

Trace metals (Cd, Pb, Cu, Zn and Ni) in sediment of the submarine pit Dragon ear (Soline Bay, Rogoznica, Croatia)

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Abstract Vertical profiles of trace metal (Cd, Pb, Zn, Cu, Ni) concentrations, organic matter content, carbonate content and granulometric composition were determined in two sediment cores from the submarine pit Dragon Ear (Middle Adriatic). Concentrations of the analyzed metals (Cd: 0.06–0.12 mg kg⁻¹, Pb: 28.5–67.3 mg kg⁻¹, Zn: 17.0–65.4 mg kg⁻¹, Cu: 21.1–51.9 mg kg⁻¹, Ni: 27.8–40.2 mg kg⁻¹) were in usual range for Adriatic carbonate marine sediments. Nevertheless, concentrations of Cu, Zn, and especially Pb in the upper layer of sediments (top 12 cm) were higher than in bottom layer, while Cd and Ni concentration profiles were uniform. Regression analysis and principal component analysis were used to interpret distribution of trace metals, organic matter and carbonate content in sediment cores. Results of both analysis showed that concentrations of all trace metals in the core below the entrance to the pit were significantly positively correlated with organic matter and negatively correlated with carbonate, while in the core more distant from the entrance only Pb showed significant positive correlation with organic matter. Obtained results indicated that, except for lead which was enriched in surface sediment, in the time of sampling (before the building of the nautical marina) investigated area belonged to unpolluted areas.

Keywords Croatia · Organic matter · Sediment · Submarine pit · Trace metals

Introduction

Eastern Adriatic (Croatian) coast is a typical transgressional coast formed during the Late Pleistocene–Holocene sea level rise by flooding of the pre-existing karstified surface (Surić et al. 2005). As a result, numerous remarkable karstic features developed along the coast, such as karstic estuaries, marine lakes, drowned canyons, submarine springs, caves and pits. The Dragon Ear is a small submarine pit located near Rogoznica (Soline Bay, Croatia), on the middle Adriatic coast. Most of the studies in this area were focused on karstic lake Dragon's Eye located about 150 m south-west from the pit (Barić et al. 2003; Mihelčić et al. 1996; Šestanović et al. 2005). Rare studies of the Dragon Ear pit were focused on basic geomorphological characteristics (Petricioli and Bakran-Petricioli 1997) and basic hydrographical and chemical properties of the seawater (Kušpilić and Barić 1995). The cave is located close to the coast in well-protected bay, and acts as a natural trap for all particles, natural or anthropogenic which enter it.

The study of coastal sediments (granulometric composition, geochemical characteristics, contaminant concentrations, etc.) is a widely utilized method of environmental quality assessment (Förstner and Wittmann 1979) since sediments integrate contaminants concentration over time, rendering a long-term picture of influence of different factors (natural weathering, agriculture, urbanization, etc.) on aquatic system. Sources of trace metals accumulated in marine sediments are a combination of natural weathering and/or anthropogenic influence. Industrial and urban

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activities in coastal regions commonly introduce major amounts of pollutants into the nearby marine environment. Hence, the sediments in these areas may be influenced by the local geology, but can also reflect anthropogenic discharge from neighboring areas that contribute concentrations of both organic matter and heavy metals.

In this paper, we report concentrations and vertical distributions of trace metals (Cd, Pb, Cu, Zn and Ni), organic matter content, carbonate content, and granulometric composition of two sediment cores from the submarine pit Dragon Ear, before the nautical marina (<http://www.marinafrapa.hr>) was built in the area in 1998. The aim of the study was to determine total concentrations of trace metals in vertical sediment profiles in attempt to establish the pattern of trace metals enrichment in the pit and, indirectly, in surrounding area. Furthermore, since in 1998 (5 years after sediment core sampling for this work) nautical marina was built around the pit, data obtained by this work could be used as basis for detection of changes in the surrounding area in the future.

Materials and methods

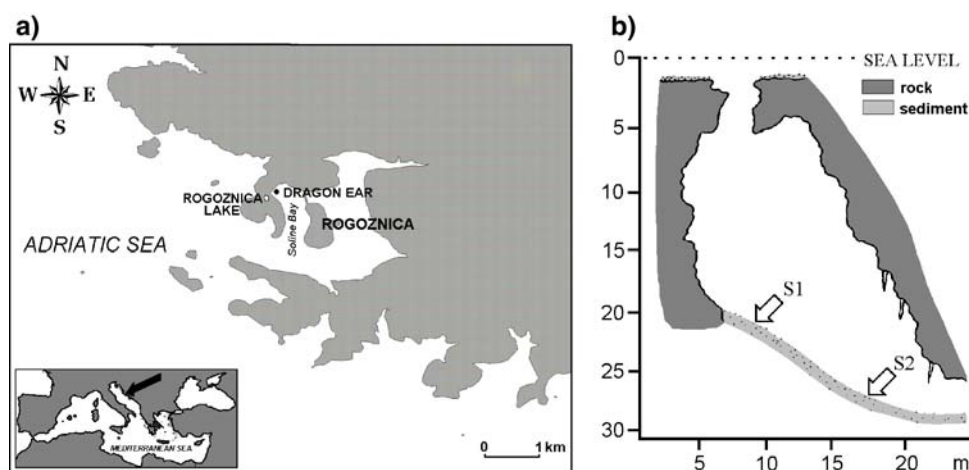
Study area

The Dragon Ear is a small submarine pit located on the Eastern Adriatic shoreline near Rogoznica (middle Adriatic, Croatia) in semi-enclosed Soline Bay (Fig. 1a). In 1998, 5 years after sediment core sampling for this work, nautical marina was built around the pit. However, even in the period before the nautical marina was built in the bay the whole area was not entirely isolated from the anthropogenic influence. The village of Rogoznica, which is situated on the coast, was populated as early as ancient times. Modern community of Rogoznica with 2,391 inhabitants is oriented towards farming, fishing and

tourism. The number of inhabitants more than doubles every summer because of the tourist activity. Semi-enclosed Soline Bay with the average depth of 13.5 m is a favorable shelter for yachts. That is why an artificial island was built in the bay in 1993–1996, literally around the pit, to be used as a marina. Nowadays major sources of pollution are assumed to be trace elements released from the antifouling paints applied on the ships in both local port and Marina Frappa (opened in 1998), sewage waste and drainage waters from agriculture.

