Potencijal ispiranja selena i metala iz nepropisno odloženog otpada šljake, pepela i Raškog ugljena u naselju Štrmac u Istri

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Leaching potential of selenium and metals from unregulated waste of slag, ash, and Raša coal (Štrmac, Istria)

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POTENCIJAL ISPIRANJA SELENA I METALA IZ NEPROPISNO ODLOŽENOG OTPADA ŠLJAKE, PEPELA I RAŠKOG UGLJENA U NASELJU ŠTRMAC U ISTRI

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Rad je izrađen: Geološki zavod, PMF, Zagreb, Horvatovac 95, 10 000 Zagreb, Republika Hrvatska

Sažetak:

U naselju Štrmac nalazi se nepropisno odloženi otpad šljake i pepela nastao tijekom četiri stoljeća eksploatacije i izgaranja ugljena. Ispitano je ispiranje elemenata iz uzoraka Raškog ugljena, otpadne šljake i okolnog tla. Ukupne koncentracije elemenata u pet uzoraka određene su u uzorcima nakon totalne digestije u mikrovalnoj pećnici. Za ekstrakciju, testirane su tri metode ekstrakcije, ASTM, EP i TCLP (pH 4.93 i 2.9). Multi-elementarna analiza razgrađenih uzoraka i ekstrakata izvršena je tehnikom spektrometrije masa visoke razlučivosti uz induktivno spregnutu plazmu (HR-ICP-MS). Svi su uzorci analizirani na 29 elemenata (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, U, V, Zn). Ukupne koncentracije kretale su se za glavne elemente od 0.005-21.1%, a za elemente u tragovima od ispod granica detekcije do 1083 mg kg^{-1}. Najviše ukupne koncentracije za većinu elemenata izmjerene su u uzorku tla. Koncentracije ekstrakata kretale su se od ispod granica detekcije do 507 mg L^{-1} i slijedile su redoslijed: ASTM < EP < TCLP < TCLP2, pri čemu su najviše koncentracije zabilježene u uzorcima otpada za većinu elemenata. V, S, U i Mn bili su iznad ograničenja u svim metodama. V, S i U su bili iznad u uzorcima brda, a Mn u uzorku tla. Relativna masa ispranih elemenata kretala se u rasponu od 0.00001% do 1.94% što je znatno manje u usporedbi sa sličnim istraživanjima. Najveći RML zabilježeni su u uzorcima brda za većinu elemenata. Na mobilnost elemenata utječu pH i mineralogija (karbonati i sulfati).

Ključne riječi: ispiranje, nepropisni otpad, Raša ugljen, Štrmac

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Master Thesis

LEACHING POTENTIAL OF SELENIUM AND METALS FROM AN UNREGULATED WASTE OF SLAG, ASH, AND RAŠA COAL (ŠTRMAC, ISTRIA)

Marija Petrović

Thesis completed in: Department of Geology, Faculty of Science, University of Zagreb, Horvatovac 95, 10 000 Zagreb, Republika Hrvatska

Abstract: Unregulated waste generated from four century long coal mining and combustion is still left in Croatian village situated on karstic area. Leaching of elements from Štrmac ash and slag heap, soil around heap and Raša coal was investigated. For total element analysis, five samples were subjected to total digestion in microwave oven. For extraction, three extraction procedures were tested, ASTM, EP and TCLP (pH 4.93 and 2.9). Multielemental analysis of bulk samples and extracts was performed by HR-ICP-MS. All samples were analysed for 29 elements (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, U, V, Zn). Total concentrations ranged from 0.0046 to 21.1% for major oxides and from below the detection limit to 1083 mgkg-1 for trace elements. The highest total concentrations were measured in the soil sample for majority of elements. The extract concentrations ranged from below the detection limit to 506.97 mg L^{-1} and followed the order: ASTM < EP < TCLP < TCLP2. The highest extract concentrations were observed in hill samples. V, S, U and Mn were above the limit in all extraction procedures. V, S, U were above in hill samples, while Mn was above in soil sample. Relative Mass Leached of elements ranged from 0.00001% to 1.94% which is much lower compared to similar studies. Highest RML were observed in hill samples. Mobility of elements is controlled by pH and mineralogy (carbonates and sulphates).

Keywords: leaching, unregulated waste, Raša coal, Štrmac

Thesis contains: 53+XXI pages, 1 figure, 7 tables, 115 references

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1. INTRODUCTION

Coal power-plants generate almost 40% of world electricity. Prior to combustion, coal has to be mined, excavated and most often cleaned. After combustion, non-combustible parts of coal are left in the form of ash and slag. All of the processes happening prior and after the combustion generate waste, which must be disposed in specific terms to not interfere with environment and human health. If the waste is not properly disposed, the environmental conditions, such as precipitation, can cause leaching of elements from ash and slag which can enter the groundwater or pollute the soil around disposal site.

Coal mining has been for four centuries one of the main industrial sectors in Croatia, but with the lack of clean coal technology, the mining and combustion of coal generated spoil heaps and illegal landfills, which are still left in villages situated on karstic area.

Those landfills consist of coal ash, slag and any waste that was left from mining. To understand how elements are leached from such lanfills and how they act in different pH conditions, it is necessary to understand in which form they come in coal and coal ash. Raša coal is considered a 'non-usual' coal, so first section describes general coal characteristics. Literature review is presented in chapter two (in section An overview of previous research) and it covers geochemistry and formation of Raša coal which was used during time when waste was created.

To determine if waste is a threat to the surrounding area, different organisations developed methods and criteria which classify waste as hazardous or non-hazardous. In this diploma thesis, three different methods were used, ASTM, EP and TCLP which differ in terms of pH and extraction time. They were used to represent different environmental conditions, e.g. ASTM has natural pH and represent conditions during rainfall, while EP and TCLP have acidic pH and they represent acidic conditions. Broader overview of used methods is presented in chapter two (in subsection Extraction procedures).

The aim of the study is to determine the total concentrations of potentially toxic elements (Se and metals) in samples of coal ash, coal and surrounding soil from the Štrmac area (Istria) as well as their concentrations in the extracts obtained by extraction procedures. The purpose of the study is to assess the risk of leaching of these elements by natural weathering on the environment and human health.

2. AN OVERVIEW OF PREVIOUS RESEARCH

In this chapter, general coal characteristics and coal combustion products are described, followed by description of extraction procedures used in this thesis. In subsection 'Previous geological research' geochemistry and environmental impact of Raša coal and its combustion is described.

2.1. THEORETICAL BASIS

2.1.1. Coal – formation and characteristics

Coal is black or brown sedimentary rock consisting primarily of carbon, hydrogen and oxygen. The physical, chemical, and other properties of coal vary considerably from sample to sample.

- Coal formation

Coal is formed by accumulation of organic materials, mostly remains of terrestrial plants like wood, roots, leaves and seeds, in a swamp environment which leads to the formation of peat. After the peat is buried under mineral sediment, the high temperatures and pressure convert the plant material to coal by the geochemical process called coalification. Coalification consists of three main steps**:** the microbiological degradation of the cellulose of the plant material, the conversion of the lignin[1] into humic substances[2], and the condensation of these humic substances into larger coal molecules (Miller, 2011; Speight, 2012). Most abundant formation of coal happened about 300 million years ago during the Carboniferous Age and 100 million years ago during the Upper Cretaceous Age (Speight, 2012). It is still not completely clear what caused first abundance of coal. Suggested theory was that fungi, that act as plant decomposers, were absent during the Carboniferous Age, resulting in massive accumulation of organic matter, originated from plants with high lignin content (Corner, 1964). New research propose that this theory lacks evidence and that coal

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[1] a complex organic polymer deposited in the cell walls of many plants, making them rigid and woody

[2] Substances formed by the microbial degradation of dead plant matter, such as lignin and charcoal

accumulation in that period is simply result of unique combination of climate and tectonics during Pangea formation (Nelsen et al. 2016).

Coalification forms different types of coal which depends on the pressure, temperature and length of time in formation. Initially the peat is converted into 'lignite' that is soft and its colour range from dark black to various shades of brown. The continuing effects of temperature and pressure transforms lignite into ‘sub-bituminous’ coals. Further chemical and physical changes occur until these coals became harder and blacker, forming the ‘bituminous’ coals and finally 'anthracite' (Tatsch, 1980). Bituminous and anthracite coals are considered ‘high rank’ coal due to higher percentage of pure carbon, lower impurities and higher fuel value than lignite.

- Coal composition

Coal is composed of organic material (primarily carbon, hydrogen and oxygen and lesser amounts of nitrogen and sulfur) and of inorganic material (wide variety of elements in mineral form and organically bound elements) (Miller, 2011). Organic constituents of coals are called macerals. Macerals are grouped according to the plant tissue that they were derived from in three main groups: vitrinite, inertinite, liptinite.

Regarding its inorganic part, five mineral groups are most abundant in coal: clay minerals, carbonate minerals, sulphide and disulphides, silica and sulphates, whereby clay, quartz, pyrite and various carbonates are the dominate minerals in most coals. Coal also contains significant quantities of many trace elements, which can occur in coal in both organic and inorganic forms. Distribution and occurrence of these elements and minerals differ between coals from different locations and even between coals from the same seams due to different conditions in peat environments (Rađenović, 2006). Table 1. summarizes findings of Querol et al. (1996) on distribution of trace elements in coals, but it should be mentioned that organic and inorganic affinity of elements varies in different types of coals, and there is no general rule in occurrence of trace elements (Vejahati et al., 2010).

Table 1. Distribution of trace elements in coal (Querol et al. 1996)

Affinity	Mineral Group	Mineral Type	Elements
Inorganic	Clay minerals and feldspars	Kaolinite Montmorillonite	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y and rare earth elements
	Iron sulphides	Pyrite Spharelite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb S, Sb, Se, Ti, W and Zn
	Carbonates	Calcite, Dolomite	Ca, Co and Mn
	Sulfates		Ba, Ca, Fe and S
	Heavy minerals		B
Organic			N, S, Be, B, Ge, V, W and Zr

2.1.2. Coal combustion products (CCP)

Coal, as a combustible material, is one of the world's most important sources of energy where 37% of world electricity comes from coal-fuelled power plants. Due to its slow formation which takes millions of years, it is considered a non-renewable resource and the deposits of coal that are now on Earth are estimated to last for another 200 years if mining and combustion of coal continues at today's rate (WCA – Link 5).

While coal is burned, combustible elements of coal (carbon, sulfur and hydrogen) react with oxygen and produce respective oxides (CO, CO_2, SO_2, H_2O) and heat which is then converted to electricity. The non-combustible part of coal remains in the form of fly ash, bottom ash, boiler slag and flue-gas desulfurization residues. Fly ash is a very fine, powdery material that floats into the exhaust stacks and can be collected with filters. It is composed mostly of silica. Bottom ash is coarsely granular product that is too heavy to float so it settles on the bottom of the boiler where it is collected. Boiler slag is the melted form of coal ash. Flue-gas desulfurization material is a residue from the process of reducing sulfur dioxide emissions. It mainly consists of calcium sulfite and sulfate. These products are waste products of coal combustion and can be considered as environmental concern if not disposed properly. The products can often be used as secondary raw materials (Speight, 2012).

Due to high temperatures in coal combustion processes (≥1000), organic and inorganic constituents of coal are transformed, which makes composition of coal combustion products different than composition of coal. Elements associated with coal organic fractions usually vaporize and adsorb on fine particles when the temperature drops. Elements associated with minerals mostly remain in the ash. In general, CCP are enriched in trace elements (Vejahati et al., 2010; Miller, 2011; Speight, 2012).

2.1.3. Extraction procedures

Extraction procedures are used to estimate potentially leached concentration of waste constituents that can enter the environment. More than twenty leaching test methods have been developed over time to simulate the leaching process (Tiwari et al., 2015). Commonly used methods include ASTM, EP and TCLP methods which are compared in this thesis.

- ASTM – extraction procedure

ASTM stands for American Society of Testing and Material where several extraction methods were developed. Most commonly used method is The Shake Extraction of Solid Waste with Water (ASTM D-3987-85), often referred to as only ‘ASTM’. The method is based on an extraction of a known weight of waste with distilled water for 48h. The test is intended to simulate conditions where the solid waste is the dominant factor in determining the pH of the leachate. This method has only been approved for certain inorganic constituents and is not applicable to organic substances and volatile organic compounds (Link 6).

- EP - The Extraction Procedure

The Resource Conservation and Recovery Act (RCRA) is United States’ primary law governing the disposal of solid and hazardous waste. It was passed by the Congress of US in 1976 to address the problems of growing municipal and industrial waste. US Environmental Protection Agency (EPA) developed a program for RCRA which consists of guidelines for transportation, treatment, storage and disposal of waste as well as laboratory procedure for determining whether the waste is hazardous or not. EP was the first procedure that was developed, while TCLP was developed later and was proposed as a replacement for the EP test. (Bricka et al., 1992).

The EP is a laboratory test originally designed to simulate leaching of components from potentially hazardous waste disposed in a municipal landfill. It uses a weak acid solution (pH 5.0 ± 0.2) and waste is considered hazardous if the extract contains any of the listed contaminants at a concentration greater than the specified value (Table 2; US EPA, 1980).

Table 2. Maximum concentration of contaminants

USEPA hazardous waste number	Contaminant	Maximum concentration (mgl^{-1})
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

- <u>TCLP – Toxicity Characteristic Leaching Procedure</u>

The TCLP is an expanded version of the EP because it covers a broader range of waste types and can be used for more organic and inorganic compounds. The test is conducted using buffered acetic acid solutions with pH=4.93 or pH=2.88 depending on the pH of the material. TCLP is the most commonly used leachate test for estimating the actual leaching potential of wastes, but the main problem associated with this method is that it can overestimate or underestimate leaching potential under other extreme conditions (e.g. alkaline waste) (Link 2).

2.2. PREVIOUS GEOLOGICAL AND ENVIRONMENTAL RESEARCH

2.2.1. Brief history of coal mining in Croatia

It is not clear when and where people first started using coal, but it is known that it was used during Bronze age in China and on a small-scale around the world during medieval period (Dodson et al., 2014). It's not until Industrial Revolution in 18th and 19th century when people started using coal on a large scale. It was used for iron and steel production, rail transportation, steamships, producing gas for gas lights and with development of electric power, it was used and still is for generating electricity.

In Croatia, the mining activities took off in 18th century on Istrian Peninsula. First mining activities started in Krapan mine, where the tar-like coal was found and used in impregnation of bottom of the boats. After intensive mining work and attempts to find hard coal, Raša coal was found, and it was the economic, social and cultural turning point for the region. The mining was the main factor in developing that part of the country which was visible in school openings, building residential areas, railways and roads that connected Raša coal mining towns (Štrmac, Labin, Vinež, Krapan, and Raša). In the mining period that lasted four centuries, Croatia was under the rule of many different governments (Venetian, Austro-Hungarian, German) which resulted in different management of mines and sometimes dissatisfaction among workers. Main facilities that were open were the coal separation facilities in Štalije, the Vlaška thermal power plant, heating plant in Raša during the 1930s, and the Plomin thermal power plant in the 1970s (Vorano, 1997; Medunić et al., 2016a). The coal combustion activity related to these facilities generated large quantities of waste ash. Last mine was closed in 1999, leaving behind generated waste from mining and combustion in former mining towns.

2.2.2. Raša coal – Croatian SHOS coal

- Superhigh-organic-sulphur (SHOS) coal

The sulphur content and forms in coals vary with location and coal rank. Sulphur in coal appears in organic form (bonded to carbon) and inorganic forms (sulphides and sulphates). Content of S in most coals ranges from 0.50% to 5.00% (Rađenović, 2004; Chou, 2012), but there are coals that are enriched in organic sulphur, usually in the range of 4.00-11.0%. Those coals form a special class of coal Superhigh-organic-sulphur (SHOS) coal, which are also found around the world, mainly in Australia (Smith and Batts, 1974; Marshall and Draycott, 1954; Ward et al., 2007) and China (Dai et al., 2008, 2013a, 2013b, 2015). SHOS coals are usually enriched in U-Se-Mo-V-Re (Shao et al., 2003; Zeng et al., 2005; Dai et al.2015). Content of inorganic sulphur, mostly in form of pyrite (FeS_2), is variable and SHOS coals can have a low or high pyritic sulfur content depending on the coal forming environment. Raša coal has a low pyrite content similar as found for Chinese Yanshan and Guidan coals (0.30% to 1.1%) (Chou, 2012).

- Formation and geochemistry of Raša coal and combustion products

Coal reservoirs in Croatia are found in south-eastern part of Istrian Peninsula and are of late Paleocene age. The rise in sea level caused the rise of fresh groundwater, submerging parts of the relief and turning them into wetlands where the initial material was deposited. Coalification process resulted in more than thirteen coal beds, where coal layers are mostly several cm to 3 meters thick, as well as vertically distanced 1 to 15 meters (Pantić and Nikolić, 1973; Nikolić and Dimitrijević, 1981; Medunić et al., 2015).

