

## Trace Metals Conservation in Morinje Bay Sediment: Historical Record of Anthropogenic Imissions into a Shallow Adriatic Bay\*

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Geochemical and sedimentological characteristics, the sediment accumulation rate (by <sup>137</sup>Cs dating) and vertical distribution of trace metals (Pb, Cu, Zn) in sediments from Morinje Bay (Central Dalmatia-Croatia) have been studied. The sediment is fine-grained, well-sorted silt throughout the investigated section. The very high average sedimentation rate (4.5 cm in 3 years, or 1.65 g dry sediment/cm<sup>2</sup> per year) in Morinje Bay, compared to the nearby coastal areas of the Rogoznica lake and the Krka river estuary, may be a result of high aeolian supply of material from the agricultural field of Donje polje, and influenced by the seasonal input from the rapid streamlet Ribnik draining the surrounding area. Concentrations of most trace metals in the Morinje Bay sediments are in the range typical of unpolluted marine carbonates. However, concentrations of Pb, Cu and Zn, in recent and subrecent (down to 50 years before the present) sediments reflect anthropogenic influences. Leaded gasoline seems to be the principal anthropogenic source of Pb enrichment, while Zn and Cu may be of urban and agricultural origin.

### INTRODUCTION

Trace metals are introduced into the aquatic environment either in soluble or in particulate form through various sources, including fallout, agricultural and urban runoff and domestic waste. In aquatic systems, sediments are their ultimate sinks. Analyses of the sediment samples collected near highly populated areas and sites with extensive industrial activity provide a record of the

pollution history. Bioturbation, redeposition, erosion and other sediment mixing processes, which can occasionally result in misleading conclusions, may disturb this sedimentary record. The vertical distribution of trace metals in sediments can be also considerably changed due to the influence of diagenetic processes.<sup>1,2</sup> In general, biogenic sediments are mainly considered to be less effective as geochemical sinks for trace metals than

\* Dedicated to the memory of the late Professor Marko Branica.

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terigenous sediments<sup>3</sup> which is even more evident in the case of anoxic sediments.<sup>4,5</sup>

Concentrations of major elements and trace metals in the sediment provide useful information about the origin and transport of terrestrial material to the sea. Trace metal concentrations in sediment profiles can be used for identification of the history and sources of pollution in a certain area. In order to evaluate the trace element pollution in sediments, it is very important to be able to distinguish between the natural trace element record derived from sedimentation and records that may reflect the anthropogenic impact. In general, the sources of major and minor elements in marine sediments are a combination of natural weathering, run-off and riverine input affected by anthropogenic impact – industrial, agricultural, communal wastes as well as the atmospheric input.<sup>4</sup>

Specific circumstances ensuing from industrial, agricultural and communal activities of a particular area may be identified from the profile of trace metals in dated sediment cores. The artificial radionuclide <sup>137</sup>Cs ( $T_{1/2} = 30.2$  years) has been sporadically appearing in traces in the environment since the beginning of the 1950s (from the first nuclear weapon testing fallout), showing two additional characteristic activity maxima in sediments, the first between 1961 and 1963 (from atmospheric nuclear weapon testing fallout maximum) and the second, more pronounced in numerous European countries, from the Chernobyl incident in 1986. The position of these maxima in the sediment column can be conveniently utilized as a geochronological marker of recent sedimentation processes.<sup>6,7,8</sup> The bulk sedimentation rate can be estimated from the sediment depth between the present surface and the bottom sediment with no <sup>137</sup>Cs activity, which corresponds to the beginning of the 1950s or 1960s. However, this is accurate only in the case when the sediment is not excessively disturbed by bioturbation or any other mixing process. The geochemical distribution of <sup>137</sup>Cs depends on various properties of solid materials. The sorption ratio of cesium is proportional to the clay content of sediments.<sup>9</sup> Albertazzi *et al.*<sup>10</sup> found that this radionuclide is particularly accumulated in the fine-grain-size fraction (0.24–16  $\mu\text{m}$ ). Chernobyl-derived <sup>137</sup>Cs was conspicuously deposited in this region of Croatia<sup>11,12,13</sup> and was therefore used to calculate the sediment accumulation rate in this study.