The first precise measurements of the Dragon Ear pit dimensions were performed in 1992 (Petricioli and Bakran-Petricioli 1997), when submarine pit was named after the karstic lake Dragons Eye located about 150 m south-west from the pit. The entrance of the pit is located on flat sea bottom, at depth of 2 m. Vertical entrance of the pit (diameter = 1.5 m) was formed by roof collapses (Surić et al. 2005). The cave extends to a depth of 29.5 m, with an average width of 10 m (Kušpilić and Barić 1995). Marine conditions in the pit were established at 4,050 cal BP when mean sea level was just 3–3.5 m lower than today (Surić et al. 2005). Basic hydrographical and chemical properties of the seawater in the cave were measured in July 1993, parallel with sediment sampling for this paper, and published elsewhere (Kušpilić and Barić 1995). Salinity profile was uniform throughout the water column and ranged from 37.83‰ in the bottom layer to 38.14‰ at 14 m depth. Salinity data indicated that there was no fresh water inflow through the walls of the cave in the time of sampling. Vertical temperature distribution in the cave was more stratified in comparison to conditions in surrounding water column (Kušpilić and Barić 1995). Upper 10 m of the water column was well oxygenated (100–105%). Oxygen saturation in the cave decreased rapidly below the thermo cline down to 37% in the bottom layer. Similar trend was also established for pH (Kušpilić and Barić 1995).

Fig. 1 **a** The location of the Dragon Ear submarine pit in the eastern middle Adriatic; **b** Locations of the sampling stations S1 (depth = 21 m) and S2 (depth = 27 m) in the pit



Sampling and analytical determinations

Sediment samples were collected by a diver, with a push-tube coring device using Plexiglas liners (i.d. = 3 cm). This type of sampling device allows the collection of relatively undisturbed sediment profiles from different substrates. Sampling of sediment was carried out in July 1993 at two depths: 21 m (Station 1, 24 cm long sediment core) and 27 m (Station 2, 26 cm long core) (Fig. 1b). The samples were placed in clean plastic bags and frozen until further analysis in laboratory. Prior to analysis samples were defrosted at room temperature, sliced into 2 cm long subsamples and dried at 60°C for 48 h. Dry samples were divided in two parts. One subsample was used to determine granulometric composition while the other subsample was ground into powder and used to determine trace metals, carbonate content and organic matter content. Granulometric composition analysis was not performed on individual subsamples due to small amount of material (2-cm slices, 3 cm in diameter). Since the method for granulometric analysis required 50 g of sediment material we had to combine few subsamples together to create samples of required weight. After that, granulometric composition of composite sediment samples was determined both by sieving (>63 µm) and the hydrometric method (<63 µm) (Strmac 1952). Sediment type was classified according to Folk (Folk 1954). The organic matter content was determined as a weight loss after H₂O₂ treatment of samples and heating at 450°C for 6 h. Carbonate content was determined as weight loss after treatment with 4 M HCl (Loring and Rantala 1992).

Concentrations of trace metals (Cd, Pb, Cu, Zn and Ni) were measured by the GF-AAS method using instrument Perkin-Elmer 1100 B. All equipment used for sample preparation and analysis was soaked in 0.1 M nitric acid for 24 h and then rinsed several times with Milli-Q deionised water (>18 MΩ) prior to use. About 0.1 g of dried sediment samples were digested with HNO₃-HF-HClO₄ mixture according to method developed previously in our laboratory (Bogner 1996; Ujević et al. 2000). The accuracy of the analytical procedure was repeatedly checked by analyzing samples of certified reference material SRM-1646 (estuarine sediment) provided by the National Bureau of Standards (NIST, USA). The compliance of obtained results with the referred values is shown in Table 1. All results are reported on a dry weight basis. As a further quality assurance measure, method blanks were performed to check for

the presence of contamination during the digestion and analytical procedures. The method blanks confirmed the absence of contamination for both procedures.

Results were analyzed using STATISTICA software modules for Windows. The regression analysis (Pearson's Product-Moment Correlation) was used to examine relationships between trace metals content in sediment cores and organic matter content, carbonate content, and granulometric composition of sediments. In all cases, the level of significance was set at *P* < 0.05. Principal component analysis (PCA) was used to investigate vertical pattern of contaminants.

Results and discussion

Classification of sediment types according to Folk (1954) and granulometric composition of sediments (Table 2) indicated that two sediment cores are considerably different although the distance between them was less than 20 m. Generally, sediment at station S1, located beneath the entrance to the pit, was coarser grained (gravely muddy sand) than sediment at station S2 (mud). Share of particles higher than 63 µm (gravel and sand) prevailed in sediment core at S1 (except in surface layer where it was 31%), while at S2 particles smaller than 63 µm prevailed (90%). Vertical distribution of granulometric composition also differed between stations. At station S1 share of coarse particles (>63 µm) increased from the surface along the sediment core accompanied with more carbonate and less organic matter, while at station S2 granulometric composition was uniform along the core. Differences in sediment type and granulometric characteristics of sediments at two stations are the result of their location in relation to pit entrance. Granulometric composition in two cores indicates that fine grained material that enters the pit is transported towards deeper station by resuspension processes.

Descriptive statistics of raw data on organic matter and carbonate content and trace metal concentrations in sediments from the cave (Fig. 2) are summarized in Table 3. Correlation matrices were also calculated to aid the interpretation of data (Table 4).

