Heavy metals in sediments of the Kaštela Bay

D. Bogner*, N. Odžak*, M. Juračic**, A. Barić* & D. Tibljas**
Institute of Oceanography and Fisheries, 21 000 Split, Croatia
E-mail: bogner@jadran.izor.hr
E-mail: odzak@jadran.izor.hr
E-mail: baric@jadran.izor.hr
***Department of Geology, Faculty of Science, University of Zagreb, 10 000 Zagreb, Croatia*
E-mail: juracic@olimp.irb.hr
E-mail: darko.tibljas@public.srce.hr

Abstract

Six sediment samples from Kaštela Bay (Adriatic sea) and 6 samples of source rocks around the bay have been taken in order to establish the dependence of heavy metal concentration on granulometric and mineral composition, on surface characteristics of the sediment, and on source rocks.

The mineral composition of sediments is homogeneous. It reflects mostly the lithology of the surrounding area (carbonates and flysch).

The concentration of cadmium is greater in parent rocks than in the sediments, which points to the partial lithogenous origin of cadmium. The increased concentration of cadmium found in top portions of sediments from locations 4 and 5 is probably a result of the anthropogenic activities.

The anthropogenic influence on Pb, Cu and Zn concentrations was identified in the all surface sediment samples.

1 Introduction

The Kaštela Bay is a semienclosed, oval-shape basin (Figure 1); the overall length is 14.8 km, width is 6.6 km, and average depth is 23 m. The surface area is 61 km^2, and total volume 1.4 km^3. The deepest part (more than 50 m) is located at the entrance of the Kaštela Bay (between the Marjan peninsula and the island of Čiovo). The area of the Kaštela Bay is densely populated, and industrially developed.

Numerous studies have demonstrated e.g. Prohić & Juračić[1], Krumgalz et al[2], Voutsinou-Taliadouri & Varnavas[3], that near shore sediments from coastal areas near industrial and urban centres are very often heavily contaminated by trace metals, such as cadmium, lead, zinc and copper. It is important to differentiate natural levels and the anthropogenic influence on heavy metal concentrations.

Heavy metals from sediment can be pollutants if crossing from sediments to the water column, as result of sediment resuspension, of biological activity, and of changing physical and chemical conditions, as suggested by Bonnevie et al.[4].

Measurement of heavy metal concentrations in parent rock may substantially help to determine the anthropogenic influence on heavy metal concentrations in sediments.

2 Methods

The samples were collected in March 1994 at 5 locations in the Kaštela Bay (Figure 1) using a plastic gravity corer. The inner diameter of the plastic corer was 3.1 cm. At the location 6 in shallow water, sediment was taken by manually operated corer in May 1995. Immediately after sampling, the samples were frozen until further treatment. On the land, samples of parent rocks were taken in March 1995 at 6 locations (Figure 1).

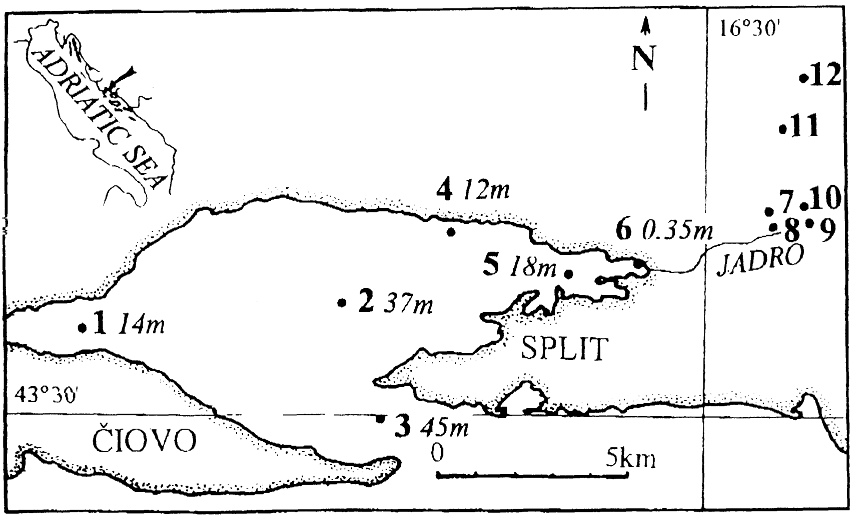

Figure 1. Map of sampling locations.

