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Sulfur, metal(loid)s, radioactivity, and cytotoxicity in abandoned karstic Raša coal-mine discharges (the north Adriatic Sea)

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Abstract
Raša coal, mined on the Istrian Peninsula (NW Croatia) for nearly 400 years up to 1999, is notable for having superhigh organic sulfur, and high levels of selenium, uranium, vanadium, and molybdenum. Selenium is the poison responsible for the widespread loss of cattle and sheep. It is essential to human health in trace amounts, but higher concentrations can be harmful. An estimated 4.4Mt. of coal remains underground within marine carbonate rocks. The study area belongs to the coastal karst of the Adriatic Sea. Several abandoned coal-mine discharges (CMDs) were released into local streams and the Raša Bay for decades. Therefore, the water quality of a natural karst spring (Fonte Gaja), the Raša Bay seawater, municipal wastewater, and the Raša CMDs were investigated, focusing on sulfur, selected metal(loid)s (major, minor, and trace), radioactivity, and cytotoxicity. The Fonte Gaja spring water, unrelated to the Raša CMD, served as a reference. Its values of Se, U, V, and Mo (µg/L) were as follows: 1.09, 0.75, 1.37, and 2.04, respectively. However, the respective levels (µg/L) were increased in the rest of the water samples as follows: 10.9, 10.8, 4.60, and 33.1. Water sulfate levels were low though. Total beta activities of the CMDs and Raša Bay water were 235 and 1320 Bq/m^3, respectively, below the guideline level of 2000 Bq/m^3. The cytotoxicity of water samples on the RTG-2 fish cells was not statistically significant. The large volumes of water involved mean the transport of rather large amounts of Se and U, and their deposition in the Adriatic Sea. Due to the complexity of the karst hydrogeology, knowledge of Se and U circulation patterns is highly needed.

Keywords:
Raša coal-mine discharges, water, selenium, radioactivity, cytotoxicity, karst.

1. Introduction

Coal is the most abundant fossil fuel, widely distributed throughout the world. Generally, its consumption could last up to 250-1000 years. In Europe, the major coal-producing countries are Serbia, Poland, Germany, the Czech Republic, Greece, Hungary, Bulgaria, Turkey, Romania, and the United Kingdom **(EIA, 2008)**. In Croatia (see **Figure 1**), the most important and biggest coal-mining district was situated in the eastern part of the Istrian Peninsula (see **Figure 1b**). It was known under the name of 'Istrian Raša coal mines' (in Croatian 'Istarski Ugljenokopi Raša', IUR), according to the name of a major coal-mining town of Raša (see **Figures 1** and **2**), which is situated close to the local Raša River. The coal-mining activities began during Venetian rule (17th to 18th centuries). In 1785, a sugar factory located in the city Rijeka (located some 50 km NE from the town of Raša) became the first permanent buyer of Raša coal, which created the basis for a continuous mining industry. The IUR went under Italian rule in 1918, when its accelerating progress followed, with the introduction of new technologies and an increased production of coal. The Raša coal-mining and coal-combustion activities ended in 1999, after some 40 million tons of coal had been excavated in total. An estimated 4.4Mt. of coal still remains underground. Given the fact that the local area is composed of highly vulnerable karst, it is important to monitor water chemistry of abandoned coal-mine discharges (CMDs). Papers **(Younger, 1997; Belmer and Wright, 2019)** have reported that water draining from

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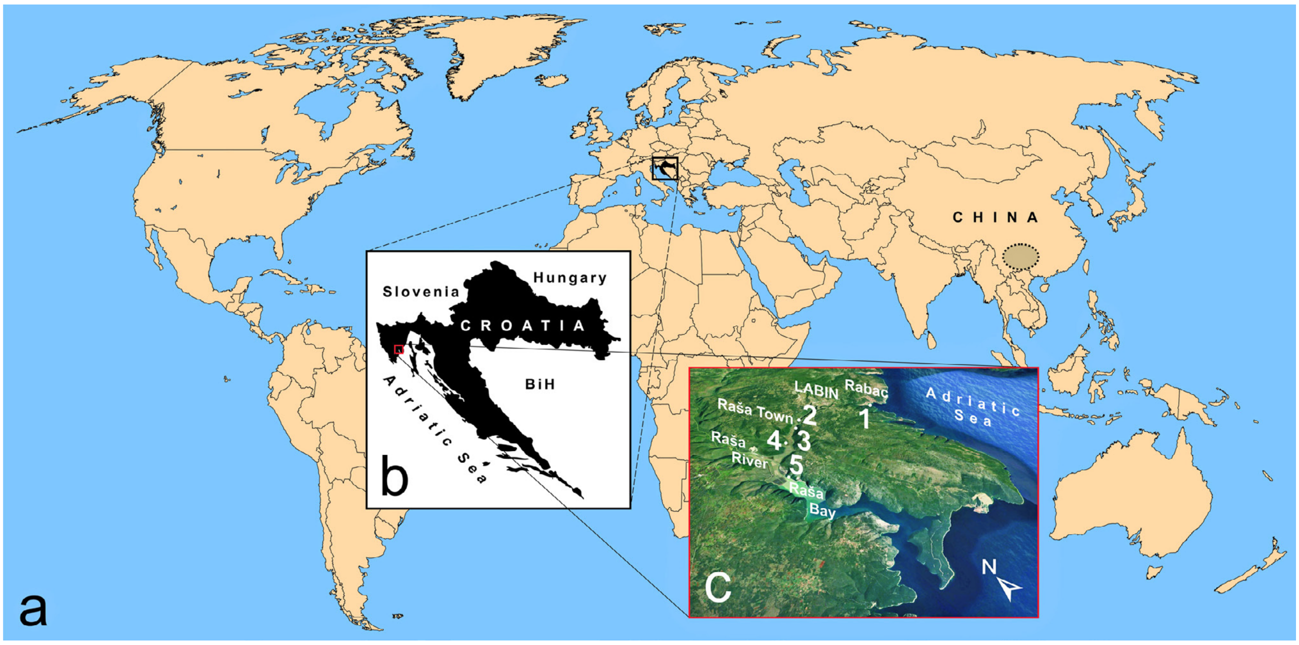

Figure 1: Map of the study area: a) global positions of Croatia (rectangle), and SHOS coal sites in SW China (dashed lined circle); b) the location of the study area (rectangle) on the eastern part of the Istrian Peninsula, i.e. a coastal part of the north Adriatic Sea; and c) a panoramic view of the Raša Bay study area with water sampling sites (no. 1.-5.).

