, posebice iz Zn-Cd baterija.

Kadmij se upotrebljava za izradu lako topivih legura, za galvanizaciju, izradu akumulatora i baterija (Ni-Cd i Ag-Cd baterije), za legure i boje, za zaštitu od korozije (postojan na atmosferilije) i kao materijal za kontrolu fisije u nuklearnim reaktorima. Osim toga, Cd-sulfat se rabi za izradu Westonovih elemenata, koji služe mjerenju napona i to kao standard.

U okoliš dospijeva preko otpada, sagorijevanjem fosilnih goriva, iz rudnika olova i cinka, razgradnjom boja i zaštitnih sredstava, iz peći za proizvodnju cementa, od trošenja automobilskih guma te iz fosfatnih mineralnih gnojiva u poljoprivredi. Značajni onečišćivači su termoelektrane. Tla se onečišćuju najčešće kroz odlaganje iz zraka i kroz fosfatna mineralna gnojiva. Kadmij se najvećim dijelom zadržava u 15 cm površinskog tla. Vrlo značajne su i industrijske emisije u zrak, pogotovo u blizini metaloprerađivačkih postrojenja (topionice, željezare).

Cadmium is a rare chalcophile, silver-white trace metal which is 65th in abundance in the Earth's crust. By its properties it is similar to zinc

Average content in the igneous rocks is as follows: ultramafic rocks 0.05 mg/kg, basalts 0.19 mg/kg, intermediary rocks 0.13 mg/kg and acid rocks 0.1 mg/kg. In shales it amounts to 0.3 mg/kg, in sandstones 0.02 mg/kg, in carbonates 0.035 mg/kg and in clays 0.42 mg/kg. The average content of this element in the soils varies from 0.06 to 1.1 mg/kg, with median of 0.5 mg/kg. In the sweet water the average is 0.08 μg/L.

Mobility of this element is very low and strongly depends on environmental pH values. It is stabile to the influence of atmospheric phenomena. Cadmium dissolves in acids, harder non-oxidizing but more easily in acids having oxidizing properties. Available cadmium forms chelates with organic matter or absorbs in the clay minerals. It is enriched in waste mud which are frequently used as fertilizers in agriculture

Cadmium is essential for some animals but only in very low concentrations. Not being a biogenic element it is toxic for people and animals. Cadmium is deemed one of the most eco-toxic metals for humans, animals and plants and its entry into the organism is by inhaling or by food or drink. Some plants accumulate cadmium in their roots. Soils with concentration of this element greater 5 mg/kg result with poorer crop. Wheat, celery and carrot accumulate cadmium whereas, for example, potato does not.

The year production of this metal is plummeting since 1990 and with the year 2003 it was 16,800 t. Cadmium is obtained as a byproduct in the production of zinc. Recently, it is intensely recycling, particularly of the Zn-Cd batteries.

Cadmium is used for the production of easily melting alloys, for galvanization, production of accumulators and (Ni-Cd and Ag-Cd batteries), for alloys and paints, for protection against corrosion (stable to atmospheric phenomena) and as material for the control of fission in the nuclear reactors. Besides, cadmium is utilized in the making of the Weston elements which serve to the measuring of voltage as a standard.

Cadmium disperses into the environment through the waste, by combustion of fossil fuels, from the lead and zinc mines, breakdown of paints and protective agents, from furnaces for the production of cement, from wasting of car tires and from the phosphate mineral fertilizers in the agriculture. The most troublesome pollutants are thermal power plants. The soils are more often by deposition from the air and through the phosphate mineral fertilizers. Cadmium is for the most part retained in the topsoil (15 cm). Industrial emissions into the air are highly important, especially close to metal-processing plants (smelteries, steelworks).

Kadmij je jedan od najotrovnijih metala u okolišu i zbog toga je potrebno posvetiti posebnu pažnju interpretaciji izmjerenih koncentracija u tlu. Na istraživanom području izmjerene koncentracije ovog elementa u uzorcima tla kreću se od 0,14 do 10,96 mg/kg s medijanom od 0,46 mg/kg. Ekstremne koncentracije registrirane su isključivo u industrijskom dijelu i to u području Željezare Sisak, Rafinerije nafte Sisak i Termoelektrane Sisak. Najveća vrijednost izmjerena je u neposrednoj blizini Termoelektrane. Ekstremna koncentracija registrirana je također i u sjeverozapadnom dijelu naselja Crnac. Prema periferiji industrijskih postrojenja, u svim pravcima, koncentracija kadmija u tlu naglo opada ispod vrijednosti medijana, što je dokaz antropogenog onečišćenja. Iznimka je područje sjeverno od Rafinerije i Termoelektrane (Travno na desnoj obali Save, Polojci na lijevoj obali Save i dalje na sjever prema naselju Galdovo). U tim područjima registrirane su anomalne do visoke vrijednosti kadmija u tlu. Područje prema naselju Budaševo na sjeveroistoku pokazuje također koncentracije kadmija u tlu iznad medijana. Sve te povišene koncentracije kadmija u tlu posljedica su emisije ovog metala u zrak iz industrijskih postrojenja na jugu i njegove kasnije depozicije na tlo, u smjeru glavnih pravaca puhanja vjetra, na sjever, odnosno sjeveroistok.

Povećane koncentracije kadmija u tlu u području Starog Siska (Siscije) i na Pogorelcu (Segestice) također se mogu protumačiti antropogenim utjecajem (jako razgranata mreža olovnih vodovodnih cijevi u doba Rimljana u kojima se nalazi i određen sadržaj kadmija).

Povišene vrijednosti ovog elementa iznad srednjih sadržaja u okolici kemijske industrije „HERBOS“ posljedica su proizvodnje raznovrsnih kemijskih proizvoda u tom postrojenju od Drugog svjetskog rata do današnjih dana.

Uzorak tla u sjevernom dijelu istraživanog područja u naselju Žabno također pokazuje povišenu koncentraciju kadmija. Tlo na tom lokalitetu je antropogeno i jako obogaćeno organskom tvari na koju je vjerojatno vezan

Cadmium is one of the most toxic metals in the environment which is why it must be paid special attention to interpretation of the measured concentrations in the soil. In the investigated area the measured concentrations of this element in the soil samples vary from 0.14 to 10.96 mg/kg with median of 0.46 mg/kg. Extreme concentrations are registered solely in the industrial zone, namely in the circle of steelworks, oil refinery and thermal power plant. The highest value is measured in the immediate vicinity of the thermal power plant. The extreme value is registered also in the northwestern part of the Crnac settlement. Toward the peripheral zones of the industrial plants in all directions the concentration of cadmium in the soil declines abruptly below the median values, which is the evidence for the anthropogenic contamination. Exception is the area to the north of the refinery and the thermal power plant (Travno on the right bank of the Sava River, Polojci on the left bank of the Sava River and more to the north toward the Galdovo settlement). In these areas are registered anomalous to high values of cadmium in the soil. The area toward Budaševo settlement to the northeast also shows the concentrations of cadmium in the soil above the median values. All these elevated values of cadmium in the soil result from the emission of this metal into the air from the industrial plant to the south and its consequent deposition on the land surface in the direction of prevailing winds, to the north and northeast.

Increased concentrations in the soil in the area of Old Sisak (Siscia) and on Pogorelec (Segestica) can be also explained by anthropogenic impact (a large network of lead conduits in the Roman times containing a certain quantity of cadmium)

Increased values of this element above the median in the surroundings of the chemical industry of „HERBOS“ are the consequence of various chemical products in that industrial plant from the WWII to the present.

The soil sample in the northern part of the investigated area in the settlement of Žabno also indicates the ele-

ovaj element. Suprotno tome, povećane koncentracije kadmija koje su registrirane u tlu na desnoj obali Kupe te u tlima oko meandra Save na sjeveru (Luka, Poloj, Bok Palanječki) su geogenog podrijetla i potječu iz deponiranog materijala na poplavnoj ravnici. Tla na aluvijalnim sedimentima toga područja su bogata mineralima glina koji na sebe vežu kadmij.

Prema prijedlogu iz *Programa trajnog motrenja tala Republike Hrvatske* (MESIĆ et al., 2008.) dozvoljene granične vrijednosti za kadmij u tlima za poljoprivredna tla su 2 mg/kg, za dječja igrališta 5 mg/kg, za područja za stanovanje 10 mg/kg, za parkove 30 mg/kg i za industrijska područja 50 mg/kg (Tab. 6.2.). Prema tim preporučenim graničnim vrijednostima izmjerene koncentracije kadmija u tlima na čitavom istraživanom području urbane cjeline Siska su u granicama dozvoljenih. Međutim, bez obzira na to, posebnu pažnju treba ipak posvetiti tlima u naselju Kanak na čijem području se nalazi mnogo privatnih vrtova zasađenih voćem i povrćem za potrebe domaćinstava, posebice zbog toga, jer neke biljake poput mrkve i celera mogu akumulirati ovaj otrovni element (KABATA-PEDIAS & MUKEHRJEE, 2007). Osim toga, pozornost treba obratiti i na poljoprivrednu površinu koja se nalazi neposredno sjeverno od Termoelektrane Sisak (Travno). Na njoj se uzgajaju žitarice koje također mogu akumulirati kadmij u većim koncentracijama (npr. pšenica).

vated concentrations of this element. Soil on this site is anthropogenic and is strongly enriched in organic matter which probably binds this element.

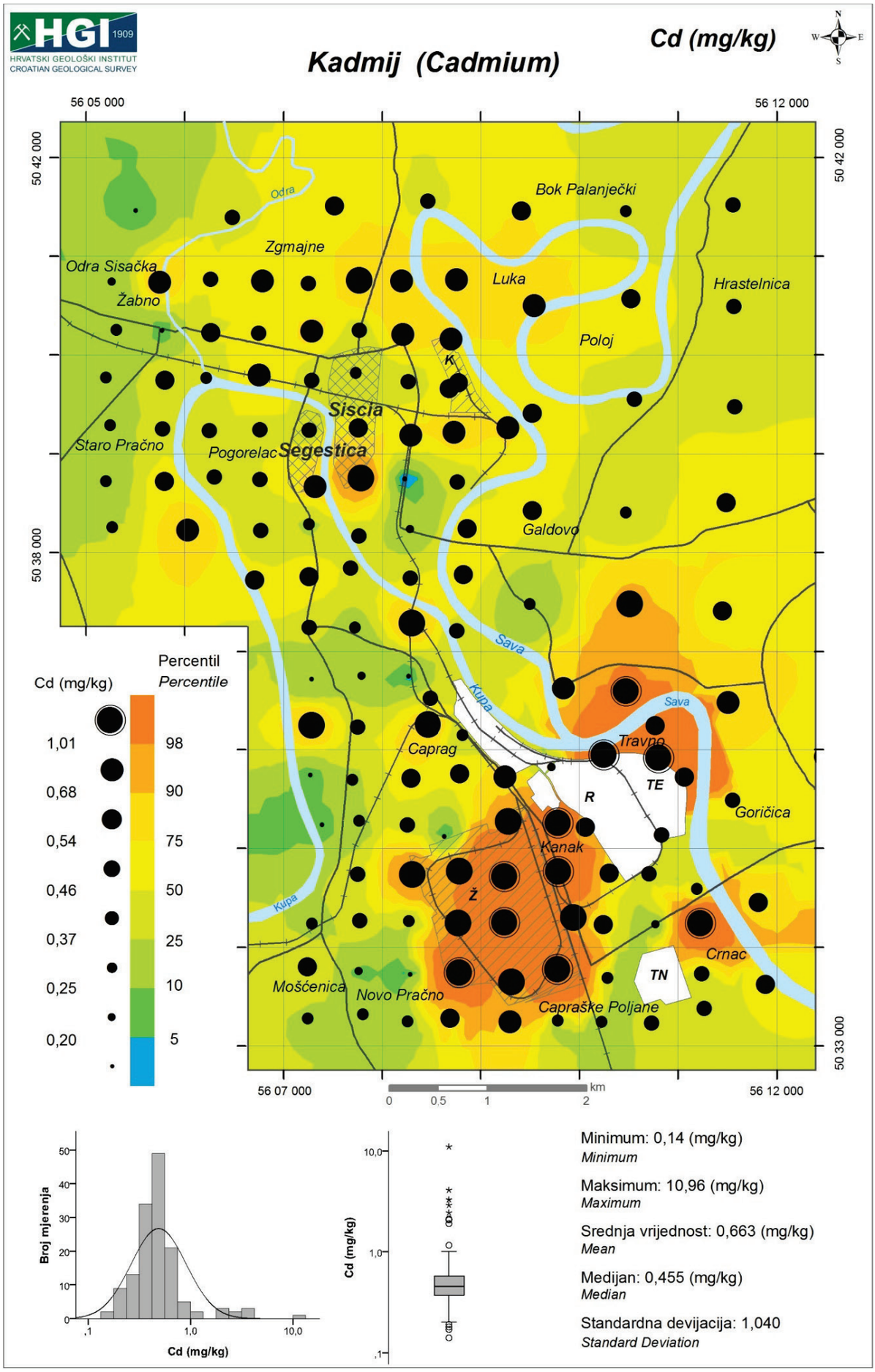
On the contrary, increased concentrations of cadmium registered in the soil on the right bank of the Kupa River as well as around the meander of the Sava River to the north (Luka, Poloj, Bok Palanječki) are of geogenic origin and originate from the material deposited on the floodplain. Soils on the alluvial sediments of this area are rich in clays which bind cadmium.

In accordance with the suggestion from the Program of the permanent monitoring of the Croatian soils with a pilot project" (MESIĆ et al., 2008) the allowed limit values for Cd in the agricultural soils are 2 mg/kg, for kindergartens 5 mg/kg, for residential areas 10 mg/kg, for parks 30 mg/kg and for industrial zones 50 mg/kg (Tab. 6.2.). According to these values the measured concentrations of cadmium on the entire territory of the urban Sisak area are within the prescribed limits. However, in spite of this the special attention must be paid to the soils in the Kanak settlement which is situated between the steelworks, refinery, and thermal power plant. On this area there are many privately owned gardens for cultivation of fruits and vegetables for the home use. This is particularly necessary due to the fact that some plant species, such as carrot and celery tend to accumulate this toxic element (KABATA-PEDIAS & MUKEHRJEE, 2007). Besides, attention must be paid also to the agricultural land situated immediately to the north of the thermal power plant (Travno) where cereals are cultivated which can also accumulate cadmium (such as wheat).



Slika 10.2. *Uzimanje uzorka na igralištu u naselju Kanak (Foto: J. Halamić).*

Figure 10.2. *Sampling at the playground in the Kanak settlement (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Kadmij (Cadmium)
Cd (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
Travno
TE
R
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
Cd (mg/kg)
1,01
0,68
0,54
0,46
0,37
0,25
0,20
98
90
75
50
25
10
5
56 07 000
56 12 000
km
0
0,5
1
2
Broj mjerenja
Cd (mg/kg)
,1
1,0
10,0
Minimum: 0,14 (mg/kg)
Minimum
Maksimum: 10,96 (mg/kg)
Maximum
Srednja vrijednost: 0,663 (mg/kg)
Mean
Medijan: 0,455 (mg/kg)
Median
Standardna devijacija: 1,040
Standard Deviation

Ce

10.10. Ce – CERIJ (atomski broj 58) CERIUM (atomic number 58)

Cerij je element iz grupe lantanida odnosno tzv. lakih rijetkih zemalja (LREEs) i u toj grupi on je najčešći element. Po učestalosti pojavljivanja u Zemljinoj kori nalazi se na 25. mjestu. Obogaćuje se s porastom alkaliniteta magme.

Srednja vrijednost cerija u magmatskim stijenama je 60 mg/kg (ultrabaziti 9 mg/kg, oceanski toleitni bazalti 10 mg/kg, bazalti 48 mg/kg i graniti 92 mg/kg). Šejlovi sadrže 50 mg/kg, pješčenjaci 20 mg/kg i karbonati 10 mg/kg. U tlu koncentracije cerija variraju od 30 do 97 mg/kg. Najmanje vrijednosti su u pjeskovitim tlima, a najveće u ilovastim tlima. U slatkoj vodi koncentracija cerija je 0,00006 mg/L. Cerij je topiv u vodi u formi karbonatnih kompleksa.

Mobilnost ovog elementa je niskaAkumulira se u pijescima teških minerala te u humusnim horizontima tala.

Cerij nije esencijalni element. Otrovnost mu je relativno niska, ali je vrlo malo literaturnih podataka za pouzdanu procjenu njegove toksičnosti. Poznato je da neke biljke, kao npr. američki orah (hickory), akumuliraju cerij. Nije poznat utjecaj cerija na biljke.

Proizvodnja lantanida (plus Sc i Y) u 2000. godini iznosila je 83 300 t, a totalna produkcija REE u 2003. godini iznosila je 75 150 t. Najviše se proizvodi iz minerala monacita i bastnesita.

Cerij ima višestruku tehničku primjenu. Upotrebljava se za proizvodnju upaljača, sredstava za brušenje, u proizvodnji stakla za bojanje, izradi slitina, baterija za punjenje, u industriji radara, katalitičkih konvertera i dr.

Disperzija u okoliš je relativno mala. Lantanidi se mogu naći u muljevima iz pročistača i to u prilično velikim koncentracijama. U kultiviranim tlima povećan sadržaj može biti posljedica intenzivnog tretiranja tla fosfatnim mineralnim gnojivima. Veće koncentracije lantanida u zraku su isključivo posljedica antropogenog unosa kroz raznorazne emisije.

Cerium is an element from the group of lanthanides or the so called light rare earths (LREEs) figuring as the most common among them. It is 25th in abundance in the Earth's crust, being enriched with increase of the magma alkalinity.

The average value of Ce in igneous rocks is 60 mg/kg (ultramafic rocks 9 mg/kg, oceanic tholeiite basalts 10 mg/kg, basalts 48 mg/kg, and granites 92 mg/kg). Shales contain 50 mg/kg, sandstones 20 mg/kg and carbonates 10 mg/kg. In soils concentrations of Ce vary from 30 to 97 mg/kg. The least values occur in sandy soils while the greatest are found in loamy soils. In the sweet water the concentration of cerium is 0.00006 mg/L. Cerium is soluble in water in the form of carbonate complexes.

Mobility of this element is low. It accumulates in sands containing heavy minerals as well as in humus in soils.

Cerium is not an essential element. Its toxicity is relatively low. However, data from literature concerning the reliable assessment of its toxicity is scarce. It is known that some plants, such as American nut (hickory) accumulate cerium. Its impact on plants is not known.

Production of lanthanides (plus Sc and Y) in the year 2000 was 83,300 t while the total production of REE u in 2003 was 75,150 t. It is mostly extracted from the monazite and bastnaesite.

Cerium has a multiple use in technology. It is utilized for the production of lighters, abrasive materials, colored glass, alloys, batteries, radars, catalytic convertors and others.

Dispersion of cerium into environment is relatively small. Lanthanides can be found in in considerable quantities in mud from cleaners. In cultivated soils the increased lanthanide content can be the consequence of intense treatment of soil by the phosphate mineral fertilizers. Higher concentrations of lanthanides in the air are solely the result of the anthropogenic input by various emissions.

Izmjerene koncentracije cerija na istraživanom području su u rasponu od 9,8 do 58,9 mg/kg vrijednošću medijana od 30,75mg/kg. Za ovaj element na čitavom području nisu izmjerene ekstremne i anomalne vrijednosti. Maksimalna izmjerena koncentracija registrirana je u tlu na aluvijalnim sedimentima na desnoj obali Kupe. Tlo na toj lokaciji je bogato mineralima glina i humusom te je cerij najvjerojatnije akumuliran u tim komponentama tla i geogenog je podrijetla.

Visoke koncentracije cerija izmjerene su u uzorcima tala neposredno oko Rafinerije nafte Sisak te dijelom u i oko Željezare Sisak. Nema dvojbe da su u tom području povišene koncentracije cerija posljedica industrijske prerade ugljikovodika i metala. Povišene vrijednosti cerija u naselju Caprag mogu se također vezati uz antropogeni industrijski unos u tlo. Međutim, visoka koncentracija cerija u tlu u Fistrovićevoj ulici nema jednoznačnog objašnjenja, jer se ta lokacija nalazi između vrlo prometne gradske ulice i željezničke pruge.

Karta raspodjele cerija u urbanim tlima grada Siska pokazuje dvije, po sadržaju ovog elementa u tlima, potpuno različite cjeline, ali sa zajedničkim geogenim podrijetlom. Očito je da tla koja su razvijena na aluvijalnim sedimentima rijeke Kupe, a dijelom i Odre imaju općenito veće koncentracije ovog elementa, dok tla razvijena na aluviju rijeke Save imaju znatno manje sadržaje cerija od medijana za istraživano područje. Tla koja se nalaze na aluviju rijeka Kupe i Odre imaju više siliciklastičnog materijala, glinovite komponente i humusa što pogoduje akumulaciji cerija u njima. Tla na poplavnim sedimentima Save su više pjeskovita i s manje organske tvari što rezultira manjim vrijednostima ovog elementa u njima.

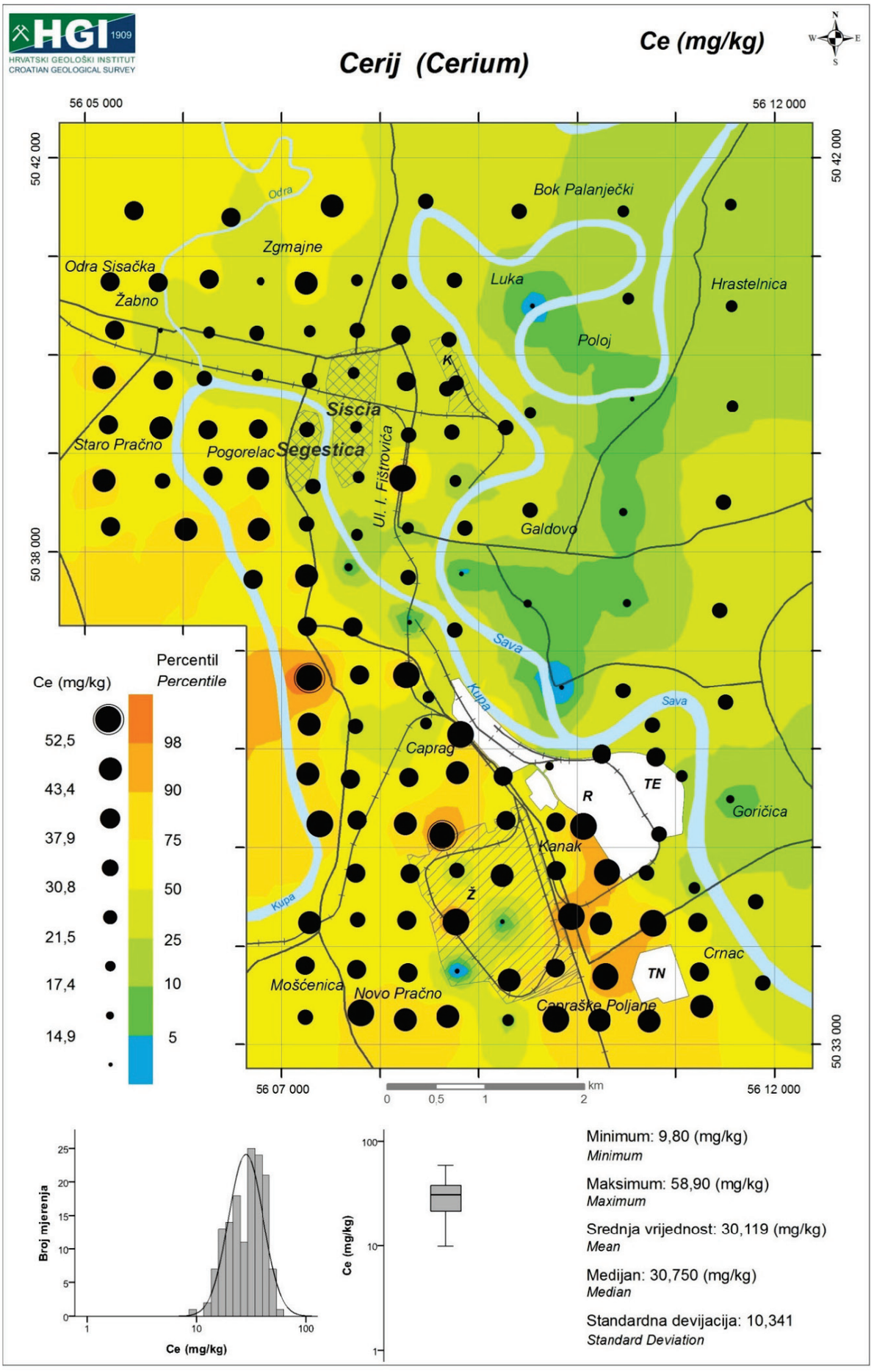
Element cerij nije visoko toksičan, pa relativno niske izmjerene koncentracije u tlima urbanog područja Siska ne predstavljaju značajniju opasnost za okoliš.

The measured concentrations of cerium in the investigated area vary between 9.8 and 58.9 mg/kg with median of 30.75 mg/kg. There is no extreme and anomalous values measured for this element in the entire area. The maximum concentration is registered in the soils developed on the alluvial sediments on the right bank of the Kupa River. The soil at this location is rich clay minerals and humus so that cerium is most probably accumulated in these components as the geogenic input.

The high concentrations of cerium are measured in the soil samples immediately around the refinery and, partly, in the zone in and around the steelworks. It is doubtless that in this area the elevated concentrations of cerium arise from the industrial production of hydrocarbons and metals. Increased values of cerium in the Caprag settlement can be also associated with anthropogenic input into the soil. However, the high concentration of Ce in the Fištrović's street can not be unequivocally explained because this location is found between the very busy city street and the railway.

The spatial distribution of cerium in the urban soils of Sisak displays two completely different whole but with common geogenic origin. It is obvious that soils developed on the alluvial sediments of the Kupa, and partially, Odra River, contain, in general, higher concentrations of this element while those developed on the Sava River alluvium show the lower contents of cerium for the investigated area. Soils on the alluvium of Kupa and Odra Rivers contain more siliciclastic material, clayey component and humus which favor the accumulation of cerium. Soils on the flood sediments of River Sava are more sandy with less content of organic material which has result by lower value of this element in them.

The element cerium is not highly toxic so that relatively low concentrations measured in the soils of the urban area of the Sisak do not represent a significant threat to the environment.


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Cerij (Cerium)
Ce (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Ul. I. Fištrovića
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Kupa
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Ce (mg/kg)
Percentil
Percentile
52,5
43,4
37,9
30,8
21,5
17,4
14,9
98
90
75
50
25
10
5
Broj mjerenja
Ce (mg/kg)
Minimum: 9,80 (mg/kg)
Minimum
Maksimum: 58,90 (mg/kg)
Maximum
Srednja vrijednost: 30,119 (mg/kg)
Mean
Medijan: 30,750 (mg/kg)
Median
Standardna devijacija: 10,341
Standard Deviation

Co

10.11. Co – KOBALT (atomski broj 27) COBALT (atomic number 27)

Kobalt je litofilni i siderofilni element u tragovima iz skupine željeza. On je prateći element nikla i po učestalosti u Zemljinoj kori nalazi se na 32. mjestu.

Srednji sadržaj kobalta u magmatskim stijenama iznosi 25 mg/kg (ultrabaziti 110 mg/kg, oceanski toleitni bazalti 32 mg/kg, bazalti 48 mg/kg, granodioriti 10 mg/kg i graniti 1 mg/kg). Šejlovi sadržavaju 19 mg/kg, pješčenjaci 0,3 mg/kg i karbonati 2 mg/kg. Koncentracija kobalta u tlima varira od 2 do 40 mg/kg. U područjima mineralizacije može biti i preko 1 000 mg/kg. Najveće koncentracije kobalta vezane su uz tla razvijena na serpentinitima (do 1 000 mg/kg kobalta). Sadržaj kobalta u tlima je najvećim dijelom nasljeđen od matičnih stijena. U slatkoj vodi ima ga 0,0001 mg/L.

Mobilnost kobalta kontrolirana je manganom i željezom. Sorpcijska veza na okside mangana jača je nego na okside željeza. Mobilni Co-ioni vežu se za minerale glina i lako se koprecipitiraju sa Fe i Mn oksi-hidroksidima. Tako kobalt ostaje mobilan samo u kiselim uvjetima.

Kobalt je esencijalni element u tragovima za sve organizme. Ako su koncentracije veće, vrlo je otrovan za biljke, a intravenozno umjereno i za sisavce. On aktivira enzime i fiksira dušik kod biljaka. Kobalt je centralni atom vitamina B_{12}. Njegov manjak može uzrokovati bolest. U područjima siromašnim kobaltom masovno oboljeva stoka na ispaši. Njegov manjak izrazito je prisutan u tlima iznad krupnozrnatih sedimenata ili iznad granita. Tlo se smatra siromašno kobaltom kada je koncentracija manja od 5 mg/kg. Uporaba Co-gnojiva povećava prinose, ali prevelike koncentracije uzrokuju osiromašenje željezom i bakrom.

Svjetska proizvodnja kobalta u 2003. godini iznosila je 43 030 t.

Većina kobalta se koristi za legure,u proizvodnji čelika (oplemenjivač), u avioindustriji, za galvanizaciju i izradu magnetskih uređaja. Manje količine služe u proizvodnji boja, tinte te kao katalizator u naftnoj industriji, učvrščivač plastike i dr. Nadalje, se koristi u medicini i veterini za lijekove. Osim toga, radionuklid ^{60}Co koristi se u medicini kao izvor gama-zračenja.

Raspršenje u okoliš je, zbog relativno niske svjetske proizvodnje, malo, ali lokalno može biti znatno (šljaka). Brojne topionice ruda mogu povećati unos u okoliš. Oko 2 % kobalta korištenog u metalurškoj industriji nalazi se u otpadnim muljevima.

Cobalt is a lithophile and siderophile trace element from the group of iron. It is associated with nickel occupying the 32nd place according to abundance in the Earth's crust.

The average content of cobalt in igneous rocks is 25 mg/kg (ultramafic rocks 110 mg/kg, oceanic tholeiite basalts 32 mg/kg, basalts 48 mg/kg, granodiorites 10 mg/kg and granites 1 mg/kg). Shales contain 19 mg/kg, sandstones 0.3 mg/kg and carbonates 2 mg/kg. Concentration of cobalt in soils varies from 2 to 40 mg/kg. In mineralization areas it can abound up to 1,000 mg/kg. The greatest concentrations of Co are associated with soils developed on serpentinites (up to 1,000 mg/kg of Co). The content of cobalt in soils is for the most part inherited from the parent rocks. In the sweet water cobalt abounds with 0.0001 mg/L.

Mobility of cobalt is controlled by manganese and iron. The sorption bonding to the manganese oxides is stronger with regard to the iron ones. Mobile Co-ions are bonding to clay minerals and easily co-precipitate with Fe and Mn oxy-hydroxides. Thus cobalt remains mobile only in acid conditions.

Cobalt is essential trace element fro all organisms. In greater concentrations it is highly poisonous to plants while interveinal can be moderately toxic for mammals. It activates enzymes and fixes nitrogen in plants. Cobalt is a central atom of the vitamin B_{12}. Owing to its shortage diseases can arise. In areas deficient in cobalt the grazing cattle get sick en masse. It scarcity is explicitly present in soils above the coarse-grained sediments and granites. Soil is deemed deficient in cobalt if concentration is less 5 mg/kg. The use of Co-fertilizers increases the crops but too great concentrations cause depletion in iron and copper.

The world production of cobalt in the year 2003 was 43,030 t.

The most portion of cobalt is utilized for alloys and in then production of steel (ennobling), aircraft production, for galvanization and production of magnetic devices. Minor quantities serve in production of

paintings, ink, as a catalyst in the oil industry, for fixer in production of plastics, etc. Further, cobalt is used in medicine and animal health for drugs. Besides, the radionuclide ^{60}Co is applied in medicine as a source of gamma radiation.

Dispersion into the environment is due to relatively low world production small but locally it can be considerable (dross). Numerous foundries can increase input of cobalt into environment. About 2 % of cobalt used in metallurgy can be found in a waste mud.

Na čitavom istraživanom području nisu registrirane veće koncentracije kobalta u tlu. Izmjerene vrijednosti su u rasponu od 4,5 do 18,5 mg/kg s medijanom od 10,4 mg/kg. Maksimalna koncentracija izmjerena je unutar velikog meandra, na aluvijalnim sedimentima rijeke Kupe.

Visoke i povišene koncentracije ovog elementa utvrđene su najvećim dijelom u uzorcima fluvisola na aluvijalnim sedimentima rijeka Kupe i Odre (područje južno od vodovoda „Kopa“, Staro Pračno, Pogorelec i sisačka Zgmajna). Tla ovih terena bogata su mineralima glina, a posebice Mn i Fe oksi-hidroksidima tako da je mobilni kobalt vezan na njih i obogaćuje se u tlu. Osim toga, jedan dio ovog elementa nalazi se i u teškoj mineralnoj frakciji. Desne pritoke Kupe u Banovini dreniraju stijene ofiolitnog kompleksa koje su bogatije ovim elementom.

Uzorak na sjevernom rubu Rafinerije nafte Sisak sadrži, također, povišenu koncentraciju kobalta, što je vjerojatno vezano uz emisiju ovog elementa u okoliš tijekom proizvodnog procesa.

Ostali dijelovi istraživanog područja imaju malo povišene vrijednosti kobalta u tlu (željezara, kemijska industrija, Caprag, Novo Pračno). Međutim, veći dio istraživanog područja ima koncentracije ovog elementa ispod ili znatno ispod vrijednosti medijana. Neka područja možemo smatrati graničnim u osiromašenju kobaltom (< 5 mg/kg).

Prema predloženim graničnim vrijednostima kobalta u tlu (MESIĆ et al., 2008.) na čitavom istraživanom području koncentracije kobalta u tlu su daleko ispod maksimalno predloženih vrijednosti za sve načine korištenja tla (Tab. 6.2.).

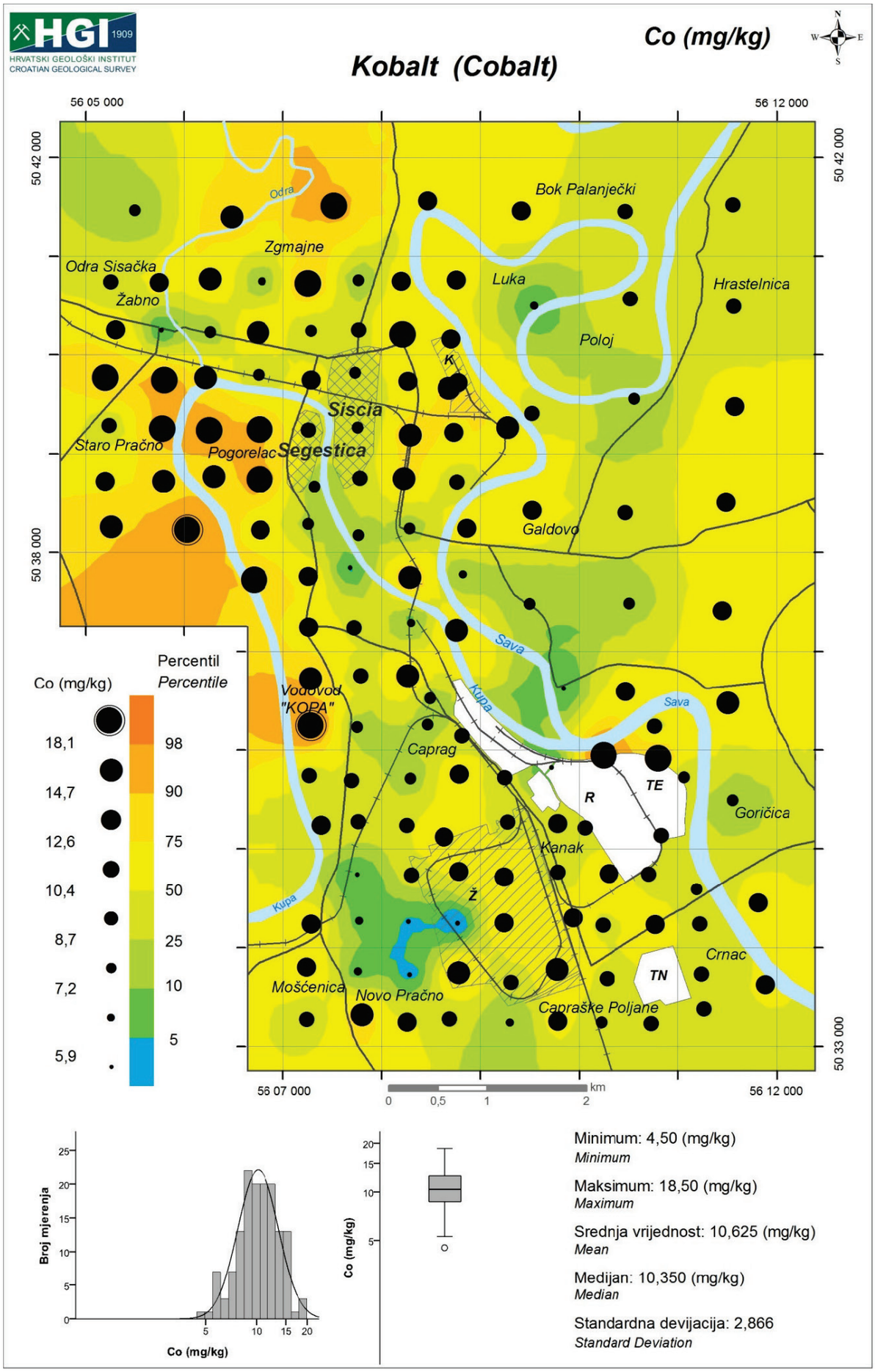
Greater concentrations of cobalt in soils are not registered in the entire area of investigation. The measured values range from 4.5 to 18.5 mg/kg with median of 10.4 mg/kg. Maximum concentration is measured inside the great meander, on the alluvial sediments of the Kupa River.

High and increased concentrations of this element are registered mostly in the samples of fluvisol on the alluvial sediments of the Kupa and Odra Rivers (area to the south of the water supply line „Kopa“, Staro Pračno, Pogorelec and Sisak Zgmajna). The soils on these terrains are rich in clay minerals and particularly with Mn and Fe oxy-hydroxides so that the mobile Co is bonded to them and is enriched in soil. Besides, one portion of this element is found in the heavy fraction. The right tributaries of the Kupa River in the Banovina drain the rocks of the ophiolite complex rich in this element.

The sample on the north rim of the refinery also contains elevated concentration of cobalt which is probably related to emission of this element into environment during the manufacturing process.

The other parts of the investigated area are characterized with slightly increased values of cobalt in soil (steelworks, chemical industry, Caprag, Novo Pračno). However, the concentrations on the greater part of investigated area are below or considerably below the median values. Some zones can be considered even at the edge of depletion of this element (< 5 mg/kg).

According to the prescribed limit values for cobalt in soils (MESIĆ et al., 2008) in the entire area the concentrations of cobalt are far below the maximum prescribed values for all manner of land use (Tab. 6.2.).


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Co (mg/kg)
Kobalt (Cobalt)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Vodovod "KOPA"
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
Co (mg/kg)
18,1
14,7
12,6
10,4
8,7
7,2
5,9
98
90
75
50
25
10
5
Broj mjerenja
Co (mg/kg)
Minimum: 4,50 (mg/kg)
Minimum
Maksimum: 18,50 (mg/kg)
Maximum
Srednja vrijednost: 10,625 (mg/kg)
Mean
Medijan: 10,350 (mg/kg)
Median
Standardna devijacija: 2,866
Standard Deviation

Cr

10.12. Cr – KROM (atomski broj 24) CHROMIUM (atomic number 24)

Krom je litofilni element u tragovima do sporedni element, karakterističan za visokotemperaturne okside. On prati Mg, Fe, Co i Ni. Geokemijski je asociran s Fe i Mn. On je element indikator za ultrabazične i bazične stijene. Prema učestalosti u Zemljinoj kori je na 21. mjestu.

Srednji sadržaj u magmatskim stijenama iznosi 100 mg/kg (ultrabaziti 3 000 mg/kg, oceanski toleitni bazalti 300 mg/kg, bazalti 170 mg/kg, granodioriti 20 mg/kg i graniti 4 mg/kg). Šejlovi sadrže 90 mg/kg, pješčenjaci 35 mg/kg i karbonatne stijene < 10 mg/kg. Koncentracija kroma u tlima u velikoj mjeri ovisi o tipu matične stijene. Srednja vrijednost je 40 mg/kg. Tla većinom sadržavaju od 5 do 1 000 mg/kg Cr, ali ponekad i manje od 5 mg/kg, ili više od 1 %. Ponaša se vrlo različito – može se reducirati, oksidirati, ostati u otopini ili adsorbirati na mineralne i organske komplekse i dr. U slatkoj vodi ga ima 0,001 mg/L.

Mobilnost kroma je mala. Najveći dio kroma nalazi se u mineralima koji nisu toliko podložni trošenju (kromit, magnetit, ilmenit). Manji dio kroma koji se oslobađa trošenjem fiksira se u mineralima glina ili se koprecipitira sa željezovim i/ili manganovim oksi-hidroksidima. U tlima je dokazana pozitivna korelacija između koncentracije kroma i granulometrijskog sastava tako da siltozna i glinova tla imaju veće sadržaje ovog elementa od krupnozrnatijih.

Krom je esencijalni mikronutrijent za energetski metabolizam organizama te je u mikrogramskim količinama važan za biljnu, životinjsku i ljudsku prehranu. Ion Cr^{3+} je u ljudskom organizmu neophodan za metabolizam šećera, a njegov nedostatak može izazvati bolest. Testiran na životinjama, nedostatak kroma uzrokovao je smetnje u rastu. U normalnim uvjetima nije otrovan, osim, možda, u tlima koja se nalaze iznad ultrabazičnih stijena i serpentinita. Otrovnost ovisi o valentnom stanju (Cr^{3+} je relativno neopasan, dok su Cr^{2+} i Cr^{6+} visoko otrovni. Cr^{2+} obično ne nalazimo u prirodi). Većina biljaka ugrađuje krom u malim količinama. Neke ga i akumuliraju, a druge opet mogu tolerirati vrlo velike koncentracije u tlima te su zbog toga od posebnog znanstvenog interesa. Glavni izvori kroma u prehrani su povrće, kompletna zrna žitarica i orašasto voće, zatim žumanjci jaja, pivski kvasac, jetra i plodovi mora.

Procijenjena svjetska produkcija ovog elementa u 2003. godini iznosila je 158 300 t.

Najveći dio kroma upotrebljava se kao oplemenjivač čelika, zatim za visokotemperaturne materijale, za galvanizaciju, pigmente i kemikalije te u nekim umjetnim gnojivima.

Onečišćuje okoliš uglavnom preko industrijskih otpadnih voda (galavanizacija, tekstilna i kožna industrija), razgradnjom legura, termoelektrana na ugljen kao i spaljivanjem komunalnog otpada. Najveći dio kroma u okolišu potječe od raznovrsnih boja i sredstava za štavljenje kože, kod čega se sredstva direktno ispuštaju u vodotoke (u tekućem ili krutom stanju).

Chromium is a lithophile trace to minor element, characteristic for high-temperature oxides. In nature it occurs with Mg, Fe, Co and Ni. Geochemically, it is associated with Fe and Mn and represents an indicator for mafic and ultramafic rocks. It occupies 21st place in abundance in the Earth's crust

The average content of chromium in igneous rocks is 100 mg/kg (ultramafic rocks 3,000 mg/kg, oceanic tholeiite basalts 300 mg/kg, basalts 170 mg/kg, granodiorites 20 mg/kg, and granites 4 mg/kg). Shales contain 90 mg/kg, sandstones 35 mg/kg and carbonate rocks < 10 mg/kg. Concentration of chromium in soils greatly depends on the type of igneous rock. The average content is 40 mg/kg. Soils mostly contain from 5 to 1,000 mg/kg Cr but sometimes also less than 5 mg/kg, or more than 1 %. Chromium behavior is various – it can be reduced, oxidized, it may remain in solution or be adsorbed on minerals and organic complexes, etc. In sweet water it is present with 0.001 mg/L.

Mobility of chromium is low. The most part of chromium is found in minerals not so prone to weathering (chromite, magnetite, ilmenite). The minor part of chromium released by weathering is fixed in clay minerals or co-precipitates with ferric and/or manganese oxy-hydroxides. It is demonstrated the positive correlation between the chromium concentration and granulometric composition of soils which is why the silty and clayey soils contain more chromium with regard to the coarse-grained soils.

Chromium is an essential micronutrient for energetic metabolism of organisms so that in microgram quantities becomes crucial for vegetable, animal and human diet. Cr^{3+} ion is in the human organism nece-

ssary for metabolism of sugar which is why its shortage can cause disease. The lack of chromium with tested animals caused disturbances in growth. In normal conditions it is not toxic except, perhaps, in soils overlying ultramafic rocks and serpentinites. Toxicity depends on state (Cr^{3+} is relatively safe while Cr^{2+} and Cr^{6+} are highly toxic. Cr^{2+} is usually not present in nature). Most plants incorporate chromium in small quantities. Some of them accumulate it while others can tolerate very high concentrations of chromium in soils which is why they are of special scientific interest. The main sources of chromium in the diet are vegetables, the whole cereal grains and nuts, egg yolks, beer yeast, liver and sea fruits.

The estimated world production of chromium in the year 2003 was 158,300 t.

The greatest portion of chromium is used for the steel ennobling, for high temperature materials, galvanization, for production of pigments and chemical as well as in some chemical fertilizers.

Chromium contaminates the environment mostly through industrial waste waters (galvanization, textile and leather industry), degradation of alloys, processes in thermal power plants, and combustion of communal waste. The most part of chromium arises from diverse paints and means for leather processing whereby the chemicals are directly emitted into the streams (in liquid or solid states).

Krom pripada grupi teških metala i kod razmatranja njegove prisutnosti u okolišu, pa tako i u tlu, više pažnje treba posvetiti njegovoj insuficijenciji nego povišenim koncentracijama (osim u ekstremnim slučajevima). Naime, element krom je esencijalni mikronutrijent te njegov nedostatak može izazvati određene poremećaje u organizmu.

Izmjerene koncentracije ovog elementa na istraživanom području kreću se od 15,2 do 462,1 mg/kg s medijanom od 30,6 mg/kg. Najveća vrijednost registrirana je u uzorku tla u krugu Željezare Sisak. Ekstremne vrijednosti izmjerene su i na nekoliko drugih lokacija u krugu tvornice. Zbog široke primjene kroma u metalurgiji ove ekstremne koncentracije bile su i očekivane. Unos ovog elementa u tlo u industrijskim postrojenjima je dijelom mehanički (industrijski otpad po krugu), a dijelom i taloženjem iz zraka. Međutim, iako ekstremne, ove vrijednosti su, prema prijedlogu graničnih vrijednosti za industrijska postrojenja (MESIĆ et al., 2008.), daleko ispod maksimalno dozvoljenih koncentracija.

Osim ekstremnih koncentracija ovog elementa u krugu Željezare Sisak, registrirana je i jedna ekstremna vrijednost u uzorku poljoprivrednog zemljišta na lijevoj obali Save, južno od naselja Goričica, u blizini gradskog odlagališta otpada. Prema Pravilniku o zaštiti poljoprivrednog zemljišta od onečišćenja (Narodne novine 9, 2014) tlo na ovoj lokaciji je zagađeno. Točka uzorkovanja na ovoj lokaciji nalazi se u blizini odlagališta otpada, ali nedaleko se nalaze i industrijska postrojenja rafinerije nafte, termoelektrane i željezare, tako da je teško procijeniti u kojoj mjeri koja industrija ima utjecaja na koncentraciju kroma. Okolni uzorci tla, međutim, ne pokazuju anomalne koncentracije ovog teškog metala, te bi radi sigurne procjene stanja ovu specifičnu lokaciju trebalo detaljnije istražiti.

Ekstremna i anomalna koncentracija kroma izmjerene su i na sjevernom rubu postrojenja Rafinerije nafte Si-

Chromium belongs to the group of heavy metals and considering its presence in the environment and in the soil on must pay more attention to its insufficiency than to its elevated concentrations (except in the extreme cases). Namely, chromium is essential micronutrient which is why its shortage can provoke certain disturbances in the organism.

Measured concentrations of this element in the investigated area range between 15.2 and 462.1 mg/kg with median of 30.6 mg/kg. The greatest value is registered in the soil sample collected in the zone of steelworks. Extreme values are measured also on several other locations around the steelworks. Owing to wide use of chromium in metallurgy these extreme concentrations were expected. Its input into the soil within the sphere of industrial plants is partly mechanic (industrial waste) and partly comes from the airborne emissions. However, although being extreme, these values are far below from the maximum allowed concentrations according to the suggested prescribed values for the industrial processing plants (MESIĆ et al., 2008).

Besides extreme concentrations of this element in the sphere of the steelworks it is also registered another extreme value in the soil sample collected from the agricultural soil on the left bank of the Sava River, to the south of the Goričica settlement close to the city waste depot. According to Regulations on the protection of agricultural soil from pollution (NN9, 2014) the soil on this location is contaminated. The sample point on this location is situated near the waste depot but oil refinery, thermal power plant and steelworks are also found close to it which is why it is hard to estimate to what extent certain industry is responsible for the chromium accumulation. Surrounding soil samples, however, are far from showing any concentrations of this metal that may be assumed as anomalous which is why the safety assessment for this specific location requires a more detailed investigation

sak i Termoelektrane Sisak, a anomalne i povišene vrijednosti registrirane su i u području sjeverno od tih postrojenja na lijevoj obali Save, između Polojaca i naselja Galdovo. Slično kao i za elemente Au, Ag, Ba, Bi i Cd, a dijelom i za As raspršenje ovog elementa u okoliš iz prethodno navedenih industrijskih postrojenja uslijedilo je vjetrom iz zraka.

Anomalne, visoke i povišene koncentracije kroma registrirane su i na skoro čitavom području naselja Caprag. One su, također, antropogenog podrijetla (blizina industrijskih postrojenja). Raspršenje u okoliš uslijedilo je iz zraka. Prema prijedlogu o graničnim vrijednostima kroma u tlu na dječjim igralištima, u stambenim područjima i parkovima (100, 200 i 500 mg/kg – MESIĆ et al., 2008.) izmjerene vrijednosti u ovom naselju su ispod predloženih za sve načine korištenja zemljišta.

Povišene vrijednosti ovog elementa izmjerene su i u tlima koja su razvijena na aluvijalnim sedimentima rijeka Kupe i Odre, što je posljedica povećanog sadržaja teške mineralne frakcije bogatije kromom u matičnom supstratu. Desne pritoke Kupe jednim dijelom dreniraju ultrabazične i bazične stijene ofiolitnog kompleksa Banovine koje su prirodno bogatije ovim teškim metalom. Osim toga, ta tla su bogata mineralima glina i Mn i Fe oksi-hidroksidima koji su potencijalni fiksatori mobilnog kroma.

Tla na poplavnim sedimentima Save imaju koncentracije kroma ispod ili znatno ispod medijana za istraživano područje, što je uvjetovano petrografskim sastavom matičnih stijena iz kojih su ta tla derivirana (šljunci, pijesci, siltovi pretežito karbonatnog sastava s malim sadržajem kroma).

Zanimljiv je pojas povišenih vrijednosti kroma u tlu koji se proteže od Starog mosta na Kupi preko Fistrovićeve ulice i kompleksa tvornice „HERBOS“ do sisačke Zgmajne na sjeveru. Ova anomalija okružuje povišeno područje oko današnjeg željezničkog kolodvora. Iako u starogradskom području, povišene kocentracije kroma su vjerojatno geogenog podrijetla i ocrtavaju pružanje nekog starog toka potoka ili rječice koja je protjecala tim područjem donoseći materijal bogatiji ovim elementom. U prilog ovoj pretpostavci govori nam i geološka građa ovog područja (Sl. 4.1.). Taj povišeni dio izgrađen je od sedimenata druge terase rijeke Save, koji su, kao što smo prethodno utvrdili, siromašniji ovim elementom.

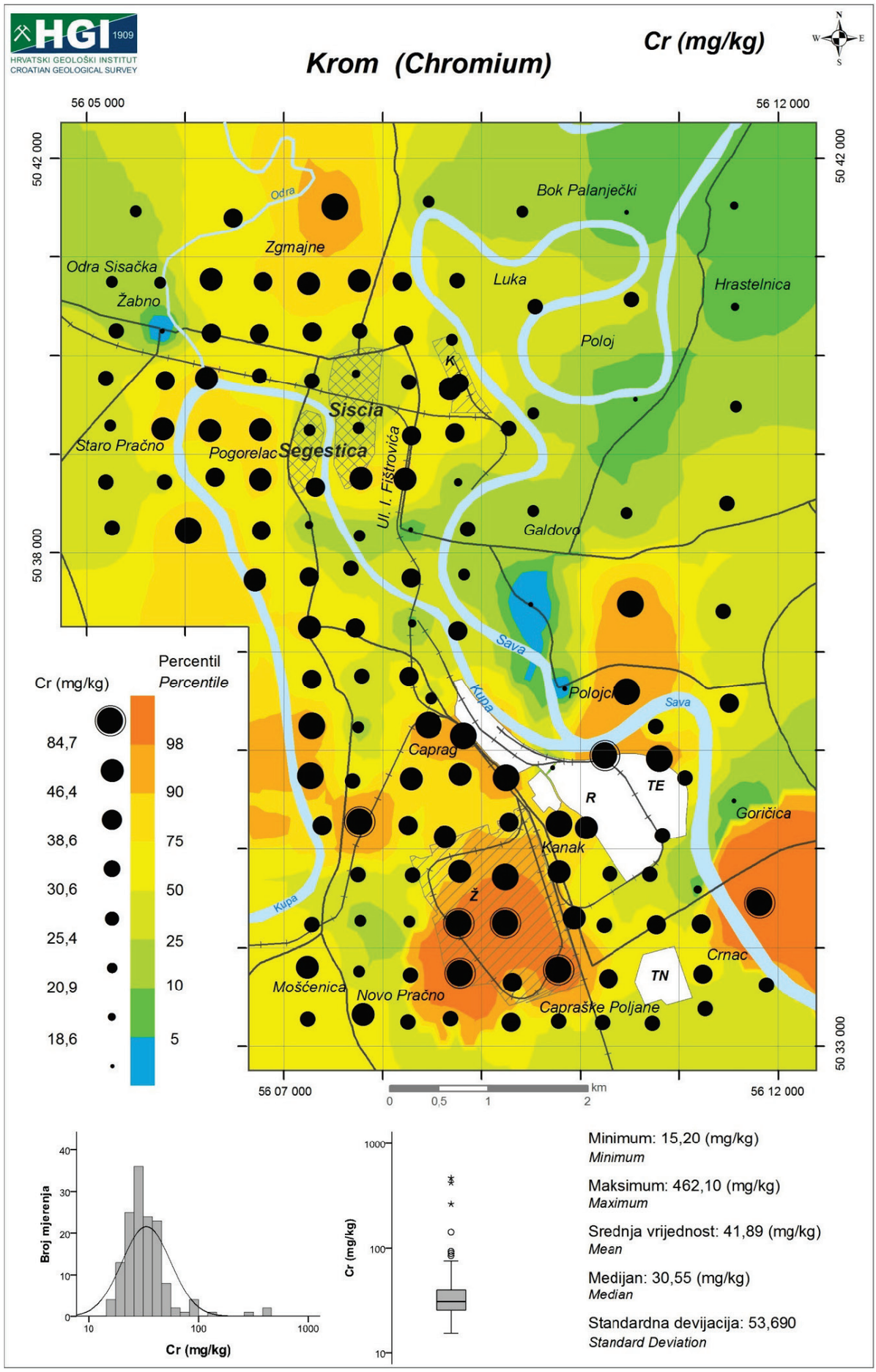
Extreme and anomalous concentration of chromium are also measured on the northern rim of the refinery and thermal power plant while anomalous and increased values are registered to the north of them on the left bank of the Sava River between Polojci and the Galdovo settlement. Analogous to Au, Ag, Ba, Bi and Cd, and partly also to As, dispersion of this element into the environment from the aforementioned industrial processing plants was from the air due to action of wind.

Anomalous, high and increased concentrations of chromium are registered also on the almost entire territory of the Caprag settlement originating doubtlessly from the anthropogenic sources (closeness to the steelworks and refinery). Dispersion into the environment was airborne in origin. According to "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" the limit values of chromium in the soils on the children playgrounds, residential areas and parks (100, 200 and 500 mg/kg - MESIĆ et al., 2008) the measured values in this settlement are below the prescribed for these land uses.

Increased values of this element are measured also in the soils on alluvial sediments of the Kupa and Odra Rivers which is the result of increased quantity of the heavy mineral fraction, rich in chromium, in the bedrock material. Right tributaries of the Kupa River partly drain the mafic and ultramafic rocks of the ophiolitic complex of Banovina which are naturally rich in that element. Besides, these soils are rich in clay minerals and Mn-Fe oxy-hydroxides which are potential fixators of the mobile chromium.

Soils on the floodplain sediments of the Sava River show the concentrations of chromium below or considerably below the median values for the investigated area which is caused by petrographic composition of the parent rocks from which those soils have been derived (gravels, sands, silts of prevalently carbonate composition with low content of chromium).

Interesting zone of the elevated values of chromium in the soil extends from the old bridge on the Kupa River across Fištrović's street and the complex of the „HERBOS“ factory to the Sisak Zgmajna to the north. This anomaly surrounds the uplifted area around the recent railway station. Although appearing in the old town area, these elevated concentrations of chromium are probably of geogenic origin delineating the direction of some olden stream or rivulet that once flowed through that zone carrying with it the material richer in that element. This suggestion is favored by the geological setting of this area (Fig. 4.1.). This uplifted zone is built of the sediments of the second terrace of the Sava River that are, as said before, slightly deficient in this element.


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Krom (Chromium)
Cr (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Ul. I. Fištrovića
Galdovo
Sava
Kupa
Polojci
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Cr (mg/kg)
Percentil
Percentile
84,7
46,4
38,6
30,6
25,4
20,9
18,6
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
Cr (mg/kg)
Minimum: 15,20 (mg/kg)
Minimum
Maksimum: 462,10 (mg/kg)
Maximum
Srednja vrijednost: 41,89 (mg/kg)
Mean
Medijan: 30,55 (mg/kg)
Median
Standardna devijacija: 53,690
Standard Deviation

Cs

10.13. Cs – CEZIJ (atomski broj 55) CESIUM (atomic number 55)

Cezij je alkalni element u tragovima s litofilnim karakteristikama i po pojavljivanju u Zemljinoj kori nalazi se na 46. mjestu. Njegove geokemijske karakteristike slične su rubidiju, ali Cs ima veći afinitet prema alumosilikatima.

Prosječni sadržaj ovog elementa u ultrabazitima je 0,1 mg/kg, bazitima 1 mg/kg, neutralnim magmataskim stijenama 0,6 mg/kg i kiselim magmatskim stijenama 5 mg/kg. Od sedimentnih stijena sadržaj cezija u šejlovima je 12 mg/kg, u pješčenjacima 0,x mg/kg i u karbonatima 0,2 mg/kg. Sadržaj cezija u ugljenu je oko 1 mg/kg. Koncentracija cezija u tlima kreće se od 0,3 do 26 mg/kg što vjerojatno ovisi o sadržaju organske tvari u tlu. U slatkoj vodi sadržaj cezij varira od 0,0004 do 0,02 μg/L.

Mobilnost cezija je niska do vrlo niska u svim okolišnim uvjetima. On ima mali elektronegativitet.

Cezij nije esencijalni element. Podaci o njegovoj otrovnosti su rijetki, ali je zato njegov izotop ^{137}Cs radiotoksičan. Pojava izotopa ^{134}Cs i ^{137}Cs je česta u nuklearnim rektorima. Mnogo pažnje izučavanju ovog elementa u okolišu posvećeno je nakon nuklearne katastrofe u Černobilu. Taloženjem iz zraka dolazi do obogaćenja cezijemu tlima s tom razlikom da izotop ^{134}Cs nije registriran u tlima nakon nuklearnih eksplozija. Otpušten izotop ^{137}Cs u atmosferu se prilikom taloženja veže na minerale glina i organsku tvar u tlu, pogotovu u vršnom organskom horizontu. Više koncentracije ^{137}Cs registrirane su u karbonatnim tlima u odnosu na ona koja su derivirana iz silicijskog matičnog supstrata. Najveće koncentracije ovog izotopa registrirane su u vršnom organskom sloju (engl. *litter*). Cezij ima afinitet istiskivanja kalija te to može imati određene posljedice radi biodostupnosti kalija.

Cezij se kao i rubidij upotrebljava za proizvodnju fotoelektričnih ćelija, izradu vakuumskih cijevi, kao dodatak raketnom gorivu te za izradu atomskih satova. Smjese cezija koriste se i kao katalizatori kod organske sinteze. Radiocezij se ugrađuje i u stanice raka tako da se u medicini koristi za testiranje na rak i u terapijske svrhe.

U okoliš se raspršuje najvećim dijelom nukleranim pokusima i akcidentima.

Cesium is an alkali trace element with lithophile characteristics occurring in the 46th place in abundance in the Earth's crust. Its geochemical characteristics are similar to rubidium but Cs has a grater affinity toward aluminosilicates.

The average content of this element in the ultramafic rocks is 0.1 mg/kg, mafic rocks 1 mg/kg, neutral igneous rocks 0.6 mg/kg and acid igneous rocks 5 mg/kg. Among the sedimentary rocks the content of Cs in shales is 12 mg/kg, in sandstones 0.x mg/kg and in carbonates 0.2 mg/kg. The content of Cs in coal is about 1 mg/kg. Concentration of cesium in soils varies between 0.3 and 26 mg/kg which probably depends on the content of organic matter. The sweet water contains cesium in quantities varying from 0.0004 to 0.02 μg/L.

Mobility of cesium is low to very low in all environmental conditions. It is characterized by low electronegativity.

Cesium is not an essential element. Data about its toxicity are scarce but its isotope ^{137}Cs is radio-toxic. Occurrence of isotopes ^{134}Cs and ^{137}Cs are very common in nuclear reactors. Much attention is paid to study of this element in the environment after the nuclear catastrophe in Černobil. Precipitation from the air causes enrichment of Cs in soils with but the isotope ^{134}Cs is not registered in soils after nuclear explosions. The isotope ^{137}Cs emitted into the atmosphere is bonded during precipitation on clay minerals and organic matter in the soil, especially in the top, organic horizon. Greater concentrations of ^{137}Cs are registered in carbonate soils with respect to those derived from the siliciclastic parent material. The greatest concentrations of this isotope are registered in the top, organic, horizon, that is, litter. Cesium shows affinity to displacement of potassium and thus generates the effects related to its bioavailability.

Cesium together with rubidium is used in industry for production of photoelectric cells, for manufacturing of vacuum tubes, as an addition to the rocket fuel and for production of atomic clocks. Mixtures of cesium are used as catalysts with inorganic synthesis. Radio-cesium is built into the carcinogenic cells, which is why it is employed in medicine for testing against cancer and for therapy.

It is dispersed into the environment mostly by the nuclear tests and accidents in nuclear power plants, that is their reactors.

Karta raspodjele cezija jasno pokazuje povezanost povišenih koncentracija u tlu s industrijskim postrojenjima (željezara, rafinerija i termoelektrana).