The Morinje Bay sediments with their geochemical, sedimentological and balneological properties can be classified as "peloid muds" according to the definition of the International Society of Medical Hydrology<sup>14,15</sup> and could be used for therapeutic and cosmetic purposes. Indeed, a considerable share of the local tourism in the Morinje Bay area is associated with the use of this peloid. However, some recent research points to the necessity of investigating the geochemical abundance of potentially toxic elements in peloids.<sup>16,17,18,19</sup>

The present study was conducted in order to determine total concentrations of the major elements and trace metals in the vertical sediment profile in an attempt to establish the pattern and history of their enrichment in Morinje Bay. Determination of the distribution and concentrations, particularly of Pb, Cu, Zn, Ni and Cr, the potentially toxic contaminants, is of great importance for identifying the principal pollution sources and their influence on the Morinje Bay at present and over time.

(According to IUPAC the quantity used here and called "concentration" should systematically be called "mass fraction",  $w$ ).<sup>32</sup>

### Site Characteristics

The Morinje Bay, with a surface area of 3 km<sup>2</sup> and a maximum depth of 21 m, is situated in the central part of the eastern Adriatic coast, 3 km SE of Šibenik (population 40,000 – Figure 1). The bay is hydrogeomorphologically divided into two parts – a shallow northern funnel (Morinje) and a deeper southern channel-shaped Jadrtovac passage. The Morinje Bay is bypassed by two major roads, one passing through the agricultural area of Donje polje located to the north of the bay, and the second crossing the southern, channel-shaped part of the bay. The community of Jadrtovac (200 inhabitants) is situated on the eastern shore of the bay.

The surrounding area of Morinje is mostly built up of Middle Eocene flysch (marly shale and sandstone),

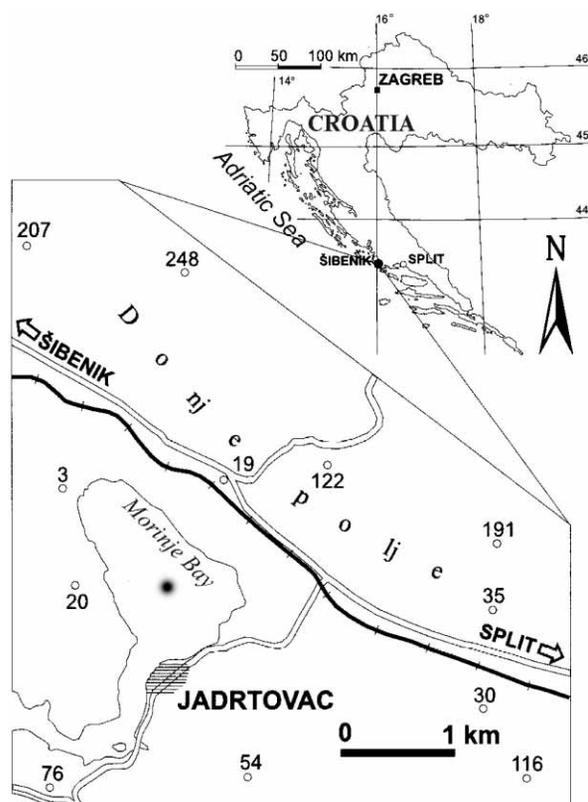


Figure 1. Map of the Morinje Bay area with the sampling site location (elevations of surrounding areas are shown in meters a.s.l.).

while Upper Cretaceous (Senonian) rudist limestone composes the Jadrtovac channel part of the bay.

Current activities in the area are primarily associated with agriculture, seasonal tourism and traffic (a major road bridge is located above the mouth of the bay and the local road passes about 100 m from the northern part of the bay).

Today, the Morinje Bay has no permanent riverine inflow into the bay, except for the insignificant and intermittent superficial inflow by one rivulet (Ribnik) and several submarine springs.

## EXPERIMENTAL

### Sampling

Sediment samples were taken by scuba diving, using hand-driven acrylic glass corers (tubes 50–120 cm long, with a 5–10 cm internal diameter), immediately deep-frozen and divided into 5 cm thick subsample slices.