Raša coal is characterised by unusually high amount of sulphur (11.8%), which is largely present in the form of anomalously high level of organic S (11.4%) (Sinninghe Damsté et al.1999). High sulphur content in Raša coal is connected to the environmental conditions during formation of Raša coal beds, which were anaerobic and alkaline (Hamrla, 1960). The alkaline marine environment fostered bacterial growth which contributed to sulphur fixation. White et al. (1990) confirmed the environmental conditions by reporting the high amount of calcite and dolomite in Raša coal as the major mineral phases. In addition, they identified the dominating maceral in Raša coal as vitrinite with some exinite or liptinite and very little inertinite. Sinninghe Damsté et al. (1999) identified the organosulfur compounds in Raša coal[3] as well as high abundance of polyaromatic sulfur compounds, which together with very low abundance of lignin-derived compounds and low oxygen values indicated that organic matter in Raša coal had not been predominantly derived from the higher terrestrial plants.

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[3] The major organosulfur compounds (OSC) present in the extract are alkylated benzo[b]- and dibenzothiophenes and in the pyrolysates alkylated thiophenes and benzo[b]thiophenes.

Bauman and Horvat (1981) reported natural U ranges in Raša coal from 14.0 mg/kg to 100 mg/kg and Valković et al. (1984) reported values of elements as follows (all in mg/kg, except for S and Ca in %) : S 13.05, K 532, Ca 1.8, Ti 380, V 43, Cr 23, Fe 3300, Ni 23, Cu 25, Zn 41, As 25, Se 43, Rb 13, Sr 412, Mo 94, and U 55. Raša coal was also characterised by an increased radioactivity. The activity of U^{-238} was 500-1200 Bq/kg in the 1970s, and 250-300 Bq/kg in the 1980s, which was 10-15 times higher than the average of other types of coal in the world (Marović et al., 2004). Valković et al. (1984) determined the bulk composition of fly ash from TPP Plomin by X-ray emission spectroscopy and the distribution pattern of different elements in individual ash particles with the proton microprobe. The X-ray spectra of fly ash showed high peaks of Ca, Fe and Sr and identified spectra of V, Zn, Cu, Cr, Ga, As, Pb, Se, Rb and Br. The magnetic separation of fly ash showed spherical particles and black irregular-shaped particles in non-magnetic fractions, and 'metallic' particles of various shape in magnetic fractions. Excitation of sample showed strong peaks of Ca and Sr in non-magnetic fraction, as well as presence of S, Se, Cu, Zn, Pb, Br and Rb. The magnetic fractions showed high peak of Fe, and presence of Ca, Sr, Ti, V, Cr, Ni, Cu, Zn and Ga. X-ray diffraction showed presence of $CaSO_4$ (anhydrite), CaO (lime), FeS_2 (pyrite and/or marcasite), $FeSO_4$ x H_2O (szmolnokite), Ca(OH), (portlandite) and amorphous material in magnetic fractions, while in non-magnetic CaO, $CaSO_4$, $Ca(OH)_2$, and $CaCO_3$ were present. Distributions of elements in particles showed three patterns. K and Ca peaked at the surface, V, Ti, Cr and Se peaked slightly below the surface and Fe was mainly in the centre of the particle. Increased levels of S, Ca, U and V was reported by Stergaršek et al. (1988), as well as that Raša coal had 15.0% of ash, which was alkaline and distributed as 70:30 fly ash: bottom ash (slag). An average composition (%) of the Raša coal ash was: SiO_2 1.90, Al_2O_3 3.27, Fe_2O_3 4.59, CaO 64.2, MgO $_{3.}$79, Na_2O 1.42, K_2O 0.19 and SO_3 20.5.

Previous study (Peco, 2018) showed that main minerals in Raša coal are calcite ($CaCO_3$), gypsum ($CaSO_4$ x $2H_2O$) and dolomite ($CaMg(CO_3)_2$), while rozenite ($FeSO_4x4H_2O$) and siderotil ($FeSO_4x4H_2O$) are found in traces. Main mineral composition in ash were anhydrite ($CaSO_4$), calcite, aragonite (polymorph modification of calcite), gypsum and bassanite ($CaSO_4$x $0.5H_2O$), with small fractions of portlandite ($Ca(OH)_2$) and in slag gypsum, portlandite, calcite, anhydrite and ternesite ($Ca_5(SiO4)_2SO_4$). Mineral composition of soils around TPP Plomin shows predominance of quartz, calcite, ilite, clinochlore and anorthite, while albite, microcline and kaolinite were found in smaller quantities. Dolomite, gypsum, gibbsite, ankerite and boehmite were found in traces, while thaumasite and fairchildite were found in soil near ash and slag landfills.

2.2.3. Environmental impact of Raša coal and combustion products

At the end of the 20th century, environmental impact of Raša coal mining and combustion began to be explored. The focus was PP Plomin as the main, and currently the only, thermal power plant in Croatia. Komlenović and Pezdirc (1987) reported mechanical damage of the needles and leaves of Austrian pine (*Pinus nigra*), Aleppo pine (*Pinus halepensis*), flowering ash (*Fraxinus ornus*) and the pubescent oak (*Quercus pubescens*) near TPP Plomin, during the use of Raša coal. They also reported higher SO_2 concentration in Austrian pines (*Pinus nigra*) near TPP Plomin, than in pines 22 kilometars away from PP Plomin. Komlenović (1989) broaden study area on whole Istria Peninsula and confirmed that culture of *Pinus nigra* near TPP Plomin is the most damaged culture of same species in Istria. Komlenović et al. (1990) continued research on concentration of sulphur in needles of *Pinus nigra*, and in addition they reported elevated levels of sulphur and lead in all and zinc in places of top five centimetres of humus-accumulative soil horizon near PP Plomin.

Lokobauer et al. (1996) investigated radon activity concentration in houses around the PP Plomin with assumption that old houses in that region were built using mortar and plaster prepared from slag and ash. They reported that the average annual radon activity concentrations in the old houses ranged from 55 Bqm^{-3} to 426 Bqm^{-3} and in more recently built houses from 16 Bqm^{-3} to 67 Bqm^{-3}. Prohić and Miko (1998) compared metals concentration (Se, As, V, Cr, Ni, Zn i Pb) in soils from the vicinity of the PP Plomin and in soils from Croatian National Park Risnjak (geochemical background). They reported the mean concentrations for <63 mm fraction of topsoil samples around the PP Plomin as follows: Se 5.64 mg kg^{-1}, As 10.3 mg kg^{-1}, V 166 mg kg^{-1}, Cr 145 mg kg^{-1}, Ni 80 mg kg^{-1}, Zn 143 mg kg^{-1}, Pb 143 mg kg^{-1}, and for the soils from Risnjak: Se 0.84 mg kg^{-1}, As 18.5 mg kg^{-1}, V 123 mg kg^{-1}, Cr 66 mg kg^{-1}, Ni 49 mg kg^{-1}, Zn 114 mg kg^{-1}, Pb 65 mg kg-1. They concluded that selenium and chromium had the most impact on the soils around the power plant. Oreščanin et al. (2009) found neither cytotoxic nor mutagenic effects of the Plomin bay sediments, and later reported that these sediments have identical chemical composition prior and following the PP Plomin activity. Ernečić et al. (2014) analysed the activity of Ra in soil in the vicinity of the TPP Plomin and reported increased activity of ^{226}Ra (64,5 Bq/kg-

202 Bq/kg) in samples collected in the dominant wind direction. Fiket et al. (2015) measured rare earth elements (REE) concentrations to assess the influence of TPP Plomin on surrounding soils. Results pointed to transfer of ash particles from the TPP to the surrounding environment, with greatest influence in the direction of the prevailing north-eastern wind. Medunić et al. (2016b) reported the elevated levels of sulphur, PAHs and potentially toxic trace elements in soils surrounding the TPP Plomin. Radić et al. (2018) conducted a study of chemical and toxicological evaluation of aqueous extracts of soil collected near a coal-fired Plomin power plant, demonstrating that Plomin soil extracts induced phytotoxic effects.

Medunić et al. (2016a) reviewed historical, geological, geochemical and environmental aspects of the Raša coal mines and generated waste, shifting the focus of research from pollution caused by TPP Plomin to pollution caused by mining and other facilities mentioned earlier. Medunić et al (2018a) reported the levels of S, Se, V, U, Hg, Sr, Cd, Cr, Pb, Cu and Zn in the two coal types (Raša coal and imported coal), their bottom ash, seawater and plant (clover, mushroom and foliage) specimens collected from the Labin City area, while the sulphate was measured in surface stream water. Values of Se were slightly increased in aquatic and herbal plant specimens. Total values of Se in Štrmac site were lower compared to relevant previous studies on SHOS Raša coal ash by-products, implying the possibility of leaching. The values of trace metals (Cd, Pb, Cr, Zn and Cu) were slightly increased in seawater compared to world values, which was attributed to the respective elevated levels in today's ash derived from the low-S coal combustion. Medunić et al. (2018b) reported values of Se, S, trace metals and BTEX in soil, water and lettuce in Raša Bay. Trace elements in soil, based on ecological indices, were in a category of an extremely high level of soil pollution. S, Se, V and U were elevated in soil, surface water and home-grown lettuce. Soil around Štrmac had anomalously high Cu, Zn and Pb levels, while low Se levels were prescribed to leaching. Medunić et al. (2018c) reported total Se, As, Cd, Cu, Cr, Hg, Pb, Sr, U, V and Zn values in lettuce, potato and tissues (liver, kidney, heart, and muscle) of three non-migratory bird species (pigeon, jay and black coot) from the Raša Bay area. Values of Mo, U, V, and Sr were increased in the majority of water samples as well as in analysed vegetables, soil, and aquatic sediments, while Cu, Zn, Pb, and V were slightly increased in liver samples of birds. Fiket et al. (2018) presented content of rare earth elements (REE) in Raša coal, in combustion products (Štrmac landfill) and in soil around those landfills. They concluded that Raša coal ash cannot be considered as the secondary raw material for rare earth elements and that Raša coal-bearing strata were influenced by both the seawater and hydrothermal solutions which both led to sulfur enrichment and REY accumulation.

3. MATERIALS AND METHODS

3.1. Study area

The study area is in village Štrmac, which is located on the south-eastern part of the Istrian peninsula, the westernmost part of Croatia (Fig. 1a, b). The geological setting of the wider study area consists of sedimentary Mesozoic (mostly Cretaceous) and Paleogene (Paleocene, Eocene) rocks (Vlahović et al., 2005) with the superhigh-organic-sulphur Raša coal seams (Medunić et al., 2016) (Attachment 1). Štrmac lays on Eocene limestones with the thrust fault going across the village (Šikić et al., 1969). The wider area is characterized with red and brown soils, while Štrmac lays on brown soils on limestones, belonging to the class of Chromic Cambisols[4] (Miko et al., 2003), with inclusions of rendzina and terra rossa (Link 1).

The samples were collected from a hill in the village (Fig.1c), which was made by dumping slag and ash, i.e. by-products of mining in the past. The hill was briefly covered with soil to prevent air spreading and the water erosion is visible on the slope of the hill (Fig.1d). About 5,5 km southeast (air-distance) of Štrmac is town Raša (Fig.1e), in which coal sample was collected from the abandoned mine (Fig.1f) mentioned in previous chapter.

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[4] Food and Agriculture Organization (FAO) has classified all soils in 30 groups, 22 of them are based on one of the factors: climate, organisms, and time. One of them are Cambisols defined as soils having a cambic B horizon (B = Subsoil; cambic = changes in horizon relative to the underlying horizons) or an umbric A horizon (A = Topsoil; umbric = dark coloured and thick) which is more than 25 cm thick; they are classified on 9 subclasses, one of them is Chromic Cambisols which are Cambisols with strong brown to red B horizon. (Link 3)

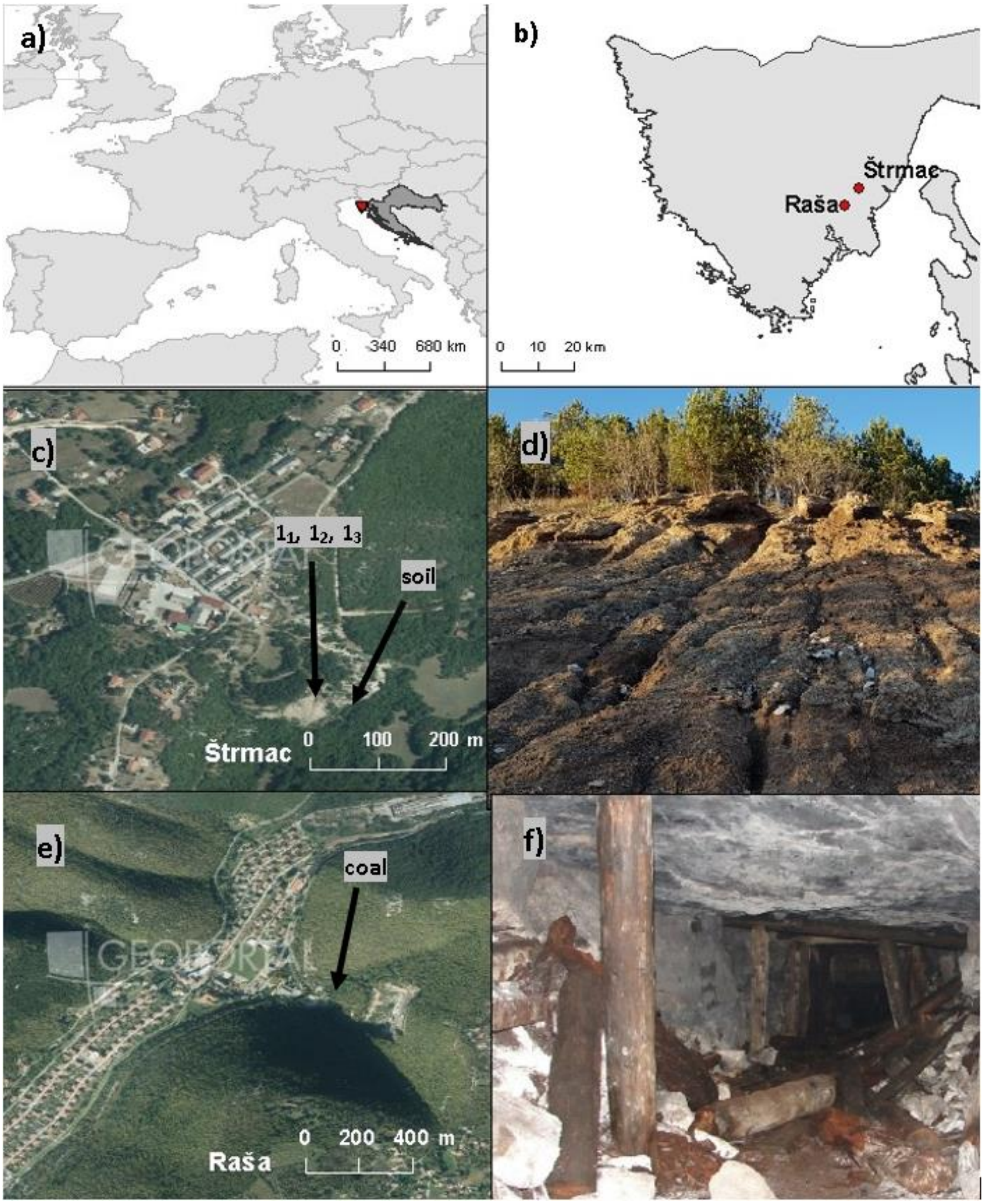

Figure 1. (a – geographical position, red is Istrian Peninsula, b – geographical relation of Raša and Štrmac on Istrian Peninsula, c – segment of Digital Orthophoto of village Štrmac, arrows pointing at the sampling sites, d – front view of the Štrmac hill (Foto: Medunić, 2018) e – segment of Digital Orthophoto of town Raša, arrow pointing at the entrance of mine, f – abandoned mine in Raša (Link 4))

3.2. Sampling and samples description

Total of five samples was collected in December 2017 on different locations (Fig.1). Three ash samples were collected from the Štrmac hill, from locations 2-3 m apart. In the first location (1_1) surface sample was collected, while at the other two (1_2 and 1_3) subsurface layer, ~20 cm deep, was sampled. Additionally, a sample of soil was collected at the bottom of the hill, in a place where rainwater, running down the hill, flew highest. A coal sample was collected in the old abandoned mine, 2 km from the entrance of the mine. The surface layer of coal was removed and subsurface layer, ca. 5 cm underneath, was collected. At all locations, samples were collected with a sampling shovel and stored in a plastic bag.

3.3. Sample preparation

All samples were air dried, sieved through a 2 mm sieve to remove the gravel fraction, and stored until further analysis.

For total element analysis, sub-samples (0.05 g), previously homogenized in an agate mill, were subjected to total digestion in the microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure consisting of digestion with a mixture of 4 mL nitric acid (HNO_3, 65 %, pro analysi, Kemika, Zagreb, Croatia) - 1 mL hydrochloric acid (HCl) - 1 mL hydrofluoric acid (HF, 48 %, pro analysi, Kemika, Zagreb, Croatia) followed by addition of 6 mL of boric acid (H_3BO_3, Fluka, Steinheim, Switzerland). Prior to analysis, digests were 10-fold diluted, acidified with 2% (v/v) HNO_3 (65%, supra pur, Fluka, Steinheim, Switzerland) and In (1 μgL^{-1}) as internal standard was added.

3.4. Extraction procedure

For extraction, sieved samples were mixed with a specified extraction medium. Three extracting methods were tested, ASTM (Method D-3987, ASTM 1995), EP (Method 1310B, US EPA 2005) and TCLP (at pH 4.9 and 2.9; Method 1311, US EPA 1993). The conditions of all extraction procedures are represented in Table 3.