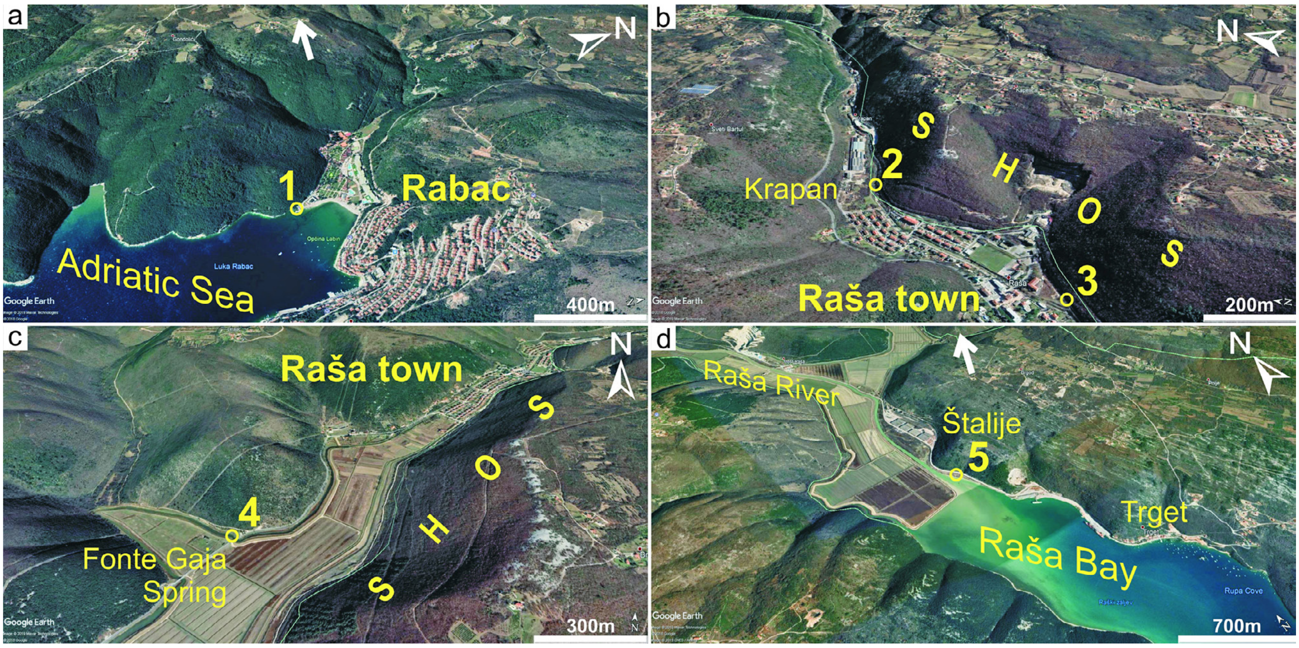

Figure 2: Water sampling locations: a) Raša CMD (no. 1.) next to a beach in the Rabac settlement; b) Raša CMD (no. 2.) in Krapan village (a Leone Klement shaft), and sewage channel water (no. 3.) in the Raša town centre; c) the location of the natural Fonte Gaja spring (no. 4.); and d) water sampling site (no. 5.) close to a former Štalije coal separation unit (the Raša Bay estuary). SHOS is indicating the approximate position of Raša coal.

abandoned as well as active coal/metal mines are a major cause of freshwater degradation.

Coal is the most complex geological material, containing most naturally occurring elements, at least in trace concentrations **(Rađenović, 2004, 2006; Singh et al., 2015; Dai et al., 2020)**. Large amounts of sulfur, selenium, and potentially hazardous trace metals are released into the environment by coal utilization, posing a health hazard **(Saikia et al., 2018)**. Raša coal belongs to a class of superhigh-organic-sulfur (SHOS) coal **(Chou, 2012)**, with S exceeding 11% in some samples **(Medunić et al., 2016a, 2018a)**. Such coal is not very common and is deposited in a special depositional environment **(Chou, 1997; Dai et al., 2015)**. According to **Chou (1997)**, all

SHOS coals show extreme enrichment in organic sulfur, but the pyritic S is variable; Croatian Raša coal, and Chinese Yanshan and Guiding coals (see **Figure 1c**) have low pyritic sulfur content (up to 1.1%), the lowest values (up to 0.3%) reported for Raša coal. Moreover, Raša coal is enriched with selenium, uranium, vanadium, and molybdenum **(Medunić et al., 2018a, 2020)**. Similarly, U-Se-Mo-Re-V assemblage was found in Chinese SHOS Guiding coals **(Dai et al., 2015)**, and Yishan coals **(Dai et al., 2017)**, while increased S, F, V, Cr, Ni, Mo, and U were found in Yanshan SHOS coal **(Dai et al., 2008)**. All these coals are preserved within marine carbonate successions. However, compared to the Late Permian age of the Chinese coals, Raša coal belongs to the Paleocene. Their mutual comparison in terms of chemical and mineralogical composition was elaborated by **Medunić et al. (2020)**. Moreover, Raša coal was renowned for its enhanced radioactivity. **Marović et al. (2004)** reported that the activities of ^{238}U were 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 coal types in the world. Also, high uranium SHOS coals from China were reported by **Dai et al. (2008, 2013a, b, 2015)**.

The geological settings of Raša coal and Chinese SHOS coals are similar as they are all hosted by carbonate lithologies. According to **Shao et al. (2003)**, it is relatively unusual for coal to be preserved within marine carbonate successions. The authors point out that coals are most commonly preserved within nonmarine siliciclastic successions or paralic, interbedded siliciclastic–carbonate successions. Particularly, the IUR's location is situated next to the Adriatic Sea coastline (see **Figure 1**), while Chinese SHOS coals (SW China) are situated inland, hundreds of km from the South China Sea (see **Figure 1a**). It is well known that karst-water systems, being sensitive to industrial and agricultural pollution, require careful exploitation and protection **(Parise et al., 2015)**. More specifically, karst environments are among the most vulnerable settings in the world from an environmental perspective, largely due to direct connections between surface waters and highly permeable aquifers **(Parise et al., 2009; Soltanian et al., 2015; Fiket et al., 2018a)**. **Li (2018)** reports that China is impacted by mine water more seriously than anywhere else in the world. The author emphasizes that in China, mine water research is becoming more complicated due to the combined impacts of environmental changes (e.g. climate change and geological evolution), and human activities (e.g. deeper mining and hydraulic fracturing). This is especially true in northwest China where natural gas, oil, and coal are abundant, while human activities are extensive, and the environment (karst) is fragile **(Wu et al., 2017)**. Currently, many Chinese hydrogeologists and civil engineers are addressing this topic. **Huang and Chen (2012)** investigated the Jiaozuo coal-mining district (Henan province, northeast China), aiming to link water-intrusion aquifers with the sources of groundwater recharge. **Gu et al. (2018)** used a mixing model to assess mining-affected groundwater dynamics.

China will continue to be among the largest coal producers and users in the world. **Dai et al. (2012)** reviewed Chinese coals in the context of medical geology, and summarized papers on endemic selenosis in Enshi county (Hubei province) due to high Se in local carbonaceous rocks and shales ('stone coal'). Along with the local inhabitants, domestic animals (chickens and pigs) also suffered from Se poisoning, and only a few animals survived once they developed the disease. Selenium is essential to the health of humans and other animals in trace amounts only, but is toxic in excess. **Fordyce (2013)** reports that chronic selenium intoxication leads to two conditions known as alkali disease and blind staggers in grazing animals. Generally, selenium toxicity in humans is far less widespread than selenium deficiency. In seleniferus areas, a higher incidence of gastrointestinal problems, poor dental health, diseased nails, and skin discoloration were reported **(Fordyce, 2013)**. On the other hand, **Haug et al. (2007)** emphasize that the world's scarce Se resources need to be managed carefully so that this vulnerable resource is not wasted. Namely, selenium is the rarest micronutrient, and there are no ores from which Se could be mined as a primary product. CMDs are the initial route of release of Se into surface watercourses **(Etteieb et al., 2020)**. Apart from selenium, radioactivity derived from uranium in coal is also a serious environmental hazard. **Bauman and Horvat (1981)** reported natural U ranges in Raša coal from 14.0 mg/kg to 100 mg/kg (occasionally up to 1500 mg/kg), while the natural radioactivity of ash and slag was enhanced by a factor of ten. Also, the authors found higher values of ^{210}Pb in urine and chromosome aberrations of an exposed group of workers in the local Plomin coal-fired power plant.

Multidisciplinary studies of the fate of metal(loid)s in the environment are necessary due to their long-lasting cycles there, and consequences for human, animal, and plant health. Bioassays have proven very attractive in this regard. By examining the bioaccumulation of pollutants and their interactions, it is possible to get an insight into the cytotoxic and genotoxic potential of an environmental compartment (water, soil and sediment) affecting living organisms (**Sasmaz et al., 2019; Ternjej et al., 2013**). It has been shown that interactions of coal and coal combustion by-products with biological systems can induce cytotoxic, phytotoxic, and genotoxic effects in several organisms (**Awoyemi and Dzantor, 2017; Medunić et al., 2016; Nordin et al., 2018; Radić et al., 2018**).

Medunić et al. (2020) determined that the Raša coal weathering by groundwater is constantly affecting the environment around the IUR (see **Figure 1c**). By comparison with the eastern part of Croatia (see **Figure 1**), where the soil and food contents of selenium were found to be lower compared to other European countries and the USA **(Klapec et al., 1998, 2004)**, **Medunić et al. (2018c)** reported increased Se levels in locally grown vegetables from the Raša town area. **Lemly (1997)** reviewed the environmental implications of excessive Se and the associated threats to fish and wildlife. The author discussed how rain-driven leachate and overflow rich in Se from coal piles and ash ponds could make its way into rivers and streams. Afterwards, Se gets bioaccumulated in aquatic food chains, contaminating the diet of fish, wildlife, and sometimes humans. Since neither radioactivity levels in water nor cytotoxic potential of water from the Raša area have not been reported so far, the main objective of this study was to examine the two mentioned variables along sulphur and selected metal(loid)s (major, minor, and trace) in several types of water collected across the study area (see **Figures 1c, 2**). Hydrogeology of the Raša area has been scarcely characterized so far **(Baturić, 1962; Šarin and Tomašić, 1991)** as the IUR was largely inaccessible for research in the past. Due to the complexity of the karst hydrogeology, selenium and uranium circulation patterns are essentially unknown. Herewith, this study should be accompanied by future complex hydrogeochemical research. The process of the mixing of freshwater and seawater should be examined in order to plan an effective monitoring of environmental contaminants derived from the Raša CMD as well as to apply a suitable concomitant treatment strategy **(Aman et al., 2011)**.

