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Source / Izvornik: **Geologia Croatica, 2022, 75(3), 411 - 420**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:237:696550

Geologia Croatica
Journal of the Croatian Geological Survey and the Croatian Geological Society
2022 | 75/3 | 411–420 | 2 Figs. | 5 Tabs. | www.geologia-croatica.hr

Distribution of sulphur, phosphorous, iron, and trace elements in bottom sediment cores, mussels and fish from the Punat Bay (Island of Krk, Croatia)

Tatjana Ivošević[1]*, Ivan Halkijević[2], Nina Bilandžić[3], Katarina Licht[2], Marija Sedak[3], Ivica Orlić[4], Damir Bucković[5] and Štefica Kampić[5]

[1] University of Rijeka, Faculty of Maritime Studies, Rijeka, Croatia (*corresponding author: tatjana.ivosevic@pfri.uniri.hr ; tatjana.ivosevic14@gmail.com)
[2] University of Zagreb, Faculty of Civil Engineering, Zagreb, Croatia
[3] Croatian Veterinary Institute, Zagreb, Croatia
[4] Independent researcher, Krk, Croatia
[5] University of Zagreb, Faculty of Science, Department of Geology, Zagreb, Croatia

doi: 10.4154/gc.2022.29

Article history:
Manuscript received June 17, 2022
Revised manuscript accepted September 02, 2022
Available online October 26, 2022

Abstract

Ships and associated anthropogenic activities release a number of contaminant elements into the marine environment which can be particularly concentrated in restricted circulatory environments including Bays and marinas. One such locality is a Punat Bay, situated at the southern coastline of the island of Krk (west Croatia), which is the largest Croatian marina. The aim of this study was to examine depth profiles of sulfur (S), phosporous (P), iron (Fe), and trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sn, Sr, Ti, U, V, Y, and Zn) in six sediment cores (down to 20-30 cm), and from mussels and fish from Punat Bay, by determining their levels with ICP-OES. Data analysis showed that the majority of variables were elevated in a sediment core located closest a port of the marina. Minimum to maximum S, P, and Fe levels in sediments were as follows: 0.4-2.4%, 0.04-320 mg/kg, and 0.2-2.3%, respectively. Correlations among S, P, Fe, and various trace elements were mostly positive ($p<0.05$). Trace elements were not increased in mussels and fish. This paper shows that the Punat marina has only a limited impact on the environmental status. Several potentially toxic trace elemens (Pb, Cu, etc.) were found to be elevated in a sediment core located closest to the marina.

Keywords: sulfur; phosporous; iron; sediment cores; mussels; marina; contamination

1. INTRODUCTION

Harbours are important for the economic and social development of coastal areas. However, they also represent anthropogenic sources of contaminant emissions CUKROV et al., 2011). The increase in global trade and the consequent increase in the demand of port-services make harbours and ships key sources of wastewater input into the marine environment (SHU et al., 2022). Oily wastewater from shipping waste and marine activities are polluting the marine environment across the globe, and solving such a complex problem by using treatment technologies is very challenging (HAN et al., 2019; RAĐENOVIĆ & MEDUNIĆ, 2015; SAHIN & VARDAR, 2020). Wastewater emissions contain a number of variously toxic and harmful substances, that can impact the reproductive and growth characteristics of marine organisms and life and the environment in general (TERNJEJ et al., 2013; BUSKEY et al., 2016; WU et al., 2017; SASMAZ et al., 2019). This is particularly hazardous in the case of karst-water systems (FIKET et al., 2017a), which are quite sensitive to the pollution caused by wastewater effluents. Karst requires careful exploitation and effective, efficient protection, mostly due to direct connections between the surface waters and highly permeable aquifers (PARISE et al., 2009, 2015; JEBREEN et al., 2018).

Coastal marine environments are particularly vulnerable to pollution by trace elements directly discharged into them. Multidisciplinary studies of their fate in such settings are necessary due to their long-lasting cycles, and consequences for human, animal, and plant health. In this regard, sediment cores provide a historical record of activities occurring in the watershed of a particular bay or estuary (CINDRIĆ et al., 2015; FIKET et al., 2017a). Namely, sedimentary geochemical composition enables an estimate to be made of background levels and changes in input over a period of time (KANG et al., 2022).

One such environment is the Croatian Punat marina (Fig. 1), which is among the leading nautical tourism centres on the Croatian coast. It is the oldest and one of the leading marinas in the Adriatic, also containing a shipyard. Ports are important transport hubs that contribute to the social and economic development of coastal areas with an impact on commerce, tourism and often, with potential negative effects on pollution and health. VALKOVIĆ et al. (2007) investigated the Punat locality and discovered anthropogenic loads of Cu, Zn, and Pb from the local marina and the shipyard. The main sources of contamination from the chemical compositions of the sediments in the Punat Bay were antifouling paints. These contaminations were reflected in the elevated concentrations of Zn, Cu, and Pb in the upper sediments in the vicinity of marina working area and the shipyard. The contamination of the coastal environments with Sn completely originates from tributyltin (TBT) antifouling paints. FURDEK TURK et al. (2020) determined that TBT input via antifouling paints resulted in high enrichment of coastal Punat sediments with inorganic Sn. OREŠČANIN et al. (2002) gave a detailed account of the evaluation of the anthropogenic influence on the chemical compositions of the sediments in Punat Bay. They determined that the antifouling paints were the main source of contamination which was reflected in the elevated levels of Zn, Cu, and Pb in the four uppermost centimetres of fine-grained