### Sample Preparation and Analyses

Determination of the sediment grain-size distribution was performed by a combination of wet sieving using ASTM sieves and measuring the fine-grained silt and clay fractions (< 30  $\mu\text{m}$ ) using a Sedigraph 500 ET.

Mineralogical identification and a semi-quantitative estimate of principal minerals were made using a Philips 1050/25 PW X-ray diffractometer, equipped with a proportional counter, using Cu-K $\alpha$  radiation.

Concentrations of major (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P) and minor (Cu, Pb, Zn, Ni, Cr) elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a high-resolution VG Elemental Axiom SC machine. Reproducibility of the method was tested using the marine sediment reference standard MAG-1 (US National Bureau of Standards) and was about 10 % at the 95 % confidence level.

The  $^{137}\text{Cs}$  activity in dried samples was analyzed by gamma-spectrometry. Spectra were collected between 80,000 and 100,000 seconds, and a calibrated HPGe detector system coupled to a 4096 channel analyzer (Canberra) was used.  $^{137}\text{Cs}$  activities were calculated using the Canberra Genie-2000 software from the 661.6 keV peak.

The redox potential ( $E_h$ ) and pH in sediments were measured on-site, immediately after coring, using a Eh-pH-meter model Mettler MP-12 with INLAB 501 and INLAB 427 electrodes, which were inserted into the core through 1 cm-wide horizontally positioned holes in the tube, covered with plastic adhesive tape during coring.

Elemental sulfur was analyzed after CS<sub>2</sub> extraction, following the procedure of Troelson and Jorgenson.<sup>20</sup> Organic carbon was analyzed using a LECO IR-212 carbon analyzer, after removal of carbonates with phosphoric acid.

## RESULTS AND DISCUSSION

### Grain-size Distribution

The mean size (Md), sorting (So) and the contribution of the <30  $\mu\text{m}$  fraction in the sediment profile are presented in Table I. The sediment type is defined as fine-grained silt, since the distribution spectrum is found to be between 5.2 and 6.3  $\mu\text{m}$ . All subsamples can be classified as well sorted (So between 2.3 and 2.5) as a consequence of unimodal distribution. The share of the "total" fine-grained fraction (<30  $\mu\text{m}$ ) is relatively high at ca. 88 %. Granulometric parameters indicate constant patterns in recent and subrecent sedimentation of accumulated material.

### Mineralogical Composition and Sediment Sources

A semiquantitative estimate of major minerals detected by X-ray diffraction in the sediment core is given in Table II A. Table II B presents the mineral composition of

TABLE I. Granulometric parameters of Morinje Bay sediments<sup>(a)</sup>

Depth/cm	Md/ $\mu\text{m}$	So	Sk	Fgf/%
0–5	5.5	2.5	1.6	87.6
20–25	5.9	2.3	1.4	87.6
40–45	6.3	2.5	1.2	87.8
65–70	5.2	2.3	1.3	88.2

<sup>(a)</sup> Md = mean size, So = sorting, Sk = skew, Fgf = fine-grained fraction (< 30  $\mu\text{m}$ ).

TABLE II A. Semiquantitative estimate of the Morinje Bay sediment by X-ray diffraction

Depth/cm	Ca	Ar	D	Q	I	Chl	H	F
0–5	+++	++	trace	++	+	trace	+	trace
20–25	+++	++	trace	++	+	trace	+	trace
40–45	+++	++	trace	++	+	trace	+	trace

<sup>(a)</sup> Ca = calcite, Q = quartz, Ar = aragonite, D = dolomite, I = illite, Chl = chlorite, H = halite, F = feldspar; +++ = very abundant (<30%), ++ = abundant (10–30%), + = fairly abundant (2–10 %).

TABLE II B. Mineral composition<sup>(a)</sup> of the sediment (HCl resistant fraction)<sup>(b)</sup>

Depth/cm	Q	F	D	Op	Zo	Am	Py	G	T	Zr	Ap
0–5	54	21	+	7	+	6	3	3	1	1	+
20–25	58	20	+	6	+	5	2	2	2	1	+
40–45	56	21	+	7	+	6	2	3	1	1	+
65–70	55	20	+	7	+	5	3	4	1	1	+

<sup>(a)</sup> Mass fractions, w/%.