2. Materials and methods

2.1. Geological and hydrogeological characteristics of the study area

The study area belongs to the wider surroundings of the Raša Bay (see **Figure 1c**) at the eastern part of the Istrian Peninsula (see **Figure 1b**). The details in terms of pedology, geography, and climate were presented in previous papers **(Medunić et al. 2016a, 2018a, b)**. Briefly, the climate is Mediterranean, with a highest average temperature of 24°C in August, and a lowest one of 5°C in January. Summers are dry and warm with more than 10 hours of sunshine a day. Temperatures above 10°C have been recorded for more than 240 days a year. Extreme heat (above 30°C) can last for a maximum of three weeks. Two types of winds are present there: 1) the particularly strong bora (from the NE towards the SW) bringing cold and clear weather in winter, and rain in summer (from S to N directions), and 2) the maestral, which is a light summer breeze blowing from land to sea **(Croatian Waters, 2016)**. The water supply at the study localities is managed by the city of Labin (see **Figure 1c**), which is the administrative center of the study area. The existing water supply at the Istrian Peninsula is satisfactory, reaching 99% of the local population, which is above the average compared with other basins of the northern Adriatic Sea.

The Istrian Peninsula (see **Figure 1b**) is largely composed of Middle Jurassic to Upper Cretaceous limestones. From a geological point of view, it can be divided into three regions as follows: (a) the Jurassic–Cretaceous–Eocene carbonate plain of southern and western Istria, (b) the Cretaceous–Eocene carbonate–clastic zone, characterised by overthrust structures in eastern and north-eastern Istria, and (c) the Eocene flysch basin in central Istria **(Velić et al., 2003)**. In the Raša River Basin (see **Figure 3**), the following four lithologically distinct units can be distinguished: (1) the Carbonate unit, (2) the Transitional beds unit (i.e., Transitional to Flysch unit); (3) the Flysch unit; and (4) the Quaternary unit. They are described in the text below.

(1) The Carbonate unit includes Upper Cretaceous and Upper Paleocene to Lower Eocene beds. The Upper Cretaceous beds ($K_2^{1,2}$ and $K_2^{2,3}$) include shallow-water Cenomanian to Santonian/Campanian homogeneous plate limestones with sporadic crystalline and/or rudist limestone lenses/intercalations **(Šikić and Polšak, 1973)**. Following the deposition of the youngest beds, a long emersion phase took place lasting up to the Late Paleocene when the deposition was renewed. The Upper Cretaceous emerged area was transgressively overlain, first locally by Late Paleocene deposits and then, during the Early Eocene, the transgression covered the entire area. In general, these transgressive deposits can be divided into the so-called Liburnian beds (Pc, E) and Foraminiferal limestones (E_1, $E_{1,2}$) **(Šikić and Polšak, 1973)**. The Liburnian beds, only locally present, were deposited in the lowest parts of the Upper Cretaceous palaeorelief during Late Paleocene. They are characterised by freshwater to brackish, lagoonal brown to dark grey, dense and homogeneous, predominantly bituminous limestones with varied freshwater and brackish fauna and flora. In the upper parts of the Liburnian beds, there are thinly bedded, light to dark grey limestones, which represent the transition towards the upcoming marine Foraminiferal limestones. The Foraminiferal limestone series can be divided into four lithostratigraphic types which are mostly in superpositional relationships. These are Miliolidae-, Alveolina-, Nummulite-, and Discocyclina- limestones. They are mostly composed of whole and broken larger foraminiferal tests, with subordinate detritus of molluscs, ostracods, echinoderms, bryozoans, and corallinacean algae, as well as glauconite grains and planktonic foraminifera in the uppermost part.

(2) The Transitional beds unit overlies the Lower Eocene Foraminiferal limestones. Their lower parts, composed of marly limestones, are commonly referred to as the "Marls with Crabs", and are interpreted as reflecting the gradual deepening from shelf to bathyal environments, representing hemipelagic beds **(Ćosović et al. 2004, 2006)**. The upper part of the Transitional beds consists of several tens of meters of the hemipelagic Globigerina Marls, which are conformably overlain by coarser detrital deposits known as the Flysch.

(3) The Flysch unit of Middle to Upper Eocene ($E_{2,3}$) is generally characterized by hemipelagic marls interbedded with calcarenites, sandstones, and carbonate breccias of gravity-flow origin **(Magdalenić, 1972)**.

(4) The Quaternary unit of the Raša River valley is typically composed of a variety of alluvial materials, including fine particles of silt and clay, and larger particles of carbonate sand and gravel **(Šikić and Polšak, 1973)**.

Hydrogeologically, the following two groups of rocks are of interest in the area of the Raša River Basin, due to their distribution and permeability (see **Figure 3**): (a) permeable Upper Cretaceous to Lower Eocene carbonates on one side, and (b) Middle to Upper Eocene Transitional beds, Flysch and Quaternary clastites on the other side. Upper Cretaceous carbonates are widespread and highly permeable, characterised by pronounced secondary porosity **(Babić & Čakarun, 1966)**. They can be found next to joints, numerous microtectonic cracks, and bedding plane contacts formed by dissolution. Their vast thickness allowed for the development of deep and irregular karstification with numerous solution holes and possibly interconnected aquifers of various sizes. Upper Paleocene Liburnian beds and Lower Eocene Foraminiferal limestones occupy a smaller surface area, representing somewhat less permeable parts of the Carbonate unit due to their significantly less tectonical disturbance and karstification **(Babić & Čakarun, 1966)**. Finally, regarding the presence of clay within the Transitional beds unit, the Flysch unit, and the Quaternary unit, they all represent impermeable parts of the Raša River Basin. The Upper Cretaceous to Lower Eocene carbonate units facilitate the accumulation of considerable quantities of groundwater and have a dual role, as a collector and a conductor. It receives the water from the surface through the following mechanisms: (a) by diffuse or point infiltration of rainwater from the surface into the underground, and (b) by diffuse or point infiltration of surface water flowing over the impermeable clay-rich Transitional beds and Flysch, entering into the underground at the points of contact with carbonates **(Babić & Čakarun, 1966)**.

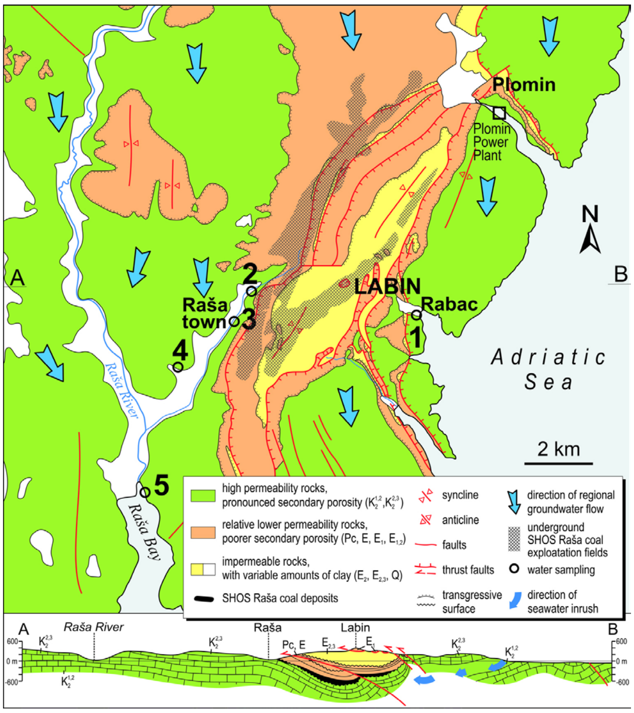

Figure 3: A simplified hydrogeological map with a cross section of the study area and its surroundings (**Šikić et al., 1973**). K21,2 – Turonian; K22,3 - Coniacian and Santonian/ Campanian; Pc, E - Liburnian beds; E1, E1,2 - Foraminiferal limestones; E2 - Transitional beds; E2,3 - Flysch unit; Q - Quaternary.