Izmjerene vrijednosti ovog elementa na istraživanom području su u rasponu od 0,46 do 7,92 mg/kg s medijanom od 0,97 mg/kg. Najveća koncentracija cezija registrirana je na južnom obodu odlagališta ostataka taljevina iz visokih peći željezare. Nedvojbeno je da ova ekstremna vrijednost potječe iz odlagališta, jer ono se drenira površinskim vodama te se cezij akumulira u tlu ispod i okolo haldišta. Druga ekstremna koncentracija ovog elementa izmjerena je na sjevernom rubu industrijskog kompleksa Termoelektrane i Rafinerije nafte Sisak, što je posljedica emisije cezija tijekom spaljivanja fosilnih goriva i prerade ugljikovodika u tim postrojenjima. Skoro na čitavom području industrijske zone i u njenoj neposrednoj blizini (južno, zapadno i sjeverozapadno od željezare i rafinerije) registrirane su anomalne i visoke koncentracije ovog elementa u tlu. Visoku vrijednost cezija u tlu na području naselja Crnac također treba vezati uz utjecaj industrijske aktivnosti u neposrednoj blizini.

Ekstremnu i anomalnu koncentraciju cezija u području naselja Mošćenica se ne može jednoznačno interpretirati, jer je između tih lokacija i industrijskog postrojenja Željezare Sisak, na istoku, jedan pojas s nižim vrijednostima cezija u tlu. Tla na lokaciji Mošćenica su šumska tla, jako bogata organskom tvari na koju se preferirano veže ovaj element, posebice njegov izotop ^{137}Cs.

Cezij ima i afinitet prema alumosilikatima (K-feldspati, tinjci) pa su stoga povećane vrijednosti u tlima na aluvijalnim sedimentima rijeke Kupe i povećana kocentracija u tlu sisačke Zgmajne geogenog podrijetla, jer su ta tla bogatija alumosilikatima od onih na sedimentima Save.

U ostalim dijelovima istraživanog područja (pretežito sjeverni i istočni dio) registrirane kocentracije cezija su oko ili znatno ispod medijana (posebice predjeli istočno od Save na istoku terena).

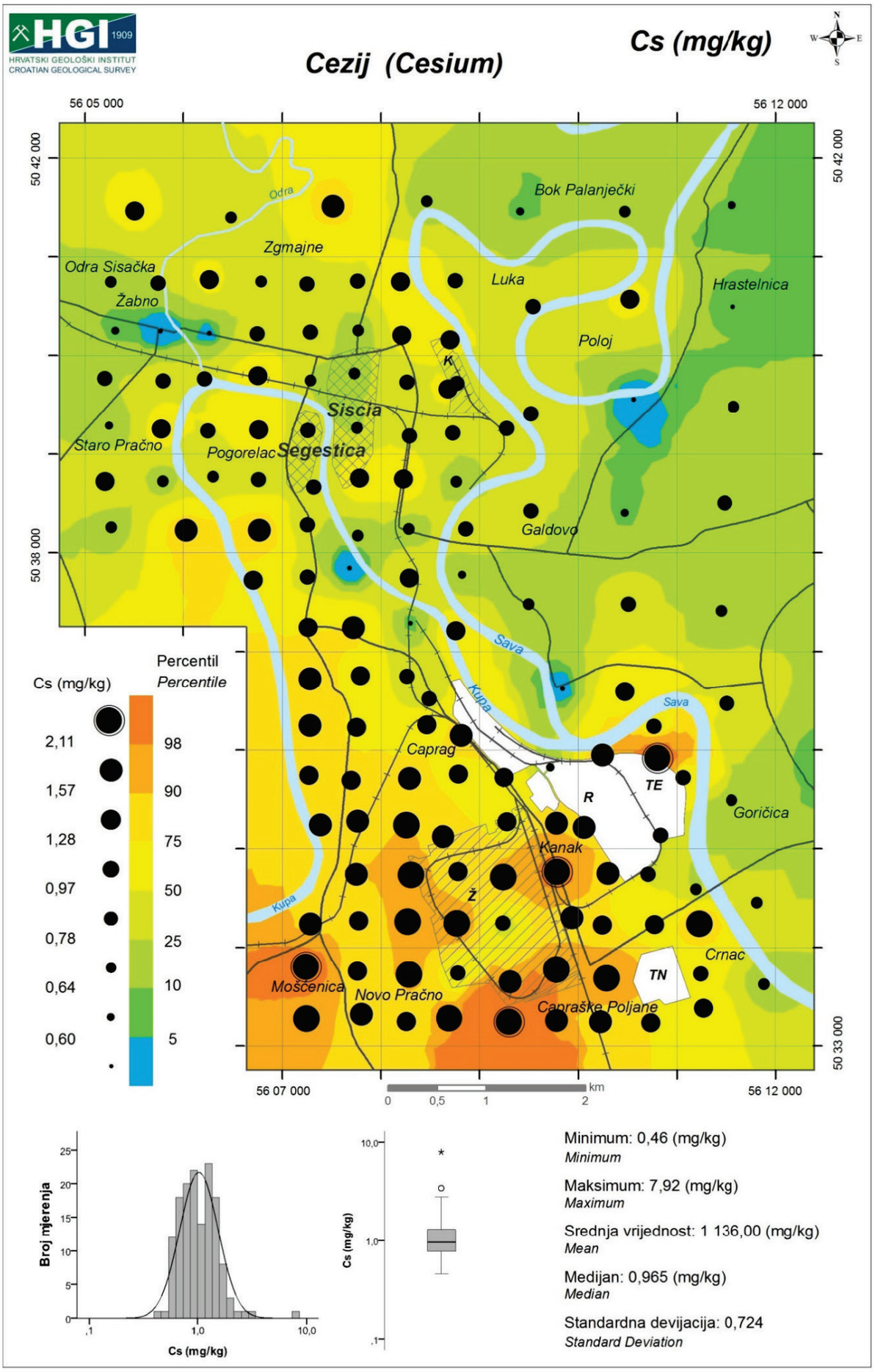
The map of spatial distribution of cesium clearly shows the link between the elevated concentrations in the soil and industrial processing plants (steelworks, oil refinery and thermal power plant).

The measured values of this element in the investigated area vary between 0.46 and 7.92 mg/kg with median of 0.97 mg/kg. The greatest concentration of Cs is registered in the southern margin of the depot containing the remnants of dross form the steelworks chimneys. This extreme value arises doubtlessly from the depot because the latter is drained by the surface waters accumulating cesium in the soil underneath and around the depot. Another extreme concentration of this element is measured on the northern rim of the industrial complex encompassing the thermal power plant and refinery. It results form emissions of cesium during combustion fossil fuels and hydrocarbon processing in the mentioned plants. In the almost entire industrial zone and in its immediate vicinity (to the south, west and northwest of steelworks and oil refinery anomalous and high concentrations of this element in the soils have been registered. The high cesium content in the soil in the zone of the Crnac settlement must be also related to the impact of industrial activity in the immediate surroundings.

Extreme and anomalous concentration of Cs in the zone of the Mošćenica settlement cannot be irrevocably interpreted because between these locations and the steelworks processing plants to the east there is a belt with lower values of cesium in the soil. The soils on the location of Mošćenica are the forest soils rich in organic matter on which this element is preferably bonding, especially its ^{137}Cs isotope.

Cesium has also an affinity toward aluminosilicates (K-feldspars, micas) so that the increased values both in the soils on alluvial sediments of the Kupa River and in the soil of the Sisak Zgmajna are of geogenic origin due to the fact that these sols are richer in aluminosilicates than those on the Sava River sediments.

In other parts of the investigated area (predominantly to the north and to the south) are registered the Cs concentrations about or considerably below the median values (particularly the landscapes to the east of the Sava River occupying the east side of the investigated terrain).


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Cezij (Cesium)
Cs (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
Cs (mg/kg)
2,11
1,57
1,28
0,97
0,78
0,64
0,60
98
90
75
50
25
10
5
Broj mjerenja
Cs (mg/kg)
10,0
1,0
,1
Minimum: 0,46 (mg/kg)
Minimum
Maksimum: 7,92 (mg/kg)
Maximum
Srednja vrijednost: 1 136,00 (mg/kg)
Mean
Medijan: 0,965 (mg/kg)
Median
Standardna devijacija: 0,724
Standard Deviation

Cu

10.14. Cu – BAKAR (atomski broj 29) COPPER (atomic number 29)

Bakar je halkofilni element u tragovima asociran s drugim prijelaznim elementima kao Cr, Fe, Ni, Co te As. U Zemljinoj kori se po učestalosti nalazi na 26. mjestu. Najveći sadržaji su mu u bazičnim i intermedijarnim tipovima stijena u obliku sulfida. On ima jaki afinitet prema sumporu.

U magmatskim stijenama njegov srednji sadržaj iznosi 55 mg/kg (ultrabaziti 10 mg/kg, bazalti 87 mg/kg, granodioriti 30 mg/kg i graniti 10 mg/kg). Srednja vrijednost u šejlovima 45 mg/kg (crni šejlovi mogu imati znatne koncentracije ovog elementa), u pješčenjacima je 5 mg/kg, a u karbonatima 4 mg/kg. Koncentracija u tlima varira od 2 do 250 mg/kg, sa srednjom vrijednošću oko 30 mg/kg. Količina Cu u tlu znatno ovisi o klimatskim značajkama – najveće koncentracije zabilježene su u tropskim područjima (lateritska tla), a najmanje u umjerenim i hladnim klimatskim zonama. Veći sadržaji bakra zabilježeni su u ilovastim tlima, dok pjeskovita tla imaju relativno manji sadržaj ovog elementa. Koncentracija bakra u tlu kontrolirana je i pH vrijednostima te sadržajem organske tvari. U slatkoj vodi je dobro topiv kao Cu^{+} i Cu^{2+} (0,003 mg/kg).

Sulfidi se lako troše u kiselim uvjetima (pH < 5) i nakon oslobađanja bakar je srednje mobilan. Sulfidne rude oksidiraju u okside, sulfate, karbonate, fosfate, arsenate i dr. Mobilnost bakra je uvjetovana prisustvom humusne kiseline, organskih liganada, minerala glina, hidričnih oksida i topivih karbonata. Nadalje, njegova mobilnost u tlima jako ovisi o sadržaju organskog ugljika i pH. U sedimentu je pretežito vezan za sitnu frakciju.

Bakar je esencijalni bioelement za biljke i životinje. U visokim koncentracijama on je otrovan za sve kralježnjake, ali manje za sisavce. Bakar je sastavni dio metalnih enzima. Ljudi i svinje mogu podnijeti relativno visoke koncentracije ovog elementa, dok su ovce i krave jako osjetljive na trovanje bakrom. Glavni izvori bakra su sve vrste hrane i voda. Kod uzgoja svinja $CuSO_4$ se koristi kao dodatak ishrani. To može dovesti do povećanih koncentracija u tlima koja se tretiraju gnojivom s takvih svinjogojskih farmi. Previsok sadržaj bakra u tlu dovodi do nedostatka cinka i obrnuto. Previsok sadržaj molibdena izaziva nedostatak bakra. Radi pomanjkanja bakra u tlu (< 10 mg/kg) mogu se pojaviti bolesti. Tla sa sadržajem bakra < 5 mg/kg smatraju se osiromašena. Biljke podnose visoke koncentracije bakra u tlu i to ako je tlo bogato organskim ugljikom.

Svjetska proizvodnja bakra u 2003. godini iznosila je oko 13,7 milijuna tona.

Bakar ima široku primjenu, kako u industriji tako i u drugim granama. Koristi se za izradu vodovodnih i toplovodnih cijevi, bakrene žice, elektromagneta, krovnih limova, statua, kovanog novca i dr. Osim toga, ima široku primjenu u poljoprivredi (mineralna gnojiva i pesticidi), a dodaje se i hrani za perad i stoku.

Utječe na okoliš u procesima taljenja, industrijskoj prašini, otpadu i upotrebi kemikalija (npr. fungicida u poljodjelstvu). Izvori onečišćenja atmosfere bakrom su talionice, kako ruda metala tako i nemetala, sagorijevanje fosilnih goriva, ljevaonice, cementare i otpadni muljevi.

Copper is a chalcophile trace element associated with other transition elements such as Cr, Fe, Ni, Co and As. It is 26th in abundance in the Earth's crust. The greatest contents of copper are in the basic and intermediary types of rocks in the form of sulfides. Cooper has a strong affinity with sulfur.

In igneous rocks its average content is 55 mg/kg (ultramafic rocks 10 mg/kg, basalts 87 mg/kg, granodiorites 30 mg/kg and granites 10 mg/kg). The average content in shales is 45 mg/kg (black shales can contain considerable concentrations of this element), in sandstones 5 mg/kg, and in carbonates 4 mg/kg. Concentration in soils varies from 2 to 250 mg/kg, with median of 30 mg/kg. The quantity of Cu in the soil significantly depends on climate characteristics – the greatest concentrations are registered in tropical regions (laterite soils) and the smallest in temperate and cold climate zones. Major contents of copper are registered in loamy soils while sandy soils contain relatively lower quantities of this element. Concentration of copper in soils is regulated both by pH values and the content of organic matter. It is easily soluble in the sweet water both as Cu^{+} and Cu^{2+} ion (0.003 mg/kg).

Sulfides are easily weathered under acid conditions (pH < 5) and after being released Cu is moderately mobile. Sulfide ores are oxidized into oxides, carbonates, sulfates, phosphates, arsenates, etc. Mobility of copper is controlled by the presence of the humic acid, organic ligands, hydric oxides and soluble carbo-

nates. Further, its mobility in soils strongly depends on the content of organic carbon and pH. In the sediment it is prevalently associated with fine fraction.

Copper is essential bioelement for plants and animals. In high concentrations it is toxic for all vertebrates but less toxic for mammals. Copper is a component part of metal enzymes. Humans and pigs can tolerate relatively great concentrations of this element while ship and cows are highly sensitive to copper poisoning. Chief sources of Cu are all types of food and water. With pig farming $CuSO_4$ is used as a food supplement. This can lead to increased contents of copper in soils which are treated by fertilizers from these farms. Excessive quantities of copper in the soil lead to zinc shortage and vice versa. Excessive contents of molybdenum cause the copper deficiency. Due to the lack of copper in the soil (< 10 mg/kg) diseases can appear. Soils with the copper content less than 5 mg/kg are deemed depleted. Plants tolerate high concentrations of Cu in the soil but only if soil is rich in organic carbon.

The world production of copper in the year 2003 was about 13.7 millions of tons.

Copper has a broad application both in industry and other economy branches. It is used for production of water-pipe and hydronic tubes, copper wires, electromagnets, roof plates, statues, coins, etc. Besides, copper is widely used in agriculture (mineral fertilizers and pesticides) and as a food supplement for poultry and cattle.

Its impact on environment comes through the processes of melting, through industrial dust, waste, and application of chemicals (for instance, fungicides in agriculture). The sources of atmospheric pollution by copper are foundries, both of metal and non-metal ores, combustion of fossil fuels, cast houses, cement factories and waste mud.

Na karti raspodjele bakra u urbanim tlima grada Siska jasno se odvajaju dva područja s anomalnim koncentracijama. Na sjeveru je jedno područje, gdje su se nalazila antička naselja Segestica i Siscija, a drugo je na jugu, u području industrijske zone sa željezarom, rafinerijom i termoelektranom.

Izmjerene koncentracije na istraživanom području kreću se od 12,27 do 944,89 mg/kg s vrijednošću medijana od 26,18 mg/kg. Maksimalna koncentracija registrirana je u industrijskoj zoni, na sjevernom rubu Rafinerije nafte Sisak. U neposrednoj blizini postrojenja Rafinerije i Termoelektrane, na lijevoj obali Save registrirano je i nekoliko drugih ekstremnih i anomalnih vrijednopsti bakra u tlu (područje Polojci). Isto tako, na većini lokacija u krugu Željezare Sisak te u naselju Kanak, registrirane su ekstremne i anomalne koncentracije bakra. Povišene vrijednosti ovog elementa u tlu, koje su također vezane na industriju, registrirane su u uzorcima tla u naselju Caprag. Kao i kod nekih drugih elemenata i pri distribuciji bakra u industrijskoj zoni evidentan je utjecaj vjetra na raspršenje ovog metala u okoliš. Naime, izduženje anomalnih područja je u smjeru vjetra tj. *SSI-JJZ*. Osim toga, prema distribuciji bakra u tlima oko industrijske zone vidljivo je da se on iz zraka taloži u krugu promjera maksimalno do 3 km.

Drugo područje na kojem se nalazi niz lokacija s ekstremnim i anomalnim koncentracijama bakra u tlu je područje antičkih naselja Segestice i Siscije (Sl. 10.3.). Ove vrijednosti su također posljedica antropogenog unosa bakra u tlo u to doba (kovnice novca, nakita i raznih predmeta za kućanstvo i obrt). Povećan sadržaj

On the map of the spatial distribution of copper in the urban soils of the Sisak city two zones with anomalous concentrations are clearly separated. One is to the north where once existed the ancient settlements of Segestica and Siscia and the other is to the south in the area occupied by the industry – steelworks, oil refinery and thermal power plant.

Measured concentrations in the investigated area vary from 12.27 to 944.89 mg/kg with median of 26.18 mg/kg. Maximum concentration is registered in the industrial zone, on the northern edge of refinery. In the immediate vicinity of the refinery and the thermal power plant on the left bank of the Sava River a few other extreme and anomalous values of copper in the soil are registered (Polojci area). The same is on the majority of locations in the sphere of steelworks and in the Kanak settlement where the extreme and anomalous concentrations are also registered. Increased values of this element in the soil, being also associated with industry, are registered in the soil samples form the Caprag settlement. Similar to some other elements the spatial distribution of copper in the industrial zone is evidently controlled by the course of wind. Namely, elongation of the anomalous zones is in the direction of wind, that is, NNE-SSW. Besides, from distribution of copper in the soils around the industrial zone it is obvious that precipitation of airborne copper is present in the circle of the 3 km perimeter at most.

Another area with a number of locations showing extreme and anomalous concentrations of copper in the soil is occupied by ancient settlements of Segestica and Sis-

bakra u krugu i oko kemijske industrije „HERBOS“ može se vezati uz proizvodnju fungicida i drugih zaštitih sredstava u tim postrojenjima.

Oba navedena područja s ekstremnim i anomalnim koncentracijama bakra su jasno odvojena jedno od drugog, a prema njihovoj periferiji sadržaj ovog metala u tlu naglo opada na vrijednosti ispod medijana.

U rubnim dijelovima istraživanog područja kao i u zoni Brzaj-Galdovo-Hrastelnica registrirane koncentracije bakra u tlu su ispod, a u području Novog Pračna i daleko ispod vrijednosti medijana.

Bakar je jedan od teških metala koji su obuhvaćeni *Prijedlogom o graničnim vrijednostima onečišćujućih tvari u tlu* (MESIĆ et al., 2008). Prema toj preporuci samo uzorak tla u industrijskoj zoni na sjevernom rubu Rafinerije treba smatrati onešišćenim (sadržaj Cu > 500 mg/kg). Pošto nam nije bilo dopušteno uzimanje uzoraka u krugu Rafinerije i Termoelektrane, na temelju ovog podatka, pretpostavlja se da jedan dio uzoraka unutar rafinerije ima povišene vrijednosti bakra. Svi ostali analizirani uzorci, iako s ekstremnim ili anomalnim koncentracijama, su ispod zadanih vrijednosti za sve namjene zemljišta.

cia (Fig. 10.3.). These values are also result of anthropogenic input during these times (coin mintages, jewelry, and various articles for household and crafts). Increased content of copper in the zone of chemical processing plant „HERBOS“ and its surrounding can be related to the production of fungicides and other protection means.

Both mentioned areas with extreme and anomalous concentrations of copper are clearly separated from each other and toward their peripheries the content of this metal falls abruptly below the median value.

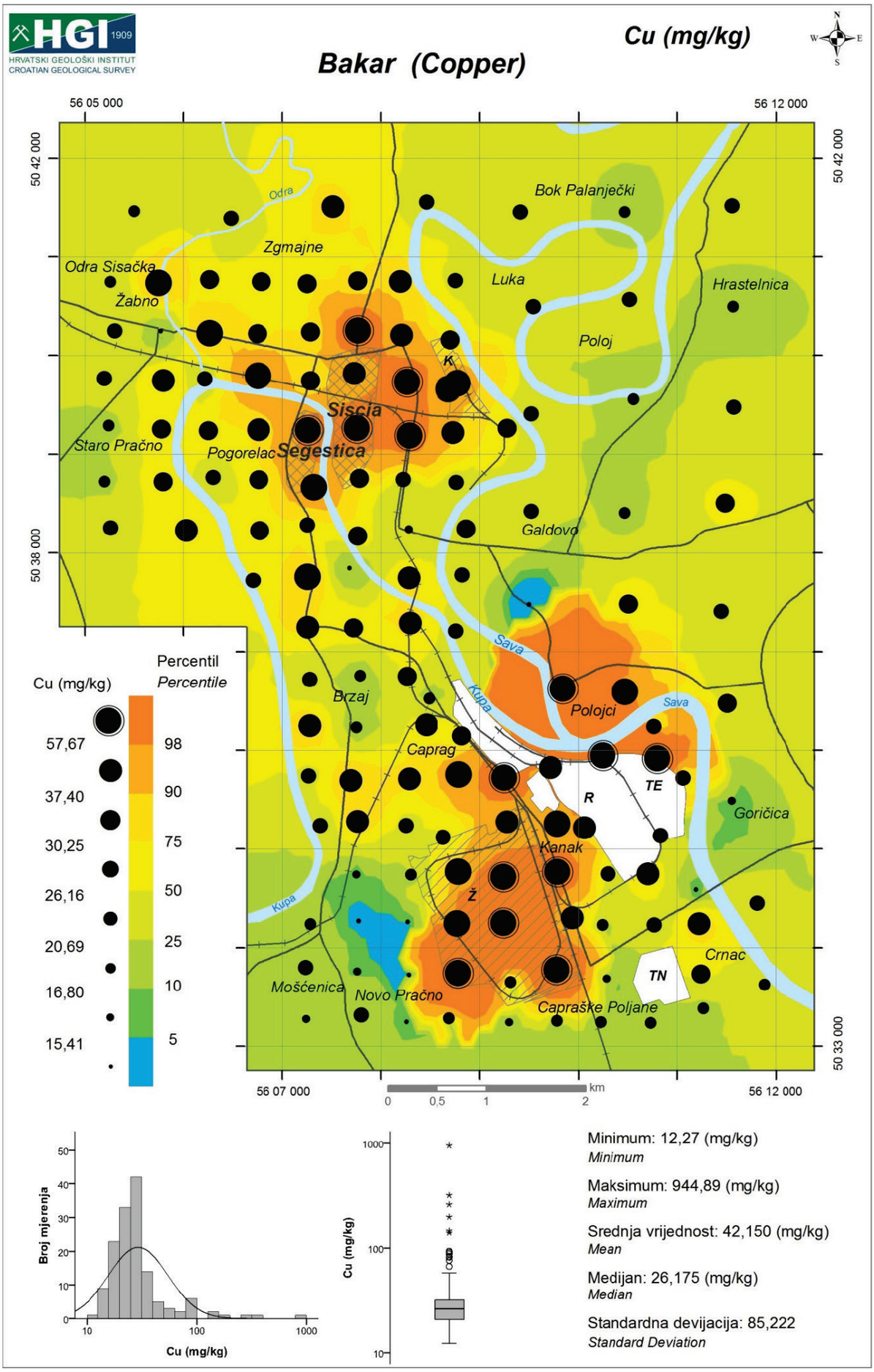
In the peripheral zones of the investigated area as well as in the zone Brzaj-Galdovo-Hrastelnica the concentrations of copper are below and in the area of Novo Pračno far below the median values.

Copper is one of heavy metals which are included by “Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use” (MESIĆ et al., 2008). According to this recommendation only the sample in the industrial zone on the northern edge of oil refinery should be considered polluted (content Cu > 500 mg/kg). Since we were not allowed to collect samples in the circle of refinery and thermal power plant it can be assumed based on this information that one portion of samples within refinery also shows increased values of copper. All other analyzed samples, albeit with extreme and anomalous concentrations, are below the prescribed values for all types of land use.



Slika 10.3. *Novčić iz kovnice novca u Sisciji (Theodosius I (379-395) (http://www.numismall.com/acc/AE4-of-Theodosius-I-379-395-AD-Siscia-mint-Roman-Empire-v7217.html, zadnji pristup 9.10.2013.).*

Figure 10.3. *Coin from the coin mint in Siscia (Theodosius I (379-395) http://www.numismall.com/acc/AE4-of-Theodosius-I-379-395-AD-Siscia-mint-Roman-Empire-v7217.html, last access 9.10.2013)*


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Bakar (Copper)
Cu (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Segestica
Staro Pračno
Pogorelac
Galdovo
Sava
Kupa
Brzaj
Polojci
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Cu (mg/kg)
Percentil
Percentile
57,67
37,40
30,25
26,16
20,69
16,80
15,41
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Cu (mg/kg)
Minimum: 12,27 (mg/kg)
Minimum
Maksimum: 944,89 (mg/kg)
Maximum
Srednja vrijednost: 42,150 (mg/kg)
Mean
Medijan: 26,175 (mg/kg)
Median
Standardna devijacija: 85,222
Standard Deviation

Fe

10.15. Fe – ŽELJEZO (atomski broj 26) IRON (atomic number 26)

Željezo je litofilni glavni element, 4. po učestalosti u Zemljinoj kori, a 3. u omotaču. Ono je udruženo s drugim prijelaznim elementima kao što su Mg, Sc, Ti, V, Cr, Mn, Ni, Co, Cu i Zn. Željezo je sulfofilni rudni element.

Srednji sadržaj u magmatskim stijenama iznosi 5,6 % (ultrabaziti 9,4 %, oceanski toleitni bazalti 6 %, bazalti 8,65 %, granodioriti 2,7 % i graniti 1,4 %). Šejlovi imaju srednji sadržaj Fe 4,8 %, pješčenjaci 1,0 %, a karbonati 0,4 %. Srednji sadržaj željeza u tlima je oko 2,1 %. Za njegovu pojavu u tlu vrlo je važna činjenica da je glavni sastojak u feromagnezijskim alumosilikatima. U slatkoj vodi ga ima oko 0,1 mg/L Fe^{2+}.

Često se nalazi u mnogim oksidima (magnetit, hematit, maghemit i ilmenit); hidroksidima (limonit); željeznom karbonatu (siderit), sulfidima (pirit i markazit) i pirhotit i Fe-Mg silikatima (olivini, pirokseni, amfiboli, biotiti, almandin).

Željezo je umjereno mobilno kao Fe^{2+}, a nije mobilno kao Fe^{3+}. Njegova dostupnost u sekundarnom okolišu u mnogome ovisi o pH/Eh odnosu. U oksidirajućem okolišu dolazi do oksidacije željeza (Fe^{3+}) i njegove precipitacije kao hidroksida u vidu koloidne suspenzije (iznad pH 2 – 3). U kiselim i reducirajućim uvjetima Fe^{2+} ion je jako topiv. Tako su potoci, koji dreniraju kisele ili močvarne terene (reduktivni uvjeti), obogaćeni otopljenim željezom. S porastom pH i Eh vrijednosti koncentracije Fe rastu i precipitacija je relativno brza. Tako nastaju vrlo raširene Fe-hidrične oksidne prevlake koje kontroliraju mobilnost i mnogih drugih adsorbiranih ili koprecipitiranih elemenata (npr. Ba, Mo, As, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn). U podzolima tlo je tipično osiromašeno željezom u E-horizontu, a obogaćeno u B-horizontu. Koloidni hidroksidi pokazuju visoka sorpcijska svojstva za anionske komplekse AsO_3^{2-}, PO_4^{2-}, SeO_3^{2}, VO_4^{3-} i dr. Željezo ima tendenciju vezivanja na organsku tvar.

Željezo je biogeni i esencijalni element za sve organizme, no u velikim koncentracijama je otrovno. Nužno je za enzimsku sintezu klorofila i kao sastavni dio hemoglobina. Nedostatak željeza je raširen problem. Ako nema dovoljno željeza, rast biljaka je poremećen (kalcitizacija). Dostupnost željeza u tlu ovisi o pH vrijednosti, sadržaju fosfata i sadržaju drugih metala (npr. Co). Fe-sulfat se upotrebljava za prihranu i kao herbicid. Nedostatak željeza izaziva anemiju i smanjenje dostupnosti drugih hranjivih tvari u organizmu te povećava osjetljivost prema infekcijama. Najviše dostupnog željeza ima u majčinom mlijeku i mesu (posebice jetri), a manje ga ima u biljkama.

Svjetska produkcija željeza u 2000. godini procijenjena je na 571 milijuna tona. Preko 90 % dobivenog željeza taljenjem iz ruda koristi se za proizvodnju čelika i legura. Željezo kao metal lako oksidira i korodira u dodiru s kisikom.

Željezo je već preko 3 000 godina najčešće upotrebljavni metal u svim civilizacijama.

Onečišćenje okoliša željezom nastaje preko željeznog otpada, hrđom, pigmentima i prašinom u tehnološkom procesu taljenja te prašinom prilikom sagorijevanja ugljena.

Iron is a major lithophile, the fourth in abundance in the Earth's crust and the third in the mantle. It is associated with other transition elements such as Mg, Sc, Ti, V, Cr, Mn, Ni, Co, Cu and Zn. Iron is also sulphophilic ore forming element.

The average content of iron in igneous rocks is 5.6 % (ultramafic rocks 9.4 %, oceanic tholeiite basalts 6 %, basalts 8.65 %, granodiorites 2.7 % and granites 1.4 %). Shales contain typically 4.8 %, sandstones 1.0 %, and carbonates 0.4 % of Fe. Average content of iron in the soils is about 2.1 %. Important information related to its occurrence in the soils is that it represents the main component in ferromagnesian aluminosilicates. Its content in the sweet water is around 0.1 mg/L Fe^{2+}.

Iron is very common in many oxides (magnetite, haematite, maghemite and ilmenite); hydroxides (limonite); ferric carbonate (siderite), sulfides (pyrite and marcasite) and pyrrhotite and Fe-Mg silicates (olivine, pyroxene, amphibole, biotitie, and almandine).

Iron is moderate mobile as Fe^{2+}, and immobile as Fe^{3+}. Its availability in the secondary environment mostly depends on pH/Eh relationship. In oxidizing environment forms Fe^{3+} which is then precipitated as hydroxide in the form of colloidal suspension (pH > 2 - 3). In acid and reducing conditions Fe^{2+} ion is highly soluble. This is why streams draining acid or marshy terrains (reducing conditions), are enriched in

dissolved iron. With increase of pH and Eh values the concentrations of Fe also raise so that precipitation is relatively fast. In this way form very common Fe-hydric oxide coatings which also control mobility of many other adsorbed or co-precipitated elements (e.g. Ba, Mo, As, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn). In podzols the soils is typically depleted in iron in E-horizon and enriched in B-horizon. Colloidal hydroxides show high sorption features concerning the anionic complexes of AsO_3^{2-}, PO_4^{2-}, SeO_3^{2}, VO_4^{3-} etc. Iron is prone of bonding to organic matter.

Iron is a biogenic and essential element for all organisms but in great concentrations it is toxic. It is necessary for the enzyme synthesis of chlorophyll and as a component part of hemoglobin. The iron deficiency is a common problem. If Fe is lacking the plant growth is disturbed (calcification). Availability of Fe in soil depends on pH value, content of phosphates, and content of other metals (such as Co). Fe-sulfate is used for a supplementary diet and as herbicide. The shortage of iron causes anemia and decrease of availability of other nutrients in the organism developing the sensibility to infections. The most of the available Fe can be found in the mother's milk, in meat (especially liver), the less in plants.

The world production of Fe in the year 2000 is estimated to 571 millions of tons. More than 90 % of iron obtained by the ore smelting is utilized in the production of steel and alloys. Iron as a pure metal is easily oxidizing in the contact with oxygen.

Fore more than 3,000 years iron is the most utilized metal in all civilizations.

Contamination of environment by iron occurs through the iron waste, by rust, pigments, and by dust in the technological process of melting and by dust form the coal combustion.

Kao što je i očekivano, područja s ekstremnim i anomalnim koncentracijama željeza nalaze se u industrijskoj zoni, a vezana su za željezaru, rafineriju i termoelektranu.

Koncentracije željeza na istraživanom području su u rasponu od 1,10 do 11,50 % s medijanom od 2,47 %. Najveća vrijednost ovog elementa u tlu izmjerena je u uzorku u krugu Željezare Sisak. Većina drugih uzoraka tla iz kruga Željezare pokazali su ekstremne i anomalne koncentracije ovog elementa. Također, vezana za željezaru je i ekstremna koncentracija željeza u uzorku tla u naselju Kanak. Drugo područje s ekstremnim vrijednostima željeza u tlu nalazi se na sjevernom rubu Termoelektrane Sisak. Po distribuciji ovog metala u tlu na toj lokaciji vidljivo je da je njegov unos u okoliš potječe velikim dijelom od spaljivanja fosilnih goriva u termoelektrani.

Anomalne i povećane koncentracije željeza u tlima razvijenim na aluvijalnim, sitnozrnatim sedimentima rijeka Kupe i Odre imaju geogeno podrijetlo. Naime, tla na ovim lokacijama su hidromorfnog karaktera te bogata organskom tvari i Fe oksi-hidroksidima.

Područje oko kemijske industrije „HERBOS" pokazuje također povišene koncentracije ovog elementa u tlu u odnosu na okolno područje. Ta razlika je geogenog podrijetla i uvjetovana je granulometrijom i petrografskim sastavom matičnog supstrata koji je u tom području izgrađen od siltova i glina (područje nekadašnjih ciglana). Na tom supstratu su se razvila hidromorfna tla u kojima su povoljni uvjeti za vezanje željeza i tvorbu Fe oksi-hidroksida.

As was expected the areas with extreme and anomalous concentrations of iron are found in the industrial zone and are associated with the steelworks, oil refinery and the thermal power plant.

Concentrations of Fe in the investigated area vary between 1.10 and 11.50 % with median of 2.47 %. The greatest value of this element in the soil is measured in the sample from the factory yard of the steelworks. A majority of other samples from the same circle show the extreme and anomalous concentration of this element as well. Related to the steelworks is also the extreme concentration of Fe in the Kanak settlement. Another zone with extreme values of iron is on the northern rim of the thermal power plant. According to spatial distribution of this element in the soil it is clear that its input into the environment arises for the most part from the combustion of the fossil fuels in the thermal power plant.

Anomalous and increased values of Fe in the soils on alluvial fine-grained sediments of the Kupa and Odra Rivers are geogenic in origin. Namely, soils on these locations are hydromorphic in character and rich in organic matter and Fe oxy-hydroxides.

The area around the chemical industry of „HERBOS" also shows the increased concentrations of this element in soil with respect to the surrounding area. This difference is of geogenic character and is caused by granulometric and petrographic composition of the bedrock material which in this area is composed of silts and clays (the place once occupied by brickyards). On this bedrock hydromorphic soils have developed with favora-

Ostala područja, posebice ona uz donji tok Kupe te uz Savu imaju niske vrijednosti željeza ili koncentracije daleko ispod vrijednosti medijana. Matični supstrat za ova tla izgrađen je od pjeskovito-šljunkovitog, pretežito karbonatnog materijala koji je dobro dreniran te se je mobilno željezo relativno lako premještalo u dublje horizonte tla.

ble conditions for bonding of iron and formation of Fe oxy-hydroxides.

Other areas, particularly those by the lower course of the Kupa River and along the Sava River show the low values of Fe or the concentrations far below the median values. The parent material for these soils is composed of sandy-gravel predominantly carbonate material which is well drained so that the mobile iron relatively easily relocated into the deeper soil horizons.



Slika 10.4. *Skulptura iz Parka skulptura koji se nalazi pored Željezare Sisak (Foto: J. Halamić).*

Figure 10.4. *Sculpture from the Sculpture park next to the steelweorks Sisak (Photo: J. Halamić).*



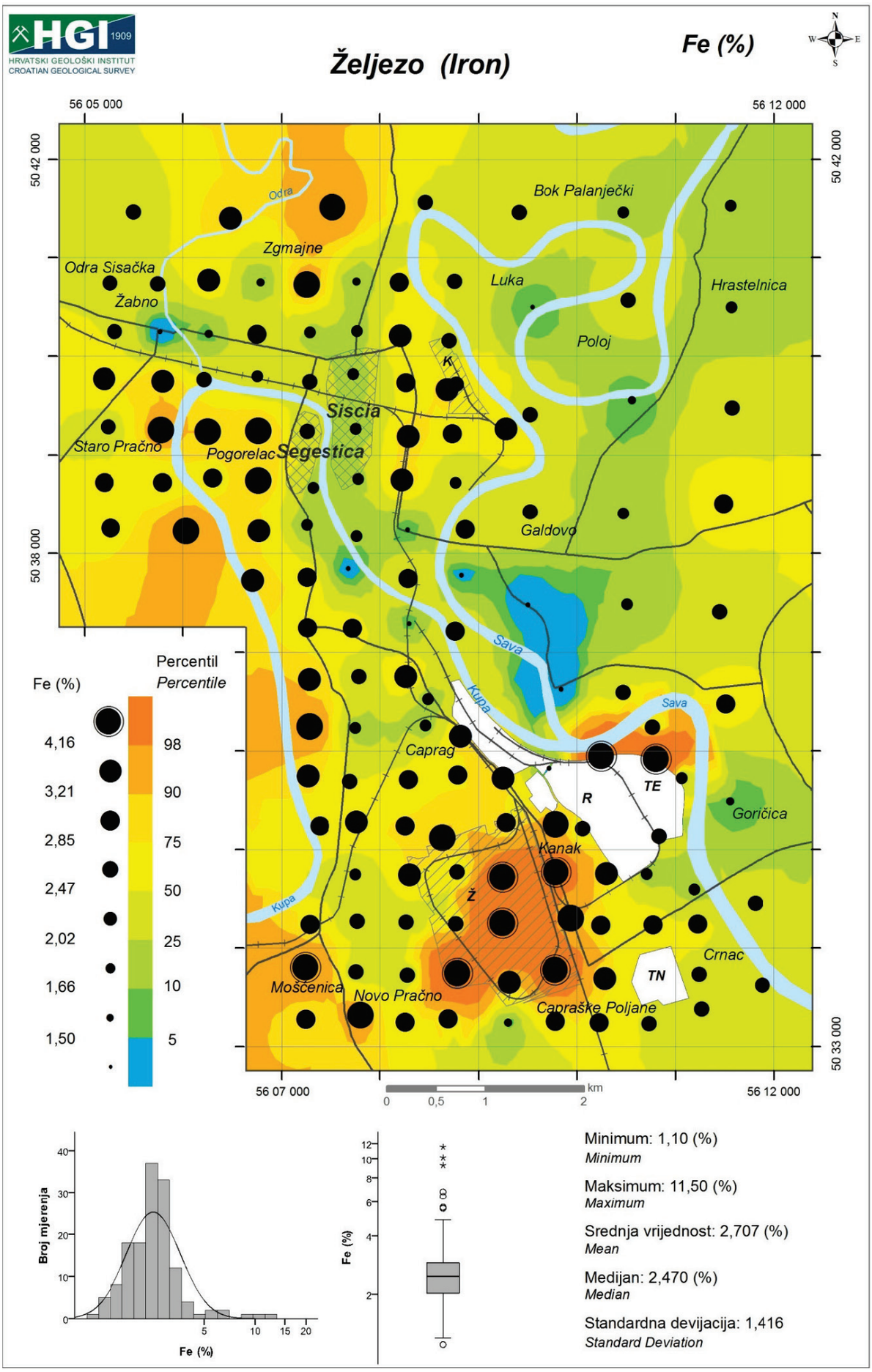
Slika 10.5. *Skulptura iz Parka skulptura (Foto: J. Halamić).*

Figure 10.5. *Sculpture from the Sculpture park (Photo: J. Halamić).*



Slika 10.6. *Skulptura iz Parka skulptura (Foto: J. Halamić).*

Figure 10.6. *Sculpture from the Sculpture park (Photo: J. Halamić).*


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CROATIAN GEOLOGICAL SURVEY
Željezo (Iron)
Fe (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
Fe (%)
Percentil
Percentile
4,16
3,21
2,85
2,47
2,02
1,66
1,50
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Fe (%)
Minimum: 1,10 (%)
Minimum
Maksimum: 11,50 (%)
Maximum
Srednja vrijednost: 2,707 (%)
Mean
Medijan: 2,470 (%)
Median
Standardna devijacija: 1,416
Standard Deviation

Ga

10.16. Ga – GALIJ (atomski broj 31) GALLIUM (atomic number 31)

Galij je litofilni element u tragovima i po pojavljivanju u Zemljinoj kori zauzima 34. mjesto. Često je prikriven aluminijem. Obogaćen je u alkalnim magmama, diferencijatima i fluidnoj fazi. U srednje do niskim hidrotermalnim otopinama pokazuje halkofilne osobine. Po geokemijskom karakteru nalikuje cinku.

Prosječni sadržaj galija u magmatskim stijenama je 15 mg/kg (ultrabaziti 5 mg/kg, bazalti 17-30 mg/kg i graniti 18 mg/kg). U sedimentnim stijenama najviše ga ima u šejlovima (19 mg/kg). Pješčenjaci imaju 12 mg/kg, a karbonati 1 mg/kg. On se koncentrira i u ugljenu. Sadržaj u tlima kreće se od 1 do 70 mg/kg (srednja vrijednost 28 mg/kg). U slatkoj vodi koncentracija je ispod 0,001 mg/L.

Mobilnost galija u sekundarnom okolišu je mala. Akumulira se u organskoj tvari u tlu, detritusu feldspata, mineralima glina i sekundarnim Fe i Mn oksi-hidroksidima.

Za sada još nema dovoljno podataka o štetnosti ovog metala za ljude. Postoje neki podaci o nefrotoksičnosti, iritaciji kože i oštećenju sluznice.

Ne postoje pouzdani podaci o svjetskoj proizvodnji ovog metala, ali se procjenjuje da je ona 2003. godine iznosila oko 203 t.

Galij je industrijski otkriven kao sporedni proizvod kod proizvodnje cinka (sfalerit) i aluminija. Relativno visoke koncentracije galija nalazimo u boksitima (maksimalna koncentracija u tropskim boksitima do 0,08 %). Povećana je potražnja za ovim metalom radi proizvodnje poluvodiča. On se još upotrebljava za izradu elektronskih intergralnih kola, fotodetektora i solarnih ćelija. Manji dio troši se za izradu legura i u laboratorijske svrhe. U medicini se raznovrsni sastojci na temelju galija koriste pri terapiji raka.

Ovaj element se kao onečišćivalo raspršuje u okoliš pri proizvodnji aluminija, spaljivanju ugljena (toplane i termoelektrane), otpadnim vodama i muljevima.

Gallium is a lithophile trace element 34th in abundance in the Earth's crust. It is often screened by aluminum. Enriched in alkali magmas differentiates and in the fluid phase. In the middle to low hydrothermal solutions shows the chalcophile characteristics. In geochemical character is similar to zinc.

The average content of gallium in igneous rocks is 15 mg/kg (ultramafic rocks 5 mg/kg basalts 17 – 30 mg/kg and granites 18 mg/kg). In sedimentary rocks the most abundant is in shales (19 mg/kg). Sandstones contain 12 mg/kg and carbonates 1 mg/kg. Gallium is also concentrated in coal. Its content in soils is from 1 to 70 mg/kg (average is 28 mg/kg). In sweet water the concentration is below 0.001 mg/L.

Mobility of gallium in the environment is low. It accumulates in organic matter in the soil, in feldspar detritus, clay minerals and, secondary, in Fe and Mn oxy-hydroxides.

Up to now there is not enough information concerning its harm for people. Some data exist about its nephrotoxicity, skin irritation and damage of mucosa.

No reliable data exist on the world production of this metal but it is estimated that in the year 2003 it amounted to about 203 t.

Gallium is industrially discovered as a byproduct of production of zinc (sphalerite) and aluminum. Relatively high concentrations can be found in bauxites (maximum concentration in tropical bauxites up to 0.08 %). Increased demand exists for this metal due to production of semiconductors. Additionally, it is employed in production of electronic integrated circles, photo detectors, and solar cells. A minor part is spent in production of alloys and for laboratory purposes. In medicine, there are various compounds based on gallium which are used in the cancer therapy.

As a contaminant, this element is dispersed into environment during aluminum production, by the coal combustion (heating and thermal power plants), by the waste waters and waste mud.

Na čitavom istraživanom području nisu registrirane niti ekstremnne, a niti anomalne koncentracije galija u tlu.

Izmjerene vrijednosti ovog elementa kreću se od 1,4 do 8,2 mg/kg s medijanom od 4,4 mg/kg. Visoke koncentarcije galija registrirane su na aluviju rijeka Kupe i Odre. Ova tla su fluvisoli bogati mineralima glina te Fe i Mn oksi-hidroksidima, koji na sebe vežu element galij. Povećane koncentracije u području Mošćenice i Novog Pračna su također vezane na ilovasta tla bogata humusom (Mošćenica) te mineralima glina i Fe i Mn oksihidroksidima (Novo Pračno). Relativno visoka koncentracija galija u uzorku tla na Capraškim Poljanama je posljedica sastava tla i industrijske aktivnosti. Povišene vrijednosti oko Rafinerije te u sjeveroistočnom dijelu kruga Željezare i naselju Caprag su antropogenog podrijetla.

Distribucija galija u području kemijske industrije je jako slična onoj za željezo i vjerojatno je istog geogenog podrijetla (siltozno-glinoviti matični supstrat i hidromorfno tlo na njemu). Jako niske koncentracije galija, željeza i nekih drugih elemenata u donjem toku Kupe, prije ušća u Savu, posljedica su prirodnog miješanja aluvijalnih sedimenata jedne i druge rijeke pri visokim vodostajima. Kao što je vidljivo poplavni sedimenti Save osiromašeni su s navedenim elementima.

Sjeveroistočni dio istraživanog područja, gdje su tla razvijena na aluvijalnim poplavnim sedimentima rijeke Save, imaju niske ili jako niske koncentracije ovog elementa. Takve vrijednosti su posljedica petrografskog i granulometrijskog sastava matičnog supstrata na kojima su razvijena uzorkovana tla.

On the entire territory of investigation neither extreme nor anomalous concentrations of gallium in the soil have been registered.

The measured values of this element vary between 1.4 and 8.2 mg/kg with median of 4.4 mg/kg. High concentrations of gallium are registered on alluvium of the Kupa and Odra Rivers. These soils are fluvisols rich in clay minerals and Fe-Mn oxy-hydroxides which bond gallium. Increased concentrations in the zone of Mošćenica and Novo Pračno are also associated with loamy soils rich in humus (Mošćenica), clay minerals and Fe-Mn oxy-hydroxides (Novo Pračno). Relatively high concentration of Ga in the soil sample from the Capraške Poljane is a result of the soil composition and industrial activity. Elevated values around the oil refinery and in the northeastern part of steelworks circle are of anthropogenic origin.

Distribution of gallium in the zone of chemical industry is very similar to that for iron and is probably of the same geogenic origin (silty-clayey parent material and hydromorphic soils developed over it. Very low concentrations of gallium, iron, and certain other elements in the lower part of the Kupa River before its confluence with the Sava River, are the consequence of mixing between the alluvial sediments of both rivers during the high water levels. As can be seen from the map the floodplain sediments of the Sava River are depleted in these elements

The northeastern parts of the investigated area, where the soils are developed on the alluvial floodplain sediments of the Sava River, are characterized by low or very low concentrations of this element. These values result from petrographic and granulometric composition of the bedrock overlain by the sampled soils.



Slika 10.7. *Uzimanje uzorka u park-šumi pored Željezare Sisak (Foto: A. Šorša).*

Figure 10.7. *Sampling in the forest park next to the steelworks Sisak (Photo: A. Šorša).*



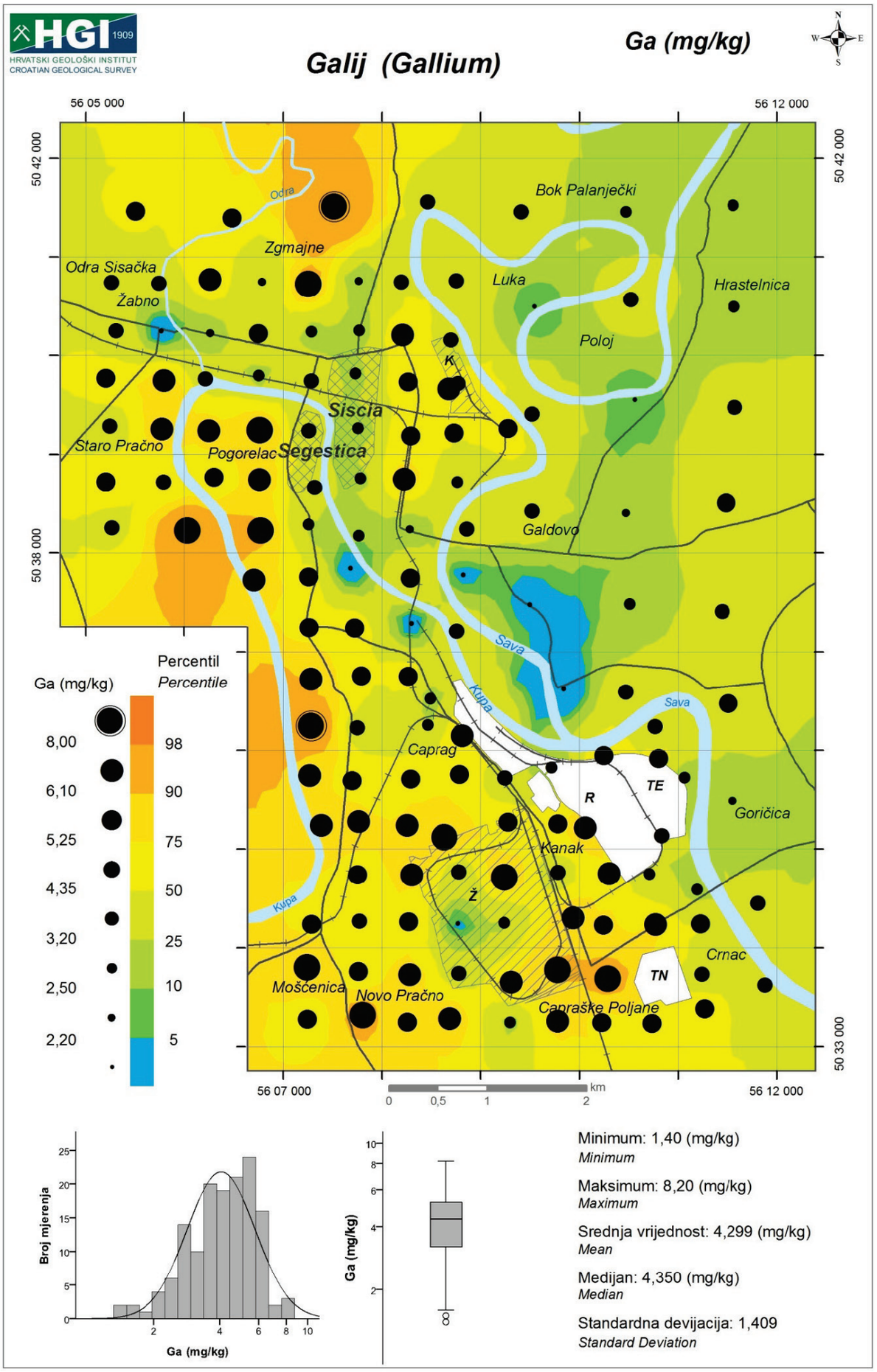
Slika 10.8. *Uzimanje uzorka u krugu Željezare Sisak (Foto: J. Halamić).*

Figure 10.8. *Sampling in the factory premises of the steelworks Sisak (Photo: J. Halamić).*



Slika 10.9. *Proljeće u park-šumi pored Željezare Sisak (Foto: J. Halamić).*

Figure 10.9. *Springtime in the forest park next to the steelworks Sisak (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Galij (Gallium)
Ga (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Ga (mg/kg)
Percentil
Percentile
8,00
6,10
5,25
4,35
3,20
2,50
2,20
98
90
75
50
25
10
5
Broj mjerenja
Ga (mg/kg)
Minimum: 1,40 (mg/kg)
Minimum
Maksimum: 8,20 (mg/kg)
Maximum
Srednja vrijednost: 4,299 (mg/kg)
Mean
Medijan: 4,350 (mg/kg)
Median
Standardna devijacija: 1,409
Standard Deviation

Hg

10.17. Hg – ŽIVA (atomski broj 80) MERCURY (atomic number 80)

Živa ili popularno nazvana tekuće srebro je element u tragovima. Nalazimo je samorodnu u vidu impregnacija, no uglavnom se pojavljuje kao sulfid. To je jedini metal u prirodi koji se pri normalnim uvjetima nalazi u tekućem stanju. Najvažnije odlike žive su njezina izrazito halkofilna svojstva i velika mobilnost, što je posljedica niske točke taljenja.

Srednji sadržaj u magmatskim stijenama je kod ultrabazita 10 μg/kg, bazalta 90 μg/kg, neutralnih stijena 50 μg/kg i kiselih stijena 80 μg/kg. Od sedimentnih stijena šejlovi imaju srednji sadržaj žive od 400 μg/kg, pješčenjaci 30 μg/kg, karbonati 40 μg/kg i gline 700 μg/kg. Ona se najviše koncentrira u sitnozrnatim sedimentima i ugljenu. Raspon koncentracije žive u ugljenu je od 10 do 8 500 μg/kg, a kod nafte od 20 do 2 000 μg/kg. Koncentracija žive u tlima je 50 μg/kg. Sadržaj ovog elementa u slatkoj vodi kreće se od 1 do 7 μg/L.

Najčešći kemijski oblici žive su: elementarna živa (Hg^0) s visokim pritiskom para i niskom topivošću u vodi; dvovalentna anorganska živa (Hg^{2+}) sa snažnim afinitetom prema mnogim anorganskim i organskim ligandima, ponajprije onima koji sadržavaju sumpor; metil-živa te dimetil-živa. Metil-živa otporna je na degradaciju u prirodnoj sredini, obogaćuje se u živim organizmima i može prolaziti kroz važne biološke barijere. Nalazi se vezana u kloridnim kompleksima i tada je vrlo mobilna. Zadržavanje žive u tlu i sedimentima uzrokuje vezivanje na okside mangana i željeza, čestice glina i organsku materiju te uvjetuje precipitaciju sulfida, a ovisi o količini žive, količini gline i humusne tvari, pH, mikrobiološkoj i biokemijskoj aktivnosti, kao i o prozračivanju tla (ANDERSSON, 1979.). U dubljim slojevima tla živa se najčešće veže za minerale glina, posebno za montmorilonit i kaolinit. U gornjim slojevima živa i njezini kompleksi vežu se na organsku tvar (KROMER et al., 1981.).

Ovaj element je vrlo otrovan za biljni i životinjski svijet. Trovanje živom kod ljudi može izazvati mutagene, kancerogene i teratogene efekte, oštećenje imunološkog sustava, krvnih žila i centralnog živčanog sustava, deformacije DNK, smanjenje reprodukcije i ometanje rasta i razvoja djece. Posebnu pažnju treba posvetiti ovom elementu kada se koristi za tretiranje prehrambenih proizvoda (fungicidi i dr.).

Živa je poznata od predbiblijskih vremena i zauzima jedinstveno mjesto u ljudskoj civilizaciji. Procijenjena godišnja svjetska proizvodnja ovog metala u 2000. godini iznosila je 1 800 t. Zbog njezine otrovnosti u mnogim zemljama obustavljena je proizvodnja.

Živa se upotrebaljava u mjernoj tehnici (termostati, pumpe i dr.), medicini, proizvodnji insekticida i fungicida, pri procesu amalgamiranja zlata u rudnicima zlata te za proizvodnju kaustične sode i klora.

Raspršenje u okoliš (osobito u vode) događa se preko otpada kemijske industrije i sve veće upotrebe za amalgmaciju zlata.U okoliš dospijeva i postupnim taloženjem iz zraka, putem kiše, zatim kroz otpadne muljeve iz taložnica i pročistača, pesticide bazirane na živi i raznovrsni industrijski i kućanski otpad. Osim toga, relativno veliki unos u okoliš događa se spaljivanjem fosilnih goriva (ugljena, mazuta i nafte).

Mercury, or quicksilver, popularly called, is a trace element. It can be found in natural state or in the form of impregnations but it mostly appears as a sulfide. This is the only metal in nature occurring in the liquid state under the normal conditions. The most important features of mercury are specifically chalcophile characteristics and great mobility, which is a result of the low melting point.

The average content in igneous rocks is 10 μg/kg, basalts 90 μg/kg, neutral rocks 50 μg/kg and acid rocks 80 μg/kg. Among sedimentary rocks shales contain on average 400 μg/kg of mercury, sandstones 30 μg/kg carbonates 40 μg/kg and clays 700 μg/kg. It is mostly concentrated in fine-grained sediments and in coal. The concentration range in coal is between 10 and 8,500 μg/kg, while in oil it mounts to between 20 and 2,000 μg/kg. Concentration of mercury in soils is 50 μg/kg. The content of this element in the sweet water is between 1 and 7 μg/L.

The most common forms of mercury are as follows: elementary mercury (Hg^0) with high steam pressure and low solubility in water; bivalent inorganic mercury (Hg^{2+}) with stronger affinity toward many inorganic and organic ligands, especially those containing sulfur; methyl-mercury and dimethyl-mercury. Methyl-mercury is resistant to degradation in the natural environment; it is enriched in living organisms and can

pass through important biologic barriers. It is found bonded in the chloride complexes and then it is highly mobile. If retained in soils and sediments it can bond to oxides of manganese and iron, clay particles and organic matter causing precipitation of sulfides. The retention depends on the content of mercury, content of clay and humic matter, pH, microbiological and biochemical activity, as well as soil airing (ANDERSSON, 1979). In deeper horizons mercury is most frequently bonded to the clay minerals, montmorillonite and kaolinite in particular. In upper horizons mercury and its complexes are bonded to the organic matter (KROMER et al., 1981).

This element is highly toxic for both plant and animal world. Mercury poisoning with people can provoke mutagenic, carcinogenic and teratogenic effects, damage to immune system, blood vessels and central nervous system, deformations of DNK, reduced reproduction and interference with children growth and development. Particular attention must be paid to this element if used for treatment of (fungicides etc.).

Mercury is notorious from the biblical times (alchemists in the ancient China!) and it occupies the unique place in the human civilization. The estimated yearly world production in 2000 was 1,800 t. Because of its toxicity in many countries its production is stopped.

Mercury is used in the measuring technique (thermostats, pumps etc.), in medicine, in production of insecticides and fungicides, in the process of gold amalgamating in the gold mines, and for the production of caustic soda and chlorine.

Dispersion of mercury into environment (water in particular) is conducted by the chemical industry waste and all the more utilization of mercury in the gold amalgamation. Further, it comes into the environment by the precipitation from the air, also by raining, through the waste mud from the deposition tanks and cleaners, by the pesticides based on mercury, and various industrial and household wastes. Besides, relatively great input into the environment, that is, air and indirectly into the soil is due to combustion of fossil fuels (coal, crude oil, and oil).

Na karti prostorne raspodjele žive vidljiva su dva područja s visokim sadržajem ovog elementa u tlu. Jedno područje je industrijska zona u južnom i jugoistočnom dijelu grada, a drugo se nalazi oko kemijske industrije „HERBOS“ i u predjelu antičkih naselja Segestica i Siscija.

Koncentracije žive u analiziranim uzorcima tla na istraživanom području variraju od 44 do 4 438 μg/kg s medijanom od 119 μg/kg. Maksimalna koncentracija registrirana je u uzorku neposredno sjeverno od Termoelektrane Sisak. U tom okružju izmjerene su ekstremne i anomalne koncentracije i na drugim lokacijama, tako da čitavo područje oko Rafinerije nafte Sisak i Termoelektrane pokazuje visoke, anomalne i ekstremne vrijednosti žive u tlu. Vezane uz to su visoke i anomalne koncentracije na lijevoj obali Save, sjeverno od navedenih industrijskih postrojenja (predio Polojci i područje prema naselju Galdovo). Raspodjela žive u tlu na ovim lokacijama nedvojbeno pokazuje da se njen unos u okoliš događa spaljivanjem fosilnih goriva u termoelektrani i preradom ugljikovodika u rafineriji. Glavni pravac raspršenja je prema sjeveru u smjeru vjetra (Sl. 9.1.). Ekstremna koncentracija žive u uzorku tla na području naselja Crnac te anomalne vrijednosti u naselju Kanak i u jugoistočnom dijelu željezare vezane su također za ova industrijska postrojenja. Povišene koncentracije izmjerene su i u krugu Željezare Sisak, zatim u njenom neposrednom zapadnom susjedstvu i u naselju Caprag. Te vrijednosti su samo jednim dijelom ve-

Two zones with high content of mercury in the soil are visible on the map of spatial distribution of mercury. One is industrial zone in the south and southeastern part of the city while another is found around the chemical industry of „HERBOS“ and in the area around the ancient settlements of Segestica and Siscia.

Concentrations of mercury in the analyzed soil samples in the investigated area vary between 44 and 4,438 μg/kg with median of 119 μg/kg. Maximum concentration is registered in the sample immediately to the north of the thermal power plant. In this surrounding extreme and anomalous concentrations are measured on other locations as well so that the whole area around the refinery and the thermal power plant shows high, anomalous and extreme values of the mercury in the soil. These are associated with high and anomalous concentrations on the left bank of the Sava River to the north of the aforementioned industrial processing plants (zone of Polojci and area toward the Galdovo settlement). Distribution of Hg in the soil on these locations indubitably shows that its input into the environment, that is, in the air and indirectly into the soil is due to combustion of fossil fuels in the thermal power plant and due to processing of hydrocarbons in the oil refinery. The main direction of dispersion is toward the north, in the direction of the wind (Fig. 9.1.). Extreme concentration of Hg in the soil sample in the area of the Crnac settlement as well as anomalous values in both the Kanak settlement and the southeastern part of the

zane uz željezaru te nešto udaljenije rafineriju i termoelektranu, dok jedan dio vjerojatno potječe i od spaljivanja fosilnih goriva u kućanstvima i stambenim naseljima (grijanje na ugljen).

Druga cjelina koja ima ekstremne i anomalne koncentracije žive u tlu nalazi se u sjevernom dijelu grada. Najveći dio onečišćenja u istočnom dijelu te cjeline vezan je za proizvodna postrojenja kemijske tvornice „HERBOS". Naime, u HERBOSU je donedavno bio aktivan pogon za proizvodnju žive. Anomalne vrijednosti na području Starog Siska, istočnom dijelu Pogorelca i Zelenom brijegu, prema sisačkoj Zgmajni, velikim dijelom su vezane za antički Sisak (naselja Segestica i Siscija). Vjerojatno su Rimljani upotrebljavali živu u proizvodnji nakita i drugih predmeta od zlata i drugih kovina. K tomu se mora pribrojiti i onečišćenje spaljivanjem ugljena, koji je donedavno bio glavno ogrijevno sredstvo u tom gusto naseljenom dijelu grada. Na temelju toga su ove povećane i anomalne koncentracije žive u tlu u tim dijelovima grada i očekivane.

Od urbanih cjelina grada prema ruralnim područjima koncentracija žive u uzorcima tla naglo opada ispod vrijednosti medijana.