Carbonates in marine sediments are the result of both weathering of surrounding limestone rocks (carbonate and flysch are predominant source rocks in the hinterland of Dalmatian coastal area) and sedimentation of different biogenous particles (calcite and aragonite minerals)

Table 1 Comparison of the certified and obtained values (mg kg⁻¹ dry wt) for trace metal concentrations in standard reference material SRM 1646

	Cu	Zn	Cd	Pb	Ni
Certified	18.0 ± 1.5	138 ± 6	0.360 ± 0.070	28.2 ± 1.8	32 ± 3
Obtained	17.3 ± 1.2	137 ± 13	0.405 ± 0.053	27.1 ± 1.1	30 ± 2

(Mihelčić et al. 1996). Carbonate content of the samples in this work (Fig. 2; Table 3) was found to be comparable with data previously reported in the literature for the Croatian coast (Table 5). Along the coast, which is made mainly of carbonate and flysch, carbonate content ranges in wide range, from 16 to 90% (Bogner et al. 2005; Bogner et al. 2004b) Values higher than 60% are often found at off-shore stations (Island Vis, open sea) (Bogner et al. 2004b) or estuaries of karstic rivers (e.g. river Neretva) (Bogner et al. 2005), as a result of granulometric composition e.g.

prevalence of coarse-grained particles. Accordingly, the highest carbonate content (93%) determined in deep layer of station S1 is probably the consequence of the prevailing coarse grained particles.

Organic matter in marine sediments may be derived from terrestrial, marine and anthropogenic sources. It is mostly deposited in near shore areas (deltas, shelves and upper slopes). Except that organic matter in marine sediments provides a significant reservoir in the global carbon cycle, it influences the chemical conditions during early

Table 2 Granulometric composition, median size (Md) and sediment type (according to Folk's classification) of sediment cores from two locations in the Dragon Ear pit

Subsamples (cm)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Md (μm)	Sediment type (Folk 1954)
S1 (depth = 21 m)						
0–12	11	20	65	4	34.3	Gravelly mud
13–16	24	48	25.5	2.5	207	Gravelly muddy sand
17–20	17	65	17	1	187	Gravelly muddy sand
21–24	11	66	22.5	0.5	283	Gravelly muddy sand
S2 (depth = 27 m)						
0–12	0	8	77	15	48.5	Mud
12–22	0	10	66	24	73.5	Mud
22–26	0	10	74	16	64	Mud

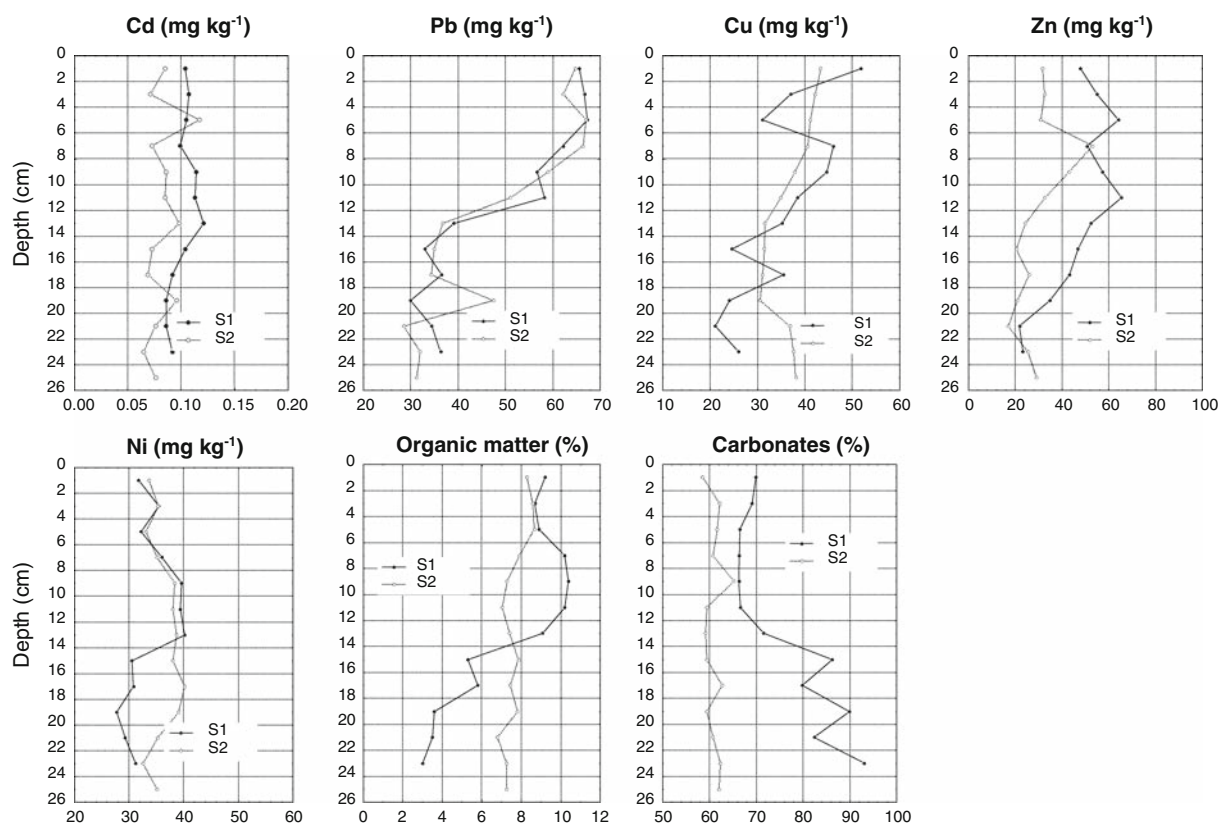


Fig. 2 Trace metal concentrations (mg kg^{-1}), organic matter (%) and carbonate content (%) in sediment cores at investigated stations

diagenesis in sediment (Chester 2003). Organic matter content of samples in this work (3–10.4%) is comparable with data previously reported for the Croatian coast