The locality is characterised by 1100 mm of rainfall per year, and about half of it gets infiltrated through the Carbonate unit into the underground **(Šarin and Tomašić, 1991)**. Due to a general NNE-SSW strike of most linear structural features in a wider area, such as beds, folds, faults and fractures, groundwater predominantly flows in the southern direction (see **Figure 3**). It also moves laterally, towards the impermeable Quaternary

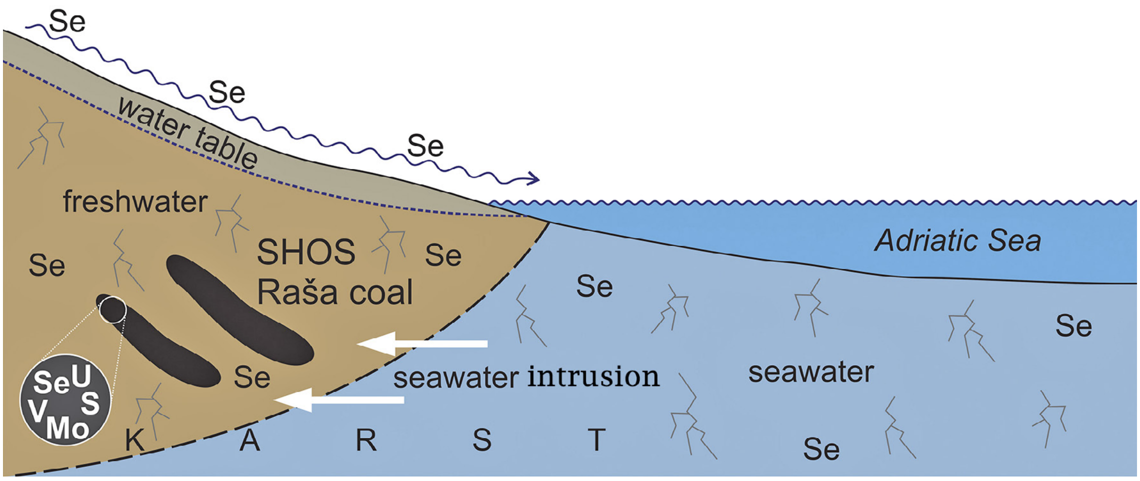

Figure 4: A scheme showing the mechanism of water-driven weathering of Raša coal in a karstic environment, and a concomitant enrichment of water with selenium derived from SHOS Raša coal.

alluvial deposits of the Raša River valley, which represents a relative barrier to groundwater that flows in the direction of the lowest erosional base. There, it forms a series of springs on the left and right side of the valley. The springs are fed by groundwater from different areas, i.e. different hydrogeological units. Compared to the right side, the springs on the left side of the valley have a smaller catchment area and the length of the groundwater movement is shorter. Furthermore, the groundwater on the left side often contains not only freshwater derived from the surface infiltration, but also saline water as a consequence of the seawater intrusion. Namely, the hydrogeological units are situated in close proximity to the Adriatic Sea coastline (see **Figures 1** and **3**). Some 25,000 years ago, the Adriatic sea level was lower (-96.5 m) compared to the present one, and the karstification depth was far below the present sea level. This has resulted in the expansion of the zone of possible contacts between freshwater and seawater (see **Figure 4**). Moreover, on the left side of the Raša River valley, there are pronounced synclinal structures with the Liburnian beds, which contain Raša coal deposits in their base. Since these deposits are over- and underlain by highly permeable carbonates, chemically mixed groundwater is circulating through the system **(Šarin and Tomašić, 1991)**. Herewith, it is expected that the left side of the Raša River valley is very susceptible to the influence of saline groundwater intrusion and/or groundwater enriched in various contaminants derived from Raša coal. On the other hand, the right side of the valley belongs to much larger hydrogeological units, and is solely influenced by groundwater derived from the catchment area located on the north and northwest parts of the Istrian Peninsula (see **Figure 1c**, sample no. 4, i.e. Fonte Gaja spring). Herewith, the groundwater contamination derived from the abandoned Raša coal deposits is of a major concern due to seawater and freshwater mixing as well as the lack of a natural filtration system in the karst. Namely, the heavily karstified bedrock is overlain by either a scarce protective cover (Transitional beds unit, Flysch unit, and Quaternary unit) or not protected at all. Therefore, groundwater is considerably vulnerable to any sort of contamination at the study locality.

2.2. Water sampling and sample preparation

For the purpose of element (major, minor, and trace) analyses, water sampling was conducted at five sites (see **Figures 1c** and **2**) in late October and early December 2019 (n = 1 per site). Also, one tap water sample was taken from a randomly selected building in the town of Raša. The amount of rainfall during the sampling period was not high at all as the CMD and channel stream water flow levels were mediocre. Site no. 1. (see **Figure 2a**) is a place where the Raša CMD is entering seawater in a Rabac settlement. Site no. 2. (see **Figure 2b**) is a place where the CMD is entering an artificial stream (a sewage channel) transporting Labin's partly treated municipal wastewater. Site no. 3. (see **Figure 2b**) is located in the Raša town centre (downstream of site no. 2.), where the municipal wastewater was collected; that water is a mixture of sewage and the CMDs. Site no. 4. (see **Figure 2c**) is the location of the Fonte Gaja natural karst spring that served as a reference. Site no. 5. (see **Figure 2d**) is close to a former Štalije coal separation unit, where huge quantities of coal-washing waste had ended up in the Raša Bay estuary in the past. Also, the sewage channel is inflowing into the Raša Bay. Sites no. 1. and 4. were not sampled during the previous field campaigns by **Medunić et al. (2018a, b, 2019)**. Water samples (300 mL per sample) were collected from the surface at a maximum depth of 10 cm in acid-cleansed plastic bottles. Following the sampling, they were immediately filtered and acidified with nitric acid, 1% s.p. HNO_3 (v/v), and then stored at 4°C until analysis. Prior to analysis, salinity was determined using a handheld refractometer (Atago, S-10E, Tokio, Japan), and the samples were, if necessary, further diluted 10 times.

At sites no. 1. and 5., additional nonfiltered water was collected in 30L canisters for the purpose of radioactivity measurements. It was evaporated in a laboratory to a final volume of 1L and then packed in an airtight 1L container. It was packed to secure the secular equilibrium of the daughters of ^{226}Ra in a naturally occurring radioactive uranium series (at least for 30 days).

2.3. Water multielement and radioactivity analyses

Mulitielemental analysis of the prepared water samples was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). A detailed method description was given in **Fiket et al. (2007)**. An external calibration was used for quantification. Standards for the multielement analysis were prepared by an appropriate dilution of a multielemental reference standard (Analytika, Prague, Czech Republic) containing As, Ba, Co, Cr, Fe, Li, Mn, Mo, Ni, Rb, Sr, Ti, and V, in which single element standard solutions of U (Aldrich, Milwaukee, WI, USA) and Sb (Analytika, Prague, Czech Republic) were added. Prior to analysis, In (1 μg/L) as an internal standard was added to samples. All samples were analysed for total concentration of following elements: Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, U, V, Y, and Zn. A quality control of the analytical procedure was performed by simultaneous analysis of the blank and certified reference materials for water (SLRS-4, NRC, Canada). A good agreement among the analysed and certified concentrations within their analytical uncertainties for all elements was obtained (± 10%).

The measurements and calculations of activity concentrations in water were performed using high–resolution gamma-ray spectrometry. The activity of a sample was measured using a coaxial high purity Ge detector (Ortec GMX with a relative efficiency of 74.2%, and a resolution of 2.24 keV at 1.33 MeV of ^{60}Co. All the necessary calculations were performed using the Ortec GammaVision software. The counting time was 250,000 seconds. The energy and efficiency calibration procedures were performed by using the Czech Metrology Institute certified standards. The method is accredited according to the requirements of the ISO/IEC 17025 standard. A quality assurance was carried out by systematic participation in proficiency tests and intercomparison exercises organized by the International Atomic Energy Agency and the EC Joint Research Centre.

2.4. Cytotoxicity of water samples

Cytotoxicity assessment was carried out on the water samples no. 2, 4, 5, and the Raša town tap water. It was performed using the RTG-2 cells (ATCC CCL-55). The cells were routinely grown in DMEM medium (Sigma, St. Louis, MO, USA) supplemented with 10% inactivated fetal bovine serum (FBS) (GIBCO, Paisley, Scotland, UK) at the optimal growth temperature of 22°C. For the cytotoxicity assays, the RTG-2 cells from the exponential growth phase were plated in 96-well plates at an initial concentration of $5x10^4$ cells/well during 24h. The culture medium was then replaced with a medium containing 10-40% of tested water samples, and the cells were further cultured for 72h. Control cells were exposed to distilled water in order to exclude the effects of medium dilution. Following the exposure, 10 µL of CellTiter 96® AQueous One Solution Assay (Promega, Madison, WI, USA) was added to each well and the cells were incubated for a further 4h. The absorbance was then measured at 490 nm using a microplate reader (Tecan, Switzerland). All the experiments were performed in triplicate. Cell viability was presented as a percentage of absorbance of the treated cells compared to the absorbance of the control cells.

