RGNZ/MGPB

Levels of hazardous trace elements in estuarine sediments, fish, mussels and wild boar collected from the Raša Bay area (Croatia)

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Abstract

A part of the Raša Bay (western Croatia) is an estuary that is fed by the sediment load from the Raša River. The local area had been affected by the former Raša coal industry. The aim of this study was to determine levels of hazardous trace elements (HTEs) in bottom estuarine sediments, fish and mussels collected from two sites downstream of the Raša River mouth, and a wild boar's kidney donated by hunters. The pseudo-total concentrations of 21 HTEs in sediments were obtained by the X-ray fluorescence (XRF) technique. The results showed that sediment collected closest to the former Raša coal separation unit Štalije was enriched in V, Sr, Ni, Cu, and Pb. Concentrations of HTEs in flathead grey mullet, wild blue mussels, and wild boar were obtained by inductively coupled plasma mass spectrometry (ICP-MS). The results showed that Pb, Cd and Hg in fish and wild mussels were not elevated compared to the Regulation levels of contaminants in food. Lead and Cd in the kidney of a wild boar exceeded the prescribed maximum values for food. This study warrants further geochemical investigations of the Raša Bay environment.

Keywords:

Raša River estuary; estuarine sediments; fish; mussels; wild boar

1. Introduction

Marine coastal zones are particularly vulnerable to environmental degradation (**Uddin et al., 2022**) and climate change (**Behbehani et al., 2019**). Namely, more than 60% of the global population live within 100 km of the coast, and the large growth of associated urban centres is commonly in disparity with management plans towards the protection of the ecosystem (**Oreščanin et al., 2006**). Estuaries, where freshwater from the land mixes with seawater, are highly productive habitats teeming with aquatic life (**Mackenzie, 1997**). Such aquatic ecosystems are often contaminated by a range of hazardous substances found in sediment, soil, water and organisms (**Förstner and Wittmann, 1981; Al-Salem et al., 2020; Jakovljević et al., 2022**).

One such case is the Raša Bay, located at the eastern coast of the Istrian Peninsula in western Croatia (see **Figure 1**). The region belongs to the northern part of the Adriatic Sea. The Raša Bay area is a locality that has exemplified insufficient environmental protection measures in terms of the waste legacy of its Raša coal industry (**Medunić et al., 2018b, 2019; Fiket et al., 2020**). Locally exploited superhigh-organic-sulfur Raša coal was used for the production of electricity. Its waste legacy has affected the local ecosystem (**Prevendar Crnić et al., 2022**), and the environment (**Jakovljević et al., 2022, Medunić et al., 2020a, 2021**).

The accumulation of hazardous trace elements (HTE) adsorbed on fast sedimenting clay grade particles dominates in a restricted upper part of the estuary, and therefore their transport into adjacent marine areas is prevented. According to **Sondi et al**. **(1994)**, the anthropogenic HTEs load on the estuary was modest, and no indication of their critical levels was found. Later, **Sondi et al. (2008)** confirmed that enrichment of sediments with HTEs and organic matter of terrestrial origin in the upper part of the estuary was related to salt-induced coagulation of colloidal inorganic and organic materials, and the precipitation of both humid substances and iron and manganese oxyhydroxides at the clay mineral surfaces. The latter ones were more efficient in binding HTEs. Recently, **Fiket et al. (2021)** investigated the water and sediment of the Raša River estuary in terms of oxyanion mobility's in sediments estimated by the diffusion gradients in thin films (DGTs) technique. The authors determined that the geochemical composition of the water and sediment at the studied locations did not reflect the impact of past mining activities.

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Figure 1: Map of study area: a) position of Croatia in Europe; b) Istrian Peninsula with Raša Bay and the sampling sites labelled RS (10 km); c) sampling sites RS#1 (45°2.195'N 14°2.796'E), RS#2 (45°2.003'N 14°2.838'E) and RS#3 (45°1.859'N 14°2.803'E), M – mussels, F- fish, WB – wild boar, GM1 and GM2 – sampling sites **Medunić et al, 2018a** (400 m) CSB – coal-separation building;

According to **Förstner and Wittmann (1981)**, sediment analysis alone provides little information regarding the amount of HTEs which enters the biomass in water. Therefore, they suggest that it is necessary to determine the HTE concentrations in as many trophic levels as possible in the aquatic system. Such organisms (mussels, fish, etc.) are bioindicators that are used to screen the health of the natural ecosystem in the environment (**Losso and Ghirardini, 2010; Ouali et al., 2018; Förstner and Wittmann, 1981; Regoli, 1998; Krmpotić et al., 2015**). HTEs are resistant to degradation and they can accumulate in microorganisms, aquatic flora and fauna, but also in terrestrial organisms (including free-living wild animals, such as wild boar) through the food chain (**Milošković et al., 2013**). HTEs, such as Fe, Cu, Zn, Se, Ni, Mn, Cr, Co, V, etc., are essential trace elements in biological systems because they play an essential role in metabolism and growth, but they can produce toxic effects on organisms in high concentrations. On the other hand, HTEs, such as Hg, Pb, Cd, As, Ba, Sb, Al, Ag, etc., are hazardous even in traces (**Antović et al., 2019**). Therefore, the aim of this study was to present levels of HTEs in fish, wild blue mussels and wild boar potentially affected by Raša coal mine water that inflows into the Raša Bay, for the first-time. The flathead grey mullet (*Mugil cephalus*) is a filter-feeder inhabiting the coastal estuaries. Among the mussels, wild blue mussels *M. Galloprovincialis* is one of the most commonly consumed bivalve molluscs (**Goldberg, 1986**) and the determination of HTEs in this species is of considerable interest.

Wild boars, especially their kidneys, can serve as bioindicators of HTEs pollution due to their relatively long life and consequently, long period of bioaccumulation. The accumulation of HTEs in plant and water may increase the risk of transfer to wild animals. Non-essential HTEs, such as Pb, As, and Cd, are highly toxic for the animal organism. Following oral exposure to Cd in food and water, it is accumulated in the kidneys of wild animals (**Wlostowski et al., 2006**).

2. Methods

2.1. Main characteristics of the Raša River estuary

The Raša River estuary in the south-eastern part of the Istrian peninsula, the westernmost part of Croatia (45°02' N 14°03'E) is a coastal environment that receives contaminants and natural substances, mainly from the inflowing Raša River (see **Figure 1**). The Raša River is characterized by large variations in water flow and variable loads of mineral particles. More than 90% of the load is brought into the estuary as fine-grained (>63 um) suspended matter, consisting of only 24-36% of carbonates, while the rest relates to clays. Its sedimentation occurs at the salt wedge, resulting in a prograding estuarine delta. The estuary is being infilled with sediment, thus classifying it as a disequilibrium estuary (**Sondi et al., 1995**). Briefly, the Raša River estuary is a small, rock-bounded, micro-tidal (tidal range up to 2 m), low-wave-energy karstic estuary. Agricultural activities are recognizable and involve the use of fertilizers which arrive to the sea dissolved in water. The embankments were built to protect agricultural land because this part of the river is under a significant storm surge. Its sedimentological, geochemical and environmental characteristics have been thoroughly described elsewhere (**Sondi et al., 2008; Durn et al., 2021**).

2.2. Sampling and preparation of estuarine sediments samples

Estuarine sediment samples were collected on November 2nd, 2020. It was cloudy. The air temperature was

14°C and humidity was 52%. The temperature of the surface layer of sea water was 15°C and the temperature of water above the bottom was 19.5°C.

Samples were collected at three locations RS#1, RS#2 and RS3# (see **Figure 1**) by a homemade core sampler. The inner diameter of the tube is 10 cm. The lengths of samples collected with this sampler were typically in the range of 30 – 50 cm. Immediately after collection, each sample was cut into 2 cm slices using a guillotine and stored in a plastic bag. Only the top layers with an approximate thickness of 1 cm were further processed and analysed in this study as shown in **Figure 2a.** Sediment samples were crushed in an agate mortar, homogenized and dried in an oven at 105°C for 24 h (see **Figure 2b**). After drying, each sample was placed on a nest of sieves of 2 mm, 250 μm, 125 μm and 63 μm, stacked top to bottom in descending order of aperture size. The stack was placed on an electronic *Retsch Sieve Shaker AS200* sieve shaker to separate the sediment into different sized fractions.