For ASTM procedure, the extraction medium was Milli-Q (MQ) water with a liquid-to-solid ratio 4:1 (40 mL MQ, 10 g sample). For EP procedure, an appropriate quantity of MQ water was added to the sample and pH was adjusted to 5.0 by adding 0.5 N acetic acid. For TCLP procedure, the extraction medium was prepared at pH 4.9 and pH 2.9. In the first case, the puffer was made by adding 2.85 mL acetic acid, 250 mL MQ water, 3.2 mL 10 N NaOH and diluting it to a volume of 500 mL. In the second case, the puffer was made by adding 2.85 mL acetic acid to a 500 mL of MQ water. In both cases, the liquid-to-solid ratio for extraction procedure was 20:1 (40 mL puffer, 2 g sample).

Prepared samples were agitated with a horizontal shaker for a specified period, 48h (ASTM), 24h (EP), and 18h (TCLP). After extraction time finished, the leachates (20 mL) were separated from the solids by filtration through 0.45 µm filters and acidified with 1% (v/v) HNO_3 (supra pur, Fluka, Steinheim, Switzerland).

Prior to analysis samples were 100-fold diluted, acidified with 2% (v/v) HNO_3 (65%, supra pur, Fluka, Steinheim, Switzerland) and In (1 μgL^{-1}) as internal standard was added.

Table 3. Conditions of four different extraction methods (EP, TCLP, TCLP2, ASTM)

	EP	TCLP	TCLP2	ASTM
Medium:sample ratio	20:1	20:1	20:1	4:1
Extraction medium	0.5 N acetic acid	Acetic acid	Acetic acid	Milli-Q water
pH	5.0	4.93	2.9	Neutral
Extraction time	24 h	18 h	18 h	48 h
Agitation method	Horizontal shaker	Horizontal shaker	Horizontal shaker	Horizontal shaker

3.5. Multi-element analysis

Multielemental analysis of bulk samples and extracts was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). Typical instrument conditions and measurement parameters used throughout the work are reported earlier (Fiket et al., 2017). All samples were analyzed for total concentration and extract concentration of 29 elements (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, U, V, Zn).

Quality control of analytical procedure was performed by simultaneous analysis of the blank and certified reference material for soil (NCS DC 77302, China National Analysis Center for Iron and Steel, Beijing, China). Good agreement between the analyzed and certified concentrations within their analytical uncertainties for all elements was obtained (~ 10%).

4. RESULTS

4.1. Total concentrations

Total concentrations of twenty-nine elements (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, U, V, Zn) in five analysed samples are shown in Table 1 (major elements) and Table 2 (trace elements).

4.1.1. Major elements

Table 4 shows concentrations of major elements (Al, Fe, Mn, Ti, P, S) expressed as oxides. The content of Al_2O_3, Fe_2O_3, MnO, TiO_2, P_2O_5 and SO_3 in all analysed samples ranged from 0.0046% (MnO) to 21.1% (SO_3). The content of all elements was highest in the soil sample, with the exception of S exhibiting the lowest value. Contrary, coal sample had the highest value of S (21.1%), while other elements exhibit lower concentrations. In soil and ash samples, Al was present at highest concentrations (0.87 – 13.1%), followed by Fe (0.34 - 5.93%) and Ti (0.05 – 1.10%), while Mn and P were present at concentrations < 1%. In coal sample, S was present in two orders of magnitude higher concentrations compared to other major oxides which followed the similar decreasing order as in soil and ash samples.

Comparing three samples from Štrmac spoil heap, all oxides had highest values in 1_3 sample, while 1_1 sample had the lowest values of listed oxides. Still, samples 1_1 and 1_2 displayed similar levels of major oxides.

Table 4. The content of major oxides (%) in analysed samples and CRM (NCS DC 77302). Bolded are the highest values per oxide.

	1_1	1_2	1_3	Soil	Coal	CRM soil
Al_2O_3	2.1534	2.2938	5.4135	**13.054**	0.8724	14.448
Fe_2O_3	1.2537	1.5836	2.6932	**5.9353**	0.3427	4.6647
MnO	0.0046	0.0062	0.0118	**0.2918**	0.0039	0.1007
TiO_2	0.1289	0.1338	0.3051	**1.1067**	0.0509	0.8460
P_2O_5	0.0158	0.0162	0.0325	**0.1496**	0.0062	0.0951
SO_3	5.2815	5.8358	7.3250	0.5138	**21.088**	0.1201

4.1.2. Trace elements

Table 5 shows total concentrations of trace elements in all analysed samples. Concentrations ranged from below the detection limit (Be in coal subsample) to 1083 mg kg^{-1} (Sr in the 1_1 sample). Bismuth had the lowest concentrations in all samples, from below the detection limit in 1_3 to 0.47 mg kg^{-1} in soil sample.

Majority of trace elements (As, Ba, Be, Bi, Cd, Co, Cr, Cs, Li, Ni, Pb, Rb, Sb, Sc, Sn, Tl, Zn) had the highest concentration in the soil sample. The Bi, Co, Cs, Pb, and Rb were present in 7 – 30 times higher concentrations in soil compared to other samples, while, Cu, Mo, Se, Sr, U, V had highest concentrations in one of the three samples from the hill. In general, majority of elements had the lowest concentration in the coal sample. Only Bi, Cd, Pb, Se, Tl, Rb, and Zn had the lowest levels in one of the samples from the hill, while Sr showed the lowest concentration in the soil sample.

Table 5. Average total concentration (mg kg^{-1}) in five samples (1_1, 1_2, 1_3, soil and coal) and CRM (NCS DC 77302). Bolded are the highest values per element.

	1_1	1_2	1_3	Soil	Coal	CRM soil
As	4.28	8.74	8.76	**14.8**	2.68	12.3
Ba	64.3	88.5	144	**381**	17.7	641
Be	0.37	0.53	1.19	**2.36**	0.06	2.09
Bi	0.02	0.02	0.00	**0.47**	0.04	0.38
Cd	0.19	0.42	0.15	**0.83**	0.20	0.13
Co	3.30	4.20	7.87	**41.5**	1.62	14.4
Cr	55.8	63.6	141	**167**	14.1	66.5
Cs	0.50	0.48	0.61	**7.14**	0.42	7.43
Cu	32.5	32.6	**57.4**	37.8	8.93	28.6
Li	25.5	21.7	32.6	**53.8**	10.5	35.2
Mo	11.1	15.5	**28.6**	2.89	2.75	1.12
Ni	27.9	35.6	64.5	**96.3**	8.92	32.5
Pb	2.23	8.02	1.70	**48.2**	1.82	30.2
Rb	2.67	2.52	3.74	**108**	3.05	111
Sb	0.21	0.53	0.45	**1.64**	0.15	1.49
Sc	3.36	3.72	7.47	**16.1**	0.95	12.3
Se	27.3	**35.9**	5.39	21.8	31.80	5.56
Sn	1.33	1.55	1.98	**4.70**	1.08	5.05
Sr	**1083**	971	984	128	199	222
Tl	0.08	0.31	0.07	**1.04**	0.09	0.62
U	15.2	21.1	**30.3**	4.86	0.79	2.36
V	128	136	**262**	183	16.8	95.0
Zn	12.1	21.2	20.1	**120**	17.7	101

4.2. Extract concentrations

Results of three extraction procedures are shown in Table 6 as extract concentrations (mg L^{-1}) and Table 7 as Relative Mass Leached (%).

- ASTM method

In ASTM method, extract concentrations ranged from 0.0001 mg L^{-1} to 507 mg L^{-1}. The highest concentrations were observed for S and Sr in all measured samples and the lowest for Be and Tl along with Bi and Sc found below the detection limit in all samples. In total, fourteen elements (Be, Bi, Cd, Co, Cr, Cs, Fe, Mn, P, Pb, Sb, Sc, Ti, and Tl) were below the detection limit in one of the samples.

Generally, the highest concentrations for majority of elements were observed in hill samples with exception to Cu, Fe, Ni and Ti which had the highest concentrations in soil sample and P in coal sample. For Al, Ba, Cd, Co, Mn, Pb, Sn, Tl, and Zn there wasn’t a major difference in extract concentration between samples.

The lowest extract concentrations for majority of elements were measured in coal samples, while for some elements (As, Cs, Li, Mo, S, Se, Sb, Sr, U, and V) the lowest concentrations were similar in both coal and soil samples.

- EP method

In EP method, the extract concentrations ranged from 0.0001 mg L^{-1} to 292.85 mg L^{-1}. The highest concentrations were observed for S and Sr in hill samples and coal sample, while in soil sample the highest concentrations were observed for Mn and S. The lowest concentrations were observed for Sb and Tl along with Be, Bi, and Sc being below the detection limit in all samples. In total, fourteen elements (Al, Be, Bi, Cd, Cr, Cs, Cu, Fe, Mo, P, Pb, Sb, Sc, Ti, and Tl) were below the detection limit in at least one of the samples.

The highest concentrations were in hill samples for majority of elements, with exception to Al, Ba, Cd, Co, Fe, Mn, P and Pb which had the highest extract concentrations in soil sample. For Sn, Tl and Zn there wasn’t a major difference in extract concentration between samples. The lowest extract concentrations of all measured elements were measured in coal sample, while for some elements (Cs, Li, Mo, S, Se, Sr, and U) the lowest concentrations were similar in both soil and coal samples.

- TCLP method

In TCLP (pH=4.93) method, extract concentrations ranged from 0.0001 mg L^{-1} to 427 mg L^{-1}. The highest concentrations were observed for S and Sr in hill samples and coal sample, while in soil sample the highest concentrations were observed for Mn and S. The lowest extract concentrations were observed for Sb, Tl and Be along with Bi and Sc below the detection limit in all samples. In total, twelve elements (Be, Bi, Cr, Cs, Mo, P, Pb, Sb, Sc,Se, Ti, and Tl) were below the detection limit in at least one of the samples.

The highest extract concentrations for majority of elements were observed in hill samples, with exceptions to Ba, Be, Cd, Co, and Mn which had the highest concentrations in soil sample and P in coal sample. For Cu, Sn, Tl and Zn there wasn't a significant difference in extract concentrations between samples.

The lowest concentrations of elements were observed for coal and soil sample, while Cd, Co, Mn and P had the lowest concentrations in one of the hill samples.

In TCLP (pH=2.9) method, extract concentrations ranged from 0.0001 mg L^{-1} to 271,75 mg L^{-1}(S). The highest concentrations were observed for S and Sr in hill samples and coal sample, while in soil sample the highest concentrations were observed for Mn and S. The lowest concentrations were observed for Sb, Sc and Tl along with Bi found below the detection limit in all samples. In total, nine elements (Be, Bi, Cs, Mo, Pb, Sb, Sc, Se, and Tl) were below the detection limit in at least one of the samples.

The highest extract concentrations for most elements were observed in hill samples, with exception to Ba, Be, Cd, Co, Cu, Mn, P, Pb and Zn which had the highest concentration in soil sample. For Sn and Tl there wasn't a major difference in concentrations between samples.

The lowest concentrations of elements were observed in coal sample, while for some elements (As, Cr, Li, S, Sb, Sc, Ti, U, V) the lowest concentration was in both soil and coal sample. The lowest concentration in hill samples were observed for Cd, Co and P. In conclusion, ASTM method resulted in lowest extract concentrations of measured elements, followed by EP method. Concentrations in TCLP and TCLP2 extracts were mostly one to two orders of magnitude higher than in ASTM and EP extracts, with exceptions to S and Mo which had the highest extract concentrations in ASTM method.

Table 6. Extract concentrations (mg L^{-1}) of twenty-nine elements in five analysed samples and limit values (mg L^{-1}) from Croatian regulation or other regulations noted in parenthesis. Bolded values are above the limit. (DW = Drinking Water; IRG = irrigation)

El	Method	1_1	1_2	1_3	Soil	Coal	Limit	El	Method	1_1	1_2	1_3	Soil	Coal	Limit
Al	ASTM	0.2553	0.2654	0.1215	0.0413	0.2960	3.0	As	ASTM	0.0007	0.0016	0.0010	0.0007	0.0002	0.1
	EP	0.0378	<LOD	0.0150	0.1516	0.0276			EP	0.0009	0.0016	0.0016	0.0008	0.0003	
	TCLP	1.1201	0.0521	0.0312	0.5709	0.2454			TCLP	0.0013	0.0022	0.0024	0.0007	0.0012	
	TCLP2	**5.2630**	**4.0946**	**3.5368**	2.8682	1.3000			TCLP2	0.0043	0.0052	0.0027	0.0005	0.0006	
Ba	ASTM	0.0390	0.0378	0.0298	0.0258	0.0215	5.0	Be	ASTM	0.0001	<LOD	<LOD	<LOD	<LOD	0.1 FAO IRG
	EP	0.0923	0.0745	0.0783	0.1673	0.0171			EP	<LOD	<LOD	<LOD	<LOD	<LOD	
	TCLP	0.1284	0.1232	0.0883	0.3431	0.0548			TCLP	0.0004	0.0004	0.0001	<LOD	0.0003	
	TCLP2	0.4570	0.4418	0.3267	1.3627	0.0725			TCLP2	<LOD	<LOD	<LOD	0.0082	<LOD	
Bi	ASTM	<LOD	<LOD	<LOD	<LOD	<LOD	/	Cd	ASTM	0.0003	0.0004	0.0005	0.0001	<LOD	0.1
	EP	<LOD	<LOD	<LOD	<LOD	<LOD			EP	0.0002	0.0001	0.0002	0.0011	<LOD	
	TCLP	<LOD	<LOD	<LOD	<LOD	<LOD			TCLP	0.0001	0.0001	0.0002	0.0025	0.0011	
	TCLP2	<LOD	<LOD	<LOD	<LOD	<LOD			TCLP2	0.0009	0.0016	0.0009	0.0082	0.0017	
Co	ASTM	0.0001	<LOD	0.0001	0.0004	<LOD	1.0	Cr	ASTM	<LOD	<LOD	0.0191	<LOD	<LOD	0.5
	EP	0.0003	0.0001	0.0014	0.0077	0.0002			EP	<LOD	<LOD	0.0006	<LOD	<LOD	
	TCLP	0.0005	0.0002	0.0014	0.0102	0.0066			TCLP	0.0012	<LOD	0.0010	0.0002	0.0002	
	TCLP2	0.0055	0.0048	0.0137	0.0709	0.0110			TCLP2	0.0521	0.0383	0.0600	0.0038	0.0023	
Cs	ASTM	0.0010	0.0007	0.0010	<LOD	<LOD	/	Cu	ASTM	0.0050	0.0006	0.0062	0.0106	0.0006	0.2 Greece IRG
	EP	0.0006	0.0006	0.0008	<LOD	<LOD			EP	0.0031	0.0027	0.0133	0.0047	<LOD	
	TCLP	0.0019	0.0017	0.0030	<LOD	0.0001			TCLP	0.0051	0.0031	0.0037	0.0080	0.0032	
	TCLP2	0.0013	0.0011	0.0015	<LOD	<LOD			TCLP2	0.0156	0.0143	0.0276	0.0596	0.0130	

El	Method	1_1	1_2	1_3	Soil	Coal	Limit	El	Method	1_1	1_2	1_3	Soil	Coal	Limit
Fe	ASTM	0.0037	<LOD	0.0019	0.0460	<LOD	2.0	Li	ASTM	0.0570	0.0429	0.0396	0.0004	0.0006	2.5 Greece IRG
	EP	0.0163	<LOD	0.0046	0.0989	0.0399			EP	0.0540	0.0373	0.0533	0.0006	0.0003	
	TCLP	0.0969	0.0420	0.0174	0.0513	0.0858			TCLP	0.0551	0.0444	0.0588	0.0004	0.0003	
	TCLP2	1.1926	0.7322	0.7577	0.1605	0.3882			TCLP2	0.1364	0.1143	0.1121	0.0031	0.0010	
Mn	ASTM	0.0025	0.0010	<LOD	0.0043	0.0037	2.0	Mo	ASTM	0.0630	0.0715	0.1280	0.0038	0.0030	0.2 Italy IRG
	EP	0.0178	0.0093	0.0432	**3.844**	0.0274			EP	0.0234	0.0214	0.0457	<LOD	<LOD	
	TCLP	0.0262	0.0223	0.0439	**5.1448**	0.1316			TCLP	0.0269	0.0332	0.0570	<LOD	<LOD	
	TCLP2	0.2037	0.2490	0.3749	**13.693**	0.3026			TCLP2	0.0882	0.1052	0.1129	0.0030	<LOD	
Ni	ASTM	0.0004	0.0005	0.0023	0.0048	0.0008	0.5	P	ASTM	<LOD	<LOD	<LOD	0.0737	0.2999	2.0
	EP	0.0059	0.0018	0.0309	0.0086	0.0005			EP	<LOD	0.0210	0.1429	0.9007	<LOD	
	TCLP	0.0066	0.0024	0.0328	0.0120	0.0060			TCLP	<LOD	<LOD	0.0099	0.1135	0.2271	
	TCLP2	0.0675	0.0517	0.2046	0.0656	0.0116			TCLP2	0.0423	0.0042	0.1391	0.5039	0.0275	
Pb	ASTM	<LOD	0.0003	<LOD	0.0005	<LOD	0.5	Rb	ASTM	0.0139	0.0103	0.0142	0.0034	0.0009	/
	EP	0.0004	<LOD	<LOD	0.0081	<LOD			EP	0.0056	0.0050	0.0095	0.0047	0.0006	
	TCLP	0.0003	0.0223	<LOD	0.0013	0.0044			TCLP	0.0106	0.0083	0.0220	0.0045	0.0016	
	TCLP2	0.0002	0.0016	<LOD	0.0125	0.0083			TCLP2	0.0105	0.0093	0.0167	0.0059	0.0010	
S	ASTM	**397.36**	**454.29**	**506.97**	11.846	10.585	250 (SO_4^{2-})	Sb	ASTM	0.0001	0.0005	0.0004	<LOD	<LOD	0.006 EPA DW
	EP	102.71	176.01	**292.85**	3.3330	2.1235			EP	<LOD	0.0002	<LOD	<LOD	<LOD	
	TCLP	122.63	194.43	**426.86**	2.7623	2.2260			TCLP	<LOD	0.0003	<LOD	<LOD	<LOD	
	TCLP2	183.85	211.52	**271.75**	4.0532	2.3931			TCLP2	0.0004	0.0010	0.0007	<LOD	<LOD	
Sc	ASTM	<LOD	<LOD	<LOD	<LOD	<LOD	/	Se	ASTM	0.0107	0.0013	0.0119	0.0004	0.0005	0.02
	EP	<LOD	<LOD	<LOD	<LOD	<LOD			EP	0.0104	0.0084	0.0125	0.0005	0.0001	
	TCLP	<LOD	<LOD	<LOD	<LOD	<LOD			TCLP	0.0070	0.0105	0.0110	<LOD	0.0007	
	TCLP2	0.0002	0.0004	0.0005	<LOD	<LOD			TCLP2	**0.0263**	**0.0513**	**0.0418**	0.0001	<LOD	