3. Results and discussion

The data for all elements analysed is summarised in **Tables 1–4**. Its evaluation should answer two basic questions as follows: 1) does water chemistry indicate a marine influence (seawater intrusion), and 2) are selenium and uranium levels, along with the rest of the analysed elements, similar to the ones previously reported by **Medunić et al. (2018a, b, 2019)**. In relation to marine influence, the conceptual framework for the IUR hydrogeology was elaborated by **Šarin and Tomašić (1991)**. They emphasized that the Raša coal mine represented a valuable and unique case for the understanding of coastal karst hydrogeology, particularly its dynamics of groundwater flow in the karst aquifer. They also noted that the deepest galleries of the Raša mine reached a depth of about 200-250m below the land surface, and about 180m below sea level. As the IUR's mines represent a huge drainage area, some $18m^3$/min of water were pumped from the Raša mine back in the 1980s. Since 1934, when a major seawater inrush happened **(Baturić, 1962)**, the coal-mining activities were ceased in the affected part of the mine (field no. 5) leaving some 1Mt. of coal confined by freshwater and seawater **(Šarin and Tomašić, 1991)**. The authors pointed out that seawater has good hydraulic contact with fresh groundwater of field no. 5 in some places, and with the mine itself through caverns and fissures developed particularly along the fault zones.

Selected element levels (see **Table 1**) in sample no. 4 (the control Fonte Gaja spring) were fairly comparable with respective levels reported by **Fiket et al. (2015, 2018a)** for uncontaminated water samples from Croatian karst sites. Phosphorous levels were slightly increased compared to world groundwater P concentrations though **(Reimann and de Caritat, 1998)**. **Tables 2** and **3** also show fairly low metal(loid) levels in the Fonte Gaja spring. **Table 4** shows that U, Mo, V, and Se concentrations in the spring, although low compared to the Raša CMDs, were slightly above the corresponding Croatian karst **(Fiket et al., 2018a)**, world stream water **(Reimann and de Caritat, 1998)**, and the US CMD **(Cravotta, 2008)** levels. This points to a strong influence of the regional litho- and hydrogeochemical processes, which had been reflected in the Raša coal and host rock chemistry, i.e. enrichment in Se, U, V, and Mo **(Medunić et al., 2018a, 2020)**. Despite low S concentrations in US coal (0.6–2.2%), the corresponding CMD sulfur levels were 87,000–193,000 µg/L **(Cravotta, 2008)**, i.e. four- to ten-fold the Raša CMD sulfur levels. This can be explained by much higher quantities of pyritic S in US coal compared to SHOS Raša coal **(Medunić et al., 2020)**. Upon exposure to air and water, pyritic S gets oxidised and dissolved in water. By recalculating the S levels (see **Table 4**) to sulfate levels for samples no. 1.–5., the respective values (mg/L) were as follows: 63, 65, 62, 15, and 460. Only the Fonte Gaja sulfate was similar to global average sulfate concentration of 11 mg/L in river water. In contrast, the median SO_4 concentration in the US CMD was 520 mg/L **(Cravotta, 2008)**.

Table 1 shows that concentrations of the selected elements in water samples no. 1., 2. (both CMDs), 3. (CMD plus sewage), and 5. (brackish water affected by the CMD and sewage) were highly variable. In such a geomorphological setting (see **Figures 1–4**), characterised by the close proximity to seawater, sodium in the CMD is likely indicating a marine influence. Its values in the analysed samples were generally increased compared to Croatian karst **(Fiket et al., 2015)** and world stream water **(Reimann and de Caritat, 1998)**. One stronger indication of a marine influence is the Sr/Ba ratio. According to **Dai et al. (2020**, and references therein), the Sr/Ba ratio is an indicator of the depositional environment for

Table 1: Total element concentrations (μg/L) in water samples from five locations (see **Figures 1** and **2**) compared with relevant guideline and literature values

	Na	Mg	Ca	K	P	Al	Mn	Fe	Sr	Ba	Reference
1. Rabac (coal mine water)	88,100	11,200	101,000	2940	70.4	8.67	1.17	225	1940	74.5	This study (1.-5.)
2. Krapan (coal mine water)	13,900	8810	122,000	2350	23.7	13.2	0.86	6.01	1045	34.4	
3. The town of Raša (municipal wastewater/sewage)	58,050	8790	104,000	7540	355	22.6	1.07	8.15	774	29.1	
4. Fonte Gaja (natural freshwater spring)	18,800	3380	122,000	1980	96.1	17.3	0.65	14.3	191	14.6	
5. Raša Bay (brackish water)					4.5	6.5	2.2	2.1	1797	31.3	
Rttw (Raša town tap water)					40.0	2.29	1.67	0.24	122	13.5	
Fonte Gaja spring (monitored during 2003-2014)	73,900	19,100	129,000	5630		3-37	0.5-25	1-390			**Croatian Waters (2016)**
World ocean water	10,800,000	1,290,000	412,000	399,000	60.0	2.00	0.20	2.00	7900	13.0	**Reimann and de Caritat (1998)**
Stream water (Harz region)	3400	2065	5400	700	20.0	108	22.0	285	30.0	32.0	
Groundwater (Norway)	17,300	4250	25,700	2170	5.40	12.0	7.50	25.0	179	16.6	
Drinking water quality						200	400			700	**WHO (2011)**
Drinking water standards	200,000					200	50.0	200		1000	**EPA (2012)**
China's groundwater quality (category III)										≤0.70	**GB/T 14848 (2017)**
Croatian tap water from karst	2560	6970	61,300	740		28.8	0.75	17.8	101	17.6	**Fiket et al. (2015)**
Zrmanja River (surface sample Z1), karst river						0.33	0.19	10.1	295	15.6	**Fiket et al. (2018a)**
Zrmanja River estuary (surface sample N1), sea						2.11	0.01	2.50	1780	13.3	**Fiket et al. (2018a)**
Italian karst groundwater	35,200	35,900	105,000	5670						56.2	**Cangemi et al. (2019)**
Palestinian karst aquifer						3.90		250	118	32.2	**Jebreen et al. (2018)**
Chinese carbonate aquifer	14,150	25,300	49,700	670		14.1	2.56	70.0	450	166	**Ma et al. (2011)**
US abandoned coal-mine discharges	15,000	38,000	88,000	2800	<0.001	1250	2350	32,000	720	15.0	**Cravotta (2008)**
Groundwater (NW India)					1.2		82	1.3			**Bajaj et al. (2011)**
Croatian limits for wastewater discharged into streams					1000	3000	2000	2000		5000	**OG (2010)**
Croatian limits for wastewater discharged into public sewage system							4000			5000	**OG (2010)**
Chinese discharge limits for wastewater treatment plants (GB 18918-2002)							2000				**Zhou et al. (2018)**

sedimentary rocks and coal. It can be used as an indicator of seawater (>1), freshwater (<1), and their mixtures. Based on Raša coal data in **Medunić et al. (2020)**, that ratio was 23, which is in accordance with the fact that Raša coal was formed in a marine-influenced paleoenvironment (**Medunić et al., 2018a**, and references therein). The ratio values, calculated for the Raša coal and its fly- and bottom ash data **(Medunić et al., 2016b)** were 29, 45, and 57, respectively. Also, by using data for soil affected by Raša coal combustion **(Medunić et al. (2016b)**, the ratio values for control, less polluted, and more polluted soil samples were 0.29, 0.35, and 0.54, respectively, which is in line with the fact that coal combustion by-products can leave a strong impact on the environment for a long time **(Fiket et al., 2016, 2018b, 2019; Zhang et al., 2019)**. **Medunić et al. (2020)** reported a notably increased Sr value (2600 mg/kg) in weathered Raša coal compared to world coal levels (110 mg/kg). The authors emphasized that Sr values were up to 400 mg/kg in Raša coal not exposed to the CMD **(Medunić et al., 2018a)**. Hence, weathered Raša coal chemistry could be indicative of today's seawater intrusion (see **Figure 4**). On the basis of experiments, **Cabon et al. (2007)** revealed that most hazardous trace metals