Table 3 Descriptive statistics [minimum (Min), maximum (Max), mean, and median values, standard deviation (SD), and coefficient of variation (CV)] of raw data on trace metal concentrations (mg kg⁻¹ dry wt), and carbonate and organic matter content (%) in two sediment cores from the Dragon Ear pit

	Min	Max	Mean	Median	SD	CV (%)
S1 (depth = 21 m)						
Cd	0.086	0.121	0.102	0.104	0.011	11
Pb	29.9	67.3	48.8	47.9	15.0	31
Cu	21.1	51.9	34.6	35.3	9.7	28
Ni	27.8	40.2	33.7	32.0	4.3	13
Zn	21.9	65.4	46.9	49.3	14.1	30
Organic matter (%)	3.0	10.4	7.3	8.8	2.9	39
Carbonates (%)	66.3	93.1	75.7	70.8	10.1	13
S2 (depth = 27 m)						
Cd	0.065	0.117	0.082	0.076	0.015	18
Pb	28.5	67.0	47.4	47.5	15.0	32
Cu	30.6	43.4	36.7	37.6	4.5	12
Ni	32.6	40.2	36.4	35.4	2.5	7
Zn	17.0	53.1	28.8	29.0	8.9	31
Organic matter (%)	6.8	8.7	7.7	7.4	0.6	8
Carbonates (%)	58.5	65.2	61.1	60.8	1.9	3

(Table 5). OM content higher than 4% was usually found in highly productive areas and sediments with prevailing small-size particles (Bogner et al. 2005; Ujević 2002; Ujević et al. 2000). We observed positive trend between OM content and the percentage of mud ($r_{S1} = 0.864$; $r_{S2} = 0.963$), and the negative trend between OM content and the mean diameter of particles ($r_{S1} = -0.894$; $r_{S2} = -0.791$) at both stations. This could be expected since it is well documented that the proportion of total organic matter generally increases as the mean grain size decreases (Bogner et al. 2005; Chen et al. 2004; Förstner and Wittmann 1979; Lin et al. 2002; Ujević et al. 1998a; Zhang et al. 2002).

Comparison of trace metal concentrations in the sediment cores from the Dragon Ear pit with the values frequently used to evaluate natural levels of these elements and with values from different parts of Adriatic, Mediterranean and other world areas (Table 5) showed that concentrations of trace metals in sediments of the Dragon Ear pit were not significantly elevated. More exact, concentrations of Cu, Pb and Zn are higher than those in average carbonate rocks or shale rocks (Bogner 1996; Prohić and Juračić 1989), while concentrations of Cd and Ni are similar to or even lower than concentrations in source limestone and carbonate rocks (Bogner 1996).

Cadmium concentrations in the Dragon Ear pit (0.06–0.12 mg kg⁻¹) were very low in comparison to nearby Rogoznica Lake (Mihelčić et al. 1996) located 140 m from the pit, or other areas on the Dalmatian coast (Table 5). For

Table 4 Linear correlation coefficients between carbonate content, organic matter content and trace metals in sediment from two sampling stations in the Dragon Ear pit

	Cd	Pb	Cu	Ni	Zn	OM (%)
Station S1 [#] (21 m)						
Pb	0.485	1.000				
Cu	0.514	0.736*	1.000			
Ni	0.872**	0.468	0.571	1.000		
Zn	0.790**	0.710*	0.572	0.672	1.000	
OM (%)	0.801**	0.817**	0.827**	0.810**	0.883**	1.000
Carbonate (%)	-0.694*	-0.859**	-0.759*	-0.725*	-0.834**	-0.960**
Station S2 (27 m)						
Pb	0.400	1.000				
Cu	0.011	0.646	1.000			
Ni	0.007	-0.254	-0.801	1.000		
Zn	-0.068	0.685*	0.560	-0.264	1.000	
OM (%)	0.339	0.709**	0.480	-0.329	0.338	1.000
Carbonate (%)	-0.211	0.028	0.192	-0.018	0.092	-0.120

Statistically important correlations ($P < 0.05$) are marked with *bold letters*

[#] Data from Ujević et al. (1998a)

* Correlations significant at level $P < 0.01$

** Correlations significant at level $P < 0.001$

Table 5 Comparison of trace metals concentrations in sediments from the Dragon ear with previously published values for sediments and source rocks from the Adriatic, Mediterranean and other world areas