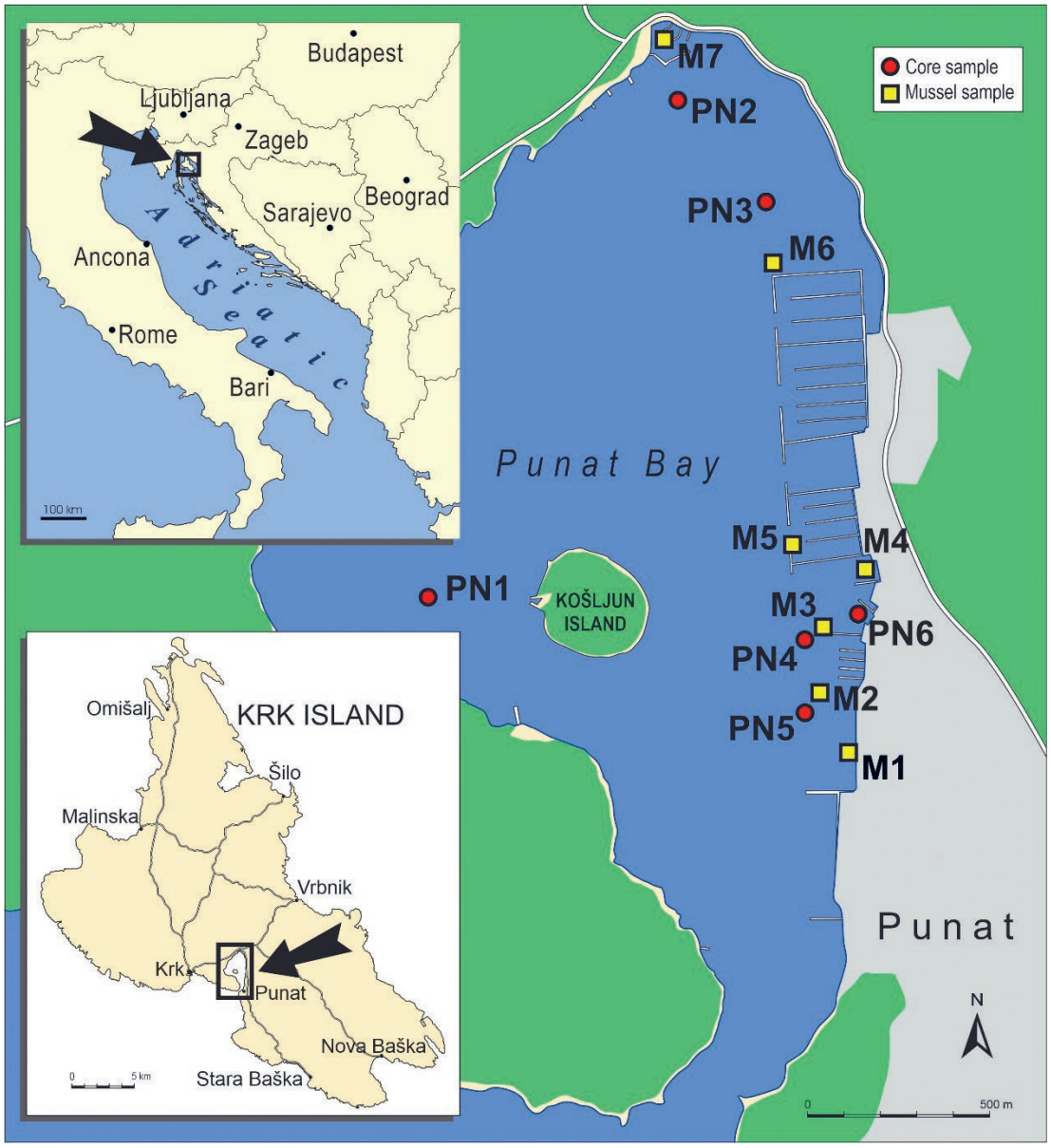

Figure 1. Map of the study area.

sediments in the vicinity of the marina working area and the shipyard. Their results also showed the influence of the marina on distant parts of Punat Bay as a consequence of the morphology and the climate conditions influencing the efficiency of the cleaning mechanisms.

As global consumption of seafood rises (FOX et al, 2018), it's important to research the potential hazardous trace element content, especially of non-essential metals Pb, Cd, As and Hg in fish samples and wild mussels. Trace elements concentrations of Zn, Cu, As, Pb, Cd and Hg in wild blue mussels collected from 2005 to 2007 were measured from the coastal areas of the southeastern Adriatic (MARKOVIĆ et al, 2012). The obtained data for Cd and Pb indicated that metal levels from the Montenegrin coastal areas were much higher than the concentrations reported for other Adriatic and Ionian Sea areas (CARDELLICCHIO et al., 2008; KLJAKOVIĆ-GASPIĆ et al., 2006; KLAKOVIĆ-GASPIĆ et al., 2007). Against the toxicities of Cd and Pb, zinc is one of the essential trace elements for humans and its toxicity is rare. The concentrations of Zn in Montenegrin mussels were higher than ones in the Ionian Sea in southern Italy (CARDELLICCHIO et al., 2008) but lower than those sampled from the eastern Adriatic coast (KLJAKOVIĆ-GASPIĆ et al., 2006), or from the Mali Ston Bay coast (KLAKOVIĆ-GASPIĆ et al., 2007). More recently, trace elements in blue mussels including Al, Fe, Zn, Cu, Ni, Mn, Cr, As, Pb, Cd, etc. were measured in the Gulf of Trieste (BAJC & KIRBIŠ, 2019), Raša Bay (IVOŠEVIĆ et al, 2022), Šibenik Bay (BOGDANOVIĆ et al, 2014) and Boka Kotorska Bay (PEROŠEVIĆ et al., 2018). The highest measured concentrations of Al and Fe were in Raša Bay. These concentrations were up to five times higher than the concentrations of these elements in other sites. Other measured trace element concentrations were differences within 30% of earlier measurements of the same elements. The Pb and Cd concentrations did not exceed prescribed values for Pb of 1.5 mg/kg ww, and for Cd of 1 mg/kg ww (REGULATION, 2006).

Different fish tissues such as muscle tissue or liver are commonly used as indicators of the degree of contamination of the marine environment by hazardous trace elements. Cadmium and lead were determined in the muscle tissue of fish species sampled in 1995 from the eastern Adriatic. In the muscle tissue, Cd and

Pb concentrations were among the range of concentrations for fish samples in the Mediterranean and these results provided no proof of the general pollution of the Adriatic (KLJAKOVIĆ-GAŠPIĆ et al, 2002). SALIMANEC GRGEC et al (2022) reported total Hg, total As and Se in fish samples (e.g. Sparus aurata) available in a Croatian market which were characterized by their origin from the Adriatic Sea. Wild-caught fish had generally higher levels of As (11 times) and Hg (29 times) and Se (1.6 times) than farmed fish of the same species.

The aim of this study was to examine the depth profiles of sulfur (S), phosphorous (P), iron (Fe), and trace elements (Al, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sn, Sr, Ti, U, V, Y, and Zn) in six sediment cores (down to 20-30 cm), wild blue mussels and fish sampled and caught in Punat Bay, in the context of possible anthropogenic influences on the marina's environment and other port and tourism activities such as boat painting, domestic waste etc.