El	Method	1_1	1_2	1_3	Soil	Coal	Limit	El	Method	1_1	1_2	1_3	Soil	Coal	Limit
Sn	ASTM	0.0019	0.0007	0.0029	0.0042	0.0020	2.0	Sr	ASTM	4.1722	4.1676	4.1367	0.1466	0.6315	7.0 EPA DW
	EP	0.0018	0.0016	0.0019	0.0012	0.0026			EP	4.1833	3.4925	4.4566	0.4081	0.3524	
	TCLP	0.0027	0.0013	0.0020	0.0020	0.0018			TCLP	4.9312	5.0927	5.8975	0.4433	3.1261	
	TCLP2	0.0009	0.0031	0.0015	0.0029	0.0017			TCLP2	**19.556**	**17.389**	**15.298**	0.8400	3.6244	
Ti	ASTM	<LOD	0.0002	<LOD	0.0012	0.0004	/	Tl	ASTM	<LOD	0.0001	<LOD	<LOD	<LOD	0.001 Italy IRG
	EP	0.0057	0.0013	0.0038	0.0006	<LOD			EP	<LOD	0.0001	<LOD	0.0001	<LOD	
	TCLP	0.0068	0.0034	0.0031	0.0025	<LOD			TCLP	0.0001	0.0003	<LOD	0.0001	0.0001	
	TCLP2	0.1132	0.0696	0.0489	0.0016	0.0042			TCLP2	0.0001	0.0005	<LOD	0.0001	0.0001	
U	ASTM	0.0296	0.0275	0.0018	0.0001	0.0003	0.03 EPA DW	V	ASTM	0.0106	0.0099	**0.0628**	0.0023	0.0023	0.05
	EP	0.0207	0.0233	**0.0427**	0.0003	0.0002			EP	0.0209	0.0141	0.0370	0.0015	0.0005	
	TCLP	0.0223	**0.0341**	**0.0577**	0.0009	0.0006			TCLP	0.0306	0.0222	**0.0566**	0.0011	0.0033	
	TCLP2	**0.1110**	**0.1387**	**0.1641**	0.0036	0.0011			TCLP2	**0.1055**	**0.0722**	**0.0997**	0.0035	0.0048	
Zn	ASTM	0.0302	0.0244	0.0333	0.0788	0.0297	2.0								
	EP	0.0411	0.0307	0.0391	0.0388	0.0307									
	TCLP	0.0484	0.0330	0.0323	0.0493	0.0402									
	TCLP2	0.0270	0.0362	0.0360	0.1553	0.0610									

Table 7. Mobility of elements in five analyzed samples expressed by Relative Mass Leached (%). Bolded values show high mobility (RML>0.5%)

El	**Method**	**1_1**	**1_2**	**1_3**	**Soil**	**Coal**	**El**	**Method**	**1_1**	**1_2**	**1_3**	**Soil**	**Coal**
Al	ASTM	0.0022	0.0022	0.0004	0.0001	0.0064	As	ASTM	0.0164	0.0183	0.0114	0.0047	0.0075
	EP	0.0003	<LOD	0.0001	0.0002	0.0006		EP	0.0210	0.0183	0.0183	0.0054	0.0112
	TCLP	0.0098	0.0004	0.0001	0.0008	0.0053		TCLP	0.0304	0.0252	0.0274	0.0047	0.0448
	TCLP2	0.0462	0.0337	0.0123	0.0042	0.0282		TCLP2	0.1005	0.0595	0.0308	0.0034	0.0224
Ba	ASTM	0.0607	0.0427	0.0207	0.0068	0.1215	Be	ASTM	0.0274	<LOD	<LOD	<LOD	<LOD
	EP	0.1436	0.0842	0.0543	0.0440	0.0966		EP	<LOD	<LOD	<LOD	<LOD	<LOD
	TCLP	0.1997	0.1392	0.0612	0.0902	0.3096		TCLP	0.1096	0.0756	0.0084	<LOD	0.4860
	TCLP2	**0.7109**	0.4991	0.2266	0.3581	0.4095		TCLP2	<LOD	<LOD	<LOD	0.3471	<LOD
Bi	ASTM	<LOD	<LOD	<LOD	<LOD	<LOD	Cd	ASTM	0.1565	0.0958	0.3287	0.0120	<LOD
	EP	<LOD	<LOD	<LOD	<LOD	<LOD		EP	0.1043	0.0239	0.1315	0.1318	<LOD
	TCLP	<LOD	<LOD	<LOD	<LOD	<LOD		TCLP	0.0522	0.0239	0.1315	0.2994	**0.5413**
	TCLP2	<LOD	<LOD	<LOD	<LOD	<LOD		TCLP2	0.4694	0.3831	**0.5916**	**0.9821**	**0.8365**
Co	ASTM	0.0030	<LOD	0.0013	0.0010	<LOD	Cr	ASTM	<LOD	<LOD	0.0136	<LOD	<LOD
	EP	0.0091	0.0024	0.0178	0.0186	0.0123		EP	<LOD	<LOD	0.0004	<LOD	<LOD
	TCLP	0.0152	0.0048	0.0178	0.0246	0.4070		TCLP	0.0022	<LOD	0.0007	0.0001	0.0014
	TCLP2	0.1669	0.1143	0.1741	0.1708	**0.6784**		TCLP2	0.0934	0.0602	0.0427	0.0023	0.0163
Cs	ASTM	0.1998	0.1448	0.1643	<LOD	<LOD	Cu	ASTM	0.0154	0.0018	0.0108	0.0281	0.0067
	EP	0.1199	0.1241	0.1315	<LOD	<LOD		EP	0.0095	0.0083	0.0232	0.0124	<LOD
	TCLP	0.3796	0.3516	0.4930	<LOD	0.0238		TCLP	0.0157	0.0095	0.0064	0.0212	0.0358
	TCLP2	0.2598	0.2275	0.2465	<LOD	<LOD		TCLP2	0.0480	0.0438	0.0481	0.1577	0.1456

El	Method	1_1	1_2	1_3	Soil	Coal	El	Method	1_1	1_2	1_3	Soil	Coal
Fe	ASTM	0.00004	<LOD	0.00001	0.0001	<LOD	Li	ASTM	0.2232	0.1974	0.1213	0.0007	0.0057
	EP	0.0002	<LOD	0.0000	0.0002	0.0017		EP	0.2115	0.1716	0.1633	0.0011	0.0029
	TCLP	0.0011	0.0004	0.0001	0.0001	0.0036		TCLP	0.2158	0.2043	0.1801	0.0007	0.0029
	TCLP2	0.0136	0.0066	0.0040	0.0004	0.0162		TCLP2	**0.5341**	**0.5259**	0.3434	0.0058	0.0095
Mn	ASTM	0.0068	0.0021	<LOD	0.0002	0.0122	Mo	ASTM	**0.5702**	0.4618	0.4474	0.1313	0.1092
	EP	0.0482	0.0193	0.0472	0.1701	0.0900		EP	0.2118	0.1382	0.1597	<LOD	<LOD
	TCLP	0.0709	0.0463	0.0480	0.2276	0.4323		TCLP	0.2435	0.2145	0.1993	<LOD	<LOD
	TCLP2	**0.5515**	**0.5175**	0.4098	**0.6058**	**0.9939**		TCLP2	**0.7983**	**0.6795**	0.3947	0.1037	<LOD
Ni	ASTM	0.0014	0.0014	0.0036	0.0050	0.0090	P	ASTM	<LOD	<LOD	<LOD	0.0113	**1.1085**
	EP	0.0211	0.0051	0.0479	0.0089	0.0056		EP	<LOD	0.0297	0.1008	0.1379	<LOD
	TCLP	0.0236	0.0067	0.0508	0.0125	0.0673		TCLP	<LOD	<LOD	0.0070	0.0174	**0.8394**
	TCLP2	0.2416	0.1451	0.3170	0.0681	0.1301		TCLP2	0.0612	0.0059	0.0981	0.0772	0.1016
Pb	ASTM	<LOD	0.0037	<LOD	0.0010	<LOD	Rb	ASTM	**0.5204**	0.4093	0.3794	0.0032	0.0295
	EP	0.0179	<LOD	<LOD	0.0168	<LOD		EP	0.2096	0.1987	0.2538	0.0044	0.0197
	TCLP	0.0135	0.2779	<LOD	0.0027	0.2419		TCLP	0.3968	0.3299	**0.5879**	0.0042	0.0525
	TCLP2	0.0090	0.0199	<LOD	0.0260	0.4564		TCLP2	0.3931	0.3696	0.4462	0.0055	0.0328
S	ASTM	**1.8786**	**1.9437**	**1.7282**	**0.5755**	0.0125	Sb	ASTM	0.0482	0.0939	0.0880	<LOD	<LOD
	EP	0.4856	**0.7531**	**0.9983**	0.1619	0.0025		EP	<LOD	0.0376	<LOD	<LOD	<LOD
	TCLP	**0.5798**	**0.8319**	**1.4551**	0.1342	0.0026		TCLP	<LOD	0.0563	<LOD	<LOD	<LOD
	TCLP2	**0.8692**	**0.9050**	**0.9263**	0.1969	0.0028		TCLP2	0.1927	0.1878	0.1540	<LOD	<LOD
Sc	ASTM	<LOD	<LOD	<LOD	<LOD	<LOD	Se	ASTM	0.0392	0.0036	0.2206	0.0018	0.0016
	EP	<LOD	<LOD	<LOD	<LOD	<LOD		EP	0.0381	0.0233	0.2317	0.0023	0.0003
	TCLP	<LOD	<LOD	<LOD	<LOD	<LOD		TCLP	0.0257	0.0292	0.2039	<LOD	0.0022
	TCLP2	0.0060	0.0108	0.0067	<LOD	<LOD		TCLP2	0.0964	0.1426	**0.7748**	0.0005	<LOD

El	**Method**	**1_1**	**1_2**	**1_3**	**Soil**	**Coal**	**El**	**Method**	**1_1**	**1_2**	**1_3**	**Soil**	**Coal**
Sn	ASTM	0.1430	0.0452	0.1468	0.0894	0.1856	Sr	ASTM	0.3854	0.4294	0.4203	0.1146	0.3166
	EP	0.1354	0.1034	0.0962	0.0256	0.2412		EP	0.3864	0.3599	0.4528	0.3191	0.1767
	TCLP	0.2032	0.0840	0.1012	0.0426	0.1670		TCLP	0.4537	**0.5247**	**0.5992**	0.3466	**1.5675**
	TCLP2	0.0677	0.2003	0.0759	0.0617	0.1577		TCLP2	**1.8063**	**1.7917**	**1.5543**	**0.6568**	**1.8174**
Ti	ASTM	<LOD	0.00002	<LOD	0.00002	0.0001	Tl	ASTM	<LOD	0.0323	<LOD	<LOD	<LOD
	EP	0.0007	0.0002	0.0002	0.00001	<LOD		EP	<LOD	0.0323	<LOD	0.0096	<LOD
	TCLP	0.0009	0.0004	0.0002	0.00004	<LOD		TCLP	0.1197	0.0970	<LOD	0.0096	0.1121
	TCLP2	0.0147	0.0087	0.0027	0.00002	0.0014		TCLP2	0.1197	0.1617	<LOD	0.0096	0.1121
U	ASTM	0.1947	0.1303	0.0059	0.0021	0.0382	V	ASTM	0.0083	0.0073	0.0240	0.0013	0.0137
	EP	0.1362	0.1104	0.1411	0.0062	0.0255		EP	0.0163	0.0104	0.0141	0.0008	0.0030
	TCLP	0.1467	0.1616	0.1907	0.0185	0.0764		TCLP	0.0239	0.0163	0.0216	0.0006	0.0196
	TCLP2	**0.7302**	**0.6572**	**0.5422**	0.0741	0.1400		TCLP2	0.0823	0.0531	0.0381	0.0019	0.0285
Zn	ASTM	0.2495	0.1153	0.1660	0.0655	0.1677							
	EP	0.3396	0.1450	0.1950	0.0322	0.1734							
	TCLP	0.3999	0.1559	0.1610	0.0410	0.2270							
	TCLP2	0.2231	0.1710	0.1795	0.1290	0.3445							

5. DISCUSSION

In this chapter, total values of all samples were compared to previous studies, extract concentrations were compared to prescribed limit values, mobility of elements was discussed as function of pH and mineralogy, and lastly risk assessment was carried out for soil sample.

5.1. Geochemistry of Štrmac hill, soil and Raša coal

Total values of analysed elements in samples were compared to the values measured in the same or wider study area to see if there is any inconsistency.

- Štrmac hill samples

The content of major elements and several trace elements (Cd, Cu, Pb, Sr, U, V, and Zn) in hill samples are mostly in the same range as reported by previous studies of wider study area (Fiket et al.,2018, Medunić et al., 2018a). More than two times higher values were observed for Cr and Sr, and six times higher values for Se in 1_1 and 1_2 samples, while in the third sample Se value was in agreement with previously reported values. Study by Medunić et al (2018a) showed that values of trace elements in Štrmac hill were generally lower than lowest measured values in ash landfill in central Croatia reported by Oreščanin et al. (2012), while the maximum values were either similar or higher than those reported. Lower values of Se and other elements reported by previous studies (Medunić et al., 2018a) were prescribed to leaching and oxidation. In this study values of Se showed variability in samples, ranging from 5.39 to 35.9 mg/kg, which are all higher than previously reported. This variability could be, along with heterogeneity of samples, due to leaching and secondary adsorption, after Se originally leached, which is discussed in Section 6.3. Overall, most elements are below Clarke ash values (Ketris and Yudovich, 2009), except for Se and Sr that showed elevated values.

Increase with depth was observed for all oxides and most trace elements. Lower concentrations in 1_1 sample, is probably due to direct exposure of surface layer to rainfall.

- Soil sample

The content of major elements and several trace elements (Cd, Cr, U, and V) in soil samples are mostly in the agreement with previous studies (Fiket et al., 2018, Medunić et al., 2018b). In contrary, more than two times lower values of Pb, Zn, Sr and Cu and ten times higher values of Se were observed. Overall, values of fifteen elements (Al, Ba, Co, Cr, Cu, Fe, Ni, Pb, Sc, Sr, Ti, V, and Zn), out of seventeen elements listed in Geochemical atlas of Croatia (regional background values) (Halamić & Miko, 2009), had higher values than the median, while As and Cd were found at slightly lower levels. Previous study (Medunić et al., 2018b) visualized the spatial distribution of trace elements (Cd, Cu, U, Se, Zn, Sb, As, Be, Cr, Pb, Sr, and V) of wider study area with contour maps, indicating soil pollution of the area, which is in agreement with values from this study.

The highest concentration of almost all elements (except S, Cu, Mo, Se Sr, U, and V) was in soil sample. It is noticeable that elements with values not highest in soil sample are elements usually elevated in SHOS coal and ash.

- Coal sample

The content of major elements and majority of trace elements is in the agreement with previously reported values (Jakšić et al. 1993, Valković et al. 1995; Peco 2018). However, some trace elements (As, Cr, Mo, Ni, Pb, Sr, U, and V) were more than two times lower than those reported.

All trace elements, except for Cd, Se, Sn, Sr, and Tl, were lower than Clarke values. Since Raša coal is usually enriched in Sr, U, V, Mo, which is an anomaly common for SHOS coal (Querol et al., 1996), it is unusual that values of U and V are lower than worlds average, and values of Sr and Mo close to average. Lower values of other trace elements in Raša coal were attributed to different peat conditions during coalification, like alkaline pH or lower yield of detrital material (Orem & Finkelman, 2003).