Table 2: Total element concentrations (μg/L) in water samples from five locations (see **Figures 1** and **2**) compared with relevant guideline and literature values

	Li	Be	Rb	Sc	Ti	Y	Cs	Tl	Bi	Co	Reference
1. Rabac (coal mine water)	17.6	0.006	1.49	0.02	0.26	0.02	0.005	0.08	0.001	0.07	This study (1.-5.)
2. Krapan (coal mine water)	0.83	0.008	0.98	0.02	0.23	0.05	0.003	0.04	0.000	0.05	
3. The town of Raša (municipal wastewater/sewage)	2.36	0.006	5.18	0.02	0.26	0.02	0.020	0.03	0.001	0.15	
4. Fonte Gaja (natural freshwater spring)	0.46	0.007	1.04	0.02	0.37	0.09	0.004	0.01	0.000	0.04	
5. Raša Bay (brackish water)	27.5	0.08	19.5		0.10	0.02	0.04	0.04	0.001	0.06	
Rttw (Raša town tap water)	0.40		0.72	0.01	0.13	0.03				0.04	
World ocean water	180	0.01	120	0.0006	1.00	0.01	0.30	0.020	0.020	0.02	**Reimann and de Caritat (1998)**
Stream water (Harz region)	2.30	0.18	2.10	3.80	3.70	0.74	0.05	0.020	0.020	0.37	
Groundwater (Norway)	3.60	0.04	2.20	1.96	0.60	0.14	0.10	0.003	0.001	0.06	
Drinking water standards		4.00						2.000			**EPA (2012)**
China's groundwater quality (category III)		≤0.002						≤0.0001		≤0.05	**GB/T 14848 (2017)**
Croatian tap water from karst	0.43	0.002	0.64		1.73	0.02	0.01	0.014	0.002	0.02	**Fiket et al. (2015)**
Zrmanja River (surface sample Z1), karst river	4.97		3.53				0.01			0.01	**Fiket et al. (2018a)**
Zrmanja River estuary (surface sample N1), sea	33.6		26.0				0.06			0.01	**Fiket et al. (2018a)**
Palestinian karst aquifer	1.48		2.27								**Jebreen et al. (2018)**
Chinese carbonate aquifer	9.32									0.13	**Ma et al. (2011)**
US abandoned coal-mine discharges	69.0	1.6	6.3	5.0	5.8	8.7	0.11	0.072	0.01	58	**Cravotta (2008)**
Croatian limits for wastewater discharged into streams										1000	**OG (2010)**
Croatian limits for wastewater discharged into public sewage system										1000	**OG (2010)**

were not released from coal into seawater and, on the contrary would be likely removed from seawater solutions in the presence of coal having a high calcite content. The Sr/Ba ratio values, calculated for the analysed water samples no. 1.–3., 4., and 5., were 26-30, 13, and 60, respectively. The ratio was lowest in the Fonte Gaja spring, which is apparently not connected to the Adriatic Sea. Generally, this study suggests that the Sr/Ba ratios reflect primarily the bedrock carbonate geochemistry, but today's marine influence on local as well as regional hydrogeochemical patterns cannot be ruled out.

Tables 2 and **3** show that the selected trace metal(loid) data were either similar or less than the respective levels in Croatian karst water **(Fiket et al., 2015, 2018a)**, world water **(Reimann and de Caritat, 1998)**, and the CMD in Pennsylvania, USA **(Cravotta, 2008)**. The same holds true when comparing them with previous water sampling campaigns at the study area **(Medunić et al., 2018b, c, 2019)**. Similarly, **Cravotta (2008)** noted that the US CMD samples had lower concentrations of total base metals (Zn, Cu, Cd, Pb, Co, Ni) compared to drainage from many metal mines in western USA. **Tables 2** and **3** also primarily show the narrow range of element data, which was also found for the US CMD **(Cravotta, 2008)**. The author explained it in the context of limited variability in the mineralogy of typical coal-bearing sedimentary rocks (non-carbonate), less abundance of sulfide minerals, and a presence of some metals as relatively inert organic compounds. The author emphasized that Fe-sulfide and calcareous minerals, regardless of their low levels in US coal-bearing strata, are highly reactive and are mainly responsible for the CMD chemistry. Considering Raša coal, a unique coal in world terms, its organic sulphur is among the highest ones (along Chinese SHOS coals; up to 11.0%), while its pyritic and sulphate S is the lowest one (below 0.50%) **(Chou, 1997)**. **Medunić et al. (2020)** reported major crystalline phases in Raša coal as follows: calcite, ankerite, dolomite and magnesite. As the levels of Cd, Pb, Cu, and Zn in Raša coal are similar to coal Clarke values, and are low in host rocks **(Medunić et al., 2018a, 2020)**, neither underground nor surface water from the Raša locality could be expected to violate various aquatic protection criteria in terms of the elements listed in **Tables 2** and **3**.

Table 4 shows the data for elements highly enriched in Raša coal **(Medunić et al., 2018a, 2020)**. Therefore, their levels in the Raša CMDs were expectedly elevated compared to Croatian karst **(Fiket et al., 2015, 2018a)**,

Table 3: Total element concentrations (μg/L) in water samples from five locations (see **Figures 1** and **2**) compared with relevant guideline and literature values

	As	**Cd**	**Cr**	**Cu**	**Zn**	**Pb**	**Ni**	**Sb**	**Sn**	**Reference**
1. Rabac (coal mine water)	0.43	0.18	0.37	1.36	47.2	0.44	4.06	0.31	0.07	This study (1.-5.)
2. Krapan (coal mine water)	0.22	0.11	0.74	0.80	14.2	0.56	1.46	0.19	0.02	
3. The town of Raša (municipal wastewater/sewage)	0.76	0.09	0.53	2.63	4.08	0.18	1.14	0.33	0.10	
4. Fonte Gaja (natural freshwater spring)	0.40	0.03	0.55	0.43	13.7	0.09	0.35	0.07	0.06	
5. Raša Bay (brackish water)		0.21	0.60	0.60	4.20	0.20	1.30	0.37	0.35	
Rttw (Raša town tap water)	0.18	0.05	0.37	9.03	133	0.23	0.46	0.04	0.08	
Fonte Gaja spring (monitored during 2003-2014)	1.40	0.05-0.2	0.5-5	0.5-10	2.5-267	0.5-1	0.5-20			**Croatian Waters (2016)**
World ocean water	3.70	0.11	0.30	0.25	4.9	0.03	0.56	0.24	0.004	**Reimann and de Caritat (1998)**
Stream water (Harz region)	0.60	0.29	0.41	1.20	26.0	2.10	2.90	0.13	0.030	
Groundwater (Norway)	0.20	0.03	0.54	11.70	23.0	0.30	0.74	0.03	0.005	
Croatia (law, MAC)	10.00	5.00	50.00	2000	3000	10.00	20.00	5.00		**OG (2013)**
Drinking water quality	10.00	3.00	50.00	2000	3000	10.00	70.00	20.00		**WHO (2011)**
Drinking water standards	10.00	5.00	50.00	1000	5000	10.00	20.00	6.00		**EPA (2012)**
China's groundwater quality (category III)	≤0.01	≤0.005		≤1.00	≤1.00	≤0.01	≤0.02	≤0.005		**GB/T 14848 (2017)**
Croatian tap water from karst	0.32	0.04	3.14	5.60	45.0	0.91	0.55	0.05	0.013	**Fiket et al. (2015)**
Zrmanja River (surface sample Z1), karst river	0.18		0.19	0.03			0.02			**Fiket et al. (2018a)**
Zrmanja River estuary (surface sample N1), sea	0.37		0.24	0.03			0.09			**Fiket et al. (2018a)**
Italian karst groundwater	0.33		0.29	0.96		0.16	2.32	0.10		**Cangemi et al. (2019)**
Palestinian karst aquifer				1.57			0.50			**Jebreen et al. (2018)**
Chinese carbonate aquifer	0.43	0.01		0.61	1.7		0.33	1.45		**Ma et al. (2011)**
US abandoned coal-mine discharges	1.70	0.12	1.20	2.00	140	0.20	85.0	0.01	≤0.1	**Cravotta (2008)**
Groundwater (NW India)	1.30	0.10		1.30	60.0	2.40	0.20			**Bajaj et al. (2011)**
Croatian limits for wastewater discharged into streams	100	100	500	500	2000	500	500		2000	**OG (2010)**
Croatian limits for wastewater discharged into public sewage system	100	100	500	500	2000	500	500		2000	**OG (2010)**
Chinese discharge limits for wastewater treatment plants (GB 18918-2002)	100	10	100	500	1,000	100	50			**Zhou et al. (2018)**