2. MATERIALS AND METHODS

2.1. Geological characteristics of the study area

The island of Krk is the northernmost large island in the Mediterranean, and is located in Kvarner Bay. It is the largest island of the Adriatic Sea with a surface area of 409.9 km^2. It belongs to the western part of the Outer Dinarides, composed mainly of Cretaceous shallow-water carbonates of the Adriatic Carbonate Platform (VLAHOVIĆ et al., 2005). These deposits are overlain by Palaeogene carbonate ramp shallow-marine carbonates in certain locations, and later by flysch (deep-sea trough marls in alternation with carbonate conglomerates, arenites, and siltstones), which formed when ramp carbonate production couldn't keep up with subsidence (ĆOSOVIĆ et al., 2008; GULAM et al, 2014). The youngest Palaeogene deposits at Krk island are represented by the so-called Jelar carbonate breccias formed by poly-phase tectonic fracturing of the apical parts of the overturned anticline, resulting in the crushing of clasts and collapse into a complex system of deep fractures largely without surficial transport (VLAHOVIĆ et al., 2007).

The Punat Bay study area's immediate environment is made up of Upper Cretaceous and Palaeogene to Quaternary deposits (ŠUŠNJAR et al., 1970). The west and south coast of Punat bay is predominantly built of microcrystalline dolomite with frequent intercalations of fossiliferous limestone beds containing numerous foraminifera species, e.g., *Nummoloculina heimi* BONET, *Nezzazata simplex* OMARA as well as with frequent occurrences of mollusc shells such as Chondrodonta and Nerinea, indicating a Cenomanian/lowermost Turonian age. These carbonates have a different degree of fissuring and karstification and form the typical karstic landscape. The east coast of the bay is covered by Pliocene to Quaternary talus breccias composed of silty clay and carbonate fragments and a little further to the east, by the Oligocene Jelar breccias.

2.2. Sampling of bottom sediments

Sampling locations of marine sediments in Punat Bay were selected to be at a depth of 3 to 4 m due to a home-made core sampler dimension. Its main elements are a plastic pipe with a diameter of 9,5 cm and a non-return valve that prevents the loss of sediment when drawing the pipe from the sea. The lengths of samples collected with this sampler were typically in the range of 30 to 60 cm. The six core samples were collected during October 20th, 2020 sampling excursions. The sampling locations are shown on the map in Figure 1 and are labelled PN1-PN6 in a clockwise sequence within the lagoon. The seawater depths at these locations vary from 3.5 m (PN1, PN2) to 4 m (PN3, PN4, PN5, PN6).

Immediately after their collection, each core sample was cut into 1 cm segments for the first 10 cm, and then about 10 cm sections below 10 cm core depth using a specially designed guillotine in order to obtain the concentration depth profiles of the pollutants in the sediment.

2.3 Sampling of biota

Wild blue mussels (*M. galloprovincialis*) were sampled at 1 m below sea level where the depth of Punat Bay, is about 3m, on the 26th January 2021. Sampling sites are numbered M1 to M7 on Figure 1. Around 0.5 kg of mussels were collected at each site, placed into polyethylene bags with seawater and transported to the Laboratory for Determination of Residues at the Croatian Veterinary Institute in Zagreb. The 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.

The fish samples (*Sparus aurata* and *Lophius piscatorius*) were collected in Punat Bay close to the sediment sampling sites PN1 on the 26th January 2021. The fish were beheaded, gutted, washed, and filleted. Only the edible portions were utilized for the analysis. Fish fillets (tissue) were carefully removed from the fish bones without any contact with guts and roes. This was to prevent any contamination being introduced to fish tissue. Fish fillet was also homogenised in a blender and stored at − 20 °C until analysis.

2.4. Analytical work

2.4.1. Sediment samples

All glassware and containers used were previously cleaned by soaking for 48 hours in 10% HNO_3 solution and rinsed with high-purity water before use. Sediment core samples, were sieved to <0.063 mm and weighed. Afterwards, 5 mL of HNO_3 and 15 mL of HCL were added. A wet digestion of the samples was performed on a hot plate for 4 h. It should be noted that this is not a complete digestion method (Potts, 1992). The samples were filtered through a blue coloured filter paper and the precipitate was washed with distilled water. After the cooling step, the filtrate was quantitatively transferred to a 50 mL volumetric flask and filled to the mark with distilled water.

An Inductively coupled plasma optical emission spectrometer (ICP-OES) was used for elemental analysis. All measurements were performed using the Agilent 5900 SVDV ICP-OES system equipped with a Sea spray concentric glass nebulizer and a double-pass glass spray chamber. Simultaneous axial and radial viewing mode was used for element determination, while fitted background correction and 3 replicates were used to measure the analytical signal. Quantification was performed by linear weighted regression of the calibration curves. The appropriate emission lines were selected using the IntelliQuant Screening feature in the ICP Expert software, which allows full spectrum measurement of each sample and determines which wavelengths provide the best result. Calibration standards (0.01, 1, 10 µg/L) were prepared by diluting the 10 µg L-1 stock multi-element standard solutions (71A and 71B, Inorganic Ventures, USA) in 2% HNO_3 and 1% HCl. For quantification of concentrated elements, samples were diluted 10-fold and measurements were re-

peated. All solvents and reagents used were of analytical purity and were manufactured by VWR Chemicals BDH (USA).