<sup>(b)</sup> Q = quartz, F = feldspar, D = dolomite, Op = opaque minerals, Zo = zoisite, Am = amphibole, Py = pyroxene, G = garnet, T = tourmaline, Zr = zircon, Ap = apatite, + = trace amount.

TABLE III. Chemical composition<sup>(a)</sup> of the Morinje Bay sediment

Depth cm	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI	tot.	C	S
0–5	29.8	8.9	2.0	1.8	0.04	1.9	20.8	2.7	1.7	0.4	0.2	28.4	98.7	7.7	1.2
5–10	30.7	9.6	1.6	2.3	0.04	2.0	19.6	2.7	1.8	0.5	0.1	27.4	98.2	7.5	1.3
10–15	33.1	10.5	2.0	2.3	0.04	2.1	17.8	2.4	2.1	0.5	0.1	25.5	98.5	7.0	1.5
15–20	33.2	10.7	2.2	2.2	0.04	2.1	17.7	2.4	2.0	0.5	0.1	25.2	98.4	6.6	1.4
20–25	30.9	9.9	2.5	1.6	0.04	2.0	19.5	2.5	1.9	0.5	0.1	27.4	98.7	7.7	1.4
25–30	25.7	7.9	1.6	1.8	0.03	1.7	24.7	2.5	1.6	0.4	0.1	30.4	98.4	8.3	1.2
30–35	28.6	9.3	1.2	2.3	0.03	2.0	20.5	3.1	2.0	0.4	0.1	29.6	98.9	8.2	1.2
35–40	26.1	8.4	1.8	1.6	0.03	1.9	21.7	3.1	1.8	0.4	0.1	31.7	98.5	9.2	1.2
40–45	26.9	8.3	1.0	2.4	0.03	2.0	20.5	3.2	1.7	0.4	0.1	32.5	99.1	9.4	1.2
45–50	25.1	8.1	0.7	2.2	0.02	1.8	21.3	3.0	1.7	0.4	0.1	35.0	99.4	9.4	1.2
50–55	30.3	9.5	0.8	2.8	0.03	2.0	18.3	2.7	1.9	0.5	0.1	29.7	98.5	8.6	1.4

<sup>(a)</sup> Mass fractions, w/% dry weight.

the HCl resistant fractions from the same sediment core. There is no significant difference between the mineralogical compositions along the core. The presence of substantial amounts of calcite is due to the authigenic-biogenic origin of the sediment and biological and physical weathering of carbonate rocks around the bay. Aragonite is entirely biogenic in origin since aragonite-forming organisms are relatively abundant in the Adriatic Sea.<sup>21,22</sup> Quartz is also present in substantial amounts and is mostly of terrigenous (most likely from flysch deposits) and partially of biogenic origin (opalized material). Other terrigenous minerals such as chlorite and feldspars were detected only in minor amounts.

According to mineralogical composition, four different sources of sediments can be recognized: (i) terrigenous material from aeolian supply and atmospheric deposition, (ii) terrigenous material from the Ribnik streamlet inflow, (iii) biogenic material of authigenic origin (*i.e.*, calcareous and siliceous organisms), (iv) terrigenous material from biological and/or physical weathering of the carbonate banks of the bay. The said sources were ordered according to their estimated share of the total sediment material accumulated in the bay.

### Chemical Composition

Concentrations of major elements, expressed as oxides, largely correspond to the mineral composition of the sediment as determined by X-ray diffraction. An exception is the relatively high mean SiO<sub>2</sub> concentration (biogenic in origin, from *Diatomeae sp.* algae), which could not be detected by X-ray diffraction analysis because of its amorphous form (Table III). Concentrations of major elements reflect the strong influence of terrigenous sedimentation as well as a relatively high average percentage (mass fractions, *w*) of FeO (2.1 %), Fe<sub>2</sub>O<sub>3</sub> (1.6 %), and K<sub>2</sub>O (1.8 %). The average concentration of CaO

TABLE IV. Trace metal concentrations<sup>(a)</sup> in the Morinje Bay sediment

Depth / cm	Cu	Pb	Zn
0–5	25	15	67
5–10	33	23	84
10–15	30	19	95
15–20	24	16	81
20–25	28	22	78
25–30	20	17	62
30–35	22	19	70
35–40	19	14	58
40–45	27	12	69
45–50	21	9	59
50–55	18	10	57

<sup>(a)</sup> w/μg g<sup>-1</sup> dry weight.