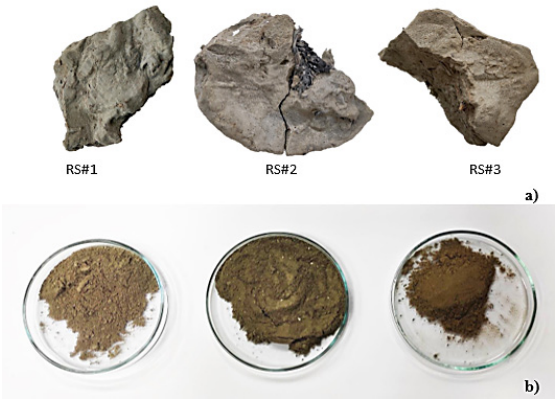

Figure 2: a) parts of the top layers (1cm) of sediment samples from three different locations from RS#1 to RS#3; b) ground samples prepared for XRF

2.3. XRF measurements of estuarine sediment samples

The X-ray fluorescence (XRF) analysis of sediment samples were conducted with an energy dispersive portable XRF analyser Niton XL3t Goldd+. Calibrations were performed with soil standard reference materials (SRM) with certified metal concentrations (National Institute of Standards and Technology standard NIST-2709a and ISE sample 979), and coal materials from USGS (Lower Bakerstown CLB-1).

Ground soil samples of different sizes were added to polypropylene sample cups and capped with a thick polypropylene film (Premier Lab Supply model TF-240-255). The centre of each inverted vial was aligned with the centre of the analyser window on the XRF stand. For this study, the instrument was operated in 'Soil Mode' with a 3 mm primary X-Ray beam diameter. The XRF analyser is equipped with excitation filters (main, low, high) that optimize the sensitivity for various elements. Three energy filter modes are automatically changed at 30-second intervals, and measurements are made for at least 90 seconds per sample, so the optimal analysis conditions were established while changing the measurement time. XRF analysis examined five different points on the sample surface to test the homogeneity of the samples and standards. The obtained results for 21 pseudo-total concentrations of HTEs, such as Sc, Mn, Sr, Ba, Zr, Cs, V, Cr, Ni, Cu, Rb, Sb, Sn, Te, Pb, Zn, As, Mo, Ag, Cd and Th are presented in the form of the average values of five measurements with standard deviation (SD). The concentrations of major elements (S, K, Ca, Ti and Fe) were also measured for calculation enrichment factors and accumulation indexes. Further, the concentrations of HTEs in four size fractions with diameters >250 μm, >125 μm >63 μm and < 63 μm were also measured and presented in **Table 2**.

2.3.1. ICP -MS measurements of estuarine sediments samples

The results of two techniques applied on the same estuarine sediment samples from locations RS#1 to RS#3 were compared. The pseudo-total concentrations of elements in these samples were obtained by a high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS). Fiket et al. (2021.) performed these measurements using an Element 2 instrument (Thermo, Bremen, Germany). Multielemental analysis of the prepared digestions and extracts was performed by typical instrument conditions and measurement parameters used throughout the work have been reported previously in Fiket et al. (2021). All samples were analysed for the total concentration of 26 elements (As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Li, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Tl, U, V and Zn).

2.4. Evaluation of sediment pollution

To assess the levels of trace metal contamination and the possible anthropogenic impact on the sediments, two of the most commonly calculated pollution indices were applied: Enrichment Factor (*EF*) and Index of geoaccumulation (*Igeo*).

Mean concentrations for elements measured in riverine and estuarine sediments were taken from **Frančišković-Bilinski et al. (2014)**. Calcium was used as a reference element and the element of choice for normalization purposes because it is the most abundant element in stream sediment (fraction <63 μm) with 10.81%. The *EF* is defined as the observed metal/Ca ratio in the sample divided by the background metal/Ca ratio. The equation for calculating *EF* is as follows:

$$EF = \frac{(\frac{c_x}{c_{ref}})_{sample}}{(\frac{c_x}{c_{ref}})_{bkg}} \quad (1)$$

Where:

c_x – the concentration of element of interest (x) in sample and background,

c_{ref} – the concentration of a reference element for the purpose of normalization in sample and background.

Five degrees of enrichments are commonly defined in **Sutherland (2000)**: low enrichment *(EF* < 2), moderate enrichment (2 < *EF* < 5), significant enrichment (5 < *EF* < 20), very high enrichment (20 < *EF* < 40), extremely high enrichment (*EF* > 40).

A method for identifying elements to quantify the levels of potential contamination of sediments is the geoaccumulation index (*lgeo*) by **Muller (1979)**. The *Igeo* is defined as

$$I_{geo} = log_2 \frac{c_x}{1.5 \cdot (c_x)_{bkg}} \quad (2)$$

Where:

c_x – the measured concentration of element of interest (x),

$(c_x)_{bkg}$ – the geochemical background of the element (x).

Factor 1.5 is used as the background matrix correction factor due to lithogenic effects. **Muller (1979)** defined six classes of sediment pollution status (see **Table 1**).

Table 1: Six classes of polluted sediment

Class	*Igeo*	Sediment
0	< 0	unpolluted
1	0-1	unpolluted to moderate polluted
2	1-2	moderate polluted
3	2-3	moderate to heavily polluted
4	3-4	heavily polluted
5	4-5	heavily to extremely polluted
6	> 5	extremely polluted

2.5. Sampling and preparation of fish, mussels and kidney of a wild boar samples

Wild blue mussels (*M. galloprovincialis*) were sampled at 1 m below sea level on the 4 m depth of the Raša Bay, near the mussel farm on November 2nd, 2020. The sampling site marked as M in **Figure 1** is 1 km from RS#3. Around 1 kg of *mussels* were collected, placed into polyethylene bags with seawater and transported into the Laboratory for Determination of Residues at Croatian Veterinary Institute in Zagreb. The flathead grey mullet (*Mugil cephalus)* were collected in the Raša estuary (marked as F in **Figure 1**) close to sediment sampling sites RS#1 and RS#3 on November 2nd, 2020.

The fish samples were beheaded, gutted, washed, and filleted. Only the edible portions were utilized for the analysis. Fish fillet (tissue) was carefully removed from the fish bone without any contact with guts and roes. This is to prevent any contamination being introduced to fish tissue. The fish fillet and was then homogenised in a blender and stored at − 20°C until analysis.

The wild blue mussel samples were first unshelled and the soft tissues were pooled and thoroughly rinsed with deionised water to remove extraneous impurities. The whole mussel tissues were homogenised in a blender and stored at − 20°C until analysis.

Homogenized tissue samples (0.5 g) were weighed into a Teflon liner with the addition of 3 mL distilled H_2O and 2.5 mL HNO_3 (65%). The wet digestion of the samples was performed using a high-pressure microwave oven Multiwave 3000 (Anton Paar, Graz, Austria), in three steps: I) 2.5 minutes at 500 W; II) 20 minutes at 1000 W, and III) 30 minutes at 1200 W. Following the cooling step, the digested clear solution was quantitatively transferred to a 50 mL volumetric flask and filled up to the mark with ultra-pure water. Since we did an on-line introduction of an internal standard by peristaltic pump, the internal standard solution must be prepared separately from the sample and the calibration curve standard solutions. The inner diameter of the internal standard introduction tubing is much smaller than the inner diameter of the sample introduction tubing and so the uptake rate of the internal standard solution is about 1/20 of the sample uptake rate. A mixture of internal standard solution (ISTD) of 200 ppb containing In, Bi, and Sc (Inorganic Ventures, Blacksburg, VA, USA) was added on-line using the standard ISTD mixing tee connector.