2.3.2. Fish and mussels

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%). 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

Table 1. Basic statistical parameters of analysed variables in six sediment cores (PN1-6). (The concentrations are presented in mg/kg. The concentrations of Fe and S are presented in g/kg*)

Elements		As	Ba	Cd	Cr	Cu	Fe*	Hg	Mn	Mo	Ni	P	Pb	S*	Sn	U	V	Zn
PN1	N	12	12	12	12	12	12	12	12	12	12	12	12	12	4	12	12	12
	Min	0.160	18.1	0.860	14.0	9.04	3.05	0.060	61.2	3.40	5.30	0.090	2.37	3.89	0.500	2.38	11.6	27.1
	Max	10.5	28.0	1.88	21.1	46.2	4.93	4.59	81.5	15.8	13.5	111	12.9	12.8	2.96	32.2	21.0	111
	Mean	4.25	23.0	1.33	17.2	25.3	3.96	1.39	70.3	7.08	9.72	40.0	7.84	7.17	1.55	14.5	17.2	67.3
	Stdev	3.68	2.58	0.370	1.70	11.2	627	1.37	6.27	3.94	3.09	48.4	4.47	3.65	1.04	10.6	2.88	24.3
	Median	3.52	23.2	1.25	17.2	26.1	3.80	1.13	70.2	5.93	10.9	12.3	8.80	4.94	1.37	14.9	17.0	65.4
	25 prcntil	1.03	21.0	0.955	16.3	14.8	3.46	0.193	64.4	3.83	5.87	0.670	2.52	4.69	0.665	3.95	15.2	49.9
	75 prcntil	6.45	24.8	1.64	17.7	33.8	4.65	2.05	76.0	9.77	11.75	103	12.0	11.7	2.62	22.7	20.3	84.8
	Coeff. var	86.7	11.2	27.9	9.93	44.1	15.8	99.0	9.12	55.6	31.7	121	57.0	50.9	67.1	72.9	16.7	36.1
PN2	N-	14	14	14	14	14	14	14	14	14	14	14	14	14	3	14	14	14
	Min	0.5	21.4	0.910	21.8	14.8	6.61	0.180	76.0	2.94	13.1	0.220	4.11	5.53	2.51	4.71	25.0	40.3
	Max	15.6	33.1	2.05	46.4	60.8	10.1	3.89	117	27.3	47.2	144	32.1	22.4	20.5	27.5	50.0	167
	Mean	6.99	24.9	1.32	32.5	30.2	8.51	1.42	93.6	14.5	20.4	38.5	13.2	11.2	9.19	12.8	37.5	76.4
	Stdev	4.55	3.610	0.320	5.76	14.8	1.18	1.22	11.3	7.75	8.25	50.7	8.58	5.67	9.86	7.11	6.27	35.4
	Median	8.74	23.7	1.29	31.4	26.4	8.32	1.04	9.15	14.3	18.4	122	11.5	8.83	4.55	9.75	38.2	68.7
	25 prcntil	2.68	22.0	1.04	29.7	17.6	7.47	0.25	85.4	7.66	16.5	43.9	5.5	8.17	2.51	7.66	33.4	46.4
	75 prcntil	9.74	26.5	1.52	34.2	40.3	9.65	2.46	101	21.7	20.7	96.9	16.0	13.4	18.5	19.8	40.0	92.3
	Coeff. var	65.0	14.5	2.47	17.7	48.9	13.8	86.1	12.02	53.6	40.5	131.8	65.1	50.4	107	55.4	16.7	46.3
PN3	N	13	13	13	13	13	13	13	13	13	13	13	13	13	4	13	13	13
	Min	1.00	18.4	0.900	29.9	13.3	7.00	0.060	76.8	5.83	17.1	1.24	6.30	6.40	1.56	6.05	26.1	42.8
	Max	11.5	34.9	4.49	51.1	52.8	11.8	2.78	106	27.7	30.0	180	41.8	24.3	2.57	25.3	51.9	163
	Mean	5.62	26.7	2.30	39.8	28.0	9.41	1.06	92.7	15.5	21.7	110	16.7	13.4	1.95	14.0	42.5	93.5
	Stdev	3.370	6.4	1.160	5.50	14.72	1.31	0.966	9.6	7.6	3.39	62.50	10.3	5.43	0.470	6.1	7.0	40.4
	Median	4.34	26.0	2.31	39.5	21.7	9.26	0.920	91.0	16.5	20.9	129	11.8	11.7	1.84	11.7	41.3	82.5
	25 prcntil	3.02	20.3	0.975	36.0	15.8	8.39	0.225	83.7	7.71	19.6	67.1	10.1	9.47	1.57	9.80	38.4	61.1
	75 prcntil	8.38	33.7	3.11	41.9	41.8	10.4	1.86	100	21.8	22.6	146	24.4	18.4	2.45	18.3	48.6	138
	Coeff. var	59.9	23.9	5.04	13.8	52.6	1.39	90.6	10.3	48.6	15.7	56.7	60.8	40.5	2.43	43.6	16.6	43.2
PN4	N -PN4	12	12	12	12	12	12	12	12	12	12	12	12	12	8	12	12	12
	Min	0.39	19.9	0.82	18.7	13.0	5.51	0.030	70.7	2.93	8.91	0.040	4.51	7.20	0.500	2.95	21.1	39.5
	Max	13.2	40.6	4.43	33.0	386	9.80	3.00	85.0	47.8	21.7	156	37.8	24.5	9.91	24.1	46.4	121
	Mean	4.96	24.7	2.39	26.4	57.7	7.10	0.946	75.6	21.1	15.6	79.2	11.8	13.7	2.41	10.3	29.8	89.0
	Stdev	4.45	5.64	1.00	4.05	104	1.39	1.21	4.3	16.50	3.6	51.0	9.1	6.32	3.18	6.24	8.35	27.9
	Median	2.61	22.9	2.61	27.3	24.4	6.79	0.295	75.7	16.9	15.6	93.4	8.67	11.7	1.20	9.33	26.1	88.5
	25 prcntil	1.36	21.6	1.44	22.7	17.3	5.91	0.053	71.1	5.00	12.30	22.5	6.63	7.68	0.523	5.14	23.6	71.8
	75 prcntil	9.62	27.4	2.87	29.1	41.9	8.17	2.35	77.5	34.4	18.6	112	13.3	19.3	2.94	15.0	37.1	117
	Coeff. var	89.7	23.0	42.2	153	18.1	196	128	5.69	78.5	23.4	64.4	77.3	46.1	132	60.4	28.0	31.3
PN5	N	13	13	13	13	13	13	13	13	13	13	13	13	13		13	13	13
	Min	1.26	26.0	1.07	12.0	11.7	3.82	0.27	66.9	1.85	12.4	0.270	0.060	4.97		12.4	4.37	52.4
	Max	10.3	44.0	4.97	24.2	34.9	8.71	3.68	147	16.7	55.1	123	11.4	17.9		26.1	7.40	103
	Mean	5.86	34.8	2.35	19.1	20.7	5.47	1.83	98.1	11.4	19.2	25.1	3.28	8.22		18.4	5.57	74.6
	Stdev	3.24	5.6	1.41	3.6	7.4	1.44	1.15	22.5	4.4	10.9	38.4	3.34	3.21		7.1	3.74	12.8
	Median	5.59	35.8	1.46	19.7	17.6	4.84	1.74	99.1	12.1	16.7	8.73	2.46	7.51		18.7	5.47	69.8
	25 prcntil	2.57	29.6	1.34	17.0	14.9	4.56	0.73	80.9	8.12	14.5	25.5	0.295	6.65		15.6	4.94	68.5
	75 prcntil	9.17	38.5	3.38	22.1	26.7	6.19	2.84	111	15.4	18.1	34.8	5.00	8.91		20.2	6.14	78.5
	Coeff. var	55.4	15.9	60.0	19.0	35.7	2.65	6.29	23.0	38.2	57.2	153	102	39.0		20.3	16.1	17.2
PN6	N	4	4	4	4	4	4	4	4	4	4	4	4	4	1	4	4	4
	Min	12.1	118	1.10	57.6	243	18.1	0.260	148	2.78	31.0	0.370	101	10.0	12.0	9.46	55.4	410
	Max	21.8	435	3.83	70.4	519	23.2	3.97	184	6.05	48.8	320	372	22.2	12.0	20.6	67.6	586
	Mean	17.4	229	3.13	66.0	384	20.4	2.79	162	4.70	43.0	81.3	209	13.5	12.0	16.5	60.8	472
	Stdev	6.3	115.0	1.35	24.8	142.3	7.64	1.390	61.0	1.72	15.5	127.0	97.8	5.48	0	6.11	23.1	171.0
	Median	17.8	181	3.79	67.9	387	20.2	3.47	159	4.98	46.0	2.56	182	10.8	12.0	18.0	60.0	446
	25 prcntil	13.3	130	1.77	59.9	267	18.5	10.6	149	3.30	34.4	0.728	116	10.1	12.0	11.1	56.5	411
	75 prcntil	21.1	376	3.82	70.1	498	22.6	3.85	179	5.81	48.5	240	330	19.4	12.0	19.4	65.8	560
	Coeff. var	23.4	61.8	43.2	87.6	31.1	10.5	61.1	10.0	29.3	19.1	196	55.7	4.3	0	31.0	83.4	17.5