world water **(Reimann and de Caritat, 1998)**, Mediterranean karst **(Jebreen et al., 2018, Cangemi et al., 2019)**, and the US CMD **(Cravotta, 2008)**, but lower compared to an Indian locality severely polluted with selenium and uranium **(Bajaj et al., 2011)**. The data from **Table 4** was mostly similar to, or slightly less than the respective ones reported by previous sampling campaigns **(Medunić et al., 2018b, c, 2019)**. Selenium is a particularly interesting element due to its multiple roles in the environment. It is essential to human health in trace amounts but is harmful in excess. According to research (**Etteieb et al., 2020**, and references therein), possible harmful effects of long-term, low level exposure to selenium should be studied. Selenium deficiency, which is more common, is regarded as a major health problem for 0.5 to 1 billion people worldwide **(Haug et al., 2007)**. Even more of them are consuming less Se than required for optimal protection against cancer, cardiovascular diseases, and severe viral infections. On the other hand, studies **(Lemly, 1997)** have shown that Se levels of 2–5 μg/L pose concern, and certain toxicological and reproductive effects are related to Se >5 μg/L in water. Compared to world stream water Se levels of 0.2–0.6 μg/L, total Se values found by **Medunić et al. (2018a, b, 2019)** in the Raša CMDs and local water bodies have been 10–15 μg/L (occasionally even higher), thus exceeding a Croatian regulatory limit value for Se in drinking water of 10 μg/L. Most of the Se levels (see **Table 4**) exceeded the existing selenium water quality guidelines for the protection of freshwater and marine aquatic life (1 μg/L) set by the Canadian Council of Ministers of Environment (**Etteieb et al., 2020**, and references therein), and the upper limit value (≤0.01 μg/L) of the Type III Chinese groundwater quality standard

Table 4: Total element concentrations (µg/L) in water samples from five locations (see **Figures 1** and **2**) compared with relevant guideline and literature values

	S	U	Mo	V	Se	Reference
1. Rabac (coal mine water)	21,200	2.77	28.7	4.60	5.10	This study (1.-5.)
2. Krapan (coal mine water)	21,600	2.56	15.1	3.61	10.9	
3. The town of Raša (municipal wastewater/sewage)	20,800	2.05	11.2	4.29	8.01	
4. Fonte Gaja (natural freshwater spring)	5100	0.75	2.04	1.37	1.09	
5. Raša Bay (brackish water)	153,106	10.8	33.1	1.70	3.50	
Rttw (Raša town tap water)	3653	0.49	0.83	0.77	0.60	
World ocean water	905,000	3.20	10.00	2.50	0.20	**Reimann and de Caritat (1998)**
Stream water (Harz region)	5000	0.05	0.05	0.50	0.60	
Groundwater (Norway)		3.50	1.63	0.50	0.30	
Croatia (law, MAC)				5.00	10.00	**OG (2013)**
Drinking water quality		30.00	70.00		40.00	**WHO (2011)**
Drinking water standards		30.00			50.00	**EPA (2012)**
China's groundwater quality (category III)			≤0.07		≤0.01	**GB/T 14848 (2017)**
Croatian tap water from karst		0.72	2.34	1.12	0.13	**Fiket et al. (2015)**
Zrmanja River (surface sample Z1), karst river		0.42	0.47	0.39		**Fiket et al. (2018a)**
Zrmanja River estuary (surface sample N1), sea		0.96	2.27	1.33		**Fiket et al. (2018a)**
Italian karst groundwater		3.30			0.83	**Cangemi et al. (2019)**
Palestinian karst aquifer			0.50	2.86		**Jebreen et al. (2018)**
Chinese carbonate aquifer			1.67			**Ma et al. (2011)**
US abandoned coal-mine discharges		0.17	0.20	0.30	0.6	**Cravotta (2008)**
Groundwater (NW India)		16.2	4.7		341	**Bajaj et al. (2011)**
Croatian limits for wastewater discharged into streams				50	20	**OG (2010)**
Croatian limits for wastewater discharged into public sewage system				100	100	**OG (2010)**
Chinese discharge limits for wastewater treatment plants (GB 18918-2002)					100	**Zhou et al. (2018)**

(GB/T, 2017). Freshwater guidelines for Se set by The Netherlands Water pollution control are 0.09 µg/L and 5.40 µg/L for long-term and short-term occurrences, respectively (**Etteieb et al., 2020**, and references therein). They have been mostly violated by the Raša CMDs **(Medunić et al., 2018a, b, 2019**, and the data in **Table 4)**. Moreover, selenium concentrations in the three samples (see **Table 4**) exceeded the criteria continuous concentration (CCC) value of 5 µg/L **(EPA, 2002)**. Herewith, based on previous observations **(Medunić et al., 2018b, c, 2019)** and the results from this study (see **Table 4**), it is clear that Raša water Se values are constantly increased, well above various water-quality criteria. This was clearly supported by the study published in **Medunić et al. (2020)**. The authors elaborated environmental implications of Raša coal weathering by groundwater. It was discovered that Se, U, and Mo were highly enriched in dripstone compared to world limestone up to 756, 2.2, and 14 times, respectively, as a consequence of the leaching of Raša coal.

Considering the Raša CMD sulfur levels (see **Table 4**), they could have been influenced by seawater intrusion processes (see **Figure 4**) and, to a lesser extent, the dissolution of S-containing minerals. As described above, Raša coal sulfur is primarily in organic form which proved to be very difficult to bioremediate with bacteria **(Medunić et al., 2019)**, and is possibly not as soluble as inorganic S. As described above, the Raša CMD sulfur was quite low compared to the US CMD sulfur **(Cravotta, 2008)**, due to the arguably low solubility of organic S from Raša coal. Nevertheless, we carried out the normalization of element concentrations of S (the so-called Coal/CMD$_S$ ratio) in order to distinguish constituent mobilities in a coal-mine environment (details of the calculation and interpretation can be found in **Cravotta, 2008**); due to a small number of samples and different sampling settings (freshwater vs brackish water), the calculation only has an approximative significance. Briefly, the ratio of the element in coal and CMD is divided by (normalized to) the ratio of S in coal and CMD. If the Coal/CMD$_S$ ratio is ≤1.0, it indicates greater or equal mobility of the element compared to sulfate, which itself is highly soluble and mobile. Herewith, mostly immobile constituents in the Raša CMDs could be as follows (max

Table 5: Gamma-ray spectrometry analysis of radionuclides in water samples from sites no. 1 and no. 5.

Radionuclide	Site no. 1.	Site no. 5
	Activity concentration [Bqm^{-3}]	
^{238}U	169 ± 8	33 ± 4
^{226}Ra	88 ± 1	8.6 ± 0.3
^{210}Pb	53 ± 24	< (15 ± 3)
^{235}U	12.8 ± 0.9	< (1.2 ± 0.4)
^{232}Th	56 ± 2	7.6 ± 0.9
^{228}Ra	56 ± 2	7.6 ± 0.9
^{40}K	2756 ± 23	70 ± 4
^{7}Be*	387 ± 21	55 ± 15
^{137}Cs	28.2 ± 0.7	< (1.0 ± 0.4)
^{134}Cs	< (1.2 ± 0.5)	< (1.0 ± 0.3)
	Total activity [Bqm^{-3}]	
α – emitters	1777.6	319.6
β – emitters	4073.4	305.1
β - emitters, no ^{40}K	1317.4	235.4

* time-corrected to sampling date

values of the Coal/CMD$_S$ ratio in brackets): Co (164), V (91), Y (42), Ni (26), Cs (16), Cr (10), and Be (2). In contrast, mostly mobile constituents in the Raša CMD could be as follows (max values of the Coal/CMD$_S$ ratio in brackets): Sr (0.7), Ba (0.8), Li (0.6), Rb (0.02), Tl (0.7), As (1), Cd (0.7), Cu (0.3), Zn (0.2), U (0.4), and Se (0.2). Regarding the US CMD, **Cravotta (2008)** reported the largest ratios (i.e. the lowest solubilities) for Ti (2100), In (2120), Zr (5690), and Au (8090). The author noted that the majority of analysed elements (REEs, metals, metalloids, nonmetals, and the transition metals) were difficult to mobilize from geological materials, despite their enrichment in coal, based on their large Coal/CMD$_S$ ratios. Hereby, the respective ratio values for Se, U, and V in the US CMD were 55, 51, and 996. Their maximum values (μg/L) in the CMDs were as follows: 7.6, 1.0, and 18, respectively.