The wild boar sampling position is marked as WB on **Figure 1**. Only kidneys were separated for hazardous trace element analyses. Upon delivery to the laboratory, the tissues of the kidney were also homogenised and stored at -18°C until analysis. Samples (0.5 g) were wet-digested with 2.5 mL of HNO_3 (65% v/v), 1 mL of H_2O_2 (30% v/v), and 2 mL of H_2O using a Multiwave 3000 microwave oven (Anton Paar, Ostfildern, Germany). Three microwave digestion conditions used in mineralization were in three steps with potency: the first step: 500 W for 4 min; the second step: 1000 W for 5 min; the third step: 1200 W for 10 min. The digested clear solutions were first left to cool to room temperature and then diluted with ultrapure water to a final volume of 50 mL. The solution, containing a mixture of the internal standard (ISTD; In, Bi, and Sc), was added online using the standard ISTD mixing tee-connector (**Bilandžić et al., 2020**).

2.6. Multi-elemental analysis of fish, mussels' tissue and kidney of a wild boar

Fish and mussel samples were analysed after microwave digestion with nitric acid. The decomposed samples were diluted with demi water and the final volume content of nitric acid was 5%. Also, calibration standards were done in 5% nitric acid. Concentrations of HTEs in

fish and mussels were determined by inductively coupled plasma with a mass detector Agilent ICP-MS Model 7900 (Agilent, Palo Alto, CA, USA). High purity argon was used throughout (99.999%, White Martins, Brazil). Calibration of the instrument was done using certified standards of 99.99% purity for all elements (Se, Cd, Pb, Cu, Zn) at a concentration of 10 mg/L (Environmental Calibration Standard, Agilent Technologies, USA). Data quality was checked by analysis of the recovery rate using certified reference materials: mussel's tissue (2976, NIST, USA) and dogfish muscle (DORM-4, National Research Council, Canada). We obtained 15 element concentrations V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Mo, Cd, Ba, Pb and Hg in white fish and 13 HTEs (without Ag and Hg) in wild blue mussels and different sizes of mussels. All data are expressed in mg/kg on a wet basis (w.wt.).

Determination of Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, and Zn in the wild boar kidney was performed by ICP-MS instrument with the mass detector Agilent ICP-MS system Model 7900 (Agilent, Palo Alto, CA, USA). The peristaltic pump of the ICP-MS was set at 0.40 rps. High-purity argon (99.999%, White Martins, Rio de Janeiro, Brazil) was used throughout. The ICP-MS optimization of conditions was achieved by adjusting the torch position and tuning for reduced oxide and doubly charged ion formation with a standard tuning solution containing Li, Y, Ce, and Tl in 2% HNO_3 (**Bilandžić et al., 2020**).

3. Results and Discussion

3.1. The concentrations of analysed HTEs in Raša estuarine sediments

The 21 average pseudo-total concentrations in different particle fractions (>250 μm, >125 μm, >63 μm and <63 μm) obtained for Raša River estuarine sediments are presented in **Table 2**. From the obtained data, the average concentrations decrease in the following order: Mn>Ba>Sc>Sr>Zr>Cs>Ni>V>Te>Rb>Cr>Cu>Sb>Sn >Pb>Zn>Mo>Th>Cd>Ag>As. According to measured concentrations, the elements can be classified into three groups; the first group with c ≤ 10 ppm (Ag, Cd, As, Mo, and Th), the second group with 10 ppm < c ≤100 ppm (Zn, Sb, Pb, Sn, Cu, Te, Cr, Rb, V and Ni) and the third group with c > 100 ppm (Cs, Zr, Ba, Sr, Sc, and Mn) where c presents the concentration of HTEs. The major

Table 2: Pseudo-element concentrations and standard deviation (SD) in sediment (ppm) collected from the Raša River estuary on November 2nd, 2020 obtained by XRF technique (BDL- below detection limit)

***c* ± SD**	**RS#1 (*d*/μm)**					**RS#2 (*d*/μm)**					**RS#3 (*d*/μm)**			
(ppm)	**total**	**>250**	**>125**	**>63**	**<63**	**total**	**>250**	**>125**	**> 63**	**<63**	**total**	**>250**	**>125**	**>63**
Ag	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	7±1	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	8±10	BDL	BDL	BDL
As	6.7±0.2	BDL	10±1	BDL	10±1	0.2±0.2	2±0.1	6±0.3	2±0.1	8±0.4	8.3±0.3	10±1	8±2	10±2
Mo	10±1	10±1	10±1	10±1	10±1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	10±2	10±2
Th	10±0.3	10±1	10±1.2	10±1.1	BDL	10±2	BDL	BDL	10±2	BDL	8.3±0.3	BDL	BDL	6±0.2
Zn	15±3	15±1	20±2	10±1	20±2	BDL	BDL	BDL	BDL	20±2	BDL	BDL	BDL	BDL
Sb	15±10	BDL	BDL	BDL	BDL	38±10	BDL	BDL	BDL	BDL	36±10	BDL	BDL	BDL
Pb	18±1	20±2	14±1	10±1	18±2	15±1	14±1	16±1	12±1	20±2	12±1	10±1	10±3	10±0.4
Sn	22±10	BDL	BDL	BDL	BDL	28±10	BDL	BDL	20±10	BDL	26±10	BDL	BDL	BDL
Cu	41±6	34±3	34±3	40±3	70±4	30±7	BDL	30±6	BDL	33±7	25±10	BDL	BDL	BDL
Te	42±10	BDL	BDL	BDL	BDL	57±10	BDL	BDL	BDL	BDL	58±10	BDL	BDL	BDL
Cr	47±10	36±10	38±10	40±10	55±10	37±10	28±10	30±10	48±10	82±10	48±10	40±10	40±10	62±10
Rb	75±8	76±9	80±7	56±8	68±8	50±2	52±3	56±3	50±3	62±4	55±2	60±2	70±3	60±3
V	80±20	46±10	48±19	42±10	42±10	42±10	40±10	42±10	38±10	42±10	51±15	42±10	46±11	46±10
Ni	88±10	BDL	BDL	BDL	BDL	62±20	BDL	BDL	BDL	BDL	53±20	BDL	BDL	BDL
Cs	102±10	BDL	BDL	BDL	BDL	128±15	BDL	BDL	BDL	BDL	128±15	BDL	BDL	BDL
Zr	110±12	106±12	106±10	86±15	134±12	130±5	104±4	116±5	110±5	272±10	127±5	120±5	118±5	142±6
Ba	290±20	53±30	BDL	BDL	BDL	323±28	BDL	BDL	BDL	BDL	345±25	BDL	BDL	BDL
Sr	310±28	254±30	270±24	202±27	242±34	250±10	242±10	258±10	238±10	262±10	270±10	266±10	286±11	258±10
Sc	340±90	214±50	194±50	208±50	198±54	237±60	154±42	180±50	164±50	188±60	258±80	224±60	244±60	208±57
Mn	420±50	262±50	224±50	175±45	242±53	337±50	166±46	222±50	542±50	300±58	380±50	322±50	310±50	278±50

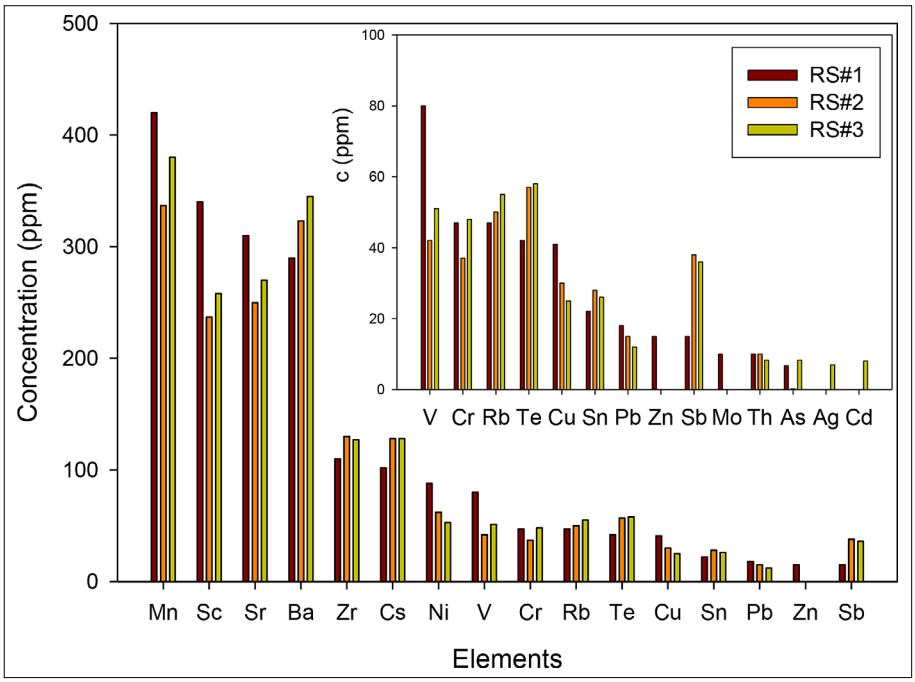

Figure 3: Comparison of HTE concentrations for three locations: RS#1, R#2 and RS#3

elements, such as S, K, Ca, Fe and Ti, were also measured by XRF for calculation of enrichment factors and geoaccumulation index. The pseudo-total concentrations of Ag and Cd were obtained only in RS#3 location. Argentum is of particular concern for sustainable estuary management because it is the most toxic metal suspected of causing toxic effect (**Coynel et al., 2016**).