a 50 mL volumetric flask and filled up to the mark with ultra-pure water. Because on-line introduction of an internal standard by peristaltic pump was carried out, 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 fish and mussel samples were analysed after microwave digestion with nitric acid. The decomposed samples were diluted with demineralized 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 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.).

2.5. Data analysis

Data analysis was conducted with the free PAST software (HAMMER et al., 2001). It included calculations of basic statistical parameters, and nonparametric Kendall's tau correlation coefficients, and Kruskal–Wallis test (level of significance was lower than 0.05).

3. RESULTS AND DISCUSSION

3.1. Element levels in bottom sediment cores

Basic statistical parameters of analysed variables in six sediment cores are shown in Table 1. The range of values of S, P and Fe across all cores are as follows: 0.4-2.4%, 0.04-320 mg/kg, and 0.2-2.3%, respectively. They are either comparable to or lower than the respective values reported by BRUNOVIĆ et al. (2019) as follows: 0.1-4.3%, 100-1000 mg/kg, and 0.6-5.2%. The authors interpreted high S values as resulting from the development of a restricted and oxygen poor water body (Island of Cres). REIMANN & DE CARITAT (1998) report natural S levels in stream overbank sediments (marine bottom sediments are not included in the publication) at 0.01%. MU et al. (2021) report fractionation and availability of P in sediments of Xiaowan and Nuozhadu reservoirs in the middle and lower reaches of the Lancang River (China). Their P levels ranged 490-550 mg/kg, which is slightly above the maximum P value in Punat Bay in the PN6 core (320 mg/kg, Table 1). They also interpreted sediment column P levels in the context of the release of Fe and S from reactive phases. The behaviour of Fe, Mn, and P in sediments mostly depends on redox processes, and P (and S as well) mostly originates from the breakdown of organic matter, which also affects redox conditions (SALOMONS & FOERSTNER, 1984). The same is true for S levels, BRUNOVIĆ et al. (2019) interpreted high Mo values (0.1-45 mg/kg) as being due to oxygen depleted conditions. Since Mo values in this study ranged between 1.4-48 mg/kg, a similar interpretation could be ascribed to the Punat bottom sediments as S and Mo levels (Table 1) are fairly comparable with their respective values in the paper by BRUNOVIĆ et al. (2019). This study reports higher Cu (9-519 mg/kg) and Pb (0.1-372 mg/kg) values than respective ones in BRUNOVIĆ et al. (2019), i.e., 5.3-33.2 mg/kg, and 5.8-86.8 mg/kg. Also, Punat sediment Cu and Pb levels are much higher than their respective values (up to 64 mg/kg and 74 mg/kg) found in sediment polluted with fly and bottom ash (OREŠČANIN et al., 2005a). Herewith, the Punat sediments of the PN6 core (Fig. 1) can be considered as being polluted with Cu and Pb as the levels of both elements naturally are mostly well below 100 mg/kg in Adriatic sediments (FIKET et al., 2021; MEDUNIĆ et al., 2018), and below 50 mg/kg in river sediments (OREŠČANIN et al., 2005b). MIKULIĆ et al. (2004) reported four sources of Cu, Zn and Pb in sediments, not only the antifouling paints, but also arising from traffic, long-range transport of aerosols and eroded materials. Also, a few samples had quite high Hg levels (3-4.6 mg/kg) that are slightly less than the maximum Hg value (6.5 mg/kg) in the Sava River sediment, polluted by weathering of Hg-Pb-Ba ores (PAVLOVIĆ et al., 2004). According to PAVLOVIĆ et al. (2005), such high levels of Hg represent on average a 100-fold increase with respect to clean sediments. STANKOVIĆ et al. (2014) report an Hg max value of 0.1 mg/kg in surface Adriatic sediments. Levels (mg/kg) of As, Ba, Cr, Mn, Mo, Ni, Sn, U, V, and Zn in Raša Bay sediments are reported by FIKET et al. (2021) as follows: 6, 150, 120, 500, 2, 50, 0.3, 3, 70-100, and 60-90, respectively. Respective levels (mg/kg) in this study were the following: 0.2-22, 18-434, 5-70, 16-183, 1.4-48, 5.3-55, 0.5-20, 0.3-32, 5.1-68, and 27-586. Their comparison clearly shows that the Punat sediments are slightly enriched in As, Ba, Cu, Mo, Pb, Sn, U, and Zn, likely due to the influence of anthropogenic activities related to the marina. Furthermore, Table 1 shows the largest RSD values for As, Cu, Hg, P, Pb, Sn, and U as a consequence of anthropogenic processes, which usually result in high RSD values of trace elements in the environment, causing their skewed distributions (REIMANN & FILZMOSER, 2000; PAVLOVIĆ et al., 2004, 2005).