Lowest concentrations of majority of elements was observed in coal sample. Ash samples are generally enriched in trace elements in comparison to coal sample. Only exception was sulphur which had the highest concentrations in coal sample. Ash samples had lower values of S due to forming of SO_x during combustion, which can then be absorbed on fly ash or released in the atmosphere (Müller, 2013).

5.2. Impact of Štrmac landfill on the environment

- Selection of extraction procedures

Extraction procedures resulted in different extract concentrations of analysed elements (ASTM < EP < TCLP < TCLP2), which indicates that pH is an important parameter affecting the leaching rate of elements. It also raises a question which procedure is the most effective in predicting subsurface contamination due to leaching.

Selection of a method that can closely simulate the real-life scenario depends on different factors – physical properties of wastes, the composition of the source, age of waste disposal, and the climatic conditions of the disposal area (Tiwari et al., 2015). Most authors agree that ASTM is the best method in representing natural weathering, since the waste is the dominant factor in determining pH of the extract (US EPA, 1987; EPA – Link1, Baba & Kaya, 2004). EP and TCLP method are considered too aggressive for majority of wastes, which often results in misinterpreting the results and wrongly classifying waste (Izquierdo & Querol, 2012; Miguel et al., 2012; Tiwari et al., 2015). In addition, TCLP and EP methods are shown to mask leaching of oxyanionic species, like As and Se which are usually more mobile in neutral to alkaline conditions (Thorneloe et al., 2010; Tiwari et al., 2015). However, results showed that extract concentrations of As and Se are higher in TCLP than in ASTM, meaning that TCLP method wouldn't 'mask' the leaching if only that method was used for evaluating Štrmac hill waste. Although TCLP may not always be the most accurate method for representing natural weathering, using it is a great way to gain knowledge on the mobility of elements under acidic conditions, especially in parts of the world affected by acid rain (Kalembkiewicz & Sitarz-Palczakm 2015). For the first half of 2019, pH of rainfall measured in Rijeka (Croatia) ranged from 4.88-7.72, while in 1996 pH of 3.02 was reported (DHMZ, 1996, 2019), therefore measured concentrations from all methods should be considered.

- Limit values

The extract concentrations, compared to EPA toxicity levels listed in the second chapter, define Štrmac landfill as non-hazardous. However, extract concentrations of several elements are above limit values listed in Croatian regulation of wastewater treatment[5] (Ministry of Agriculture, Croatian Government. 2010).

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[5] Regulation is in accordance with European Directives 2000/60/EC, 2006/118/EC and 2006/11/EC. It covers limit values of pollutants in technological wastewaters prior to their release into public sewers, or into septic or aggregate pit and in all purified or untreated wastewater

The regulation covers seventeen of twenty-nine analyzed elements, and five of them (Al, Mn, S, Se, and V) are above the limit in certain extraction methods. The concentrations of As, Pb, Ni, and Cd in extracts are below the limit values, but according to this Regulation, it is forbidden to release water of such element composition in the environment. Other elements covered by the Regulation (Ba, Co, Cr, Cu, Fe, P, Sn, and Zn) are below the limit values in all samples. Twelve elements not covered by the Croatian regulation (Be, Bi, Cs, Li, Mo, Rb, Sb, Sc, Sr, Ti, Tl, and U) are also not globally regulated. For several elements, there are limitations in drinking water (U, Sb, and Sr) (EPA, 2018) or limit values for treated wastewater which is used in agriculture irrigation[6] (Be, Cu, Li, Mo, and Tl). Several elements (Rb, Sc, and Ti) were not compared due to lack of defined limit values. This is because some elements are not considered as elements of major environmental concern.

In all extraction procedure, similar elements are above the limit, the difference is that the concentrations are much higher as the pH decreases. Elements that showed elevated values are V and S in ASTM procedure, Mn, S and U in EP procedure, Mn, S, U and V in TCLP, and Al, Mn, S, Se, Sr, U and V in TCLP2. All elements are above the limit in hill samples, except for Mn which is above the limit in soil sample.

Elements that are above prescribed limits in almost all extracts (V, S, U, and Mn) are elements commonly elevated in SHOS coal varieties (Querol et al., 1996). Elevated values of mentioned elements are also in agreement with previous studies of wider area, where U, V and Sr were increased in the majority of water samples, vegetables, soil and aquatic sediment (Medunić et al, 2018c). In mentioned study, V was also found slightly increased in liver samples of non-migratory birds from this area, as well as Cu, Zn and Pb which were below the limit value in this study. The elevated values of same elements indicate that

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discharged into water. Regulation has seventeen appendixes with limit values for wastewater from certain technological activity. In this diploma thesis, extract concentrations are compared to limit values from Appendix 1 which is covering wastewater from non-specified activity.

[6] Different countries have different limit values for treated wastewater which is used in agriculture irrigation and they were compared and summarized by Jeong (2016). Limit values from Italy (Angelakis et al., 2008), Greece (Kalavrouziotis et al., 2015) and FAO[6] (Ayers & Westcot, FAO 1985) were used for comparison to extract concentrations.

leaching of Štrmac hill could be one of the sources of pollution for area impacted by Raša coal usage. Elements that are above the limit may have entered the groundwater, highlighting the need for future study.

Selenium was above prescribed limits only in TCLP2 extracts which indicates that it could be environmental threat for groundwater and local soil in case of acid rain. Previous research of Se pollution in wider study area showed elevated selenium values in stream water and associated bottom sediment as well as in seawater, clover and foliage (Medunić et al., 2018a, 2018b), implying that Se probably leached from coal, ash and coal-polluted soil. It could be that Se leached during more acidic rainfall reported in the past.

5.3. Mobility of elements

To determine the leaching potential of elements, Relative Mass Leached (RML) was calculated for each element in each extraction procedure. Since Bi was below the detection limit in all samples, it was omitted from the discussion.

Mobility of elements is expressed by RML and elements were grouped[7] according to their mobility. Elements with RML 0.5% or higher were referred to as high mobility class, elements with RML between 0.5% and 0.05% as moderate mobility class and elements with RML below 0.05% as low mobility class. Most of the elements changed mobility groups depending on the extraction procedure and sample type (Tab. 7).

In ASTM method, most samples showed low to moderate mobility for majority of elements, with exception to Mo, P and Rb that showed high mobility. Similar mobility showed EP for most elements, with exception to Mn and Ni that changed groups from low to moderate mobility, while mobility of Mo, P, Rb decreased. In contrast, TCLP showed

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[7] Groups were made according to the results in this diploma thesis. They are made to relatively express mobility of elements and to compare the samples to one another. In other publications 1% would probably be considered low leaching, but here is considered high because there are only few elements that had leaching percentage above 1% and their percentage is high compared to other elements in this thesis.

significantly higher mobility at both pH tested, where in conditions of lower pH leaching potential is more than 10 times higher for majority of elements. Several elements showed similar mobility regardless of the conditions of pH. In all extraction procedures, low mobility was observed for Al, Fe, Sc, Ti, medium mobility for Sn and Zn and high mobility for S.

Comparing the samples, the highest RML values were observed for U, Mo, Li, S in hill samples, S in soil sample, and P and Co in coal sample, while Mn, Sr and Cd had high mobility in all samples.

The behaviour of elements during leaching is mainly controlled by pH and mineralogy (Yue and Zhao, 2008). Generally, elements under different pH conditions show one out of three main leaching pattern – cationic, oxyanionic and amphoteric leaching pattern. Elements with cationic pattern have the highest mobility in acidic pH, which decreases as pH increases. Mobility of elements with oxyanionic pattern only slightly increases at acidic pH and significantly increases at alkaline pH. Elements with amphoteric pattern have high mobility at both alkaline and acidic pH values (Izquierdo and Querol, 2012; Komonweeraket et al., 2015; Zhang et al., 2019). Association with mineral and organic matter can alter the pattern, causing the change of the usually leaching pattern of elements.

5.3.1. Leaching characteristics under different pH conditions

Lowest mobility of majority of elements in ASTM method is due to most trace elements being in a cation state, adsorbed to minerals. As pH decreases, intensity of attack on the metal-bearing minerals increases due to acidic conditions, resulting in higher extract concentrations of elements in TCLP method (Fleming et al., 1996; Tiruta-Barna et al., 2004). Cationic pattern was observed for As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sc, Se, Sr, Tl, U, and V.

Rb is the only element that showed oxyanionic pattern, although it is not an oxyanion. Oxyanion species (Mo, As and Se) showed amphoteric pattern (Mo) and cationic pattern (As, Se). High mobility of Rb and Mo in ASTM method is mostly in agreement with other publications (Zhang et.al 2019, Izquierdo and Querol, 2012). Rb is considered highly soluble species in coal ashes, due to association with soluble species like sulphates and chlorides. Sulphates are one of the constituents of Raša ash (Peco et al., 2018), probably responsible for high mobility of Rb in hill samples. Mo is an oxyanion species, so high mobility in ASTM was expected. However, Mo also showed high mobility in TCLP2 which would indicate that

Mo has amphoteric pattern. In acidic conditions, concentration of Mo usually decrease as it is absorbed by Fe and Al oxyhydroxides at pH >3.5 (Jones, 1995), which may happened in EP and TCLP, while in TCLP2 precipitation may be reduced.

Contrary to other publications, which reported that other oxyanion species (As, Se) usually have similar leaching pattern as Mo (Zhang et.al 2019, Izquierdo and Querol, 2012), As and Se had low mobility in ASTM. Raša ash is alkaline due to its main mineralogical phases being alkaline minerals like calcite, aragonite and portlandite (Peco, 2018). Although alkaline conditions enhance desorption of oxyanions, they also decrease dissolved As and Se through incorporation into secondary calcium precipitates, like ettriginite (Wang et al., 2009; Izquierdo and Querol, 2012; Schwartz et al, 2018). Sulphur concentration hasn't decreased in ASTM conditions, applying that ettriginite may not have formed, but that does not exclude forming of other secondary calcium precipitates. Uptake of Mo by secondary precipitates is usually lower due to its larger size (Kumarathasan et al., 1989), explaining why Mo had high mobility in ASTM unlike other oxyanions. Uptake of Se by Ca-precipitates could be one of the reasons why 1_1 and 1_2 samples showed higher total values of Se in comparison to the 1_3 and previous publication (Medunić et al., 2018a).

Several elements showed similar mobility regardless of the conditions of pH. In all extraction procedures, low mobility was observed for Al, Fe, Sc and Ti, medium mobility for Sn and Zn and high mobility for S, which was mostly affected by mineralogy.

In conclusion, majority of elements had cationic pattern, Rb had oxyanionic pattern, Mo had amphoteric pattern and Al, Fe, Sc, Ti, Sn, Zn and Sn showed the same mobility regardless of pH.

5.3.2. Leaching characteristics in different samples

Except pH, mineralogy of samples can affect leaching rate of elements. In different pH conditions, dissolution and reprecipitation of certain mineral phases occur, causing the release or adsorption of trace elements associated with the mineral (Komonweeraket et al., 2015). Raša coal and ash consist mainly of carbonates and sulphates, while soil sample consist of carbonates and aluminosilicates detailed in Chapter 2. The pH of water eluates from Raša ash and slag measured by Peco, (2018) ranged from 10 to 12.5, while for coal and soil amounted to 7-8.

All elements had noticeably lower RML values (0.00001% to 1.94%), compared to the literature (Baba & Kaya, 2004; Equeenuddin, 2015; Kierczak & Chudy, 2014, Zhang et al., 2019) where RML ranged from 0.1 to >10.0%. High content of carbonates and low pyritic value of samples are probably responsible for low RML. Presence of carbonates may be responsible for alkalinity of Raša ash, which can have buffering capacity and cause Ca-precipitates to occur, causing the precipitation of trace elements (Fruchter, 1990; Jones, 1995). Pyrite gives acidic discharge, making the samples more acidic, and therefore causing higher mobility of majority of elements, which is not the case in this study (Equeenuddin, 2015). Leaching pattern of elements in different samples is probably controlled by solubility (dissolution-precipitation) and sorption processes of main minerals (carbonates, sulphates and silicates in samples of this study) (Komonweeraket et al., 2015).

Regardless of low RML values compared to other publications, terms ‘high, moderate and low mobility’ are used to show which elements had the highest mobility in samples. Most elements that had high mobility in samples are probably associated with sulphates and soluble salts. But considering overall low RML values, it is likely that elements precipitated with Ca-precipitates and Al and Fe oxyhydroxides, or were immobile due to some other factor.

- <u>Similar mobility in all samples</u>

High mobility of Mn, Sr, Cd and moderate mobility of Zn and Ba is probably due to association with carbonates and sulphates which are soluble in acid (calcite) and water (gypsum) and are found in all samples (Swaine, 1990; Finkelmanetal., 2018; Peco, 2018). Substitution of Mn^{2+} and Sr^{2+} for Ca^{2+} in calcite was observed in many coals (Swaine,1990) and Sr is also often associated with gypsum (Spivak-Birndorf, 2012). Cadmium and zinc are usually associated with sulphides and considered immobile in neutral to alkaline conditions (Izquierdo and Querol, 2012; Zhang et al., 2019). But considering that mobility of Cd and Zn in all samples and extraction procedures was moderate to high, it is likely that Cd and Zn are associated with sulphates or soluble salts like $CdSO_4$ and $ZnSO_4$ (Querol et al., 1996). Ba also forms soluble compounds with carbonates and sulphates, and it is reported that its mobility usually depends on the presence of Ca rather than pH. In the presence of large amounts of Ca, Ba precipitates as $Ba(Sr)SO_4$ or $BaSO_4$ (Fruchter et al., 1990), which could be the reason why Ba in ASTM leached only 0.006%.

High mobility of S in hill and soil samples is probably due to high amounts of soluble sulphates, while low mobility of S in coal sample is probably due to sulphur being in organic form which is immobile in some coals (Markuszewski, 1981).

Low mobility of Al, Fe and Ti in all samples is usually prescribed to slow dissolution rate of aluminosilicates. Titanium commonly replaces Si in clays and is usually retained within the aluminosilicate glassy matrix. Al and Fe precipitate at pH >3.5, which could affect overall low RML values of elements in all samples due to high surface area of mentioned precipitates (Warren and Dudas 1988).

- <u>Hill samples</u>

Alkali metals Cs, Li and Rb showed the same leaching pattern - moderate to high leaching in all three hill samples, and low mobility in coal and soil, indicating that they probably have the same association in samples. High mobility in hill samples is associated with sulphates, where those elements form water-soluble compounds with common anions (carbonate, oxide, nitrate, sulphate, etc.) (Butterman and Reese 2003). This association is also in agreement with previous research by Valković (1984) where peak of Rb was present in non-magnetic fraction of fly ash where $CaCO_3$ and $CaSO_4$ were main constituents. Raša coal also has high amount of sulphates, but low mobility of Rb, Cs and Li may be due to elements being bound to small pyritic fraction, clay minerals or organic fraction (Izquierdo and Querol, 2012; Zhao, 2017). In soil samples, those elements are probably absorbed on potassium alumino-silicates (e.g. ilite) due to common substitution of those elements for K ion in mentioned minerals (Butterman and Reese 2003).

Mo and U also showed high mobility in hill samples. Mobility of Mo is mostly affected by pH mentioned earlier. Mo is usually associated with fly ash because it is a volatile element and during coal combustion it condenses on the surface of fly ash particles. Because it is on the surface of fly ash, it is easily leached. Occurrence of Mo in bottom ash is not usually discussed, but Querol et al. (1996) reported that Mo and U could also have high mobility in coal ash due to association with sulphates, oxides and salts.

Most elements showed higher mobility in hill samples, compared to coal and soil. This is probably due to transformation of minerals during coal combustion (Unver & Terzi, 2018), as well as higher content of water-soluble sulphates, unlike in soil where main minerals are clay minerals (Peco, 2018).

All three hill samples, 1_1, 1_2 and 1_3, showed similar mobility for most elements, most likely due to the same composition. Lower total values of elements in outer layer are most likely caused by direct exposure to natural weathering.

- Soil sample

Although total values of elements were highest in soil samples, mobility of elements was lower in this sample than in hill samples. This is probably due to slow dissolution rate of silicates in acid conditions and to association of elements with clay minerals, which adsorb trace elements, especially in alkaline conditions (Komonweeraket, 2015). All elements that had high mobility in soil sample (Mn, Sr, S, and Cd) where discussed earlier due to high mobility in other samples, mostly associated with sulphates.

- Coal sample

In coal sample, P and Co showed high mobility. Phosphorus in coal usually occurs as organically bound P or as inorganic in apatite and aluminophosphates. Usually one mineral group dominates, depending on the factors such as pH and metal availability during coalification (Ward et al., 1995). Apatite is more likely to form in natural to alkaline conditions, meaning that apatite is more likely to appear in Raša coal due to alkaline conditions prevailing during coalification of Raša coal (Medunić et al., 2016). However, mobility of P was the highest in ASTM procedure, which is contrary to solubility of apatite which has lower solubility as pH increases (Williams et al., 1976; Smith et al., 1977). Reason of high mobility of P in coal sample can’t be concluded without too much uncertainty, due to lack of literature about mobility of phosphorus from coal. Cobalt is usually associated with pyrite, calcite and dolomite. Considering low pyrite value of Raša coal, high mobility of Co in coal could be due to solubility of carbonates in acidic conditions.