(20 %) is mostly a result of sedimentation of biogenic calcareous remains (shells, tests, *etc.*). It is likely that most of the calcium is biogenic, although chemical precipitation of CaCO<sub>3</sub> in shallow and warm waters of the bay is possible, but of minor significance. The MgCO<sub>3</sub> (1.9 %) originates from weathered dolomite lenses of the Upper Cretaceous age. Mg-calcite (MGC) was not detected, although its presence was expected. The relatively high concentrations of organic carbon (8.1 %) can be explained by the high accumulation rate of the sediment, resulting in preservation of the rapidly buried organic material. Total sulfur concentrations are relatively high (1.3 %) and probably mainly associated with iron sulfides (pyrite).

### Trace Metals Concentrations

Concentrations of Pb, Cu and Zn in the sediment core are presented in Table IV. Low concentrations of all trace metals analyzed in the sediment reflect a low anthropogenic impact. Table V presents the concentrations of trace

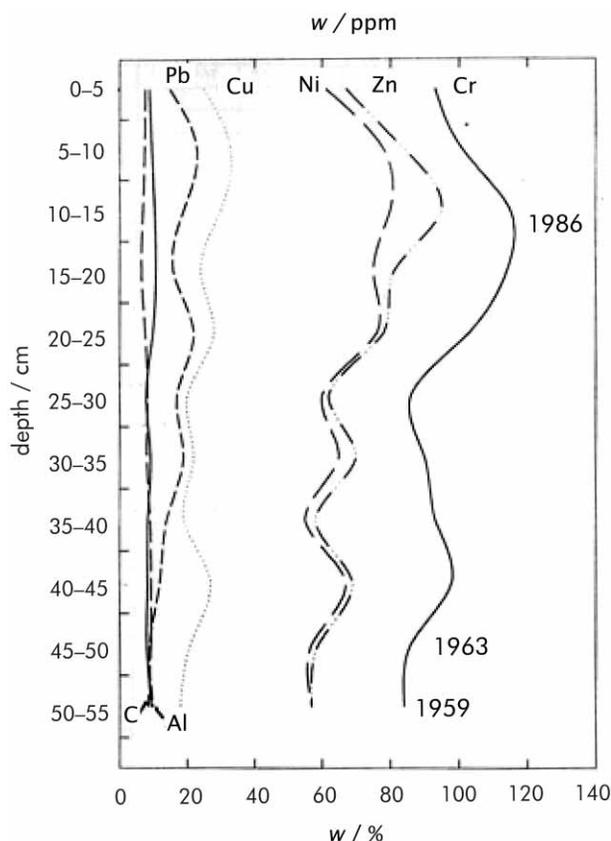
TABLE V. Trace metal concentrations<sup>(a)</sup> in different natural sediments

Reference	Cu	Pb	Zn
Limestone <sup>26</sup>	4.0	5.0	23.0
Shale <sup>26</sup>	43.0	22.0	95.0
Kornati <sup>25</sup>	13.7	12.4	23.0
Krka River <sup>25</sup>	9.6	28.8	40.7
Rogoznica lake <sup>8</sup>	2.63–14.20	8.45–23.28	9.18–32.51
This study	18–33	9–23	57–95

(a) w/ $\mu\text{g g}^{-1}$  dry weight.TABLE VI. pH and  $E_h$  values in the vertical sediment section