Samples were defrosted at room temperature, sliced into 1 cm long subsamples, dried at 60 °C and, after cooling to room temperature, chrushed in a mortar.

In these paper results on granulometric and mineral composition of 4 cm surface layer are presented, where as concentrations heavy metals, organic matter and carbonate are presented for 5 cm surface layer.

The granulometric composition of sediment was determined by sieving (>63 μm) and areometring (Casagrande) (<63 μm).

The mineral composition was determined by X-ray diffractometer. Heavy minerals were determined in the 63-125 μm fraction, using a polarisation microscope. Carbonate content was determined as weight loss after treatment with 4M HCl according to Loring & Rantala[5].

The concentrations of heavy metals (Cd, Pb, Cu, Zn) were measured by the ET-AAS method using a Perkin-Elmer 1100 B. For trace metal determination, samples of the dry sediments were digested with a mixture of HF, HNO_3 and $HClO_4$ according to Bogner[6].

The organic matter content was determined as a weight loss after H_2O_2 treatment and heating at 450° C for 6 h.

3 Results

The results of granulometric analysis and organic matter content are presented in Table 1, while parent rock characteristics are presented in Table 2. At the shallower stations (1, 4 and 6), the sediment is composed mainly of fine sand and silt. The average particle size (Mz = 78.1 - 113 μm) correspond to very fine sand. Sediment samples taken from the deeper locations (2, 3 and 5) are silts (Mz = 20.5 - 37.3 μm).

Table 1. Granulometric characteristic of sediment samples and organic matter content. (Sediment type according to Shepard[7])

Location	*Bottom depth (m)*	*Clay (<4 μm) (%)*	*Mz (μm)*	*Sediment type*	*Organic matter (%)*
1	14	1	113	silty sand	5.26
2	37	16	22.8	silt	8.89
3	45	17	20.5	silt	6.05
4	12		93.1	sandy silt	8.78
5	18	3	37.3	silt	8.68
6	0.35		78.1	silty sand	2.52

X-ray diffraction method has revealed that mineral composition of sediment samples taken from the Kaštela Bay is uniform. Calcite and quartz are more abundant then aragonite, illite and feldspar. Under the polarising microscope opaque as well as, transparent grains and skeletal debris were observed. In transparent heavy mineral fraction grains of hornblende, garnet, augite and epidote are most abundant.

Table 2. Parent rock characteristics. (Age ascribed after Marinčić et al.[8])

Location	*Age*	*Geological unit*	*Rock-samples*
7	$^2E_{2,3}$	flysch	marl
8	$^2E_{2,3}$	flysch	marl
9	Ol	breccia	different carbonate fragments
10	E_3^2	Promina deposit	marl
11	K_2^3	limestone	limestone
12	K_2^1	limestone with dolomite lens	limestone

Organic matters vary in the range from 2.52 to 8.89 % (Table 1). The lowest is in coarse grained sediment sample from the location 6, while the highest share is found at locations 2 and 5.

The carbonate share is very high, both in the parent rocks and marine sediments. It varies from 39 % in marl to 99.9 % in limestone, while in marine sediments it varies from 45.2 to 61.8 % (Figure 2).

The results obtained for cadmium in the sediment and parent rocks concentration are illustrated in Figure 3. This figure shows that parent rocks in general, (except from the location 10) have considerably higher concentrations of cadmium than the sediments.

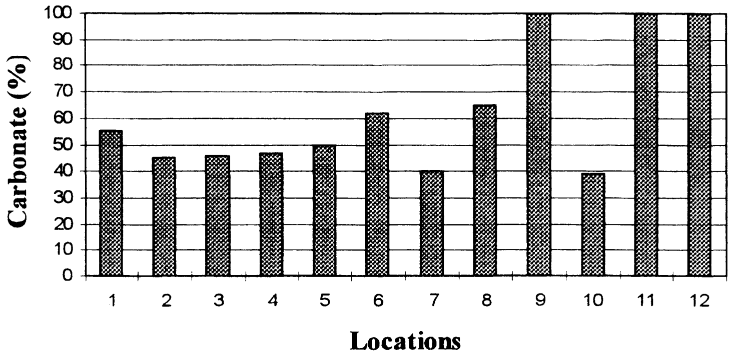

Figure 2. Average carbonate contents (%)