	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Organic matter (%)	Carbonates (%)
Rogoznica lake (Mihelčić et al. 1996)	0.4–0.7	8.5–23.3	2.6–14.2	9–32			
River Krka area-sediment (Prohić and Juračić 1989)		16–70	2–65	20–50	42–100		55.1–91.7
River Krka area-flysch (Prohić and Juračić 1989)		6	9	90	200		68.6
River Krka area-limestone (Prohić and Juračić 1989)		10	14	30	41		95.6
River Krka estuary (Martincic et al. 1990)	0.47	12.4	13.7	23			
Šibenik (1995, 0–10 cm) River Krka estuary (Bikić 1995)	0.48–0.72	71–116	36–54	61–186		7.5–10.3	
Carbonate rocks near Bacina lakes (Bogner et al. 2004a)	0.19–0.27	0.11–0.3					
Bacina lakes sediments (Bogner et al. 2004a)	0.21–1.37	2.3–30.2					65–80
Carbonate rocks near Kaštela Bay (Bogner 1996)	0.653–1.109	0.6–1.01	2.67–4.96	5.4–7.1	11.33–35.46		99.8
Kaštela Bay sediments (Bogner 1996)	0.21–0.87	11.05–76.83	11.89–74.88	22–211	19.27–71.34	1.95–9.98	35–63
Morinje Bay sedim-top 25 cm (Mihelčić et al. 1996)		15–23	24–28	67–95			
Soline Bay (Obhodaš et al. 2006)		24–29	9.8–18.2	22–62			
Adriatic Sea, offshore station (Ujević et al.1998b)	0.18–0.27	6.12–13.23	8.31–11.74	38–54		2.4–2.8	
Adriatic Sea, Šolta Island, control samples (Mikulčić et al. 2008)		16.0 ± 1.4	23.7 ± 1.9	24.8 ± 1.5			
Adriatic Sea, northern Adriatic Slovenia, (Ščančar et al. 2007)	0.085–0.126	8–18	15–31	35–140	12–83		
Mediterranean, South Italy, Naples (Sprovieri et al. 2007)	0.01–3.00	19–3083	12–5743	17–7234	4–362		
Marmara Sea, Izmit Bay (Pekey, 2006)	2.5–9.5	55.2–172	24.5–102.4	440–1900			
Mediterranean, Spain, Barcelona (Guevara-Riba eta al.2004)	0.4–1.4	85–130	70–195	180–300	18–27		
Atlantic Ocean, Spain, Bay of Cadis (Ligero et al. 2002)	0.05–0.5	10–45		50–150			
Hong Kong, South China Sea (Choi et al. 2006)	1.5–2.5	20–108	112–202	77–225			
Mazatlan Harbour (SE Gulf of California) (Jara-Marini et al. 2008)	3.1–3.3	49.6–54.0	31.9–44.9	217.8–323.5			
China, Quanzhou Bay (Ruilian et al. 2008)	0.28–0.89	34.3–100.9	24.8–119.7	105–241	16.1–45.7		
Dragon ear 21 m	0.086–0.121	29.9–67.3	21.1–51.9	21–65	27.8–40.2	3–10.4	66–93
Dragon ear 27 m	0.065–0.117	28.5–67	30.6–43.4	17–53	32.6–40.2	6.8–8.7	59–65

illustration, cadmium content in sediments of the Kaštela Bay, located 50 km SE from investigated area and heavily contaminated by urban and industrial wastewater, is at least five times higher in comparison to the Dragon Ear pit (Ujević et al. 2000). The low cadmium concentrations in the pit indicate natural origin of Cd, or negligible anthropogenic influence, owing to somewhat higher concentration in core at station S1 in comparison to S2.

Lead concentrations in the pit were higher than in the Dragon Ear lake (Mihelčić et al. 1996), and more in the range recorded in sediments from the polluted areas such as Kaštela Bay (Ujević et al. 2000). Dominant pollution sources of lead in the past were vehicles which used leaded gasoline (Piron-Frenet et al. 1994; Viard et al. 2004). After substitution of this gasoline with unleaded gasoline, main anthropogenic input of Pb to the coastal area is considered to be from industrial and domestic wastes (Dolenec et al. 1998). According to Obhodaš et al. (2006), the main source of contamination with lead in the Soline bay are antifouling paints used in the port of the town of Rogoznica, whose inhabitants are using small boats for fishing and recreational purposes.

Copper concentrations ($21.1\text{--}51.9\text{ mg kg}^{-1}$) in two cores were higher than in source rocks (the River Krka area flysch and limestones) (Table 5) and sediment from nearby Rogoznica Lake ($3\text{--}14\text{ mg kg}^{-1}$), and partially higher than average values for shale rocks (Förstner and Wittmann 1979). Copper may be introduced to the aquatic environment through natural sources (e.g. from the weathering of or the solution of copper minerals), or through different anthropogenic sources, among which fungicide formulations used in vineyards (wine making is one of the traditional activities in the surrounding area) or antifouling copper based compounds in marinas (Obhodaš et al. 2006) are the most frequent in the surrounding area.

Zinc content at both stations ($17\text{--}65.4\text{ mg kg}^{-1}$) was higher than the values recorded for Rogoznica Lake and the river Krka area, but lower than the highest values determined in front of town of Šibenik (Table 5). Increased zinc concentrations in sediment indicate partially anthropogenic influence. According to Mihelčić et al. (1996), elevated value of zinc in Rogoznica Lake coincides with increase of domestic waste. Recent work of Obhodaš et al. (2006) pointed out that the main source of contamination with zinc in the Soline bay is small port of the town of Rogoznica (zinc is important constituent of antifouling paints).

Nickel concentrations in sediments from the pit ($27.8\text{--}40.2\text{ mg kg}^{-1}$) agree well with data of Prohić and Juračić 1989 for the limestone (source rocks) in the river Krka area (41 mg kg^{-1}) (Table 5), who suggested that nickel in the river Krka area is of natural origin. According to Vukadin et al. (1994), in sediment from the eastern Adriatic coast nickel is bound to fine particles, terrigenous in origin and is

naturally enriched near submarine springs and rivers. In addition to relatively low concentrations of nickel in the pit, the distribution of nickel in both cores was uniform and varied in a narrow range ($CV = 7\text{--}13\%$). Also, there were no differences between sediment cores at two stations (Fig. 2). Absolute values and spatial and vertical distribution combined with chemical composition of source rocks in surrounding coastal area (prevalent carbonate rocks) support the idea of natural origin of nickel in the pit suggesting that anthropogenic inputs have been negligible.

In conclusion, concentrations of trace metals in sediments of the Dragon Ear pit (Tables 3, 5) were not significantly elevated; they were in the range usual for unpolluted marine carbonate sediments. Our results agree well with the results of Obhodaš et al. (2006), who have shown that even after Marina Frapa was built in the area (literally around the pit), the new-built marina has not become the most important source of contamination with some of analyzed metals. According to their results, local port of the town of Rogoznica, located on the east side of the bay, remained the main source of contamination with Cu, Pb and Zn. Namely, contribution of Zn from the town was an order of magnitude higher, and of Pb and Cu five times higher in comparison to new marina.