Interval cm	pH	$E_h$ mV
0–1	8.4	72
1–2	8.2	18
2–3	7.7	–264
3–4	7.6	–293
4–5	7.6	–300
5–6	7.4	–332
6–7	7.4	–326
7–8	7.4	–359
8–9	7.3	–345
9–10	7.2	–360
10–11	6.9	–382
11–12	7.0	–375
12–13	6.9	–384
13–14	6.4	–414
14–15	6.5	–405
15–16	6.5	–416
16–17	6.4	–412
17–18	6.4	–407
18–19	6.5	–411
19–20	6.4	–407

metals in coastal sediments of the islands of Kornati, the Rogoznica Lake (not subject to anthropogenic influence, *i.e.*, to a point-source of contamination) and the Krka river estuary.<sup>8,23,24,25</sup> Comparison of the average concentrations of trace metals in the sediment core from the Morinje Bay with the values frequently used to evaluate natural levels of these elements (concentration in an average limestone and shale – appropriate for sediments containing aluminosilicates as the major mineral phase,<sup>26</sup> Table V) shows that contents of all investigated trace metals are higher than those in an average limestone and generally lower than in an average shale. However, it is possible that the metal enrichment above this baseline may not be solely due to anthropogenic input. This enrichment in the sediments (with redox interface within the sediment column) may be explained by the recycling of Fe and Mn hydrous oxides, which control the exchange of trace metals between sediments and the water column.<sup>27</sup> In the anoxic

Figure 2. Downcore concentrations of trace metals (w/ppm), organic matter and  $\text{Al}_2\text{O}_3$  (w/%) in the dated sediment core profile.

part of the sediment column (below 2 cm depth – Table VI), this enrichment is determined by the adsorptive properties of organic matter and sulfide precipitation, and can be attributed not only to diagenesis but also to anthropogenic sources.<sup>28</sup> On the other hand, diagenesis may enhance trace metal mobility, even causing their remobilization from anoxic sediments.<sup>4,5,29</sup> This also explains the decrease of trace metal concentrations in the downward sediment column.

In the sediment core profile (Figure 2), a downward decrease of Pb, Cu and Zn appears to a depth of 45 cm, remaining practically constant. Taking into consideration the chemical composition of the sediment (Table III), it is obvious that the concentrations of organic matter and  $\text{Al}_2\text{O}_3$  are practically constant (Figure 2). It is therefore obvious that the organic matter and aluminosilicates are not the main factor controlling the metal distribution. All three metals have a constant concentration at the same depth, which indicates the final depth at which Fe sulfides are precipitated from the pore water. Hence, the Pb, Cu and Zn enrichment is probably of anthropogenic origin.

#### Sediment Accumulation Rate and History of Metal Pollution

The <sup>137</sup>Cs activities were measured down to the 75 cm deep sediment profile compartment. The measured <sup>137</sup>Cs

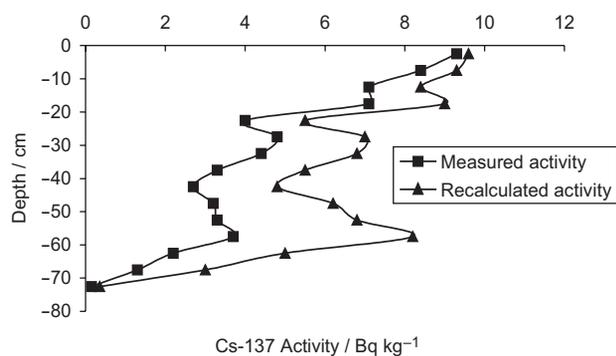


Figure 3. Activities of  $^{137}\text{Cs}$  in the vertical sediment profile.