Based on p values 0.003 and 0.01, Kruskal-Wallis test confirmed for S and P, respectively, that six sediment cores were mutually significantly different. Similar p values were found for As, Cr, Cu, Fe, Mo, Ni, Pb, Ti, V, and Zn as follows: 0.03, 8E-10, 0.002, 1E-08, 0.001, 2E-07, 1E-06, 8E-07, 3E-09, and 0.002, respectively. Such low numbers are indicative of a very strong difference among the sediment cores. Based on Mann-Whitney pairwise test, either all six sediment cores were mutually significantly different or cores PN1-5 were significantly different from the PN6 core. Analysed variables were elevated mostly in core PN6, situated closest to the ships in the marina (Fig. 1), as shown in Fig. 2. It presents a comparison of variable levels in sediment cores, and this is fairly in accordance with the aforementioned results of the Kruskal-Wallis test. Generally, box-plot patterns are fairly similar to each other (a convex 'curve' PN1-5 that peaks in PN6), except for U where in this case the null hypothesis was accepted (no difference among groups). Interestingly, U levels in the Punat sediments are fairly increased in all six sediment cores compared with U levels in the Adriatic sediments that are mostly less than a few mg/kg (FIKET et al., 2021; MEDUNIĆ et al., 2018). From Fig. 2 it can be assumed that mostly natural geochemical pro-

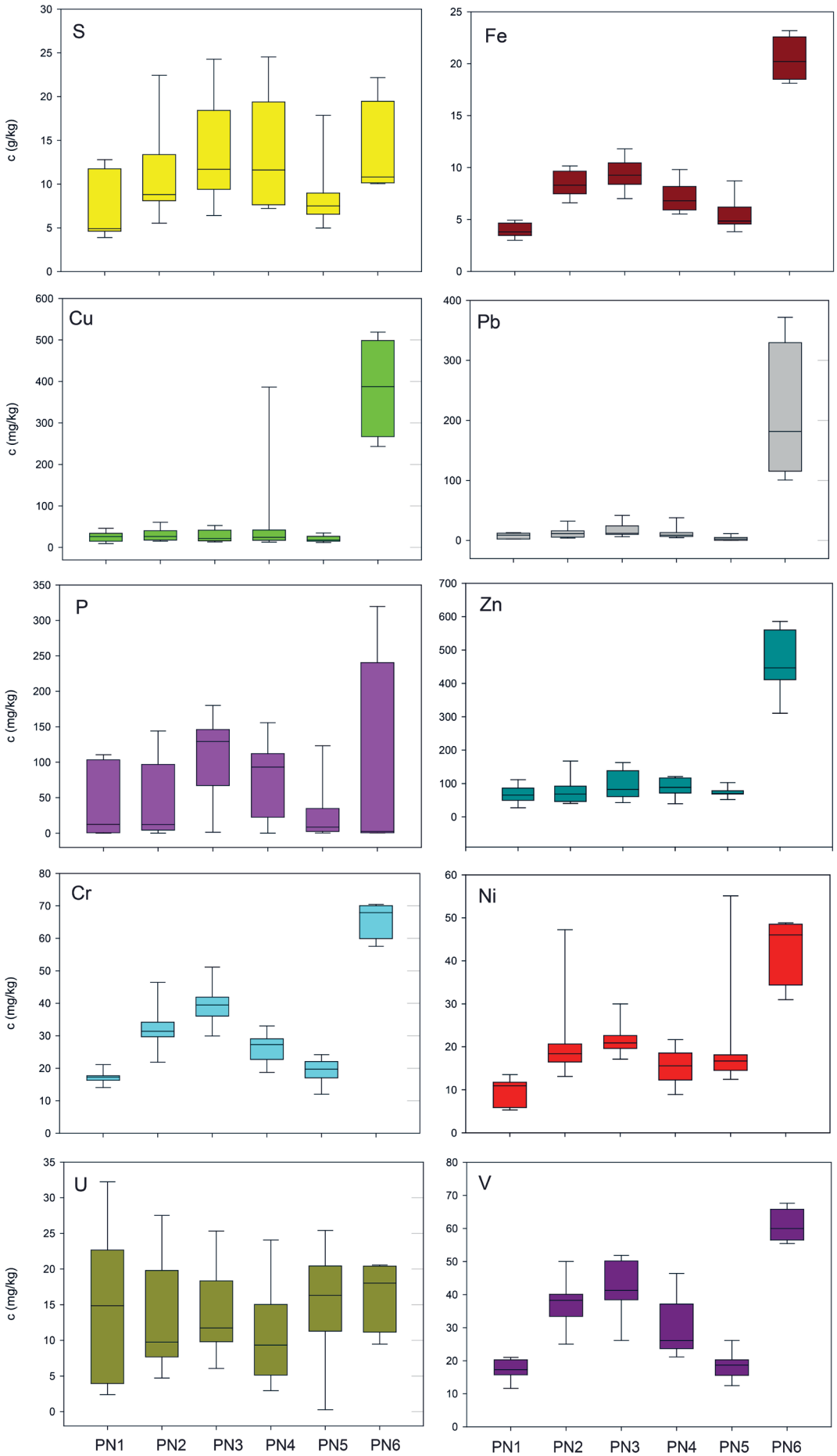

Figure 2. Descriptive statistical parameters for concentrations of selected elements obtained in sediment cores (PN1-6).

cesses have governed the distribution of the analysed variables in the Punat bottom sediments at the sites PN1-5, while site PN6 has been adversely impacted by the port and marina.