Vertical distribution

Trace metal concentrations in two cores from the Dragon Ear pit where in most cases higher in the upper sediment layer (top 12 cm) of both cores than in deeper sediment layers (Fig. 2). Unlike other metals, vertical distribution of lead was very similar at both stations, values being two times higher in upper 12 cm in comparison to bottom sediment. Described vertical profiles characterized by elevated concentrations in upper layer of sediment are typical for process of sediment loading by input from the surrounding area (Ujević et al. 1998a, 2000).

Concentrations and vertical distributions of trace metals in sediment may be controlled by numerous factors such as: particle size (granulometric composition), mineral composition of sediments, carrier substances (e.g. hydroxides, carbonates, sulfides), sediment surface area, organic matter content, individual and combined effects of Eh and pH, etc. (Förstner and Wittmann 1979). The efficiency of the various influencing factors on the bonding and enrichment of heavy metals in aquatic sediments is dependent on depositional environment, characterized by the chemical composition (particularly concentration of dissolved iron and carbonate available for reaction), salinity, pH, redox potential and hydrodynamic conditions.

Results of the regression analysis (Table 4) showed that at station S1 concentrations of all trace metals were significantly positively correlated with concentration of

organic matter (Table 4), while at station S2 statistically significant correlation was determined only between OM content and lead concentration. These differences between stations are probably the result of significant differences between vertical profiles of OM at two stations (Fig. 2; Table 3). Namely, at station S1 located beneath the entrance organic matter content (3–10.4%) decreased with depth, while at S2 vertical distribution of OM was mostly uniform and ranged from 6.8 to 8.7% (CV = 8%). Strong positive associations between OM and trace metal concentrations have often been related to the adsorption and complexation of metals by organic matter of both terrestrial and marine origin (Libes 1992), indicating that the interaction between organic matter and trace metals is an important process for the removal and fixation of metals in sediment at station S1. In addition, strong correlation between organic matter content and trace metal concentration in certain location, similar to one we have found for S1 (Table 4), usually indicates pollution of investigated area (Ujević et al. 1998a, 2000).

Granulometric composition may also control concentrations of metals in sediment (Förstner and Wittmann 1979). Elevated concentrations of trace metals can be usually find in sediments with fine grained particles, particularly those in the silt and clay fractions, in both freshwater and marine sediments (Förstner and Wittmann 1979), although metals have been shown to accumulate on the surfaces of coarser materials, like sand and pebbles. Our results showed that organic matter content and trace metal concentrations were higher at S1 than at S2, although sediment at S1 was coarser grained. Namely, share of coarse grained particles increased with depth in core at S1 (especially from 13 to 24 cm of the sediment core) while Pb, Cu and Zn concentrations decreased (Fig. 2; Table 2). This was probably due to effect of new-settled particles on surface sediment. In fact, new-settled smaller particles are the main carriers of contaminants, such as organic matter and trace metals (Bogner et al. 2005; Chen et al. 2004; Förstner and Wittmann 1979; Lin et al. 2002; Ujević et al. 1998a, 2000; Zhang et al. 2002).

Increased concentration of metals in sediments can be also caused by coprecipitation of metal cations with carbonates, where heavy metal cations adsorbed onto the surface become a part of the crystal lattice. This mechanism appears to be important for limitation of metal concentrations in marine environment in cases when carbonate contents occur as a major component i.e., when other substrates (hydrous iron oxides or organic substances) are less abundant (Förstner and Wittmann 1979). With respect to possible influence of carbonates on trace metals vertical distribution in the pit sediments, we observed negative trend between carbonate content and concentrations of all trace metals only at station S1

(Table 4). This difference between stations was probably resulting from differences in carbonate content and granulometric composition of sediments at two stations. Namely, vertical profiles of carbonate content in two cores from the pit differed significantly (Fig. 2; Table 3). At station S1 carbonate content (66.3–93.1%) varied in wider range in comparison to S2. At S1 carbonate content increased with depth, as share of coarse particles increased (Fig. 2), while at S2 vertical distribution of carbonates was mostly uniform and ranged from 58.5 to 65.2% (CV = 3%), respectively.

A possible way to estimate anthropogenic input is to compare concentrations of metals in upper-most layers of sediment with concentrations of the same elements from deeper layers of sediment (Ujević 2002; Obhodaš et al. 2006). Therefore, we compared means of the results for the 0–12 cm and 12–24 (26) cm depth intervals with the use of simple *t* tests. Results indicated that there were no significant between-depth differences ($P > 0.05$) for Cd and Ni at both stations, and organic matter and carbonate content at station S2. Other parameters (Pb, Cu, Zn at both stations, and OM and carbonate content at S1) differed significantly between depths (0–12 cm versus 12–24 cm), values usually being higher in the upper sediment layer (except for carbonates which increased with depth at S1). In additional attempt to evaluate the metal enrichment in the sediment, a concentration factor (CF) was calculated as the ratio between the sediment metal content for top 12 cm of sediment cores at a given sampling station and the last 2 cm of sediment cores (22–24 cm at S1; 23–25 cm at S2). Values of CF higher than 1 were found for Pb (1.7 at S1; 1.8 at S2) in both cores, and for Cu (1.7) and Zn (2.5) at S1, which indicates that these elements, especially at the station below the entrance to the pit, might be introduced to the area not only from natural sources but also by some sources of anthropogenic input. Metal enrichment in the upper layer of sediment and obtained sediment profiles are not necessarily due to anthropogenic input (Obhodaš et al. 2006). This enrichment may be explained by the redox processes on redox boundaries which control the exchange of trace metals between sediments and the water column. According to Foster and Charlesworth (1996), the fundamental question relating to an interpretation of the chemical record in bottom sediments is whether the sediment record solely reflects the historical influx of metals to the investigating area or the pH and/or redox conditions which control post-depositional mobility within the sediment column. Foster and Charlesworth (1996) hold that, in reality the sediment core record will undoubtedly reflect both processes in addition to the effects of physical mixing by bioturbation, which will not be readily separable by phase-specific or pore water chemical analysis.