Transactions on Ecology and the Environment vol 14, © 1997 WIT Press, www.witpress.com, ISSN 1743-3541

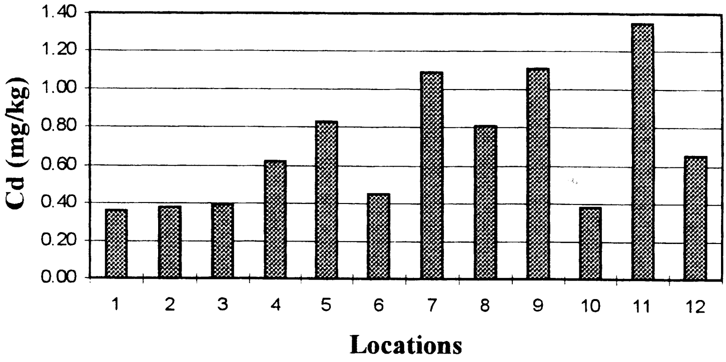

Figure 3. Average cadmium concentrations (mg/kg)

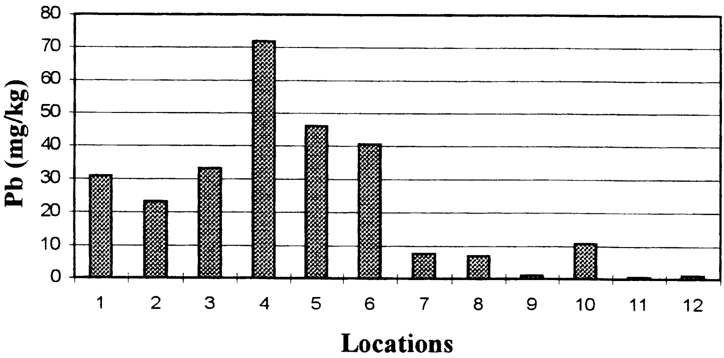

Figure 4. Average lead concentrations (mg/kg)

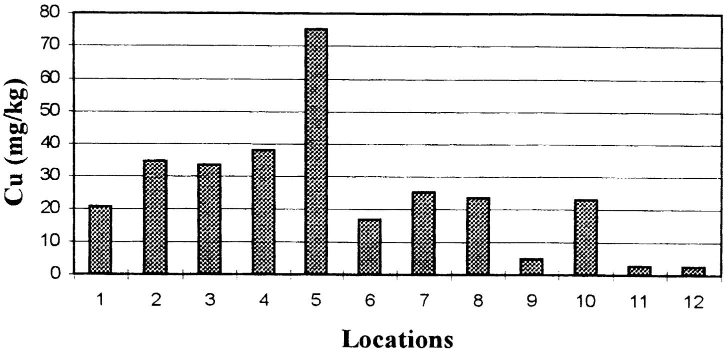

Figure 5. Average copper concentrations (mg/kg)

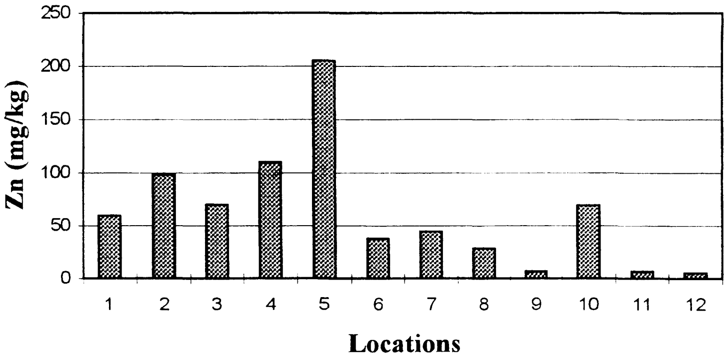

Figure 6. Average zinc concentrations (mg/kg)

The lead, copper and zinc concentrations in marine sediment samples were much higher than in the parent rocks (Figures 4, 5 and 6). The average lead concentration in sediment samples was a 8.7 times higher then the average concentration in the parent rocks. For copper and zinc, the increase was 2.7 and 3.6 respectively.