The activity concentrations of natural and artificial radionuclides are shown in **Table 5**. In water sample no. 1. (the Rabac site, see **Figure 2a**), the activity concentrations of all analysed radionuclides were within the range of previously conducted measurements in the Plomin Bay seawater **(Marović and Senčar, 1999; Marović et al, 2019)**. In water sample no. 5. the activity concentrations were also in the range of usual levels for groundwater in the investigated area (e.g. water from piezometers in the vicinity of the Plomin coal-fired power plant) **(Marović et al., 2004; Bituh et al., 2017)**. This was expected as the coal-mining activities in the area ceased in 1999, hence any significant leaching of radionuclides by groundwater has not been detected. At the moment in Croatia, there are no legislative limits set for radionuclide levels either for seawater or non-drinkable groundwater.

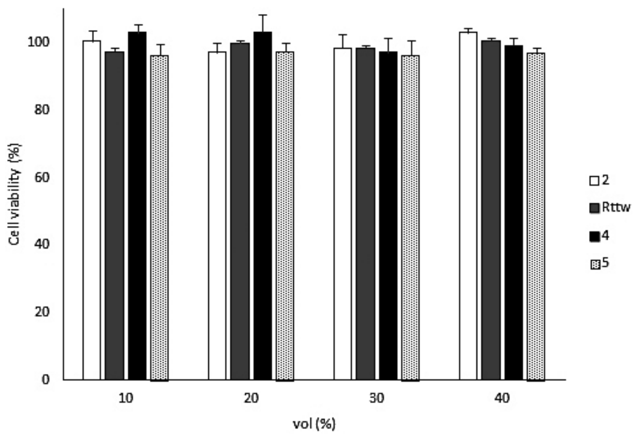

Figure 5: Effects of different water samples (10-40 vol%) on the RTG-2 cell viability following 72h exposure using MTS assay. Data is expressed as a percentage of unexposed control cells ± SD of three replicates for each concentration.

Although the results (see **Table 5**) show no increase in radionuclide levels in comparison to water from the wider area, the low number of analyses is insufficient to state firm conclusions. Further investigations taking into account seasonal variations as well as data on precipitation are needed to obtain more data on radionuclide levels in surface water and groundwater from the study area.

The application of cell lines in the evaluation of toxicity can be of paramount importance in elucidating intracellular, molecular, or physiological mechanism induced by different xenobiotics. In aquatic toxicology, cytotoxicity tests with the continuous fish cell lines have been used as a tool for toxicity ranking of anthropogenic chemicals, compound mixtures and environmental samples (Fent, 2001; Ternjej et al 2013). Herewith, several water samples selected from the Raša area were tested for the fish RTG-2 cells viability (see **Figure 5**). The obtained results did not show statistically significant cytotoxic effects. The results show how the fish cell cultures could be used for evaluation of the toxicity of environmental water samples. Moreover, this strategy can serve as a replacement for *in vivo* toxicity testings using fish or other organisms.

4. Conclusion

This paper summarizes data on the element and radioactivity levels of a few abandoned Raša coal-mine discharges (CMDs) that were sampled in October and December 2019. The main objectives of the study were the following: 1) did water element levels indicate seawater intrusion, i.e. the mixing of fresh groundwater and seawater, reflected in elevated elements (Na, Sr) characteristic for a marine environment, 2) did selenium and uranium, along with the rest of the analysed elements, show trends similar to previously reported ones **(Medunić et al., 2018a, b, 2019)**, 3) was the radioactivity of collected water samples low regardless of a potentially adverse impact of Raša coal, and 4) was the cytotoxic potential of water low despite its elevated Se levels. It can be concluded that the answer to all four questions would be mostly affirmative. Sodium and particularly Sr were increased in water samples, thus reflecting marine influence on the CMDs. The majority of element concentrations were consistent with respective ones reported by previously conducted campaigns. Although sulfur and potentially toxic trace metal(loid)s were low in water samples, selenium, U, Mo, and V were consistently increased due to Raša coal leaching. Despite the fact that Raša coal was known for elevated radioactivity, its levels found by this study should not pose any health concerns. Cytotoxicity of water samples on the RTG-2 fish cells was not statistically significant. Nevertheless, selenium circulation pathways through the Raša coal mine hydraulical system should be investigated further, especially in the context of future sea level rise. Namely, selenium as well as uranium are highly mobile in oxidative and alkaline conditions, which prevail in the study locality. High-Se groundwater should be monitored so as to prevent natural hazards, whereas remediation measures should help collect selenium for future generations as selenium is a valuable element in terms of human/animal health and its utilization in the electronic industry.

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SAŽETAK

Razine sumpora, metala, polumetala, radioaktivnosti i citotoksičnosti u krškim ispustima vode iz napuštenih raških ugljenokopa (sjeverni dio Jadranskoga mora)

Pridobivanje raškoga ugljena u Istri (SZ Hrvatska) trajalo je gotovo 400 godina, sve do 1999. godine. Raški ugljen poznat je po iznimno visokim koncentracijama organskoga sumpora te visokim razinama selena, urana, vanadija i molibdena. Otprije je poznata toksičnost selena na primjerima goveda i ovaca. Za ljudsko zdravlje selen je od presudne važnosti, ali u povišenim je količinama štetan. Procjenjuje se da je još 4,4 milijuna tona raškoga ugljena ostalo pod površinom, unutar marinskih karbonatnih stijena. Područje istraživanja pripada obalnome krškom pojasu Jadranskoga mora. Na nekoliko mjesta nalaze se ispusti podzemne vode iz napuštenih rudnika ugljena (engl. CMD), gdje ta voda desetljećima izbija van na površinu te se izravno ulijeva u lokalne vodotoke i na kraju u Raški zaljev. Stoga su uzeti uzorci vode prirodnoga krškog izvora, morske vode Raškoga zaljeva, komunalne otpadne vode te CMD. U uzorcima su izmjerene koncentracije sumpora, odabranih metala i polumetala (glavnih, sporednih i u tragovima), radioaktivnost te citotoksičnost. Izvorska voda, koja nije u dodiru s CMD-om, poslužila je u referentne svrhe. Njezine odgovarajuće vrijednosti Se, U, V i Mo (μg/L) bile su sljedeće: 1,09, 0,75, 1,37 i 2,04. Međutim, odgovarajuće razine tih četiriju elemenata (μg/L) bile su povišene u ostatku uzoraka vode: 10,9, 10,8, 4,60 i 33,1. Razina sumpora u vodi bila je niska. Ukupne beta aktivnosti CMD-a i vode Raškoga zaljeva iznosile su 235 i 1320 Bq/m^3, čime nije bila premašena dopuštena vrijednost od 2000 Bq/m^3. Citotoksičnost nekoliko odabranih uzoraka vode nije se pokazala statistički značajnom. Velike količine vode podrazumijevaju transport prilično velikih količina Se i U te njihovo taloženje u Jadranskome podmorju. Zbog složenosti krške hidrogeologije nužno je istražiti obrasce cirkuliranja selena i urana na spomenutome području.

Ključne riječi:
ispusti vode iz rudnika Raškoga ugljena, voda, selen, radioaktivnost, citotoksičnost, krš

Authors contribution

Gordana Medunić (Full Professor, PhD, Earth Sciences) participated in water sampling campaigns and drafted the manuscript. **Damir Bucković** (Full Professor, PhD, Earth Sciences) was responsible for art-work and drafting the geology/hydrogeology chapter. **Andreja Prevendar Crnić** (Full Professor, PhD, Veterinary Toxicology) provided financial funds for field work and participated in water sampling campaigns. **Tomislav Bituh** (Senior Research Associate, PhD, Occupational Medicine) carried out radioactive analyses and drafted a respective interpretation. **Višnja Gaurina Srček** (Full Professor, PhD, Biotechnology) and **Kristina Radošević** (Associate Professor, PhD, Biotechnology) conducted cytotoxicity analyses on water samples. **Mladen Bajramović** (a head of the today's IUR heritage organization) helped with the sampling campaign in the Raša coal mine. **Željka Zgorelec** (Associate Professor, PhD, Plant science) participated in the October water sampling campaign.