Kendal tau correlation coefficients ($p<0.05$) among analysed variables can be found in Table 2. Primarily, the focus was put on relationships among S as a fingerprint element of the presence of organic matter, and the rest of variables. It is well established that the organic fractions of sediments act as reservoirs of trace elements (PAVLOVIĆ et al., 2004; OREŠČANIN et al., 2005b), especially potentially toxic ones such as Ba, Cr, Cd, Cu, Ni, Pb, V, and Zn. Correlations in Table 2 are mostly positive, and they can be interpreted by various natural physico-chemical processes in sediments (MIHELČIĆ et al., 1996; MILLER et al., 1998; PAVLOVIĆ et al., 2005). It is noteworthy that S and Hg are mostly negatively correlated, and this might be explained by possible discrete Hg particles. Mercury is commonly lost to the environment as Hg^0 is characterized by low mobility and high density (LACERDA et al., 1995; MILLER et al., 1998), and therefore Hg distribution in aquatic environments is mainly controlled by physical and gravimetric parameters.

3.2. Element levels in mussels

Trace elements can accumulate in 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 potential danger to their health.

Concentrations of 16 trace elements in blue mussel samples (*Mytilus galloprovincialis*) sampled in Punat Bay are shown in Table 3. Their average concentrations decrease in the following order: Fe>Al>Zn>Cu>As>Mn>Mo>Se>V>Pb>Cr>Ba>Ni>Co>Cd>Ag. The levels of Fe, Al, Zn, Cu, Mn and As were higher than 1 mg/kg ww (ww-wet weight), and concentrations of the remaining elements were lower than 1 mg/kg ww.

According to the Croatian Regulation (2006), the maximum permissible limits set for Cd (1 mg/kg ww) and Pb (1.5 mg/kg ww) were higher than the concentrations of Cd and Pb in the Punat Bay wild mussels. As can be seen from Table 4, the mean concentrations of Pb, Zn and Cd in Punat Bay wild mussels were lower than in the mussel samples in Raša Bay (IVOŠEVIĆ et al., 2022), Gulf of Trieste, Seča (BAJC & KIRBIŠ, 2019), Šibenik Bay (BOGDANOVIĆ et al., 2014) or Boka Kotorska Bay (PEROŠEVIĆ et al., 2018). The mean concentrations of Cu and Mo in the Punat mussels were higher than those in the selected sites. Mean Cu and Mo concentrations were 1.5 higher than corresponding concentrations sampled in Raša mussels (IVOŠEVIĆ et al., 2022). Further, the mean Cu concentration in mussels were also 3 times higher than in Trieste mussels (BAJC & KIRBIŠ, 2019) and in Boka Kotorska mussels (PEROŠEVIĆ et al., 2018).

Table 2. Kendal tau correlation coefficients ($p<0.05$) among analysed variables (PN1-6 are sediment cores; +, and - signs mark positive and negative correlations (>0.7), respectively).

PN1		PN2		PN3		PN4		PN5		PN6	
+	-	+	-	+	-	+	-	+	-	+	-
Correlations ($p<0.05$) with sulfur:											
Al, Ba, Cr, Cu, Fe, Mn, P, V	Hg	Cu, Fe, P, Zn	Be, Cd, Hg, K	Ba, Co, Cu, Fe, Mn, Ni, P, Pb, V, Y, Zn		Co, Fe	Hg	Ba, Co, Ni	Be, Hg, U		
As-Be Al-Cr Fe-Cu Mn-Cu Mn-Fe	As-Co Cu-Mo P-U	P-Cu P-Fe Pb-Cr P-Zn		Cr-Ni P-Cu Pb-Cu P-Zn	Pb-Mo	Ni-Cr		Cd-Hg Mn-Fe Pb-Cd Pb-P P-Sr		Cu-Fe Pb-Ba	

Table 3. Concentrations of trace elements in wild blue mussels (mg/kg w. w.) from seven locations. Essential elements are listed above the drawn line, and non-essential ones are listed below it.

c(mg/kg w.w.)	M1	M2	M3	M4	M5	M6	M7
Fe	34.2	27.3	25.9	22.9	12.3	11.1	96.2
Zn	11.1	15.7	14.6	17.5	12.1	9.95	12.0
Se	0.353	0.404	0.309	0.262	0.248	0.242	0.289
Cu	3.10	3.74	4.36	5.34	2.89	2.37	10.9
Ni	0.115	0.140	0.074	0.155	0.069	0.066	0.074
Mn	2.33	1.36	0.71	1.49	0.689	0.762	1.42
Cr	0.189	0.203	0.109	0.108	0.078	0.058	0.264
Co	0.066	0.066	0.056	0.081	0.055	0.044	0.043
Mo	0.492	0.585	0.427	0.318	0.200	0.152	0.089
V	0.343	0.201	0.124	0.139	0.076	0.062	0.110
Al	42.1	31.8	17.7	25.3	11.2	6.24	21.2
As	2.67	2.42	2.65	2.00	1.91	1.76	1.69
Ba	0.258	0.137	0.117	0.136	0.051	0.029	0.079
Cd	0.029	0.038	0.034	0.032	0.025	0.023	0.028
Ag	0.004	0.009	0.006	0.004	0.004	0.002	0.012
Pb	0.168	0.165	0.157	0.276	0.097	0.075	0.078

Table 4. Comparison of concentrations (mean, min, max) of trace elements in wild blue mussels (mg/kg ww) with literature data from different sites in Adriatic Sea (a - IVOŠEVIĆ et al., 2022; b - BAJC & KIRBIŠ, 2019; c - BOGDANOVIĆ et al., 2014; d - PEROŠEVIĆ et al., 2018; e – Regulation, 2006).

c /(mg/kg w.w.)	Mean	Min	Max	Raša Bay[a]	Gulf of Trieste[b]	Šibenik Bay[c]	Boka Kotorska Bay[d]	Cro. Regulation[e]
Fe	32.8	11.1	96.2	175.7	42		55	
Zn	13.3	10.0	17.5	14.3	20		14.9	
Se	0.301	0.242	0.404	1.42				
Cu	4.67	2.37	10.9	3.65	1.3		1.49	
Ni	0.099	0.066	0.155	0.669	0.4		0.36	
Mn	1.25	0.69	2.33	4.21	1.80		1.59	
Cr	0.144	0.058	0.264	0.555	0.36		0.22	
Co	0.059	0.044	0.081	0.174	0.2		0.13	
Mo	0.323	0.089	0.585	0.215				
V	0.151	0.062	0.342	0.898				
Al	22.2	6.21	42.1	205.1			81.5	
As	2.15	1.69	2.63	3.16	4.0	2.29		
Pb	0.145	0.075	0.276	0.197	0.1	1.06	0.46	1.5
Ba	0.115	0.029	0.258	0.694			0.23	
Cd	0.030	0.023	0.038	0.140	0.2	0.19	0.17	1
Ag	0.006	0.002	0.012					
Sampling year	2021			2020	2015	2011	2015	

Cooper is toxic when it is present in higher concentrations than those necessary for organisms (MARIA & BEBIANNO, 2011). Higher concentrations of Cu in Punat Bay mussels could indicate a nanoform of copper from various applications such as liquid filtration, wood preservation, bioactive coating, etc. (GOMES et al., 2011) used for boat and yacht maintenance.