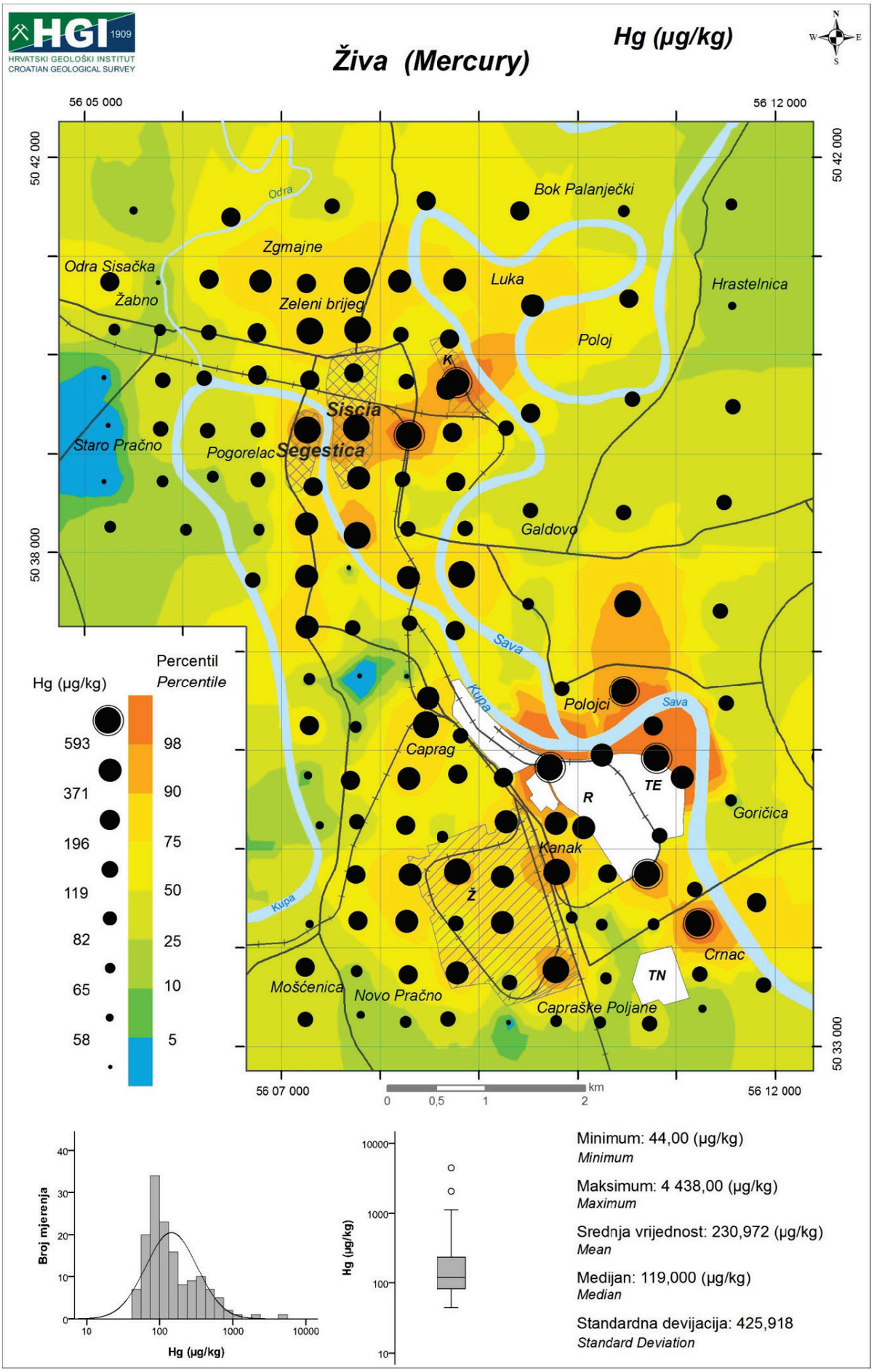
Prema *Prijedlogu o graničnim vrijednostima onečišćujućih tvari u tlu* (MESIĆ et al., 2008) te prema *Pravilniku o zaštiti poljoprivrednog zemljišta od onečišćenja* (Narodne novine 9, 2014) čitavo istraživano područje ima koncentracije ovog elementa u tlu ispod MDK (maksimalno dopuštena koncentracija) i to prema svim načinima korištenja zemljišta. Iznimku čini jedan uzorak tla u Polojcima na lijevoj obali Save neposredno sjeverno od termoelektrane, u kojem je prema Pravilniku (Narodne novine 9, 2014) registrirana veća koncentracija žive od MDK za pjeskovita tla.

steelworks are also related to these two industrial processing plants. Increased values are also measured in the circle of the steelworks, in its immediate western surroundings and in the Caprag settlement. These values are only partially related to the steelworks and to the somewhat more distant refinery and thermal power plant while one portion probably arises from the combustion of fossil fuels in the households and residential quarters (coal heating).

Another area with extreme and anomalous mercury concentrations in the soil is found in the northern part of the city. The greatest part of the contamination in the eastern part of that whole is associated with the processing plants of the chemical factory of „HERBOS". Namely, in this factory mercury was produced until lately. Anomalous values in the territory of the Old Sisak, east portion of Pogorelec and Zeleni Brijeg toward the Sisak Zgmajna are to the great part associated with the ancient Sisak (settlements of Segestica and Siscia). Romans probably also utilized mercury in the production of jewelry and other things made of gold and other metals. In addition, there is also the contribution of the coal combustion which until lately was the chief means of heating in this thickly populated portion of the city. Based on this the increased and anomalous concentrations of mercury in the soil in these parts of the city are expected

From the urban parts of the town toward the rural areas the concentration of mercury in the soil samples fall below the median value.

According to "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" (MESIĆ et al., 2008) and the Regulations on the protection of the agricultural soil against pollution (NN9, 2014) the whole investigated area is characterized by the concentration of this element below MPC (maximum permitted concentration) considering all means of land use. There is only one exception represented by the soil sample in Polojci on the left bank of the Sava River immediately to north of the thermal power plant in which, according to the Regulations (NN9, 2014), the registered concentration is higher than MPC for sandy soils.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Živa (Mercury)
Hg (µg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
Odra
Zgmajne
Odra Sisačka
Žabno
Zeleni brijeg
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Sisc ia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Polojci
Caprag
TE
R
Goričica
Kanak
Ž
Kupa
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Hg (µg/kg)
Percentil
Percentile
593
371
196
119
82
65
58
98
90
75
50
25
10
5
56 07 000
56 12 000
km
0
0,5
1
2
Broj mjerenja
Hg (µg/kg)
Minimum: 44,00 (µg/kg)
Minimum
Maksimum: 4 438,00 (µg/kg)
Maximum
Srednja vrijednost: 230,972 (µg/kg)
Mean
Medijan: 119,000 (µg/kg)
Median
Standardna devijacija: 425,918
Standard Deviation

In

10.18. In – INDIJ (atomski broj 49) INDIUM (atomic number 49)

Indij je halkofilni element u tragovima i formira sulfidne minerale.

Prosječni sadržaj indija u Zemljinoj kori je 0,25 mg/kg. U magmatskim stijenama koncentracija indija varira od 0,02 do 0,2 mg/kg (bazične stijene 0,02 do 0,22 mg/kg, a kisele stijene od 0,04 do 0,2 mg/kg). Od sedimentnih stijena najveći sadržaj imaju siltovi i gline (0,05 do 0,07 mg/kg), dok pješčenjaci imaju koncentracije od 0,02 mg/kg i vapnenci 0,03 mg/kg. Sadržaj indija u tlu najčešće varira od 0,01 do 0,5 mg/kg i on je veći u ilovastim i glinovitim tlima od pjeskovitih. Relativno visoke koncentracije registrirane su u ugljenu i sirovoj nafti što je posljedica vezivanja ovog metala na organsku tvar.

Minerali indija su indit ($FeInS_4$) i roquésit ($CuInS_2$). Česti su također i selenidi i teluridi. Radi sorpcijskih procesa indij je asociran i s mineralima željeza. Međutim, od ekonomskog značaja za dobivanje indija su sfalerit (ZnS), galenit (PbS) i halkopirit ($CuFeS_2$). Koncentracija In u tim mineralima može biti relativno visoka (do 10 g/kg u sfaleritu, do 1,5 g/kg u halkopiritu i do 0,1 g/kg u galenitu, ali najčešće se ona kreće od 10 do 20 mg/kg).

Topivi indij u tlu nalazi se u formi $InCl^{2+}$ i $In(OH)^{2+}$,mobilniji je u kiselim uvjetima i kod neutralnih pH vrijednosti. Prema distribuciji In u tlu može se zaključiti da je on asociran pretežito s glinovitijom frakcijom te da se lako apsorbira u Fe i Mn hidrokside. Također se ovaj metal veže i na organsku tvar te su zbog toga njegove koncentracije više u vršnim horizontima tla. Takve povišene koncentracije mogu nam indicirati onečišćenje.

Indij je toksični metal, a njegova otrovnost ovisi o topivosti spojeva. On može ometati sintezu proteina što onda izaziva neurološke efekte kao što je paraliza udova te oštećenje bubrega i jetre. Njegovi kloridni spojevi su nefrotoksični, a koloidne forme hepatoksične. Indij može prouzročiti i probleme s apetitom.

Svjetska produkcija indija u 2002. godini iznosila je oko 335 t i ovaj metal se dobivao pretežito preradom galenita i sfalerita i to iz rezidua, taloga, prašine i pepela tijekom produkcije Zn, Pb i Sn.

Indij se upotrebljava za proizvodnju legura, sredstava za lemljenje i u elektronskoj industriji. Jedna vrsta legure koristi se i kao termalno-neuronski apsorber u nuklearnim reaktorima. Nadalje, on se koristi i u Na-žaruljama, a njegovi spojevi služe kao zamjena žive u alkalinskim baterijama.

Antropogena disperzija u okoliš je pretežito preko spaljivanja otpada i fosilnih goriva kao što su ugljen i sirova nafta (mazut).

Indium is a chalcophile trace element which forms the sulfide minerals.

The average content of indium in the Earth's crust is 0.25 mg/kg. In igneous rocks the concentration of indium varies from 0.02 to 0.2 mg/kg (mafic rocks from 0.02 to 0.22 mg/kg and acid rocks from 0.04 to 0.2 mg/kg). Among sedimentary rocks the greatest contents is present in silts and clays (0.05 to 0.07 mg/kg) while sandstones contain 0.02 mg/kg and carbonates 0.03 mg/kg. The content of indium in soil most often varies between 0.01 and 0.5 mg/kg which is more than in loamy and clayey than in sandy soils. Relatively high concentrations are registered in the crude oils which is a result of indium bonding on organic matter.

Indium minerals are indite ($FeInS_4$) and roquésite ($CuInS_2$). Commom are also selenides and telurides. Owing to sorption processes indium is also associated with iron minerals. However, economically important for obtaining indium are sphalerite (ZnS), galena (PbS) and chalcopyrite ($CuFeS_2$). Concentration of indium in those minerals can be relatively high (up to 10 g/kg in sphalerite, 1.5 g/kg u chalcopyrite and 0.1 g/kg u galena but most often it varies between 10 and 20 mg/kg).

Soluble indium is found in the form of $InCl^{2+}$ and $In(OH)^{2+}$. It is more mobile in acid conditions and neutral pH values. According to distribution of indium in soils it can be said that it is associated predominantly with clayey fraction and is easily adsorbed on Fe and Mn hydroxides. This metal is also bonded on organic matter which is why its concentrations are higher in the topsoil. Increased concentrations can indicate contamination.

Indium is a toxic metal and its toxicity depends on solubility of compounds. It can interfere with a protein synthesis which subsequently causes neurologic effects such as limb paralysis and damage to kidneys

and liver. Its chloride compounds are nephrotoxic and colloidal forms are hepatoxic. Indium can also cause problems with the appetite.

The world production of indium in the year 2002 was about 335 t and this metal was mainly obtained by processing of galena ad sphalerite from the residua, dust, and ashes during production of Zn, Pb and Sn.

Indium is used for the production of alloys, soldering products, and in the electronic industry. One type of alloy is also utilized as a thermal-neutron absorber in nuclear reactors. Further, it is used in Na-lamps while its compounds serve as a substitute for mercury in alkaline batteries.

Anthropogenic dispersion into environment is associated with combustion of waste and fossil fuels such as coal and crude oil.

Karta prostorne raspodjele indija na istraživanom području jasno pokazuje da su povećane koncentracije ovog elementa isključivo vezane za industrijsko područje.

Izmjerene koncentracije u analiziranim uzorcima tla variraju od 0,01 mg/kg do 1,51 mg/kg s vrijednosti medijana od 0,03 mg/kg što je u granicama prosječnih koncentracija za tla općenito. Maksimalna koncentracija registrirana je u uzorku neposredno uz Termoelektranu Sisak. Spaljivanje organskih fosilnih goriva ima za posljedicu i povećane koncentracije ovog elementa u tlu u neposrednoj blizini postrojenja termoelektrane. Povećane vrijednosti indija u Polojcima na lijevoj obali Save također treba vezati uz termoelektranu. Ekstremne, anomalne i visoke koncentracije indija u tlu izmjerene su i u uzorcima tla u krugu Željezare Sisak, zatim u naseljima Kanak, Crnac i Caprag te u području sjeverozapadno od Željezare prema Kupi. Ove koncentracije posljedica su industrijske aktivnosti u željezari.

Povećani sadržaji indija u pojedinim uzorcima tla razvijenih na aluvijalnim sedimentima rijeka Kupe, Odre i Save su pretežito geogenog podrijetla.

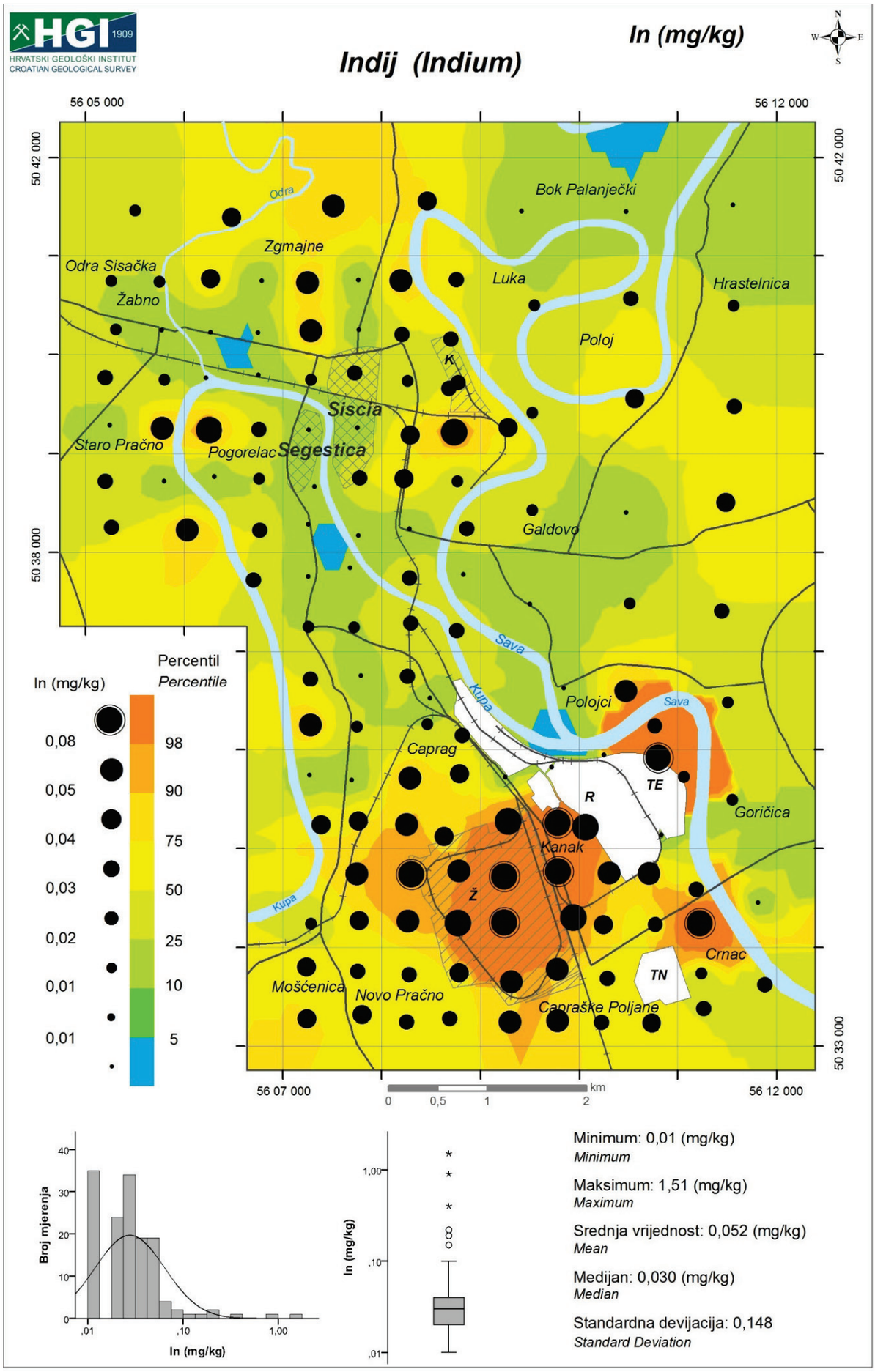
Najveći dio istraživanog terena ima koncentracije ovog elementa ispod ili daleko ispod vrijednosti medijana.

The map of spatial distribution of indium in the investigated area clearly shows that the increased concentrations of this element are related solely to industrial zone.

The measured concentrations in the analyzed samples vary from 0.01 mg/kg to 1.51 mg/kg with median of 0.03 mg/kg which is within the limits of average concentrations for the soils in general. The maximum concentration is registered in the sample immediately nearby the thermal power plant. Combustion of organic fossil fuels results with increased concentrations of this element in the soil immediately by the processing plant. Increased values of indium in Polojci on the left bank of the Sava River must be also associated with the thermal power plant. Extreme, anomalous and high concentrations of indium in the soil are measured also in the soil samples collected in the circle of the steelworks, in the settlements of Kanak, Crnac and Caprag as well as in the area to the northwest of the steelworks toward the Kupa River. These concentrations are the consequence of the industrial activity in the steelworks itself.

The elevated contents of indium in some soil samples developed on the alluvial sediments of the Kupa, Odra and Sava Rivers are dominantly of geogenic origin.

The most part of the investigated terrain shows concentrations of this element below or considerably below the median value.


HGI 1909
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Indij (Indium)
ln (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Polojci
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
ln (mg/kg)
Percentil
Percentile
0,08
0,05
0,04
0,03
0,02
0,01
0,01
98
90
75
50
25
10
5
56 07 000
56 12 000
km
0
0,5
1
2
Broj mjerenja
ln (mg/kg)
,01
,10
1,00
Minimum: 0,01 (mg/kg)
Minimum
Maksimum: 1,51 (mg/kg)
Maximum
Srednja vrijednost: 0,052 (mg/kg)
Mean
Medijan: 0,030 (mg/kg)
Median
Standardna devijacija: 0,148
Standard Deviation

K

10.19. K – KALIJ (atomski broj 19) POTASSIUM (atomic number 19)

Kalij je litofilni glavni element koji se tijekom magmatske diferencijacije obogaćuje u kiselim magmatskim stijenama u odnosu na bazične. Po učestalosti u Zemljinoj kori nalazi se na 8. mjestu i nadmašuje natrij. Glavna je komponenta u raznim važnim stijenskim mineralima. Prate ga elementi u tragovima, primjerice Rb, Cs, Tl, Sr, Ba i Pb.

Srednji sadržaj u magmatskim stijenama je 2,1 % (ultrabaziti 0,00 3%, oceanski toleitni bazalti 0,4 %, bazalti 0,8 %, granodioriti 2,5 % i graniti 4,2 %). Od sedimentnih stijena šejlovi imaju najveći srednji sadržaj kalija od 2,7 %, slijede ih pješčenjaci s 1,1 %, a karbonati imaju najmanje srednje sadržaje s 0,27 %. U tlima se kalij najčešće akumulira u mineralima glina (npr. u tlima bogatim ilitom). Koncentracija u tlima varira od 0,05 do 9 % (u obliku K_2O), sa srednjom vrijednošću od 1,68 %. U slatkoj vodi ga kao K^{1+} ima u prosjeku 2,3 mg/L.

Nakon oslobađanja iz minerala, K^+ je relativno mobilan, ali se obično vrlo brzo adsorbira na minerale glina. Koncentracija kalija je veća u biljkama nego u tlu te se manjak u tlu nadoknađuje umjetnim gnojivima. Tinjci poput muskovita, ilita i hidromuskovita relativno su postojani.

Kalij je esencijalan za sve biljke i praktički je u normalnim koncentracijama neotrovan. Međutim, koncentrirane K-soli uništavaju biljke. Uz dušik i fosfor važan je hranjivi sastojak. Ima elektrokemijsku i katalitičku funkciju u biološkim sustavima i ubraja se među primarne katione u citoplazmi.

Kalijske soli upotrebljavaju se kao sirovina za umjetna gnojiva kao KCl, K_2SO_4, K_2CO_3 i KNO_3, zatim kemikalije i dr.

Tehnogeno raspršenje u okoliš zbog geogenih i biogenih svojstava se ne zamjećuje.

Potassium is a major element which is enriched during magmatic differentiation in acid igneous rocks with respect to mafic rocks. It is 8th in abundance in the Earth's crust and thus it surpasses sodium. It is the chief component in various important rock minerals. It is associated with trace elements such as Rb, Cs, Tl, Sr, Ba and Pb.

The average potassium content in igneous rocks is 2.1 % (ultramafic rocks 0.003 %, oceanic tholeiite basalts 0.4 %, basalts 0.8 %, granodiorites 2.5 % and granites 4.2 %). Of sedimentary rocks shales contain the greatest average content of potassium amounting to 2.7 %, followed by sandstones with 1.1 % while carbonates have the least average contents of 0.27 %. In the soils potassium most often accumulates in the clay minerals (such as in the soils rich in illite). Concentration in soils varies between 0.05 and 9 % (in the form of K_2O), averaging 1.68 %. In the sweet water it occurs as K^{1+} averaging 2.3 mg/L.

After releasing from the minerals, K^+ is relatively mobile bit it is usually very soon adsorbed on the clay minerals. Concentration of potassium is higher in plants than in the soil which is why the deficit in the soil is supplied by chemical fertilizers. Micas such as muscovite, illite and hydromuscovite are relatively stabile.

Potassium is essential for all plants and is practically not toxic in normal concentrations. However, the concentrated K-salts destroy the plants. Along with nitrogen and phosphorus potassium is an important nutrient. It has electrochemical and catalytic function in the biological systems and belongs to the primary cations in the cytoplasm.

Potassium salts are utilized as a raw material for the chemical fertilizers in the form of KCl, K_2SO_4, K_2CO_3 and KNO_3. It is also used in the production of chemicals etc.

Technogenic dispersion into the environment is insignificant due to its geogenic and biogenic properties.

Izmjerene koncentracije kalija u tlu na čitavom istraživanom području su relativno niske ili su daleko ispod prosječnih za raznovrsne tipove tala. One variraju od 0,05 do 0,76 % s medijanom od 0,12 %. Maksimalna vrijednost registrirana je u krugu Željezare Sisak. Za željezaru su vezane i ekstremne i anomalne koncentracije ovog elementa što je posljedica proizvodnog procesa. Iako ekstremne i anomalne ove vrijednosti nemaju većeg utjecaja na stanje okoliša.

Područje Starog Pračna, Pogorelca i oko kemijske industrije u sjevernim dijelovima grada imaju anomalne i povišene koncentracije kalija u tlu. One su pretežito geogenog podrijetla i uvjetovane mineralnim sadržajem matičnog supstrata iz kojeg su ta tla derivirana. Matični supstrat je izgrađen od sitnozrnatijih naplavnih aluvijalnih sedimenata koji su bogatiji tinjcima.

Tla ostalih dijelova istraživanog područja (Mošćenica, Novo Pračno, dijelovi južno od Željezare Sisak, Goričica, Galdovo, Poloj, Luka, Bok Palanječki i Hrastelnica) osiromašena su ovim elementom. Jedan od razloga tomu je da biljke akumuliraju kalij i tako smanjuju njegov sadržaj u tlu. Za poljoprivrednu proizvodnju u tim bi područjima bila potrebna prihrana putem mineralnih gnojiva bogatih kalijem.

The measured concentrations of potassium in the soil on the whole investigated area are relatively low or they are considerably below the average for diverse soil types. They vary 0.05 to 0.76 % with median of 0.12 %. Maximum value is registered within the circle of the steelworks. With the latter are also associated extreme and anomalous concentrations of this element which is the result of the production process in the steelworks. Although being extreme and anomalous these values are without major impact on the environment conditions.

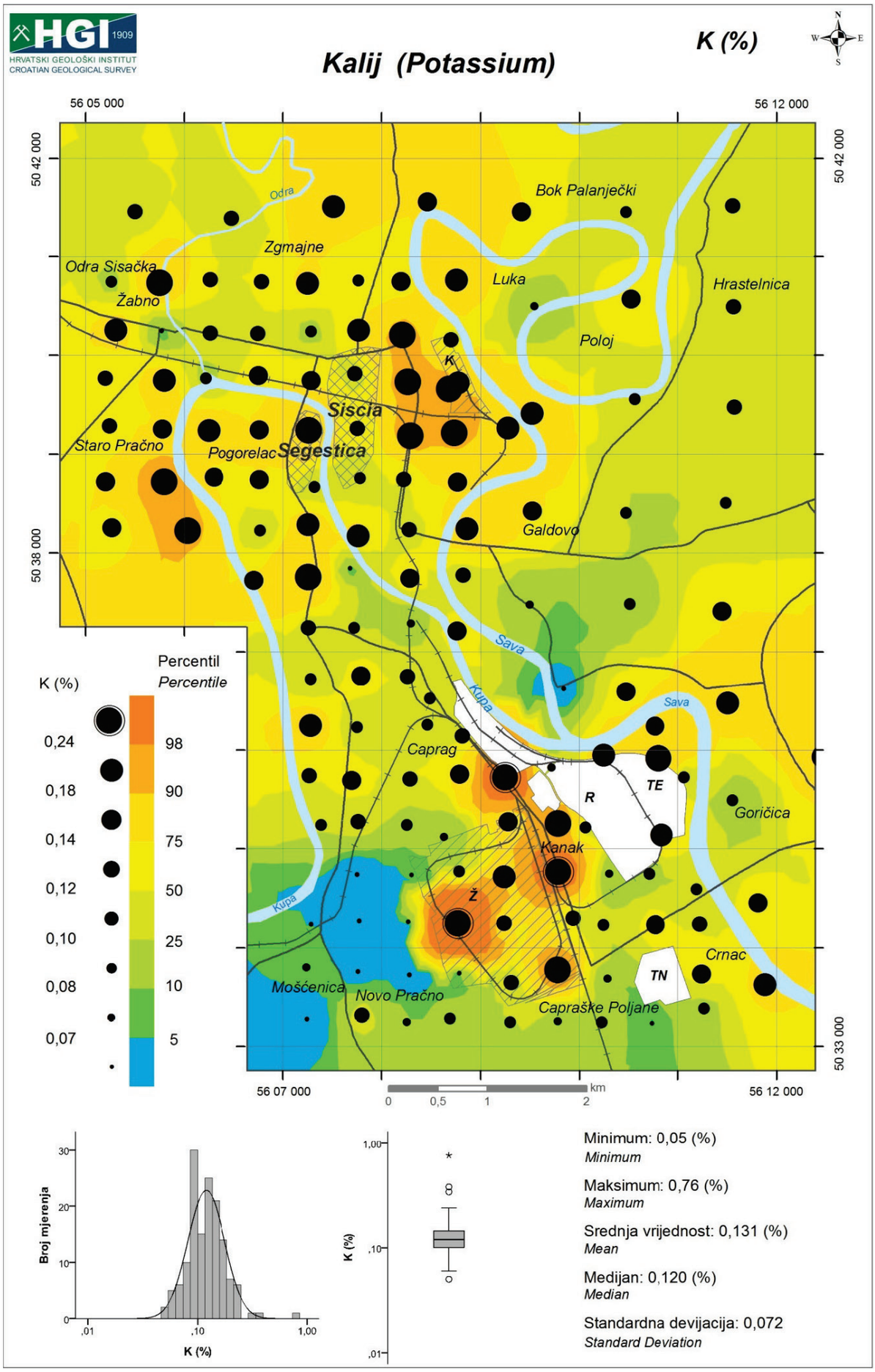
The zone of Staro Pračno, Pogorelec and around the chemical processing plants in the northern parts of the city shows anomalous and increased concentrations of potassium in the soil. They are mostly of geogenic origin and are caused by mineral composition of the parent materials from which the soils have been derived. The parent material is built of more fine-grained floodplain alluvial sediment enriched in micas.

The soils of other parts of the investigated area (Mošćenica, Novo Pračno, and portions to the south of the steelworks, Goričica, Galdovo, Poloj, Luka, Bok Palanječki and Hrastelnica) are depleted in this element. One of the reasons for that is plants accumulate potassium thus reducing its content in the soil. For agricultural production these areas would require additional nutrients through the use of mineral fertilizers rich in potassium.



Slika 10.10. *Uzorkovanje poljoprivrednog zemljišta (Foto: J. Halamić).*

Figure 10.10. *Sampling of the agriculture soil (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
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Kalij (Potassium)
K (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Segestica
Staro Pračno
Pogorelac
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
K (%)
0,24
0,18
0,14
0,12
0,10
0,08
0,07
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
K (%)
,01
,10
1,00
Minimum: 0,05 (%)
Minimum
Maksimum: 0,76 (%)
Maximum
Srednja vrijednost: 0,131 (%)
Mean
Medijan: 0,120 (%)
Median
Standardna devijacija: 0,072
Standard Deviation

La

10.20. La – LANTAN (atomski broj 57) LANTHANUM (atomic number 57)

Lantan pripada skupini rijetkih zemalja (REE) tj. lantanidima. Obogaćuje se povećanjem alkaliniteta magme. Prema učestalosti u Zemljinoj kori nalazi se na 28. mjestu.

Srednji sadržaj u magmatskim stijenama je oko 30 mg/kg (ultrabaziti 3 mg/kg, bazalti 17 mg/kg i graniti 55 mg/kg). Šejlovi sadržavaju oko 20 mg/kg, pješčenjaci oko 7,5 mg/kg, a karbonati oko 4 mg/kg. U tlima je srednji sadržaj lantana oko 30 mg/kg. U slatkoj vodi ga ima oko 0,0002 mg/L i topiv je kao karbonatni kompleks.

Smatra se da je lantan u sekundarnom okolišu vrlo slabo mobilan. Kada se oslobodi, adsorbira se na minerale glina i/ili hidrokside, ili pri visokim pH-vrijednostima precipitira u autigene karbonate.

Lantan nije esencijalan element. Pretpostavlja se da mu je otrovnost mala, ali nema podataka o njoj, odnosno o otrovnosti rijetkih zemalja. Neke biljke, npr. američki orah, akumuliraju lantan, ali utjecaj na biljke općenito nije poznat.

Svjetska produkcija rijetkih zemalja u 2003. godini iznosila je oko 751 500 t.

Lantan ima mnogostruku tehničku upotrbu, najčešće s Ce i drugim rijetkim zemljama u obliku legura u upaljačima, sredstvima za poliranje te staklima. Lantan ima specifičnu primjenu u visokoj tehnologiji.

Antropogeni utjecaj na okoliš nije poznat.

Lanthanum belongs to the group of rare earth elements (REE), that is, lanthanides. It is enriched by the increasing magma alkalinity. In abundance it is 28th element in the Earth's crust.

The average content in igneous rocks is about 30 mg/kg (ultramafic rocks 3 mg/kg, basalts 17 mg/kg and granites 55 mg/kg). Shales contain around 20 mg/kg, sandstones 7.5 mg/kg and carbonates 4 mg/kg. In soils the average content of lanthanum is around 30 mg/kg. In the sweet water lanthanum is present with circa 0.0002 mg/L. There, it is soluble in the form of the carbonate complex.

Lanthanum is considered very lowly mobile in the secondary environment. When released, it is adsorbed on clay minerals and/or hydroxides, or, at high pH-values precipitates into authigenic carbonates.

Lanthanum is not an essential element. Its toxicity is considered low but no available data exist on that matter, that is, on toxicity of rare earths. Some plants, for example American nut, accumulate lanthanum but its impact on plants in general is not known.

The world production of rare earths was about 751,500 t in the year 2003.

Lanthanum has multifarious technical application, mostly with Ce and other rare earths in the form of alloys in lighters, polishing agents and glass. Lanthanum has a specific application in the high technology.

Anthropogenic impact on the environment is unknown.

Na temelju prostorne raspodjele lantana u tlima na istraživanom području mogu se razlikovati tri područja. Prvo je industrijski dio s visokim koncentracijama lantana u odnosu na srednju vrijednost istraživanog područja. Drugo područje čine tla koja su razvijena na aluvijalnim sedimentima rijeke Kupe s povišenim sadržajem ovog elementa. Treće područje se proteže od naselja Odra Sisačka na zapadu, preko sjevernog dijela grada, potom Hrastelnice i Galdova do Goričice na istoku, a karakteriziraju ga niske ili jako niske koncentracije lantana u analiziranim tlima.

Three zones can be distinguished based on the spatial distribution of lanthanum in the soils of the investigated area. The first is the industrial part with high concentrations of La with regard to the average content of the investigated area. The second zone forms the sols developed on the alluvial sediments of the Kupa River showing the increased content of this element. The third one is extended from the Odra Sisačka settlement to the west across the northern part of the city, including Hrastelnica and Galdovo to Goričica on the east. This zone is characterized by low or very low concentrations of lanthanum in the analyzed soils.

Izmjerene koncentracije u tlima urbane cjeline Siska su u rasponu od 5,4 do 31,8 mg/kg s medijanom od 14,2 mg/kg. Najveća koncentracija registrirana je u uzorku s južnog ruba Rafinerije nafte Sisak. Ostali uzorci tla s povećanim vrijednostima lantana u tlu nalaze se također u području oko rafinerije i željezare te u naseljima Kanak i Caprag. Te povišene koncentracije nesumnjivo su posljedica antropogenog unosa ovog elementa u tlo radi industrijske proizvodnje u navedena dva prostrojenja.

Povišene koncentracije u tlima doline rijeke Kupe te Novog i Starog Pračna i Mošćenice su geogenog podrijetla. Analizirana tla na tim lokacijama razvijena su na klastičnim aluvijalnim sedimentima bogatih teškom mineralnom frakcijom, mineralima glina i Fe i Mn oksi-hidroksidima u kojima je lantan nakupljen.

Područja u kojima je matični supstrat izgrađen od pretežito karbonatnih klastičnih sedimenata rijeka Save i Odre imaju niske ili vrlo niske koncentracije lantana u analiziranim uzorcima tla.

Zaključno se može reći da su prosječne koncentracije lantana u tlima istraživanog područja niske, tako da ovaj element u razmatranju stanja okoliša ne igra značajnu ulogu.

The measured concentrations in the soils of the urban core of the Sisak city vary in range from 5.4 to 31.8 mg/kg with median of 14.2 mg/kg. The greatest concentration is registered in the sample from the southern rim of the oil refinery. Other samples with increased values of lanthanum are also found in the area around the oil refinery and the steelworks and in the settlements of Kanak and Caprag as well. These elevated values are undoubtedly the result of the anthropogenic input of this element into the soil owing to the industrial production in both mentioned processing plants.

The higher concentrations of lanthanum in the soils of the River Kupa valley as well as of Novo and Staro Pračno and Mošćenica settlements are of geogenic origin. Analyzed soils on these locations are developed on the clastic alluvial sediments rich in heavy mineral fraction, clay minerals, and Fe-Mn oxy-hydroxides in which La is accumulated.

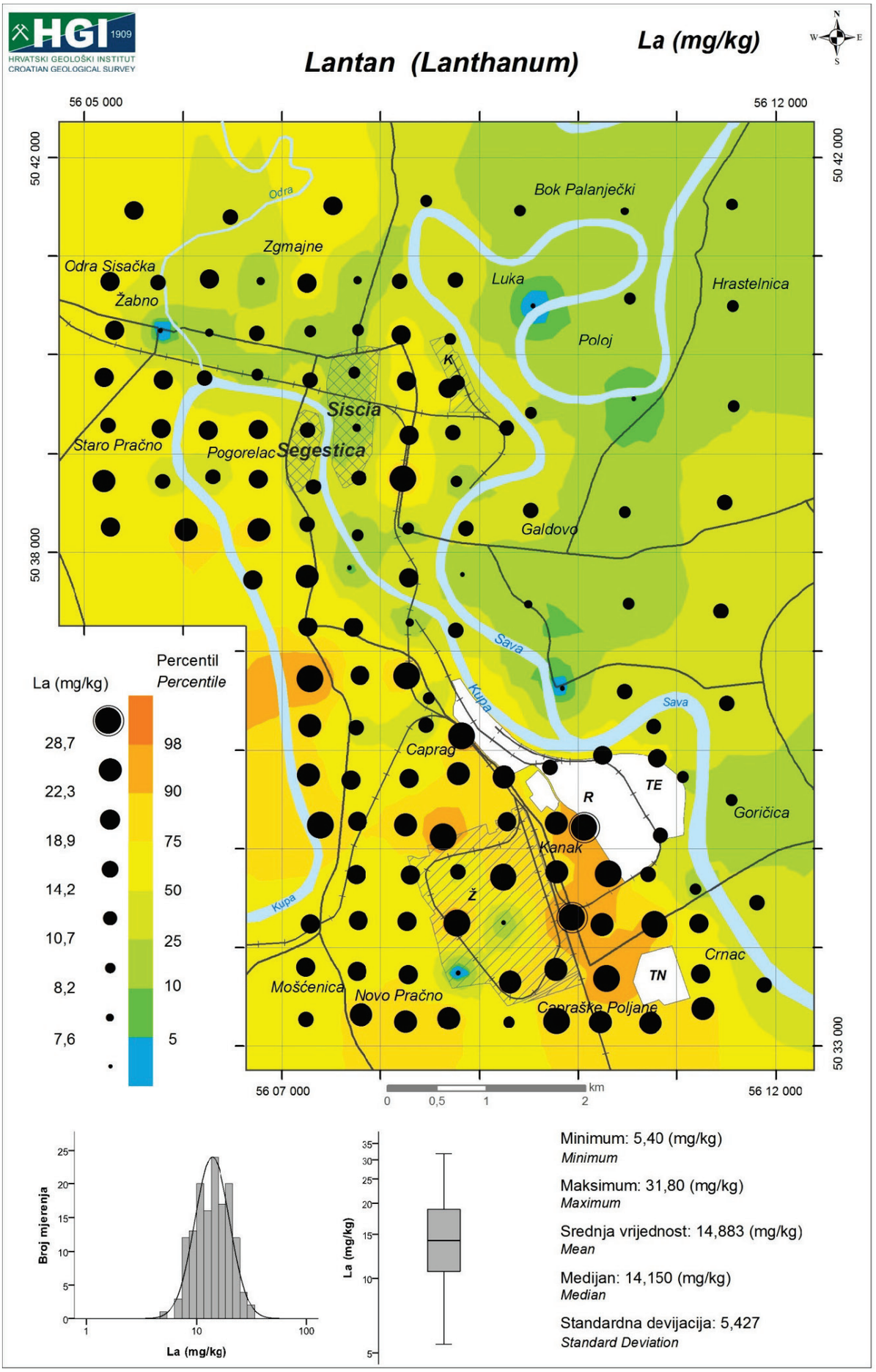
The area in which the parent material is built predominantly of carbonate clastic sediments of the Sava and Odra Rivers show low or very low concentrations of La in the analyzed soils.

In conclusion it might be said that the average concentrations of lanthanum in the soils of the investigated area are low which is why this element escapes a major role in the considerations of the environmental condition.



Slika 10.11. *Uzorkovanje tla na dječjem igralištu u blizini Rafinerije nafte Sisak (Foto: J. Halamić).*

Figure 10.11. *Soil sampling on the children's playground close to the petroleum refinery Sisak (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Lantan (Lanthanum)
La (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Bok Palanječki
Zgmajne
Odra Sisačka
Žabno
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
La (mg/kg)
Percentil
Percentile
28,7
22,3
18,9
14,2
10,7
8,2
7,6
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
La (mg/kg)
Minimum: 5,40 (mg/kg)
Minimum
Maksimum: 31,80 (mg/kg)
Maximum
Srednja vrijednost: 14,883 (mg/kg)
Mean
Medijan: 14,150 (mg/kg)
Median
Standardna devijacija: 5,427
Standard Deviation

Li

10.21. Li – LITIJ (atomski broj 3) LITHIUM (atomic number 3)

Litij je najlakši metal i pripada alkalijskoj skupini. On je ravnomjerno raspoređen u Zemljinoj kori.

Prosječni sadržaj litija u gornjem dijelu kontinentalne kore je 20 mg/kg. Srednji sadržaj u bazičnim magmatskim stijenama je 5 mg/kg, dok je on u kiselim varijetetima 27 mg/kg. Šejlovi i siltiti sadrže oko 61 mg/kg, pješčenjaci oko 25 mg/kg i karbonati 11 mg/kg. Prosječni sadržaj ovog elementa u tlu varira od 22 do 56 mg/kg pri čemu je on viši u ilovastim tlima, a manji u pjeskovitim. Radi afiniteta prema organskoj tvari koncentracije litija u ugljenu su od 0,17 do 370 mg/kg, a u sirovoj nafti od 0,02 do 3 mg/kg. Visoke koncentracije registrirane su i u ugljenoj prašini (od 50 do 1 064 mg/kg). U slatkoj vodi ga ima 1,7 μg/L.

Litij se tijekom trošenja lako oslobađa iz primarnih minerala u oksidirajućem i kiselom okruženju i lako se inkorporira u minerale glina i Fe i Mn hidrokside te se apsorbira u organsku tvar. On je jako topiv i u hipergenim uvjetima jako mobilan posebice u početku formiranja tla, a kasnije migrira kroz horizonte tla. U poodmakloj fazi pedogeneze on se veže na minerale glina, Fe i Mn hidrokside i organsku tvar. U aridnim uvjetima migrira prema površini, slično kao i soli klorita, sulfata i borata.

Smatra se esencijalnim elementom za ljude i životinje. Međutim, veće koncentracije ovog metala u hrani mogu biti otrovne za ljude i neke životinje, a u tlu i za neke biljke. Njegov nedostatak ometa proteinski metabolizam i ima efekta na različite biološke sustave (endokrini, kardiovaskularni, neuromuskulatorni, bubrežni i dermatološki). Najviše prirodnog litija dobivamo pitkom vodom, a hranom iz mesa (riba) i jaja.

Litij se pretežito dobiva iz spodumena, a svjetska proizvodnja ovog metala u 2000. godini iznosila je preko 183 000 t.

Koristi se za organsku sintezu, proizvodnju plastike i specijalnih legura, zatim u proizvodnji keramike i stakla (optika). Dodaje se raketnom gorivu, sredstvima za podmazivanje i kao rashladno sredstvo u nuklearnim reaktorima,koristi se za izradu baterija te u farmaceutskoj industriji.Ne postoje pouzdani podaci o disperziji i učinku na stanje okoliša.

Lithium is the lightest metal, belonging to the alkali group of elements. It is evenly distributed in the Earth's crust.

The average content of Li in the upper part of the continental crust is 20 mg/kg. The average content in mafic igneous rocks is 5 mg/kg and in acidic varieties it amounts to 27 mg/kg. Shales and siltstones contain about 61 mg/kg, sandstones 25 mg/kg and carbonates 11 mg/kg. Average content of this element in soil varies from 22 to 56 mg/kg being higher in loamy soils and lower in sandy ones. Owing to affinity to organic matter the concentration of lithium in coal is between 0.17 and 370 mg/kg and in crude oil from 0.02 to 3 mg/kg. High concentrations are also registered in the coal dust (from 50 to 1,064 mg/kg). In the sweet water lithium is present with 1.7 μg/L.

Lithium is easily released during weathering from primary minerals in the oxidizing and acidic environment and then it is easily incorporated in the clay minerals, Fe-Mn hydroxides and absorbed in organic matter. It is easily soluble and in hypergene conditions is highly mobile, particularly in the beginning of the soil formations while later it migrates through the soil horizons. In the advance phase of pedogenesis lithium is bonded on the clay minerals, Fe-Mn hydroxides and organic matter. In arid conditions it migrates toward the surface, similar to the salts such as chlorites, sulfates and borates.

Lithium is considered essential element for people and animals. However, greater concentrations of this metal in the food can be toxic for people and some animals while in soil it can be also toxic for some plants. Its deficiency disturbs the protein metabolism and it affect diverse biological systems (endocrine, cardiovascular, neuromuscular, kidney and dermatologic). The most of natural Li is obtained from the drinking water whereas lithium in the food is contained mostly in meat (fish) and eggs.

Lithium is mainly obtained out of spodumen. The world production of this metal during the year 2000 amounted to over 183,000 t.

Lithium is utilized for organic synthesis, production of plastics and special alloys, in production of ceramics and glass (optics). It is added to the rocket fuel, lubricants, and is used as the cooling agent in the nuclear reactors. Al-Li alloys reduce the weight of airplanes. Recently, lithium is used for production of batteries and in the pharmaceutics

No reliable data exist on its dispersion and its environmental impact.

Kao i kod mnogih drugih metala, na karti prostorne distribucije vidljiv je utjecaj industrije na raspodjelu litija u tlu. Tako se i za ovaj element mogu izdvojiti područja koja su pod utjecajem industrije (antropogeni unos ovog elementa u tlo) i područja gdje je njegov sadržaj u tlu pretežito geogenog podrijetla (tla na aluvijalnim sedimentima rijeka Kupe u Odre).

Koncentracije ovog elementa u tlima istraživanog područja kreću se od 6,8 do maksimalno 59,4 mg/kg s medijanom od 20,7 mg/kg. Najveća vrijednost izmjerena je u uzorku tla iz kruga Željezare Sisak. Ekstremni sadržaj utvrđen je i u uzorku na južnom rubu odlagališta ostataka iz visokih peći željezare. Nesumnjivo je da oborinske vode dreniraju to odlagalište (nekoliko stotina hektara) i obogaćuju tlo ispod, ne samo s ovim elementom nego i s mnogim drugim metalima. Za pretpostaviti je da procijedne vode transportiraju tako izlužene metale dalje u podzemne vode.

Anomalne koncentracije litija u tlu naselja Kanak i istočnom dijelu naselja Caprag također su posljedica industrijske djelatnosti u željezari i rafineriji u neposrednoj blizini.

Povećani sadržaji ovog elementa u tlu registrirani su također i oko kemijske industrije „HERBOS“, što je uzrokovano emisijom litija iz tih postrojenja.

As with many other metals on the map of the spatial distribution the impact of industry on the distribution of lithium in the soils is clearly visible. For this element also the areas impacted by industry (anthropogenic input of lithium in the soil) and those where its content in soil is predominantly of geogenic origin (soils on alluvial sediments of the Kupa and Odra Rivers) can distinguish.

Concentrations of this element on soils of the investigated area range from 6.8 to maximally 59.4 mg/kg with median of 20.7 mg/kg. The highest value is measured in the soil sample from the circle of the steelworks. Extreme value is registered also in the sample on the southern rim of the depot serving for the waste from the steelworks chimneys. Undoubtedly, the surface waters drain the depot (a few hundreds of hectares) and enrich the soil beneath not only with that element but also with many others. It is supposed that the percolated waters transport the leached metals further to the underground.

Anomalous concentrations of lithium in the soil of the Kanak settlement and in the eastern part of the Caprag settlements are also the consequence of the processes in the steelworks and in the oil refinery in the immediate vicinity.

Increased contents of this element in the soil are registered also around the chemical industry of „HERBOS“



Slika 10.12. *Stari most preko Kupe u Sisku (Foto: Ž. Rakarić).*

Figure 10.12. *Old bridge over the Kupa River in Sisak (Photo: Ž: Rakarić).*

Osim navedenih antropogeno uzrokovanih povećanih sadržaja litija u tlu, anomalne i visoke koncentracije ovog elementa registrirane su i u tlima razvijenim na sitnozrnatim, klastičnim aluvijalnim sedimentima rijeka Kupe i Odre i to na lokacijama Novo Pračno, Mošćenica, uzorak južno od gradskog vodovoda „Kopa“, Staro Pračno, Pogorelec i sisačka Zgmajna. Uistočnom dijelu istraživanog terena utvrđene su povišene vrijednosti litija u tlu na lokacijama Topolovac i Lazi, južno od Hrastelnice (zabarena područja nekadašnjih rukavaca rijeke Save). Tla na navedenim lokacijama bogata su mineralima glina, Fe i Mn hidroksidima i organskom tvari na koje se fiksiraju mobilni ioni litija.

Ostali dijelovi istraživanog područja imaju koncentracije litija ispod ili znatno ispod vrijednosti medijana.

Bez obzira na ekstremne i anomalne koncentracije litija u tlima urbanog područja Siska one nisu, u odnosu na prosječne vrijednosti u tlima, visoke, nego su u okviru normalnih.

which is the result of the lithium emission from those processing plants.

Besides from the mentioned man made high contents of lithium in the soil, anomalous and high concentrations of this element are registered also in the soils developed on fine-grained, clastic alluvial sediments of the Kupa River, namely on the locations of Novo Pračno, Mošćenica, to the south of the water supply line „Kopa“, Staro Pračno, Pogorelec and Sisak Zgmajna. In the eastern part of the investigated terrain the elevated values of lithium in the soils are defined on the locations of Topolovac and Lazi to the south of Hrastelnica (the zones with ponds derived from the previous armlets of the Sava River). Soils on the mentioned locations are rich in clay minerals, Fe-Mn hydroxides and organic matter fixing the mobile lithium ions.

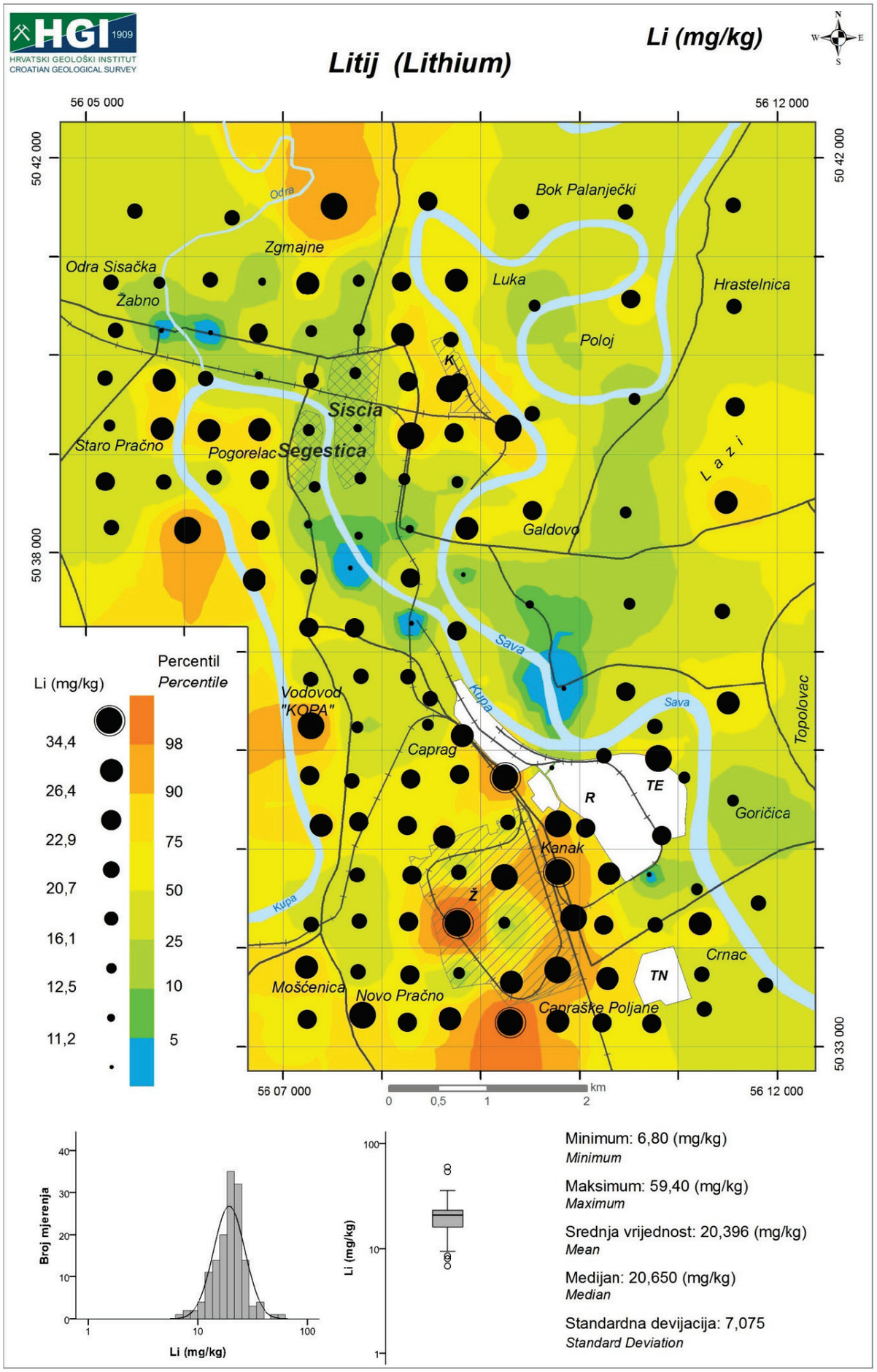
The other portions of the investigated area are characterized by concentrations below or considerably below the median values.

Regardless of extreme and anomalous concentrations of lithium in the soils of the urban core of the Sisak city these values are not, with regard to the average values in soils in general, high but within the limits of normality.



Slika 10.13. *Čamci na rijeci Kupi (Foto: J. Halamić).*

Figure 10.13. *The boats on the Kupa river (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Litij (Lithium)
Li (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Lazi
Galdovo
Sava
Kupa
Vodovod "KOPA"
Caprag
TE
R
Goričica
Topolovac
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Li (mg/kg)
Percentil
Percentile
34,4
26,4
22,9
20,7
16,1
12,5
11,2
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Li (mg/kg)
Minimum: 6,80 (mg/kg)
Minimum
Maksimum: 59,40 (mg/kg)
Maximum
Srednja vrijednost: 20,396 (mg/kg)
Mean
Medijan: 20,650 (mg/kg)
Median
Standardna devijacija: 7,075
Standard Deviation

Mg

10.22. Mg – MAGNEZIJ (atomski broj 12) MAGNESIUM (atomic number 12)

Magnezij je litofilni glavni element obogaćen u omotaču i u ultrabazičnim i bazičnim magmatskim stijenama koje imaju podrijetlo iz gornjeg omotača. On je prvi element prijelaznih elemenata, a udružen je s kalcijem. Prema učestalosti u Zemljinoj kori nalazi se na 7. mjestu.

Srednji sadržaj u magmatskim stijenama iznosi 2,3 % (ultrabaziti do 30 %, bazalti 4,6 %, granodioriti 1 % i graniti 0,16 %). Šejlovi sadržavaju oko 1,6 %, pješčenjaci 0,7 %, karbonati općenito 2,6 % i vapnenci 0,3 %. Koncentracija magnezija u tlu kreće se od 0,2 do 2 % (srednji sadržaj 0,5 %). U tlu se ponaša slično kalciju, no za razliku od njega, u kiselim tlima izluženi magnezij lako se nadoknađuje trošenjem matične stijene. U slatkoj vodi srednji sadržaj iznosi oko 0,0004 mg/L.

Magnezij je vrlo mobilan i lako se oslobađa tijekom trošenja stijena i minerala domaćina. Otopljeni Mg-ioni mogu se vezati na minerale glina ili na aktivnu organsku tvar.

Magnezij je esencijalni bioelement s elektrokemijskim, katalitičkim i strukturnim funkcijama i u normalnim uvjetima praktički je neotrovan. Sastavni je element klorofila.Nedostatak ili višak magnezija kod biljaka, ljudi i životinja može uzrokovati bolesti. Nedostatak magnezija može biti i u tlima iznad stijena bogatih tim elementom kada se sadržaj izmjenjivog magnezija smanji ispod 5 % kapaciteta kationske izmjene. U poljoprivredi se obnavlja u tlu primjenom umjetnih gnojiva. U tu svrhu često se rabe $MgSO_4$, $MgCl_2$ i $(Ca, Mg)CO_3$ (dolomit).

Magnezij se kao metal proizvodi najvećim dijelom iz morske vode.

U okoliš dolazi u obliku gnojiva, punila (talk), građevinskog materijala, otpada od visokotemperaturnih materijala, kemikalija i dr., ali to ne narušava prirodnu raspodjelu magnezija.

Magnesium is a lithophile major element enriched in the mantle and in ultramafic and mafic rocks deriving their origin from the upper mantle. It is the first of the transitory elements, occurring in association with calcium. It is 7th in abundance in the Earth's crust.

The average content of magnesium in igneous rocks is 2.3 % (ultramafic rocks up to 30 %, basalts 4.6 %, granodiorites 1 % and granites 0.16 %). Shales contain about 1.6 %, sandstones 0.7 %, carbonates in general 2.6 % and limestones 0.3 %. Concentration of Mg in soil is from 0.2 to 2 % (average value is 0.5 %). In soil it behaves similar to calcium but, in contradistinction, in acid soils the leached magnesium is easily supplied by weathering of the parent rocks. In the sweet water its content is about 0.0004 mg/L.

Magnesium is highly mobile and is easily released during the weathering of rocks and host minerals. Dissolved Mg-ions can be bonded on the clay minerals or active organic matter

Magnesium is an essential bioelement with electrochemical, catalyst, and structural functions and in normal conditions it is practically non-toxic. It is a compositional part of chlorophyll (greenness of leaves). Diseases can arise due to deficiency or excessiveness of magnesium in plants, animal and humans. Lack of magnesium can also appear in the soils developed on rocks rich in this element if the content of exchangeable Mg is reduced the 5% cation exchange capacity (CEC). In agriculture it is replenished in soil by application of chemical fertilizers. For that purpose are often used $MgSO_4$, $MgCl_2$ and $(Ca, Mg)CO_3$ (dolomite).

Magnesium as a metal is produced mostly from the sea water.

Its input into the environment is realized by fertilizers, fillers (talcum), building material, high temperature resistant materials, and chemicals etc., which, however, do not interfere with the natural distribution of magnesium.

Magnezij zauzima relativno visoko mjesto po zastupljenosti u Zemljinoj kori tako da njegova prostorna raspodjela u tlu najvećim dijelom ovisi o geološkoj podlozi, odnosno matičnom supstratu iz kojeg je dotično tlo

Magnesium is relatively highly placed with respect to its abundance in the Earth's crust which is why its spatial distribution in the soil is for the most part dependant on geological setting, that is, the bedrock lithology from

derivirano. Tako i raspodjela magnezija istraživanog područja pokazuje dva različita područja. Jedno, gdje u podlozi tla prevladavaju siliciklastični sedimenti Kupe i Odre, a drugo gdje kao matični supstrat prevladavaju karbonatni aluvijalni sedimenti (pretežito dolomit) Save.

Izmjerene koncentracije magnezija u tlu istraživanog područja variraju od 0,27 do 5,69 % s medijanom od 1,06 %. Maksimalna vrijednost magnezija izmjerena je u tlu na sjevernom rubu postrojenja Rafinerije nafte Sisak. Uzorak je uzet u neposrednoj blizini ceste koja je nasuta pretežito dolomitnim materijalom, tako da se anomalna koncentracija u tom uzorku može vezati na taj nasuti materijal.

Kao što je prethodno napomenuto tla razvijena na siliciklastičnim sedimentima rijeka Kupe i Odre imaju koncentracije ovog elementa ispod ili znatno ispod medijana, što je uvjetovano mineralnim sastavom matičnog supstrata. Suprotno tomu, područja gdje je matični supstrat izgrađen pretežito od karbonatnih aluvijalnih sedimenata (pretežito dolomit) rijeke Save, imaju povećane i visoke koncentracije magnezija.

Element magnezij raširen je u svim medijima u okolišu, pa i u tlu, tako da izmjerene koncentracije na istraživanom području ne narušavaju njegovu prirodnu distribuciju.

which it derives its origin. This is why the magnesium distribution in the investigated area indicates two different areas. One refers to the terrain characterized by the prevalently siliciclastic sediments of the Kupa and Odra Rivers while another represents the terrain with predominantly carbonate alluvial sediments of the Sava River in the bedrock (mostly dolomite).

The measured concentrations of Mg in the soils of the investigated area vary between 0.27 and 5.69 % with median of 1.06 %. Maximum value of Mg is measured in the soil on the north rim of the oil refinery. The sample is collected close to the road which is covered by the predominantly dolomite material so that anomalous concentration in that sample can be associated with it.

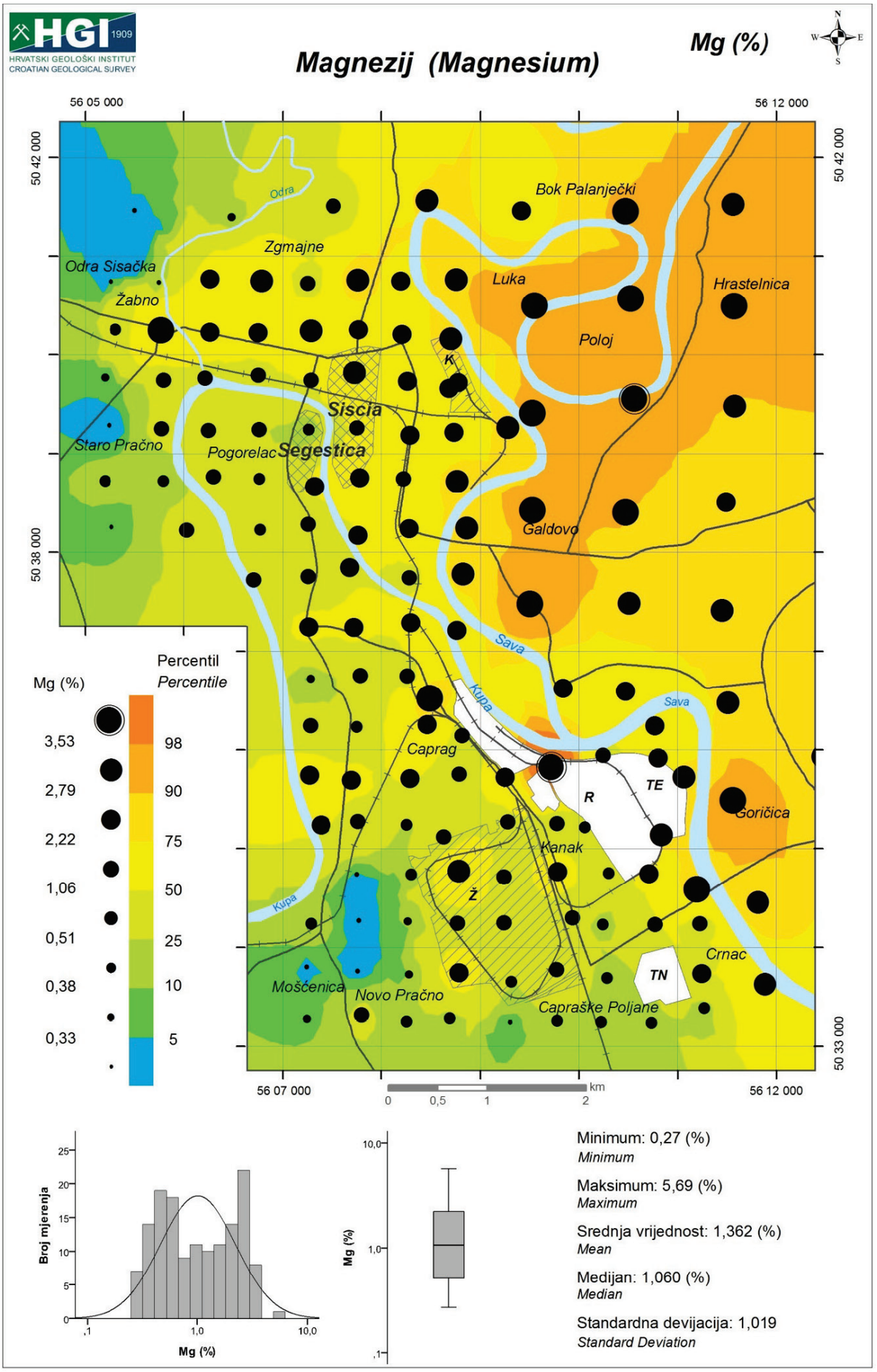
As said before the soils developed on the siliciclastic sediments of the Kupa and Odra Rivers show concentrations of this element below or considerably below the median value which results from the mineral composition of the parent material. On the contrary, the area where the parent material is composed prevalently of carbonate alluvial sediments (mostly dolomite) of the Sava River is characterized by elevated and high concentrations of magnesium.