activities, as well as recalculated activities for the estimated time of sediment deposition, are represented in Figure 3. The  $^{137}\text{Cs}$  activity is below the detection limit in the sediment below 70 cm depth. Maximum activity was detected in the uppermost 20 cm, with the first peak from the surface down to 5 cm, and the second between 15 and 20 cm, while a third maximum was found between 55 and 60 cm, which coincides with the  $^{137}\text{Cs}$  global fallout maximum in the early sixties of the twentieth century. The recalculated  $^{137}\text{Cs}$  vertical sediment profile clearly shows that the fallout contamination in the early 1960s and the Chernobyl-derived contamination in 1986 were very similar in this region. At the same time, it seems that sediment mixing caused by bioturbation and resuspension processes is very strong in the surface sediment down to some 20 cm depth. The sediment accumulation rate of 1.65 g (dry material)/cm<sup>2</sup> per year, corresponding to *ca.* 4.5 cm over a 3-year period) was calculated from these data. The relatively high average accumulation rate compared to the nearby coastal areas of the Rogoznica Lake (0.093 (g/cm<sup>2</sup>)/year or 0.45 cm/year)<sup>8</sup> and the Krka river estuary (0.024 cm/year)<sup>31</sup> can be a result of the high aeolian supply of material from the adjacent agricultural area of the Donje polje field, as well as of the influence of the rapid seasonal streamlet Ribnik, which drains the surrounding area. Figure 2 illustrates the Pb, Cu and Zn concentrations in the sediment profile, dated by vertical distribution of  $^{137}\text{Cs}$  activities. The lead profile strongly indicates that leaded gasoline is the principal anthropogenic source of Pb enrichment. The Pb concentrations increased up to the 1980s, decreasing thereafter because of the retreat of traffic in the vicinity of the village of Jadrtovac (an alternative route was put to use in the early 1980s). The upward increase in Pb concentrations is related to the increased traffic frequency as a consequence of a significant growth of tourism in nearby areas. A pronounced decrease of traffic commenced in 1991 with the beginning of the war in Croatia, almost isolating this area. Since gasoline with a very high level of lead (0.6 g Pb/l)<sup>31</sup> was phased out only in 2005, the decrease in Pb accumulation cannot be attributed to its substitution with unleaded gasoline like in western Eu-

rope. It was not possible to clearly assess whether the main Cu enrichments were due to the anthropogenic sources of an airborne origin (from aeolian and rivulet supply or agricultural use of copper-based plant protection agents) or from Cu-based antifouling paints from numerous boats moored in the Morinje Bay. There is no satisfactory explanation for the copper concentration maximum within the depth interval between 5 and 15 cm (whether it is caused by an alternative input of Cu into the Morinje Bay or is due to different diagenetic behavior). The oscillations of Zn and Pb concentrations may reflect tourist activities in this area, but also the development of housing and infrastructure utilities such as plumbing and galvanized iron fixtures. The main source of Zn is communal waste, while anthropogenic Pb is primarily airborne. The Morinje Bay peloid mud has a good potential to be used for medicinal and cosmetic purposes, since the measured trace metal levels are well below detrimental levels, though higher than the natural background values. Further conclusions about the enrichment of sediments with trace metals through anthropogenic sources, as well as their diagenetic distribution in the Morinje Bay, will be possible when more dated trace metal profiles become available in the future.

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## SAŽETAK

### Metali u tragovima u sedimentu iz Morinjskog zaljeva: Povijesni prikaz antropogenih imisija u plitki Jadranski zaljev

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Istraživane su geokemijske i sedimentološke značajke sedimenta iz Morinjskog zaljeva (srednja Dalmacija, Hrvatska), te brzina sedimentacije datiranjem izotopom  $^{137}\text{Cs}$  i vertikalna raspodjela metala u tragovima (Pb, Cu i Zn). Sediment Morinjskog zaljeva je sitno-zrnati, dobro sortirani mulj, a prosječna brzina sedimentacije je vrlo velika (4,5 cm kroz 3 godine, ili 1,65 g suhog sedimenta/cm<sup>2</sup> godišnje) u odnosu na brzinu sedimentacije u obližnjem Rogozničkom jezeru ili estuariju rijeke Krke. Razlog tomu je vjerojatno izraženi eolski donos materijala s poljoprivrednog područja Donje polje, a vjerojatan je i utjecaj sezonski aktivnog potoka Ribnik koji se prihranjuje s područja oko Morinja. Sadržaj ispitivanih teških metala u sedimentu Morinjskog zaljeva odgovara nezagađenim morskim karbonatnim sedimentima, iako koncentracije olova, bakra i cinka u recentnom i subrecentnom dijelu sedimentnog stupca (odgovara vremenskom rasponu od posljednjih 50 godina) odražavaju antropogeni utjecaj. Uporaba olovnog benzina osnovni je izvor Pb u sedimentu, dok su komunalna djelatnost i poljoprivreda izvor Zn i Cu.