Additional statistical analysis of the data was carried out using the PCA (Grant and Middleton 1990; Ujević et al. 2000). The PCA was performed on the entire data set (trace metal concentrations, organic matter content, and carbonate content) to identify the major processes that determine trace metal distribution in two sediment cores. The PC analysis of data for sediment core at station S1 determined only one principal component (PC), which explained 77% of the total variance (Table 6). Results of PCA for station S1 agreed well with results of regression analysis (significant positive correlations between trace metals and organic matter, and significant negative correlations between trace metals and carbonate) (Table 4), which indicates that all analyzed metals at station S1 are strongly bound to the organic matter, and generally have similar vertical distribution path.

For core at station S2 two significant principal components were extracted. They explained little more than 65% of the total variance (Table 6) indicating that these axes should be useful for examining the major differences between metal distributions. At station S2 the first group includes lead, copper, zinc and organic matter, indicating that organic matter has strong influence on removal and binding of these metals in sediment of station S2. Nickel also belongs to this group. However, diametrically different loading of the first component for nickel suggests that its distribution is opposite to distribution of organic matter and other metals (e.g. lowest at surface). The second group (Factor 2) includes cadmium and carbonate, whose components are diametrically opposite due to their opposing vertical distributions. Carbonate content and Cd were extracted in separate factor probably due to fact that between-layer differences and absolute values of Cd and carbonates at S2 ($CV_{Cd\ S2} = 7\%$; $CV_{Carb\ S2} = 3\%$) are very low in comparison to other variables (Table 3). This supports suggestion on natural cadmium origin.

Table 6 PCA results: table of loadings of the principal components obtained in the analysis

	S1	S2	
	Factor 1	Factor 1	Factor 2
Cd	0.838	-0.261	0.784
Pb	0.827	-0.881	0.246
Cu	0.808	-0.881	-0.338
Zn	0.892	-0.714	-0.204
Ni	0.831	0.646	0.336
Organic matter	0.993	-0.749	0.370
Carbonate	-0.952	-0.060	-0.624
Prp. total (%)	77.39	44.45	20.99

Conclusions

The results of this study are the first measurements of trace metals in sediment of karstic submarine pit Dragon Ear. Obtained trace metal concentrations, except for lead enrichment in surface sediment, indicate that, in the time of sampling (before the building of the nautical marina), investigated area was not seriously polluted.

Although the two sampling sites were situated in distance less than 20 m, granulometric composition between sites was considerably different, as well as vertical pattern of metals, organic matter and carbonate content. Generally, higher concentrations of trace metals, organic matter and carbonate content were found at station beneath the entrance to the pit. This indicates that, due to its position in the pit, this station is under stronger impact of the surrounding area despite the more coarse grained composition of the sediment.

Results of statistical analysis obtained using entire data set (trace metal concentrations, organic matter content, and carbonate content) indicate that investigated trace metals could be, according to origin, separated in three groups: Cd and Ni, which are primarily derived from natural sources; Pb, originating primarily from human activities; and Cu and Zn, originating from both natural and anthropogenic sources.

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References

- Barić A, Grbec B, Kušpilić G, Marasović I, Ninčević Ž, Grubelić I (2003) Mass mortality event in a small saline lake (Lake Rogoznica) caused by unusual holomictic conditions. *Sci Mar* 67:129–141
- Bikić S (1995) Sadržaj i raspodjela kadmija, olova, bakra i cinka u priobalnom području srednjeg Jadrana (Distribution of cadmium, lead, copper and zinc in inshore sediments in the middle Adriatic). B. Sc, University of Split, Croatia (in Croatian)
- Bogner D (1996) Površinski sedimenti i utjecaj njihovih fizičko-kemijskih svojstava na raspodjelu teških kovina u Kaštelanskom zaljevu (Surface sediments and influence of their physico-chemical characteristics on the distribution of heavy metals in sediment of the Kaštela bay). M. Sc University of Zagreb, Croatia (in Croatian)
- Bogner D, Ujević I, Barić A (2005) Trace metal (Cd, Pb, Cu, Zn and Cr) distribution in sediments along east coast of the Adriatic Sea (Croatia). *Fresen Environ Bull* 14:50–58
- Bogner D, Ujević I, Odžak N, Crmarić R, Barić A (2004a) Cadmium and lead distribution in sediment of the Bačina lakes (Croatia). *Fresen Environ Bull* 13:626–632
- Bogner D, Ujević I, Zvonarić T, Barić A (2004b) Distribution of selected trace metals in coastal surface sediments from the middle and south Adriatic Sea. *Fresen Environ Bull* 13:1281–1287