The element magnesium is widespread in all media in the environment, including the soil, which is why the measured concentrations in the investigated area do not disrupt its natural distribution.



Slika 10.14. *Rijeka Sava (Foto: J. Halamić)*

Figure 10.14. *River Sava (Photo: J. Halamić)*


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Magnezij (Magnesium)
Mg (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
Mg (%)
3,53
2,79
2,22
1,06
0,51
0,38
0,33
98
90
75
50
25
10
5
Broj mjerenja
Mg (%)
10,0
1,0
,1
Minimum: 0,27 (%)
Minimum
Maksimum: 5,69 (%)
Maximum
Srednja vrijednost: 1,362 (%)
Mean
Medijan: 1,060 (%)
Median
Standardna devijacija: 1,019
Standard Deviation

Mn

10.23. Mn – MANGAN (atomski broj 25) MANGANESE (atomic number 25)

Mangan je litofilni sporedni element, a kao prijelazni element blizak je skupini željeza. On je i oksifilan element u rudnim mineralima. Prema učestalosti u Zemljinoj kori nalazi se na 12. mjestu.

Njegov srednji sadržaj u magmatskim stijenama je 950 mg/kg (ultrabaziti 1 040 mg/kg, bazalti 1 500 mg/kg, granodioriti 540 mg/kg i graniti 390 mg/kg). Šejlovi sadržavaju 850 mg/kg, pješčenjaci 50 mg/kg i karbonati 700 mg/kg. Koncentracija mangana u tlu kreće se od 20 mg/kg do 1 % sa srednjom vrijednošću oko 1 000 mg/kg i on nije ravnomjerno raspoređen u horizontima tla. Nakuplja se u formi oksidnih i hidroksidnih prevlaka, nakupina i nodula. Najčešći tipovi tla imaju maksimalnu koncentraciju mangana oko 0,4 %. U slatkoj vodi ima ga oko 0,015 mg/L.

Mangan je mobilan samo u kiselom reducirajućem okolišu. U geokemijskom ciklusu slijedi željezo. Koloidna suspenzija $Mn(OH)_4$ pokazuje visoka sorpcijska svojstva za katione poput Co^{2+}, Zn^{2+} i dr. On sudjeluje i u procesima oksidacije i redukcije i tvori veliki broj oksida i hidroksida koji mobiliziraju relativno veliki broj drugih metala (osim ostalih i anorganskih onečišćivača).

Esencijalni je bioelement za većinu biljaka i životinja i praktički je neotrovan u normalnim uvjetima. Aktivira mnoge reakcije koje potiču stvaranje enzima u metabolizmu biljaka. Nedostatak mangana uočava se u tlima s pH > 6. Manjak mangana uzrokuje neplodnost kod sisavaca. U većim koncentracijama umjereno je otrovan, a nakuplja se u jetri i bubrezima. Nedostatak mangana u biljkama dovodi do poremećaja u rastu.

Svjetska produkcija mangana u 2003. godini iznosila je 243 500 000 t.

Služi kao oplemenjivač čelika i kao metal za legure, za proizvodnju kemikalija, baterija, boja, keramike, stakla i dr. Legure s manganom koriste se u elektroindustriji (suhe baterije). Manganov sulfat ($MnSO_4$) služi kao gnojivo i kao dodatak stočnoj hrani. Ima široku primjenu i kao fungicid, pretežito za tretman sjemenja. Od 1970. godine mangan se koristi u formi organskih spojeva i u benzinu (kao zamjena olovu). Kalijev permanganat ($KMnO_4$) se dugo koristio kao oksidacijski katalizator u kemijskim procesima i kao dezinfekcijsko sredstvo u medicini te za purifikaciju voda. U farmaceutskoj industriji koristi se Mn-glukonat i sulfat.

Onečišćenje okoliša, osim šljakom, manje je značajno. Značajni antropogeni izvori unosa mangana u okoliš su otpadne vode, otpadni muljevi iz pročistača i talionice Mn-rude. Izgaranje goriva s Mn-aditivima manje je značajno.

Manganese is minor lithophile element and as a transitory element it is close to the iron group. It is oxyphile element in the ore minerals and 12th in abundance in the Earth's crust.

Its average content in igneous rocks is 950 mg/kg (ultramafic rocks 1,040 mg/kg, basalts 1,500 mg/kg, granodiorites 540 mg/kg and granites 390 mg/kg). Shales contain 850 mg/kg, sandstones 50 mg/kg and carbonates 700 mg/kg. Concentration of manganese in the soil varies from 20 mg/kg to 1 % with mean value of about 1,000 mg/kg and it is not evenly distributed in the soil horizons. It is accumulated in the form of oxide and hydroxide coatings, lumps and nodules. The most common types of soils contain the maximum concentration of Mn around 0.4 %. The sweet water contains around 0.015 mg/L.

Manganese is mobile only in acidic reducing environment. In the geochemical cycle it follows iron. The colloidal suspension of $Mn(OH)_4$ exhibits the high sorption properties for cations such as Co^{2+}, Zn^{2+} and others. It also participates in the oxidation and reduction processes and forms the great number of oxides and hydroxides which mobilize relatively high number of other metals (inorganic contaminants, among others).

It is essential for the most of plants and animals and is practically harmless under normal conditions. It activates many reactions instigating the formation of enzymes in the plant metabolism. Deficiency of Mn is observed in soils with pH > 6. Deficiency of manganese causes infertility of mammalians. In greater concentrations is moderately toxic and is accumulated in liver and in kidneys. In plants the lack of manganese leads to disturbance in growth.

The world production of manganese amounted 243.5 million of tons in the year 2003.

Manganese serves for the steel ennoblement and as the metal for alloys, for the production of chemicals, batteries, paints, ceramics, glass etc. The manganese alloys serve in electro industry (dry batteries). Manganese sulfate ($MnSO_4$) is utilized as fertilizer and as the supplement to the cattle food. It has also wide application as a fungicide, particularly in the seed treatment. Since 1970 manganese is used in the form of organic compounds and in gasoline (as the substitute for lead). Potassium permanganate ($KMnO_4$) has been used long since as an oxidizing catalyst in the chemical processes and as a disinfection agent in medicine as well as for the purification of water. In pharmaceutics manganese is used as Mn-gluconate and sulfate.

Contamination of environment by manganese, except form the dross, is less significant. Important anthropogenic sources of manganese into the environment are the waste waters, waste mud from the separators, and foundries of Mn ores. Fuel combustion with Mn-additives is of lesser importance.

U prostornoj raspodjeli mangana na istraživanom području jasno je vidljiv utjecaj industrijske aktivnosti na koncentracije ovog elementa u tlu. Ekstremne i anomalne koncentracije mangana u tlu vezane su isključivo za željezaru, rafineriju i termoelektranu. Izmjerene vrijednosti kreću se od 267 mg/kg do preko 10 000 mg/kg, tako da maksimalna vrijednost prekoračuje gornju granicu detekcije analitičke metode (ICP-MS) za ovaj element. Medijan je 669 mg/kg.

Osim u industrijskim pogonima anomalne koncentracije ovog metala registrirane su u naseljima Caprag, Kanak i Crnac. Nesumnjivo je da su visoki sadržaji mangana u tlu na ovim lokacijama također posljedica industrijske aktivnosti u Željezari Sisak, Rafineriji nafte Sisak i Termoelektrani Sisak.

Područja s tlima razvijenim na siliciklastičnim aluvijalnim sedimentima rijeke Kupe pokazuju povećane koncentracije mangana, ali su one ovdje isključivo geogenog podrijetla i vezane su za geokemijske uvjete koji na ovim lokacijama pogoduju mobilizaciji i obaranju mangana u vidu prevlaka, nakupina i Mn oksida i hidroksida.

Tla razvijena na aluvijalnim poplavnim sedimentima rijeke Save imaju koncentracije mangana ispod medijana, a neki tereni (južno od naselja Galdovo i Luka) pokazuju čak i nedostatak ovog elementa u tlu. To je posljedica dobre dreniranosti tala i mobilizacije mangana u dublje horizonte tla ili u podzemne vode.

Iako je mangan u normalnim uvjetima neotrovan, tlima naselja Kanak, a dijelom i Capraga, treba posvetiti pažnju zbog visokih koncentracija ovog metala u njima (uzgoj povrća i voća u privatnim vrtovima).

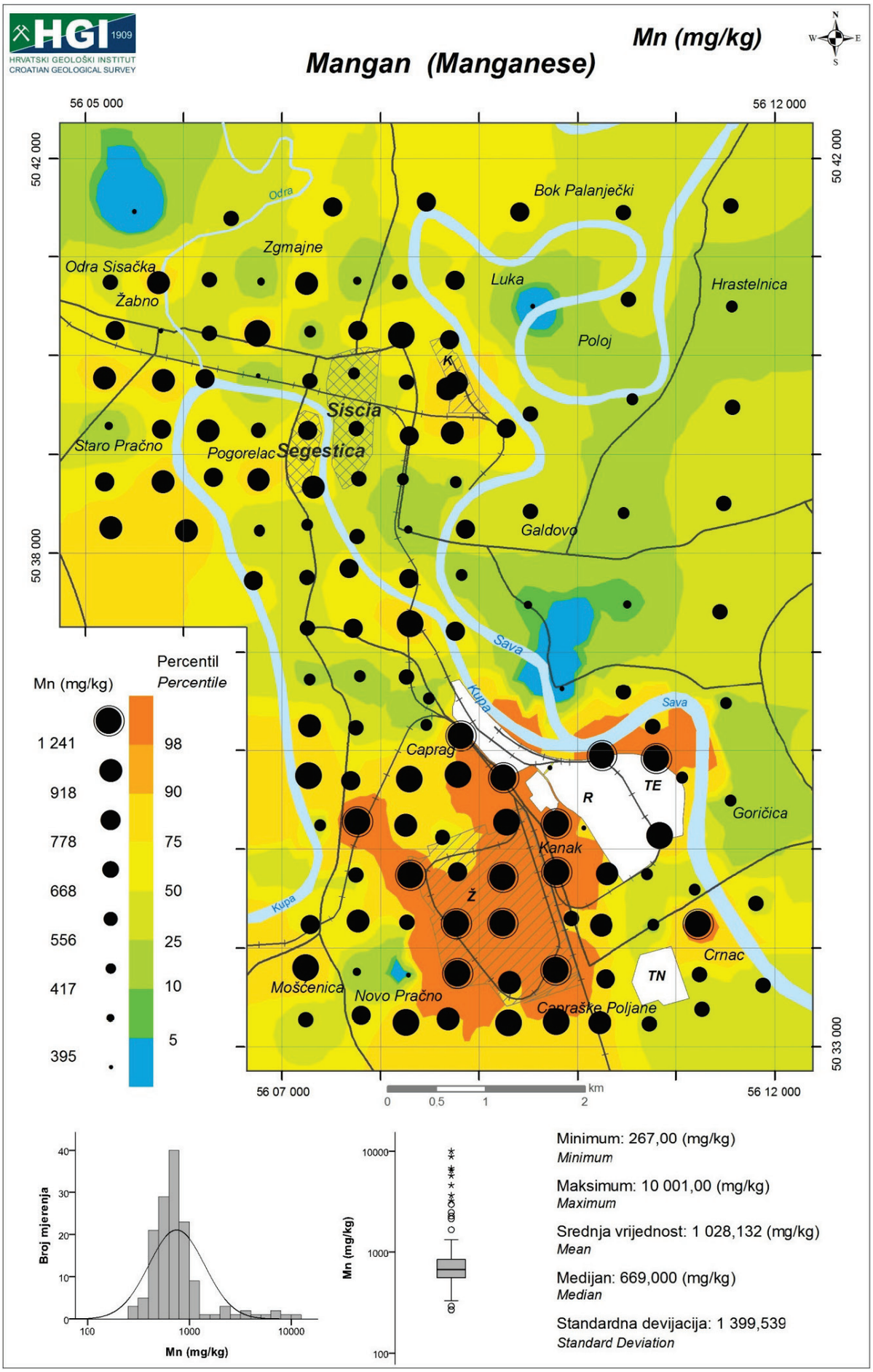
With the spatial distribution of manganese in the investigated area the impact of industrial activity on concentration of this element in the soil is clearly visible. Extreme and anomalous concentrations of Mn in the soil are associated solely with the steelworks, oil refinery and thermal power plant. The measured values range from 267 mg/kg to over 10,000 mg/kg, so that the maximum value exceeds the upper limit of detection for the analytical method (ICP-MS) of this element. Median is 669 mg/kg.

Besides from industrial processing plants the anomalous concentrations of this element are registered in the Caprag, Kanak and Crnac settlements. Indubitably, the high contents of manganese on these locations are also the consequence of industrial activity in the steelworks, oil refinery and thermal power plant.

The zones with soils developed on siliciclastic alluvial sediments of the Kupa River indicate increased concentrations of manganese but in this case these are solely of geogenic origin and related to geochemical controls favoring in these locations the mobilization and precipitation of manganese in the form of coatings, lumps and Mn oxy-hydroxides.

Soils developed on alluvial floodplain sediments of the Sava River show concentrations of Mn below the median value while some terrains (to the south of the Galdovo and Luka settlements) exhibit event the deficiency of this element in the soil. This is a result of the well drained soils, mobilization of manganese and its transport to the deeper soil horizons or into the underground water.

Albeit manganese under normal conditions is harmless attention must be paid to the soils in the Kanak settlement and, partly, in the Caprag settlement because of the high concentrations of this metal (fruit and vegetable cultivation in the privately owned gardens).


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Mangan (Manganese)
Mn (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
Mn (mg/kg)
Percentil
Percentile
1 241
918
778
668
556
417
395
98
90
75
50
25
10
5
km
0
0.5
1
2
Broj mjerenja
Mn (mg/kg)
100
1000
10000
Minimum: 267,00 (mg/kg)
Minimum
Maksimum: 10 001,00 (mg/kg)
Maximum
Srednja vrijednost: 1 028,132 (mg/kg)
Mean
Medijan: 669,000 (mg/kg)
Median
Standardna devijacija: 1 399,539
Standard Deviation

Mo

10.24. Mo – MOLIBDEN (atomski broj 42) MOLYBDENUM (atomic number 42)

Molibden je litofilan i halkofilan element u tragovima asociran s W i Re, a po učestalosti u Zemljinoj kori nalazi se na 54. mjestu (slično kao i arsen).

Srednji sadržaj molibdena u magmatskim stijenama je 1,5 mg/kg (ultrabaziti 0,3 mg/kg, bazalti 1,5 mg/kg i graniti 1,3 mg/kg). Od sedimentnih stijena molibdena ima u glinjacima 2,6 mg/kg (posebice u crnim škriljavcima – veza na organsku tvar), pješčenjacima 0,2 mg/kg i karbonatima 0,4 mg/kg. Prosječan sadržaj molibdena u tlima je 2 mg/kg. On može formirati i nodule u tlu koje mogu imati i do 410 mg/kg Mo. U tragovima ga nalazimo i u bitumenu. U nekim ugljenima nalazimo dosta visoke koncentracije ovog elementa. U slatkoj vodi ga ima 0,0015 mg/L, a nalazi se kao molibdat (MoO_4^{2-}) i u formi organskih kompleksa.

Molibden je u sekundarnim uvjetima u kiselom okolišu relativno mobilan, dok je u alkalnoj sredini (pH > 6,5) lako pokretljiv. Tako topivi Mo-anioni lako se koprecipitiraju s organskom tvari, $CaCO_3$ i Fe i Mn te Cu, Zn i Pb. Najviše je topiv u uvjetima visokih vrijednosti Eh i pH. Precipitira zajedno s oksi-hidroksidima Fe, Mn i Al u kiselim uvjetima. Adsorbira se na Fe-hidrokside kod pH 2,5 – 7, minerale glina kod pH 2 – 4 i organsku tvar. Obara se u reducirajućim uvjetima kao MoS_2. Osim toga, veže se na Fe-sulfide i formira jake komplekse s organskom tvari tako da se može reći da je molibden u sekundarnom okolišu više imobilan nego mobilan.

Molibden je mikronutrijent i esencijalni element (osim za neke zelene alge i bakterije). Umjereno je otrovan. Jače je otrovan za krave i ovce nego za ljude. Manje količine molibdena u tlu su važne za optimalan rast biljki. Zamjetan je nedostatk molibdena u kiselim tlima. Povrće koje raste na alkalnim tlima može sadržavati visoke koncentracije ovog elementa. Previsoki sadržaji molibdena u tlu mogu prouzorčiti smanjenu proizvodnju u stočarstvu (krave i ovce). Mnoga umjetna gnojiva sadrže komponente s molibdenom (natrijmolidat (engl. *sodiummolydate)*, amonijmolidat (engl. *ammoniummolydate)*). Glavni izvor molibdena u ljudskoj prehrani su mahunarke, povrće tamnog lista i meso. Višak molibdena akumulira se u serumu, urinu i kosi.

Molibden se dobiva pretežito iz molibdenita i kao nusprodukt u rudnicima bakra. Godišnja svjetska proizvodnja 2003. godine iznosila je 127 400 t.

U indistrijskoj proizvodnji ovaj element služi kao oplemenjivač čelika i očvrščivač legura. On ima i široku primjenu u elektronici i kemijskoj industriji (katalizator).

U okoliš se raspršuje iz talionica, šljakom, otpadnim vodama, uljima za podmazivanje (molykot) i dr.

Molybdenum is a lithophile and chalcophile trace element associated with W and Re, which is 54th in abundance in the Earth's crust (similarly to arsenic).

The average content of Mo in igneous rocks is 1.5 mg/kg (ultramafic rocks 0.3 mg/kg, basalts 1.5 mg/kg and granites 1.3 mg/kg). Among the sedimentary rocks molybdenum is present in claystone 2.6 mg/kg (particularly in black shales – bonding on organic matter), sandstones 0.2 mg/kg and carbonates 0.4 mg/kg. Average content of molybdenum in soils is 2 mg/kg. It can form nodules in the soil which can contain up to 410 mg/kg of Mo. In traces it can be found in bitumen. Some coals can show pretty high concentrations of this element. In the sweet water it is present with 0.0015 mg/L in the form of molybdate (MoO_4^{2-}) and in the form of organic complexes.

Molybdenum in the secondary conditions in the acidic environment is relatively mobile while in the alkaline environment (pH > 6.5) is easily mobile. Thus the soluble Mo-anions easily co-precipitate with organic matter, $CaCO_3$, Fe and Mn, as well as with Cu, Zn and Pb. The most soluble is at the high Eh and pH values. It precipitates together with oxy-hydroxides of Fe, Mn and Al in acidic conditions. It is adsorbed on Fe-hydroxides at pH 2.5 - 7, clay minerals at pH 2 - 4 and organic matter. In reducing conditions it precipitates as MoS_2. Besides, it is bonded on Fe-sulfides and forms strong complexes with organic matter so that molybdenum in secondary environment is more immobile than mobile.

Molybdenum is a micronutrient and essential element (besides for some green algae and bacteria). It is moderately toxic. More toxic it appears to cows and sheep than to humans. The small quantities of mol-

ybdenum in the soil are important for optimum growth of plants. Deficiency of molybdenum in acid soils is noticeable. Vegetables growing on the alkaline soils can contain high concentrations of this element. Too high contents of molybdenum in the soil can cause reduced production in the livestock farming (cows, sheep). Many chemical fertilizers contain components with molybdenum (sodiummolydate, ammoniummolydate). The main source of molybdenum for the human diet is pulses, dark green vegetables and meat. Excessive molybdenum is accumulated in serum, urine and hair. It can be associated with the stomach cancer.

Molybdenum is obtained predominantly from molybdenite and as a byproduct in the copper mines. The annual world production in 2003 was 127,400 t.

In industrial production this element serves for the steel ennoblement and solidification of alloys. It is widely used in electronics and chemical industry (catalyst)

Its dispersion into the environment is through the smelting process, dross, waste waters, oil for oiling (molykot) etc.

Na temelju raspodjele molibdena u tlima istraživanog područja može se reći da su povišene, visoke, anomalne i ekstremne koncentracije najvećim dijelom vezane uz uže urbano i industrijsko područje te da je najveći dio molibdena u tlu antropogenog podrijetla. Na karti distribucije mogu se izdvojiti tri područja s visokim sadržajem ovog elementa u tlu. Najveće područje zauzima industrijska zona sa svojim satelitskim stambenim naseljima Kanak i Caprag. Drugo područje se nalazi na sjeveru i dijelom je vezano uz kemijsku industriju, a dijelom uz urbani dio. Treće područje je naselje Mošćenica, na jugozapadu, koje po distribuciji molibdena u tlu nema izravnu vezu s industrijskom zonom na istoku.

Izmjerene koncentracije na istraživanom području su u rasponu od 0,36 do 33,54 mg/kg s medijanom od 0,65 mg/kg. Najveći sadržaj registriran je u krugu Željezare Sisak. Ekstremne i anomalne vrijednosti utvrđene su u tlima u željezari te u neposrednoj blizini Rafinerije i Termoelektrane, ali i u naseljima Kanak i Caprag. Vezano za rafineriju i termoelektranu također su povišene vrijednosti na lijevoj obali Save, neposredno sjeverno od tih postrojenja. Po prostornoj distribuciji ovog elementa na tim lokacijama jasno je vidljivo da on prvo dospijeva u zrak te se nakon toga vjetrom raspršuje u okoliš.

Drugo područje s ekstremnim, anomalnim i visokim koncentracijama molibdena proteže se od željezničkog ranžirnog kolodvora i pristaništa na zapadu do kemijske industrije na istoku. Ovi sadržaji najvjerojatnije imaju antropogeno podrijetlo, ali izvori onečišćenja nisu jasni.

Ekstremne koncentracije ovog elementa registrirane su i na dvije lokacije u naselju Mošćenica. Kao što je na karti vidljivo, ne postoji izravna veza sa Željezarom, jer uzorci tala u Novom Pračnu imaju vrijednosti molibdena u tlu ispod medijana. Tla na ovoj lokaciji su šumska tla, izuzetno bogata humusom na koji bi molibden mogao biti vezan i tako akumuliran u tlu.

The molybdenum distribution in the soils of the investigated area shows that increased, high, anomalous and extreme concentrations are mostly confined to the urban and industrial zone and that the most portion of Mo in the soil is of anthropogenic origin. On the map of spatial distribution three zones can be isolated with high content of this element in the soil. The greatest area occupies the industrial zone with its satellite residential quarters of Kanak and Caprag. Another area is situated to the north and is partly associated with chemical industry and partly with urban terrain. Still another area is the settlement of Mošćenica to the southwest which, judging by the distribution of Mo in the soil, is not directly related to the industrial zone to the east.

The measured concentrations on the investigated area range from 0.36 to 33.54 mg/kg with median of 0.65 mg/kg. The greatest content is registered in the circle of the steelworks. Extreme and anomalous values are also determined in the soils in the immediate vicinity of oil refinery and thermal power plant but also in the Kanak and Caprag settlements which are situated very close to their processing plants. Increased values on the left bank of the Sava River immediately to the north of these plants are also related to them. Spatial distribution of molybdenum on these locations clearly shows its airborne dispersion into the environment due to the action of wind.

Another area with extreme, anomalous and high concentrations of molybdenum is extended from the freight-yard and the docks on the west to the chemical industry to the east. Most probably these contents are of anthropogenic origin but the sources of contamination are not clear.

Extreme concentrations of this element are registered on two locations in the Mošćenica settlement. As seen from the map no direct relationship exists with the steelworks since the soil samples in Novo Pračno are cha-

Povišene vrijednosti molibdena u tlima razvijenim na aluviju rijeka Kupe i Odre su geogenog podrijetla i ovdje je molibden vjerojatno vezan za glinovitu mineralnu komponentu, Fe i Mn oksi-hidrokside te organsku tvar.

Tla na aluviju rijeke Save, gdje je taložen pretežito karbonatni materijal, imaju koncentracije molibdena ispod ili znatno ispod vrijednosti medijana (Galdovo, Hrastelnica, Luka). Za istraživano područje karakteristično je da koncentracije molibdena u tlu naglo opadaju od urbanih cjelina prema ruralnim, što je još jedan pokazatelj za antropogeni unos ovog elementa u tlo.

Pošto molibden spada u grupu PTE-a potrebno je prokomentirati njegovu distribuciju u tlu istraživanog područja s aspekta zaštite okoliša i čovjekova zdravlja. Prema *Prijedlogu graničnih koncentracija onečišćujućih tvari u tlima za raznovrsnu namjenu* (MESIĆ et al., 2008.) sadržaji molibdena u tlima na cijelom istraživanom području su ispod predloženih maksimalnih koncentracija (Tab. 6.2.). Međutim, ekstremne i anomalne koncentracije utvrđene su u naseljima Caprag, Kanak i Mošćenica, gdje postoji mogućnost akumulacije tog potencijalno toksičnog elementa u voću i povrću (privatni vrtovi i voćnjaci) te bi bilo uputno analizirati i tla na površinama koje se koriste za proizvodnju tih kultura.

racterized by values of Mo in the soil below the median. Soils on this location are represented by the forest soils which are particularly rich in humus to that molybdenum could be bonded and thus accumulated in soil.

Increased values of Mo in soils developed on the alluvium of the Kupa and Odra Rivers are geogenic in their origin and this is where Mo is probably bonded on clayey mineral component, Fe-Mn oxy-hydroxides and organic matter.

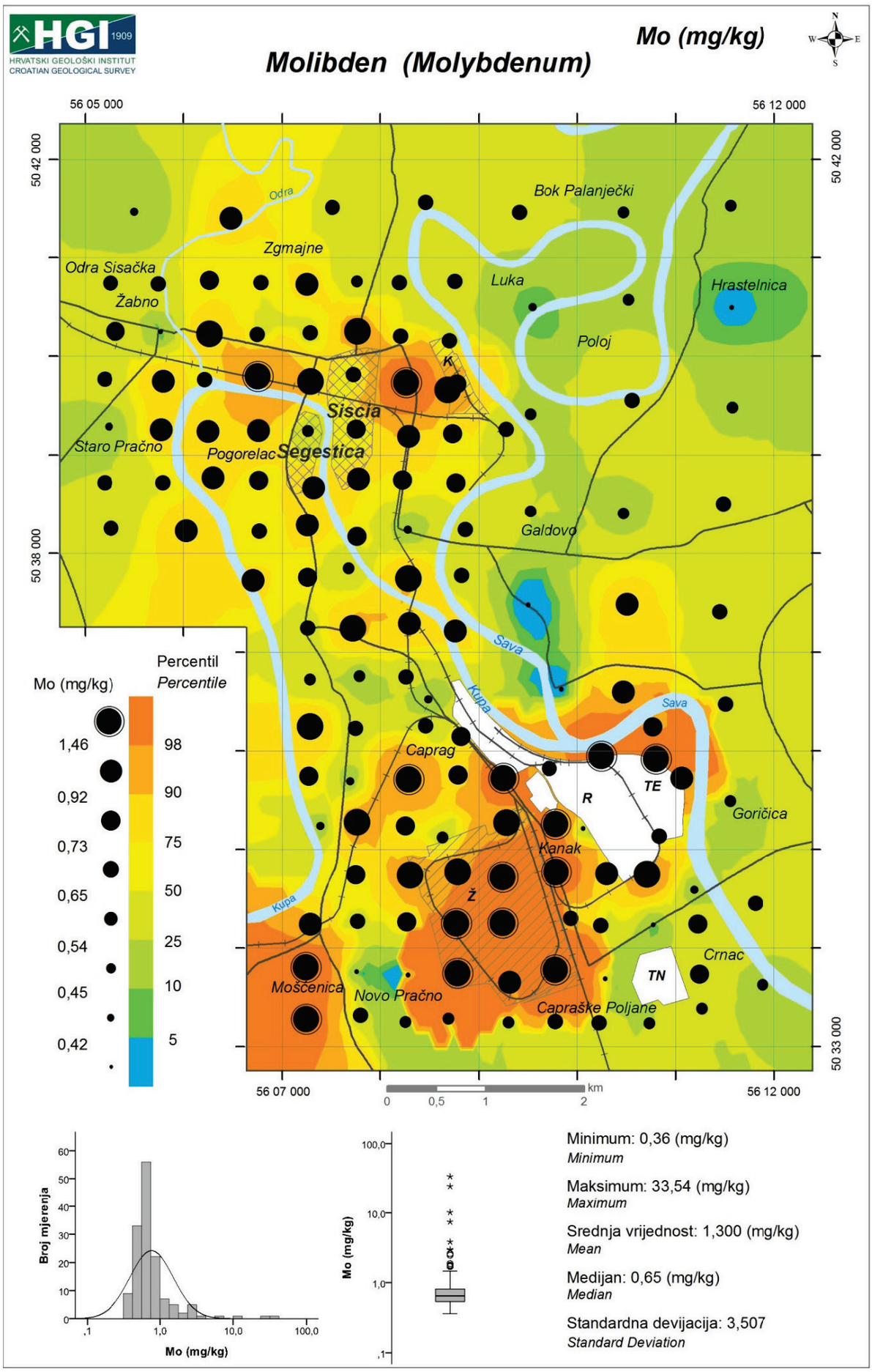
Soils on the alluvium of the Sava River where predominantly carbonate material is deposited show concentrations of molybdenum below or considerably below the median value (Galdovo, Hrastelnica, Luka). It is characteristic for the investigated area that concentrations of molybdenum abruptly decrease from the urban core to the rural terrains which is another indicator of anthropogenic ingress of this element into the soil.

Since molybdenum fall into the group of PTEs it is necessary here to discuss its distribution in the soil from the standpoint of environmental and human health protection. According to "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" (MESIĆ et al., 2008) the contents of molybdenum in the soils on the entire investigated area are below the suggested maximum concentrations (Tab. 6.2.). However, extreme and anomalous concentrations are also found in the Caprag, Kanak and Mošćenica settlements where there is a possibility of accumulation of this potentially toxic element in fruit (privately owned gardens and orchards) which is why it would be also advisable to analyze soils on the terrains used for production of these cultures.



Slika 10.15. *Uzimanje uzorka na poljoprivrednom zemljištu u Boku Palanječkom (Foto: A. Šorša).*

Figure 10.15. *Sampling on the agriculture land in Bok Palanječki (Photo: A. Šorša).*


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Molibden (Molybdenum)
Mo (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
Mo (mg/kg)
Percentil
Percentile
1,46
0,92
0,73
0,65
0,54
0,45
0,42
98
90
75
50
25
10
5
56 07 000
56 12 000
km
0
0,5
1
2
Broj mjerenja
Mo (mg/kg)
,1
1,0
10,0
100,0
Minimum: 0,36 (mg/kg)
Minimum
Maksimum: 33,54 (mg/kg)
Maximum
Srednja vrijednost: 1,300 (mg/kg)
Mean
Medijan: 0,65 (mg/kg)
Median
Standardna devijacija: 3,507
Standard Deviation

Na

10.25. Na – NATRIJ (atomski broj 11) SODIUM (atomic number 11)

Natrij je litofilni glavni element. Prema učestalosti u Zemljinoj kori nalazi se na 6. mjestu. Postoji blizak kristalokemijski odnos s kalcijem, što omogućuje međusobnu zamjenu (npr. u feldspatima). Koncentriran je u morskoj vodi.

Srednji sadržaj natrija u magmatskim stijenama iznosi 2,36 % (ultrabaziti 0,1 %, baziti 1,8 %, oceanski toleiitni bazalti 2,8 %, granodioriti 2,5 % i graniti 0,5 %). Šejlovi sadržavaju oko 0,96 %, pješčenjaci 0,3 % i karbonati 0,04 %. Najveća količina natrija u tlu sadržana je u mineralima plagioklasa. Koncentracija (u obliku Na_2O) se kreće od 0,03 do 5,1 % s medijanom 0,3 %. U morskoj vodi ga ima oko 1,05 %, a u slatkoj vodi 6,3 mg/L (ekstremno je topiv u vodi).

Natrij je jedan od najmobilnijih metala. Na osnovi toga, nakon oslobađanja iz minerala domaćina (najčešće iz plagioklasa, tinjaca i mafitnih minerala) biva transportiran u oceane. Zbog evaporacije dolazi do obogaćenja natrijem i nastaju ležišta evaporita. Ta ležišta sastoje se pretežito od soli (NaCl) i sode (Na_2CO_3). Kemijsko trošenje uzrok je malim koncentracijama natrija u sedimentu.

Esencijalni je element za sve životinje, ali ne i za sve biljke. Ima katalitička svojstva. Aktivira enzime i glavni je sastojak krvne plazme (izuzev kod većine insekata). Nakuplja se u korijenju biljaka. U velikim koncentracijama je otrovan za biljke i životinje. Na-nitrati i molibdenati često su sastavni dio umjetnih gnojiva.

Kamena i kuhinjska sol upotrebljava se u prehrani i industriji (proizvodnja klora i metala natrija, zatim sode, stakla, boja i dr.).

Njegovo raspršenje u okoliš je prikriveno zbog visokog udjela natrija u stijenskim mineralima.

Sodium is a lithophile major element. It is 6th in the Earth's crust according to abundance. There is a close crystal-chemical relationship with calcium which enables mutual substitution (such as in feldspars). It is concentrated in the sea water.

The average content of sodium in igneous rocks is 2.36 % (ultramafic rocks 0.1 %, mafic rocks 1.8 %, oceanic tholeiite basalts 2.8 %, granodiorites 2.5 % and granites 0.5 %). Shales contain about 0.96 %, sandstones 0.3 % and carbonates 0.04 %. The greatest quantity of a Na in soil is contained in the plagioclase mineral. Concentration (in the form of Na_2O) varies between 0.03 and 5.1 % with median of 0.3 %. In the sea water it is present with circa 1.05 % and in the sweet water circa 6.3 mg/L (it is extremely soluble in the water).

Sodium is one of the most mobile metals. Based on this, after being released from the host mineral (most often plagioclase, micas and mafic minerals) it is transported into the oceans. Owing to evaporation sodium is enriched occurring in the form of evaporite deposits. These are built mostly of natural salt (NaCl) and soda (Na_2CO_3). Chemical weathering results in small concentrations of Na in sediments.

Sodium is essential element for all animals but not for all plants. It is characterized by catalyst properties. Also, it activates enzymes and so it represents the main component of the blood plasma (save form the majority of insects). Sodium accumulates in the plant roots. In the great concentrations it is toxic for plants and animals. Na-nitrates and molybdenates are often the component parts of the chemical fertilizers.

Salt is used in diet and in industry (production of chlorine and sodium, soda, glass, paints etc.).

Sodium dispersion into environment is screened by the strong presence of this element in the rock minerals.

Koncentracije natrija u tlima istraživanog područja su relativno niske i kreću se od 0,002 do 0,136 % s vrijednosti medijana od 0,008 %. Razlog tomu je njegova velika mobilnost i topivost u hipergenim uvjetima. Maksimalna koncentracija ovog metala registrirana je u

Concentrations of sodium in soils of the investigated area are relatively low ranging between 0.002 and 0.136 % with median of 0.008 %. The reason is its high mobility and solubility in the hypergene conditions. Maximum concentration of this metal is registered in the

krugu Željezare Sisak. U industrijskom području izmjerena je i većina drugih ekstremnih i visokih koncentracija natrija, što je posljedica industrijske proizvodnje u tim pogonima.

Povišene vrijednosti u tlu registrirane su i u uzorcima uz veće prometnice što je vjerojatno uzrokovano intenzivnom upotrebom soli za posipanje ulica tijekom zimskog perioda. Ostala područja urbanog dijela grada imaju koncentracije ovog metala neznatno iznad medijana, što je samo dijelom odraz antropogenog unosa, a dijelom je odraz i mineralnog sastava matičnog supstrata (povećani sadržaj minerala plagioklasa i tinjaca koji u sebi sadrže više natrija). U rubnim dijelovima istraživanog područja utvrđene su koncentracije natrija u tlu ispod ili znatno ispod vrijednosti medijana.

Na temelju raspodjele ovog metala u tlu jasno se raspoznaje antropogeni utjecaj na njegovu koncentraciju u tlu. Naime, industrijski i uži urbani dio grada imaju povišene vrijednosti, dok ruralni dio ima znatno manje koncentracije natrija u tlu. U onim ruralnim područjima gdje su koncentracije povišene u odnosu na vrijednost medijana, a nalaze se izvan urbanih cjelina, može se sa sigurnošću tvrditi da su te vrijednosti isključivo geogenog podrijetla (povećan sadržaj minerala u tlu koji su obogaćeni natrijem).

circle of the steelworks. Industrial zone is characterized also with majority of other extreme and high concentrations of sodium which is a result of industrial production in these processing plants.

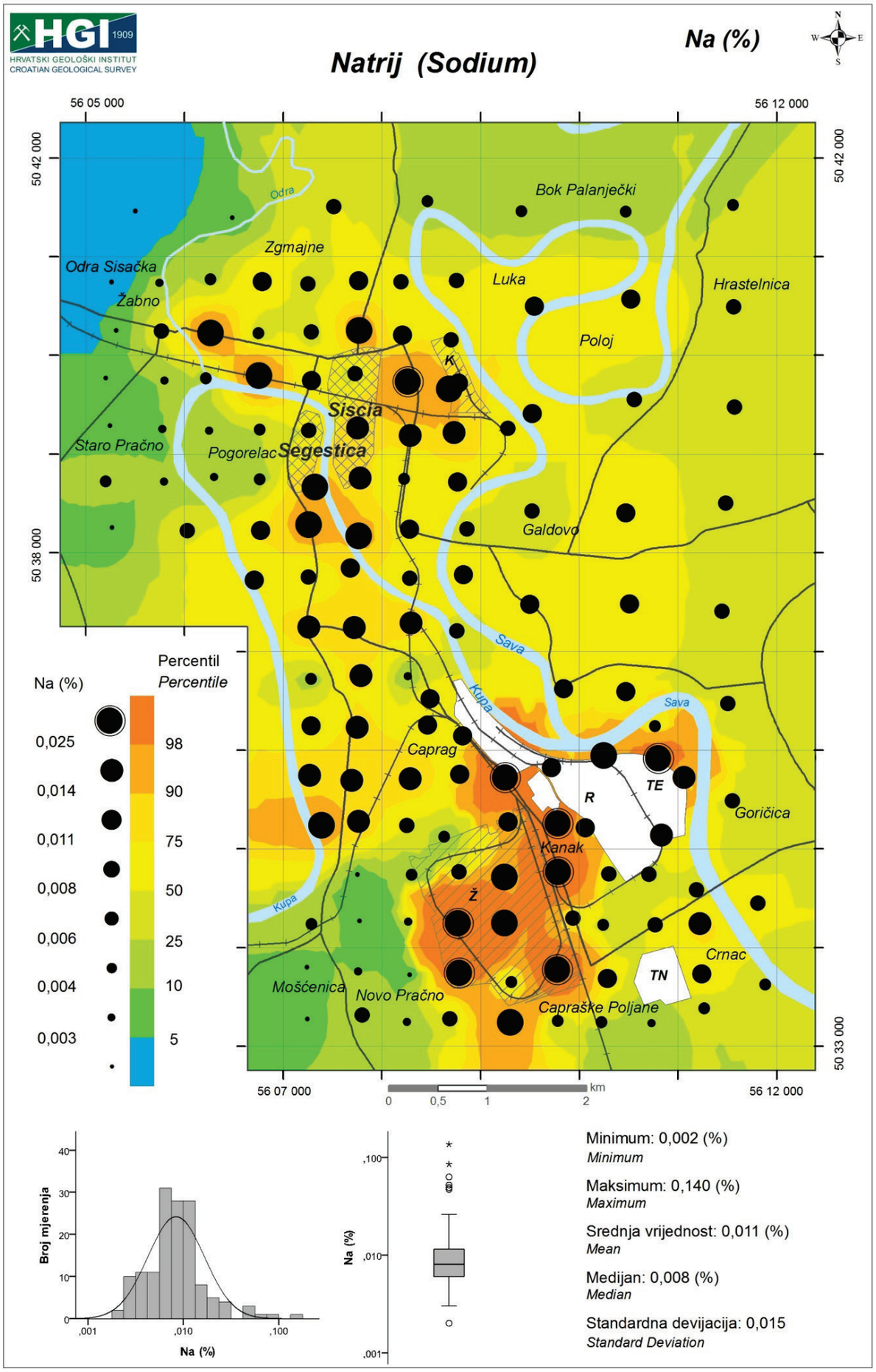
Increased values in the soil are also registered in the samples collected along the major traffic lines, which is probably caused by intense application of salt in the street salting during the winter period. The other urban parts of the town show concentrations of this element slightly above the median which only partly mirrors the anthropogenic input and partly reflects the mineral composition of the parent material (increased content of plagioclases and micas containing more sodium). In the marginal parts of the investigated area concentrations of sodium determined in the soil are below or considerably below the median value.

According to distribution of this metal in the soil the anthropogenic effect on its concentration in the soil is clearly recognized. Namely, industrial and narrow urban parts of the city are characterized by the elevated values while in the rural parts these are considerably lower. In those rural zones situated farther from the urban core, where concentrations are increased with regard to median, one can safely conclude that these values are solely of geogenic (increased content of minerals rich in sodium).



Slika 10.16. *Uzimanje uzorka tla uz prometnicu (Foto: J. Halamić)*

Figure 10.16. *Sampling along the street (Photo: J. Halamić)*


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Natrij (Sodium)
Na (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Segestica
Staro Pračno
Pogorelac
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
Na (%)
0,025
0,014
0,011
0,008
0,006
0,004
0,003
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
Na (%)
,001
,010
,100
Minimum: 0,002 (%)
Minimum
Maksimum: 0,140 (%)
Maximum
Srednja vrijednost: 0,011 (%)
Mean
Medijan: 0,008 (%)
Median
Standardna devijacija: 0,015
Standard Deviation

Nb

10.26. Nb – NIOBIJ (atomski broj 41) NIOBIUM (atomic number 41)

Niobij (drugo ime je kolumbij – Cb) je litofilni element u tragovima, a oksifilan u rudnim mineralima. Pojavljuje se i kao teški element u mineralima kiselih i bazičnih stijena te kao prateći element titanija. Obogaćuje se u jako alkalnim i karbonatitskim magmama. Udružen je s Ti, Ta, Zr, Hf, La, Ce, Sn, Y, U, W, Th i P. Prema učestalosti u Zemljinoj kori nalazi se na 33. mjestu.

Srednji sadržaj u magmatskim stijenama je 20 mg/kg (ultrabaziti 1mg/kg, oceanski toleitni bazalti 5 mg/kg, bazalti 20 mg/kg i graniti 20 mg/kg). U sedimentnim stijenama šejlovi imaju sadržaj niobija 20 mg/kg, pješčenjaci 0,05 mg/kg i karbonati 0,3 mg/kg. Srednji sadržaj u tlu iznosi 15 mg/kg. Sadržaj niobija u sirovoj nafti (mazutu) je 4 mg/kg, a u benzinu 2 mg/kg. U ugljenu može doseći i koncentracije od 70 mg/kg. U slatkoj vodi koncentracija Nb iznosi 0,001 mg/L kod pH 6,6 – 7.

Mobilnost niobija je vrlo mala. On je pretežito vezan uz teške minerale.

Ovaj element je bioelement za neke invertebrate (Ascidien), inače bez značenja. Intravenozno je umjereno otrovan za sisavce.

Godišnja svjetska produkcija niobija u 2004. godini iznosila je oko 27 000 t.

Niobij ima posebnu primjenu u metalurgiji gdje se koristi se za oplemenjivanje čelika. Osim toga, koristi se i u nuklearnoj industriji. Ima i široku primjenu u izradi cijevi za raznovrsne cjevovode. Zbog njegovih specijalnih osobina dodaje se u legure za izradu implantata te u stomatologiji.

Raspršenje u okoliš ovog elementa je zanemarivo.

Niobium (another name for it is columbium – Cb) is lithophile trace element, oxyphile in ore minerals. It also occurs as a heavy element in the minerals of acidic and mafic rocks and as an element accompanying titanium. It is enriched in ore minerals and also strongly in alkali and carbonatite magmas. It is associated with Ti, Ta, Zr, Hf, La, Ce, Sn, Y, U, W, Th and P. Niobium is 33rd in abundance in the Earth's crust.

The average content of niobium in the igneous rocks is 20 mg/kg (ultramafic rocks 1 mg/kg, oceanic tholeiite basalts 5 mg/kg, basalts 20 mg/kg and granites 20 mg/kg). In sedimentary rocks shales contain Nb 20 mg/kg, sandstones 0.05 mg/kg and carbonates 0.3 mg/kg. The average content in soils is 15 mg/kg. The content of niobium in the crude oil is 4 mg/kg, and in gasoline 2 mg/kg. In coal it can be concentrated up to 70 mg/kg. In sweet water the content of Nb is 0.001 mg/L at pH 6.6 - 7.

Mobility of niobium is very low. This element is predominantly associated with heavy minerals.

Niobium is a bioelement for some invertebrates (Ascidien), otherwise without significance. It is moderately toxic for mammals if taken intravenously

The annual production of niobium in the year 2004 was about 27,000 t.

Niobium has a special application in metallurgy where it serves for the steel ennoblement. Besides, it is used in nuclear industry. Its application is broad in the production of tubes for various conduits. Owing to its special features niobium is added to alloys for production of implants and in dental medicine.

Dispersion of this element into environment is negligible.

Ukupne izmjerene koncentracije niobija u tlima istraživanog područja su relativno niske u odnosu na srednje vrijednosti u tlima općenito (HALAMIĆ & MIKO, 2009). Razlog tomu je način kemijske pripreme uzoraka za anlizu (zlatotopka). Naime, niobij je najvećim dijelom vezan za rezistentnu tešku mineralnu frakciju, koja kod obrade uzoraka sa zlatotopkom najvećim dijelom ostaje neotopljena. No, na temelju relativnih

The total measured concentrations of niobium in soils of the investigated area are relatively low with regard to the average values in soils in general (HALAMIĆ & MIKO, 2009). The reason is the chemical preparation of samples for analysis (aqua regia). Namely, niobium is for the most part associated with the resistant heavy mineral fraction which during the treatment of samples remains mostly undissolved. However, based

odnosa koncentracija ovog elementa u tlu dobivena je realna slika njegove prostorne raspodjele u tlima istraživanog područja.

Izmjerene koncentracije variraju od 0,13 do 1,14 mg/kg s medijanom od 0,51 mg/kg. Maksimalna koncentracija ovog elementa izmjerena je u uzorku u stambenom naselju Caprag. Anomalna vrijednost u odnosu na srednju koncentraciju registrirana je istočno od Fistrovićeve ulice u sjevernom dijelu urbane cjeline. Općenito povišene koncentracije u urbanom dijelu, izmjerene su pretežito uz veće prometnice pa je moguće pretpostaviti da jedan dio niobija u tlu potječe iz goriva automobila. Povišene vrijednosti registrirane su i u naselju Kanak te oko naftnih terminala u jugoistočnom dijelu i u dijelu naselja Crnac. Pošto su u krugu Željezare Sisak koncentracije niobija oko ili ispod medijana pretpostavljamo da antropogeni unos ovog elementa u tlu ima podrijetlo iz industrijskih pogona rafinerije i naftnih terminala.

Iako su izmjerene koncentracije niobija na sjevernom rubu Termoelektrane Sisak i na lijevoj obali Save, neposredno sjeverno, niske, njihova prostorna raspodjela ipak ukazuje na antropogeno podrijetlo i njegovo raspršenje u okoliš pomoću vjetra.

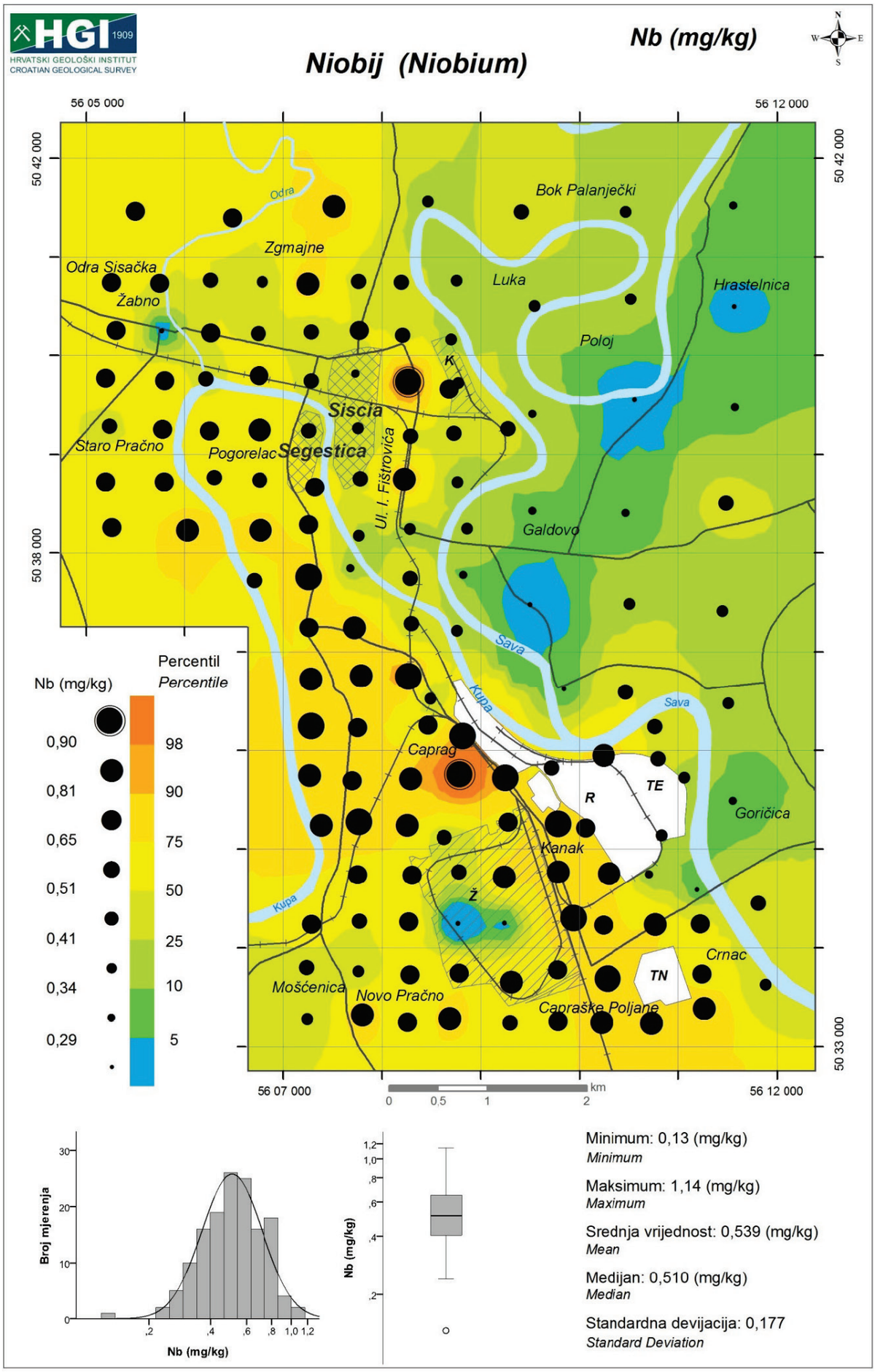
Na karti prostorne raspodjele ovog elementa u tlu istraživanog područja jasno se uočavaju geogene razlike podrijetla matičnog supstrata između rijeka Kupe i Odre na jednoj strani i Save na drugoj strani. Aluvij Kupe i Odre izgrađen je pretežito od siliciklastičnih sedimenata s većim sadržajem teške mineralne frakcije, dok je aluvij Save pretežito karbonatnog sastava i s manjim sadržajem teške mineralne frakcije. Radi navedenog, tla koja se nalaze na sedimentima rijeka Kupe i Odre, bogatija su niobijem od onih koja su nastala na sedimentima rijeke Save.

on the relative concentrations of this element in the soil a realistic picture of its spatial distribution in the soils of the investigated area was assessed.

The measured concentrations of niobium vary from 0.13 to 1.14 mg/kg with median of 0.51 mg/kg. Maximum concentration of this element is measured in the residential area of Caprag. Anomalous value with regard to the median concentration is registered to the east of Fištrović's street in the north part of the urban core. Generally, increased concentrations in the urban part are measured prevalently along the major traffic lines, which is why it can be supposed that a portion of niobium in soil derives its origin from the car fuel. Increased values are registered also in the Kanak settlement, the part of the Crnac settlement, and around the oil terminal in the southeastern part of the Crnac settlement. Since within the circle of the steelworks the concentrations of niobium are around or below the median value we suppose that the anthropogenic input of this element in the soil originates from industrial processing plants of the oil refinery and oil terminals.

Although the measured concentrations of niobium on the northern edge of the thermal power plant and the left bank of the Sava River immediately to the north are low, their spatial distribution nevertheless indicates the anthropogenic origin of this element and dispersion of this element into the environment by wind.

On the map of the spatial distribution of this element in the soils of the investigated area it is clearly observed the geogenic differences in the origin of the parent material from the area between the Kupa and Odra Rivers on the one side and the Sava River on the other. Alluvium of the Kupa and Odra Rivers is composed chiefly of siliciclastic sediments with higher content of heavy mineral fraction while alluvium of the Sava River is predominantly carbonate in its composition with lesser content of heavy mineral fraction. Due to the abovementioned the soils overlying the sediments of the Kupa and Odra Rives are richer in niobium than those developed on the sediments of the Sava River.


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Niobij (Niobium)
Nb (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Segestica
Staro Pračno
Pogorelac
Ul. I. Fištrovića
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Nb (mg/kg)
Percentil
Percentile
0,90
0,81
0,65
0,51
0,41
0,34
0,29
98
90
75
50
25
10
5
Broj mjerenja
Nb (mg/kg)
Minimum: 0,13 (mg/kg)
Minimum
Maksimum: 1,14 (mg/kg)
Maximum
Srednja vrijednost: 0,539 (mg/kg)
Mean
Medijan: 0,510 (mg/kg)
Median
Standardna devijacija: 0,177
Standard Deviation

Ni

10.27. Ni – NIKAL (atomski broj 28) NICKEL (atomic number 28)

Nikal je element u tragovima sporedni element u skupini željeza sa siderofilnim i halkofilnim svojstvima. Prema zastupljenosti u Zemljinoj kori nalazi se na 23. mjestu. U silicijem siromašnim magmama udružen je s Mg, Fe, Co, Cr i V.

Srednji sadržaj u magmatskim stijenama je 75 mg/kg (ultrabaziti 2 000 mg/kg, bazalti 130 mg/kg, granodioriti 15 mg/kg i graniti 5 mg/kg). Šejlovi imaju srednji sadržaj nikla oko 68 mg/kg, pješčenjaci 2 mg/kg i karbonati 10 mg/kg. Srednja vrijednost nikla u najčešćim tipovima tla je oko 40 mg/kg (5 – 500 mg/kg). Tla nastala na ultrabazitima mogu sadržavati koncentracije od 100 mg/kg do 0,5 %. U slatkoj vodi ga ima oko 0,0015 mg/L. Hidrolizira kod pH > 6,5.

Nikal je relativno slabo pokretljiv zbog jake tendencije adsorpcije na minerale glina i na Fe-Mn oksi-hidrokside. Osim toga, značajna je sorpcija u limonit i organsku tvar, tako da je ovaj element koncentriran u ugljenu i nafti. Feromagnezijski minerali se razmjerno lako troše pa nikal u tlima može biti mobiliziran kiselim kišama. Mnoge Ni-komponente su relativno topive kod pH < 6,5, a netopive kod pH > 6,7.

Nikal nije biogeni element, ali je esencijalan za neke organizme. Vrlo je otrovan za biljke u koncentracijama preko 50 mg/kg, uz iznimku endemskih vrsta na serpentinitskim tlima koje akumuliraju nikal. Velike koncentracije nikla u tlu otežavaju rast biljaka. Umjereno je otrovan za sisavce, pogotovo preko respiratornih organa (rak pluća i nosnica). Poznato je da je nikal alergen. Prekomjerne koncentracije nikla izazivaju razvojne smetnje i imaju genotoksične, neurološke, reproduktivne i kancerogene posljedice. Upotreba vode za piće koja sadržava puno nikla može izazvati bolove u trbuhu i oštećenje bubrega. Fosfatna umjetna gnojiva povećavaju dostupnost nikla, dok vapnenačka i kalijeva umjetna gnojiva smanjuju njegovu dostupnost. Nedostatak nikla uzrokuje retardaciju tijekom rasta životinja, a kod ljudi izaziva poremećaje metabolizma. Poznato je preko 70 biljnih vrsta koje akumuliraju nikal (npr. orasi, kakao, kelj i dr.), druge ga uopće ne uzimaju (npr. žitarice, krumpir, mrkva i dr.).

Svjetska produkcija nikla u 2003. godini iznosila je oko 1 200 000 t.

U crnoj metalurgiji nikal je oplemenjivač čelika s velikom mjerom reciklaže, zatim se upotrebljava za magnete (magnetni prekidači i permanentni magneti), legure (avioindustrija), za proizvodnju Ni-Cd baterija te za instrumente u medicini i prehrambenoj industriji. Spojevi nikla koriste se kao boje u keramičkoj i staklarskoj industriji. Također je čest katalizator za hidrogenaciju ulja i masti te za oksidaciju različitih organskih spojeva.

Onečišćenje okoliša tim metalom nastaje preko industrijske prašine, otpadom i otpadnim vodama i sagorijevanjem fosilnih goriva.

Nickel is a trace element to minor element in the iron group with siderophile and chalcophile properties. It is 23rd in abundance in the Earth's crust. In magmas poor in silicium it is associated with Mg, Fe, Co, Cr and V.

The average content of nickel in igneous rocks is 5 mg/kg (ultramafic rocks 2,000 mg/kg, basalts 130 mg/kg, granodiorites 15 mg/kg and granites 5 mg/kg). Shales contain about 68 mg/kg of nickel in average, sandstones 2 mg/kg and carbonates 10 mg/kg. The average content of Ni in the most common types of soils is about 40 mg/kg (5 – 500 mg/kg). Soils originated on ultramafic rocks can contain concentrations from 100 mg/kg to 0.5 %. In the sweet water it is present with about 0.0015 mg/L. It is hydrolized at pH > 6.5.

Nickel is relatively lowly mobile due to the strong adsorption on the clay minerals and Fe-Mn oxy-hydroxides. Besides, important is sorption in limonite and organic matter which is why this element is concentrated in coal and oil. Ferromagnesian minerals are weathered relatively easy and thus nickel in soils can be mobilized by acid rains. Many Ni-components are relatively soluble at pH < 6.5 but insoluble at pH > 6.7.

Nickel is not a biogenic element but is essential for some organisms. It is very poisonous for plants in concentrations over 50 mg/kg, with exception of endemic species on the serpentinite soils which accumulate Ni. High concentrations of nickel interfere with plant growth. It is moderately toxic for mammals, particularly through respiratory (lungs and nostrils cancer). Nickel is notoriously allergenic (nickel jewe-

lry). Excessive concentrations of nickel produce genotoxic, neurologic, reproductive and carcinogenic effects. The use of drinking water containing excessive nickel can trigger pains in stomach and can damage kidneys. Phosphate chemical fertilizers increase its availability while calcareous and potassium chemical fertilizers decrease it. Nickel deficiency causes retardation during the animal's growth while in the human world it provokes disturbances in metabolism. Over 70 plant species is known that accumulate nickel (e.g. nuts, cacao, kale etc.) while others avoid it completely (e.g. cereals, potato, carrot etc.).

The world production of nickel in the year 2003 was about 1,200,000 t.

In the black metallurgy nickel is ennobler of steel with great degree of recycling. It is used for magnets (magnetic breakers and permanent magnets), alloys (airplane industry), in production of Ni-Cd batteries, and for instruments in medicine and food industry. Compounds of nickel are used as paints in ceramic and glass industry. Additionally, nickel is a common catalyst in hydrogenation of oil and grease and in oxidation of various organic compounds.

Environmental pollution by this metal occurs through industrial dust, industrial waste and waste water, as well as by combustion of fossil fuels.

Na karti prostorne raspodjele nikla u tlima istraživanog područja, jasno se odvajaju industrijska područja koja imaju znatno veće koncentracije ovog elementa, od ostalih urbanih i ruralnih područja.

Izmjerene vrijednosti su u rasponu od 15,7 do 133,3 mg/kg s medijanom od 30,7 mg/kg. Najveća koncentracija izmjerena je u uzorku tla iz kruga Željezare. Većina ostalih uzoraka iz kruga Željezare Sisak, kao i uzorci tla na sjevernom rubu Rafinerije Nafte Sisak i Termoelektrane Sisak posjeduju ekstremne i anomalne vrijednosti nikla. One su antropogenog podrijetla i posljedica su obrade i oplemenjivanja željeza ovim metalom u pogonima željezare, zatim spaljivanja fosilnih goriva i obrade ugljikovodika u rafineriji. Po pružanju polja raspodjele anomalnih područja (izduženje prema sjeveru u smjeru vjetra) vidljivo je da je antropogeni unos ovog elementa u tlo uslijedio iz zraka. Zbog toga se područje s povišenim i visokim koncentracijama nikla u tlu proteže sjeverno od Termoelektrane preko Save na *SSI* skoro do naselja Hrastelnica. Anomalna koncentracija ovog elementa u uzorku tla neposredno kod željezničke stanice u Capragu ima dvojako podrijetlo. Jedan dio nikla u tom uzorku potječe iz željezare i bio je transportiran zrakom, a drugi dio potječe od metalne prašine koja se oslobađa s tračnica i s kotača željezničkih vagona prilikom kočenja.

Visoke vrijednosti nikla u tlu utvrđene su i u neposrednoj blizini kemijske industrije „HERBOS", što je vjerojatno uzrokovano raspršenjem nikla i njegovih spojeva u okoliš tijekom njihove upotrebe u proizvodnom procesu tih pogona.