Pseudo-total concentrations of Mn, Sc, **Sr, Ni, V**, **Cu** and **Pb** in RS#1 were 30% higher than for other sites (see **Figure 3**). Molybdenum and zinc were obtained only in the RS#1 site. The RS#1 location is closest to the former coal-separation unit Štalije (CSB in **Figure 1**) This site was fed by water coming from the coal-separation unit where iron, wood, stones and other waste were separated. The coal separation in this building was operated from 1971 to 1980 and it was closed after the mine ceased operations. **Medunić et al. (2020c)** concluded that concentrations of **V, Ni, Se** and **Sr** in Croatian SHOS Raša coal exceeded Chinese SHOS coal and world averages of 3.3, 1.2, 3.6 and 26 times, respectively. Further, **Medunić et al. (2018b)** found high positive correlation among elements Cu, Pb and Zn in soil, which is typical for soil pollution by the mining and coal-combustion industries.

The concentrations of Ni, Cu and Pb were found to continuously decrease from the Raša River mouth to the estuary. **Sondi et al. (2008)** reported that the highest concentrations of Pb and Cu were found in the uppermost part of the estuary where clay minerals predominate. This indicates the prevalent accumulation of metals is governed by the fast sedimentation rate of clay in the restricted upper part of the estuary. This could be indicating that water brought the contaminants into the estuary from local anthropogenic sources, such as foundry activities, agricultural activities, etc. The Raša River brings a lot of sediments and storm surge brings HTEs from land use into the river. The elements from riverine sediments accumulate due to the adsorption to clay minerals in estuarine sediments (**Sondi et al., 1994**). Opposite to that, the concentrations of Ba, Zr, Cs, Rb, Ag, Cd and As in RS#1 were lower than for other sites (see **Figure 3**). The concentrations of Ba, Rb and Te continuously increase from the mouth to the estuary. These could be due to removal through flocculation of colloidal particles from the water column during fresh- and saline-water interaction (**Akhtar et al., 2022**).

A detailed HTE concentrations distribution as a function of particle size has been obtained for three muddy sediments of the Raša River estuary. **Figure 4** represents part of the XRF spectrum for three different sizes.

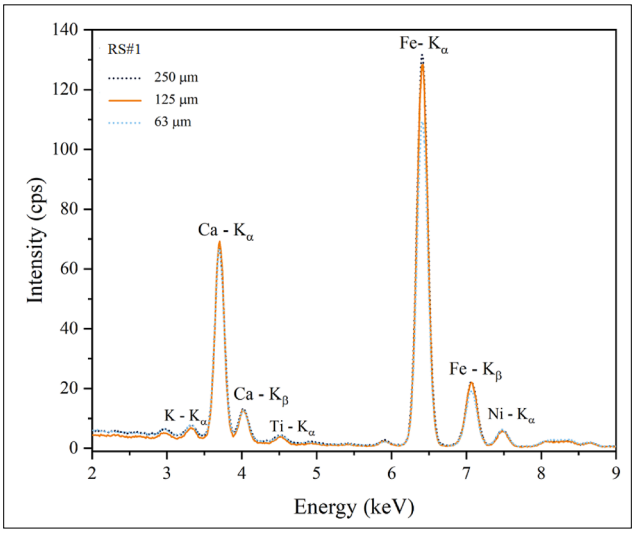

Figure 4: Part of the XRF spectrum of sample *RS#1* with different particles sizes >250 µm, >125 µm and >63 µm

The 14 HTE concentrations as a function of grain size (> 250 μm, > 125 μm, > 63 μm and < 63 μm) in sample RS#1 are shown in **Figure 5**. The other measured elements, such as Ag, Cd, Sb, Sn, Te, Ni and Cs in RS#1 were BDL. For five elements, such as Sc, V, Mo, Th and As, the concentrations in various size fractions varied within 6.7%, which is less than standard deviations of measurements. Only concentrations of Cr and Cu show a non-linear increase with a decrease in size fractions. This could be due to desorption and solubilisation of particulate metals as salinity (**Regnier et al., 1993**). The results for other elements do not clearly demonstrate an increase/decrease of concentrations with a decrease in the size fraction. The obtained Mn, Zr and Pb concentrations were decreased with a decreasing size fraction to the silt fraction.

The concentrations of eight elements, Sr, Rb, Mn, Cr, Zr, Cu, Pb and Zn were higher in the silt fraction (<63 μm) than in the sand fraction (>63 μm) for 20%, 21%, 38%, 38%, 56%, 75%, 80%, 100%, respectively. The same results for higher concentrations of Mn, Cr, Cu, Pb and Sr in the silt fraction were presented for the Sava riverine sediments in **Oreščanin et al. (2004.)**

Elements of anthropogenic origin, such as Cr, Cu and Zr had higher concentrations in the smallest fraction (d<63 μm). These small particles could be generated during high-temperature industrial processes, such as coal combustion (**Sager et al., 2012**) and entered into the river, and consequently into the estuarine sediment.

Figure 6 shows pseudo-total HTE concentrations in the same size fraction for different sampling sites. The concentrations of V, Sr and Zr in fraction >250 μm, then Zr, Rb and Mo in fraction >125 μm and V, Pb and Mo in fraction >63 μm for three locations varied within SD. The highest variations of Mn concentrations in three locations were obtained. The Pb concentrations in >250 μm and >125 μm were higher in the upper part of the mouth and decreased from river mouth to estuary. Opposite to that, the Sr, Cr and Cu concentrations in >125 μm and the Sr, Cr and Zr concentrations in >63 μm increased from river mouth to estuary. The elements Sr, Cu and Cr, are the trace elements determined in fertilizers (**Senesi et al., 1999; Lepp et al., 1994**) and these could be transported by the stream into the estuary.

Concentrations of As in the RS#3 sample were higher by 39% and 19% than in RS#2 and RS#1, respectively. The As concentrations in two fractions in sample RS#1 d>250 μm, d> 63 μm were also higher than in the samples RS#2 and RS#1 by 70% and 100%, respectively. Arsenic is a very toxic and relatively accessible, non-essential element, used as a pigment, a livestock growth promoter and as a component in pesticides (herbicides, fungicides, insecticides, etc.) and wood preservatives. (**Medunić et al., 2020b**; **Senesi et al., 1999**). Elements such as Ag, Cd, Sb, Cu, Te, Ni, Cs and Ba (see **Table 2**) were BDL in some size fractions.