Low mobility of other elements in coal sample is probably due to complex coal structure or association of trace elements with organic matter. Low mobility could also be due to soluble iron sulphates (rozenite and siderotil) reported as constituents of Raša coal (Peco, 2018). Since they contain Fe and are soluble species, Fe^{2+} may be oxidized to Fe^{3+} and then precipitated as Fe hydroxide or oxyhydroxide at pH >3.5. Fe-precipitates have a large surface area and adsorb heavy metals making them less mobile (Herbert et al., 1996; Hudson-Edwards et al., 1999; Kairies et al., 2005). Both Al and Fe precipitates could form in all samples in EP and TCLP procedures, considering total value of said elements and pH.

In conclusion, all elements that had high and moderate leaching were probably associated with sulphates and to a lesser extent with carbonates. Those elements were Mn, Sr, Cd, and Zn in all samples, Rb, Cs, Li, Mo, and U in hill samples, S in hill and soil samples, and P and Co in coal sample. Higher mobility of most elements in hill sample is probably due to more available elements than in coal samples, higher amount of soluble sulphates and lesser value of silicates which are dominant in soil sample.

Overall low RML values of all elements could probably be prescribed to:

1. Alkalinity of soil and Raša ash, which attenuates the release of elements associated with silicates (majority of analysed elements), and enhances the release of oxyanionic species (As, Cr, Sb, Se, and V) while simultaneously causes the uptake of released elements by Ca-precipitates. This is most likely to happen in ASTM procedure where the samples are the dominant factor in determining the pH of the extract.
2. Adsorption of elements by large surface area of Al and Fe oxyhydroxides, most likely happening in EP and TCLP due to pH being in the right range for precipitation.
3. Low pyritic value of Raša coal, which would generate acidic leachate and higher mobility of elements if the pyritic value was higher.

Both pH and mineralogy affect the leaching pattern of elements highlighting the complex interaction between mineral matter solubility, pH and the leaching of potentially hazardous elements. Further research should be made on possible precipitates from analysed samples, as well as trace elements associated with them.

5.4. Risk assessment

Since values in soil are above the regional values, health risk assessment was carried out for total soil values. Health risk assessment for leached extract concentrations couldn’t be carried out without too much uncertainty, due to unknown variables (aquifer hydraulic conductivity, hydraulic gradient, etc.).

Human health risk assessment was carried out using a model developed by US EPA (USEPA, 1989, 1996, 2011). Variables and equations were implemented in Octave 5.1.0. and script was made with details about variables and equations, as well as calculations (Attachment 2). This script can be opened in Octave or MATLAB and used for any future calculation, only changing several variables. Briefly, Elemental Dose (D_i) was estimated for adults and children for three different routes of exposure to potentially hazardous substance (oral exposure – D_{oral}; dermal exposure – D_{dermal}, inhalation – D_{inhal}). The non-carcinogenic effects of the elements were estimated by calculating the Hazard Quotient (HQ) and the Hazard Index (HI) using the equations:

$$HQ = \frac{Di}{Rfi} \tag{1}$$

Where *HQ* is the Hazard Quotient, *Di* is the Elemental Dose (calculated for each element) and *Rfi* is the Reference Dose (maximum acceptable daily dose of element published by US EPA).

$$HI = \sum HQi \tag{2}$$

Where *HI* is the sum of all three exposure pathways.

Hazard Quotient is the ratio of the potential exposure to a substance and the level at which no adverse effects are expected. If the HQ is >1 adverse health effects are possible.

HQ was >1 for As in all three exposures (oral, dermal and inhalation). HQ for dermal exposure and inhalation was <1 for other elements, while for oral exposure was higher for Co and V for adults, and for Co, Li, Mn and V for children. HI was >1 for As.

This indicates that soil around Štrmac spoil heap is polluted, and any contact or longer stay around it should be restricted. The As, Co and Li weren't above the prescribed limit in leachate, meaning that soil from this location does not pose a threat to local groundwater . However, calculated HQ indicate threat to human health, which highlights the importance of considering different exposures pathways. In addition, Mn and V in leachate were both above the prescribed limit, posing a threat to human health and showing that the Štrmac site represents a risk to the environment and human health through different pathways.

6. CONCLUSION

Based on the obtained results, the following can be concluded:

1. Total content of elements is mostly in the agreement with previous studies. Se values were more than six time higher in soil and coal which could be associated with uptake of Se by secondary precipitates, but it could also be due to heterogeneity of samples. Lower values of elements in soil sample (Pb, Zn, Sr, Cu, Se) and in coal sample (As, Cr, Mo, Ni, Pb, Sr, U, V) than previously reported is probably due to both leaching and heterogeneity of samples.
2. Extraction procedures resulted in different extract concentrations and followed the order: ASTM < EP < TCLP < TCLP2. TCLP2 didn't mask the results of oxyanionic species which is usually a limitation of the method. ASTM is a better method for representing field conditions, however it can't predict mobility of elements during acid rain. Every method has its limitation and a combination of all three gives valuable insight into the behaviour of elements in different scenarios.
3. Extract concentrations of V, S, U and Mn were above the prescribed limit in all extraction procedures, while Al, Se and Sr were above in TCLP2. Elements that were above the prescribed limit are usually elevated in SHOS coal and ashes. Such elements pose a risk for entering the groundwater.
4. Mobility of elements is controlled by pH and mineralogy. Majority of elements showed cationic pattern, Rb showed oxyanionic pattern, Mo showed amphoteric pattern. Generally low RML (<2%) values are probably result of alkalinity of samples and adsorption by Al and Fe. Ca-precipitates are likely to occur in alkaline conditions and bind oxyanionic species (As, Cr, Sb, Se, V). Along with that, dissolution of silicates is low in alkaline conditions, therefore alkalinity attenuates release of majority of elements. This is most likely the scenario during ASTM procedure. In acidic conditions, elements are most likely adsorbed by Al and Fe oxyhydroxides, but higher RML values than in ASTM are due to attack of acid on minerals and solubility of calcite. Elements with high mobility are probably associated with gypsum or other soluble sulphates.
5. Human health risk assessment was carried out for soil sample. Results showed non-cancerogenic risk for As (oral, inhalation and dermal exposure) and also for oral exposure for Co and V (adults), and Co, Li, Mn and V (children).

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Web Sources

Link 1: http://envi.azo.hr/ (1.3.2019.)

Link 2: http://www.hgi- cgs.hr (10.3.2019.)

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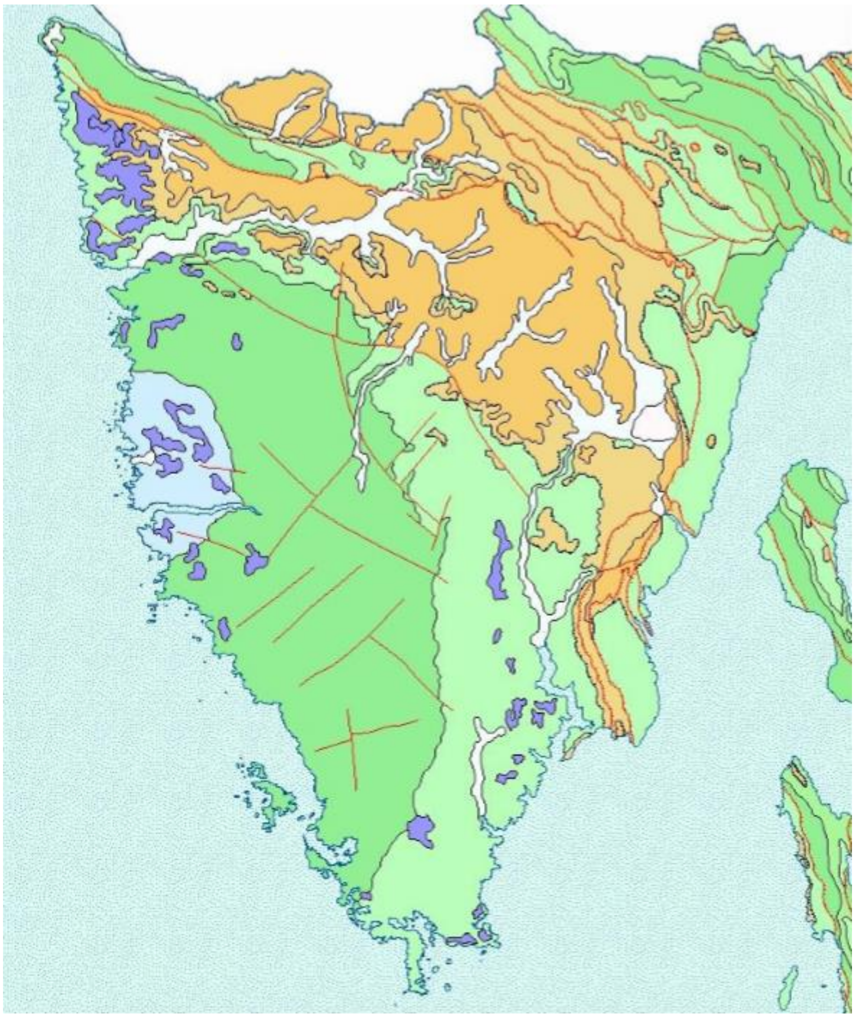
Link 5: https://www.worldcoal.org/ (29.2.2019.)

Link 6: https://www.epa.gov/sites/production/files/2016-03/documents/industrial-waste-guide.pdf (30.7.2019.)

8. LIST OF FIGURES AND TABLES

9. ATTACHMENTS

Attachment 1. Geological map of Istrian Peninsula. Segment from the basic geological map of Croatia 1:300 000 (Link 2)



Attachment 2. Octave script for calculating risk assesment

This script can be implemented in Octave or MatLab and used in future studies. Only variables C, RfDo, ABSgi, ABSd, URF, RfCi need to be changed according to the elements analayzed. C are concentrations measured in the study, while other variables can be found in Resident Soil Table and Exposure Factors Handbook (USEPA, 2019)

```
% HEALTH RISK ASSESSEMENT
% Defining the variables
% from the study
% order of elements: As, Ba, Be, Cd, Co, Cu, Li, Mo, Mn, Ni, Pb, Sb, Se, Sn, Sr, V, Zn
C=[15.8 381 2.36 0.83 41.5 37.8 53.8 2.89 2260 48.2 1.64 21.8 4.70 128 183 120]; % average concentration of element in soil in mgkg
% from USEPA (Resident Soil Value and Exposure Factors Handbook)
% upper case (adults), lower case (children)
IR=100; ir=200; % Soil Ingestion rate (mg/day)
EF=350; ef=350; % Exposure Frequency (day/year)
ED=80; ed=6 %Exposure Duration (year)
BW=80; bw=15; %Body Weight (kg)
ATNQ=9490; atnq=2190; %Averaging time for non-carcinogens (day)
ATQ=25550; atq=25550 % Averaging time for carcinogens (day)
TR=1*10e-6; tr=1*10e-6; % Target cancer risk
% Note: RfDo, ABSgi, RfDabs, Absd, URF values are taken from Resident Soil Table
% and the order of elements has to match the order of elements in variable C
RfDo=[3e-04 2.0e-01 2.0e-03 1.0e-03 3.0e-04 4.0e-02 2.0e-03 5.0e-03 1.4e-01 2.0e-02 4.02e-04 5.0e-03 6.0e-01 6.0e-01 5.0e-03 3.0e-01]; % Oral reference dose (mg/kg day), different for every element
ABSgi=[1 0.07 0.007 0.025 1 1 1 1 1 0 0.15 1 1 1 0.026 1]; % Gastro-intestinal absorption factor, different for every element
RfDabs_vec=zeros(1,length(RfDo))
for iii=1:length(RfDo)
  RfDabs=RfDo(iii)*ABSgi(iii)
  RfDabs_vec(iii)=RfDabs
end
 % Dermally adjusted reference dose (mg/kg day), different for every element
AF=0.07; af=0.2; % Skins-soil adherence factor (mg/cm2 event)
ABSd=[0.03 NaN NaN 0.001 NaN NaN NaN NaN NaN NaN NaN NaN NaN NaN NaN  NaN]; % Dermal absorption factor from soil
EvF=1; % event frequency (event/day)
SA=6.03*10e3; sa=2.37*10e3; % skin surface area (cm2)
URF= [4.3e-03 NaN 2.4e-03 1.8e-03 9.0e-03 4.0e-02 NaN NaN NaN NaN NaN NaN NaN NaN NaN NaN]; % different for every element (ug/m3)-1 ()
InhR=20; %Inhalation rate (m3/day)
RfCi=[1.5e-05 1.4e+09 2.0e-05 1.0e-03 6.0e-06 NaN NaN NaN 5.0e-05 NaN NaN 2.0e-02 NaN NaN 1.0e-04 NaN]; % Inhalation reference concentration (mg/m3); different for every elements (RST)
PEF=1.32*10e9; %Particulate emission factor (m3/kg)
%% Calculations
%Elemental Dose (Di)
D_ORAL=(C*IR*EF*ED)/(BW*ATNQ)*10E-6; % Elemental dose for oral exposure (adults)
D_oral=(C*ir*ef*ed)/(bw*atnq)*10E-6; % Elemental dose for oral exposure (children)
D_DERMAL_vec=zeros(1,length(C))
D_dermal_vec=zeros(1,length(C))

for ii=1:length(C)
D_DERMAL=(C(ii)*SA*AF*ABSd(ii)*EF*ED)/(BW*ATNQ)*10E-6; % Elemental dose for dermal exposure (adults)
D_DERMAL_vec(ii)=D_DERMAL
D_dermal=(C(ii)*sa*af*ABSd(ii)*ef*ed)/(bw*atnq)*10E-6;
```

```
D_dermal_vec(ii)=D_dermal
end

D_INHAL=(C*EF*ED)/(PEF*ATNQ); % Elemental dose for inhalation (adults)
D_inhal=(C*ef*ed)/(PEF*atnq); % Elemental dose for inhalation (children)

% Hazard Quotient for non-cancerogenus
HQ_ORAL_vec=zeros(1,length(C))
HQ_oral_vec=zeros(1,length(C))
HQ_DERMAL_vec=zeros(1,length(C))
HQ_dermal_vec=zeros(1,legnth(C))
HQ_INHAL_vec=zeros(1,length(C))
HQ_inhal_vec=zeros(1,length(C))

for i=1:length(C)
  HQ_ORAL=D_ORAL(i)/RfDo(i)
  HQ_ORAL_vec(i)=HQ_ORAL

  HQ_oral=D_oral(i)/RfDo(i)
  HQ_oral_vec(i)=HQ_oral
  HQ_DERMAL=D_DERMAL_vec(i)/RfDabs_vec(i)
  HQ_DERMAL_vec(i)=HQ_DERMAL
  HQ_dermal=D_dermal_vec(i)/RfDabs_vec(i)
  HQ_dermal_vec(i)=HQ_dermal
  HQ_INHAL=D_INHAL(i)/RfCi(i)
  HQ_INHAL_vec(i)=HQ_INHAL
  HQ_inhal=D_inhal(i)/RfCi(i)
  HQ_inhal_vec(i)=HQ_inhal
end

% Find which elements are the threat to human health:
ElementsHealthThreat_ORAL=find(HQ_ORAL_vec>1)
ElementsHealthThreat_oral=find(HQ_oral_vec>1)
ElementsHealthThreat_DERMAL=find(HQ_DERMAL_vec>1)
ElementsHealthThreat_dermal=find(HQ_dermal_vec>1)
ElementsHealthThreat_INHAL=find(HQ_INHAL_vec>1)
ElementsHealthThreat_inhal=find(HQ_inhal_vec>1)

% Hazard Index for non-cancerogenus
HI_vec=zeros(1,length(HQ_ORAL_vec))
hi_vec=zeros(1,length(HQ_ORAL_vec))

for in=1:length(HQ_ORAL_vec)
  HI=HQ_DERMAL_vec(in)+HQ_INHAL_vec(in)+HQ_ORAL_vec(in)
  HI_vec(in)=HI
  hi=HQ_dermal_vec(in)+HQ_inhal_vec(in)+HQ_oral_vec(in)
  hi_vec(in)=hi
end

HI_HealthThreat=find(HI_vec>1)
hi_HealthThreat=find(hi_vec>1)
```

10. SUMMARY (IN CROATIAN)

U uvodnom dijelu rada, definirani su svrha i cilj rada. Cilj rada je utvrditi ukupne koncentracije potencijalno toksičnih elemenata (Se i metala) u uzorcima pepela, ugljena i okolnog tla sa područja Štrmca (Istra), kao i njihove koncentracije u ekstraktima dobivenim ekstrakcijskim metodama. Svrha rada je procijeniti rizik ispiranja elemenata uzrokovanog oborinama na okoliš i zdravlje ljudi. Rad se sastoji od nekoliko poglavlja od kojih su glavni – Pregled dosadašnjih istraživanja, Materijali i metode, Rezultati i Rasprava.

Poglavlje 'Pregled dosadašnjih istraživanja' sastoji se od dva dijela – 'Teorijska osnova' i 'Prijašnja geološka i okolišna istraživanja'. U potpoglavlju 'Teorijska osnova' detaljno su opisani nastanak ugljena, karakteristike nusprodukata izgaranja ugljena te ekstrakcijske metode korištene u radu.