Osim industrijskih zona, tla razvijena na aluvijalnim sedimentima rijeka Kupe i Odre posjeduju također povišene i visoke koncentracije nikla u tlu (područje južno od gradskog vodovoda „Kopa", Staro Pračno, Pogorelec i sisačka Zgmajna). Tla ovih područja bogata su mineralima glina i Fe i Mn oksi-hidroksidima. Mobilni

On the map of the spatial distribution of nickel in soils of the investigated area industrial zones are clearly separated containing considerably greater concentrations of this element with respect to other urban and rural terrains.

The measured values range from 15.7 to 133.3 mg/kg with median of 30.7 mg/kg. The greatest concentration is measured in the soil sample from the circle of the steelworks. The majority of other samples from within the circle of the steelworks, as well as those on the northern edge of the oil refinery and the thermal power plant also show extreme and anomalous values of nickel. These values are anthropogenic in origin and result from iron processing and ennoblement by this metal in the steelworks, combustion of fossil fuels and hydrocarbon processing in the oil refinery. According to direction of elongated fields of distribution of the anomalous area (northward elongation in the direction of wind) it is obvious that the anthropogenic ingress of this element in the soil is from the air. Owing to this the area with increased and high concentrations of nickel in the soil is extended north of the thermal power plant across the Sava River to NNE almost to the Hrastelnica settlement. Anomalous concentration of this element in the sample immediately by the railway station of Caprag is of a two-sided origin. A portion of nickel in this sample originates from the steelworks and was transported airborne while another part derives from the metal dust releasing from the rails and wheels of the railway carriages caused by breaking.

The high values of nickel in the soil are also determined in the close vicinity of chemical industry which is probably caused by dispersion of nickel and its compounds into environment during their application in the production process of the chemical plants.

Except for industrial zones the sols developed on the alluvial sediments of the Kupa and Odra Rivers also

ioni nikla imaju jaku tendenciju vezivanja na gline i oksi-hidrokside tako da se taj element koncentrira u tlima bogatim tim mineralnim sastojcima i spojevima. Te koncentracije su neosporno geogenog podrijetla, tim više jer se između tih područja i industrijske zone na jugoistoku nalazi široki pojas s tlima koja imaju niske ili vrlo niske sadržaje ovog elementa.

Tla ruralnih dijelova istraživanog područja na jugu, sjeverozapadu i sjeveroistoku te područje od Viktorovca do Galdova, u urbanoj cjelini imaju koncentracije nikla ispod ili znatno ispod medijana, što je uvjetovano različitim tipovima tala te podrijetlom matičnog supstrata iz kojeg su dotična tla derivirana (aluvij rijeke Save koji je prirodno siromašniji ovim metalom).

Nikal pripada grupi teških metala i on je u većim koncentracijama otrovan za biljke i životinje. Prema *Pravilniku o zaštiti poljoprivrednog zemljišta od onečišćenja* (Narodne novine 9, 2014) i *Prijedlogu graničnih koncentracija onečišćujućih tvari u tlu iz Programa trajnog motrenja tala Republike Hrvatske* (MESIĆ et al., 2008.) nekoliko uzoraka iz ruralnog područja, a koja spadaju u grupu poljoprivrednih tala, imaju koncentracije nikla iznad MDK za tu vrstu tla i smatraju se onečišćenim. Trenutno se ta područja koriste za proizvodnju stočne hrane (sijeno), ali bi u slučaju intenzivnije poljoprivredne proizvodnje trebalo obratiti pozornost na sadržaj nikla u tim tlima.

show elevated and high concentrations of nickel in soil (area to the south of the water supply line „Kopa", Staro Pračno, Pogorelec and Sisačka Zgmajna). Soils of these areas are rich in clay minerals and Fe-Mn oxy-hydroxides. Mobile nickel ions show strong tendency to bond on clays oxy-hydroxides which is why this element is being concentrated in soils rich in these mineral components and compounds. These concentrations are undoubtedly of geogenic origin, all the more because between these areas and industrial zone to the southeast there is a wide belt with soils with low or very low contents of this element.

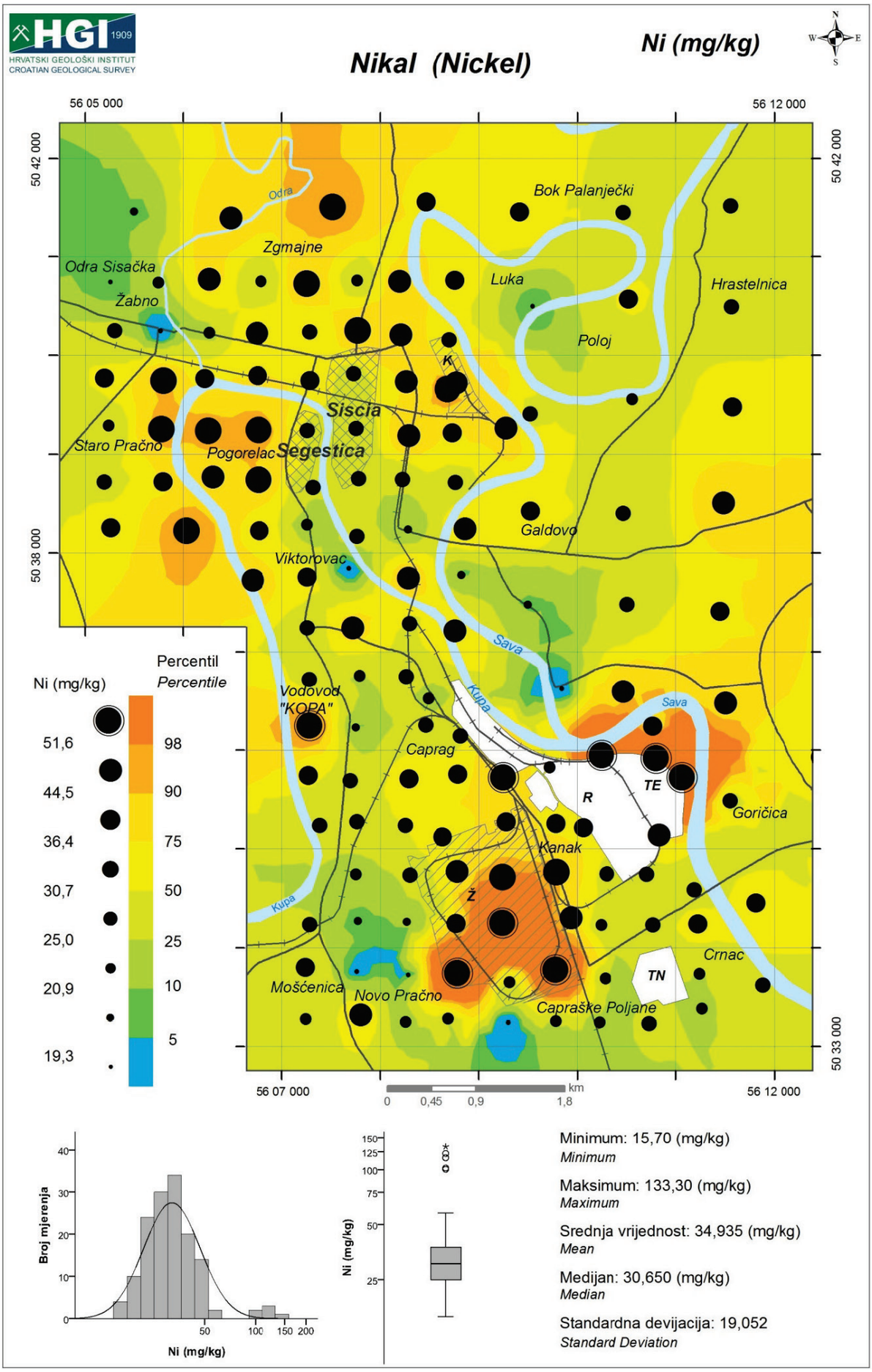
The soils of rural parts of the investigated area to the south, northwest, and northeast as well as area stretching from Viktorovac to Galdovo in the urban core show the concentrations of nickel below or considerably below the median value. This is caused by various types of soils and by the origin of the parent materials from which the former have been derived (alluvium of the Sava River is naturally more deficient in this metal).

Nickel belongs to the group of heavy metals and if occurring in higher concentrations it is toxic for plants and animals. In accordance with Regulations on protection of agricultural land from pollution (NN9, 2014) and "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" from the Program of permanent monitoring of soils in Croatia (MESIĆ et al., 2008) several samples from the rural area, which fall into the group of agricultural soils, show concentrations of nickel above MPC for that soil type and thus are considered polluted. Presently, these areas are used for the production of animal feeding stuff (hay) but in the case of more intense agricultural production (farming of other cultures) attention ought to be paid on their content of nickel.



Slika 10.17. *Odlagalište industrijskog otpada u sklopu Željezare Sisak (Foto: J. Halamić).*

Figure 10.17. *Dumpsite of industrial waste in the factory premises of the Sisak steelworks (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Nikal (Nickel)
Ni (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Viktorovac
Sava
Kupa
Vodovod "KOPA"
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
51,6
44,5
36,4
30,7
25,0
20,9
19,3
98
90
75
50
25
10
5
km
0
0,45
0,9
1,8
Broj mjerenja
Ni (mg/kg)
Minimum: 15,70 (mg/kg)
Minimum
Maksimum: 133,30 (mg/kg)
Maximum
Srednja vrijednost: 34,935 (mg/kg)
Mean
Medijan: 30,650 (mg/kg)
Median
Standardna devijacija: 19,052
Standard Deviation

P

10.28. P – FOSFOR (atomski broj 15) PHOSPHORUS (atomic number 15)

Fosfor je litofilni element u tragovima, sa sklonošću nakupljanju u akcesornim mineralima. Prema učestalosti u Zemljinoj kori nalazi se na 11. mjestu.

U ultrabazičnim stijenama njegova srednja vrijednost je 220 mg/kg, u bazitima 1 100 mg/kg, u granodioritima 920 mg/kg, a u granitima 600 mg/kg. Šejlovi sadržavaju oko 700 mg/kg, pješčenjaci 170 mg/kg, a karbonati 200 mg/kg. Srednji sadržaj u tlima iznosi oko 650 mg/kg. Uz dovoljne količine dvovalentnog željeza i fosfora u tlima u reduktivnim uvjetima nastaje mineral vivianit $Fe_3^{2+}ŠPO_4Ć_2{\cdot}8H_2O$. U slatkoj vodi fosfora ima oko 0,02 mg/kg.

Mobilnost fosfora je mala do umjerena i određena je topivošću fosfata. Apatit se lako troši, dok su drugi fosfati, posebice REE-fosfati rezistentniji i nakupljaju se u sekundarnim ležištima teških minerala. Otopljeni fosfor vezan je uz aktivnu organsku tvar ili se precipitira pomoću Ca i Fe tvoreći sekundarne fosfate. Fosfor je najbolje topiv kod vrijednosti pH oko 7.

Fosfor je esencijalan element za sve organizme, ali otrovan u većim količinama. Mnogi tehnički proizvedeni P-spojevi su visoko otrovni. Ugrađuje se u skelete. Zajedno s dušikom i kalijem on je jedan od najvažnijih prihrambenih komponenata za biljnu prehranu. Zbog ugradnje u biljke, tlo osiromašuje fosforom pa je u širokoj primjeni u poljodjeljstvu kao umjetno gnojivo. Fosfor može biti obogaćen nepoželjnim toksičnim elementima kao što su kadmij i uran.

Fosfati se upotrebljavaju u proizvodnji umjetnih gnojiva (90 %), fosforne kiseline, fosforne soli, sredstava za pranje rublja, a crveni fosfor se rabi za izradu žigica.

U okoliš se najčešće unosi u obliku umjetnih gnojiva i sredstava za pranje rublja.

Phosphorus is a lithophile trace element prone to accumulating in the accessory minerals. According to abundance it is 11th in the Earth's crust.

In ultramafic rocks its average content is 220 mg/kg, in mafic rocks 1,100 mg/kg, in granodiorites 920 mg/kg, and in granites 600 mg/kg. Shales contain about 700 mg/kg, sandstones 170 mg/kg, and carbonates 200 mg/kg. The average content in soils is about 650 mg/kg. With sufficient quantities of the bivalent iron and phosphorus in the reducing conditions in soils is formed the mineral vivianite $Fe_3^{2+}ŠPO_4Ć_2{\cdot}8H_2O$. In the sweet water phosphorus is present with about 0.02 mg/kg.

Mobility of phosphorus is low to moderate which is defined by solubility of phosphates. Apatite is easily weathered while other phosphates, REE-phosphates in particular, are more resistant and accumulate in secondary deposits of heavy minerals. Dissolved phosphorus is bonded on active organic matter or is precipitated by means of Ca and Fe forming secondary phosphates. Phosphorus is best soluble if pH value is around 7.

Phosphorus is essential element for all organisms but poisonous in greater quantities. Many technically produced P-compounds are highly toxic. Phosphorus is incorporated into the skeletons. Together with nitrogen and potassium it is one of the most important food components in the plant diet. Due to its being incorporated into the plants the soil becomes deficient in phosphorus which is why the phosphors-based chemical fertilizers are in wide application in agriculture. Phosphorus can be enriched in unwanted toxic elements such as cadmium and uranium.

Phosphates are utilized in the production of chemical fertilizers (90 %), phosphorus acid, phosphorus salt, and laundry washing agents while the red phosphorus is used in production of matches.

This element is most often dispersed into the environment in the form of chemical fertilizers and laundry washing agents.

Fosfor je uz magnezij jedini analizirani element čije su koncentracije u tlu u industrijskoj zoni ispod ili znatno ispod vrijednosti medijana. Iznimku čine dva uzorka koji se nalaze u naseljima Caprag i Kanak, u neposred-

Phosphorus, together with magnesium, is the only analyzed element whose concentrations in the soils of the industrial zone are below or considerably below the median value. Exception is two samples from the Ca-

noj blizini industrijskih postrojenja. Anomalne koncentracije na tim lokacijama nisu posljedica industrijske aktivnosti nego imaju drugo antropogeno podrijetlo.

Raspon mjerenih koncentracija ovog elementa na istraživanom području kreće se od 0,026 do 0,300 % s medijanom od 0,071 %. Maksimalna vrijednost registrirana je u uzorku tla u Pogorelcu. Zanimljivo je da su na području antičkih naselja Segestica i Siscija registrirane i druge visoke, anomalne i ekstremne vrijednosti fosfora u tlu, tako da se na temelju prostorne raspodjele tog elementa u tlu na tom području mogu rekonstruirati obrisi spomenutih naselja. U nekim aktivnim rimskim iskopinama na tom području, registrirana je pojava željezno-fosfatnog minerala vivijanita, a pretpostavlja se i prisutnost minerala struvita koji je također karakterističan za tla u blizini nekadašnjih kanalizacijskih odvoda.

Tla na području naselja Mošćenice, Starog Pračna i Žabna imaju također ekstremne i anomalne sadržaje ovog elementa u tlu. Te visoke vrijednosti su najvjerojatnije, osim geogenog podrijetla, gdje je fosfor vezan na organsku tvar kojom su tla na tim terenima bogata, posljedica antropogenog unosa kroz mineralna gnojiva.

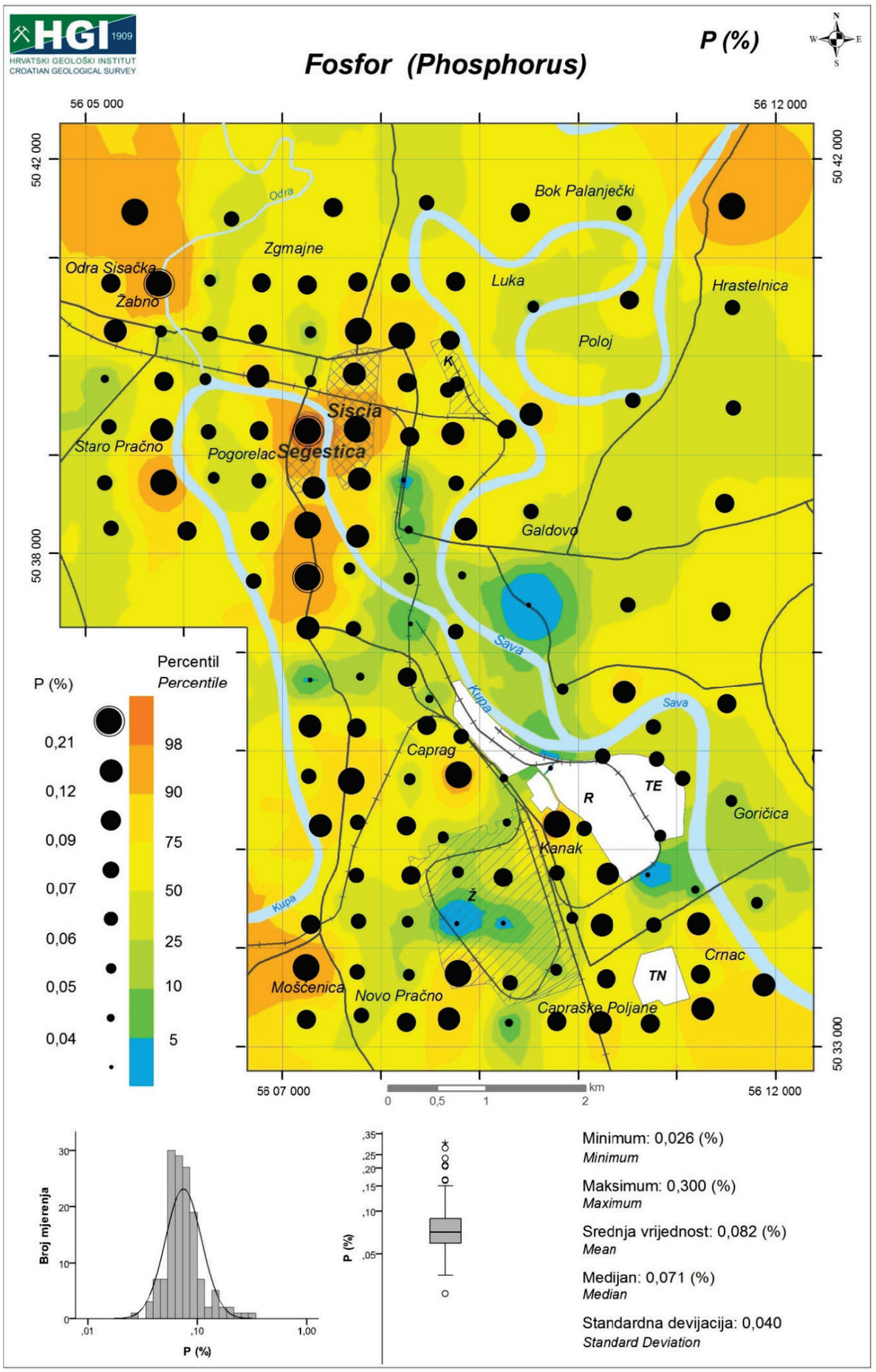
Anomalna koncentracija fosfora u tlu, sjeverno od Hrastelnice, na istoku i sjeverno od Odre Sisačke, na zapadu, te povišene vrijednosti, na većini intenzivno obradivih površina u ruralnom dijelu istraživanog terena, vjerojatno su posljedica primjene fosfatnih mineralnih gnojiva u poljoprivrednoj proizvodnji. Uz već navedeno područje industrijske zone na jugu (željezara i rafinerija), naselje Galdovo te urbano područje od Viktorovca do obrtničke zone imaju sadržaje fosfora u tlu ispod ili znatno ispod vrijednosti medijana.

prag and Kanak settlements in the close vicinity of the industrial processing plants. Anomalous concentrations on these locations are not result of the industrial activity but derive from different anthropogenic source.

The range of measured concentrations of this element in the investigated area is between 0.026 and 0.300 % with median of 0.071 %. Maximum value is registered in the soil sample from Pogorelec. Interestingly, in the areas of ancient settlements of Segestica and Siscia some other high, anomalous and extreme values of phosphorus in the soil have been registered so that based on the spatial distribution of this element in the soil one can reconstruct the outlines of these settlements. Occurrence of the iron-phosphate mineral vivianite is registered in certain active Roman excavations in this area and it is also supposed the presence of the mineral struvite which is characteristic for soils in the vicinity of the previous sewage outfalls.

The soils in the zones of Mošćenica, Staro Pračno and Žabno settlements also show extreme and anomalous contents of this element in the soil. The high values are most probably not only geogenic in origin as a result of phosphorus bonded on the organic matter enriching the soils on those terrains but also reflect the anthropogenic input by the chemical fertilizers.

Anomalous concentrations of phosphorus in the soil to the north both of Hrastelnica situated on the east portion of the investigated terrain and Odra Sisačka occupying its west part, including the elevated values on the most of the intensely cultivated lands in the rural area, are probably the result of application of the phosphate mineral fertilizers in agriculture. In addition to already mentioned industrial zone on the south (steelworks and oil refinery), the Galdovo settlement and the urban area from Viktorovac to the crafts zone also contain the concentrations of phosphorus in the soil below or considerably below the median value.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Fosfor (Phosphorus)
P (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Bok Palanječki
Zgmajne
Odra Sisačka
Žabno
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
P (%)
0,21
0,12
0,09
0,07
0,06
0,05
0,04
98
90
75
50
25
10
5
km
0
0,5
1
2
Broj mjerenja
P (%)
Minimum: 0,026 (%)
Minimum
Maksimum: 0,300 (%)
Maximum
Srednja vrijednost: 0,082 (%)
Mean
Medijan: 0,071 (%)
Median
Standardna devijacija: 0,040
Standard Deviation

Pb

10.29. Pb – OLOVO (atomski broj 82) LEAD (atomic number 82)

Olovo je oksifilan element u tragovima i po pojavljivanju u Zemljinoj kori je na 36. mjestu. Obogaćuje se porastom alkaliniteta magme. U stijenskim alumosilikatima pojavljuje uz glavni element kalij, a prikriven je kalcijem. U kristalima minerala stijena često zamijenjuje K^+, ali i Sr^{2+}, Ba^{2+} pa čak Ca^{2+} i Na^+.

Srednji sadržaj u magmatskim stijenama iznosi 12,5 mg/kg (ultrabaziti 0,05 mg/kg, bazalti 4 mg/kg, granodioriti 15 mg/kg i graniti 19 mg/kg). U sedimentnim stijenama srednji sadržaj u šejlovima iznosi 20 mg/kg, u pješčenjacima 7 mg/kg, a u karbonatima 9 mg/kg. Koncentracija u tlima kreće se od 2,6 do 83 mg/kg sa srednjom vrijednošću oko 14 mg/kg. Olovopokazuje sklonost prema organskoj materiji pa se nakuplja u ugljenu i crnim šejlovima. Tla bogata organskom materijom sadržavaju oko tri puta veću koncentraciju olova od prosječne srednje vrijednosti. Koncentracije > 100 mg/kg smatraju se anomalnima i upućuju na moguće onečišćenje. Koncentracije olova u riječnim vodama variraju od 0,007 do 3,8 μg/L, a kod podzemnih voda od 0,1 do 8 μg/L.

Mobilnost olova je mala. Sulfidne rude oksidiraju u teže topiv sulfat, karbonat, arsenat, vanadat, molibdat i kromat. Mobilnost je ograničena s tendencijom k adsorpciji na Fe i Mn oksi-hidrokside, minerale glina i netopivu organsku tvar, a olakšana stvaranjem topivih organskih kompleksa i anionskih kompleksa. Olovo nije ravnomjerno raspoređeno u horizontima tala i ono pokazuje obogaćenje u onim horizontima koji su bogatiji Fe i Mn hidroksidima i nalaze se bliže površini (engl. *topsoil*).

Olovo je najpoznatiji onečišćivač okoliša. Nije esencijalan element, ali je štetan. Vrlo je otrovan za biljke i životinje. Olovo je kancerogeno, otrovno već u malim koncentracijama i akumulira se u organizmu. U organizam ga se može unijeti hranom, vodom ili udisanjem prašine. Do otrovanja olovom dolazi ako je njegov sadržaja u krvi visok. Ono može uzrokovati neurološka oštećenja, posebno kod male djece. Izloženost organizma olovu može uzrokovati bolesti bubrega i jetre, povišen krvni tlak, anemiju, rak i reproduktivne probleme.

Svjetska godišnja proizvodnja olova u 2003. godini iznosila je oko 2 900 000 t, a po nekim izvorima i preko 6 820 000 t. Najveća proizvodnja metala olova je iz rudnog minerala galenita.

Unatoč njegovoj otrovnosti olovo ima široku tehničku primjenu. Upotrebljava se kod izrade baterija, kao dodatak bojama, staklu, kremici, legurama, u industriji guma, za izradu projektila, koristi se kao štit protiv radijacije, za izradu elektroda, a prije je služilo i kao aditiv u nafti i benzinu. Veliki je postotak reciklaže iz starog olova.

Olovo se raspršuje u okoliš iz benzina, spaljivanjem fosilnih goriva i otpada, rudarenjem i radom talionica. Osim toga, raspršenje u okoliš događa se i preko baterija, muljeva iz pročistača (kolektora) te uporabom pigmenata, kemikalija, stabilizatora u plastici, akumulatora, sačme i olovnog stakla. Visoki unosi u zrak i indirektno u tlo, su u blizini termoelektrana na ugljen i mazut. Moguće je raspršenje i preko umjetnih gnojiva (fosfati).

Lead is an oxyphile trace element, 36th in abundance in the Earth's crust. It is enriched by increasing alkalinity of magma. In the rock aluminosilicates it occurs together with the major element potassium but is screened by calcium. In the crystals of rock minerals lead is often the substitute for K^+ but also Sr^{2+}, Ba^{2+} and even Ca^{2+} and Na^+.

The average content of lead in igneous rocks is 12.5 mg/kg (ultramafic rocks 0.05 mg/kg, basalts 4 mg/kg, granodiorites 15 mg/kg and granites 19 mg/kg). Among sedimentary rocks, the average content in shales is 20 mg/kg, sandstones 7 mg/kg, and carbonates 9 mg/kg. Concentration in soils varies from 2.6 to 83 mg/kg with mean value of about 14 mg/kg. Pb is affiliated to organic matter which is why it accumulates in coal and black shales. Soils rich in organic matter contain the concentrations of lead about thrice above the average value. Concentrations > 100 mg/kg are deemed anomalous and indicate the possible contamination. Concentrations of lead in stream waters vary from 0.007 to 3.8 μg/L and in underground water from 0.1 to 8 μg/L.

Mobility of lead is low. Sulfide ores oxidize into low soluble sulfate, carbonate, arsenate, vanadate, molybdate and chromate. On the one side mobility is limited with tendency to adsorption on Fe-Mn oxy-

hydroxides, clay minerals and insoluble organic matter while on the other it is alleviated by formation of the soluble organic and anionic complexes. Lead is not evenly distributed in the soil horizons showing enrichment in those more rich in Fe-Mn hydroxides and closer to surface (topsoil).

Lead is the most infamous environmental pollutant. It is not an essential element and it is very harmful. Lead is very toxic to plants and animals. It is carcinogenic and toxic already in small concentrations, accumulating within the organism. There it can enter by food, water, or by inhaling the dust. The poisoning by lead occurs if its content in blood is high. Lead can trigger neurologic damage, particularly with small children who can become retarded due to brain damage. Exposition of organism to lead can provoke diseases of kidneys and liver, increased blood pressure, anemia, cancer and problems with reproduction.

The world production of lead in the year 2003 was about 2,900,000 t. According to certain sources it even exceeded 6,820,000 t. The greatest production of this metal is from the ore mineral galena.

Notwithstanding its toxicity lead has a wide technical application. It is commonly used in the production of batteries, as a chemical addition to paints, glass, ceramics, alloys, in the tire industry, for the production of projectiles. It is also utilized as shield against radiation, for production of electrodes. Formerly, it was used as an additive in oil and gasoline. There is a great percentage of recycling from the old lead.

There is a strong dispersion of lead into environment from the gasoline (70s and 80s of the last century). It is also disseminated by combustion of fossil fuels and waste, by mining and work of foundries. Besides, dispersion of lead into environment is happening by disposing of batteries, waste mud form collectors, by the use of pigments, chemicals, stabilizers in plastics, accumulators, buckshot and leaded glass. High inputs into the air and thereby into the soil appear close to the thermal power plants powered by coal and crude oil. Dispersion by the chemical fertilizers is also possible (phosphates).

Prostorna raspodjela olova na istraživanom području slična je raspodjeli bakra, srebra, kositra i cinka. Jasno se ističu dva područja s ekstremnim i anomalnim koncentracijama olova u tlu. Jedno je vezano za industrijsku zonu na jugu, dok se drugo nalazi u sjevernom dijelu i poklapa se s lokacijom antičkih naselja Siscije i Segestice (Sl. 3.1.). Ta dva područja jasno su odvojena zonom Viktorovac-Galdovo-Hrastelnica koja ima niske sadržaje olova u tlu.

Raspon izmjerenih koncentracija ovog teškog metala u analiziranim tlima kreće se od 19,54 do 2 409,43 mg/kg s vrijednosti medijana od 37,15 mg/kg. Maksimalni sadržaj olova izmjeren je u uzorku na sjevernom rubu Termoelektrane. Susjedni uzorci, također, imaju anomalne i ekstremne sadržaje olova. Kao i kod mnogih drugih potencijalno toksičnih elemenata i ovdje je jasno vidljiva disprezija olova u zrak te njegovog naknadnog transporta u smjeru vjetra (prema sjeveru i sjeveroistoku). Međutim, kod ovog elementa je lepeza distribucije puno šira, pa zaključujemo da izvor onečišćenja nije samo termoelektrana, nego da i rafinerija doprinosi jednim dijelom povećanju sadržaja olova u tlima na lijevoj obali Save, između Polojaca i naselja Galdovo.

U krugu Željezare Sisak skoro svi uzorci tla imaju anomalne i ekstremne koncentracije ovog elementa.

U blizini industrijskih postrojenja na jugu (željezara, rafinerija, termoelektrana i naftni terminali) u naseljima Kanak, Crnac i Caprag, također su registrirane ekstremne i anomalne vrijednosti olova u tlu. Sve te vrijednosti posljedica su industrijskog onečišćenja. Ekstremna

Spatial distribution of lead in the investigated area is similar to distribution of copper, silver, tin and zinc. Two zones with extreme and anomalous concentrations of lead in the soil are clearly indicated. One is associated with industrial zone on the south (steelworks, oil refinery and thermal power plant) while the other is situated in the northern part and overlaps with extent of ancient settlement of Siscia and Segestica (Fig. 3.1.). These two zones are clearly divided by the belt of Viktorovac-Galdovo-Hrastelnica which is characterized by low contents of lead in the soil.

The range of measured concentrations of this heavy metal in the analyzed soils is between 19.54 and 2,409.43 mg/kg with median value of 37.15 mg/kg. Maximum content of Pb is measured in the sample at the northern edge of the thermal power plant. The neighboring samples also contain anomalous and extreme contents of lead. As in the case of many other potentially toxic elements, dispersion of lead into the air together with the subsequent transport in the direction of wind (toward north and northeast) is also clearly evident. However, with this element distribution on the form of fan is much wider leading to conclusion that the source of contamination is not only the thermal power plant but also the oil refinery contributes partly to increased content of lead in the soils on the left bank of the Sava River between Polojci and Galdovo settlement.

Within the steelworks circle almost all soil samples show anomalous and extreme concentrations of this element.

koncentracija olova u uzorku u blizini željezničkog mosta preko Kupe (pješačka staza iz Capraga prema centru grada na sjevernom rubu postrojenja rafinerije) također je posljedica prerade ugljikovodika u rafineriji.

Uzorak s ekstremnom vrijednošću olova (178,51 mg/kg) nalazi se neposredno uz Caprašku ulicu, koja spaja naselje Caprag s Petrinjskom ulicom na zapadu. To je vrlo frekventna ulica, a tako visoka koncentracija olova u tlu potječe od olovnih aditiva iz ispušnih plinova automobila. Iako benzin s olovnim aditivima već petnaestak godina nije u upotrebi, ovdje se radi o olovu koje je vjerojatno ostalo fiksirano na Fe i Mn oksi-hidrokside te minerale glina u tlu. Naime, vezivanjem na te spojeve i minerale mobilnost olova je ograničena. No, tako vezano olovo može naknadno biti mobilizirano stvaranjem topivih organskih kompleksa. Slična situacija zabilježena je i u uzorku koji se nalazi neposredno uz Zagrebačku ulicu. Ta prometnica je glavni ulaz u grad sa sjevera (a bila je to i u vrijeme Rimljana) i izuzetno je prometno frekventna, tako da najveći dio olova u tlu u tom uzorku potječe iz ispušnih plinova automobila.

Drugo spomenuto područje s ekstremnim i anomalnim koncentracijama olova nalazi se u urbanoj cjelini koja pokriva terene antičkih naselja Siscije i Segestice. Dobro je poznato da je olovo u antičko doba bilo široko upotrebljavan metal, tako da visoke vrijednosti olova u tlu potječu iz tog doba, a samo mali dio je recentnog podrijetla.

Povećana koncentracija olova u uzorcima u naselju Mošćenica posljedica je fiksiranja tog elementa na organsku tvar. Uzorkovana tla su šumska tla bogata organskom materijom. To olovo je također antropogenog podrijetla, a u okoliš je dispergirano putem vjetra iz industrijskih postrojenja na istoku.

Ostali, pretežito ruralni dijelovi istraživanog područja imaju koncentracije olova ispod ili znatno ispod medijana (posebno se ističe područje gdje je matični supstrat tla izgrađen od aluvijalnih sedimenata rijeke Save).

Na temelju prostorne raspodjele olova u tlu jasno je vidljivo da su njegove visoke koncentracije isključivo antropogenog podrijetla. Od urbanih i industrijskih cjelina prema ruralnim područjima, sadržaj olova u tlu naglo opada ispod ili znantno ispod medijana.

Na temelju *Pravilnika o zaštiti poljoprivrednog zemljišta od onečišćenja* (Narodne novine 9, 2014) i *Programa trajnog motrenja tala Republike Hrvatske* (MESIĆ et al., 2008) na istraživanom području urbane cjeline grada Siska imamo nekoliko žarišnih točaka s koncentracija-

Close to the industrial processing plants on the south (steelworks, oil refinery, thermal power plant and oil terminal) in the Kanak, Crnac and Caprag settlements extreme and anomalous values of lead in the soils are also registered. All these values are the result of industrial pollution. Extreme concentration of lead in the sample close to the railroad bridge across the Kupa River (pedestrian lane from Caprag toward the city center on the northern rim of the refinery processing plants) is also the result of hydrocarbon processing in the refinery.

The sample with extreme value of lead (178.51 mg/kg) is situated immediately near the Capraška Street connecting the Caprag settlement with Petrinjska Street to the west. That is a very busy street and the high concentration of lead in the soil originates from the lead additives present in the gaseous emissions from the cars. Albeit the leaded gasoline is not in use for already fifteen years this lead probably remained fixed on Fe-Mn oxy-hydroxides and clay minerals in the soil. Namely, by bonding on these compounds and minerals the mobility of lead becomes constrained. However, thus bonded, lead can afterwards become mobile again by formation of soluble organic complexes. The similar situation is registered also in the sample from the immediate vicinity of the Zagrebačka Cesta road. This traffic line is the main entrance into the city (as it was in the times of Romans) and is extremely crowded so that the most part of lead in the soil from this sample arise from gaseous emissions of the automobiles.

Another mentioned area with extreme and anomalous concentrations of this heavy metal is situated in the urban core which covers the terrains of ancient settlements of Siscia and Segestica. It is well known that lead in the ancient times was a metal widely applied (water conduits and many other things for wide application so that the high values of lead in the soils are related to this era and only a small part is of recent origin. This recent portion is also screened by high values form the ancient times.

Elevated concentration of lead in the samples from the Mošćenica settlement arise form fixing on the organic matter because the sampled soils are the forest soils rich in organic matter. This lead is also of anthropogenic origin which was delivered into environment from the industrial processing plants on the east by wind.

Other, predominantly rural parts of the investigated area show the concentrations of lead below or considerably below the median value (the area is particularly indicated where the soil parent material is built of alluvial sediments of the Sava River).

ma olova u tlu koje prelaze MDK. Tla na tim lokacijama mogu se smatrati onečišćenim.

Stambena područja u kojima je zabilježen povećan sadržaj olova u tlu (MDK za stambeni dio je 100 mg/kg) su u sjevernom dijelu grada uz Zagrebačku ulicu, u Pogorelcu, u sjevernom i zapadnom dijelu Capraga te naseljima Kanak i Crnac na jugu. U naseljima Kanak i Crnac zabilježene su povećane koncentracije olova i na nekim poljoprivrednim površinama (MDK za poljoprivredno zemljište iznosi 150 mg/kg).

Uzorak sjeveroistočno od Termoelektrane Sisak i Rafinerije nafte Sisak sa sadržajem olova od 2 409,43 mg/kg višestruko prelazi MDK za industrijsku namjenu (MDK za industriju je 1 000 mg/kg).

Based on the spatial distribution of lead in the soil it is obvious that its high concentrations are exclusively anthropogenic in origin because going from urban and industrial cores toward the rural areas the lead content in soil decreases abruptly below or considerably below the median value.

According to Regulations on protection of agricultural land from pollution (NN9, 2014) and "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" (MESIĆ et al., 2008) there are several focal points in the investigated area of the urban core of the city of Sisak with concentrations of lead in the soil that exceed MPC. Soils on these locations can be deemed contaminated.

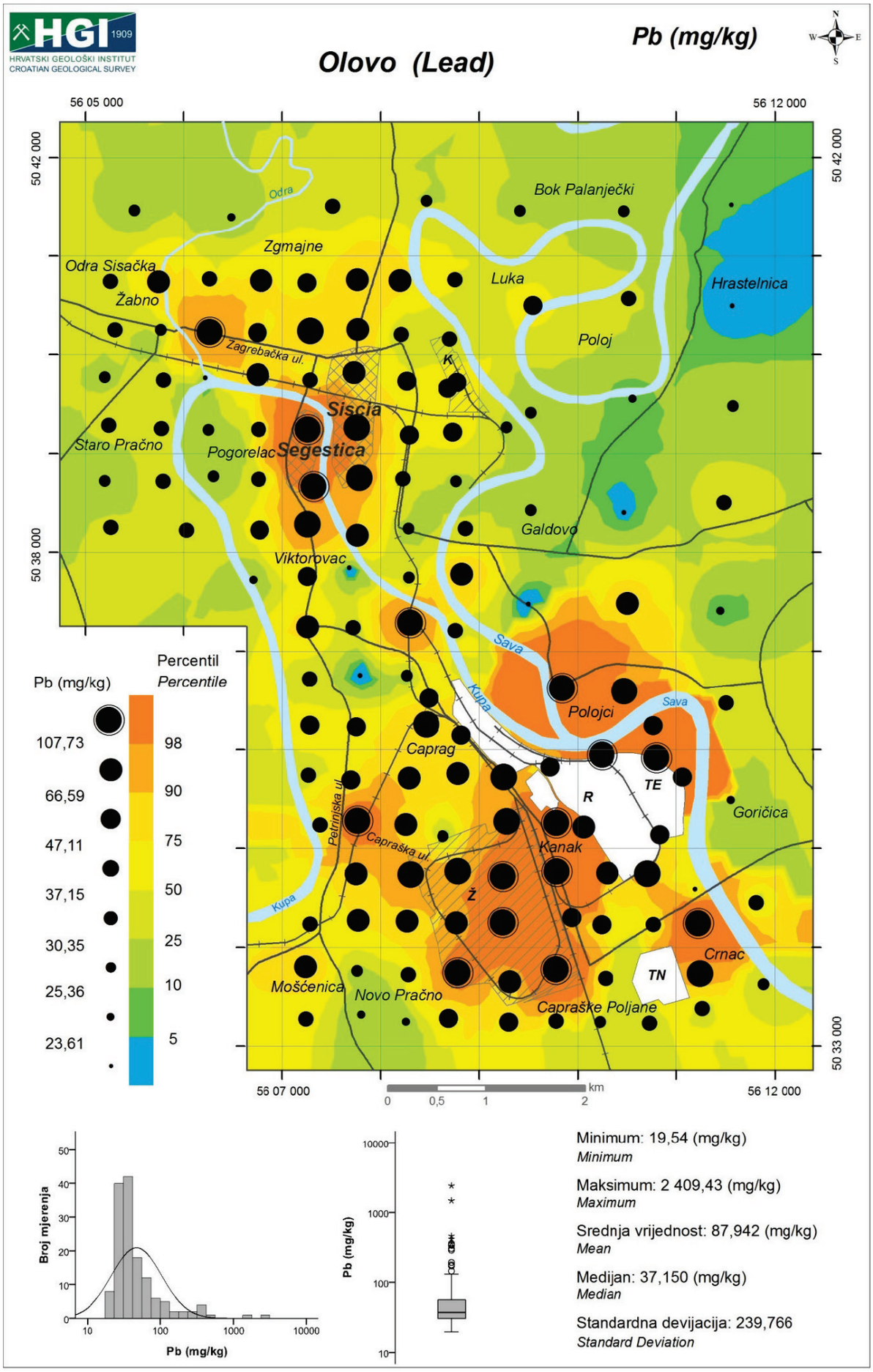
Residential areas where the elevated content of lead in the soil has been registered (MPC for the residential part is 100 mg/kg) are: in the northern part of the city alongside the Zagrebačka Cesta street and in Pogorelec; then in the northern and western part of the Caprag settlement as well as in the settlements of Kanak and Crnac on the south. In the Kanak and Crnac settlements increased concentrations of lead on some agricultural lands are also registered (MPC for agricultural land is 150 mg/kg).

The sample to the northeast of the thermal power plant and oil refinery having the content of lead of 2,409.43 mg/kg exceeds for many times MPC for industrial purposes (MPC for industry is 1,000 mg/kg).



Slika 10.18. *Olovna cijev iz rimske Siscie (Foto: J. Halamić)*

Figure 10.18. *Lead tube from Roman Siscia (Photo: J. Halamić)*


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Olovo (Lead)
Pb (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
Zagrebačka ul.
K
Siscia
Segestica
Staro Pračno
Pogorelac
Galdovo
Viktorovac
Sava
Kupa
Polojci
Caprag
Petrinjska ul.
Capraška ul.
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Pb (mg/kg)
Percentil
Percentile
107,73
66,59
47,11
37,15
30,35
25,36
23,61
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Pb (mg/kg)
Minimum: 19,54 (mg/kg)
Minimum
Maksimum: 2 409,43 (mg/kg)
Maximum
Srednja vrijednost: 87,942 (mg/kg)
Mean
Medijan: 37,150 (mg/kg)
Median
Standardna devijacija: 239,766
Standard Deviation

Rb

10.30. Rb – RUBIDIJ (atomski broj 37) RUBIDIUM (atomic number 37)

Rubidij je litofilni element u tragovima i rijedak alkalijski element. Često je prikriven kalijem, slično kao i Cs i Tl. Rubidij zauzima 22. mjesto po učestalosti pojavljivanja u Zemljinoj kori. Geokemijski se ponaša vrlo slično litiju.

Prosječna vrijednost u magmatskim stijenama iznosi 90 mg/kg (ultrabaziti 0,1 mg/kg, oceanski toleitni bazalti 1 mg/kg, bazalti 32 mg/kg, granodioriti 110 mg/kg i graniti 100 mg/kg). Kod sedimenata šejlovi imaju prosječni sadržaj rubidija 140 mg/kg, pješčenjaci 40 mg/kg, a karbonati većinom < 1 mg/kg. Sadržaj ovog elementa u tlu varira od 20 do 500 mg/kg s prosječnom vrijednošću od 100 mg/kg. Tla koja imaju veće sadržaje tinjaca pokazuju i veće koncentracije rubidija u odnosu na tla koja su krupnozrnatija. Sadržaj rubidija u slatkoj vodi je 0.001 mg/L, a u morskoj vodi ga ima 0,125 mg/L. Otopljen je kao Rb^{1+}.

Tijekom trošenja i metamorfizma rubidij se lako oslobađa iz minerala domaćina te je on dosta mobilan u svim okolišima. Mobilan rubidij najčešće se veže na minerale glina. Adsorpcija na minerale glina pospješena je visokim pH vrijednostima. Visoko je reaktivan, moguće je spontano samozapaljenje na zraku.

Rubidij nije esencijalni element i nije otrovan, ali s druge strane on je usko vezan s kalijem, koji je esencijalni element za sve organizme. U odsutnosti kalija ovaj element je otrovan. U koncentracijama preko 1 000 mg/kg u hrani može imati zdravstvene posljedice. U malim koncentracijama može djelovati stimulirajuće. U biljkama je odnos K/Rb oko 1 000, pa u onim biljkama koje prioritetno uzimaju K dolazi do povišenih sadržaja rubidija.

Svjetska produkcija ovog elementa je u 1997. godini procijenjena na 5 t. Rubidij se proizvodi kao sporedni produkt kalijskih soli i pri obradi litijskih i cezijskih rudača.

Upotrebljava se za kemikalije, za izradu fotoelektričnih ćelija, poluvodiča, za izradu specijalnih stakala, u elektronici te se koristi u svrhu znanstvenih istraživanja.

Disperzija rubidija u okoliš se ne raspoznaje.

Rubidium is a lithophile trace element and a rare alkali element. It is commonly screened by potassium much in the way as are Cs and Tl. Rubidium is 22nd in abundance in the Earth's crust. Geochemically, its behavior is similar to lithium.

The average content of rubidium in igneous rocks is 90 mg/kg (ultramafic rocks 0.1 mg/kg, oceanic tholeiite basalts 1 mg/kg, basalts 32 mg/kg, granodiorites 110 mg/kg and granites 100 mg/kg). Among sedimentary rocks shales contain in average 140 mg/kg Rb, sandstones 40 mg/kg and carbonates mostly < 1 mg/kg. The content of this element in soil varies from 20 to 500 mg/kg averaging 100 mg/kg. Soils that have greater contents of micas show higher concentrations of rubidium with regard to the coarse-grained soils. The content of rubidium in the sweet water is 0.125 mg/L. It is dissolved as Rb^{1+}.

During weathering and metamorphism Rb is easily released from the host minerals. Afterwards, it is relatively mobile in all environments. Mobile Rb is most often bonded on clay minerals. Adsorption to the clay minerals is enhanced by high pH values. Rubidium is highly reactive and if found in the air it experiences the spontaneous self-ignition.

Rb is not an essential element and is not toxic. However, on the other side, it is closely associated with potassium which is essential element for all organisms. In the absence of potassium this element is toxic. In concentrations exceeding 1,000 mg/kg in the food it can provoke the troubles with health. In small quantities it can be stimulating. In plants, the K / Rb ratio is around 1,000 which is why in those plants that take potassium as a priority the content of Rb is increased.

The world production of this element in the year 1997 was estimated to 5 t. Rubidium is produced as a byproduct of the potassium salts during processing of the lithium and cesium ores.

It is used for production of chemicals, photoelectric cells, semiconductors, special glass, in electronics and for the purpose of scientific investigations.

Dispersion of rubidium into environment is unknown.

Koncentracije rubidija na čitavom istraživanom području su relativno niske u odnosu na prosječne vrijednosti tog elementa u Zemljinoj kori (150 mg/kg) te u odnosu njegove prosječne sadržaje u tlu (100 mg/kg).

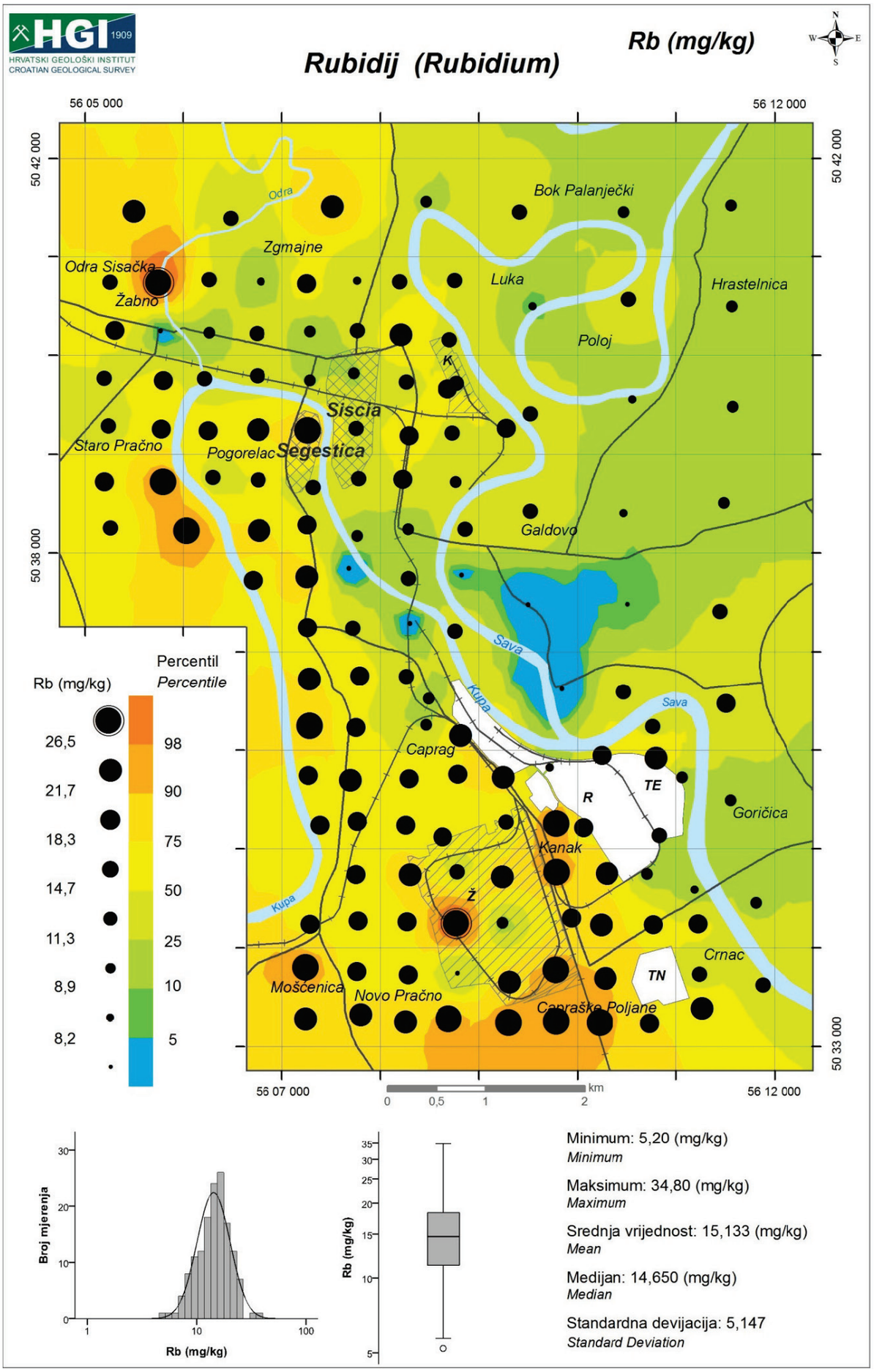
Raspon izmjerenih sadržaja u tlu kreće se od 5,2 do 34,8 mg/kg s medijanom od 14,7 mg/kg. Maksimalna koncentracija registrirana je u krugu Željezare Sisak. U urbanoj cjelini Siska jasno se odvaja područje s tlima koja su razvijena na aluvijalnim sedimentima rijeke Save od urbanog područja užeg dijela grada, industrijske zone te područja s tlima deriviranim iz poplavnih sedimenata rijeka Kupe i Odre. Očito je da je rubidij u tlima najvećim dijelom naslijeđen iz matičnog supstrata, dok je samo manjim dijelom antropogenog podrijetla (industrijska zona na jugu).

Općenito je područje industrijske zone obogaćeno ovim elementom u tlu, a što je posljedica proizvodnih procesa u postrojenjima željezare. Područja koja su pod utjecajem rafinerije, termoelektrane i kemijske industrije imaju koncentracije oko ili ispod vrijednosti medijana. Aluvijalni poplavni sedimenti Kupe i Odre imaju relativno visoke sadržaje tinjaca (biotit, muskovit) i minerala glina na koje je vezan rubidij tako da su povećane koncentracije rubidija u tlima tih područja geogenog podrijetla, a potječu iz tih minerala. Suprotno tomu, tla na poplavnim sedimentima Save (pretežito istočni dio istraživanog područja) imaju koncentracije ovog elementa u tlu ispod ili znatno ispod medijana, što je posljedica petrografskog sastava matičnog supstrata (pretežito karbonatni sedimenti s manjim sadržajem tinjaca).

Concentrations of rubidium on the entire investigated area are relatively low with regard to both the average content of this element in the Earth's crust (150 mg/kg) and in soil (100 mg/kg).

The range of contents measured in the sol is between 5.2 to 34.8 mg/kg with median of 14.7 mg/kg. Maximum concentration is registered within the circle of steelworks. In the urban core of the city of Sisak there is a clear distinction between the area with soils developed on alluvial sediments of the Sava River on the one side, and the strictly urban zone, industrial zone and areas with soils derived from the floodplain sediments of the Kupa and Odra Rivers on the other. Obviously, rubidium in the soil is for the most part inherited from the parent material and only its minor part is of anthropogenic origin (industrial zone on the south).

Generally, soils in the industrial zone are enriched in this element which is the result of the production processes in the steelworks. Areas impacted by the oil refinery, thermal power plant and chemical industry show concentrations around or below the median. Alluvial floodplain sediments of the Kupa and Odra Rivers contain relatively high quantities of micas (biotite, muscovite) and clay minerals on which rubidium is bonded so that increased concentration of rubidium in the soils of these areas are of geogenic origin, deriving from the mentioned minerals. On the contrary, the soils on the floodplain sediments of the Sava River (predominantly eastern part of the investigated area) are characterized by concentrations of this element in the soil below or considerably below the median which results from the petrographic composition of the parent material (predominantly carbonate sediments with minor quantities of micas).


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Rubidij (Rubidium)
Rb (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Rb (mg/kg)
Percentil
Percentile
26,5
21,7
18,3
14,7
11,3
8,9
8,2
98
90
75
50
25
10
5
Broj mjerenja
Rb (mg/kg)
Minimum: 5,20 (mg/kg)
Minimum
Maksimum: 34,80 (mg/kg)
Maximum
Srednja vrijednost: 15,133 (mg/kg)
Mean
Medijan: 14,650 (mg/kg)
Median
Standardna devijacija: 5,147
Standard Deviation

S

10.31. S – SUMPOR (atomski broj 16) SULPHUR (atomic number 16)

Sumpor je sporedni element u geosferi, ali je zato glavni element u biosferi. On je specifičan element po načinima pojavljivanja u raznim mineralima i supstancama te svom kruženju u prirodi. Sumpor se nalazi u evaporitima i vulkanskim naslagama, asociran je s prirodnim plinom, naftom i sulfidima metala. Ima ga puno u gipsu i anhidritu, u ugljenu, naftnim šejlovima i ostalim šejlovima bogatim organskom tvari. Zato je teško mjerljiv te procjene njegovog sadržaja, posebno u stijenama, jako variraju. Prema jednoj procjeni njegov ukupan sadržaj u Zemljinoj kori iznosi 260 mg/kg (0,026 %) te je po zastupljenosti 16. element u Zemljinoj kori. Druge procjene su da ga ima 480 mg/kg (0,048 %) u litosferi što ga čini 15. elementom po zastupljenosti. Međutim iz više izvora je procijenjeno da je čak 13. element u litosferi s udjelom od 600 mg/kg (0,06 %). Veće koncentracije sumpora registrirane su u ultrabazičnim i bazičnim stijenama u odnosu na kisele varijetete. Veće sadržaje ovog elementa nalazimo u šejlovima. Ako je prisutna organska tvar onda koncentracije sumpora mogu doseći i nekoliko postotaka. Ne temelju bušotina oceanskog dna utvrđen je prosječni sadržaj sumpora i u ocenaskoj kori. On iznosi: u gabrima 1 590 mg/kg (0,159 %), gabronoritima 760 mg/kg (0,076 %), harzburgitima 200 mg/kg (0,02 %) i dunitima 400 mg/kg (0,04 %). U morskoj vodi ga ima oko 2,65 mg/mL (0,265 %). Najvažniji minerali sumpora, koji sadrže većinu tog elementa u Zemljinoj kori su pirit (FeS_2) i pirhotit (Fe_7S_8). Sumpor ne ulazi lako u kristalne rešetke silikatnih minerala, tako da je u njima podređeno zastupljen (nekoliko stotinki postotka). Sulfidi imaju tendenciju separacije od oksida i formiranja vlastitih rudnih ležišta.

Mobilnost sumpora je vrlo visoka u svim uvjetima. Međutim, ona znatno varira u odnosu na vrstu spojeva sumpora (sulfati u odnosu na sulfide). Redukcija (tvorba sulfida s različitim metalima), precipitacija sulfata s nekim ionima kao npr. Ba i vezanje ovog elementa na organsku tvar ograničavaju mobilnost ovog elementa.

Sumpor je esencijalni element za sve organizme. Čisti sumpor nije otrovan, ali su zato mnogi njegovi spojevi otrovni (npr. SO_2 i H_2S). Nedostatak sumpora u organizmima je rijetkost, ali je čest u tlima (biljke ga uzimaju i tako osiromašuju tlo). Biljke podnose visoke sadržaje ovog elementa u tlu (SO_4 vezan u gipsu), ali su jako osjetljive na SO_2 u zraku.

Upotreba sumpora je velika. Koristi se za proizvodnju sumporne kiseline, prihranu biljaka, prilikom prerade nafte i plina, prerade celuloze i papira, sintetičkih guma, fungicida, kao dodatak prihrani životinja, dodatak tlu za smanjenje njegove alkalnosti i slično. Sumporna kiselina se upotrebljva za izluživanje bakra iz rudače, proizvodnju fosfatnih gnojiva i drugih kemijskih proizvoda za poljoprivredu, pri preradi nafte i plina i dr.

Sumpor u atmosferu može dospjeti prirodnim putem kao što su vulkanske erupcije ili antropogenim unosom. Glavnina antropogenog unosa je putem SO_2 koji nastaje kao rezultat izgaranja fosilnih goriva (ugljena, nafte i plina), otpada iz rudnika i drugih industrijskih procesa. U tlo dospijeva velikim dijelom taloženjem i adsorbiranjem iz zraka.

Ukupna svjetska proizvodnja sumpora u 2011. godini iznosila je 69 000 000 t. Dobivanje sumpora rudarenjem skoro je prestalo, jer se on jednostavno dobiva kao nusproizvod prilikom prerade nafte i plina, a sumporna kiselina prilikom topljenja metala. Recikliranje sumpora je veliko.

Sulfur is a minor element in the geosphere but major in the biosphere. It is specific element by its occurrence since it can be found in various minerals and substances but it is also characteristic by its circling in nature. Sulfur is found in evaporites and volcanic deposits. It is associated with natural gas, oil, and metal sulfides. It is abundant in gypsum and anhydrite, coal, oil shales, and other shales rich in organic matter. This is why it is problematical for measuring so that its assessment, particularly in rocks, varies considerably. According to some evaluations its total content in the Earth's crust is 260 mg/kg (0.026 %) placing it as the 16th element according to abundance in the Earth's crust. Some other estimations yield 480 mg/kg (0.048 %) in the lithosphere which makes it the 15th element according to its abundance. However, from a number of sources it is even the 13th element in the lithosphere with the content up to 600 mg/kg (0.06 %). Major concentrations of sulfur are registered in ultramafic and mafic rocks with respect to the acid varieties.

Also, major contents of sulfur are found in shales. If organic matter is present the concentrations of sulfur can amount to several percents. Based on the borehole data from the ocean bottom it is determined the average content of sulfur in the oceanic crust. It is as follows: in gabbros 1,590 mg/kg (0.159 %), gabbronorites 760 mg/kg (0.076 %), harzburgites 200 mg/kg (0.02 %) and dunites 400 mg/kg (0.04 %). In the sea water it is present with about 2.65 mg/mL (0.265 %). The most important sulfur minerals containing the major part of this element in the Earth's crust are pyrite (FeS_2) and pyrrhotite (Fe_7S_8). Sulfur is not easily built into the crystal lattices of silicate minerals, which is why in them it is of secondary importance (several hundredths of percent). Sulfides tend to separate form oxides and form then ore deposits of their own.

Mobility of sulfur is very high in all conditions. However, it varies greatly with regard to the type of sulfur compounds (sulfates with respect to sulfides). The processes such as reduction (formation of sulfides with various metals), precipitation of sulfates with some ions such as Ba, and bonding of this element on the organic matter limit its mobility.

Sulfur is essential element for all organisms. Pure sulfur is not toxic but many of its compounds (e.g. SO_2 and H_2S) are. Deficiency of sulfur in organisms is not common but it is known in soils (plants intake sulfur and thus deplete the soil). Pants tolerate high concentrations of this element in the soil (SO_4 bonded in gypsum) but are very sensitive to SO_2 in the air.

Application of sulfur is large. It is used for production of sulfuric acid, as food addition for plants and animals, in the process of oil and gas refinement, production of cellulose and paper, production of synthetic rubbers, production of fungicides, as addition to soil in order to reduce its alkalinity etc. Sulfuric acid is utilized for leaching of copper from the ore, production of chemical fertilizers and other chemical products for the use in agriculture, in the refinement of oil and gas etc.

Sulfur can enter atmosphere naturally by volcanic eruptions but also by anthropogenic input. The majority of anthropogenic input is due to SO_2 which is produced as a result of combustion of fossil fuels (coal, oil and gas), mine waste and other industrial processes. It enters the soil mostly by precipitation and adsorption from the air.

The total world production of sulfur in the year 2011 was 69,000,000 t. Exploitation of sulfur by mining almost ceased because it is simply obtained as a byproduct of oil and gas refinement. Simultaneously, sulfuric acid is obtained during the melting of metals. Recycling of sulfur is also considerable.

Prostorna raspodjela sumpora na istraživanom području jasno pokazuje njegovo antropogeno podrijetlo, koje se posebice ističe u ili u blizini industrijskih postrojenja na jugu.

Izmjerene koncentracije ovog elementa u tlu kreću se od 0,01 do 0,54 % s medijanom od 0,05 %. Maksimalna vrijednost registrirana je u krugu Željezare Sisak. I ostala postrojenja industrijske zone (rafinerija i termoelektrana) imaju ekstremne i anomalne vrijednosti sumpora u tlu. Isto tako i naselja u neposrednoj blizini tih postrojenja (Caprag, Kanak i Crnac) imaju anomalne sadržaje sumpora. Te koncentracije su samo jednim dijelom industrijskog podrijetla, dok drugim dijelom potječu od spaljivanja fosilnih goriva u toplanama i kućanstvima.Povišeni sadržaji ovog elementa u tlima u sjevernom dijelu grada (sjeverno od Viktorovca) također su rezultat spaljivanja fosilnih goriva za grijanje stambenih objekata.

Po prostornoj raspodjeli ovog elementa vidljivo je da se on iz postrojenja rafinerije, a posebice iz termoelektrane raspršuje u okoliš putem vjetra u pravcu sjevera i sjeveroistoka. Anomalne vrijednosti sumpora u tlu, neposredno sjeverno od Termoelektrane Sisak i Rafi-

Spatial distribution of sulfur in the investigated area clearly indicates its anthropogenic origin. It is particularly emphasized within the circle of, or close to, the industrial processing plants on the south.

The measured concentrations of this element in the soil vary between 0.01 and 0.54 % with median of 0.05 %. Maximum value is registered within the circle of the steelworks. Other areas occupied by industrial processing plants also show extreme and anomalous values of sulfur in the soil. The same is with the settlements in their immediate vicinity (Caprag, Kanak and Crnac). These concentrations are only partly industrial in origin while the other part originates from the combustion of fossil fuels in the heating plants and households (heating of the residential objects). Increased contents of this element in the soils of the northern part of the city (to the north of Viktorovac) also derive their origin from the fossil fuels for the heating of residential objects.