The twelve HTE concentrations were compared with literature data and reference values (**Francisković-Bilinski et al., 2014**) and the results are presented in **Table 3**. Non-presented elements in samples or reference background were BDL. The measured concentrations of Cd in the Raša River estuary were 20 times higher over 12 years (**Sondi et al., 2008**). The measured concentrations of As, Cr, Ni and Cd in the Raša River estuary were 2.5, 3, 6 and 29 times higher than in the Zrmanja River Estuary (**Fiket, et al, 2017**). The obtained concentrations of Cr and Ni were 1.5 times higher than in the Plomin Bay with an active thermal plant powered by local coal (**Oreščanin et al., 2009**). Cromium and nickel were found in

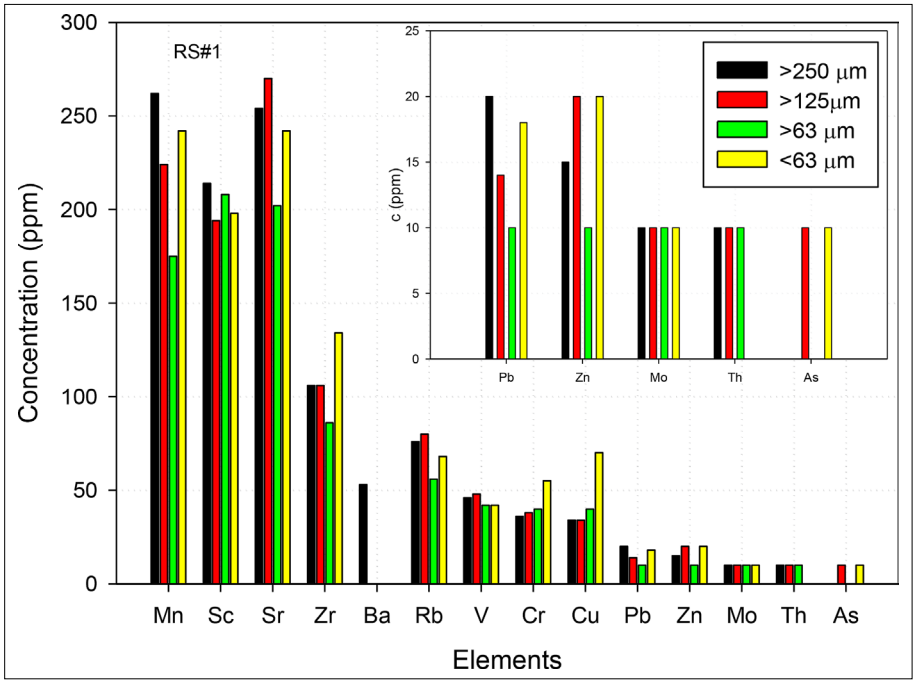

Figure 5: Comparison of HTE concentrations in various size fractions of an estuarine sediment sample collected in the RS#1 location

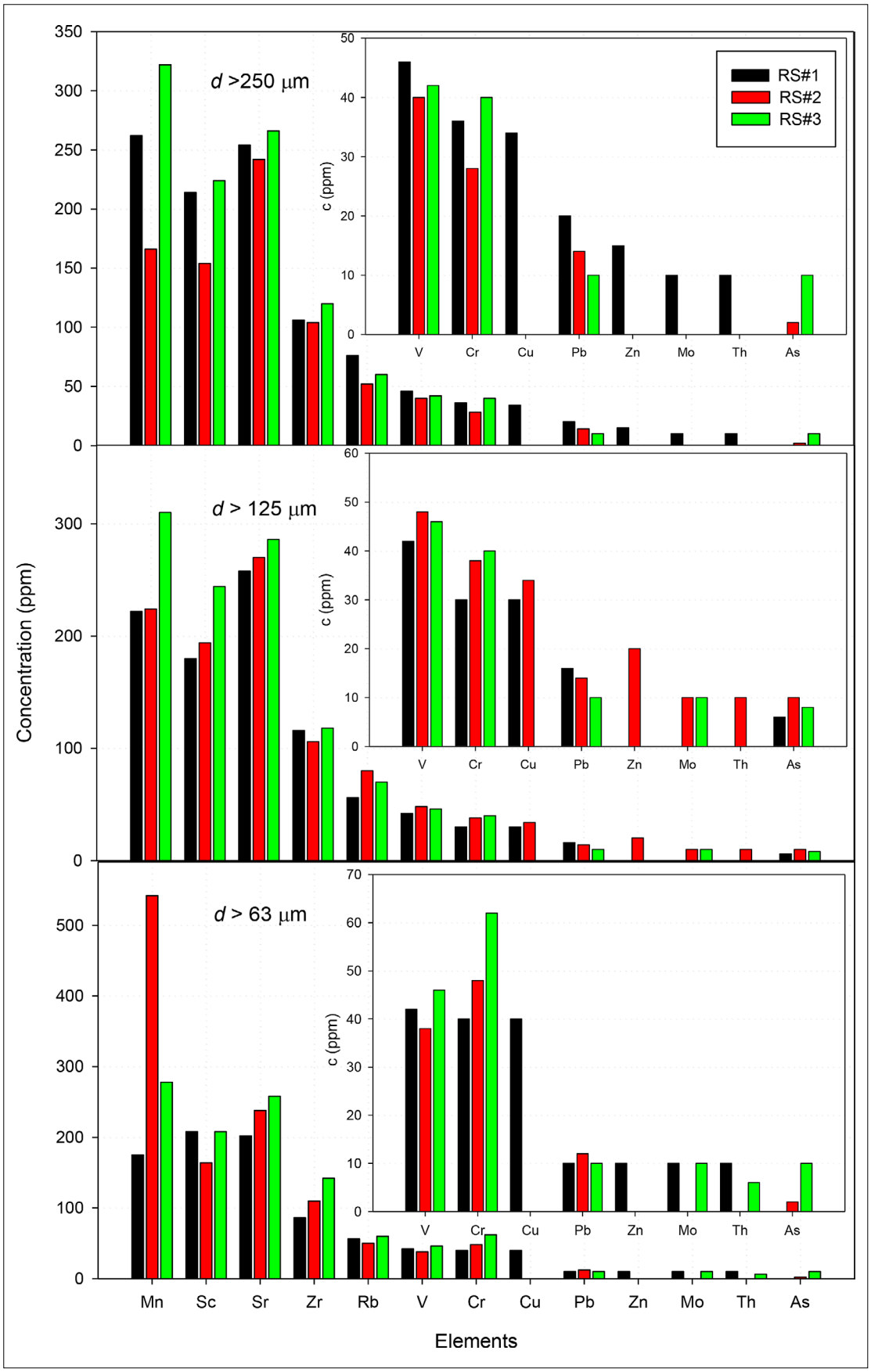

Figure 6: Comparison of HTE concentrations in the same size fraction of three sediment samples collected in the Raša River estuary (black RS#1, red RS#2, green RS#3)

Table 3: Comparison of HTE concentrations with data[a-c] ([a]**Sondi et al., 2008;** [b]**Fiket, et al., 2017;** [c]**Oreščanin, V, et al., 2009**) and reference values: **Fransciskovic-Bilinski et al., 2014**[d]. Underlined values exceed relevant reference levels.

c/ppm	RS#1	RS#2	RS#3	Raša[a]	Zrmanja[b]	Plomin Bay[c]	Sed[d]	RS#1/Sed	RS#2/Sed	RS#3/Sed
As	BDL	2	10		4.06	10.6	6.536		0.31	1.53
Cd	BDL	BDL	8	0.4	0.274					
Cr	40	48	62		20.5	40.2	44.9	0.89	1.07	1.38
Cu	40	BDL	BDL	145	6.85	33.2	28.9	1.38		
Mn	175	542	278		111	759	968.8	0.18	0.56	0.29
Ni	88	62	53		8.49	34.4				
Pb	10	12	10	130	13.1	10.9	21.2	0.47	0.57	0.47
Rb	56	50	60				16.9	3.3	3	3.5
Sn	BDL	20	BDL		1.06		1.109		18	
Sr	202	238	258		96.7	353	224.7	0.9	1.06	1.15
Th	10	BDL	6				2.577	3.9		2.3
V	42	38	46			97.6	32.8	1.28	1.16	1.4
Zn	10	BDL	BDL	20		84.1	70.4	0.14		
Zr	86	110	142				1.205	71	91	118
Ca	73600	84500	104200				108090			

It is shown that the concentrations of Zr, Sn, Sr, Rb, As, Cu, Cr and V in estuarine sediments exceeded background values. The highest incidences of elevated levels obtained from sample and background concentration ratios, were for Zr (71 -118) and Sn (18). Zirconium is resistant to weathering and it is invariably present in soil/estuarine sediments (**Chen et al., 2020**).