Ugljen je crna ili smeđa sedimentna stijena koja se sastoji uglavnom od ugljika, vodika i kisika. Fizička, kemijska i druga svojstva ugljena znatno se razlikuju od uzorka do uzorka jer ovise o okolišnim uvjetima koji su vladali tijekom nastanka. Ugljen nastaje nakupljanjem organskih materijala, uglavnom ostataka biljaka poput drveta, korijena, lišća i sjemena, u močvarnom okruženju što dovodi do stvaranja treseta. Nakon što je treset pokopan mineralnim sedimentom, visoke temperature i tlak pretvaraju biljni materijal u ugljen. Najobilnija sedimentacija ugljena dogodila se prije otprilike 300 milijuna godina tijekom karbona i prije 100 milijuna godina tijekom gornje krede. Postoje različite vrste ugljena što ovisi o tlaku, temperaturi i duljini vremena nastanka. U početku se treset pretvara u 'lignit' koji je mekan i crne do smeđe boje. Konstantno visoka temperatura i tlak pretvaraju lignit u „sub bituminozne“ ugljene. Daljnje kemijske i fizikalne promjene događaju se sve dok ugljen ne postane tvrđi i crniji, tvoreći „bituminozne“ ugljene i na kraju „antracitne“ ugljene. Bituminozni i antracitni ugljeni smatraju se ugljeni visokog ranga zbog većeg postotka čistog ugljika, manjih nečistoća i veće vrijednosti goriva.

Ugljen se sastoji od organskih materijala (prvenstveno ugljika, vodika i kisika i manjih količina dušika i sumpora) i od anorganskog materijala (elemenata u mineralnom obliku i organski vezanih elemenata). Organski sastojci ugljena nazivaju se maceralima. Macerali su grupirani prema biljnom tkivu iz kojeg su izvedeni u tri glavne skupine: vitrinit, inertinit, liptinit. S obzirom na anorganski sastav, glavne mineralne skupine su minerali gline, karbonatni minerali, sulfidi i disulfidi, silicijev dioksid i sulfati, pri čemu glina, kvarc, pirit i razni karbonati dominiraju u većini ugljena. Ugljen također sadrži značajne količine mnogih elemenata u tragovima, koji se mogu pojaviti u ugljenu i u organskom i u anorganskom obliku. Raspodjela i pojavljivanje elemenata i minerala razlikuje se između ugljena s istih i različitih lokacija.

Ugljen kao zapaljivi materijal jedan je od najvažnijih svjetskih izvora energije gdje 37% svjetske električne energije dolazi iz elektrana na ugljen. Zbog sporog formiranja koje traje milijunama godina, smatra se neobnovljivim resursom, a procjenjuju se da će naslage ugljena koje su sada na Zemlji potrajati još 200 godina ako se sagorijavanje ugljena nastavi današnjim tempom. Sagorijevanjem ugljena, zapaljivi elementi ugljena (ugljik, sumpor i vodik) reagiraju s kisikom i stvaraju okside (CO, CO_2, SO_2, H_2O) i toplinu koja se zatim pretvara u električnu energiju. Negorivi dio ugljena ostaje u obliku pepela, šljake i ostataka odsumporavanja dimnih plinova. Ti proizvodi su otpadni proizvodi izgaranja ugljena i mogu se smatrati opasnima za okoliš ako se ne odlažu pravilno jer, okolišni uvjeti, poput oborina, mogu prouzročiti ispiranje elemenata iz pepela i šljake koji mogu zagaditi tlo i podzemne vode. Zbog visokih temperatura u procesima izgaranja ugljena (≥1000), organski i anorganski sastojci ugljena se transformiraju, što čini sastav produkata izgaranja ugljena drugačijim od sastava ugljena. Elementi povezani s organskim frakcijama ugljena obično isparavaju i adsorbiraju se na sitnim česticama kada temperatura padne. Elementi povezani s mineralima uglavnom ostaju u pepelu.

Ekstrakcijske metode koriste se za procjenu potencijalno ispranih koncentracija otpadnih sastojaka koji mogu ući u okoliš. Tijekom vremena razvijeno je više od dvadeset ekstrakcijskih metoda kako bi se simuliralo proces ispiranja. Najčešće korištene metode uključuju ASTM, EP i TCLP metode koje se uspoređuju u ovom radu. ASTM je kratica za Američko društvo za ispitavanje i materijale gdje je razvijeno nekoliko ekstrakcijskih metoda. Najčešće korištena metoda je ASTM D-3987-85 (The Shake Extraction of Solid Waste with Water), koja se često naziva i samo „ASTM”. Metoda se temelji na ekstrakciji poznate mase otpada destiliranom vodom u trajanju od 48 sati. Namjera je ispitivanja da simulira uvjete u kojima je kruti otpad dominantan faktor u određivanju pH procjedne vode. Ova je metoda odobrena samo za neke anorganske sastojke i nije primjenjiva na organske tvari i isparljive organske spojeve. Američka agencija za zaštitu okoliša (EPA) razvila je dvije metode EP (Extraction Procedure) i TCLP (Toxicity Characteristic Leaching Procedure). EP metoda je razvijena prva, a TCLP metoda je razvijena kasnije i predložena kao zamjena za EP. EP je laboratorijski test izvorno osmišljen da simulira ispiranje komponenata iz potencijalno opasnog otpada odloženog na komunalno odlagalište. Koristi slabu otopinu kiseline (pH 5,0 ± 0,2), a otpad se smatra opasnim ako ekstrakt sadrži bilo koji od navedenih nečistoća u koncentraciji većoj od određene vrijednosti. Za osam elemenata su definirane maksimalne koncentracije (mgl^{-1}) u ekstraktu: arsen (5.0), barij (100.0), kadmij (1.0), krom (5.0), olovo (5.0), živa (0.2), selen (1.0) i srebro (5.0). TCLP je proširena verzija EP-a jer obuhvaća širi spektar vrsta otpada i može se koristiti za više organskih i anorganskih spojeva. Ispitivanje se provodi pomoću puferske otopine octene kiseline pH = 4,93 ili pH = 2,88, ovisno o pH ispitivanog otpada. TCLP je najčešće korištena metoda za procjenu stvarnog potencijala ispiranja otpada, ali glavni problem povezan s ovom metodom je taj što može precijeniti ili podcijeniti potencijal ispiranja u drugim ekstremnim uvjetima (npr. Alkalni otpad).

U potpoglavlju 'Prijašnja geološka i okolišna istraživanja' opisana je povijest rudarenja ugljena u Hrvatskoj i karakteristika raškog ugljena te je dan pregled istraživanja okolišnog učinka Raškog ugljena i produkata izgaranja.

Rudarenje ugljena u Hrvatskoj trajalo je četiri stoljeća i predstavljalo je jednu od glavnih industrijskih grana, vidljivo u otvaranju škola, izgradnji stambenih područja, željeznica i prometnica koja su spajala glavna rudarska naselja (Štrmac, Labin, Vinež, Krapan i Raša). Zbog nedostatka čiste tehnologije, iskopavanje i sagorijevanje ugljena stvorilo je gomilu nepropisno odloženog otpada, koji se još uvijek nalazi u naseljima na krškom području. Ta odlagališta sastoje se od ugljenog pepela, šljake i bilo kojeg otpada preostalog od rudarenja. Specifičnost ovog područja je što se iskopavao i spaljivao raški ugljen, kojeg su prijašnji autori nazvali 'neobični' ugljen, zbog svojstava koja odstupaju od uobičajenih karakteristika ugljena.

Raški ugljen karakterizira visoka koncentracija organskog sumpora (11.4%). Sadržaj sumpora u većini ugljene kreće se od 0.50% do 5.00%, no pojedini ugljeni su obogaćeni organskim sumporom, obično u rasponu od 4.00-11.00%. Takvi ugljeni pronađeni su u Australiji i Kini te u Hrvatskoj te su obično obogaćeni i na U-Se-Mo-V-Re. Sadržaj anorganskog sumpora, uglavnom pirita (FeS_2), varira, te SHOS ugljeni mogu imati nizak ili visok sadržaj piritnog sumpora, ovisno o okolišnim uvjetima koji su vladali tijekom formiranja ugljena. Raški ugljen ima nizak sadržaj pirita sličan onome u kineskom ugljenju Yanshan i Guidan (0,30% do 1,1%). Visok udio sumpora u raškom ugljenu posljedica je anaerobnih i alkalnih uvjeta okoliša tijekom nastanka raškog ugljena, što potvrđuju i glavne mineralne faze – kalcit i dolomit.

Istraživanja vezana za utjecaj raškog ugljena i nusprodukata spaljivanja na okoliš počela su se provoditi krajem 20. stoljeća s fokusom na termoelektranu Plomin. Istraživanja u okolici Plomina pokazala su da je spaljivanje ugljena negativno utjecalo na okoliš (mehanička šteta iglica i listova borova i hrastova, povećana koncentracija sumpora u iglicama borova i tlu, povećane koncentracije metala i PAHova u tlu). Nakon 2016., istraživanja su se fokusirala i na ostala naselja povezana s raškim ugljenom. Vrijednosti pojedinih metala izmjerena su iznad dozvoljene granice u uzorcima tla, vode, različitih biljaka (djetelina, povrće) te pojedinim organima ptica.

U poglavlju 'Materijali i metode' opisano je područje istraživanja, sakupljanje uzoraka, priprema uzoraka, postupak ekstrakcije i multi-elementa analiza.

Područje istraživanja nalazi se u naselju Štrmac, koje se nalazi na jugoistočnm dijelu Istarskog poluotoka, u najzapadnijem dijelu Hrvatske. Naselje Štrmac jedno je od brojnih rudarskih naselja te se u njemu nalazi nepropisno odložen otpad koji se pretežno sastoji od šljake i pepela, prekriveno tlom kako bi se spriječilo širenje pepela zrakom. Na padini brda (odlagališta) vidljivi su tragovi vodene erozije. Oko 5,5 km jugoistočno (zračna udaljenost) od Štrmca je grad Raša, u kojem se nalazi napušteni rudnik iz kojeg se vadio raški ugljen.

Ukupno je prikupljeno pet uzoraka u prosincu 2017. na različitih lokacijama. Sa brda Štrmac sa udaljenosti 2-3 m prikupljena su tri uzorka pepela. Na prvom mjestu (1_1) prikupljen je površinski uzorak, dok je na druga dva (1_2 i 1_3) uzorkovan potpovršinski sloj, dubok ~ 20 cm. Uz to, uzorak tla prikupljen je na dnu brda. Uzorak ugljena prikupljen je u starom napuštenom rudniku u Raši, 2 km od ulaza u rudnik. Prikupljen je potpovršinski sloj, ca. 5 cm ispod površinskog sloja. Na svim mjestima, uzorci su prikupljeni lopatom za uzorkovanje i pohranjeni u plastičnu vrećicu.

Ukupne koncentracije elemenata u pet uzoraka određene su u uzorcima nakon totalne digestije u mikrovalnoj pećnici. Za ekstrakciju, testirane su tri metode ekstrakcije, ASTM, EP i TCLP (pH 4.93 i 2.9). Multi-elementarna analiza razgrađenih uzoraka i ekstrakata izvršena je tehnikom spektrometrije masa visoke razlučivosti uz induktivno spregnutu plazmu (HR-ICP-MS). Svi su uzorci analizirani na 29 elemenata (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, U, V, Zn).

U poglavlju 'Rezultati' tablicama su prikazane totalne i ekstrahirane koncentracije elemenata. Ukupne koncentracije kretale su se za glavne elemente (Al_2O_3, Fe_2O_3, MnO, TiO_2, P_2O_5 and SO_3) od 0.005-21.1%, a za elemente u tragovima od ispod granica detekcije do 1083 mg kg^{-1}. Najviše ukupne koncentracije za većinu elemenata izmjerene su u uzorku tla. Sumpor je imao najmanju koncentraciju u tlu, a najvišu u ugljenu gdje je većina elemenata imala najnižu koncentraciju

Koncentracije ekstrakata kretale su se od ispod granica detekcije do 507 mg L^{-1} i slijedile su redoslijed: ASTM < EP < TCLP < TCLP2, pri čemu su najviše koncentracije zabilježene u uzorcima brda za većinu elemenata, s izuzetkom Ba, Be, Cd, Co, Cu, Mn, P, Pb i Zn koji su imali najveću koncentraciju u uzorku tla. Za Sn i Tl nije bilo velike razlike u koncentraciji između uzoraka. Najniže koncentracije elemenata zabilježene su u uzorku ugljena, dok je za neke elemente (As, Cr, Li, S, Sb, Sc, Ti, U, V) najniža koncentracija bila i u uzorku tla i ugljena. Koncentracije u TCLP i TCLP2 ekstraktima uglavnom su bile za jedan do dva reda veće nego u ASTM i EP ekstraktima, s izuzetkom S i Mo koji su imali najveću koncentraciju ekstrakta u ASTM metodi.

U poglavlju 'Rasprava', ukupne vrijednosti svih uzoraka uspoređene su s prethodnim istraživanjima, koncentracije ekstrakata uspoređene su s propisanim graničnim vrijednostima, mobilnost elemenata raspravljena je kao funkcija pH i mineralogije, a na kraju je provedena procjena rizika za uzorak tla.

Sadržaj glavnih elemenata i nekoliko elemenata u tragovima (Cd, Cu, Pb, Sr, U, V i Zn) u uzorcima brda uglavnom su istog raspona kao u prethodnim istraživanjem šireg područja. Više od dva puta veće vrijednosti primijećene su za Cr i Sr, i šest puta veće vrijednosti za Se u 1_1 i 1_2, dok je u trećem uzorku vrijednost Se bila u skladu s ranije prijavljenim vrijednostima. Prijašnje istraživanje pokazalo je da su vrijednosti elemenata u tragovima na brdu Štrmac općenito niže od najnižih izmjerenih vrijednosti na deponiji pepela u središnjoj Hrvatskoj. Niže vrijednosti Se i drugih elemenata pripisane su ispiranju i oksidaciji. U ovom radu, vrijednosti Se pokazuju varijabilnost u uzorcima, u rasponu od 5,39 do 35,9 mg / kg, koje su veće od ranije prijavljenih. Ova varijabilnost mogla bi biti zbog heterogenosti uzoraka te kao rezultat zajedničkog djelovanja ispiranja i sekundarne adsorpcije. Većina elemenata je ispod Clarkovih vrijednosti za pepeo, osim Se i Sr koji su pokazali povišene vrijednosti. Povećanje s dubinom primijećeno je za sve okside i većinu elemenata u tragovima. Niže koncentracije u 1_1 vjerojatno su posljedica izravne izloženosti površinskog sloja oborinama.

Sadržaj glavnih elemenata i nekoliko elemenata u tragovima (Cd, Cr, U i V) u uzorcima tla uglavnom je u skladu s prethodnim istraživanjima. Suprotno tome, opažene su više od dva puta niže vrijednosti Pb, Zn, Sr i Cu i deset puta veće vrijednosti Se. Vrijednosti petnaest elemenata (Al, Ba, Co, Cr, Cu, Fe, Ni, Pb, Sc, Sr, Ti, V i Zn) od sedamnaest elemenata navedenih u Geokemijskom atlasu Hrvatske (regionalne pozadinske vrijednosti) (Halamić i Miko, 2009) imaju više vrijednosti od navedene srednje vrijednosti, a As i Cd imaju nešto niže vrijednosti.

Najveća koncentracija gotovo svih elemenata (osim S, Cu, Mo, Se Sr, U i V) bila je u uzorku tla. Uočljivo je da su elementi, čija vrijednost nije najviša u uzorku tla, elementi obično povišeni u ugljenima i pepelima s povišenim koncentracijama organskog sumpora.

Sadržaj glavnih elemenata i većina elemenata u tragovima u uzorku ugljena u skladu je s ranije izmjerenim vrijednostima. Međutim, neki elementi u tragovima (As, Cr, Mo, Ni, Pb, Sr, U i V) su i do dva puta niži od onih prijašnje izmjerenih. Svi elementi u tragovima, osim Cd, Se, Sn, Sr i Tl, niži su od Clarkovih vrijednosti. Budući da je raški ugljen obično obogaćen Sr, U, V, Mo, neobično je da su vrijednosti U i V niže od svjetskih prosjeka, a vrijednosti Sr i Mo blizu prosjeka. Niže vrijednosti ostalih elemenata u tragovima ugljena Raše pripisane su različitim okolišnim uvjetima tijekom formiranja ugljena. Najniže koncentracije većine elemenata zabilježene su u uzorku ugljena. Uzorci pepela općenito su obogaćeni elementima u tragovima u odnosu na uzorak ugljena. Jedina iznimka bio je sumpor koji je imao najviše koncentracije u uzorku ugljena. Uzorci pepela imali su niže vrijednosti S zbog stvaranja SOx-a tijekom izgaranja, koji se apsorbira na leteći pepeo ili ispušta u atmosferu.