According to the spatial distribution of this element it is also evident that it is dispersed from the oil refinery and, especially, from the thermal power plant into the environment by means of wind in the north and northeast direction. Anomalous values of sulfur immedia-

nerije nafte Sisak na lijevoj obali Save (područje Polojci-Galdovo) te visoke vrijednosti u tlu područja prema naselju Hrastelnica, potječu također iz Termoelektrane i Rafinerije (Sl. 10.19.).

Tla koja su razvijena na aluviju rijeka Kupe i Odre i ne nalaze se u pravcu vjetra imaju vrlo niske koncentracije sumpora. Za poljoprivredna tla na području između naselja Staro Pračno i Odra Sisačka može se reći da su osiromašena ovim elementom.

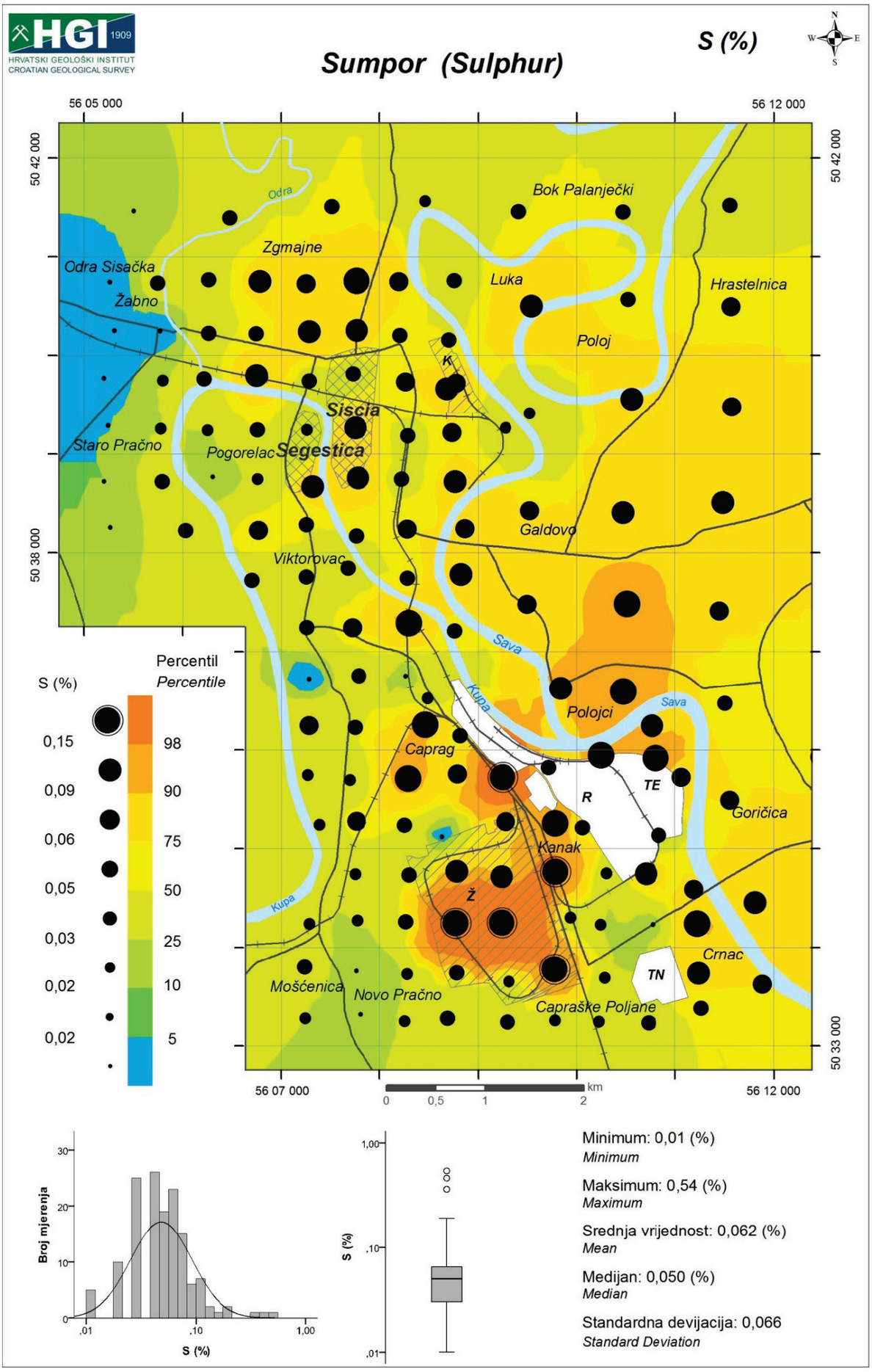
tely to the north of the thermal power plant and oil refinery, occupying the left bank of the Sava River (the area Polojci-Galdovo) as well as high values in the soil close to the Hrastelnica settlement originate also from the thermal power plant and the oil refinery where the fossil fuels are incinerated and the hydrocarbons are processed (Fig. 10.19.).

Soils developed on the alluvium of the Kupa and Odra Rivers but not in the direction of wind show very low concentrations of sulfur. For the agricultural soils in the zone between the settlements of Staro Pračno and Odra Sisačka it can be even said that they are depleted in this element.



Slika 10.19. *Poljoprivredne površine u sjeni dimnjaka Termoelektrane Sisak (Foto: J. Halamić).*

Figure 10.19. *Agriculture areas in the shadow of the chimneys of the thermo power-plant Sisak (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Sumpor (Sulphur)
S (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
Odra
Bok Palanječki
Zgmajne
Odra Sisačka
Žabno
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Viktorovac
Sava
Kupa
Polojci
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
S (%)
Percentil
Percentile
0,15
0,09
0,06
0,05
0,03
0,02
0,02
98
90
75
50
25
10
5
56 07 000
56 12 000
km
0
0,5
1
2
Broj mjerenja
S (%)
,01
,10
1,00
Minimum: 0,01 (%)
Minimum
Maksimum: 0,54 (%)
Maximum
Srednja vrijednost: 0,062 (%)
Mean
Medijan: 0,050 (%)
Median
Standardna devijacija: 0,066
Standard Deviation

Sb

10.32. Sb – ANTIMON (atomski broj 51) ANTIMONY (atomic number 51)

Antimon je oksihalkofilan element u tragovima, a po sadržaju u Zemljinoj kori nalazi se na 63. mjestu. On je produkt isplinjavanja iz Zemlje kao i As. Asociran je s As, Hg, Tl, W, Au, Ag, Pb i Zn.

U magmatskim stijenama prosječni sadržaj antimona iznosi 0,2 mg/kg (ultrabaziti 0,1 mg/kg, bazalti 0,1 mg/kg i graniti 0,2 mg/kg). Od sedimetnih stijena šejlovi imaju prosječni sadržaj Sb 1,5 mg/kg, pješčenjaci 0,05 mg/kg i karbonati 0,2 mg/kg. U tlu ga ima 2 mg/kg. Prosječni sadržaj antimona u slatkoj vodi je 0,002 mg/L, a nalazi se otopljen kao SbO_2^{1-} i $HSbO_2^0$.

Antimon je slabije mobilan od As. U kiseloj sredini i oksidirajućim uvjetima većina antimonskih minerala se brzo troši. Mobilni antimon je sklon precipitaciji u formi netopivih soli ili adsorpciji na Fe, Mn ili Al oksi-hidrokside kod pH 4 – 8. Adsorbira se, također, i na minerale glina, a obogaćuje se i u sitnozrnatijoj frakciji.

Antimon nije esencijalan element, ali je otrovan i ima karakteristiku akumuliranja u organizmu. Mnoge biljke akumuliraju antimon, trava i lišće voćaka. U manjim količinama antimon može pospješiti rast, no u većim koncentracijama on je toksičan. Kemijske i toksične osobine antimona slične su arsenu. U stara vremena antimonovispojevi koristili su se u medicinske svrhe. Zdravstveni efekti toksikacije antimonom su kancerogeni i mutageni problemi, dijarea, nefropatija, encefalopatija, bolovi mišića i zglobova, gastrointestinalni problemi, anemija i srčani problemi.

Svjetska proizvodnja antimona u 2003. godini procijenjena je na 155 000 t. Glavni rudni mineral je stibnit. Antimon se osim iz primarnih koncentrata dobiva iz recikliranog otpada i Pb-baterija koje imaju ugrađen ovaj element.

Antimon se industrijski koristi za izradu legura obojenih metala, izradu baterija, u proizvodnji keramike i stakla, plastičnih masa otpornih na temperaturu, kao aditiv kaučuku, dodatak pigmentima i bojama. Ovaj element povećava tvrdoću i krtost olovnih legura i koristi se u legurama za izradu Pb-kiselinskih baterija. Osim toga, koristi se i kod izrade kočionih feroda i diskova.

Radi široke industrijske primjene raspršenje u okoliš oko proizvodnih pogona je vjerojatno. Osim toga, on može, isto kao i arsen, biti prisutan i u nemetaličnim rudama i zato je vjerojatno onečišćivač tala u blizini talionica tih ruda. Znatno onečišćenje okoliša ovim elementom treba očekivati u blizini termoelektrana.

Antimony is an oxy-chalcophile trace element which is 63rd in abundance in the Earths crust. Much in the same way as As it is product of emanation from the Earth's crust. It is associated with As, Hg, Tl, W, Au, Ag, Pb and Zn.

In igneous rocks the average content of antimony is 0.2 mg/kg (ultramafic rocks 0.1 mg/kg, basalts 0.1 mg/kg and granites 0.2 mg/kg). Among sedimentary rocks shale contain in average 1.5 mg/kg of Sb, sandstones 0.05 mg/kg and carbonates 0.2 mg/kg. In soil antimony is present with 2 mg/kg while the average content in the fresh water is 0.002 mg/L dissolved as SbO_2^{1-} and $HSbO_2^0$.

Antimony shows lower mobility with respect to As. In acidic environment and under oxidizing conditions most of Sb minerals weather quickly. Mobile Sb is prone to precipitation in the form of insoluble salts or to adsorption on Fe, Mn or Al oxy-hydroxides at pH 4 - 8. It is also adsorbed on the clay minerals and is enriched in the fine-grained fraction.

Antimony is not an essential element but it is toxic and characterized by accumulating in organisms in time. Many plants accumulate Sb such as grass and fruit-tree leaves. In minor quantities Sb can enhance growth but in greater concentrations it is toxic. Chemical and toxic properties of antimony are similar to arsenic. On old times Sb-compounds were used in medicine. The health effects in the case of intoxication by antimony are as follows: carcinogenic and mutagenic troubles, diarrhea, nephropathy, and encephalopathy, muscle and ankle pains, gastrointestinal problems, anemia and heart troubles.

The world production of antimony in the year 2003 was estimated at 155,000 t. The chief ore mineral is stibnite. Save for the primary concentrates antimony is also obtained form the recycled waste and Pb-batteries with this element inbuilt.

Industrially, antimony is used for production of alloys of light metals, batteries, ceramics and glass, plastic resistant to temperature (antimony is present in plastic bottles for drinking water), as an addition to natural rubber, pigments and paints. This element increase hardness and brittleness of lead alloys and is used in alloys for production of Pb-acidic batteries. Besides, it is utilized in production of breaking linings and discs.

Owing to its wide industrial application its dispersion into environment around the processing plants is quite probable. In addition, it can be present, similar to arsenic, in non-metallic ores which is why it is probably the soil contaminant in the vicinity of foundries. Considerable contamination of environment by this element should be expected in the vicinity of the thermal power plants.

Prostorna raspodjela antimona vrlo je slična distribuciji sumpora, a dijelom i olova. Isto tako na temelju te raspodjele vidljivo je njegovo antropogeno podrijetlo u tlu, koje je najvećim dijelom vezano uz industriju.

Koncentracije ovog elementa u tlu na istraživanom području kreću se od 0,11 do 8,16 mg/kg s medijanom od 0,29 mg/kg. Maksimalna koncentracija izmjerena je u uzorku tla u jugozapadnom dijelu kruga Željezare Sisak. Visoke, anomalne i ekstremne sadržaje antimona u tlu imaju i svi drugi uzorci u željezari. Visoke vrijednosti antimona u tlu u ovom industrijskom postrojenju potječu od procesa prerade rudače i drugih komponenti koje se koriste pri taljenju i oplemenjivanju čelika te kod izrade drugih proizvoda od željeza.

Isto tako i tla na sjevernom rubu postrojenja Termoelektrane Sisak i Rafinerije nafte Sisak sadrže ekstremne koncentracije ovog elementa, a koje potječu od spaljivanja fosilnih goriva i prerade ugljikovodika. Ekstremna vrijednost antimona u tlu, u uzorku sjeverno od rafinerije, iznad željezničke pruge, vezana je za proizvodne procese u rafineriji, ali i za promet parnih lokomotiva u prošlosti. Industrijska proizvodnja u tim pogonima također uzrokuje visoke i ekstremne koncentracije antimona u tlu u naseljima Caprag i Kanak.

Visoke i ekstremne koncentracije antimona u tlima na lijevoj obali Save, sjeverno od postrojenja Termoelektrane Sisak i Rafinerije nafte Sisak potječu iz tih proizvodnih pogona. Antimon se dispergira u okoliš iz dimnjaka proizvodnih pogona vjetrom u smjeru sjevera i sjeveroistoka. Slično kao i sumpor, on se raspršuje po relativno širokom području, od Termoelektrane i Rafinerije na jugu, pa sve do naselja Hrastelnica i Bok Palanječki na sjeveru.

Ekstremna koncentracija antimona u uzorku tla na željezničkom kolodvoru kod pristaništa potječe vjerojatno od metalne prašine koja se stvara kod kočenja željezničkih kompozicija i vagona. Anomalna vrijednost u uzorku tla neposredno uz Zagrebačku cestu, slično kao i kod prethodno opisanog uzorka, posljedica je habanja kočionih feroda i diskova automobila te automobilskih guma.

Spatial distribution of antimony is very similar to that of sulfur and, partly, of lead. Also, based on that distribution it is evident that its origin in soil is anthropogenic which is mainly related to industry.

Concentrations of this element in the soil of the investigated area vary between 0.11 to 8.16 mg/kg with median of 0.29 mg/kg. Maximum concentration is measured in the soil sample from the southwestern part of the steelworks. All remaining samples within the circle of the steelworks also contain high, anomalous and extreme contents of Sb in the soil. High values of Sb in the soil in this industrial plant originate from the production process of the ore refining and processing of other components which are used in smelting and ennobling of steel and in production of other iron products.

In the same manner, the soils on the northern edge of the thermal power plant and oil refinery contain extreme concentrations of this element. These also derive their origin form combustion of the fossil fuels and hydrocarbon processing. Extreme value of Sb in the soil sample collected to the north of the oil refinery and close to the railroad is related to the both production processes in the oil refinery and traffic of the steam powered trains in the past. Industrial production in these plants is also the reason for high and extreme concentrations of Sb in the soils of the Caprag and Kanak settlements.

High and extreme concentrations of antimony in the soils on the left bank of the Sava River, to the north of the thermal power plant and the oil refinery arise from these processing plants. Antimony is dispersed into environment from the chimney of the processing plants blown by in the direction of north and northeast. Similar to sulfur, antimony is also dispersed over the relatively wide area, from the thermal power plant and refinery on the south all the way to the Hrastelnica settlement and Bok Palanječki on the north.

Extreme concentrations of antimony in the soil sample from the railroad station near the docks originate probably from the metal dust forming due to breaking of

Povišene i visoke koncentracije antimona u tlima užeg centra grada (gdje su se nalazila antička naselja Segestica i Siscija) mogu se, slično kao i za olovo, vezati uz tadašnju upotrebu tih metala. Naime, proizvodi od olova (olovne cijevi), zbog povezanosti antimona s rudnim mineralom olova, galenitom, sadrže u određenoj mjeri i element antimon.

Područja uz Kupu i Odru imaju koncentracije ovog elementa niže ili znatno niže od vrijednosti medijana, što je predisponirano geološkim materijalom matičnog supstrata tla na tom području (aluvijalni sedimenti tih rijeka izvorno posjeduju samo male koncentracije antimona).

the train compositions and wagons. Anomalous value in the soil sample immediately nearby the Zagrebačka Cesta street, much in the same way as in the case of the previously described sample, is a result of wearing of brake lining and discs of cars and tires.

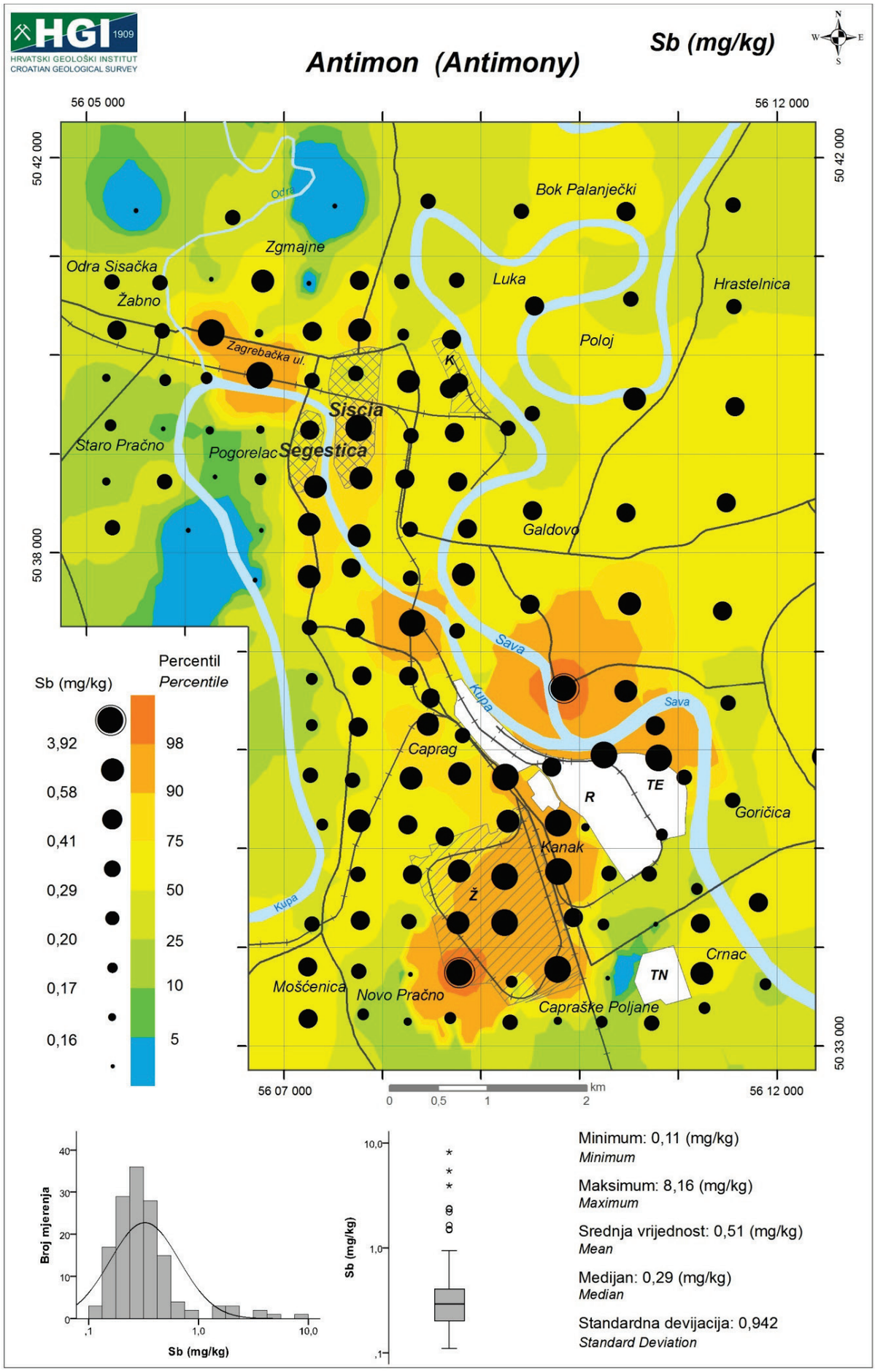
Increased and high concentrations of antimony in the soils of the narrow urban core (with former ancient settlements of Segestica and Siscia) can be, similar to lead, related to application of this metal in those times. Namely, products of lead (lead tubes and other things) contain antimony to some extent due to relationship between antimony and galena which is the lead ore mineral.

The terrains along the Kupa and Odra Rivers are characterized by concentrations of this element that are lower or considerably lower than median which is predefined by the geologic parent material underlying soil in this area (alluvial sediments of these rivers contain originally only the small concentrations of antimony).



Slika 10.20. *Uzorkovanje u dvorištu dječjeg vrtića Sisak Stari (Foto: J. Halamić).*

Figure 10.20. *Sampling in the kindergarten yard Sisak Stari (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Antimon (Antimony)
Sb (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Zagrebačka ul.
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Segestica
Staro Pračno
Pogorelac
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
Sb (mg/kg)
3,92
0,58
0,41
0,29
0,20
0,17
0,16
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Sb (mg/kg)
Minimum: 0,11 (mg/kg)
Minimum
Maksimum: 8,16 (mg/kg)
Maximum
Srednja vrijednost: 0,51 (mg/kg)
Mean
Medijan: 0,29 (mg/kg)
Median
Standardna devijacija: 0,942
Standard Deviation

Sc

10.33. Sc – SKANDIJ (atomski broj 21) SCANDIUM (atomic number 21)

Skandij je litofilni element u tragovima. On je prijelazni element koji prati željezo, a podređeno i aluminij. Prema učestalosti u Zemljinoj kori nalazi se na 35. mjestu (slično kao i olovo ili kobalt).

Srednji sadržaj u magmatskim stijenama je 22 mg/kg (ultrabaziti 15 mg/kg, pirokseniti do 200 mg/kg, oceanski toleitni bazalti > 30 mg/kg, bazalti 30 mg/kg, granodioriti 14 mg/kg i graniti 7 mg/kg). Šejlovi imaju srednji sadržaj oko 15 mg/kg, pješčenjaci 1 mg/kg i karbonati 1 mg/kg. Srednji sadržaj u tlima je 16 mg/kg. Prosječni sadržaj ovog elementa u vodi je oko 1,2 μg/L.

Skandij nije esencijalan element. On je element ravnoteže kao i Al. Relativno malo je poznato o njegovoj otrovnosti. Može biti kancerogen. Ljudske kosti mogu akumulirati skandij . Ovaj element je u određenoj mjeri opasan za ljudsko zdravlje, ali uglavnom u proizvodnom procesu. Zato se pri proizvodnji moraju primjenjivati stroge zaštitne mjere. Veće koncentracije u organizmu mogu prouzročiti plućnu emboliju, oštećenje jetre i membrane stanica.

Skandij se proizvodi u vrlo malim količinama. dobiva se kao nusprodukt u proizvodnji uranija. Procijenjena svjetska proizvodnja u 1998. godini bila je oko 537 000 t.

Koristi se pri izradi rentgenskih katodnih cijevi, lasera i fluorescentnih materijala.

Skandij može dospijeti u okolišu blizini termoelektrana, gdje se spaljuje ugljen i mazut. Fosfatna mineralna gnojiva mogu također sadržavati veće količine skandija, tako da njihova upotreba može povećati koncentraciju ovog elementa u poljoprivrednim tlima.

Scandium is a lithophile trace element. It represents a transitory element accompanying iron and, secondarily, aluminum. It is 35th element in abundance in the Earth's crust (similarly to lead and cobalt).

The average content of scandium in igneous rocks is 22 mg/kg (ultramafic rocks 15 mg/kg, pyroxenites up to 200 mg/kg, oceanic tholeiite basalts > 30 mg/kg, basalts 30 mg/kg, granodiorites 14 mg/kg, and granites 7 mg/kg). Shales contain about 15 mg/kg of scandium in average, sandstones 1 mg/kg and carbonates 1 mg/kg. Its average content in soils is 16 mg/kg, and in sweet water it is about 1.2 μg/L.

Scandium is not an essential element. It is an element of balance just as Al. Relatively little is known about its toxicity. It may be carcinogenic. The human bones tend to accumulate scandium. To certain extent this element is dangerous to the human health but mainly during the process of production. This is why strict protection measures have to be undertaken on the working places where everything comes into contact with this element. Major concentrations in organism can provoke pulmonary embolism, liver and cells damage.

Scandium is produced in very small quantities. It is obtained as a byproduct during the production of uranium. The estimated world production in the year 1988 was about 537,000 t.

Scandium is used in production of roentgen cathode tubes, lasers and fluorescent materials (high intensity lights and color TV).

Its dispersion into environment in greater quantities occurs in the vicinity of thermal power plants where coal and crude oil is incinerated. Phosphate mineral fertilizers can also contain greater quantities of scandium so that their application can increase the concentration of this element in the agricultural soils.

Skandij u analiziranim tlima ima dvojako podrijetlo. Jedno je antropogeno (industrija, kućanstva), a drugo geogeno. Industrijska područja (željezara, rafinerija, termoelektrana i kemijska industrija) pokazuju povišene sadržaja skandija u tlu, što je nesumnjivo posljedica industrijske proizvodnje u tim pogonima. Povišene i visoke koncentracije skandija u tlu na području dolina

Scandium in the analyzed soils derives its origin from two sources. One is anthropogenic (industry, households) and the other is geogenic. Industrial zones (steelworks, oil refinery, thermal power plant and chemical industry) show increased contents of Sc in the soil which is indubitably the result of industrial production in their processing plants. Elevated and high concentra-

rijeka Kupe i Odre su geogenog podrijetla i posljedica su geološke podloge. Na poplavnoj ravnici Kupe, u nekoliko uzoraka uzetih na poljopriverednom zemljištu koncentacije skandija su visoke. Vjerovatno je na njegov tako visoki sadržaj, osim geološke podloge, utjecala i upotreba umjetnih gnojiva. U dolini rijeke Save pretežito su niski sadržaji skandija u tlu, osim na nekim točkama gdje se oni kreću oko srednjih vrijednosti i vjerojatno su posljedica grijanja kućanstava na ugljen i upotrebe umjetnih gnojiva.

Raspon izmjerenih koncentracija na istraživanom području je od 1,2 do 9,1 mg/kg s medijanom od 3 mg/kg. Općenito gledano, izmjereni sadržaji u tlima sisačke regije su niži (posebice u tlima izvan industrijskih zona), što je vjerojatno posljedica metode razaranja uzoraka (zlatotopka). Naime, skandij se velikim dijelom na ovom području nalazi sadržan u mineralima teške frakcije (cirkonu, volframitu, kasiteritu, rutilu i dr.) koji se u zlatotopki ne razaraju u potpunosti.

Najveća koncentracija skandija izmjerena je u krugu Željezare Sisak, ali i uz postrojenja Rafinerije nafte Sisak i Termoelektrane Sisak. Uz industrijsku aktivnost vezani su i visoki sadržaji skandija u naselju Kanak. U blizini kemijske industrije „HERBOS“ također su registrirani povišeni sadržaji skandija u tlu. Sve navedene koncentracije su antropogenog podrijetla.

Suprotno prethodno navedenom, visoke i anomalne koncentracije skandija u tlima koja su nastala na aluvijalnim sedimentima rijeka Kupe i Odre geogenog su podrijetla. Ta tla su prirodno bogatija teškom mineralnom frakcijom, čiji minerali su nositelji skandija. Tla u dolini Save su siromašnija skandijem i koncentracije ovog elementa na tom području su ispod ili znatno ispod medijana (< 3 mg/kg). Ti sadržaji su također uvjetovani petrografskim sastavom matičnog supstrata iz kojeg su ta tla derivirana (pretežito karbonatni materijal).

Uža urbana cjelina grada ima relativno niske koncentracije skandija u tlu,većinom ispod vrijednosti medijana.

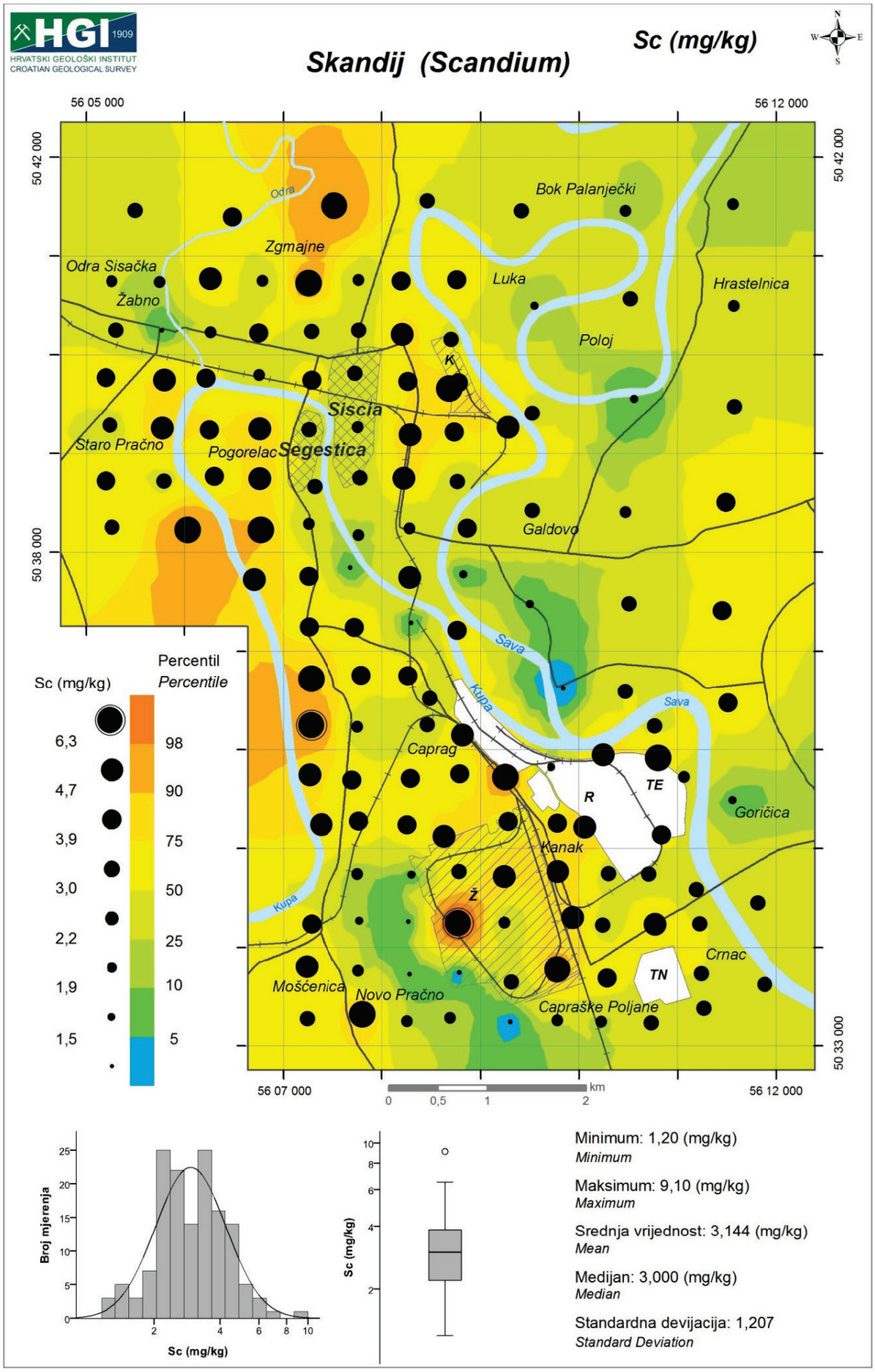
tions of scandium in the soil in the valleys of the Kupa and Odra Rivers are geogenic in origin deriving from the geologic bedrock. In several samples collected on the agricultural land of the Kupa floodplain the concentrations of scandium are high. This high concentration was probably impacted, apart from the geologic bedrock, by the utilization of chemical fertilizers. In the valley of the Sava River the contents of scandium in the soil are predominantly low except on some sites where they are around the median value most probably as a result of, among other things, the household heating based on coal, and application of chemical fertilizers.

The range of measured concentrations in the investigated area is between 1.2 and 9.1 mg/kg with median of 3 mg/kg. Generally, the measured contents of scandium in the soils of the Sisak region are lower (especially outside the industrial zones) which is probably the result of the digestion method in the sample analysis (aqua regia). Namely, scandium is in this area contained for the most part in the heavy mineral fraction (zircon, wolframite, cassiterite, rutile, etc.)

The greatest concentration of scandium is measured within the circle of the steelworks. Other high values of this element in the soil are also registered in the same circle but located closer to the oil refinery and thermal power plant. The high contents of scandium in the Kanak settlement situated between the steelworks and oil refinery are also associated with industrial activity. Close to the chemical industry of „HERBOS“ elevated contents of scandium in the soil are also registered. All aforementioned concentrations are of anthropogenic origin.

To the contrary of the above mentioned, the high and anomalous concentrations of scandium in the soils developed on the alluvial sediments of the Kupa and Odra Rivers are geogenic in their origin. These soils are naturally richer in heavy mineral fraction whose minerals are scandium-hosting. Soils in the valley of the Sava River are more deficient in scandium so that concentrations of this element in this area are below or considerably below the median value (< 3mg/kg). Those contents are also caused by petrographic composition of the parent material from which the soils have been derived (predominantly carbonate material).

The narrow urban core is characterized by relatively low concentrations of scandium in the soil (mostly below the median).


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Skandij (Scandium)
Sc (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Sc (mg/kg)
6,3
4,7
3,9
3,0
2,2
1,9
1,5
Percentil
Percentile
98
90
75
50
25
10
5
Broj mjerenja
Sc (mg/kg)
Minimum: 1,20 (mg/kg)
Minimum
Maksimum: 9,10 (mg/kg)
Maximum
Srednja vrijednost: 3,144 (mg/kg)
Mean
Medijan: 3,000 (mg/kg)
Median
Standardna devijacija: 1,207
Standard Deviation

Se

10.34. Se – SELENIJ (atomski broj 34) SELENIUM (atomic number 34)

Selenij je halkofilni i siderofilni element u tragovima. U Zemljinoj kori je po pojavljivanju na 67. mjestu, slično kao i živa. Kemijske osobine su mu slične sumporu.

Clarke vrijednost za selenij je 0,05 mg/kg. Srednji sadržaj selenija u ultrabazičnim stijenama je 0,05 mg/kg, bazaltima 0,05 mg/kg, neutralnim stijenama 0,05 mg/kg te kiselim magmatima, također, 0,05 mg/kg. Od sedimentnih stijena šejlovi imaju 0,6 mg/kg, pješčenjaci 0,08 mg/kg, a karbonati (vapnenci i dolomiti) 0,1 mg/kg. Visoki sadržaji selenija registrirani su i u crnim šejlovima i ugljenu. Kao i sumpor, selenij pokazuje jaku sklonost vezivanja na organsku tvar. Selenija u ugljenu ima i do 10,7 mg/kg, a u sirovoj nafti do 1,4 mg/kg. Prosječni sadržaj selenija u svjetskim tlima je 0,33 mg/kg. Sadržaj selenija u slatkoj vodi je < 1 μg/L.

Pod oksidativnim uvjetima minerali koji sadrže selenij troše se relativno brzo. Mobilni selenij je sklon precipitaciji u formi netopivih soli (reduktivni uvjeti), adsorbciji na Fe-oksi-hidrokside ili minerale glina te vezivanju na organsku tvar. Mobilnost selenija najveća je u alkalijskim tlima, dok je on u kiselim tlima, radi tvorbe stabilnih mineralnih i organskih spojeva, skoro imobilan.

Selenij je esencijalni kemijski element za mnoge organizme, ali isto tako u većim količinama i otrovan. Uska je granica između korisnog djelovanja i toksičnosti. Selenij je jedan od rijetkih elemenata kod kojeg postoji direktna uzročno posljedična veza između prirodnih uvjeta, odnosno koncentracije selenija u tlu, hrane uzgojene na tom tlu, kvalitete vode i ljudskog zdravlja. Toksičnost mnogih elemenata kao što su As, Cd, Hg i Tl može biti smanjena konzumacijom određene količine selenija. Neke biljke akumuliraju Se, a neke mogu podnijeti i vrlo visoke koncentracije tog elementa u tlu. Tla bogata selenijem formiraju se u aridnoj klimi. Konji, krave, svinje i kokoši osjetljivi su na trovanje selenijem. Selenij u tlu najvećim dijelom potječe iz litološke podloge, nakupljanjem tijekom pedogenetskih procesa, fiksacijom na organsku tvar, deponiranjem iz atmosfere (evaporacija oceana i mora, vulkanske erupcije i industrija), fitogenetskom volatilizacijom iz biljaka i mikroorganizama, spaljivanjem vegetacije koja sadrži selenij, antropogenim unosom u tlo kroz prihranu, prskanjem preko lista biljaka, tretiranjem zrna umjetnim mineralnim fosfatnim gnojivima te industrijskim onečišćenjem talioničkim pepelom, šljakom i otpadnim muljevima.

Svjetska produkcija selenija u 1995. godini procijenjena je na 23 100 t.

Spojevi selenija koriste se za izradu fotoelektričnih ćelija. Upotrebljava se i kao pigment u bojama (kestenjasta i narančasta boja) u proizvodnji plastike i stakla. Služi i kao vulkanizirajući i galvanizirajući reaktant. Dodaje se čeliku (npr. u formi WSe_2). Veliki dio svjetske proizvodnje selenija (do 20 %) koristi se kao dodatak hrani za ljude i životinje. Osim toga, upotrebljava se u kozmetici i medicini, gdje u novije vrijeme služi u kardiologiji kao antioksidant. U poljoprivredi se Na-selenit (Na_2SeO_3) dodaje insekticidima, mineralnim gnojivima te u sprejeve za prihranu preko lista.

Značajna emisija u okoliš događa se tijekom spaljivanja fosilnih goriva, posebice onih s povećanim koncentracijama selenija. Osim toga, povećana disperzija u okoliš je za očekivati i oko većih industrijskih postrojenja kao što su talionice.

Selenium is a chalcophile and siderophile trace element which is 67th in abundance in the Earth's crust, similar to mercury. Its chemical properties are similar to sulfur.

Clarke value for Se is 0.05 mg/kg. Its average content in ultramafic rocks is 0.05 mg/kg, basalts 0.05 mg/kg, neutral and acid igneous rocks also 0.05 mg/kg. Among sedimentary rocks shales contain 0.6 mg/kg, sandstones 0.08 mg/kg and carbonate rocks (limestones and dolomites) 0.1 mg/kg. High contents of Se are also registered in black shales and in coal. Similar to sulfur, selenium is very prone to bonding on organic matter. In coal selenium can be present with up to 10.7 mg/kg while in the crude oil up to 1.4 mg/kg. Average content of Se in the world soils is 0.33 mg/kg. In the sweet water it is present with < 1 μg/L.

In oxidizing conditions minerals containing Se are weathering relatively quickly. Mobile Se tend to precipitate in the form of insoluble salts (reducing conditions), adsorb on Fe oxy-hydroxides or clay minerals as well as to bond on organic matter. Mobility of selenium is the highest in the alkaline soils while in the acidic soils, due to formation of stable mineral and organic compounds, it is almost immobile.

Selenium is essential chemical element for many organisms but also toxic in greater quantities. It is very close to the border between being useful and toxic. Selenium is thus one of the rare elements showing direct cause-and-effect relationship between natural conditions, that is, concentration of Se in the soil, on the on side and cultivated food on that soil, water quality and human health on the other. Toxicity of many elements such as As, Cd, Hg and Tl can be reduced by consuming a certain quantity of selenium. Some plants accumulate selenium and other can even tolerate very high concentrations of that element in the soil. Soils rich in selenium are formed in arid climate. Horses, cattle, pigs and hens are very sensitive to selenium poisoning. Selenium in soil originates for the most part from lithologic bedrock. It accumulates during the pedogenetic processes, by fixation on organic matter, deposition from the (evaporation from the oceans and seas, volcanic eruptions and industry), phitogenetic volatilization from plants and microorganisms, incinerating of vegetation that contains selenium. Anthropogenic input into the soil occurs through the sprinkling of leaves with purpose o supplying the additional food to plants, treating of grain by chemical and mineral fertilizers food, and industrial contamination including ashes from the foundries, dross and various waste muds.

The world production of selenium in the year 1995 was estimated to 23,100 t.

Selenium compounds are used in the manufacturing photoelectric cells. It is also utilized as a pigment in paints (chestnut and orange color) mostly in the production of plastic and glass. It is also applied as vulcanizing and galvanizing reactant. It is added to steel (e.g. in the form of WSe_2). Great portion of the world selenium production (up to 20 %) is used as a food additive for people and animals. Besides, selenium is used in cosmetics and medicine where recently serves in cardiology as an antioxidant. In agriculture Na-selenite (Na_2SeO_3) is added to insecticides, mineral fertilizers and sprays for feeding the plants through leaves.

Significant emission into the environment occurs owing to the combustion of fossil fuels, particularly those with significant concentration of selenium. Besides, increased dispersion into environment can be expected around the major industrial processing plants such as foundries etc.

Prostorna raspodjela selenija pokazuje dva tipa izvorišta za područja s povećanim koncentracijama tog elementa u istraživanim tlima. Jedno područje nalazi se na jugu i pokazuje izraziti utjecaj industrije, dok druga područja ukazuju na geogeno podrijetlo selenija u tlu.

Izmjerene koncentracije ovog elementa variraju od 0,1 do 2,1 mg/kg s medijanom od 0,5 mg/kg, što je iznad prosječnog sadržaja u tlima općenito. Najveća izmjerena vrijednost registrirana je u uzorku na sjevernom rubu postrojenja Termoelektrane Sisak, dok ostali susjedni uzorci imaju anomalne koncentracije selenija. Vjetrom se dispergira prema sjeveru i naknadno taloži na tlo.

Ekstremne i anomalne koncentracije selenija izmjerene su i u tlima u željezari te u uzorku na sjeverozapadnom rubu tog industrijskog pogona. Te vrijednosti su antropogenog podrijetla i posljedica su prerade željezne rude i metalurške proizvodnje u željezari.

Anomalna koncentracija selenija u uzorku u neposrednoj blizini željezničkog kolodvora u Capragu također je antropogenog podrijetla. Akumulacija ovog elementa u tlu vjerojatno potječe iz vremena parnih lokomotiva, kojima je pogonsko gorivo bio ugljen (u ugljenu su akumulirane znatne količine selenija). Pri pokretanju i pri ranžiranju vlakova emitirane su velike količine ispušnih plinova iz lokomotiva uzrokujući posrednu disperziju ovog elementa u tlo.

Spatial distribution of selenium indicates two types of sources for the areas of the increased concentrations of this element in the investigated soils. One is situated on the south showing distinct impact of industry while others indicate the geogenic origin of selenium in the soil.

The measured concentrations of this element vary from 0.1 to 2.1 mg/kg with median of 0.5 mg/kg which is above the average content in the soils in general. The greatest measured value is registered in the sample from the northern edge of the thermal power plant. The neighboring samples also show anomalous concentrations of selenium. Its transfer from the thermal power plant and input into the soil is from the air. It is dispersed by wind toward the north and subsequently precipitated on the land.

Extreme and anomalous concentrations of selenium are also measured within the circle of the steelworks including the sample from the northwestern rim of that industrial plant. These values are anthropogenic in origin and result from processing and refinement of iron ore and metallurgic production in the steelworks.

Anomalous concentration of selenium in the sample collected in the immediate vicinity of the railway station of Caprag is also of anthropogenic origin. Accumulation of this element in soil probably originates from

Ekstremna i anomalne koncentracije selenija u području naselja Mošćenica su pretežito geogenog podrijetla i ovdje je ovaj element najvećim dijelom akumuliran u organskoj tvari. Naime, uzorkovana tla na tom području su pretežito šumska tla jako bogata humusom i organskom tvari.

Anomalne koncentracije u dolini rijeka Kupe, Odre i Save (uzorak južno od gradskog vodovoda „Kopa", Staro Pračno, Pogorelec, sisačka Zgmajna, Luka i jugoistočno od kemijske industrije) također su pretežito geogenog podrijetla, a vezane su za Mn i Fe oksi-hidrokside i minerale glina u tlu.

Područja oko naselja Bok Palanječki i Hrastelnica te prema jugu do naselja Goričica, pokazuju povišene koncentracije ovog elementa u tlu. Pošto se radi o ruralnom, pretežito poljoprivrednom zemljištu, selenij vjerojatno potječe od upotrebe fosfatnih mineralnih gnojiva i također je antropogenog podrijetla.

Urbana područja grada Siska te naselja Galdovo, sjeverni dio Starog Pračna, Žabno i naselje Capraške Poljane imaju koncentracije selenija u tlu ispod ili znatno ispod medijana. Za područje oko naselja Žabno može se čak reći da je osiromašeno ovim elementom.

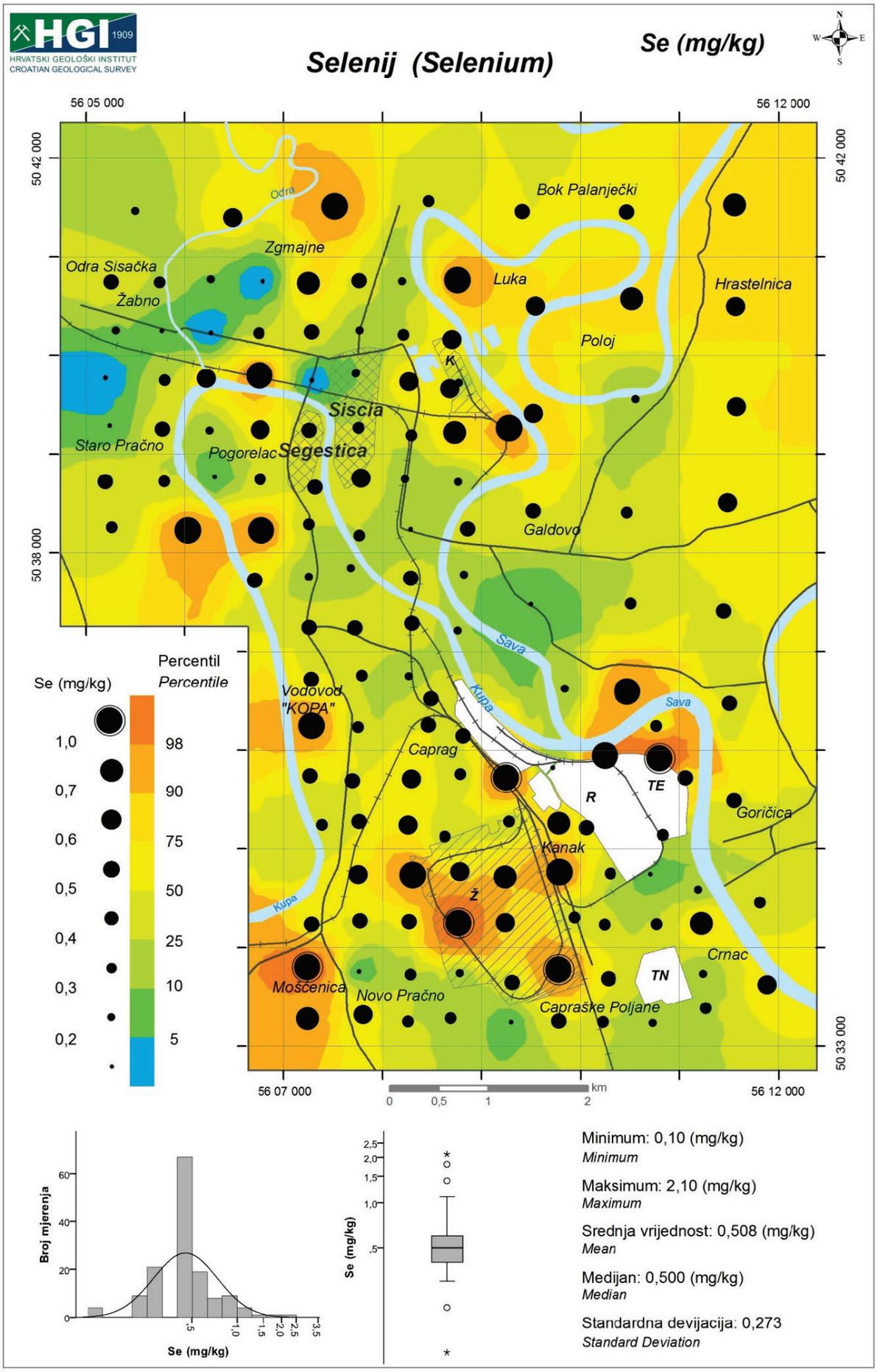
the times of steam engines to which coal was the driving fuel (considerable quantities of selenium are accumulated in coal). Starting and relocation of trains produced great emissions of gases from the steam engines and subsequent dispersion of this element into the soil.

Extreme and anomalous concentrations of Se in the zone of Mošćenica settlement are predominantly of geogenic origin which is why here this element is for the most part accumulated in the organic matter. Namely, the sampled soils on this area are prevalently forest soils very rich in humus and organic matter.

Anomalous concentrations in the valley of the Kupa, Odra and Sava Rivers (sample collected to the south of the city water supply line „Kopa", settlements of Staro Pračno, Pogorelec, Sisačka Zgmajna, Luka and area to the southeast of the chemical industry) are also predominantly of geogenic origin, associated with Fe-Mn oxy-hydroxides and clay minerals in the soil.

Areas around the settlements of Bok Palanječki and Hrastelnica as well as those southward to the Goričica settlement show increased concentrations of this element in the soil. Since in this case the land is predominantly rural, that is, agricultural, selenium probably originates from the application of phosphate mineral fertilizers indicating once more its anthropogenic origin.

Urban areas of Sisak Old City and the Galdovo settlement, northern part of Staro Pračno, Žabno and Capraške Poljane settlement show the concentrations of selenium in the soil below or considerably below the median value. It can be said that the area around the Žabno settlement is even depleted in this element.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Selenij (Selenium)
Se (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Vodovod "KOPA"
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Se (mg/kg)
Percentil
Percentile
1,0
0,7
0,6
0,5
0,4
0,3
0,2
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Se (mg/kg)
Minimum: 0,10 (mg/kg)
Minimum
Maksimum: 2,10 (mg/kg)
Maximum
Srednja vrijednost: 0,508 (mg/kg)
Mean
Medijan: 0,500 (mg/kg)
Median
Standardna devijacija: 0,273
Standard Deviation

Sn

10.35. Sn – KOSITAR (atomski broj 50) TIN (atomic number 50)

Kositar je oksihalkofilni element mobilan u rezidualnim otopinama kiselih magmi. Pokazuje tendenciju formiranja geokemijskih provincija kositra. On zauzima 49. mjesto po pojavljivanju u Zemljinoj kori.

Clarke vrijednost za kositar je 2,5 mg/kg. Srednja vrijednost sadržaja kositra u magmatskim stijenama je 2 mg/kg (ultrabaziti 0,5 mg/kg, bazalti 1,5 mg/kg i graniti 3 mg/kg). Šejlovi sadrže 6 mg/kg, pješčenjaci 0,x mg/kg i karbonati 0,5 mg/kg. Ugljeni mogu sadržavati relativno visoke koncentracije kositra što ukazuje na njegovu vezu s organskom tvari. U tlima prosječna koncentracija kositra iznosi 10 mg/kg. U slatkoj vodi sadržaj Sn je 0,0009 mg/L i on tvori organokomplekse.

Mobilnost kositra u sekundarnom okolišu je vrlo mala i uvelike ovisi o pH vrijednostima. Kasiterit kao mineral je jako otporan na trošenje i mala količina kositra koji se oslobađa prilikom trošenja precipitira se s aluminijem bogatim hidrolizatima ili se veže na organsku tvar i minerale glina.

Kositar je vjerojatno esencijalan za neke više organizme (ljude), ali za niže organizme Sn je jako otrovan (Sn^{2+} ion je jako otrovan za biljke). Metal kositar praktički je neotrovan. Može se akumulirati u organizmima koji žive u vodi. U organizam kositar može dospijeti inhalacijom, putem hrane i pića te kroz kožu. Organokositri kao npr. trietilni kositar (Et_3SnOAc) su otrovni. U organizam dospijevaju putem hrane iz konzervi (posebice iz voćnih konzervi), vodom iz vodovoda (metalne cijevi) i dodataka hrani u vidu stabilizatora i konzervansa. Povećan unos kositra hranom može izazvati akutan gastritis, smanjenje reproduktivnosti i oštećenje kostiju. Neki organokositri uzrokuju jake iritacije kože.

Kositar se eksploatira već od brončanog doba.Jedan je od prvih metala koje je čovjek poznavao (pretežito kao komponenta bronce). Svjetska proizvodnja kositra u 2003. godini procijenjena je na 258 000 t. Kositar se pretežito dobiva iz rudnog minerala kasiterita.

Kositar je obojeni metal s mnogostrukom tehničkom primjenom. Upotrebljava se većinom za poboljšanje svojstava legura, kao metal za lemljenje, PVC stabilizator (pretežito organokositar), pesticide i zaštitu drva. Potrošnja visoko toksičnih Sn-smjesa (organokositar) je u alarmantnom porastu. Upotreba boja za brodove, koje spriječavaju obraštanje trupa, a sadrže organokositar, znatno povećava rizik za organizme koji žive u vodenoj sredini.

Dispergira se u okoliš kao sastojak pokositrenih željeznih limova, limenki, staniola, materijala za lemljenje, muljeva iz pročistača otpadnih voda, pepela iz spalionica smeća. te spaljivanjem fosilnih energenata.

Tin is an oxychalcophile element mobile in residual solutions of acid magmas which shows the tendency of forming the geochemical provinces of tin. It is 49^{th} in abundance in the Earth's crust.

Clarke value of Sn is 2.5 mg/kg. Its average content in igneous rocks is 2 mg/kg (ultramafic rocks 0.5 mg/kg, basalts 1.5 mg/kg and granites 3 mg/kg). Shales contain 6 mg/kg, sandstones 0.x mg/kg and carbonates 0.5 mg/kg. Coals can contain relatively high concentrations of Sn which points at its association with organic matter. In soils the average content of tin is 10 mg/kg while in the sweet water it is 0.0009 mg/L where it forms the organic complexes.

Mobility of tin in the secondary environment is very low depending greatly on pH values. Cassiterite as a mineral is very resistant to weathering so that a small quantity of tin that is released during weathering is precipitated with hydrolisates rich in aluminium or is bonding on organic matter and clay minerals.

Tin is probably an essential element for some higher organisms (humans) but for the lower ones it is very toxic (Sn^{2+} ion is highly toxic for plants). Tin as a metal is practically harmless. It can be accumulated in organisms living in water. Tin can enter the organism by inhaling, by food and drink, or through the skin. Organic tins such as trietil tin (Et_3SnOAc) are highly poisonous. They enter the organism by food from the cans (especially fruit cans) and other cans containing food, by water from the water lines (metal conduits), and by the food additives in the form of stabilizers and food preservatives. Increasing input of tin can cause acute gastritis, decreased reproductive abilities, and damage of the bones. Some organic tins are very irritating to the skin.

Tin is exploited already since the Bronze Age (Phoenicians) representing one of the first metal known by men (mostly as bronze component). The world production of tin in the year 2003 was estimated to 258,000 t. It is predominantly obtained from the ore mineral cassiterite.

Tin is a light metal with multiple technical applications. It is used mostly for enhancing the properties of alloys, as a metal for soldering, as a PVC stabilizer (chiefly organic tin), as pesticide, for wood protection etc. Consumption of highly toxic Sn-mixtures (organic tin) is in alarming increase. Application of the paints for ships which prevent the overgrowing of its hull, containing the organic tin, considerably increases the risk for organisms living in the water environment.

Dispersion into environment is by tinned iron sheets, tins, tinfoil, soldering material, mud from aquatrons, as well as ashes from the refuse-incineration plants. Besides, considerable dispersion into environment comes from combustion of fossil fuels (coal, crude oil, peat etc.).

Povećane koncentracije kositra u tlima istraživanog terena isključivo su vezane za urbana i industrijska područja i sve su antropogenog podrijetla.

Raspon izmjerenih vrijednosti je od 0,4 do 56,3 mg/kg s medijanom od 1,3 mg/kg. Najveća koncentracija registrirana je u blizini Termoelektrane Sisak i Rafinerije nafte Sisak. Tla u čitavoj industrijskoj zoni imaju najvećim dijelom ektremne i anomalne koncentracije kositra. Kositar se emitira iz dimnjaka i proizvodnih pogona u zrak, a zatim dispergira u smjeru ruže vjetrova i taloži na tlo. Radi toga na tom području imamo dva glavna pravca disperzije: *SSI – JJZ* i *JI – SZ* (koji je slabijeg intenziteta). Zbog toga su koncentarcije kositra u

Increased concentrations of tin in the soils of the investigated terrain are exclusively associated with urban and industrial zones and are all of anthropogenic origin.

The range of measured values is between 0.4 and 56.3 mg/kg with median of 1.3 mg/kg. The greatest concentration is registered in the vicinity of the thermal power plant and oil refinery. The soils in the whole industrial zone (thermal power plant, oil refinery, oil terminals, and steelworks) are characterized mostly by extreme and anomalous concentrations of tin. It originates from air emissions of the chimneys and processing plants and is subsequently dispersed according to the prevalent winds and precipitate on the land. Owing to this there



Slika 10.21. *Arheološke iskopine rimske Siscije (Foto: J. Halamić).*

Figure 10.21. *Archeological excavation site of the Roman Siscia (Photo: J. Halamić).*

tlu u naselju Kanak, daleko veće (ekstremne vrijednosti) od onih u naselju Caprag. Nema dvojbe da su visoke koncentracije kositra u tlu na tom području posljedica industrijske proizvodnje i spaljivanja fosilnih energenata.

Drugo područje s visokim, anomalnim i ekstremnim koncentracijama kositra u tlu je područje nekadašnjih gradova Segestice i Siscije (Sl. 3.1.). Na temelju prostorne raspodjele ovog elementa u tlu moguće je odrediti vanjske granice tih antičkih naselja. Neupitno je da je za vrijeme Kelta i Rimljana metal kositar bio u širokoj primjeni, što je rezultiralo njegovim povišenim sadržajem u tlu. Očito je da je kositar akumuliran u tlu u minerale glina, Mn i Fe oksi-hidrokside i organsku komponentu, kroz duži vremenski period, gdje je ostao fiksiran do danas.

Počevši od opisanih područja, prema rubnim ruralnim dijelovima istraživanog područja, koncentracija kositra naglo opada, što je još jedan dokaz da je u urbanom dijelu isključivo antropogenog podrijetla.

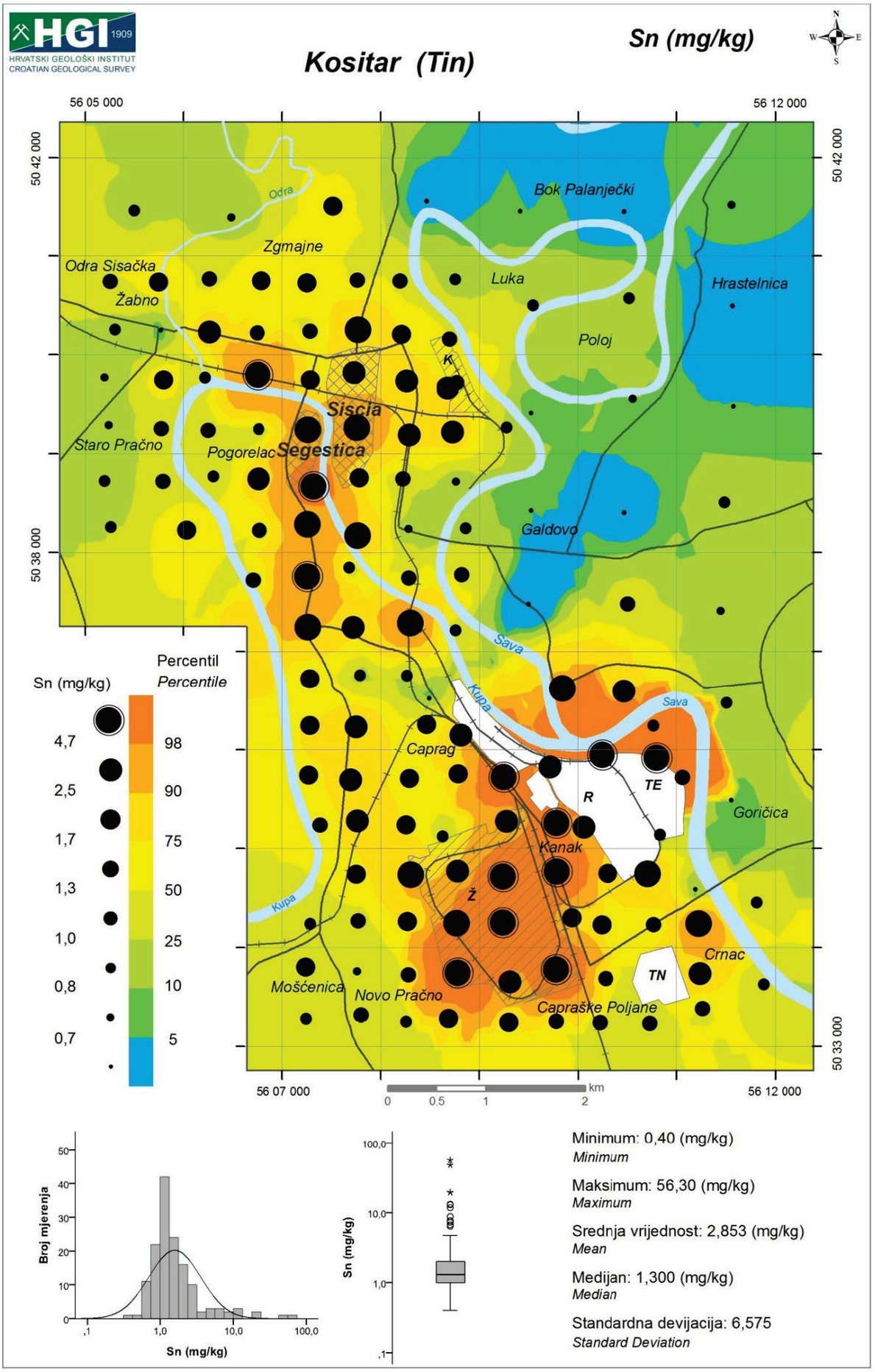
Po prostornoj raspodjeli ovog elementa u tlu vidljiva je i razlika u njegovom geogenom podrijetlu odnosno izvorištu. Naime, tla razvijena na aluvijalnim sedimentima rijeka Kupe, Mošćenice i Odre (pretežito siliciklastični materijal s većim sadržajem minerala gline i Mn i Fe oksi-hidroksida) imaju relativno veće sadržaje kositra u tlu od onih koja su se razvila na aluviju rijeke Save (pretežito karbonatni materijal). Tako su tla na području Galdova, Hrastelnice i Boka Palanječkog u poplavnom području Save osiromašena kositrom.

are two main lines of dispersion: one is NNE-SSW and the other is SE-NW which is of lower intensity. This is why the concentrations of tin in the soil of the Kanak settlement, situated between the steelworks on the one side and the thermal power plant and oil refinery on the other, are far greater (extreme values) than those in the Caprag settlement. There is no doubt at all that high concentrations of tin in this area result from the industrial production and combustion of fossil fuels.