4 Discussion

The sediment type varies with locations. In the shallower part of the Bay (at locations 1, 4 and 6, above the wave base), the sediment was coarse-grained, while fine-grained sediment prevailed at the deeper locations (2, 3 and 5).

Increased carbonate concentration at the location 6 is very probably a result of the deposition of terrigenous and biogenic material (mainly remnants of benthic organisms). In terms of numbers, Foraminifera and Ostracoda were the most frequent, but certain quantity of sea urchins, spines, some shells and snails were also found.

Differences in organic matter concentrations are mainly result of different grain sizes of sediment as described by Horowitz & Elrick[9]. High organic matter content in sediment can be result of eutrophication phenomena induced by the discharge of sewage waters near Vranjic (location 5). Intensive summer phythoplankton bloom (dominated by red-pigmented dinoflagelates), known as "red tide", is a usual event in this area, as described by Kušpilić et al.[10].

The studied heavy metals may have different origins, including the anthrophogenic ones. A comparison between trace metals concentration in surface sediment and in source rocks may show a significant difference. The higher concentration of heavy metals in marine sediments than in parent rock may be attributed to the anthropogenic influence. In this case lead, zinc and copper concentrations are much higher in the marine sediments then in the parent rocks. At the same time, the metal concentrations are decreasing with the sediment depth according to Bogner[6]. This may lead to the conclusion that these metals in marine sediments are mostly of the anthrophogenic orgin. Contrary to this, the cadmium concentrations in parent carbonate rocks in general are higher than in the marine sediments. But, at the locations 4 and 5 (nearby location of urban waste discharge outlets), the cadmium concentration in upper sediment layers is increased compared to other sediments. This, may indicate an area of a limited cadmium contamination by urban weste.

5 Conclusions

All of the locations contained more lead, zinc and copper in the upper sediment layer then in parent rocks. Urban waste water is probably the main source of metal contribution.

Contamination of marine sediments by cadmium is limited only to the eastern part of the Bay. This part receives the major portion of domestic and industrial waste waters discharged into the bay.

References

1. Prohić, E. & Juračić, M. Heavy Metals in Sediments-Problems Concerning Determination of the Anthropogenic Influence. Study in the Krka River Estuary, Eastern Adriatic Coast, Yugoslavia, *Environ. Geol. Water Sci.*, 1989, **13 (2)**, 145-151.

2. Krumgalz, B. S., Fainshtein G. & Cohen, A. Grain size effect on anthropogenic trace metal and organic matter distribution in marine sediments, *Sci. Total Environ.*, 1992, **116**, 15-30.

3. Voutsinou - Taliadouri, F. & Varnavas, S.P. Geochemical and sedimentological patterns in the Thermaikos Gulf, north-west Aegean sea, formed from a multisource of elements, *Estuar. Coast. Shelf Sci.*, 1995, **40**, 295-320.

4. Bonnevie, N.L., Huntley, S.L., Found, B.W. and Wenning, R.J. Trace metal contamination in surfical sediments from Newark Bay, New Jersey, *Sci. Total. Environ.*, 1994, **144**, 1-16.

5. Loring, D.H. & Rantala, R.T.T. Manual for geochemical analyses of marine sediments and suspended particulate matter, *Earth-Science Reviews,* 1992, **32**, 235-283.

6. Bogner, D. Površinski sedimenti i utjecaj njihovih fizičko-kemijskih svojstava na raspodjelu teških kovina u Kaštelanskom zaljevu. Magistarski rad, Sveučilište u Zagrebu. 1996.

7. Shepard, F.P. Nomenclature based on sand-silt-clay relations, *J. Sediment. Petrol,* 1954, **24**, 151-158.

8. Marinčić, S., Korolija, B. & Majcen, Ž. Osnovna geološka karta SFRJ 1:100000, List Omiš K 33-22, Inst. za geol.istraž. Zagreb, Savezni geol. zavod, Beograd,1976.

9. Horowitz A.J. & Elrick K.A. The relation of stream sediments surface area, grain size and composition to trace element chemistry, *Appl. Geochem.,* 1987, **2**, 437-451.

10. Kušpilić, G., Marasović, I., Vukadin, I., Odžak, N. & Stojanoski L. Hydrographic conditions and nutrient requirements during red tide in the Kaštela bay (middle Adriatic), *Acta Adriatica*, 1991, **32 (2)**, 813-826.