Higher concentrations of As in location RS#3 than in location RS#2 could be due to river flow direction. The RS#3 site is away from the direct stream and this could affect the accumulation of particles. The lower course of the Raša River flows through a wide valley where agricultural production takes place. Arsenic can originate from coal combustion, fertilizers in agriculture because As-components are part of herbicides, fungicides and insecticides (**Halamić et al., 2009**). The toxicity of As depends on its chemical form and its bioavailability. Arsenic is among a list of contaminants of emerging concern in seafood, for which there is insufficient data on levels in seafood for risk to be assessed (**Vandermeersch et al., 2015**). Opposite to that, concentrations of Th, Pb, Zn and Mn did not exceed reference values.

3.2. Enrichment factors for HTEs in the Raša River estuary

The enrichment factors were calculated from the pseudo-total concentrations of 12 trace elements (Zr, Sn, Th, Rb, Cu, V, Sr, Cr, As, Pb, Mn and Zn) for three locations (see **Table 4**) and the reference values for estuarine sediments (**Fransciskovic-Bilinski et al., 2014**) were calculated using Equation 1. The EFs for other measured elements were not calculated because their concentrations did not report into the background.

Calcium was used as a reference element because it is the most abundant element in flysch riverine sediments. The measured Ca concentrations from RS#1 to RS#3 presented in **Table 3** were used for calculating *EF*s (Equation 1). Based on the calculated *EF* values (>40), Zr was the major contaminant among the measured elements in the Raša River estuary samples. The *EF* of Sn in RS#2 indicated very high enrichment and the *EF* of Th in RS#1 indicated significant enrichment. The calculated EFs of Rb and Cu indicated moderate enrichment. The calculated EFs of V, Sr, Cr, As, Pb, Mn and Zn less than 2 indicated low enrichment.

Table 4: Enrichment factors for 17 trace elements in the Raša estuarine sediments presented from highest to lowest. (Extremely high enrichment (*EF*>40) is highlighted in dark grey, very high enrichment 20<EF<40 in grey, significant enrichment (5<*ER*<20) in light grey, moderate enrichments (2<*EF*<5) and low enrichments (*EF* <2) are not highlighted.)

EF	RS#1	RS#2	RS#3
Zr	105	117	122
Sn		23	
Th	5.7		2.4
Rb	4.9	3.8	3.7
Cu	2.1		
V	1.88	1.48	1.46
Sr	1.32	1.35	1.19
Cr	1.31	1.37	1.43
As		0.391	1.587
Pb	0.694	0.725	0.490
Mn	0.265	0.716	0.298
Zn	0.209		

The two elements, Zr and Th are often concentrated in the mineral of zircon, which is widely distributed in sedimentary rocks due to its strong weathering resistance. Paleo sedimentary flysch rocks are represented in this area. The water permeability of the terrain is low and during intense precipitation, the material is intensively transferred to the mouth (**Peh et al., 2003**).

Very high enrichment of Sn may be reflected in the anthropogenic influence of boat paints and boat repair materials. **Furdek Turk et al. (2020)** concluded that Adriatic coastal sediments were moderate to significantly contaminated by Sn as a result of using antifouling paints in ports, shipyards and marinas. They calculated EFs of Sn in sediments in ports, shipyards and marinas up to 20, 40 and 80, respectively. Such anthropogenic activities also take place in the Raša Bay at Bršica port for loading of livestock and timber, Trget port for commercial traffic or nautical tourism and, several local ports for small fishing boats.

3.3. Geoaccumulation index

According to the calculated *Igeo* values (see **Table 5**), Zr and Sn are the major pollutants among the measured elements in the Raša River estuarine sediments. The values of *Igeo* for Zr were higher than 5, which indicate extremely contaminated sediment. The value for Sn (RS#2) was between 3 and 4, which indicates heavily contaminated sediments. Values of *Igeo* for Rb and Th were higher than 1, which indicate moderately polluted sediment.

It is evident from **Table 4** that most elements in the estuarine sediment samples, such as Pb, As, Zn, Cu, Mn, Cr, V and Sr had negative *Igeo*, which indicates that the sediments in the Raša River estuary have lower values than those found in the material that was used as a background. These geoaccumulation indexes correspond to the uncontaminated samples.

Table 5: Geoaccumulation index *Igeo* for measured elements in sediments. (Extremely polluted *Igeo*>5 is highlighted in dark grey, heavily polluted 3<*Igeo*<4 in grey, moderately polluted 2<*Igeo*<1 in light grey and unpolluted to moderate 0<*Igeo*<1 and unpolluted *Igeo*<0 are not highlighted)

Igeo	RS#1	RS#2	RS#3
Zr	5.6	5.9	6.3
Sn		3.6	
Rb	1.14	0.9	1.24
Th	1.37		0.634
Pb	-1.66	-1.40	-1.66
As		-2.3	0.028
Zn	-3.4		
Cu	-0.115		
Mn	-3.1	-1.4	-2.4
Cr	-0.752	-0.488	-0.119
V	-0.227	-0.372	-0.096
Sr	-0.738	-0.502	-0.385

The chemical composition of these Raša estuarine sediments also reflects the geological and hydrogeological background (**Fiket et al., 2021**).

3.4. Comparison of XRF and ICP-MS concentration of the estuarine sediment samples

These estuarine samples were also analysed by ICP-MS in **Fiket et al. (2021)**. The concentrations of twelve common HTEs (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Rb, Sr, Ti and V) obtained by XRF and ICP-MS were compared (see **Table 6**). The XRF concentrations of Sn, Cs, Sb were up to 64 times higher than the ICP-MS concentrations. These huge differences in concentrations come from the matrix effects during XRF analysis. The measured XRF concentrations of Sn were 64 times higher than ICP-MS. This is the reason for various calculated EF and *Igeo* of Sn.

Table 6: Agreement between ICP-MS and XRF concentrations for the same set of sediments

	RS#5		RS#6		RS#7	
c/ppm	ICP	XRF	ICP	XRF	ICP	XRF
As	6.52	6.7	6.37	5	6.12	8.3
Ba	168	290	148	323	156	345
Cr	125	47	106	37	119	48
Cu	32	41	22.4	30	22	25
Fe	24700	16100	20200	16000	19000	12800
Mn	507	420	504	337	511	380
Ni	72.3	88	53.6	62	54.6	53
Pb	18.4	18	17.7	15	18.5	12
Rb	93.7	75	68.3	50	67.2	55
Sr	313	310	317	250	312	270
Ti	3012	2075	2534	1208	2635	1580
V	101	80	84.2	42	74.2	51

The XRF/ICP median ratios in the range of 0.3 – 2.2 were presented in Figure 7. Good agreements of two techniques were calculated for As, Ni, Pb and Sr. The concentrations of Ba, Cu and Ni were higher, and Cr, Ti and V were lower obtained by XRF than by ICP.

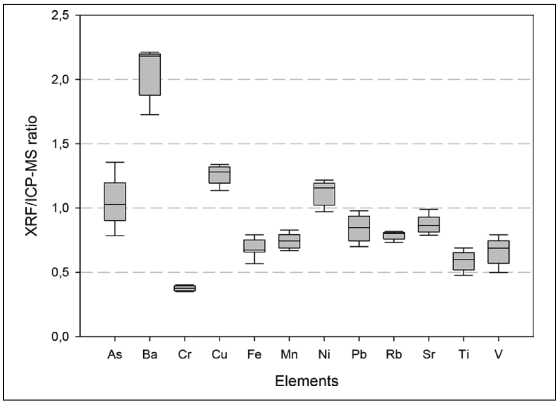

Figure 7: XRF to ICP-MS ratios of the measured elemental concentrations

3.4.1 Comparison of HTE concentrations in the Raša River estuarine sediments over three years

The concentrations of HTEs were compared with data for this area**. Medunić et al. (2018a)** collected estuarine sediments in GM1 and GM2 locations (see **Figure 1**) in 2017. The location RS#2 is less than 5 m away from GM1, and RS#3 is less than 200 m away from GM2. The location of GM2 was positioned in Bršica port. Bršica port served as a loading port for Raša coal in the past, and is specialized for the export of livestock and dangerous goods today (**Medunić et al., 2018a,b**). **Medunić et al. (2018)** used the ICP-MS technique for multi-elemental analysis of estuarine sediments.