The other area with high, anomalous and extreme concentrations of tin in the soil is the old city occupied by former cities of Segestica and Siscia (Fig. 3.1.). Almost only on the basis of the spatial distribution of this element in the soil one can define the outer limits of these ancient settlements. It is out of question that in the Celtic and Roman times tin as a metal was broadly applied which resulted with its higher content in the soil. Obviously, tin is accumulated in the soil through the longer time period and remained fixed until the recent times.

From the aforementioned areas toward the peripheral rural parts of the investigated area the concentration of tin abruptly falls which is still another evidence of its exclusively anthropogenic origin in the urban area.

In accordance with the spatial distribution of this element in the soil on can observe the difference in its geogenic origin, that is, its source area. Namely, the soils developed on the alluvial sediments of the Kupa, Mošćenica and Odra Rivers (prevalently siliciclastic material with greater content of clay minerals and Fe-Mn oxy-hydroxides) show relatively higher content of Sn in the soil than those developed on the alluvium of the Sava River (predominantly carbonate material). This is why the soils in the area of Galdovo, Hrastelnica and Bok Palanječki in the floodplain area of the Sava River are deficient in tin.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Kositar (Tin)
Sn (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Kupa
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0.5
1
2
Sn (mg/kg)
Percentil
Percentile
4,7
2,5
1,7
1,3
1,0
0,8
0,7
98
90
75
50
25
10
5
Broj mjerenja
Sn (mg/kg)
Minimum: 0,40 (mg/kg)
Minimum
Maksimum: 56,30 (mg/kg)
Maximum
Srednja vrijednost: 2,853 (mg/kg)
Mean
Medijan: 1,300 (mg/kg)
Median
Standardna devijacija: 6,575
Standard Deviation

Sr

10.36. Sr – STRONCIJ (atomski broj 38) STRONTIUM (atomic number 38)

Stroncij je litofilni element u tragovima, prikriven kalcijem i barijem, a u magmatskom okolišu vezan uz kalcij. Prema učestalosti u Zemljinoj kori nalazi se na 16. mjestu.

Srednji sadržaj u magmatskim stijenama je 375 mg/kg (ultrabaziti 9,8 mg/kg, baziti 465 mg/kg i graniti 100 mg/kg). Od sedimentnih stijena šejlovi imaju srednji sadržaj stroncija 300 mg/kg, pješčenjaci 20 mg/kg, a karbonati 610 mg/kg. Srednji sadržaj tog elementa u tlu iznosi 300 mg/kg. U morskoj vodi ga ima oko 8,1 mg /L (Ca / Sr = 50), a u slatkoj vodi 0,08 mg/L (Ca / Sr = 200 – 250).

Stroncij je po svojstvima mobilnosti između Ca i Ba. Oslobađanje stroncija iz feldspata tijekom trošenja teče razmjerno polako. Tako dugo dok pH vrijednost ostaje ispod 5,5 oslobođeni Sr^{2+} ion će ostati vrlo mobilan ili će uz prisutnost CO_2 precipitirati kao karbonat. Tijekom trošenja i transporta stroncij se ugrađuje u minerale glina, u Mn i Fe oksi-hidrokside i fiksira se na organsku tvar. Međutim, većina tog elementa taloži se u formi organskih karbonata (ljušture školjakaša).

Stroncij nije biogeni element za većinu organizama. Supstituira Ca, a u njegovoj prisutnosti je gotovo neotrovan. No, veće koncentracije u hrani i vodi za piće mogu utjecati na metaboličke procese u organizmu. Starije osobe su manje osjetljive na povećane sadržaje stroncija. Taj element sam po sebi praktički je neotrovan, ali Sr-izotop ^{90}Sr je visoko radiotoksičan. Koncentrira se u morskim plavim algama.

Svjetska proizvodnja stroncija u 2000. godini iznosila je 320 000 t.

Ovaj element nema direktnu primjenu kao čisti metal, ali se upotrebljava u mnogim spojevima u proizvodnji keramike, stakla, TV katodnih cijevi i pirotehničkog materijala. Osim toga, nalazi primjenu u metalurgiji, u luminiscirajućim pigmentima boja te u medicini za suzbijanje osteoporoze i osteoartritisa.

Antropogeni utjecaj na okoliš ostvaruje se kao posljedica spaljivanja fosilnih goriva te kod eksploatacije sumpora. Visoke koncentracije stroncija nalazimo i u fosforitima tako da on u okoliš dospijeva i putem fosfatnih mineralnih gnojiva. Povećani sadržaji stroncija u tlu mogu se očekivati i kod kalcitizacije, gnojidbe gnojnicom, komunalnim i industrijskim muljevima.

Strontium is a litophile trace element screened by calcium and barium. In magmas it is associated with calcium. It is 16th in abundance in the Earth's crust.

The average content of strontium in igneous rocks is 375 mg/kg (ultramafic rocks 9.8 mg/kg, mafic rocks 465 mg/kg and granites 100 mg/kg). Among sedimentary rocks shales contain in average 300 mg/kg of strontium, sandstones 20 mg/kg and carbonates 610 mg/kg. The average content of this element in soil is 300 mg/kg. The sea water contains about 8.1 mg /L (Ca / Sr = 50) and sweet water 0.08 mg/L (Ca / Sr = 200 - 250).

Strontium is by its mobility between Ca and Ba. Releasing of strontium from feldspars during weathering is relatively slow. Until the pH value does not exceed 5.5 the released Sr^{2+} ion will stay very mobile or, in the presence of CO_2, will precipitate as carbonate. During weathering and transport Sr bonds on clay minerals, Fe-Mn oxy-hydroxides and fixes on organic matter. However, the most part of this element precipitates in the form of organic (mollusk shells).

Strontium is not a biogenic element for the most organisms. It substitutes Ca in whose presence is almost harmless. However, major concentrations in food and drinking water can affect metabolic processes in organism. Elder people are less sensitive to elevated contents of strontium than the younger ones. This element is in itself practically harmless but the Sr-isotope ^{90}Sr is highly radiotoxic. Toxic effects of this isotope are exhibited through the development of cancer, increased mineralization of bones, and reduction of white and red blood cells, occurrence of leukemia, stronger bleeding and sensitivity to infections. It is concentrated in the blue marine algae.

The world production of strontium in the year 2000 was 320,000 t.

This element has not a direct application as a pure metal bat it is used in many compounds in production of ceramics, glass, TV cathode ray tubes (it blocks the roentgen radiation) and pyrotechnic material.

Besides, it finds its application in metallurgy, in luminescent pigments and in medicine for controlling osteoporosis and osteoarthritis.

Anthropogenic impact on the environment occurs due to combustion of fossil fuels and exploitation of sulfur. The high concentrations of strontium can be also found in phosphorites, which is why it is dispersed into environment by the phosphate mineral fertilizers. Increased contents of strontium in the soil can be also expected owing to calcification, fattening by the use of slurry and communal and industrial muds.

Prosječne izmjerene koncentracije stroncija na istraživanom području su samo neznatno povećane u odnosu na srednje sadržaje tog elementa u tlima općenito. Na temelju prostorne raspodjele mogu se razlučiti dva područja s povećanim sadržajima u tlu. Jedno je industrijsko područje (antropogeno podrijetlo), a drugo su tla u dolini Save (geogeno podrijetlo).

Izmjerene koncentracije ovog elementa variraju od 6,5 do 375,6 mg/kg s medijanom od 43,3 mg/kg. Najveća vrijednost registrirana je u krugu Željezare Sisak. Većina ekstremnih i anomalnih koncentracija ovog elementa u tlu vezane su za industrijsku aktivnost u Željezari (metalurške procese ili oslobađanje stroncija iz haldišta na jugu pogona željezare).

Ekstremna koncentracija u tlu pored željezničke stanice u Capragu može imati podrijetlo u spaljivanju ugljena i dizel goriva u pogonskim željezničkim lokomotivama.

Tlo na točki uzorkovanja na križanju Petrinjske i Školske ulice, u dvorištu iza kuće, je naveženo tlo, izgrađeno pretežito od građevinskog otpada s povećanim sadržajem karbonata tako da je ekstremna koncentracija stroncija u tom uzorku antropogenog podrijetla.

Spaljivanje fosilnih goriva u termoelektrani ima također utjecaj na povećane koncentracije stroncija u tlu u okolici tog industrijskog pogona. Ovdje je vidljivo raspršenje stroncija vjetrom prema sjeveru. Visoki i povećani sadržaji stroncija u tlima u užem urbanom području grada vjerojatno se mogu vezati uz pojačani promet, korištenje raznih građevinskih materijala i na spaljivanje fosilnih goriva u kućanstvima.

Generalno gledajući tla koja su razvijena najvećim dijelom na karbonatnim sedimentima (dolina Save) imaju veće koncentracije ovog elementa nego tla koja su razvijena na aluvijalnim siliciklastičnim sedimentima dolina rijeka Kupe i Odre.

Područja Mošćenice, Starog Pračna i Odre Sisačke osiromašena su sadržajem ovog elementa u tlu.

The average measured concentrations of strontium in the investigated area are only slightly increased with respect to the average contents of this element in soils in general. Based on its spatial distribution one can separate two different zones with increased contents in the soil. One is industrial zone (anthropogenic origin) and the other is represented by the soils in the valley of the Sava River (geogenic origin).

The measured concentrations of this element vary between 6.5 and 375.6 mg/kg with median of 43.3 mg/kg. The greatest value is registered within the circle of the steelworks. The most of extreme and anomalous concentrations of this element in the soils are associated with industrial activity in the steelworks (metallurgic processes or releasing of strontium from the depots on the southern part of the processing plants.

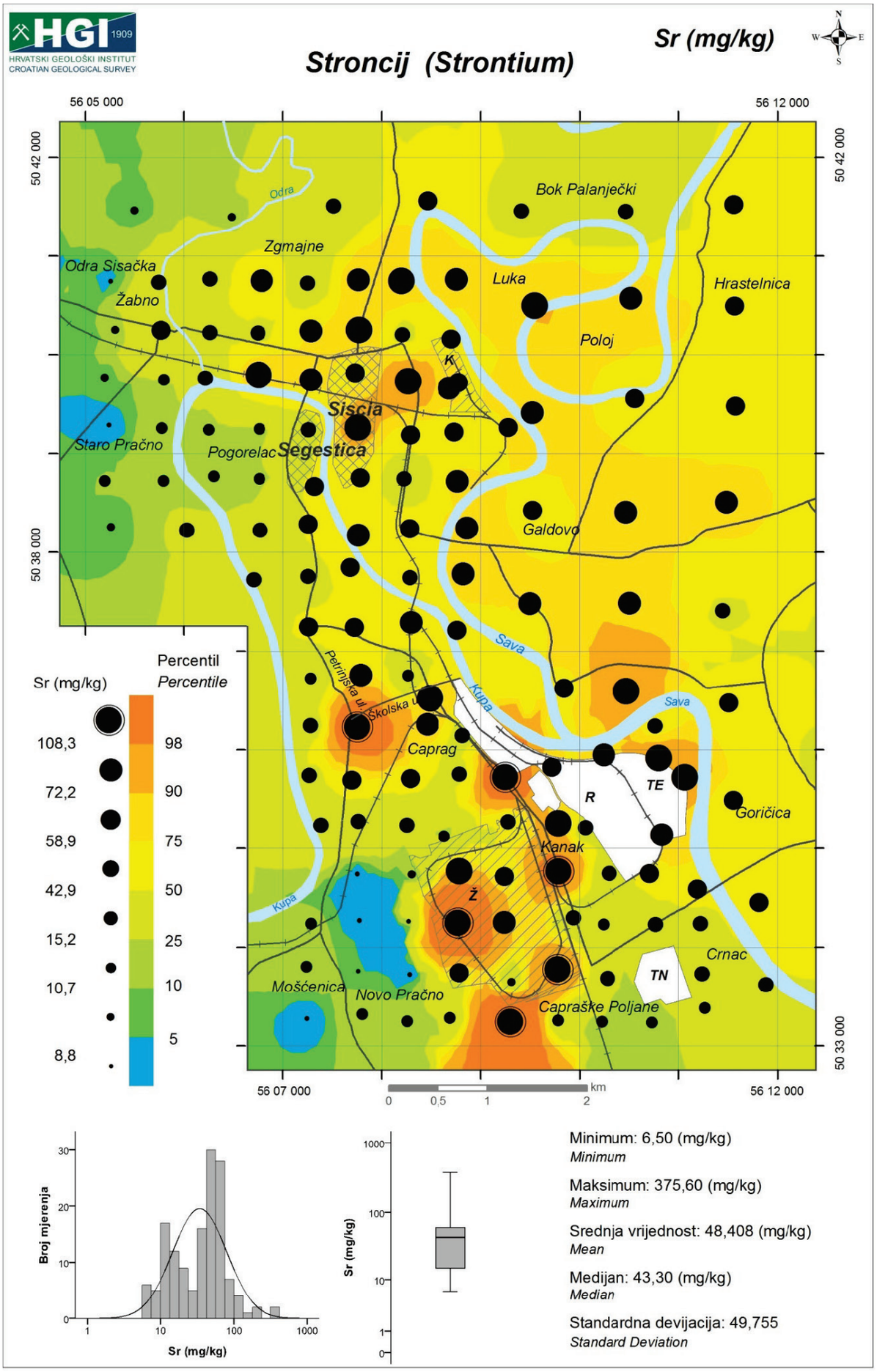
Extreme concentration in the soil near the railroad station of Caprag can originate from the combustion of coal and diesel fuel in the train engines.

Soil at the sampling point from the crossroads of Petrinjska and Školska Streets, in the courtyard behind the house is a deposited soil which is built predominantly of the constructing waste material with increased content of carbonates so that the extreme concentration of strontium in this sample is of anthropogenic origin.

Combustion of fossil fuels in the thermal power plant also affects the elevated concentrations of strontium in the soil around its processing plants. Here is evident the dispersion of strontium toward the north in the direction of wind. High and increased contents of Sr in the soils from the narrow urban core can probably be associated with the denser traffic, use of various building materials and use of fossil fuels in the households.

In general, the soils developed mostly on the carbonate sediments (valley of the Sava River) show higher concentrations of this element than soils developed on the alluvial siliciclastic sediments of the Kupa and Odra Rivers.

The soils in the area of Mošćenica, Staro Pračno and Odra Sisačka are deficient in the content of this element.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Stroncij (Strontium)
Sr (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Petrinjska ul.
Školska ul.
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Sr (mg/kg)
Percentil
Percentile
108,3
72,2
58,9
42,9
15,2
10,7
8,8
98
90
75
50
25
10
5
Broj mjerenja
Sr (mg/kg)
Minimum: 6,50 (mg/kg)
Minimum
Maksimum: 375,60 (mg/kg)
Maximum
Srednja vrijednost: 48,408 (mg/kg)
Mean
Medijan: 43,30 (mg/kg)
Median
Standardna devijacija: 49,755
Standard Deviation

Th

10.37. Th – TORIJ (atomski broj 90) THORIUM (atomic number 90)

Torij je litofilni element u tragovima iz grupe aktinida udružen s uranijem, cerijem, lantanom i drugim elementima rijetkih zemalja, a prema učestalosti u Zemljinoj kori je na 37. mjestu.

Srednji sadržaj tog elementa u ultrabazitima je 0,005 mg/kg, u bazitima 3 mg/kg, u neutralnim stijenama 7 mg/kg, a u kiselim stijenama 18 mg/kg. Od sedimentnih stijena srednji sadržaj u šejlovima je 12 mg/kg, pješčenjacima 5,5 mg/kg, a u karbonatima 1,7 mg/kg. Tla sadrže oko 13 mg/kg torija. Slatka voda ima srednji sadržaj torija 0,0001 mg/L.

Torij dolazi u mnogim rezistentnim mineralima pa se stoga ne oslobađa lako u okoliš. Mobilnost mu je vrlo malazbog velike otpornosti tih minerala na trošenje. Jedino se razmjerno lako oslobađa iz apatita i tada se može adsorbirati na minerale glina i na Al-hidrokside. U tlu se najvećim dijelom akumulira iz matičnih stijena podloge.

Torij nije esencijalni element. Neke biljke koncentriraju ovaj element pa može dospjeti u ljudski organizam preko hrane.

Godišnja svjetska produkcija torija u 1984. godini procijenjena je na oko 700 t.

U metalurgiji torij se rabi za visokotemperaturne materijale, legure, specijalna stakla i kao gorivoza reaktore.

U okoliš ovaj metal dospijeva spaljivanjem fosilnih goriva (posebice ugljena) i uslijed nuklearnih akcidenata.

Thorium is a lithophile trace element from the actinides group which is associated with uranium, cerium, lanthanum, and other rare earth elements. According to its abundance thorium is ranked 37th in the Earth's crust.

The average content of this element is 0.005 mg/kg in ultramafic rocks, 3 mg/kg in basalts, 7 mg/kg in neutral rocks and 18 mg/kg in acidic rocks. Among sedimentary rocks shales contain in average 12 mg/kg, sandstones 5.5 mg/kg and carbonates 1.7 mg/kg. Soils contain around 13 mg/kg of thorium in average and the sweet water about 0.0001 mg/L.

Thorium occurs in many resistant minerals, the fact preventing its easy released into environment. Its mobility is very low owing to the high resistance of these minerals to weathering. It is only relatively easily released from apatite and then it can be adsorbed on the clay minerals and Al-hydroxides. In soil it is mostly accumulated from the bedrock parent material.

Thorium is not an essential element. Some plants concentrate this element so that it can enter the human organism by food.

The annual world production of thorium in the year 1984 was estimated at about 700 t.

U metallurgy thorium is used for high temperature materials, alloys, special glass and fuel in reactors.

This metal appears in the environment due to the combustion of the fossil fuels (particularly coal) and nuclear accidents.

Izmjerene koncentracije torija na istraživanom području variraju od 0,5 do 7,4 mg/kg s medijanom od 2,9 mg/kg. One ne prelaze izračunate ekstremne vrijednosti. Maksimalna vrijednost ovog elementa u tlu registrirana je u krugu Željezare Sisak kao i većina drugih anomalnih koncentracija. Povišene vrijednosti registrirane su i u blizini termoelektrane. Disperzija torija iz industrijskih pogona je prema sjeveru odnosno sjeveroistoku i

The measured concentrations of thorium in the investigated area vary from 0.5 to 7.4 mg/kg with median of 2.9 mg/kg. They do not exceed the calculated extreme values. Maximum value of this element in the soil is registered within the circle of the steelworks. The majority of other anomalous concentrations are also found in the circle or in the immediate vicinity of this industrial plant. Increased values are also registered

nesumnjivo je da su te povećane koncentracije posljedica industrijske proizvodnje te da su antropogenog podrijetla.

Povećani sadržaji torija u Fistrovićevoj ulici vjerojatno su posljedica željezničkog prometa, jer su uzorci tla u tom području uzeti između željezničke pruge i prometne ulice.

Anomalna koncentracija torija zabilježena je i u krugu gradskog vodovoda „Kopa“. Podrijetlo torija na toj lokaciji i na lokacijama prema istoku najvjerojatnije je geogeno.

Na temelju prostorne raspodjele ovog elementa u tlu vidljiva je jasna razlika u koncentraciji torija između tala koja su nastala iz siliciklastičnih aluvijalnih sedimenata rijeka Kupe i Odre (više minerala gline i teške mineralne frakcije, npr. cirkona) i onih koja su nastala na poplavnim sedimentima rijeke Save. Koncentracije torija u tlima u dolinama Kupe i Odre su povišene do visoke, dok su one u tlima na aluviju rijeke Save ispod vrijednosti medijana.

Urbana cjelina grada Siska (lokacije antičkih naselja) ima niske vrijednosti torija, što je vjerojatno posljedica jake urbanizacije tog područja.

Područje Mošćenice pokazuje također povišene sadržaje torija u tlu, vjerojatno vezane na organsku tvar i geogenog su podrijetla bez utjecaja industrije s istoka. Između željezare i ovih lokacija s povećanom koncentracijom torija prostire se oko dva kilometra širok pojas s vrlo niskim vrijednostima torija u tlu.

close to the thermal power plant. Dispersion of thorium from the industrial processing plants is toward the north and northeast which undoubtedly corroborates the fact that the increased concentrations are the result of industrial production and are of anthropogenic origin.

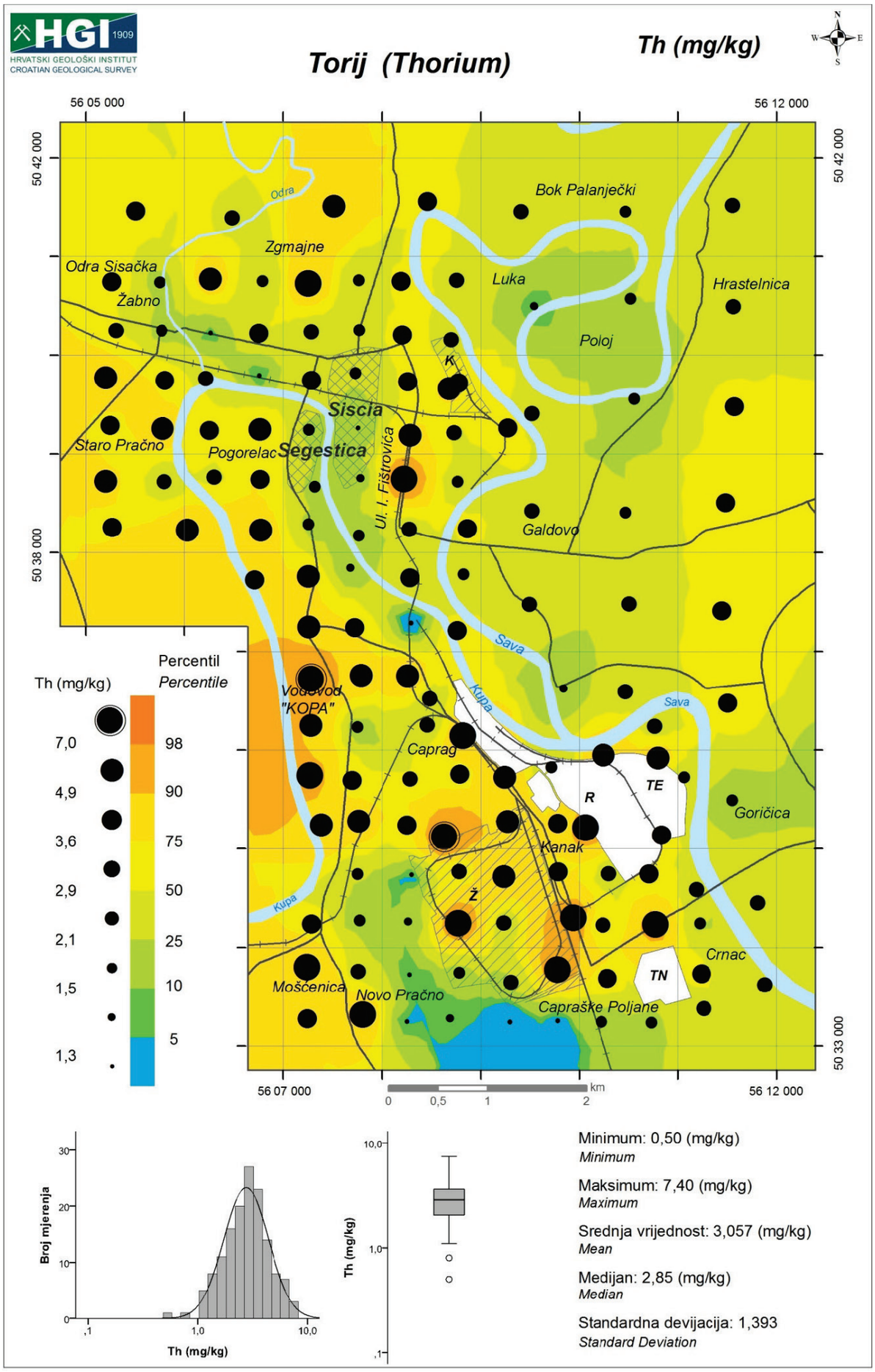
Increased contents of thorium in the Fištrović's Street are probably the result of the railroad traffic because the soil samples on this area are collected between the railroad tracks and a busy street.

Anomalous concentration of thorium is also registered in the circle of the municipal water supply line of „Kopa“. The origin of thorium on this location as well as on the locations toward the east is most probably geogenic.

Based on the spatial distribution of this element in the soil it is obvious clear difference in the thorium concentration existing between the soils developed from the siliciclastic alluvial sediments of the Kupa and Odra Rivers (more clay minerals and heavy mineral fraction such as zircon) and those originated on the floodplain sediments of the Sava River. Concentrations of thorium in the soils in the valleys of the Kupa and Odra Rivers are increased to high while those in the soils developed on the alluvium of the Sava River are below the median value.

The urban core of the Old Sisak (Siscia and Segestica) contains low thorium values which are probably the result of strong urbanization of this area.

The area of Mošćenica also shows increased contents of thorium in the soil which is here probably associated with organic matter and is of geogenic origin without the industrial impact from the east. Between the ironwork and these locations with the increased concentrations of thorium there is almost two kilometers wide belt with very low values of thorium in the soil.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Torij (Thorium)
Th (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Ul. I. Fištrovića
Galdovo
Sava
Kupa
Vodovod "KOPA"
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Th (mg/kg)
7,0
4,9
3,6
2,9
2,1
1,5
1,3
Percentil
Percentile
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Th (mg/kg)
10,0
1,0
,1
Minimum: 0,50 (mg/kg)
Minimum
Maksimum: 7,40 (mg/kg)
Maximum
Srednja vrijednost: 3,057 (mg/kg)
Mean
Medijan: 2,85 (mg/kg)
Median
Standardna devijacija: 1,393
Standard Deviation

Ti

10.38. Ti – TITANIJ (atomski broj 22) TITANIUM (atomic number 22)

Titanij je litofilni sporedni element i prema učestalosti u Zemljinoj kori je na 9. mjestu. S porastom alkaliniteta magme sadržaj titanija se povećava. Sklon je tvorbi akcesornih minerala.

U magmatskim stijenama srednji sadržaj titanija je 0,57 % (ultrabaziti 0,08 %, oceanski toleitni bazalti 0,9 %, bazalti 0,9 do 1,4 %, granodioriti 0,34 % i graniti 0,12 %). Srednji sadržaj titanija u šejlovima je 0,46 %, u pješčenjacima 0,15 %, a u karbonatima 0,04 %. U najčešćim tipovima tala koncentracija titanija kreće se od 0,1 do 1 %, sa srednjom vrijednošću oko 0,5 %. Koncentracija titanija u ugljenu kreće se od 500 do 7 400 mg/kg, a u sirovoj nafti ga ima oko 0,1 mg/kg. Veća je koncentracija u tlima tropskih krajeva (lateriti), nego u područjima umjerene klime. Kad jednom uđe u tlo, praktički je netopiv od pH 4 do pH 8. U slatkoj vodi srednji sadržaj titanija iznosi oko 0,003 mg/L. Topiv je preko organskih kompleksa.

Minerali koji sadrže titanij su jako rezistentni tako da je ovaj element slabo mobilan. Akcesorni minerali su najčešće otporni na trošenje pa se titanij u potočnom nanosu sakuplja u sitnoj frakciji (teškim mineralima). Nakon oslobađanja iz Fe-Mg silikata koji se relativno lako troše, titanij se adsorbira na minerale glina. Povećana mobilnost zapažena je u podzolima, jer pH i prisutnost organskih kiselina može imati važnu ulogu u njegovoj mobilnosti.

Titanij nije esencijalni element. Koncentrira se u nekim radiolarijama, silicijskim spužvama i ascidima. Neznatno je otrovan do neotrovan. Veće koncentracije ovog elementa mogu u tijelo dospijeti iz implantata, ali bez većih posljedica. Hrana je glavni izvor titanija u tijelu.

Procijenjena svjetska produkcija ovog metala u 2003. godini iznosila je 4 220 000 t. Ovaj metal se najčešće dobiva iz ilmenita i rutila,dodatno i kao nusprodukt kod proizvodnje željeza iz ilmenita.

Titanij se najviše primjenjuje u zrakoplovstvu i vojnoj industriji. Osim toga, upotrebljava se za boje i pigmente (bijela boja), u medicini za ortopedske implantate i proteze. Služi i kao katalizator u proizvodnji polietilena. Titanijski dioksid se koristi u kozmetici, a dodaje se i u zubne paste.

Raspršenje u okoliš se ne prepoznaje zbog njegova visokog udjela u geološkoj građi. U okoliš ovaj metal dospijeva iz industrijskih pogona (Ti-legure, Ti-boje), ali ne uzrokuje nikakve veće okolišne probleme.

Titanium is a lithophile minor element which is 9th in abundance in the Earth's crust. Its content is increasing with the increase of the magma alkalinity. Titanium is prone to formation of accessory minerals.

The average content of titanium in igneous rocks is 0.57 % (ultramafic rocks 0.08 %, oceanic tholeiite basalts 0.9 %, basalts 0.9 to 1.4 %, granodiorites 0.34 % and granites 0.12 %). Its average content in shales is 0.46 %, sandstones 0.15 %, and in carbonates 0.04 %. In the most common types of soils the concentration of Ti varies from 0.1 to 1 % with mean value of about 0.5 %. Concentration of titanium in coal is between 500 and 7,400 mg/kg and in the crude oil is 0.1 mg/kg. The concentration is higher in the soils of the tropical zones (laterites) with respect to those in the soils of the temperate climate zones. Once entered the soil it is practically insoluble within the pH range of 4 to 8. In the sweet water the content of titanium is about 0.003 mg/L. Titanium is soluble via the organic complexes.

Minerals containing titanium are very resistant which is why this element is lowly mobile. Accessory minerals are most often resistant to weathering so that Ti in the stream sediments is accumulating in the fine fraction (heavy minerals). After releasing from the Fe-Mg silicates which weather relatively easily, titanium is adsorbed on the clay minerals. Enhanced mobility is observed in the podzols since the pH value and the presence of organic acids can play an important role in its mobility.

Titanium is not an essential element. It is concentrated in some radiolarians, silica sponges and ascidia. It is slightly toxic to harmless. Greater concentrations of this element can enter organism via the implants although without major effects. Besides, the food is the main source of titanium in the body.

Estimated world production of this metal in the year 2003 was 4,220,000 t. This metal is most often produced from ilmenite and rutile. Additionally, it can be obtained as a by product in production of iron form ilmenite.

Titanium is most often applied in the aviation and in military industry. Besides, it is used for paints and pigments (white color) and in medicine (for orthopedic implants and artificial limbs). It also serves as a catalyst in the production of polyethylene. Titanium dioxide is utilized in cosmetics and is also added to the toothpastes.

Dispersion into environment is not recognized due to its great share in the geological setting. It is dispersed into the environment from the industrial plants (Ti-alloys, Ti-paints) but without causing any significant environmental problems.

Prema prostornoj raspodjeli titanija u tlima istraživanog područja vidljivo je da su ekstremne, anomalne i visoke koncentracije skoro isključivo vezane za industrijski i uži urbani dio. Izmjerene koncentracije variraju od 0,004 do 0,15 % s medijanom od 0,009 mg/kg. Relativno niske koncentracije ovog metala u tlu na čitavom istraživanom području posljedica su slabe topivosti minerala domaćina u zlatotopki (teška mineralna frakcija-ilmenit, titanit, cirkon i dr.). Maksimalna koncentracija registrirana je u krugu Željezare Sisak, što je bilo i za očekivati. U krugu Željezare i ostali analizirani uzorci tla imaju također anomalne do ekstremne koncentracije titanija.

Ekstremne vrijednosti ovog elementa registrirane su i u uzorcima uz željezničku prugu u industrijskoj zoni. U većim količinama titanij je u tlo dospio zbog industrijske proizvodnje, putem metalne prašine nastale habanjem tračnica i željezničkih kotača te sagorijevanjem fosilnih goriva (ugljen i dizelsko gorivo). Dodatni dio titanija u tlu potječe od automobilskog prometa. U blizini termoelektrane također su zabilježene anomalne vrijednosti titanija u tlu, što je posljedica spaljivanja mazuta u tom industrijskom pogonu.

Ekstremne i anomalne koncentracije titanija zabilježene su skoro na čitavom području naselja Kanak te u dijelu naselja Caprag, bliže željezari. Prema obliku rasprostiranja oko industrijskih pogona može se reći da transport ovog elementa nakon njegove emisije u zrak nije bio dug.

U skoro čitavom dijelu urbanog područja grada te uz sve veće prometnice u gradu, registrirane su povišene, visoke, a dijelom i anomalne koncentracije titanija u tlu. Jedan dio povišenih vrijednosti ovog elementa u tlu na tim lokacijama potječe od spaljivanja fosilnih goriva (ugljen za grijanje), a drugi dio od automobilskog prometa (ispušni plinovi).

Periferni dijelovi grada (Galdovo, Hrastelnica, Goričica, Mošćenica i Staro Pračno) imaju niske ili vrlo niske koncentracije titanija u tlu. Budući da su na tim loka-

According to the spatial distribution of titanium in the soils of the investigated area it is clear that extreme, anomalous and high concentrations are almost exclusively related to industrial zone urban core. The measured concentrations vary from 0.004 to 0.15 % with median of 0.009 mg/kg. Relatively low concentrations of this metal in the soil on the entire investigated area are the consequence of low solubility of the host minerals in aqua regia (heavy mineral fraction-ilmenite, titanite, zircon etc.). Maximum concentration is registered, as expected, within the circle of the steelworks. The other analyzed samples in the steelworks circle also show anomalous to extreme concentrations of titanium.

Extreme values of this element are also registered in the samples along the railroad in the industrial zone. Titanium appears in the soil in greater quantities as a result of industrial activity, metal dust produced by the wearing of railway tracks and train wheels, as well due to combustion of fossil fuels (earlier coal and recently diesel fuel in the train engines). Additional portion of titanium originates from automobile traffic. In the vicinity of the thermal power plant anomalous values of titanium are also registered which is a result of incineration of the crude oil in this processing plant.

Extreme and anomalous concentrations of titanium are recorded on almost entire area of the Kanak and, partly, Caprag settlements which are situated closer to the steelworks. According to the shape of its distribution around the industrial processing plants it can be said that the transport of this element after it had been emitted into the air was not long.

In almost entire urban part of the city as well as along the major traffic lines increased and, partly, also anomalous concentrations of titanium in the soil are registered. A portion of increased values of this element in the soil on these locations originate from the combustion of fossil fuels (coal for heating) while another part derives its origin form the automobile traffic (gaseous emissions).

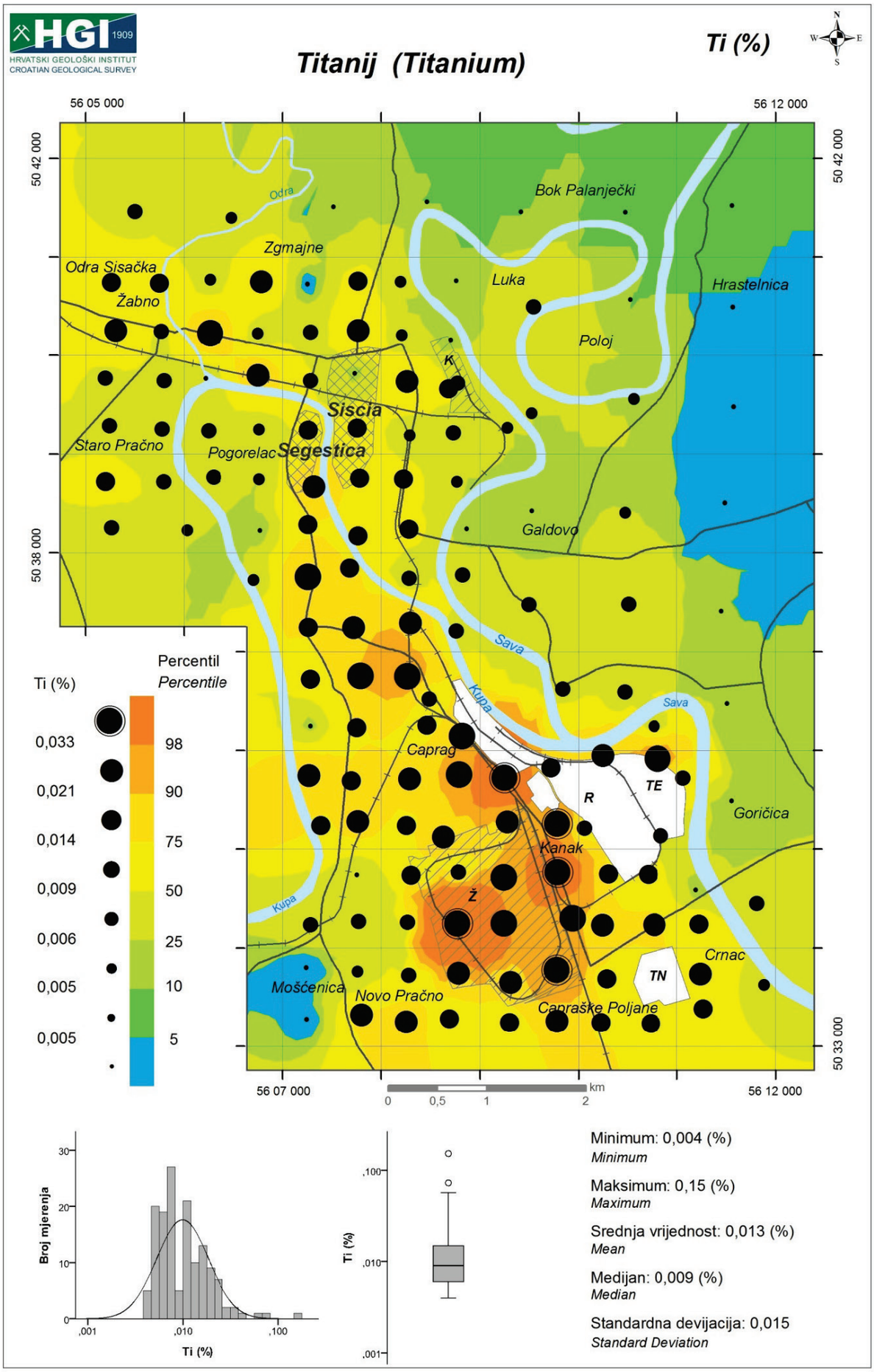
cijama sadržaji ovog elementa geogenog podrijetla, može se vidjeti razlika u sadržajima između tala na poplavnoj ravnici Save i tala na aluviju rijeka Kupe i Odre (drugačiji izvorišni materijal za matični supstrat).

Peripheral parts of the city (such as Galdovo, Hrastelnica, Goričica, Mošćenica and Staro Pračno settlements) contain low or very low concentrations of titanium in the soil. Since the contents of titanium on these locations are of geogenic origin there is clear difference visible between the contents of this element on the soil types developed on the floodplain of the Sava River on the one side and those on the alluvium of the Kupa and Odra Rivers on the other (different source area of the parent material).



Slika 10.22. *Povrtnjak u naselju Kanak između Željezare i Rafinerije nafte (Foto: J. Halamić).*

Figure 10.22. *Vegetable garden in the Kanak settlement between the steelworks and petroleum refinery (Photo: J. Halamić).*


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Titanij (Titanium)
Ti (%)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Ti (%)
Percentil
Percentile
0,033
0,021
0,014
0,009
0,006
0,005
0,005
98
90
75
50
25
10
5
Broj mjerenja
30
20
10
0
,001
,010
,100
Ti (%)
,100
,010
,001
Minimum: 0,004 (%)
Minimum
Maksimum: 0,15 (%)
Maximum
Srednja vrijednost: 0,013 (%)
Mean
Medijan: 0,009 (%)
Median
Standardna devijacija: 0,015
Standard Deviation

Tl

10.39. Tl – TALIJ (atomski broj 81) THALLIUM (atomic number 81)

Talij je rijedak litogeni i halkofilni element u tragovima i nalazi se po učestalosti pojavljivanja u Zemljinoj kori na 59. mjestu. On je često asociran s kalijem i rubidijem.

Koncentracija ovog elementa u magmatskim stijenama povećava se s kiselošću, a u sedimentima ona raste sa sadržajem glinovite komponente. Sadržaj talija u ultrabazitima kreće se od 0,05 do 0,2 mg/kg, u bazitima od 0,1 do 0,4 mg/kg, neutralnim stijenama od 0,5 do 1,4 mg/kg i kiselim stijenama od 0,6 do 2,3 mg/kg. U sedimentnim stijenama sadržaj talija u šejlovima kreće se od 0,5 do 2 mg/kg, pješčenjacima od 0,4 do 1 mg/kg i u karbonatima (vapnenci i dolomiti) od 0,01 do 0,14 mg/kg. Visoke koncentracije, zabilježene u nekim ugljenima, upućuju na njegov afinitet prema organskoj tvari. U tlima sadržaj talija varira od 0,014 do 2,4 mg/kg.

O mobilnosti talija u sekundarnom okolišu ne zna se mnogo. On se otpušta u okoliš trošenjem K-minerala ili sulfida. Slobodni talij veže se vjerojatno na minerale glina. U reduktivnim uvjetima on ulazi u kristalne rešetke novo formiranih sulfida.

Talij nije esencijalni element, ali je jako otrovan. Svrstava se po otrovnosti uz Pb, Hg i Cd. Simptomi trovanja su nesanica, glavobolja, polineuralni simptomi, umor i ćelavost. Neke biljke, kao npr. duhan, su osjetljive na trovanje talijem, dok su druge na njega otporne. Biljke vrlo lako uzimaju talij putem korijenja. Talij ima snažnu tendenciju akumulacije u vodi.

Svjetska produkcija talija je zadnjih desetljeća dosta stabilna, a 2000. godine ona je procijenjena u rasponu od 10 000 do 15 000 t na godinu. Talij se pretežito dobiva u proizvodnji cinka, a u manjoj mjeri i kod proizvodnje Pb, Cu, Fe te Au i U.

Koristi se za raznovrsne legure, ali zbog toksičnosti u ograničenim količinama. Najveći dio ovog elementa koristi se u elektroničkoj industriji. U medicini se talij koristi kao radioizotop za scintigrafiju i za dijagnozu melanoma. Ovaj element koristio se prije i u pesticidima (rodenticidima i insekticidima), ali u današnje vrijeme se zbog visoke toksičnosti ne koristi.

U okoliš se raspršuje spaljivanjem ugljena, iz talionica teških metala, proizvodnjom cementa, iz rafinerija i spaljivanjem krutog otpada. U okolici rudnika žive, cinka i olova mogu se u tlu pojaviti povišeni sadržaji ovog elementa. Koncentarcije talija u tlu > 1 mg/kg indiciraju onečišćenje te bi stoga ta vrijednost trebala predstavljati gornju dozvoljenu granicu za poljoprivredna tla.

Thallium is a rare lithogene and chalcophile trace element which is 59th in abundance in the Earth's crust. It is commonly associated with potassium and rubidium.

Concentration of this element in igneous rocks increases with increase of acidity. In sedimentary rocks it increases with increase of the clay component. The content of thallium in ultramafic rocks varies between 0.05 and 0.2 mg/kg, in mafic rocks from 0.1 to 0.4 mg/kg, neutral rocks 0.5 to 1.4 mg/kg and acidic rocks from 0.6 to 2.3 mg/kg. In sedimentary rocks the content of thallium is from 0.5 to 2 mg/kg for shales, 0.4 to 1 mg/kg for sandstones and 0.01 to 0.14 mg/kg for carbonates (limestones and dolomites). High concentrations registered in some coals indicate its affinity towards organic matter. In soils the content of thallium varies from 0.014 to 2.4 mg/kg.

Little is known about mobility of thallium in the secondary environment. It is released into environment by weathering of K-minerals or sulfides. Free Tl is probably bonded on clay minerals. In the reducing environments thallium enters the crystal lattices of the newly formed sulfides.

Thallium is not an essential element but its toxicity is very high. According to toxicity it is ranked by Pb, Hg and Cd. Symptoms of poisoning are insomnia, headache, polineural symptoms, tiredness, and baldness. Some plants such as tobacco are very sensitive to thallium poisoning while others are very resistant to it. Plants extract thallium easily through their roots. There is a strong tendency to accumulation of thallium in the water environments.

The world production of thallium in the last few decades is rather stabile. In the year 2000 it was estimated at 10,000 to 15,000 t per year. Thallium is predominantly produced as a byproduct of zinc and, to the lesser extent, during production of Pb, Cu, Fe, Au and U.

Thallium is used for various alloys but only in limited quantities due to its toxicity. The most part of this element is utilized in electronic industry. In medicine thallium is applied as a radioisotope for scintigraphy and in melanoma diagnosis. This element was formerly used in pesticides (rodenticides and insecticides) but recently is out of use owing to its high toxicity.

It is dispersed into the environment by the combustion of coal, from the metal foundries, by the production of cement and incineration of solid waste. Increased contents of this element can appear in soils around the mercury, zinc and lead mines. Concentrations of thallium in the sols > 1 mg/kg indicate pollution which is why this value should represent the upper limit allowed for agricultural soils.

Talij spada u grupu potencijalno toksičnih elemenata i obuhvaćen je preporučenim graničnim vijednostima u *Programu trajnog motrenja tala Republike Hrvatske* (MESIĆ et al., 2008.). Po prostornoj raspodjeli tog elementa na istraživanom području vidljiva su dva izvorišta povećanih koncentracija u tlu: industrijsko tj. antropogeno i geogeno.

Izmjerene koncentracije talija u tlu su u rasponu od 0,05 do 0,62 mg/kg s medijanom od 0,15 mg/kg. Maksimalna vrijednost registrirana je u neposrednoj blizini Termoelektrane Sisak. Drugi uzorci u neposrednoj blizini tog industrijskog pogona imaju povećane vrijednosti talija u tlu. Na ovom lokalitetu također je vidljiva

Thallium belongs to the group of potentially toxic elements and is included in "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" (MESIĆ et al., 2008). From the spatial distribution of this element in the investigated area one can observe two sources of elevated concentrations in soil, industrial (anthropogenic) and geogenic.

The measured concentrations of thallium in the soil vary between 0.05 and 0.62 mg/kg with median of 0.15 mg/kg. Maximum value is registered in the immediate vicinity of the thermal power plant. Other soil samples close to this industrial plant also contain increased va-



Slika 10.23. *Ušće rijeke Kupe u Savu i Stari grad u Sisku (Foto: Ž. Rakarić).*

Figure 10.23. *Confluence of the River Kupa and River Sava and the old citadel of Sisak (Photo: Ž. Rakarić).*

disperzija u okoliš pomoću vjetra, ali je transport relativno kratak. Drugo područje s anomalnim i povećanim koncentracijama ovog elementa u tlu s antropogenim podrijetlom su tla u Fistrovićevoj ulici. Lokacija se nalazi između ceste i pruge pa talij vjerojatno potječe od parnih lokomotiva koje su nekad prometovale prugom ili je zemljište naveženo prilikom gradnje ceste.

Područja Mošćenice i park-šume, zapadno od željezare, pokazuju ekstremne i anomalne koncentracije talija, ali su one vjerojatno geogenog podrijetla. Tla na tim lokacijama su pretežito šumska tla, bogata organskom komponentom i mineralima glina, na koja je ovaj element vezan.

Povećane i anomalne vrijednosti talija u tlu izmjerene su i na lokacijama u dolinama rijeka Kupe i Odre. Tla na tim područjima bogata su mineralima glina i Mn i Fe oksi-hidroksidima koji su također dobri receptori za ovaj element.

Urbano područje Siska, centralni dijelovi Željezare Sisak i Rafinerije nafte Sisak te tla na aluvijalnim sedimentima rijeke Save imaju niske ili vrlo niske koncentracije talija.

Preporučene granične vrijednosti za talij prema *Programu trajnog motrenja tala Republike Hrvatske* (MESIĆ et al., 2008.) su 1 mg/kg za poljoprivredna tla i dječja igrališta, 2 mg/kg za stambena područja, 5 mg/kg za parkove te 20 mg za industrijska područja (Tab. 6.2.). Maksimalna izmjerena koncentracija talija je 0,62 mg/kg pa se može reći da tla na istraživanom području nisu onečišćena ovim potencijalno toksičnim metalom.

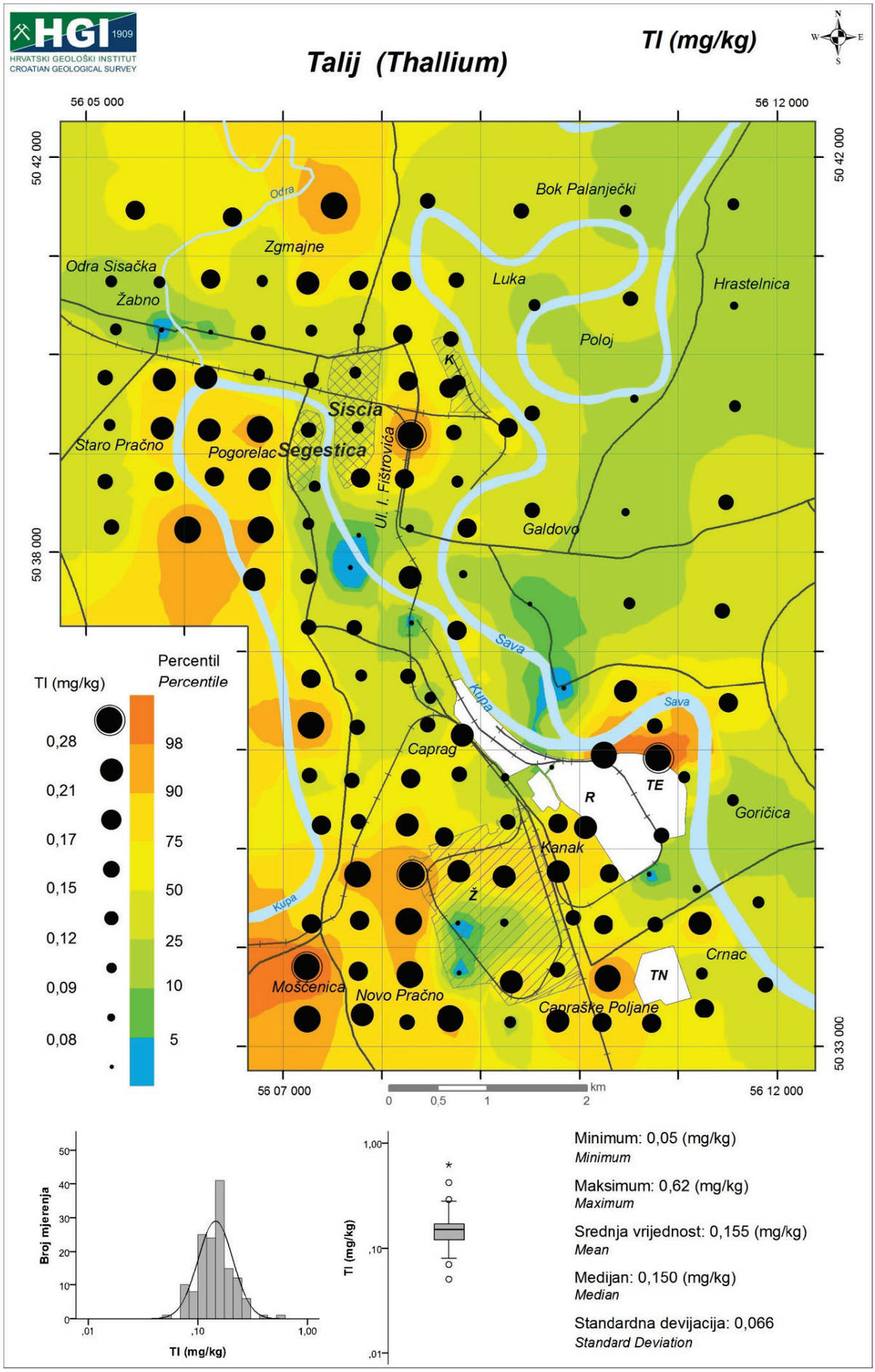
lues of thallium. On this locality is also clear the dispersion into environment by means of wind but the transport is relatively short. Another area with anomalous and increased concentrations of this element originating from anthropogenic source is the Fištrović's Street. This location is between the road and the railway so that thallium probably derives from the steam powered machines once used for the railway transport. Another possibility is that the soil is brought to the place during the road construction.

The areas of Mošćenica and the forest park on the west side of the steelworks show extreme and anomalous concentrations of thallium but these are probably geogenic in origin. Soils on these locations are predominantly the forest soils rich in organic matter and clay minerals on which this element is bonding.

Increased and anomalous values of thallium in the soil are also measured in the valleys of the Kupa and Odra Rivers. Soils on these terrains are rich in clay minerals and Fe-Mn oxy-hydroxides which are good receptors for this element as well.

Urban core of the Sisak city, central portions of the steelworks and oil refinery together with soils on the alluvial sediments of the Sava River contain low or very low concentrations of thallium.

Recommended trigger values for thallium according to the "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" (MESIĆ et al., 2008) are 1 mg/kg for agricultural soils and children playgrounds, 2 mg/kg for residential areas, 5 mg/kg for parks, and 20 mg for industrial zones (Tab. 6.2.). Maximum measured concentration of thallium is 0.62 mg/kg and on this ground one can say that the soils in the investigated area are not polluted by this potentially toxic metal.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Talij (Thallium)
Tl (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Ul. I. Fištrovića
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
Tl (mg/kg)
Percentil
Percentile
0,28
0,21
0,17
0,15
0,12
0,09
0,08
98
90
75
50
25
10
5
56 07 000
56 12 000
0
0,5
1
2
km
Broj mjerenja
Tl (mg/kg)
,01
,10
1,00
Minimum: 0,05 (mg/kg)
Minimum
Maksimum: 0,62 (mg/kg)
Maximum
Srednja vrijednost: 0,155 (mg/kg)
Mean
Medijan: 0,150 (mg/kg)
Median
Standardna devijacija: 0,066
Standard Deviation

U

10.40. U – URANIJ (atomski broj 92) URANIUM (atomic number 92)

Uranij je litofilni element u tragovima iz grupe aktinida. Obogaćuje se u kori Zemlje porastom alkaliniteta magme. Prateći je element torija (Th / U = 4). Razdvajanje nastaje tijekom hidrotermalnih procesa, u procesu trošenja i ciklusu sedimentacije. Uranij zauzima 48. mjesto po učestalosti pojavljivanja u Zemljinoj kori.

Prosječna vrijednost uranij u magmatskim stijanama je 2,7 mg/kg (ultrabaziti 0,02 mg/kg, oceanski toleitni bazalti 0,1 mg/kg, bazalti 0,1 mg/kg, granodioriti 2,3 mg/kg i graniti 4,7 mg/kg). Od sedimentnih stijena šejlovi imaju najviši sadržaj uranija 3,7 mg/kg, zatim slijede karbonati s 2,2 mg/kg i pješčenjaci s 0,45 mg/kg. U fosforitima i crnim škriljavcima asociran je s P, As, V, Mo, Se, Pb, Cu i dr. Adsorpcijom se akumulira u ugljenu, tresetu i mineralima glina. U tlima prosječna koncentracija uranija varira od 1,2 do 11 mg/kg. Sadržaj uranija u slatkoj vodi kreće se od 0,00005 do 0,005 mg/L. U humidnoj klimatskoj zoni on se u vodi nalazi otopljen kao UO_2^{2+}, a drugdje je pretežito vezan na karbonatne, fosfatne i organske komplekse.

Mnogi minerali koji sadrže uranij su otporni na trošenje. Kao posljedica toga, uranij se koncentrira u pijescima teških minerala.

Uranij je u reduktivnim uvjetima imobilan. Kao U^{6+} je jako mobilan pod oksidativnim uvjetima u kiselim i karboantnim otopinama, dok je kao U^{4+} skoro imobilan. Adsorbira se na organsku tvar, minerale glina, fosfate, a obogaćen je u precipitatima silikata, fosfata, karbonata ili vanadata. U vodotočnim sedimentima vezan je pretežito za tešku mineralnu frakciju.

Uranij nije esencijalni element. On je kemotoksičan, radiotoksičan i kancerogen (svi prirodni uranijevi izotopi emitiraju α-zrake). Osim radioaktivnog zračenja svi spojevi uranija su umjereno otrovni za sve organizme. Aktinidi, pa tako i uranij u ljudsko tijelo dospijevaju preko hrane. U organizmu se akumulira u plućima, bubrezima, jetri i kostima.

Svjetska produkcija uranija u 2003. godini procijenjena je na oko 35 370 t.

Koristi se kao gorivo u nuklearnim elektranama, u vojnoj industriji, a prije se upotrebljavao za bojanje keramike i stakla.

Dispergira se u okoliš testiranjem nuklearnih bojevih glava i streljiva, atomskih bombi te akcidentima u nuklearnim elektranama. Okoliš industrijskih postrojenja za proizvodnju umjetnih mineralnih gnojiva može imati povećane sadržaje ovog elementa u tlu. Nadalje, uranij dospijeva u okoliš spaljivanjem fosilnih goriva te upotrebom fosfatnih umjetnih gnojiva.

Uranium is a lithophile trace element from the actinide group. It is enriched in the Earth's crust with increasing alkalinity of magma. Uranium is accompanying element with thorium (Th / U = 4). Separation occurs through the hydrothermal processes, in the process of weathering and during the sedimentary cycle. Uranium is 48th element in abundance in the Earth's crust.

The average content of U in igneous rocks is 2.7 mg/kg (ultramafic rocks 0.02 mg/kg, oceanic tholeiite basalts 0.1 mg/kg, basalts 0.1 mg/kg, granodiorites 2.3 mg/kg and granites 4.7 mg/kg). Among sedimentary rocks shales contain the greatest quantities of uranium with 3.7 mg/kg followed by carbonates with 2.2 mg/kg and sandstones with 0.45 mg/kg. In phosphorites and black shales it is associated with P, As, V, Mo, Se, Pb, Cu etc. Uranium is accumulated by adsorption in coals, peat and clay minerals. The average quantity in soil varies from 1.2 to 11 mg/kg. In sweet water it is present with 0.00005 to 0.005 mg/L. In waters of the humid climate zone it is found dissolved as UO_2^{2+}, and elsewhere is predominantly bonded on carbonates, phosphates, and organic complexes.

Many minerals containing uranium are resistant to weathering. As consequence uranium is concentrated in sands of heavy minerals.

Uranium in reducing conditions is mobile. As U^{6+} it is highly mobile under oxidizing conditions in acid and carbonate solutions but U^{4+} it is almost immobile. It is adsorbed on organic matter, clay minerals and phosphates. It is enriched in precipitates of silicates, phosphates, carbonates and vanadates. In stream sediments uranium is prevalently associated with heavy mineral fraction.

Uranium is not essential element. It is chemotoxic, radiotoxic and carcinogenic (all natural uranium compounds emit α-rays. Besides radioactive radiation all uranium compounds are moderately toxic for all organisms. Actinides, uranium including, enter the human body by food. In organism it is accumulated in lungs, kidneys, liver and bones.

The world production of uranium in the year 2003 is estimated at about 35,370 t.

Uranium is used as fuel in the nuclear power plants and in military industry. Previously it was utilized for painting ceramics and glass.

It is dispersed into environment by testing of the nuclear warheads and by accidents in the nuclear power plants. In the neighborhood of industrial processing plants such as, for example, the industry of chemical mineral fertilizers, the concentration of this element in the soil can be increased. Also, the same can be expected the ports carrying out the trans-shipment of loose mineral raw materials (phosphates). Further, uranium enters the environment by combustion of fossil fuels and through the use of phosphate chemical fertilizers.

Prema prostornoj raspodjeli uranija može se zaključiti da su ekstremne i anomalne koncentracije u tlu najvećim dijelom vezane za industrijsko i uže urbano područje te su na temelju toga antropogenog podrijetla. Drugi, manji dio uzoraka s povećanim koncentracijama, nalazi se izvan industrijskog područja i urbanih cjelina te su stoga te vrijednosti geogenog podijetla.

Izmjerene koncentracije ovog elementa su u rasponu od 0,2 do 7,9 mg/kg s medijanom od 0,9 mg/kg. Maksimalna vrijednost registrirana je u krugu Željezare Sisak. Najveće koncentracije vezane su za sva tri industrijska kompleksa na jugu istraživanog područja i to Željezaru Sisak, Rafineriju nafte Sisak i Termoelektranu Sisak. Na karti prostorne distribucije vidljiva je i jasna disperzija uranija iz termoelektrane u zrak te transport vjetrom prema sjeveru sve do naselja Galdovo. Ekstremne, anomalne i visoke koncentracije uranija registrirane su i u naseljima u blizini ovih industrijskih postrojenja (Caprag i Kanak).

Ekstremne, anomalne i visoke vrijednosti uranija u tlu utvrđene su također i u naselju Zeleni brijeg u sjevernom dijelu grada. Dio s povećanim vrijednostima na tom području proteže se od željezničkog kolodvora u pristaništu na Kupi pa do postrojenja kemijske industrije „HERBOS“. Nesumnjivo je da su i ove koncentracije uranija u tlu antropogenog podrijetla.

Područje Mošćenice i tla na aluviju rijeke Kupe, prema sjeveru do Pogorelca, posjeduju također ekstremne i anomalne sadržaje ovog elementa. U Mošćenici je uranij u tlu najvjerojatnije vezan za organsku tvar (šumska tla), a u tlima u dolini Kupe na Mn i Fe oksi-hidrokside.

Južni dijelovi užeg dijela grada Siska te prigradska naselja kao i ruralna područja imaju koncentracije uranija ispod ili znatno ispod medijana.

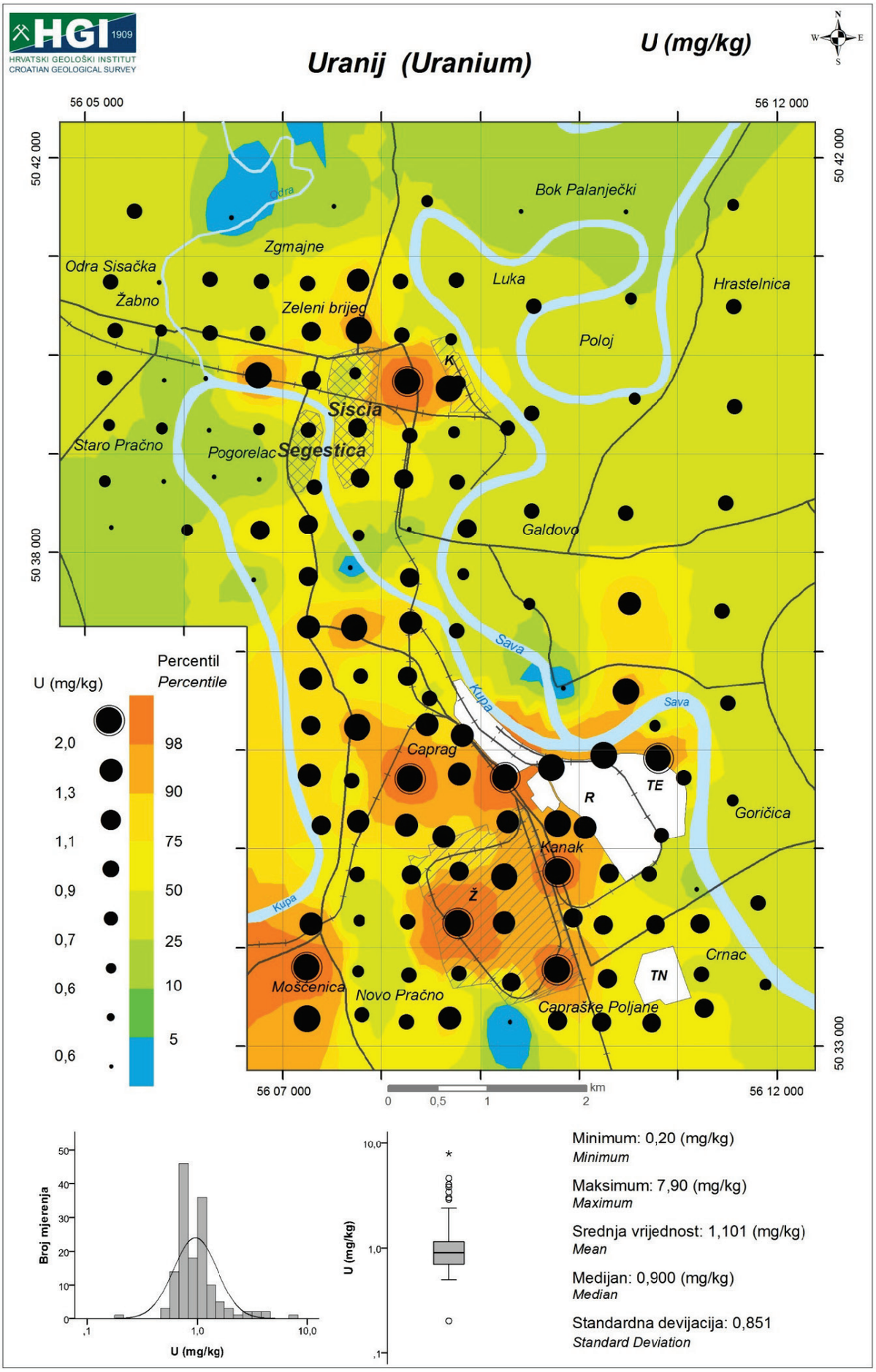
In accordance with the spatial distribution of uranium it can be deduced that extreme and anomalous concentration in the soil are for the most part associated with the industrial zone and the urban core indicating the anthropogenic origin. Another, minor part of the collected samples is found outside the industrial zone suggesting that the measured values are of geogenic origin.