Ekstrakcijske metode rezultirale su različitim koncentracijama ekstrakta analiziranih elemenata (ASTM <EP <TCLP <TCLP2), što ukazuje da je pH važan parametar koji utječe na ispiranja elemenata. Također se postavlja pitanje koja je metoda najučinkovitija u predviđanju onečišćenja uzrokovanog ispiranjem. Odabir metode koja može najbolje simulirati stvarni scenarij ovisi o različitim čimbenicima - fizičkim svojstvima otpada, izvoru otpada, starosti odloženog otpada i klimatskim uvjetima odlagališta. Većina se autora slaže da je ASTM najbolja metoda pri simuliranju vremenskih prilika, budući da je otpad

dominantan faktor u određivanju pH ekstrakta. EP i TCLP metoda smatraju se previše agresivnim za većinu otpada, što često rezultira pogrešnim tumačenjem rezultata i pogrešnom klasifikacijom otpada. Osim toga, TCLP i EP mogu 'zamaskirati' ispiranje oksianionskih vrsta, poput As i Se, koje su obično pokretnije u neutralnim do alkalnim uvjetima. Rezultati pokazuju da su koncentracije ekstrakata As i Se veće u TCLP nego u ASTM, što znači da TCLP metoda ne bi maskirala ispiranje da se samo ta metoda koristila za procjenu otpada s brda. Iako TCLP možda nije uvijek najtočnija metoda simuliranja stvarnih vremenskih prilika, korištenje te metode daje uvid u pokretljivost elemenata u kiselim uvjetima, što je važno u dijelovima svijeta koji su pod utjecajem kiselih kiša. U prvoj polovici 2019. godine,, pH kiše izmjerene u Rijeci (Hrvatska) kretale su se u rasponu od 4,88 do 7,72, dok je u 1996. izmjeren pH 3,02. Upravo zbog toga treba razmotriti izmjerene koncentracije svih metoda.

Koncentracije ekstrakata, u usporedbi s EPA razinama toksičnosti, definiraju odlagalište Štrmac kao neopasno. Međutim, koncentracije ekstrakata nekoliko elemenata su iznad graničnih vrijednosti navedenih u Pravilniku o graničnim vrijednostima emisija otpadnih voda. Pravilnik obuhvaća sedamnaest od dvadeset i devet analiziranih elemenata, a pet ih je (Al, Mn, S, Se i V) iznad granice u pojedinim ekstrakcijskim metodama. Koncentracije As, Pb, Ni i Cd ispod su graničnih vrijednosti, ali prema navedenom Pravilniku zabranjeno je ispuštanje vode s navedenim elementima u okoliš. Ostali elementi obuhvaćeni Pravilnikom (Ba, Co, Cr, Cu, Fe, P, Sn i Zn) ispod su graničnih vrijednosti u svim uzorcima. Dvanaest elemenata koji nisu obuhvaćeni hrvatskom regulativom (Be, Bi, Cs, Li, Mo, Rb, Sb, Sc, Sr, Ti, Tl i U) također nisu globalno regulirani. Za nekoliko elemenata postoje ograničenja u pitkoj vodi (U, Sb i Sr) (EPA, 2018) ili granične vrijednosti za pročišćene otpadne vode koje se koriste za navodnjavanje u poljoprivredi (Be, Cu, Li, Mo i Tl). Nekoliko elemenata (Rb, Sc i Ti) nije uspoređeno zbog nedostatka definiranih graničnih vrijednosti, jer se neki elementi ne smatraju elementima od velikog značaja za okoliš. U svim ekstrakcijskim metodama slični elementi su iznad dopuštene granice, razlika je u tome što su koncentracije veće kako se pH smanjuje. Elementi koji su pokazali povišene vrijednosti su V i S u ASTM, Mn, S i U u EP, Mn, S, U i V u TCLP, te Al, Mn, S, Se, Sr, U i V u TCLP2. Svi su elementi iznad granice u uzorcima brda, osim Mn koji je iznad granice u uzorku tla. Elementi koji su iznad propisanih granica u gotovo svim ekstraktima (V, S, U i Mn) su elementi obično povišeni u SHOS ugljenima.

Povišene vrijednosti spomenutih elemenata također su u skladu s prethodnim istraživanjima šireg područja gdje su U, V i Sr povećani u većini uzoraka vode, povrća, tla i vodenih sedimenata. U spomenutom istraživanju utvrđeno je da je V također povišen u uzorcima jetre nemigratornih ptica, kao i Cu, Zn i Pb koji su bili ispod granične vrijednosti u ovom radu. Povišene vrijednosti istih elemenata ukazuju na to da bi ispiranje elemenata s brda Štrmac moglo biti jedan od izvora onečišćenja područja korištenja raškog ugljena. Selen je bio iznad propisanih granica samo u ekstraktima TCLP2, što ukazuje na to da u slučaju kisele kiše može predstavljati opasnost za okoliš. Prethodna istraživanja Se u širem istraživanom području pokazala su povišene vrijednosti selena u tekućoj vodi i pripadajućem sedimentu, kao i u morskoj vodi, djetelini i lišću, implicirajući da je došlo do ispiranja Se iz ugljena, pepela i tla zagađenog ugljenom. Moguće je da je došlo do ispiranja Se za vrijeme kiselih kiša u 90-ima.

Za određivanje potencijala ispiranja elemenata, za svaki element izračunata je relativna masa ispiranja (RML). Relativna masa ispranih elemenata kretala se u rasponu od 0.00001% do 1.94% što je znatno manje u usporedbi sa sličnim istraživanjima. Mobilnost elemenata izražena je RML-om i elementi su grupirani prema njihovoj pokretljivosti. Elementi s RML vrijednosti 0,5% ili više svrstani su u jako mobilne elemente, elementi s RML između 0,5% i 0,05% u umjereno mobilne elemente i elementi s RML ispod 0,05% u slabo pokretljive. Većina elemenata mijenjala je grupe mobilnosti ovisno o postupku ekstrakcije i vrsti uzorka. U metodi ASTM, većina uzoraka pokazala je malu do umjerenu pokretljivost za većinu elemenata, s izuzetkom Mo, P i Rb koji pokazuju visoku pokretljivost. Slična mobilnost pokazala je EP za većinu elemenata, s izuzetkom Mn i Ni koji su mijenjali skupine iz niske u umjerenu pokretljivost, dok se mobilnost Mo, P, Rb smanjila. Suprotno tome, TCLP je pokazao značajno veću pokretljivost na oba pH testirana, gdje je u uvjetima nižeg pH potencijala ispiranje više od 10 puta veće za većinu elemenata. Nekoliko elemenata pokazalo je sličnu pokretljivost bez obzira na pH vrijednost. U svim ekstrakcijskim metodama opažena je mala pokretljivost za Al, Fe, Sc, Ti, srednja pokretljivost za Sn i Zn i visoka pokretljivost za S.

Uspoređujući uzorke, najveće vrijednosti RML uočene su za U, Mo, Li, S u uzorcima brda, S uzorak tla, te P i Co u uzorku ugljena, dok su Mn, Sr i Cd imali veliku pokretljivost u svim uzorcima. Ponašanje elemenata tijekom ispiranja uglavnom je pod utjecajem pH i mineralogije.

Općenito, elementi pod različitim pH uvjetima pokazuju jedan od tri glavna uzorka ispiranja - kationski, oksianionski i amfoterni oblik ispiranja. Elementi s kationskim uzorkom imaju najveću pokretljivost u kiselom pH, koja se smanjuje kako pH raste. Mobilnost elemenata s oksianionskim uzorkom samo se malo povećava pri kiselom pH i značajno raste pri alkalnom pH. Elementi s amfoternim uzorkom imaju visoku pokretljivost i u alkalnim i kiselim pH vrijednosti. Mineralni i organski sastav može promijeniti uzorak, uzrokujući promjenu uobičajenog uzorka elemenata.

Pokretljivost elemenata je najniža u ASTM metodi zato što je većina elemenata u kationskom stanju, adsorbirano na minerale. Kationski uzorak uočen je za As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sc, Se, Sr, Tl, U i V. Rb je jedini element koji je pokazao oksianionski uzorak, iako nije oksianion. Oksianionske vrste (Mo, As i Se) pokazale su amfoterni uzorak (Mo) i kationski uzorak (As, Se). Velika mobilnost Rb i Mo u ASTM metodi uglavnom se slaže s drugim publikacijama. Rb se smatra vrlo topljivom vrstom u pepelu zbog povezanosti s topivim vrstama poput sulfata i klorida. Sulfati su jedan od sastavnih dijelova pepela, vjerojatno odgovorni za visoku pokretljivost Rb u uzorcima brda. Mo je oksianionska vrsta, pa je velika pokretljivost u ASTM-u očekivana. Međutim, Mo je također pokazao visoku pokretljivost u TCLP2, što ukazuje da Mo ima amfoterni uzorak. U kiselim uvjetima koncentracija Mo obično se smanjuje jer ga apsorbiraju Fe i Al oksihidroksidi pri pH> 3,5, što se vjerojatno dogodilo u EP i TCLP, dok u TCLP2 adsorpcija je smanjena. Suprotno drugim publikacijama koje su izvijestile da i druge vrste oksianiona (As, Se) obično imaju sličan uzorak ispiranja kao Mo, As i Se su imali malu pokretljivost u ASTM-u. Pepeo raškog ugljena je alkalan jer su njegove glavne mineraloške faze alkalni minerali poput kalcita, aragonita i portlandita. Iako alkalni uvjeti poboljšavaju desorpciju oksianiona, oni također smanjuju topljivost As i Se ugradnjom u sekundarne precipitate kalcija. Nekoliko elemenata pokazalo je sličnu pokretljivost bez obzira na pH vrijednost. Opažena je mala pokretljivost za Al, Fe, Sc i Ti, srednja pokretljivost za Sn i Zn i visoka pokretljivost za S, na što je najviše utjecala mineralogija.

Osim pH, mineralogija uzoraka može utjecati na brzinu ispiranja elemenata. U različitim pH vrijednostma dolazi do otapanja i ponovnog taloženja određenih mineralnih vrsta, što uzrokuje oslobađanje ili adsorpciju elemenata. Raški ugljen i pepeo sastoje se uglavnom od karbonata i sulfata, dok se uzorak tla sastoji od karbonata i aluminosilikata. Svi elementi imali su niže vrijednosti RML-a (0,00001% do 1,94%) u usporedbi s literaturom, gdje se

RML kretao od 0,1 do> 10,0%. Visok sadržaj karbonata i niska piritna vrijednost uzoraka vjerojatno su odgovorni za nizak RML. Prisutnost karbonata može biti odgovoran za alkalnost pepela, koja može imati pufersku sposobnost i uzrokovati nastajanje Ca-precipitata, uzrokujući taloženje elemenata u tragovima. Pirit čini uzorke kiselijim, te stoga uzrokuje veću pokretljivost većine elemenata, što u ovom radu nije slučaj zbog malog sadržaja pirita. Uzorak ispiranja elemenata u različitim uzorcima vjerojatno je kontroliran topljivošću (otapanje-taloženje) i sorpcijskim procesima glavnih minerala (karbonata, sulfata i silikata).

Većina elemenata koji su imali veliku pokretljivost u uzorcima vjerojatno su povezani sa sulfatima i topivim solima. No s obzirom na ukupne niske vrijednosti RML-a, vjerojatno je da su se elementi taložili sa Ca-precipitatima i Al i Fe oksihidroksidima ili bili nepomični zbog nekog drugog faktora.

Visoka pokretljivost Mn, Sr, Cd i umjerena pokretljivost Zn i Ba vjerojatno je povezana s karbonatima i sulfatima koji su topljivi u kiselini (kalcit) i vodi (gips), a nalaze se u svim uzorcima. Kadmij i cink obično se povezuju sa sulfidima i smatraju se nepokretnim u neutralnim do alkalnim uvjetima. No s obzirom da je mobilnost Cd i Zn u svim uzorcima i postupcima ekstrakcije bila umjerena do visoka, vjerojatno je da su Cd i Zn povezani sa sulfatima ili topljivim solima poput $CdSO_4$ i $ZnSO_4$. Ba također tvori topive spojeve s karbonatima i sulfatima, a njegova pokretljivost obično ovisi o prisutnosti Ca, a ne o pH. U prisutnosti velikih količina Ca, Ba taloži kao $Ba(Sr)SO_4$ ili $BaSO_4$, što bi mogao biti razlog zašto je Ba u ASTM-u imao samo 0,006%.

Visoka pokretljivost S u uzorcima brda i tla vjerojatno je posljedica velike količine topivih sulfata, dok je mala pokretljivost S u uzorku ugljena vjerojatno zbog sumpora u organskom obliku koji je u nekim ugljenima nepokretan.

Niska pokretljivost Al, Fe i Ti u svim uzorcima obično se propisuje smanjenom otapanju aluminosilikata. Al i Fe precipitati talože se pri pH> 3,5, što može utjecati na niske RML vrijednosti elemenata u svim uzorcima zbog velike adsorpcijske površine precipitata.

Alkalni metali Cs, Li i Rb pokazali su isti obrazac ispiranja - umjereno do visoko ispiranje u sva tri uzorka brda, te mala pokretljivost u ugljenu i tlu, što ukazuje da su vjerojatno isto vezani u uzorcima. Velika pokretljivost u uzorcima brda povezana je sa sulfatima, gdje ti elementi tvore vodotopljive spojeve s uobičajenim anionima (karbonat, oksid, nitrat, sulfat itd.). Ova asocijacija se također slaže s prethodnim istraživanjima Valkovića (1984) gdje je Rb bio prisutan u nemagnetskoj frakciji letećeg pepela, gdje su $CaCO_3$ i $CaSO_4$ bili glavni sastojci. Raški ugljen ima i veliku količinu sulfata, ali slaba pokretljivost Rb, Cs i Li može biti posljedica toga što se elementi vežu na malu piritnu frakciju, glinene minerale ili organsku frakciju. U uzorcima tla ti se elementi vjerojatno apsorbiraju u kalijevim alumino-silikatima (npr. Ilit) zbog uobičajene zamjene tih elemenata K ionom u spomenutim mineralima. Mo i U su također pokazali visoku pokretljivost u uzorcima brda, vjerojatno zbog povezanosti sa sulfatima, oksidima i solima.

Većina elemenata pokazala je veću pokretljivost u uzorcima brda, u usporedbi s ugljenom i tlom. To je vjerojatno posljedica transformacije minerala tijekom izgaranja ugljena, kao i većeg sadržaja vodotopljivih sulfata, za razliku od tla u kojem su glavni minerali minerali glina.

Sva tri uzorka brda pokazala su sličnu pokretljivost za većinu elemenata, najvjerojatnije zbog istog sastava. Niže ukupne vrijednosti elemenata u vanjskom sloju najvjerojatnije su uzrokovane izravnim izlaganjem prirodnim vremenskim uvjetima.

Iako su ukupne vrijednosti elemenata bile najviše u uzorcima tla, pokretljivost elemenata bila je niža u ovom uzorku nego u brdskim uzorcima. To je vjerojatno zbog sporog otapanja silikata.

U uzorku ugljena, P i Co su pokazali veliku pokretljivost. Fosfor je u ugljenu obično organski vezan ili anorganski u apatitu i aluminofosfatu. Obično dominira jedna mineralna skupina, ovisno o faktorima kao što su pH. Apatit se vjerojatnije formira u prirodnim do alkalnim uvjetima, što znači da se vjerojatnije da će se apatit pojaviti u raškom ugljenu zbog alkalnih uvjeta koji su prevladavali tijekom nastanka ugljena. Međutim, pokretljivost P bila je najveća u ASTM postupku, što je suprotno topljivosti apatita koji ima manju topljivost s povećanjem pH. Kobalt se obično povezuje s piritom, kalcitom i dolomitom. S obzirom na nisku vrijednost pirita, velika pokretljivost Co u ugljenu može biti posljedica topljivosti karbonata u kiselim uvjetima.

Mala pokretljivost ostalih elemenata u uzorku ugljena vjerojatno je posljedica složene strukture ugljena ili povezanosti elemenata u tragovima s organskom tvari. Mala pokretljivost može biti posljedica topljivih željeznih sulfata (rozenita i siderotila) koji su jedni od sastojaka ugljena. Budući da sadrže Fe i topive su vrste, Fe^{2+} može oksidirati u Fe^{3+}

i potom se istaložiti u Fe hidroksid ili oksihidroksid pri pH> 3,5. Fe-precipitati imaju veliku površinu i adsorbiraju metale.

S obzirom da su vrijednosti u tlu iznad regionalnih vrijednosti, provedena je procjena rizika na ljudsko zdravlje za ukupne vrijednosti tla. Procjena rizika za koncentracije ekstrakata nije se mogla provesti bez prevelike nesigurnosti zbog nepoznatih varijabli (hidraulička vodljivost vodonosnika, hidraulički gradijent itd.). Procjena rizika za ljudsko zdravlja provedena je korištenjem modela koji je razvila EPA. Elementarna doza (Di) procijenjena je za odrasle i djecu za tri različita načina izlaganja potencijalno opasnim tvarima (oralno, dermalno, udisanje). Nekancerogeni učinci elemenata procijenjeni su izračunavanjem kvocijenta opasnosti (HQ) i indeksa opasnosti (HI).

Kvocijent opasnosti je omjer potencijalne izloženosti tvari i razine na kojoj se ne očekuju štetni učinci. Ako je HQ >1 mogući su štetni učinci na zdravlje. HQ je bio >1 za As u sva tri načina izloženosti (oralno, dermalno i inhalacijsko). HQ za dermalnu izloženost i inhalaciju bio je <1 za ostale elemente, dok je za oralna izloženost veća od 1 za Co i V za odrasle, a za djecu Co, Li, Mn i V. HI je bio> 1 za As.

Dobivene vrijednosti pokazuju da brdo u Štrmcu predstavlja rizik za okoliš i ljudsko zdravlje različitim putovima izloženosti.