The concentrations of As in Punat mussels were 1.5 and 1.8 times lower than in the Raša mussels and the Trieste mussels. The concentrations of Pb were similar in mussel samples from three sites; Punat Bay, Raša Bay and the Gulf of Trieste, but concentrations of Pb were 3.2 and 7.3 times lower than in the Boka Kotorska mussels (PEROŠEVIĆ et al., 2018) and the Šibenik mussels (BOGDANOVIĆ et al., 2014). The obtained mean Cd concentration were from 4.6 to 6.6 times lower than in other sites. Lead and Cd-contaminating compounds in water and sediments can be related to commercial ship, recreational boat traffic, etc. (NOWROUZI et al., 2012). These (Pb and Cd) could be because lower intensity of maritime traffic and lower in-port activities in Punat Bay than other ports.

The concentrations of Cr and Zn in Punat mussels were lower than in Raša Bay and Gulf of Trieste. This could indicate smaller quantities of sewage water because elements such as Cr and Zn are related in sewage sludge (SENESI et al., 1999).

3.3. Element levels in fish

The concentrations of 15 trace elements were obtained from muscle tissues of *Sparus aurata* and *Lophius piscatorius* (Table 5). 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. The Cd and Pb were lower than recommended concentrations in Regulation. 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).

The measured trace element concentrations in Table 5 (except Se) were higher in wild gilt-head breams (lat. *Sparus aurata*) up to 21 times higher than in anglerfish (lat. *Lophius piscatorius*). The V concentrations were 21 times higher in gilt-head breams than in anglerfish, Pb and Cr concentrations were 8 times higher, Ba were 4.5 times higher, than Mn, Ni, Mo, As and Cd were 2 times higher in gilt-head seabreams. So, it seems from the results obtained that wild gilt-head breams accumulated more trace elements than anglerfish.

Vanadium in trace amounts is beneficial to normal cell growth, and it is an essential element. Toxicity arises when vanadium concentrations are increased to a higher level. Vanadium porphyrin is found in the petroleum and bitumen extracted from

Table 5. Levels of analysed trace elements in fish samples caught in 2021 (a-IVOŠEVIĆ et al., 2022, b – Regulation, 2006).

c (mg/kg ww)	Sparus aurata	Lophius piscatorius	S. aurata Raša[a]	Regulation[b]
Fe	7.85	5.53	9.07	
Zn	4.86	4.77	4.87	
Se	0.356	0.465	0.417	
Cu	0.401	0.318	0.343	
Ni	0.0171	0.00873	0.231	
Mn	0.317	0.110	0.217	
Cr	0.103	0.0130	0.0567	
Co	0.00680	0.00581	0.00653	
Mo	0.00481	0.00154	0.0106	
V	0.2558	0.0115	0.0103	
Al	5.09	3.34	2.70	
As	11.3	6.39	0.883	
Ag	0.00021	0.00030	0.00093	
Cd	0.00099	0.00042	0.0012	0.3
Ba	0.107	0.0230	0.0530	
Pb	0.0444	0.00532	0.00783	0.2
l/cm	25	30	20-30	

shales, and it can be considered as an indicator of marine oil pollution (COLINA et al., 2005). ABDOLAHPUR MONIKH et al. (2011) suggested that the combustion of fossil fuels and the residual fuel oil contributes to vanadium accumulation in sediments and fish. Vanadium mean concentrations in the Punat sediments presented in Table 1 vary between 10.3 and 42.5 mg/kg ww which were up to nine times lower than the obtained vanadium concentrations in Punat Bay from 15 years ago (VALKOVIĆ & BOGDANOVIĆ, 1996) .

The vanadium means concentrations obtained in Punat Bay were between 0.01 and 0.256 mg/kg ww which were up to 10 times lower than the reported vanadium concentrations (2.7 to 3.2 mg/kg ww) for the Persian Gulf (FARD et al., 2015). AGAH et al. (2009) reported that the vanadium concentration in fish in the Persian Gulf ranges between 0.16 and 0.71 mg/kg ww, which was approximately up to three times higher than those found in the present study.

Many authors (AGAH at al., 2009; ABDOLAHPUR MONIKH et al., 2011; FARD et al, 2015) presented an increase of vanadium concentrations due to an increase of combustion of fossil fuel. When we compared vanadium mean concentrations for 1996 and 2020 in Punat Bay, a drop in concentrations is observed.

Also, Table 5 shows 25 times higher mean vanadium concentrations measured in gilt-head breams caught in Punat Bay than in Raša Bay for the year 2020.

The As mean concentration obtained in wild gilt-head breams (*Sparus aurata*) caught in Punat Bay was 2.5 times higher than mean concentrations for 151 individuals of the same species of fish caught across the Adriatic Sea (SULIMANEC GRGEC et al., 2022). Further, the As mean concentrations in wild Punat fish was 72 times higher than in farmed samples. The obtained Se mean concentration in Punat gilt-head breams were similar with other obtained Se concentrations in wild fish. (SULIMANEC GRGEC et al., 2022).

4. CONCLUSION

Data analysis (nonparametric methods) conducted on sediment cores sulfur, phosphorous, iron, and a number of trace element concentrations confirms that the Punat marina has had only a limited impact on the Bay's environment. Mostly natural geochemical processes are reflected in the marine sediments' geochemistry, at least considering the sites further away from marina's port. Several potentially toxic trace elements such as Pb and Cu, were found to be elevated in a sediment core located closest to the marina.

Of the regulated trace elements, only Pb and Cd, did not exceed recommended values in mussels and fish. It was obtained that wild gilt-head breams accumulated more hazardous trace elements such as V, Pb, Ba, As, Cd, etc. than anglerfish.

This paper shows interesting results that warrant further analytical work on the Punat bottom sediments and biota for the purpose of environmental protection.

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