For this purpose, only elements (As, Cu, Ni, Pb, Rb, Sr and V) with good agreements between two analytical techniques were compared. The concentrations of Sr increased up to 44%, while the concentrations of Cu, Cr and Pb decreased up to 60% over three years. The concentrations od As in RS#3 were 7 times higher than in GM2. The compared concentrations of V in these sites were in the SD range.

3.5. Concentrations of HTEs in fish caught downstream of the Raša River mouth

Trace metals may be accumulated by aquatic organisms such as fish and mussels, which could be a potential risk to the ecosystem. People consuming seafood could be unintentionally exposed to trace elements with a potential danger to their health. The flathead grey mullet (*Mugil cephalus*) is detritus and a filter feeder inhabiting the coastal estuaries. This species can be considered as a biological indicator for metal pollution because of its capability to accumulate heavy metals in its body (**Ouali et al., 2018**).

The concentrations of 18 HTEs in muscle tissues of *M. cephalus* sampled in the Raša estuary were obtained (see **Table 7**). From the obtained data, the average concentrations decrease in the following order: Fe>Zn< Al>As>Se>Cu>Ni>Mn>Cr>Ba>Hg>Mo>V>Pb>Co> Cd>Ag>Sb. This analysis was undertaken to examine the presence of HTEs consisting of essential elements: Fe, Zn, Se, Cu, Ni, Mn, Cr, Co, Mo and V, and non-essential elements: Al, As, Hg, Pb, Cd, Ba, Ag and Sb. Non-essential elements were considered pollutants because of their toxicity in relatively small quantities (**Rosli et al., 2018**).

Mercury, lead and cadmium prescribed in **Regulation (2006)** are considered to be the most dangerous metals and have been associated with serious adverse health effects. These elements cannot be broken down and are not biodegradable. Metal toxicity causes the formation of free radicals which causes DNA damage, alteration of sulfhydryl homeostasis, and lipid peroxidation (**Briffa et al., 2020**). The maximum values of Cd, Pb and Hg are 0.05 mg/kg w.wt., 0.3 mg/kg w.wt. and 0.5 mg/kg w.wt., respectively. These elements in caught fish samples were lower than the prescribed ones. The main sources of Pb pollution are anthropogenic. Before the use of leaded gasoline was banned, most of the lead released came from vehicle exhaust (**Abadin et al., 2007**). Fuel additives based on Pb were reduced 10 years ago, according to the **EU directive 2009/30/EZ**, and the Pb concentrations were decreased in the air (**Mao et al., 2009**; **Petit et al, 2015**). Once Pb falls onto soil, it remains in the upper layers of soil. The vegetables grown in lead-containing soils may contain traces of Pb. When soil particles are moved by rainwater, Pb may enter rivers, lakes and streams (**Abadin et al, 2007**).

Table 7: Separated HTE concentrations in fish samples (n=3) collected in the Raša River estuary compared to published data[a-b] ([a]**Antović et al., 2019;** [b]**Turkem et al., 2011**). Above the dotted line are essential and below are non-essential HTEs.

c (mg/kg w.wt.)	Mugil cephalus			Boka Kotorska Bay[a]	Paradeniz lagoon[b]
Fe	10.5	10.2	6.5	269	34.8
Zn	4.9	5.1	4.6	5.3	6.6
Se	0.31	0.41	0.53		
Cu	0.41	0.38	0.24	0.82	1.08
Ni	0.599	0.051	0.042	1.14	0.61
Mn	0.13	0.17	0.35	4.1	0.86
Cr	0.106	0.033	0.031	5.1	0.71
Co	0.0089	0.006	0.0047		0.41
Mo	0.014	0.014	0.0038		
V	0.0073	0.0095	0.0140		
Al	1.3	2.9	3.9		
As	0.36	0.99	1.3		
Hg	0.001	0.041	0.029		
Pb	0.017	0.002	0.0045	0.4	0.63
Ba	0.014	0.041	0.104		
Ag	0.0015	0.0009	0.0004		
Cd	0.0009	0.0013	0.0013	BDL	0.49
Sb	0.0008	0.0009	0.0007		
l/cm	20	25	30		

The HTE concentrations in different sizes of fish were measured. Higher concentrations of As, Cd, Ba, Pb, Mn Se and V in larger samples were obtained. This could indicate that these elements are more accumulated into tissues due to the fish size. This site was fed by water coming from the former coal-separation unit Štalije. **Medunić et al., 2018a** concluded that the estuarine sediment in location GM1 (see **Figure 1**) was highly enriched by Se and V, which reflect the presence of Raša coal particles. Selenium remains active through the cycle of return from the sediments into the water and food chain (**Lemly, 2008**). Opposite to that, lower concentrations of Cr, Co, Ni, Cu, Mo and Ag were measured in larger samples than in smaller ones.

3.6. Concentrations of trace elements in mussels sampled in the Raša Bay

The hazardous trace elements (HTEs) in the mussels can provide the measurement for the potential effects of the mixtures of pollutants in an aquatic environment. The concentrations of 15 trace elements in blue mussel samples (*Mytilus galloprovincialis*) sampled in the Raša Bay are shown in **Table 8**. The obtained results show that the tissue of mussel samples contains V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Ba and Pb. From the obtained data, the average concentrations decrease in the following order: Al>Fe>Zn>Mn>Cu>As>Se>V>Ba>Ni >Cr>Mo>Pb>Co>Cd. The Al, Fe, Zn, Mn, Cu and As concentrations were higher than 1 mg/kg w.wt and the concentrations of the remaining elements were lower. The concentrations of Al, Fe and As were higher in fish and mussel samples, which could suggest that these elements share a common accumulation process in aquatic organisms.

Table 8: Comparison of concentrations of trace elements in wild blue mussels (mg/kg w. wt.) with literature data from different sites in the Adriatic Sea[a-c] ([a]**Bajc and Kirbiš, 2019**; [b]**Bogdanović et al., 2014**; [c]**Perošević et al., 2018**.)

c /(mg/kg w.wt.)	Raša Bay	Gulf of Trieste (Italy)[a]	Šibenik Bay (Croatia)[b]	Boka Kotorska Bay (Montenegro)[c]
Fe	175.7	42		55
Zn	14.3	20		14.9
Se	1.427			
Cu	3.65	1.3		1.49
Ni	0.669	0.4		0.36
Mn	4.21	1.8		1.59
Cr	0.555	0.36		0.22
Co	0.174	0.2		0.13
Mo	0.215			
V	0.898			
Al	205.05			81.5
As	3.16	4	2.294	
Pb	0.197	0.1	1.063	0.46
Ba	0.694			0.23
Cd	0.14	0.2	0.19	0.17
Sampling year	2020	2015	2011	2015

According to **Regulation (2006)**, wherein the maximum permissions limit values set for Cd (1 mg/kg w.wt.) and Pb (1.5 mg/kg w.wt.), the concentrations of Cd and Pb in Raša wild mussels were lower than recommended. As it can be seen from **Table 8**, the concentrations of Pb, Zn and Cd in Raša wild mussels were lower than in mussel samples in the Gulf of Trieste, Seča (**Bajc and Kirbiš, 2019**), the Šibenik Bay (**Bogdanović et al., 2014**) or the Boka Kotorska Bay (**Perošević et al., 2018**). The concentrations of As, Zn and Cd in Raša mussels were up to 43% lower (21%, 40% and 43% respectively) than in Trieste mussels (**Bajc and Kirbiš, 2019**). The concentrations of Pb, Zn and Cd in Raša mussels were lower up to 2.3 times **(**4%, 21%, 230% respectively) than in Boka Kotorska mussels (**Perošević et al., 2018**). The concentrations of Pb and Cd in Raša mussels were lower than in Šibenik mussels by up to 5 times (**Bogdanović et al., 2014**). Lead and Cd-contaminating compounds in water and sediments are related to oil tankers, commercial ship, recreational boat traffic (**Nowrouzi et al., 2012**). These could be because of the lower intensity of maritime traffic and lower in-port activities in the Raša Bay than those ports.