The measured concentrations of this element range between 0.2 and 7.9 mg/kg with median of 0.9 mg/kg. Maximum value is registered within the circle of the steelworks. The greatest concentrations are related to all three industrial complexes on the south of the investigated area, namely the steelworks, oil refinery and thermal power plant. On the map of the spatial distribution an airborne dispersion of uranium form the thermal power plant into the environment is clearly displayed. It is obvious that airborne particles are transported by wind toward the north all the way to the Galdovo settlement. Extreme, anomalous and high concentrations of uranium are also registered in the settlements close to these industrial processing plants (Caprag and Kanak).

Extreme, anomalous and high values of uranium in the soil are also determined on the Zeleni Brijeg in the northern part of the town. Here, the terrain with increased values is extended from the railroad station at the Kupa river port all the way to the processing plants of the chemical industry „HERBOS“ to the east. Undoubtedly, all these concentrations of uranium in the soil derived from the geogenic origins.

The area of Mošćenica and soils on the alluvium of the Kupa River northward to Pogorelec are all characterized by extreme and anomalous contents of this element in the soil. In Mošćenica uranium in the soil is most probably bonded on organic (forest soils) while in the soils if the valley of the Kupa River on Fe-Mn oxy-hydroxides.

The southern parts of the Old Town of Sisak together with suburbia and rural areas are characterized by the concentrations of uranium below or significantly below the median.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Uranij (Uranium)
U (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Zeleni brijeg
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
R
TE
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
U (mg/kg)
2,0
1,3
1,1
0,9
0,7
0,6
0,6
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
U (mg/kg)
10,0
1,0
,1
Minimum: 0,20 (mg/kg)
Minimum
Maksimum: 7,90 (mg/kg)
Maximum
Srednja vrijednost: 1,101 (mg/kg)
Mean
Medijan: 0,900 (mg/kg)
Median
Standardna devijacija: 0,851
Standard Deviation

V

10.41. V – VANADIJ (atomski broj 23) VANADIUM (atomic number 23)

Vanadij je litofilni element u tragovima. Obogaćen je zajedno sa željezom u bazičnim i intermedijarnim (andezitsko-dioritskim) magmama. Prema učestalosti u Zemljinoj kori taj se element nalazi na 19. mjestu.

Od magmatskih stijena ultrabaziti imaju srednji sadržaj 40 mg/kg, oceanski toleitni bazalti i bazalti 250 mg/kg, granodioriti 88 mg/kg, a graniti 44 mg/kg. Šejlovi imaju srednji sadržaj 130 mg/kg, pješčenjaci 20 mg/kg, a karbonati 20 mg/kg. Kod šejlova relativno visok sadržaj tog elementa upućuje na sadržaj organske materije i na reduktivne uvjete postanka. Sadržaj ovog elementa u ugljenu je oko 20 mg/kg, sirovoj nafti 14 mg/kg, a u pogonskim gorivima oko 50 mg/kg. U oksidacijskom području tvori vanadate, ima ga u mineraliziranim pješčenjacima, u limonitnoj rudi, šejlovima, boksitima, crnim škriljavcima, fosforitima, bitumenu i ugljenu. Osim toga, vanadij može biti obogaćen u teškoj nafti, asfaltnim pijescima i u ugljenu.U tlu vanadij može zamijeniti željezo i adsorbirati se na Fe-hidrokside. Koncentracija se kreće od 3 do 500 mg/kg sa srednjom vrijednošću oko 90 mg/kg. Ukupna koncentracija vanadija u tlima koja su razvijena na pjeskovitim substratima manja je od koncentracije u tlima razvijenim na šejlovima i glinama. U slatkoj vodi vanadija ima oko 0,002 mg/L.

Vanadij je mobilan u oksidativnim uvjetima. Precipitira u prisutnosti Pb^{2+}. Sorpcija na Fe-Mn-oksi-hidrokside i organske tvari. Tijekom trošenja lako se oslobađa iz mnogih minerala domaćina te se adsorbira i apsorbira na i u minerale glina te Fe hidrokside.

Vanadij je bioelement za neke biljke, bitan za vezanje dušika (leguminoza). Široko je rasprostranjen u većini organizama. U određenim količinama otrovan je za ljude (V pentoksid – V_2O_5 je najotrovniji spoj). Potiče stvaranje klorofila i metabolizam željeza u nekim biljakama. U biljkama je sadržan u koncentracijama od 0,27 do 4,2 mg/kg (srednja vrijednost 1 mg/kg). Za biljke je u u većim koncentracijama otrovan (> 10 mg/kg u hranjivim tvarima), pri čemu otrovnost ovisi o valentnom stanju. Vanadij je važan dio prehrane za mnoge životinje i neki njegovi pripravci mogu znatno povećati prirast. Također utječe na produkciju biomase. Neke biljke (npr. krumpir, rotkva, peršin) akumuliraju vanadij, a neke gljive akumuliraju ga u vrlo velikim koncentracijama.

Svjetska produkcija ovog elementa procijenjena je u 2000. godini na 43 000 t.

Vanadij ima široku primjenu u metalurgiji gdje služi kao oplemenjivač čelika. Osim toga, njegove legure koriste se u avioindustriji. Manje količine koriste se kao katalizator kod proizvodnje kemikalija, stakla, keramike, a također i u elektroničkoj industriji. Dodaje se i nekim pesticidima a upotrebljava se i kao razvijač u fotoindustriji.

Raspršuje se u okoliš spaljivanjem ugljena i derivata nafte.

Vanadium is a lithophile trace element. Together with iron it is enriched in mafic and intermediary (andesitic-diorite) magmas. According to its abundance it is ranked 19th in the Earth's crust.

Among igneous rocks ultramafic rocks contain in average 40 mg/kg of vanadium, oceanic tholeiite basalts and basalts 250 mg/kg, granodiorites 88 mg/kg, and granites 44 mg/kg. Shales contain in average 130 mg/kg of vanadium, sandstones 20 mg/kg, and carbonates 20 mg/kg. Relatively high content of this element in shales indicates the presence of organic matter and reducing conditions of formation. The content of this element in coal is about 20 mg/kg, crude oil 14 mg/kg, and in driving fuel about 50 mg/kg. In oxidizing belt it forms vanadates. It can be found in mineralized sandstones, limonite ore, shales, bauxites, black schists, phosphorites, bitumen and coal. Besides, vanadium can be enriched in the heavy oil, asphalt sands and coal. In soil vanadium can substitute iron and be adsorbed on Fe-hydroxides. Here, the concentration varies between 3 and 500 mg/kg, averaging about 90 mg/kg. The total concentration of V in the soils developed on sandy substrates is lower than concentration in the soils evolved on shales and clays. In the sweet water vanadium is present with about 0.002 mg/L.

Vanadium is mobile in oxidizing conditions. It precipitates in the presence of Pb^{2+} and adsorbs on Fe-Mn oxy-hydroxides and organic matter. During weathering vanadium is released easily from many host minerals adsorbing on clay minerals.

Vanadium is a bioelement for some plants essential for bonding of nitrogen (leguminosis). It is widely distributed in the majority of organisms. In certain quantities it is toxic for people (V pentoxide – V_2O_5 is the most poisonous compound). Vanadium stimulates formation of chlorophyll and iron metabolism in some plants where it participates in concentrations between 0.27 and 4.2 mg/kg (average value is 1 mg/kg). In greater concentrations it is toxic for plants (> 10 mg/kg in nutrients) with toxicity depending on valence. Vanadium is a significant part of the diet for many animals so that some of its preparations can considerably enhance the gains. Also it affects the production of biomass. Some plants (e.g. potato, black radish, parsley) accumulate vanadium while some fungi accumulate it in the very high concentrations.

The world production of this element was estimated for the year 2000 at 43,000 t.

Vanadium is widely applied in metallurgy where it serves as a steel ennobler. Besides, its alloys are used in airplane industry. Minor quantities are utilized as a catalyst in production of chemicals, glass, ceramics, and it is used in the electronic industry as well. Some textile paints contain vanadium. It is added to some pesticides and is also used as a developer in the photo industry.

Dispersion of vanadium into environment occurs via combustion of coal and oil derivatives. Besides, traffic also increases the content of this element in the environment.

Koncentracije vanadija u uzorcima tla istraživanog područja variraju od 12 do 130 mg/kg s medijanom od 32,5 mg/kg. Najveća koncentracija izmjerena je u blizini Termoelektrane Sisak. I susjedni uzorci u neposrednoj blizini tog industrijskog postrojenja imaju ekstremne i anomalne koncentracije ovog elementa u tlu. Nesumnjivo je da te visoke koncentracije vanadija u tlu potječu od spaljivanja fosilnog goriva za pogon termoelektrane i da su antropogenog podrijetla. Međutim, disperzija u okoliš nije dalekog dometa, tako da uzorkovane lokacije na lijevoj obali Save, sjeverno od termoelektrane ne pokazuju povišene vrijednosti vanadija u tlu. U krugu Željezare Sisak utvrđene su na nekim lokacijama također anomalne kocentracije vanadija, što je vezano za metaluršku obradu ruda i metala.

Područje Mošćenice također pokazuje anomalne i visoke sadržaje ovog elementa u tlu, što je posljedica njegove sorpcije na organsku tvar u šumskim tlima na tom području.

Anomalne i visoke vrijednosti vanadija registrirane su i u tlima na aluvijalnim sedimentima rijeka Kupe i Odre (južno od gradskog vodovoda „Kopa“, Staro Pračno i sisačka Zgmajna). Tla na tim lokacijama bogata su Mn i Fe oksi-hidroksidima pa se vanadij u njima obogaćuje sorpcijom na te hidrokside. Povećane vrijednosti ovog elementa registrirane su i zapadno od kemijske industrije „HERBOS“, ali one su ovdje vjerojatno geogenog podrijetla. Naime, tla na ovim lokacijama imaju povećan sadržaj minerala glina, koji su dobri receptori vanadija.

Naselja Caprag i Kanak imaju povišene vrijednosti vanadija u tlu. Vjerojatno je to posljedica utjecaja industrije u neposrednoj blizini, a moguće je da je ovaj element u tlu i geogenog podrijetla.

Ostali dijelovi užeg urbanog područja grada Siska imaju koncentracije vanadija oko ili ispod medijana.

Concentrations of vanadium in the soils of the investigated area vary between 12 to 130 mg/kg with median of 32.5 mg/kg. The greatest concentration is measured in the vicinity of the thermal power plant. The neighboring samples immediately close to this processing plant also show extreme and anomalous concentrations of this element in the soil. Undoubtedly, the high concentrations of vanadium in the soil originate from combustion of fossil fuel in the thermal power plant indicating their anthropogenic origin. However, dispersion into environment is not of wide range so that the sampled locations on the left bank of the Sava River to the north of the thermal power plant do not show increased values of vanadium in the soil. Within the circle of the steelworks anomalous concentrations of vanadium are also determined on some locations, which is associated with ore and metal processing.

The area of Mošćenica also shows anomalous and high contents of this element in the soil which is the result of its sorption on organic matter in the forest samples in this area.

Anomalous and high values of vanadium are also registered in the soils on alluvial sediments of the Kupa and Odra Rivers (to the south of the city water supply line of „Kopa“, Staro Pračno and Sisačka Zgmajna). The soils on these locations are rich in Fe-Mn oxy-hydroxides so that vanadium in them is enriched by sorption on these compounds. Increased values of this element are also recorded to the west of the chemical industry of „HERBOS“, but the latter are here probably of geogenic origin. Namely, soils on these locations contain increased content of clay minerals which are the good receptors for this element.

The settlements of Caprag and Kanak contain increased values of vanadium in the soil. This is probably the



Slika 10.24. *Dogovori na terenu (s lijeva na desno: Anto Rajić, Josip Halamić, Stjepan Husnjak, Stjepan Ivoš, Drago Martinac) (Foto: A. Šorša).*

Figure 10.24. *Field consultations (from left to the right: Anto Rajić, Josip Halamić, Stjepan Husnjak, Stjepan Ivoš, Drago Martinac) (Photo: A. Šorša).*

Na temelju prostorne raspodjele vanadija na istraživanom području, vidljiva je razlika u različitim izvorišnim materijalima matičnih supstrata za tlo u dolinama Kupe i Odre na jednoj strani te aluvijalnih sedimenata Save na drugoj strani. Naime, sedimenti rijeke Save siromašniji su mineralima glina i Fe i Mn oksi-hidroksidima te stoga imaju koncentracije vanadija ispod ili znanto ispod vrijednosti medijana. Za tla južno od Galdova te Luke i Poloja može se reći da su osiromašena ovim elementom. Registrirano osiromašenje tla ovim elementom južno od naselja Žabno uzrokovano je naveženim materijalom prilikom sanacije zelene površine na tom lokalitetu, a koji je siromašan organskom komponentom, mineralima glina i Fe i Mn oksi-hidroksidima (naveženi šljunak i karbonanti tucanik).

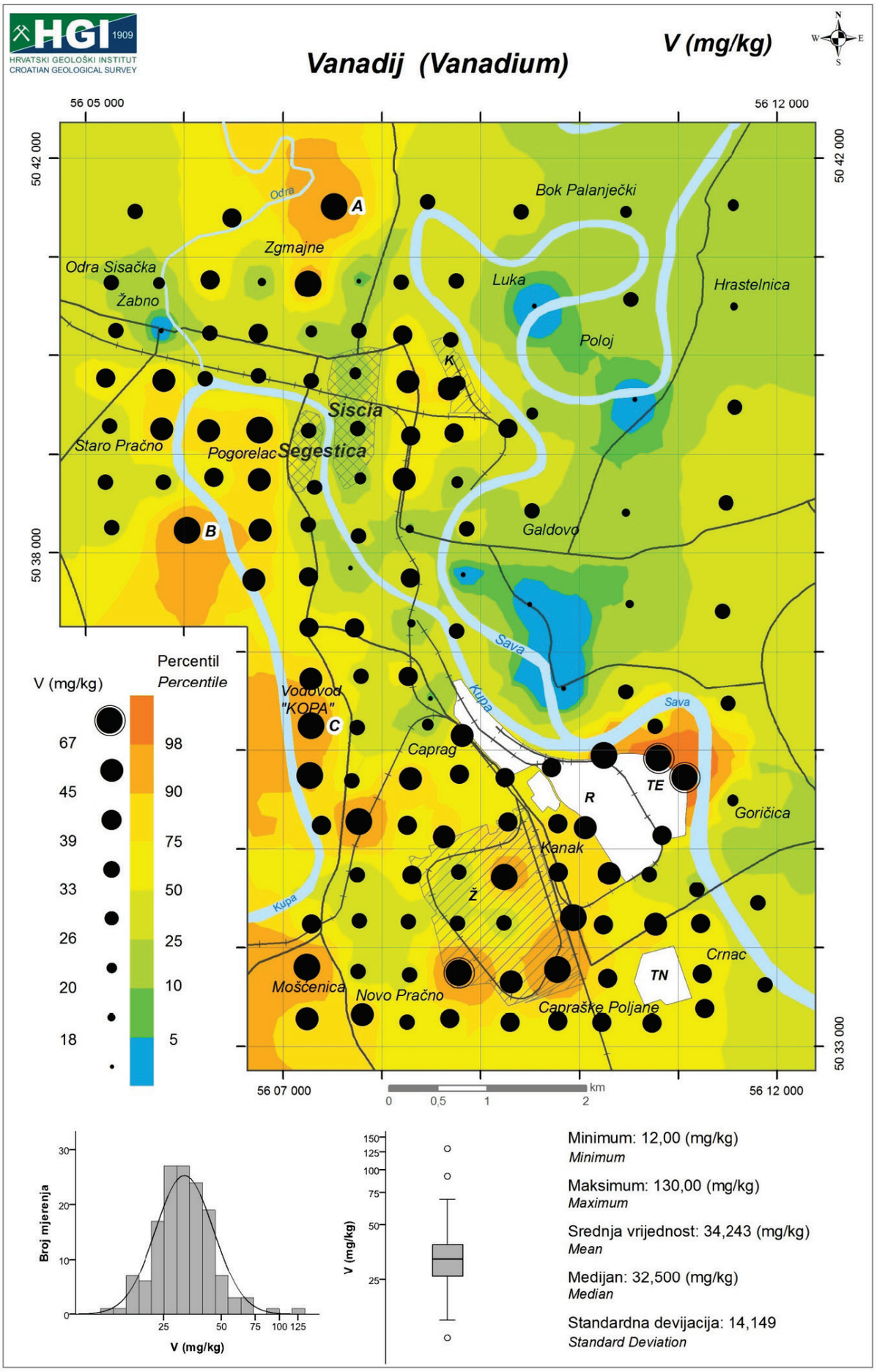
Vanadij je kao teški metal uvršten u *Program trajnog motrenja tala Republike Hrvatske* (MESIĆ et al., 2008). Prema preporučenim graničnim koncentracijama onečišćujućih tvari u tom Programu, tri uzorka poljoprivrednih tala na istraživanom području imaju koncentracije ovog teškog metala iznad preporučenih vrijednosti. To su uzorci na karti raspodjele vanadija: A, B i C. Svi uzorci potječu s livada, ali se trava na tim lokacijama kosi i upotrebljava za prehranu stoke.

consequence of industry in their immediate vicinity and, partly, it may reflect its geogenic origin.

Other parts of the urban core of the city of Sisak are characterized by concentrations around or below the median.

Based on the spatial distribution of vanadium in the investigated area one can observe the difference in various source materials of the underlying bedrock from which the soil has been derived, pertaining to the valleys of the Kupa and Odra Rivers on the one side, and alluvial sediments of the Sava River on the other. Namely, the sediments of the Sava River are more deficient in the clay minerals Fe-Mn oxy-hydroxides which is why the concentrations of vanadium are below and considerably below the median value. It can be said for the soils to the south of the Galdovo settlement, Luka and Poloj that they are deficient in this element. Deficiency of vanadium in the soil in the area to the south of the Žabno settlement is caused by the dumped material from the sanitation works of the green area on this locality. This material is depleted in organic component, clay minerals and Fe-Mn oxy-hydroxides (dumped gravel and carbonate road metal).

Since vanadium as a heavy metal is included in the "Recommendation for the trigger values of the contaminating substances in soil according to various modes of land use" (MESIĆ et al., 2008) and in accordance with recommended trigger values of the contaminating substances in that program three samples in the investigated area show the concentrations of this heavy metal above the recommended values. These are represented by the samples A, B and C on the map of spatial distribution of vanadium. All of them are sampled on the meadows but the grass is mowed and probably used as the food for cattle.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Vanadij (Vanadium)
V (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Vodovod "KOPA"
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
A
B
C
K
V (mg/kg)
Percentil
Percentile
67
45
39
33
26
20
18
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
V (mg/kg)
Minimum: 12,00 (mg/kg)
Minimum
Maksimum: 130,00 (mg/kg)
Maximum
Srednja vrijednost: 34,243 (mg/kg)
Mean
Medijan: 32,500 (mg/kg)
Median
Standardna devijacija: 14,149
Standard Deviation

Y

10.42. Y – ITRIJ (atomski broj 39) YTTRIUM (atomic number 39)

Itrij je litofilni element u tragovima, a po učestalosti u Zemljinoj kori nalazi se na 29. mjestu. On je geokemijski povezan s kalcijem. Geokemijske karakteristike itrija slične su zemnoalkalnim elementima i drugim elementima rijetkih zemalja.

Srednji sadržaj u magmatskim stijenama je 33 mg/kg (ultrabaziti 5 mg/kg, oceanski toleitni bazalti 43 mg/kg, bazalti 25 mg/kg, granodioriti 20 mg/kg i graniti 15 mg/kg). Od sedimentnih stijena šejlovi imaju srednju vrijednost ovog elementa 18 mg/kg, pješčenjaci 9 mg/kg i karbonati 4 mg/kg. Sadržaj itrija u ugljenu kreće se od 7 do 12 mg/kg. Srednja vrijednost u tlima iznosi 50 mg/kg. U slatkoj vodi ga ima 0,00007 mg/L, a topiv je u obliku karbonat-kompleksa.

Kao i sve rijetke zemlje, slabo je mobilan. U sedimentima se koncentrira pretežito kao ostatak trošenja teških minerala. Dostupni itrij ima izrazitu tendenciju adsorpcije na Fe-oksi-hidrokside i minerale glina. U neutralnom i alkalijskom okolišu tvori karbonatne komplekse. Može se precipitirati na isti način kao i aluminij.

Itrij je bez biološkog značenja. Nakuplja se u kostima. Smatra se da je slabo otrovan. Akumuliraju ga neke biljke (npr. američki orah). Itrij može zamijeniti kalcij u njegovoj biološkoj funkciji.

Prosječna svjetska proizvodnja itrija kao Y_2O_3 procijenjena je u 2001. godini na 2 400 t.

Tehnička primjena itrija je višestruka (visokotehnološki proizvodi, televizijske cijevi i ekrani). Upotrebljava se u keramičkoj i staklarskoj industriji, za izradu visokotemperaturnih opeka, lasera, a služi i kao katalizator u proizvodnji palstike. Neki spojevi itrija imaju luminiscirajuća svojstva i upotrebljavaju se za lasere.

Štetan antropogeni utjecaj na okoliš nije poznat.

Yttrium is a lithophile trace element, 29th abundance in the Earth's crust. Geochemically is associated with calcium. It geochemical characteristics are close to earth alkali elements and other rare earth elements.

The average content of yttrium in igneous rocks is 33 mg/kg (ultramafic rocks 5 mg/kg, oceanic tholeiite basalts 43 mg/kg, basalts 25 mg/kg, granodiorites 20 mg/kg and granites 15 mg/kg). Among sedimentary rocks shales contain in average 18 mg/kg of yttrium, sandstones 9 mg/kg and carbonates 4 mg/kg. The content of this element in coal is between 7 and 12 mg/kg. Its average content in soils is 50 mg/kg. In the sweet water it is present with 0.00007 mg/L, being soluble in the form of carbonate complexes.

As with all rare earths yttrium is lowly mobile. It is concentrated in sediments predominantly as a residue of the weathering of the heavy minerals. Only a few minerals containing yttrium are weathered more easily. Available yttrium is explicitly prone to adsorption on Fe oxy-hydroxides and clay minerals. In neutral and alkali environments it forms carbonate complexes. It can be precipitated in the same way as aluminium.

Yttrium is without biological significance. It is accumulated in bones. It is considered weakly toxic and it seems that is more toxic with regard to rare earths. Yttrium is accumulated by some plants (e.g. American nut). It can substitute calcium in its biological functioning.

The average world production of yttrium in the form of as Y_2O_3 is estimated for the year 2001 at 2,400 tons.

Technical application of yttrium is multifarious (highly technological products, television tubes and screens). It is also used in ceramic and glass industry, in production of high temperature bricks, and serves as catalyst in production of plastics. Some compounds of yttrium have luminescent properties and thus are utilized for lasers.

Anthropogenic impact on the environment is not recognized.

Prema prostornoj distribuciji itrija u tlima vidljivo je da su povećane koncentracije vezane za industrijsko područje na jugu, te za tla derivirana iz aluvijalnih sedimenata rijeka Kupe i Odre.

Raspon izmjerenih vrijednosti kreće se od 3,6 do 38 mg/kg s medijanom od 9,4 mg/kg. Maksimalna koncentracije registrirana je u uzorku u krugu Željezare Sisak. I ostale ekstremne i anomalne vrijednosti nalaze se u krugu Željezare te u blizini Termoelektrane Sisak. Isto tako, uzorci u blizini željezničke pruge u industrijskom dijelu (željeznička stanica Caprag) i uzorak uzet istočno od ranžirnog kolodvora željezare, pokazuju ekstremne i anomalne koncentracije ovog elementa. One su vjerojatno posljedica prijašnje upotrebe ugljena kao pogonskog goriva za lokomotive. Prema rasprostiranju povećanih vrijednosti itrija u tlima sjeverno i sjeveroistočno od termoelektrane vidljivo je da njegova disperzija u okoliš iz tog industrijskog postrojenja seže sve do naselja Hrastelnica na sjeveru.

Za razliku od ovih antropogenih sadržaja itrija u tlu, njegove anomalne i povećane koncentracije u dolini Kupe (lokacija južno od gradskog vodovoda „Kopa“ i Staro Pračno) te u dolini Odre (sisačka Zgmajna) geogenog su podrijetla. Tla na ovim lokacijama bogata su Fe i Mn oksi-hidroksidima na koje se ovaj element preferirano veže i tako obogaćuje u tlu.

Pretežito geogeno podrijetlo imaju i povećane vrijednosti itrija u tlu na lokalitetima zapadno od kemijske industrije „HERBOS“.

Ostalo urbano područje te ruralni dijelovi istraživanog područja imaju koncentracije oko ili znatno ispod vrijednosti medijana. Posebno se ističe područje park-šume zapadno od Željezare i Novo Pračno. Niže vrijednosti ovog elementa u tlima na aluviju rijeke Save posljedica su manjeg sadržaja glinovite komponente.

Šumska tla na području Mošćenice i park-šume imaju izrazito niske koncentracije itrija što ukazuje na to da ovaj element nije vezan na organsku tvar u tlu, nego da se preferirano akumulira u minerale glina i u Fe i Mn oksi-hidrokside.

According to the spatial distribution of yttrium in the soils the increased concentrations are obviously related to industrial zone on the south as well as to the soils derived from alluvial sediments of the Kupa and Odra Rivers.

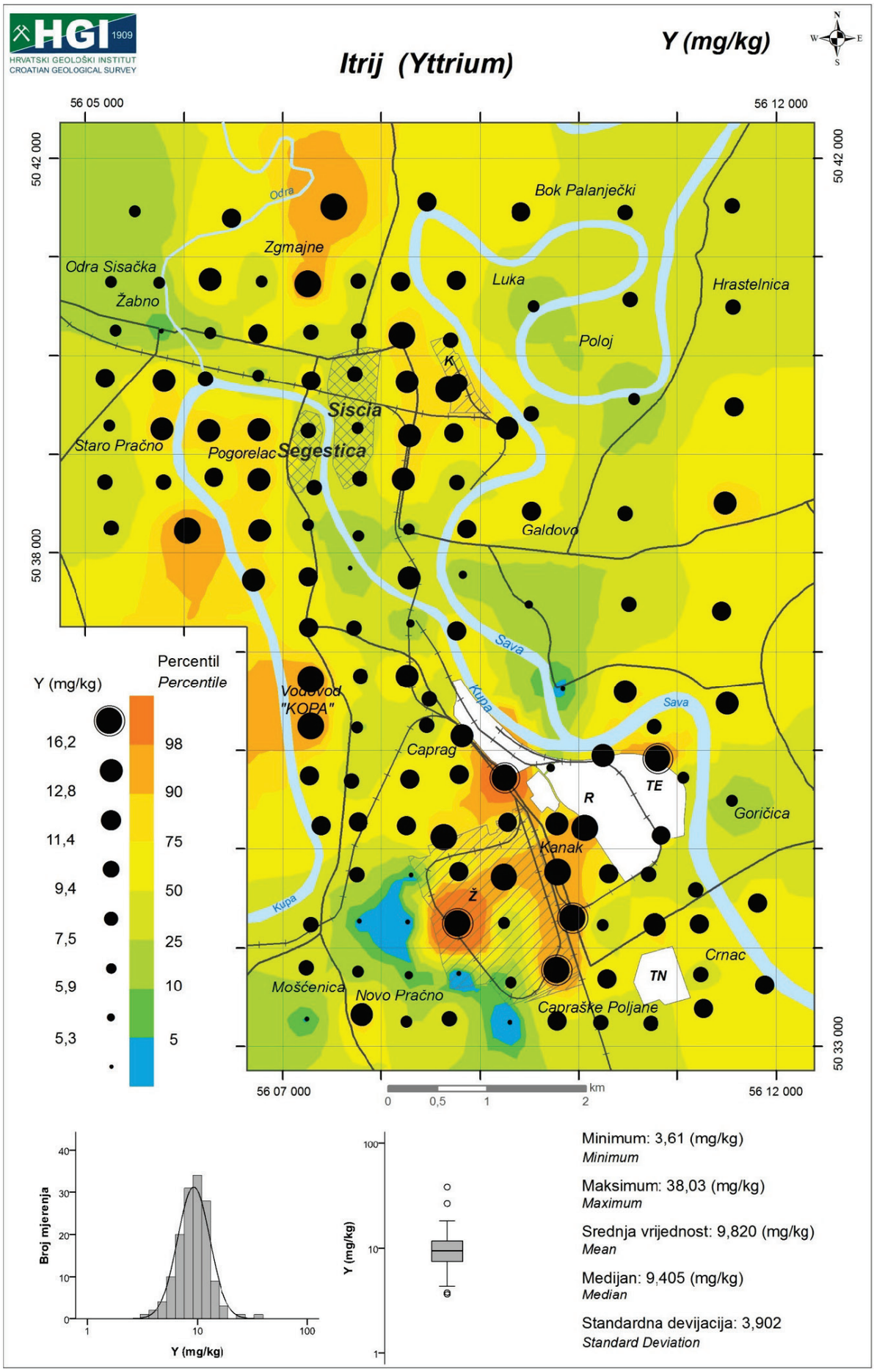
The measured values range from 3.6 to 38 mg/kg with median of 9.4 mg/kg. Maximum concentration is registered in the sample from the within the circle of steelworks. Other extreme and anomalous values are also found in this circle as well as in the vicinity of the thermal power plant. The same is with the samples close to the railroad tracks in the industrial zone (railroad station Caprag) and a single sample collected to the south of the freight-yard of the steelworks. These values are probably the result of former use of coal as a driving fuel for train engines. In accordance with distribution of increased values of yttrium in the soils to the north and northeast of the thermal power plant its dispersion into environment from this processing plant obviously reach all the way to the Hrastelnica settlement on the north.

In contrast to these anthropogenic contents of yttrium in the soil, anomalous and increased concentrations of this element in the valley of the Kupa River (location to the south of city water supply line „Kopa” and Staro Pračno) as well as in the valley of the Odra River (Sisačka Zgmajna) are geogenic in their origin. The soils on these locations are rich in Fe-Mn oxy-hydroxides on which this element is preferably bonding and thus becomes enriched in soil.

The same, predominantly geogenic origin is reflected in increased values of yttrium in the soils on the locations to the west of the chemical industry „HERBOS“.

The remaining part of urban area together with the rural parts of the investigated area shows concentrations around or considerably below the median value. The area of the forest park to the west of the steelworks Novo Pračno is particularly prominent. The lower values of this element in the soils developed on the alluvium of the Sava River result from the lower content of the clay component.

The forest soils in both the area of Mošćenica and the forest park reveal specifically low concentrations of yttrium indicating that this element is not bonded on organic matter in the soil but preferably accumulates in the clay minerals and Fe-Mn oxy-hydroxides.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Itrij (Yttrium)
Y (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Vodovod "KOPA"
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Moščenica
Novo Pračno
Capraške Poljane
Percentil
Percentile
Y (mg/kg)
16,2
12,8
11,4
9,4
7,5
5,9
5,3
98
90
75
50
25
10
5
0
0,5
1
2
km
Broj mjerenja
Y (mg/kg)
Minimum: 3,61 (mg/kg)
Minimum
Maksimum: 38,03 (mg/kg)
Maximum
Srednja vrijednost: 9,820 (mg/kg)
Mean
Medijan: 9,405 (mg/kg)
Median
Standardna devijacija: 3,902
Standard Deviation

Zn

10.43. Zn – CINK (atomski broj 30) ZINC (atomic number 30)

Cink je oksihalkofilan element u tragovima iz skupine prijelaznih elemenata. U prirodi se pojavljuje zajedno s Cu, Pb, Ag, Au, Sb, As i Se. Po učestalosti u Zemljinoj kori zauzima 24 mjesto.

Srednji sadržaj u magmatskim stijenama iznosi 70 mg/kg (ultrabaziti 50 mg/kg, bazalti 105 mg/kg, granodioriti 50 mg/kg i graniti 51 mg/kg). Srednji sadržaj u šejlovima je 100 mg/kg, pješčenjacima 40 mg/kg i karbonatima 21 mg/kg. Sadržaj cinka u ugljenu je 52 mg/kg, a u nafti 0,5 mg/kg. Uljni škriljavci, željezni ooliti i feromanganove nodule često imaju vrlo visoke koncentracije cinka. Koncentracija u tlu kreće se od 1 do 900 mg/kg (češće od 1 do 300 mg/kg) sa srednjom vrijednošću od 90 mg/kg. U najvećoj mjeri koncentracija cinka ovisi o kemizmu matičnih stijena, količini organske tvari i pH vrijednosti. U slatkoj vodi pojavljuje se otopljen kao Zn^{2+}, u obliku klorida i u organskim kompleksima (0,02 mg/L). Hidrolizira kod pH 5 – 6.

Cink je dosta mobilan u sekundarnom okolišu i to pri manjim pH vrijednostima (pH < 4,5). Sulfidne rude trošenjem tvore lako topive sulfate, teško topive karbonate i fosfate, kao i hidratizirane silikate. Cink se adsorbira na Fe-Mn-oksi-hidrokside, minerale glina i organsku tvar.

Cink je esencijalan element u tragovima za sve organizme. Prisutan je u metalnim enzimima i proteinima. Općenito je njegova otrovnost mala (povećana koncentracija je za biljke umjereno otrovna, a za sisavce slabo otrovna). Otrovnost je primjećena prilikom ispaše stoke na tlima bogatim cinkom. Ako je koncentracija cinka veća od 300mg/kg onda se primjećuje smanjenje rasta biljaka. Povećane koncentracije ovog elementa nalazimo u fosfatnim gnojivima. Pomanjkanje cinka u tlu može biti uzrokom raznih bolesti. Cinkove se komponente iskorištavaju pri uzgoju svinja i pilića kao dodaci hrani.

Svjetska produkcija ovog metala procijenjena je u 2003. godini na 9 170 000 t.

Cink ima višestruku tehničku primjenu, posebice u metalurgiji, proizvodnji boja i baterija. Nadalje, on se koristi za zaštitu od korozije, za izradu legura (npr. s bakrom se izrađuje mesing), u automobilskoj industriji, u proizvodnji guma, te za zaštitu drveta i dr.

Raspršuje se u okoliš u formi para ili čestica spaljivanjem otpada, proizvodnjom guma, pigmenta boja, pocinčanog željeza, baterija, iz otpadnih voda, topionica, iz starih haldišta na obalama rijeka i dr. Nadalje disperzija u okoliš događa se i tijekom proizvodnje cementa te spaljivanjem mazuta u termoelektranama.

Zinc is an oxychalcophile trace element from the group of transitory elements. In nature is occurs accompanied with Cu, Pb, Ag, Au, Sb, As and Se. It is 24th in abundance in the Earth's crust.

The average content of zinc in igneous rocks is 70 mg/kg (ultramafic rocks 50 mg/kg, basalts 105 mg/kg, granodiorites 50 mg/kg and granites 51 mg/kg). The average content in shales is 100 mg/kg, sandstones 40 mg/kg and carbonates 21 mg/kg. The content of zinc in coal is 52 mg/kg and in oil 0.5 mg/kg. Bituminous schists, ferric oolites, and ferromanganese nodules often contain very high concentrations of zinc. Concentration if this element in soil ranges from 1 to 900 mg/kg (more frequently from 1 to 300 mg/kg) with mean of 90 mg/kg. Concentration of zinc depends mainly on the chemistry of the parent rocks, quantity of organic matter, and pH value. In sweet water it is dissolved as Zn^{2+}, in the form of chlorides and in organic complexes (0.02 mg/L). It is hydrolyzed at pH 5 - 6.

Zinc is rather mobile in the secondary environment at lower pH values (pH < 4.5). During weathering sulfide ores form easily soluble sulfates, hardly soluble carbonates and phosphates as well as hydratized silicates. Zinc is adsorbed on Fe-Mn oxy-hydroxides, clay minerals and organic matter.

Zinc is essential trace element for all organisms. It is present in metal enzymes and proteins. Generally, its toxicity is small (increased concentration is moderately toxic for plants and slightly toxic for mammals). Its toxicity is observed during pasture on meadow soils rich in zinc. If concentration is greater than 300 mg/kg the growth of plants is reduced. Increased concentrations of this element can be found in the phosphate fertilizers. Deficiency of zinc in the soil can cause various diseases. Zinc components are utilized in pig and poultry farming as food additives.

The world production of this metal is estimated at 9,170,000 t for the year 2003.

Technical application of zinc is manifold, especially in metallurgy, production of paints and batteries. Further, it is used as protection from corrosion, for making alloys (e.g. brass in combination with copper), in automobile industry, in production of tires, wood protection etc.

Zinc is dispersed in the environment in the form of vapor or particles after combustion of waste, production of tires, paint pigments, zinc iron, batteries, waste waters, foundries, old gangue depots on the river banks etc. Further, dispersion into environment is also due to production of cement and combustion of crude oil in the thermal power plants.

Na temelju prostorne raspodjele cinka na istraživanom području jasno je vidljivo da je najveći dio ekstremnih koncentracija vezan za industrijsko područje na jugu (željezara, rafinerija, termoelektrana).

Izmjerene koncentracije ovog elementa u uzorcima analiziranih tala variraju od 44,7 do preko 10 000 mg/kg (preko 1 %!) s medijanom od 109,1 mg/kg. Izuzetno visoke koncentracije registrirane su u tlima u krugu Željezare Sisak, a maksimalna vrijednost izmjerena je u uzorku Z3 (> 10 000 mg/kg). Analizirani uzorci tla u neposrednoj blizini ovog metalurškog kompleksa imaju anomalne i ekstremne vrijednosti cinka. Međutim, osim Željezare, ekstremne koncentracije ovog elementa u tlu utvrđene su i u neposrednoj blizini Rafinerije nafte Sisak i Termoelektrane Sisak. Raspršenje cinka iz Termoelektrane odvija se prema sjeveroistoku putem vjetra tako da i uzorci tla na lijevoj obali rijeke Save, sjeverno i sjeveroistočno od postrojenja imaju visoke i ekstremne koncentracije ovog elementa u tlu.

Analizirajući prostornu raspodjelu cinka u tlu u industrijskoj zoni pokazalo se da su najrizičnija naselja Ca-

Based on the spatial distribution of zinc in the investigated area it is evident that the most part of extreme concentrations is associated with industrial zone on the south (steelworks, oil refinery, thermal power plant).

The measured concentrations of this element in analyzed soil samples vary between 44.7 to over 10,000 mg/kg (over 1 %!) with median of 109.1 mg/kg. Enormously high concentrations are registered in the soils within the circle of the steelworks with maximum value in the sample Z3 (> 10,000 mg/kg). Analyzed soil samples from the locations immediately close to this metallurgic complex also show anomalous and extreme concentrations of zinc. However, apart from the steelworks extreme concentrations of this element in the soil are also determined in the immediate vicinity of the oil refinery and thermal power plant. Dispersion of zinc from the thermal power plant is by wind toward northeast so that the samples on the left bank of the Sava River, to the north and northeast of the thermal power plant also contain high and extreme concentrations of this element in the soil.

Analyzing the spatial distribution of zinc in the soil in the industrial zone it was shown that the places most exposed to risk are the settlements of Caprag, Kanak and Crnac which are under the immediate influence of industrial processes in these plants.

In the soils of the north part of the town (ancient settlements of Siscia and Segestica) increased contents of this element are also registered. Although zinc as a metal was not utilized in these times the increased in the soils on those originate form the processing of lead with which zinc is regularly accompanied

Slightly increased to high concentrations of zinc are registered in the soils along the more frequent road routes, which is probably the result of wearing of the automobile tires into which this element is incorporated (Fig. 10.25).



Slika 10.25. *Uzorkovanje uz „Rimsku cestu" na ulazu u Sisak iz smjera Zagreba (Foto: J. Halamić).*

Figure 10.25. *Sampling along the „Roman road" on the entryway from Zagreb direction (Photo: J. Halamić).*

prag, Kanak i Crnac koja su pod neposrednim utjecajem industrijske proizvodnje u tim pogonima.

U tlima u sjevernom dijelu grada (antička naselja Siscija i Segestica) registrirani su također povećani sadržaji ovog elementa. Iako se cink u to vrijeme kao metal nije koristio, njegov povećan sadržaj u tlima tih lokacija posljedica je obrade olova čiji je cink redoviti pratitelj.

Malo povećane, do visoke koncentracije cinka, registrirane su i u tlima uzduž frekventnijih cestovnih prometnica, što je vjerojatno posljedica trošenja automobilskih guma u koje se ovaj element ugrađuje (Sl. 10.25.).

Anomalna koncentracija ovog elementa u tlu na lokaciji P1 na sjevernom dijelu istraživanog područja (prelazi i MDK vrijednost!) nema jednoznačnog objašnjenja. Naime, radi se o uzorku koji je uzet na intenzivno korištenoj livadi (djetelina), a koja se nalazi između intenzivno obrađivanih poljoprivrednih parcela (kukuruz). Jedno od mogućih objašnjenja je da povećani sadržaji cinka u tlu potječu od organskog gnojiva u kojem se može očekivati povećan sadržaj ovog elementa (svinje, perad).

Ostali dijelovi istraživanog terena imaju koncentracije cinka u tlu oko ili znatno ispod medijana. Na području Hrastelnice, Galdova, Žabna i istočno od Fistrovićeve ulice u urbanom dijelu grada tla su osiromašena ovim elementom.

Iako je cink u malim koncentracijama esencijalni element, zbog otrovnosti u većim količinama, uvršten je kao teški metal na listu za trajno motrenje tala. Za njega su propisane i granične koncentracije: za poljoprivredna tla i dječja igrališta (200 mg/kg), stambena područja (300 mg/kg), parkove (700 mg/kg) i industrijska područja (1 200 mg/kg) (MESIĆ et al., 2008.; Tab. 6.2.). Usporedbom tih graničnih vrijednosti i izmjerenih koncentracija cinka u analiziranim tlima pokazalo se je da na nekim lokacijama, a prema određenoj namjeni zemljišta, dolazi do prekoračenja MDK. Uzorci P1, P2 i P3 su na poljoprivrednom zemljištu i izmjerene koncentracije cinka prelaze 200 mg/kg. U naselju Caprag u uzorku G sadržaj cinka u tlu prelazi granicu od propisanih 300 mg/kg. Najkritičnija lokacija je u naselju Kanak (uzorak D, koji je uzet na dječjem nogometnom igralištu), gdje izmjerena koncetracija cinka u tlu četverostruko prelazi graničnu vrijednost za tu namjenu (Tab. 6.2.).

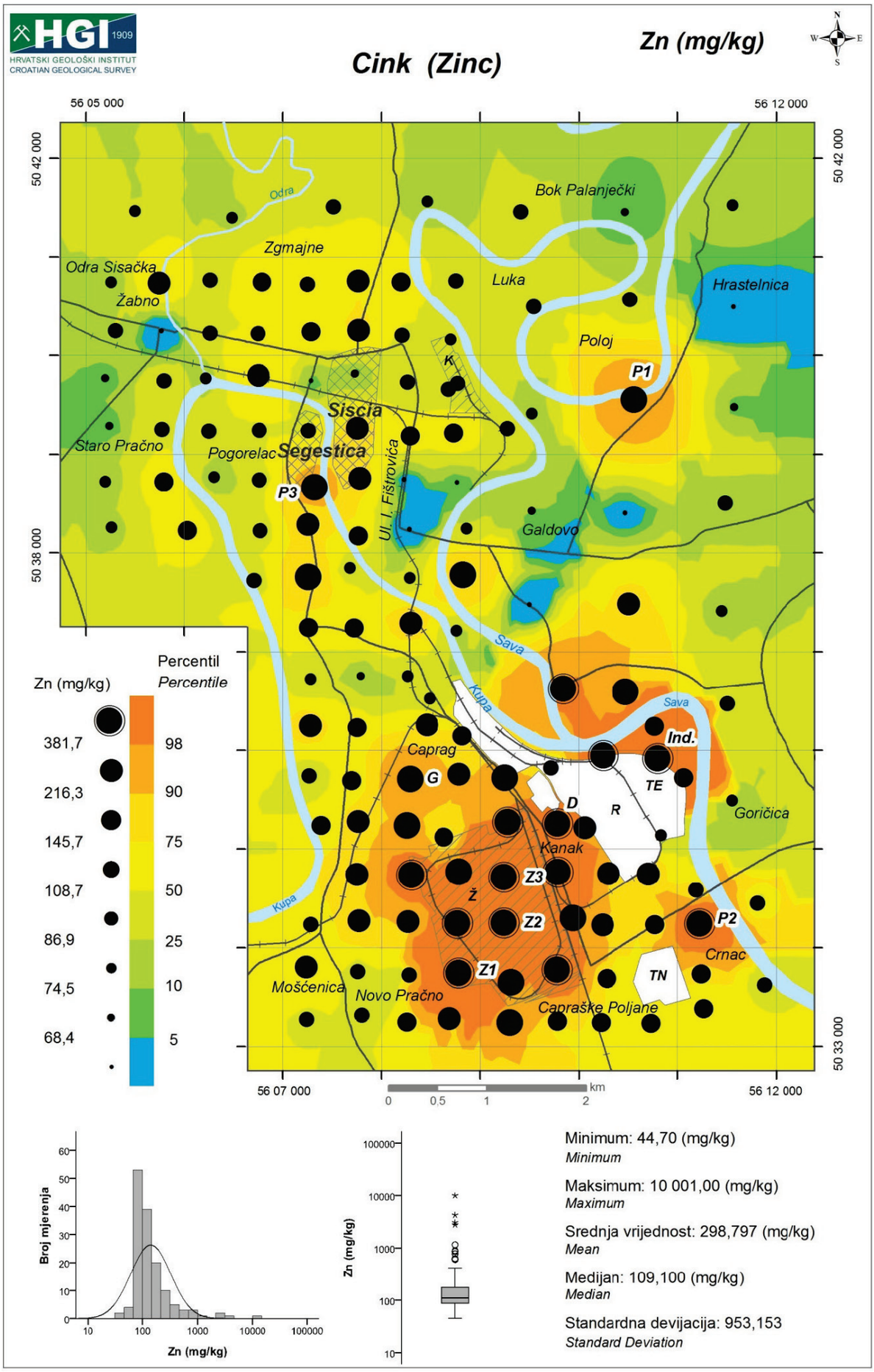
Također i tla u industrijskim postrojenjima (uzorci Z1, Z2 i Z3 te Ind.; točka Ind. se čak nalazi i izvan kruga Termoelektrane Sisak) sadrže koncentracije cinka znatno iznad propisanih.

Anomalous concentration of this element in the soil on the location P1 on the northern part of the investigated area (exceeding even the MPC value!) can not be unambiguously explained. Namely, the sample is collected on the intensely exploited meadow (currently cultivated by trefoil) which is situated between the intensely cultivated agricultural plots (currently corn). One of the possible explanations is that the elevated contents of zinc derive from organic fertilizer in which increased content of this element can be (pigs, poultry).

The other parts of the investigated area contain concentrations of zinc around or considerably below the median value. In the area of Hrastelnica, Galdovo, Žabno and to the east of Fištrović's Street in the urban core of the city the soils are deficient in this element.

Although zinc in small quantities is essential element, owing to its toxicity in greater concentrations it is included as a heavy metal on the list of the permanent monitoring of soils. The trigger values prescribed for this element are as follows: agricultural lands and children playgrounds (200 mg/kg), residential area (300 mg/kg), parks (700 mg/kg) and industrial zones (1,200 mg/kg) (MESIĆ et al., 2008; Tab. 6.2.). By comparison of these limit values and measured concentrations of zinc in the analyzed soils some soils are indicated, in accordance with previously defined land use, as those with concentrations that exceed MPC. Samples P1, P2 and P3 are on the agricultural land and measured concentrations of zinc exceed 200 mg/kg. In the Caprag settlement in the sample G the content of zinc in the soil goes beyond the level of prescribed values (300 mg/kg). The most critical location is in the Kanak settlement (sample D collected on the children soccer playground), where the measured concentration of zinc in the soil exceeds the trigger value for that allocation (Tab. 6.2.).

The soils within the circle of industrial processing plants (samples Z1, Z2 and Z3, and Ind.; the site Ind. is not even situated within the circle of the thermal power plant) also contain the concentrations of zinc considerably above the regulated values.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Cink (Zinc)
Zn (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
P1
K
Siscia
Segestica
Staro Pračno
Pogorelac
P3
Ul. I. Fištrovića
Galdovo
Sava
Kupa
Caprag
G
Ind.
TE
D
R
Goričica
Kanak
Z3
Ž
Z2
P2
Crnac
Z1
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Percentil
Percentile
Zn (mg/kg)
381,7
216,3
145,7
108,7
86,9
74,5
68,4
98
90
75
50
25
10
5
Broj mjerenja
Zn (mg/kg)
10
100
1000
10000
100000
Minimum: 44,70 (mg/kg)
Minimum
Maksimum: 10 001,00 (mg/kg)
Maximum
Srednja vrijednost: 298,797 (mg/kg)
Mean
Medijan: 109,100 (mg/kg)
Median
Standardna devijacija: 953,153
Standard Deviation

Zr

10.44. Zr – CIRKONIJ (atomski broj 40) ZIRCONIUM (atomic number 40)

Cirkonij je litofilni i oksifilni element u tragovima, a po učestalosti u Zemljinoj kori nalazi se na 18. mjestu. S povećanjem alkaliniteta magme, povećava se i koncentracija cirkonija. Udružen je s Hf, zatim s Y, La, Ce i drugim elementima rijetkih zemalja, kao i s Ti, Nb, Th i U. Cirkon kristalizira među prvim mineralima u magmatskim taljevinama.

Srednja vrijednost ovog elementa u ultrabazičnim magmatskim stijenama je 45 mg/kg, oceanskim toleitima 95 mg/kg, bazaltima 140 mg/kg, granodioritima 140 mg/kg i granitima 175 mg/kg. Šejlovi imaju srednju vrijednost od 160 mg/kg, pješčenjaci 220 mg/kg i karbonati 19 mg/kg. Srednja vrijednost u tlima je 300 mg/kg. U slatkoj vodi ga ima oko 0,001 mg/L. Topiv je u formi organskih kompleksa.

Cirkonij se smatra jednim od najimobilnijih elemenata. Ako se i oslobodi iz nekih feromagnezijskih minerala, tipično je da se brzo adsorbira na minerale glina. Teški mineral cirkon vrlo je otporan na trošenje. U teškoj frakciji (< 0,1 mm) često se pojavljuje u velikim koncentracijama.

Ovaj element je bez esencijalne važnosti. Vrlo slabo je otrovan i podaci o njegovoj otrovnosti su vrlo rijetki.

Svjetska produkcija cirkonija u 2003. godini procijenjena je na 1 100 000 t. Ovaj element dobiva se iz ležišta pijeska, ali i kao nusprodukt kod proizvodnje titanija. Pijesci su najčešće obogaćeni na U i Th, tako da proizvodnja cirkonija ima utjecaj na okoliš.

Metal cirkonij se upotrebljava za posebne visokotemperaturne legure (Fe, Ni), a oksid kao pijesak u ljevaonicama i kao sredstvo za poliranje. Osim toga, primijenjuje se u kozmetici (zubna pasta), za boje, pigmente i bljeskalice. Upotrebljava se i kao materijal za reaktore. Važnu primjenu cirkonij-metal nalazi u medicini kao dodatak materijalu za implantate za kosti i mišiće. ZrO_2 se dodaje cementu za kosti radi boljeg kontrasta kod rentgenskih snimanja.

Kao otpad je vrlo rijedak i nema utjecaja na onečišćenje okoliša.

Zirconium is a lithophile and oxyphile trace element which is 18th in abundance in the earth's crust. With increasing alkalinity of magma the concentration of zirconium also increases. It is associated with Hf, and also with Y, La, Ce and other rare earth elements as well as with Ti, Nb, Th and U. Zirconium is crystallized among the first minerals in the primary melts.

The average content of this element in ultramafic igneous rocks is 45 mg/kg, oceanic tholeiites 95 mg/kg, basalts 140 mg/kg, granodiorites 140 mg/kg and granites 175 mg/kg. Shales contain in average 160 mg/kg, sandstones 220 mg/kg and carbonates 19 mg/kg. The average content of zirconium in soils 300 mg/kg. In sweet water it is present with about 0.001 mg/L. Zirconium is soluble in the form of organic complexes.

Zirconium is considered one of the most mobile elements. Even if released from some ferromagnesian minerals it is typically quickly adsorbed on the clay minerals. The heavy mineral zircon is very resistant to weathering. In the heavy mineral fraction (< 0.1 mm) it frequently occurs in great concentrations.

This element is without essential importance. It is almost harmful and data on its toxicity are very scarce.

The world production of zirconium in the year 2003 is estimated at 1,100,000 t. This element is obtained form the sand deposits but also as a byproduct of the production of titanium. These sands are most frequently enriched in U and Th so that production of zirconium does affect the environment.

Zirconium as a metal is applied for special high temperature alloys (Fe, Ni), while its oxide is used as sand in foundries and as a polishing agent. Besides, it is used as a material for reactors. As a metal it is important in medicine as an addition to implants for bones and muscles. ZrO_2 is added to the cement for bones due to the better contrast during roentgen recordings.

As a waste material zirconium is very rare and is without impact on environment due to its frequent occurrence in the nature.

Minerali nositelji cirkonija su izuzetno otporni na trošenje u sekundarnom okolišu i jako rezistentni kod kemijske pripreme uzoraka za analizu. Kemijska priprema predmetnih uzoraka rađena je u zlatotopki, pri čemu je veći dio minerala nositelja ovog elementa ostao neotopljen. Zbog toga se koncentracije cirkonija u analiziranim tlima na istraživanom području trebaju promatrati u relativnim odnosima, a ne u apsolutnim, jer ovi posljednji ne prikazuju realno stanje.

Izmjerene koncentracije ovog elementa na istraživanom području kreću se od < 0,1 do 20 mg/kg s medijanom od 1,5 mg/kg. Najveća vrijednost registrirana je u tlu u krugu Željezare Sisak. Na druga dva lokaliteta unutar iste lokacije također su utvrđene anomalne koncentracije ovog elementa u tlu, što je nesumnjivo vezano uz proizvodne procese u tom industrijskom pogonu.

Tla u blizini Termoelektrane Sisak imaju također anomalne i visoke sadržaje cirkonija, a ujedno ukazuju na prijenos vjetrom prema sjeveroistoku.

Ekstremna koncentracija ovog elementa u uzorku između željezničke stanice u Capragu i Rafinerije nafte Sisak, vjerojatno je vezana za povećan sadržaj teške mineralne frakcije u tlu na tom lokalitetu (cirkon).

Isto tako povećani i visoki sadržaji cirkonija u tlima u dolini Kupe (Pogorelec, Staro Pračno), Odre (sisačka Zgmajna) te područja oko kompleksa kemijske industrije su geogenog podrijetla i potječu od minerala teške frakcije. Sadržaj teške mineralne frakcije je najvjerojatniji uzrok malo povećanih koncentracija ovog elementa u odnosu na vrijednost medijana na području između naselja Hrastelnice, Galdova, Budaševa i Goričice.

Veliki dio urbanog područja Siska posjeduje koncentracije cirkonija u tlu niže od medijana.

Zirconium host minerals are extremely resistant to weathering in the secondary environment and very resistant during chemical preparation of the samples for analysis. Chemical preparation of samples is carried out in the aqua regia which is why the greatest part of the host mineral is left undigested. In this regard the concentrations of zirconium in the analyzed soils of the investigated area must be considered not in absolute but relative terms since the former do not reflect the real state of affairs.

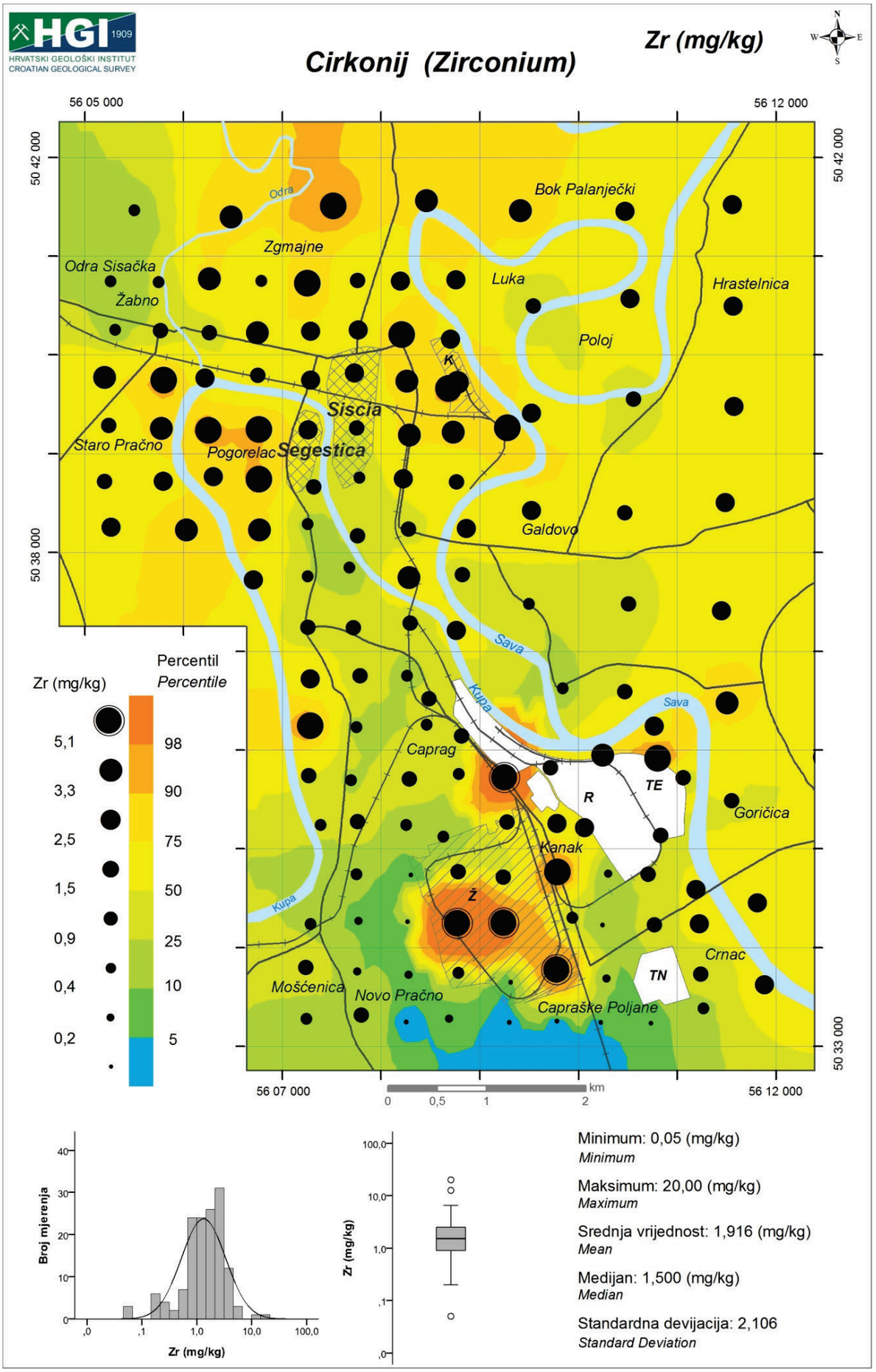
The measured concentrations of this element in the investigated area vary from < 0.1 to 20 mg/kg with median of 1.5 mg/kg. The highest value is registered within the circle of the steelworks. The two other localities within the steelworks area also contain anomalous concentrations of this element in the soil which is indubitably related to the production processes in this processing plant.

The soils in the vicinity of the thermal power plant also show anomalous and high contents of zirconium indicating the airborne transport by wind towards northeast.

Extreme concentration of this element in the sample collected between the Caprag railway station and the oil refinery is probably associated with increased content of the heavy mineral fraction in the soil on this locality (zircon).

In the same way the increased and high contents of zirconium in the soils of the Kupa and Odra valleys (Pogorelec and Staro Pračno vs. Sisačka Zgmajna) as well as in the soils in areas around the complex of chemical industry are of geogenic origin deriving from the heavy fraction minerals. The content of heavy mineral fraction is the most probable cause of the slightly increased concentrations of this element with respect to the median value in the area between the Hrastelnica, Galdovo, Budaševo and Goričica settlements.

The greatest part of the urban core of the Sisak city is characterized by the concentrations of zirconium in the soil below the median value.


HGI 1909
HRVATSKI GEOLOŠKI INSTITUT
CROATIAN GEOLOGICAL SURVEY
Cirkonij (Zirconium)
Zr (mg/kg)
N
W
E
S
56 05 000
56 12 000
50 42 000
50 38 000
50 33 000
56 07 000
Odra
Zgmajne
Odra Sisačka
Žabno
Bok Palanječki
Luka
Hrastelnica
Poloj
K
Siscia
Staro Pračno
Pogorelac
Segestica
Galdovo
Sava
Kupa
Caprag
TE
R
Goričica
Kanak
Ž
Crnac
TN
Mošćenica
Novo Pračno
Capraške Poljane
km
0
0,5
1
2
Zr (mg/kg)
Percentil
Percentile
5,1
3,3
2,5
1,5
0,9
0,4
0,2
98
90
75
50
25
10
5
Broj mjerenja
Zr (mg/kg)
Minimum: 0,05 (mg/kg)
Minimum
Maksimum: 20,00 (mg/kg)
Maximum
Srednja vrijednost: 1,916 (mg/kg)
Mean
Medijan: 1,500 (mg/kg)
Median
Standardna devijacija: 2,106
Standard Deviation

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Ajka Šorša • Josip Halamić

GEOKEMIJSKI ATLAS SISKA / GEOCHEMICAL ATLAS OF SISAK