- Chen Z, Saito Y, Kanai Y, Wei T, Li L, Yao H, Wang Z (2004) Low concentration of heavy metals in the Yangtze estuarine sediments, China: a diluting setting. *Estuar Coast Shelf Sci* 60:91–100
- Chester R (2003) *Marine Geochemistry*. Blackwell, Oxford
- Choi SC, Wai OWH, Choi TWH, Li XD, Tsang CW (2006) Distribution of cadmium, chromium, copper, lead and zinc in marine sediments in Honk Kong waters. *Environ Geol* 51:455–461
- Dolenc T, Faganeli J, Pirc S (1998) Major, minor and trace elements in surficial sediments from the open Adriatic sea: a regional geochemical study. *Geol Croat* 51:59–73
- Folk RL (1954) The distinction between grain size and mineral composition in sedimentary rock nomenclature. *J Geol* 62:344–356
- Förstner U, Wittmann GTW (1979) *Metal pollution in the aquatic environment*. Springer, Berlin
- Foster IDL, Charlesworth SM (1996) Heavy metals in the hydrological cycle: trends and explanation. *Hydrol Processes* 10:227–261
- Grant A, Middleton R (1990) An assessment of metal contamination of sediments in the Humber Estuary, UK. *Estuar Coast Shelf Sci* 31:71–85
- Jara-Marini ME, Soto-Jimenez MF, Paez-Osuna F (2008) Bulk and bioavailable metals from Mazatlan Harbor (SE Gulf of California). *Bull Environ Contam Toxicol* 80:150–153
- Kušpilić G, Barić A (1995) Basic hydrographic and chemical data from two microlocations at the eastern Adriatic coastline: The Rogoznica Lake and the Rogoznica underwater cave. Paper presented at the 34th Congress of the Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée. Malta, 27–31 March 1995
- Libes SM (1992) *An introduction to marine biogeochemistry*. Wiley, New York
- Ligero RA, Barrera M, Casas-Ruiz M, Sales D, Lopez-Aguayo F (2002) Dating of marine sediments and time evolution of heavy metal concentrations in the Bay of Cadiz, Spain. *Environ Pollut* 118:97–108
- Lin S, Hsieh I-J, Huang K-M, Wang C-H (2002) Influence of the Yangtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China Sea continental shelf sediments. *Chem Geol* 182:377–394
- Loring DH, Rantala RTT (1992) *Manual for geochemical analyses of marine sediments and suspended particulate matter*. *Earth Sci Rev* 32:235–283
- Martincic D, Kwokal Z, Branica M (1990) Distribution of zinc, lead, cadmium and copper between different size fractions of sediments. 2. The Krka river estuary and the Kornati Islands (Central Adriatic Sea). *Sci Total Environ* 95:217–225
- Mihelčić G, Šurića B, Juračić M, Barišić D, Branica M (1996) History of the accumulation of trace metals in sediments of the saline Rogoznica Lake (Croatia). *Sci Total Environ* 182:105–115
- Mikulić N, Orešćanin V, Elez L, Lj Pavičić, Pezelj Đ, Lovrenčić I, Lulić S (2008) Distribution of trace elements in the coastal sea sediment of Maslinica Bay, Croatia. *Environ Geol* 53:1413–1419
- Obhodaš J, Kutle A, Valković V (2006) Concentrations of some elements in the coastal sea sediments: bays with marinas. *J Radioanal Nucl Chem* 270:75–85
- Pekey H (2006) The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Mar Pollut Bull* 52:1197–1208
- Petricioli D, Bakran-Petricioli T (1997) Zmajevu uho, morem poplavljena jama u uvali Soline kraj Rogoznice (Dragon ear, submerged cave in Soline Bay, near Rogoznica). *Proceedings about Primošten and Rogoznica arera near Šibenik Museum* 84–92 (in Croatian)
- Piron-Frenet M, Bureau F, Pineau R (1994) Lead accumulation in surface roadside soil: its relationship to traffic density and meteorological parameters. *Sci Total Environ* 144:297–304
- Prohić E, Juračić M (1989) Heavy metals in sediments—problems concerning determination of the antropogenic influence. Study in the Krka river estuary, eastern Adriatic coast, Yugoslavia. *Environ Geol Water Sci* 13:145–151
- Ruilian Y, Xing Y, Yuanhui Z, Gongren H, Xianglin T (2008) Heavy metal pollution in intertidal sediments from Quanzhou Bay, China. *J Environ Sci* 20:664–669
- Sprovieri M, Feo ML, Prevedello L, Salvagio Manta D, Sammartino S, Tamburrino S, Marsella E (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere* 67:998–1009
- Strmac A (1952) Određivanje granulometričnog sastava tla areometaškom metodom. Po A. Casagrande-u (Determinator of granulometrical composition using hydrometric method according to A.Casagrande-u). *Građevinar* 4:23–38 (in Croatian)
- Surić M, Juračić M, Horvatinčić N, Krajcar Bronić I (2005) Late Pleistocen-Holocene sea-level rise and the pattern of coastal karst inundation—records from submerged speleothems along the Eastern Adriatic Coast (Croatia). *Mar Geol* 214:163–175
- Šestanović S, Šolić M, Krstulović N, Šegvić D, Ciglenečki I (2005) Vertical structure of microbial community in eutrophic meromictic saline lake. *Fresen Environ Bull* 14:668–675
- Ščančar J, Zuliani T, Turk T, Milač R (2007) Organotin compounds and selected metals in the marine environment of Northern Adriatic Sea. *Environ Monit Assess* 127:271–282
- Ujević I (2002) Utjecaj suspendirane tvari u moru na akumulaciju kovina u tragovima u sedimentu Kaštelanskog zaljeva (Impacts of suspended matter on the trace metal accumulation in the marine sediment of the Kaštela Bay). Ph.D, University of Zagreb, Croatia (in Croatian)
- Ujević I, Bogner D, Barić A (1998a) Trace metal accumulation in the sediment of the submarine cave “Dragon ear” (Soline bay, Croatia). Paper presented at the 35th Congress of the Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée. Dubrovnik, Croatia, 2–6 June 1998
- Ujević I, Bogner D, Zvonarić T, Barić A (1998b) Trace metal distribution in coastal sediment from the Adriatic Sea. *Fresen Environ Bull* 7:701–708
- Ujević I, Odžak N, Barić A (2000) Trace metal accumulation in different grain size fractions of the sediments from a semi-enclosed bay heavily contaminated by urban and industrial wastewaters. *Water Res* 34:3055–3061
- Viard B, Pihan F, Promeyrat S, Pihan J-C (2004) Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution: bioaccumulation in soil, *Graminaceae* and land snails. *Chemosphere* 55:1349–1359
- Vukadin I, Odžak N, Radačić J (1994) Heavy metal pollution in sediment from the eastern Adriatic coast, Croatia. *Chem Ecol* 8:265–274
- Zhang C, Wang L, Li G, Dong S, Yang J, Wang X (2002) Grain size effect on multi-element concentrations in sediments from the intertidal flats of Bohai Bay, China. *Appl Geochem* 17:59–68