The As concentrations in the Raša Bay were 37.8% higher than in the Šibenik Bay, while they were 2 times lower than in the Gulf of Trieste. The concentrations of Mn, Ni and Ba in Raša mussels were higher than in the Gulf of Trieste, the Šibenik Bay and the Boka Kotorska Bay. The concentrations of Cr, Cu and Zn in Raša mussels were lower than in the Gulf of Trieste. This could indicate smaller quantities of sewage water because elements such as Cr, Cu and Zn are related to sewage sludge (**Senesi et al., 1999**).

3.7. The concentrations of HTEs in kidney of free-living wild boar

Wild boars were confirmed as good bioindicators of trace elements in biological tissues. The concentrations of HTEs in a wild boar's kidney presented in literature (**Bilandžić et al., 2010; Prevendar Crnić et al., 2015; Pilarczyk et al., 2010; Gašparik et al., 2017**) were higher more than 5 times than in muscle or liver. In **Table 9** were presented 15 measured HTEs in the kidney of a wild boar hunted in the Raša estuary and literature data for different sites.

Regulation (2006) prescribes maximum values for Cd and Pb equal to 1 mg/kg w.wt. and 0.5 mg/kg w.wt., respectively. These elements in the analysed kidney of a Raša wild boar exceeded prescribed values. The concentrations of Pb were 85 times higher than the recommended one. The contamination of Cd and Pb could be due to mining and smelting activities (**Reglero et al., 2008; Mulero et al., 2016**).

The concentrations of Cd in an Istrian wild boar hunted in the Raša estuary area were lower than in wild boars hunted in six continental areas, such as Sisak-Moslavina, Brod-Posavina, Vukovar-Srijem, Požega-Slavonia, Virovitica-Posavina and Osijek-Baranja (**Bilandžić et al., 2010**). The concentrations of Pb in an Istrian wild boar were higher than others. These very high Pb concentrations could be from the remains of the bullets.

Table 9: The concentrations of HTEs in the kidneys of wild boars in Raša, continental Croatia, Italy, Sweden and Slovakia. ([a]**Bilandžić et al., 2010;** [b]**Amici et al., 2012;** [c]**Malmsten et al., 2021;** [d]**Gašparik et al., 2017**) The underlined values exceed maximum levels in **Regulation, 2006**. The maximum value for Pb is 0.15 mg/kg w.wt. and for Cd it is 1 mg/kg w.wt.

c (mg/kg w.wt.)	Raša	Cont. Croatia[a]	Italy[b]	Sweden[c]	Slovakia[d]
Fe	301.3			129	
Zn	23		32	25.1	19.9
Se	1.7			2.3	
Cu	4.4		5.6	6.67	3.78
Ni	<0.006				
Mn	1.4			1.66	
Cr	0.0074		0.098		
Co	0.036				
Mo	0.98				
V	0.043				
Al	2.4				
As	0.052			0.02	
Pb	43	0.1-0.4	0.298	0.14	0.345
Ba	0.021				
Cd	1.2	0.86-4.58	0.085	4.16	2.73

The concentrations of As and Fe in an Istrian wild boar's kidney were higher than in Swedish by 2.6 and 2.3 times, respectively. The concentrations of Zn and Cu were higher by 15% and Cd was lower by 2 times than in Slovak wild boar's kidneys. The Hg, Cd and Pb in wild boars should continue to be measured against the potential risk of environmental contamination by HTEs.

4. Conclusion

In this study, HTEs (As, Ba, Cd, Cr, Co, Cu, Mn, Mo, Ni, Sc, Se, Sn, Sr, V, Zn, etc.) were analysed in the estuarine sediments, fish, mussels and wild boar's kidney from the Raša River estuary. The aim was to determine whether they are a consequence of possible pollution of this area due to separation and transport of seleniferous Raša coal from Štalije to the Bršica port. The estuarine sediment collected as the closest to the former Raša coal separation unit Štalije is enriched in V, Sr, Ni, Cu and Pb. They were found to be up to 30% higher compared with the other two sediment samples. The concentrations of Cr and Ni in estuarine sediments were 1.5 times higher compared to the Plomin Bay with an active thermal plant powered by local coal. This indicates possible environmental pollution with V, Sr, Ni, Cu, Cd and Pb by waste water from the long-term use of coal separation devices.

Only the concentrations of Cr and Cu in the estuarine sediments were increased with a decrease in the size fraction (>250 μm, >120 μm, >63 μm and < 63 μm). This could be due to the desorption and solubilisation of particulate metals as salinity.

It was calculated that tin was a major contaminant which can indicate heavily contaminated sediments in the Raša River estuary. High values EF (23) and *Igeo* (3.6) of Sn could reflect the local anthropogenic influence of boat paints and boat repair materials.

The concentrations of Se and V in fish samples were found to increase as the fish grow* in size. Selenium and vanadium are the elements notably enriched in Raša coal. According to **Regulation (2006)** values for selected trace elements (Pb, Cd, and Hg) in food, concentrations of HTEs in white fish and wild blue mussels were not elevated. Cadmium and Pb in a wild boar's kidney exceed the recommended values. Lead concentrations were up to 80 times higher than the allowed recommendation, likely due to hunting tools (bullets). These results call for further geochemical investigations of the local environment.

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SAŽETAK

Razine opasnih elemenata u tragovima u sedimentima ušća, ribama, školjkama i divljoj svinji uzorkovanim na području Raškoga zaljeva (Hrvatska)

Nanos rijeke Raše gomila se na ušću koje čini dio Raškoga zaljeva (zapadna Hrvatska). Na lokalno područje prije nekoliko desetljeća neekološki je utjecala raška industrija ugljena. Cilj istraživanja bio je utvrditi razine opasnih elemenata u tragovima (HTE) u sedimentima donjega ušća, ribama i dagnjama prikupljenim s dvaju lokaliteta nizvodno od ušća rijeke Raše te doniranome bubregu ulovljene divlje svinje. Pseudototalne koncentracije 21 elementa u sedimentima određene su pomoću fluorescencije X-zrakama (XRF). Rezultati su pokazali da je sediment uzorkovan najbliže nekadašnjemu postrojenju za separaciju ugljena Štalije obogaćen V, Sr, Ni, Cu i Pb. Koncentracije elemenata u ribama, dagnjama i u bubregu divlje svinje određene su primjenom induktivno spregnute plazme – masene spektrometrije (ICP-MS tehnike) nakon digestije. Rezultati su pokazali da Pb, Cd i Hg u ribi i divljim dagnjama nisu povišeni u odnosu na razine onečišćenja u hrani propisane Uredbom. Olovo i kadmij u bubrezima divlje svinje premašili su propisane maksimalne vrijednosti za hranu. Ova studija opravdava daljnja geokemijska istraživanja okoliša Raškoga zaljeva.

Ključne riječi:
ušće rijeke Raše, sediment, ribe, školjke, divlja svinja

Author's contribution

Tatjana Ivošević (1) (Assistant Professor, PhD, Faculty of Maritime Studies, Rijeka) participated in the sampling campaign, carried out and interpreted data analysis, designed graphical and tabular presentation of the results, wrote and editing the entire manuscript. **Miloš Momčilović (2)** (Senior Research Associate, PhD, Vinča Institute) conducted XRF analysis of sediment samples and edited the entire manuscript. **Nina Bilandžić (3)** (Senior scientists, PhD, Veterinary Sciences) conducted ICP-MS chemical analysis and edited the manuscript. **Marija Sedak (4)** (Senior scientists, PhD, Veterinary Science) prepared fish, mussel samples and the kidney of a wild boar for analysis and conducted ICP-MS chemical analysis. **Jelena Petrović (5)** (Research assistant, Vinča Institute) prepared sediment samples and conducted XRF analysis of the sediment samples.