CADMIUM, LEAD AND ORGANIC MATTER DISTRIBUTION IN COASTAL SEDIMENT FROM THE ADRIATIC SEA

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Abstract

The spatial distribution of Cd, and Pb has been studied in surface sediments of the eastern Adriatic coastal region. In addition, Pb concentration has been determined in long sediment cores dating back to preindustrial time. The results indicate that trace metal concentrations in surface sediment layer depend both on pollution sources, and on local characteristics of the marine and terrestrial environment. Generally, most of the concentrations are not high revealing that the coastal area is not heavily polluted. Granulometric and geochemical data indicate the existence of some differences between sediments formed in the vicinity of fresh water input and sediments from areas without fresh water input.

1. INTRODUCTION

Coastal marine sediments are a major repository of trace metals as well as a major potential source of trace metals [1]. Man's activities (industry, agriculture, and traffic) affect the marine system, and in combination with mineralogical, morphological, granulometric and geologic characteristics of the sediment affect the chemical behaviour and distribution patterns of trace metal and organic matter in sediments. Organic matter is already known as a component of sediment directly related to trace metals distribution [2]. Behaviour of trace metals during estuarine mixing and in coastal marine sediments is largely related to their capacity for complexation with organic materials in truly dissolved, colloidal and macro-particulate phases [3]. The colloidal phase of trace metals from river and estuarine system can be removed from the water column such as small particles. Hence, the continental shelf alters the dissolved trace metals input from land into the open sea [3, 4].

2. STUDY AREA AND MATERIALS AND METHODS

Trace metals and organic matter were studied in sediments of the ecologically, economically and scientifically important eastern coastal area of the Adriatic Sea (Fig 1). The area is endangered due to untreated domestic and industrial waste discharges (stations 1, 6, 7, 8, 10 and 11) both, directly and via rivers (stations 2, 7 and 10) and streams draining storm water into the sea. Sediment samples were collected in July 1996 (Stations 1 – 5 and 7) and in July 1997 (Stations 6 – 11), using a plastic gravity corer of 6 and 3.5 cm internal diameter. The samples were frozen immediately after collection. Five centimetre long sediment samples from 11 stations were sliced horizontally into 1 cm long sections and analysed separately for Cd and Pb. In addition to this, lead and organic matter were analysed in much longer sediment cores sampled in July 1996 at stations 1-5 and 7 using a plastic gravity corer of 6 cm internal diameter. About 0,1 g of sediment sample (from each sediment layer) was digested using a mixture of acids in a Teflon vessel and heated [5]. The concentrations of lead and cadmium were measured using an atomic absorption spectrometer (Perkin-Elmer Model 1100 B, equipped with an HGA 700 graphite furnace and an AS 60/70 Autosampler System). A National

Bureau of Standards estuarine sediment (SD-M-2/TM) were treated and analysed for each trace metal in the same way as the sediment samples to evaluate the accuracy of measurement. The observed results showed great compliance with certified values: recovery was 93 % for Pb and 88 % for Cd.

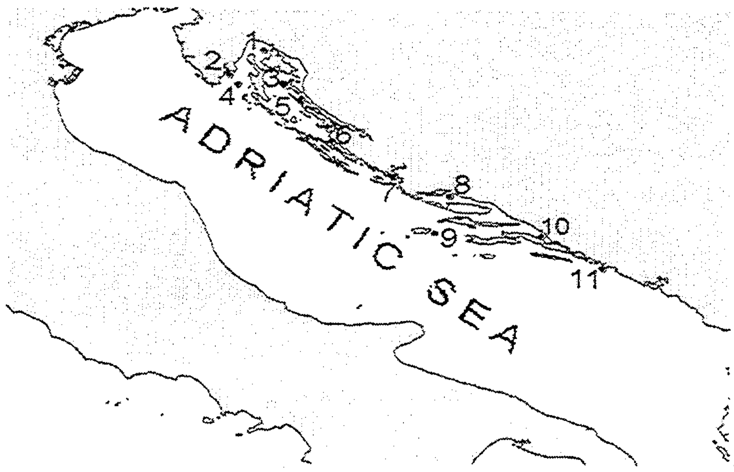

FIG 1. The study area with sampling sites

The organic matter content in the same sediment sections was determined by H_2O_2 treatment of samples at 450°C for 6 hours. The loss of weight after this treatment was assumed to be due to organic matter content [6]. Carbonate content was determined as weight loss after treatment with 4M HCl [8]. Granulometric composition was determined in 5 cm long sediment sections by sieving (>0.063 mm) and areometring (< 0.063 mm) according to Casagrande.

3. RESULTS

The content of fine fractions (< 0.032 mm) in sediment samples from all stations was relatively high and varied between 38-88 %, except from station 9, where it was only 16 % (Table 1). This station is located offshore while the others are located in channels, estuaries or near-shore areas. Organic matter is the principal component of fine-grained sediment.

The distribution patterns of Cd and Pb in the studied sediment samples revealed the existence of two zone having two different levels of trace metals. Figure. 2 shows that the Cd and Pb in general, are higher in sediment samples from the southern Adriatic, particularly from stations 7, 8 and 10 which are exposed to anthropogenic influences. The lowest concentration was found in the sediment sample taken from station 9. Station 9 is located far away from land based sources of pollution and the concentration is considered natural [8]. Station 11 is very specific. It is located close to the shore, but biological and chemical date indicate that it is under the strong influence of deep Adriatic water [9]. Cadmium concentrations were the highest at station 7 (0.487-0.747 mg/kg), located in the estuary of the river Krka. The estuary is used as a harbour for phosphate ore import and fertiliser export. On the riverbank the ferro-alloy factory was operated for more than 60 years, and raw material, products and by-products were drained directly into the estuary. The higher trace metal concentrations found in this area (three times as much as at station 9) may be related to the above mentioned activities. The discharge of untreated urban waste into the river estuary most likely also contributes to the increase in metal concentration. Organic matter content at this station is also high, 6.54 ± 1.48 %, while the sediment is of a fine-grained clayey silt type (Table 1). The main source of organic matter is the Krka river [10], but the contribution of urban wastewater generated by approx. 70,000 inhabitants, and discharged untreated into the estuary is a significant source as well.

Station 8 is located in front of the town of Split, the largest city on the Croatian coast. Urban wastewater discharged into the sea without treatment is the main source of organic matter. Organic mater content in the sediment sample is high, in the range between 5.7 and 7.2%. Station 10 is located in the area that is under the influence of the Neretva River and of the nearby town and harbour. The river drains runoff water from agricultural land. Concentrations of Cd and Pb and in the sediment sample from this station are high, while Pb is high in the sediment from station 11 (Fig. 2.).

TABLE I. GRANULOMETRIC COMPOSITION OF SEDIMENT FOR 5 CM. (SAND > 0.063 mm SILT 0.004-0.063 mm, CLAY < 0.004 mm) AND CARBONATE CONTENT (%).

Station	Sand (%)	Silt (%)	Clay (%)	Sed. type	< 0.032 mm (%)	Carbonate (%)
1	9	72	19	clayey silt	64	35
2	14	58	28	clayey silt	68	38
3	3	80	17	Silt	76	42
4	43	40	17	silty sand	41	39
5	42	48	10	sandy silt	38	57
6	16	63	21	clayey silt	62	41
7	14	62	24	clayey silt	63	55
8	8	62	30	clayey silt	80	45
9	78	15	7	Sand	16	73
10	1	68	31	clayey silt	87	39
11	3	51	46	clayey silt	88	21

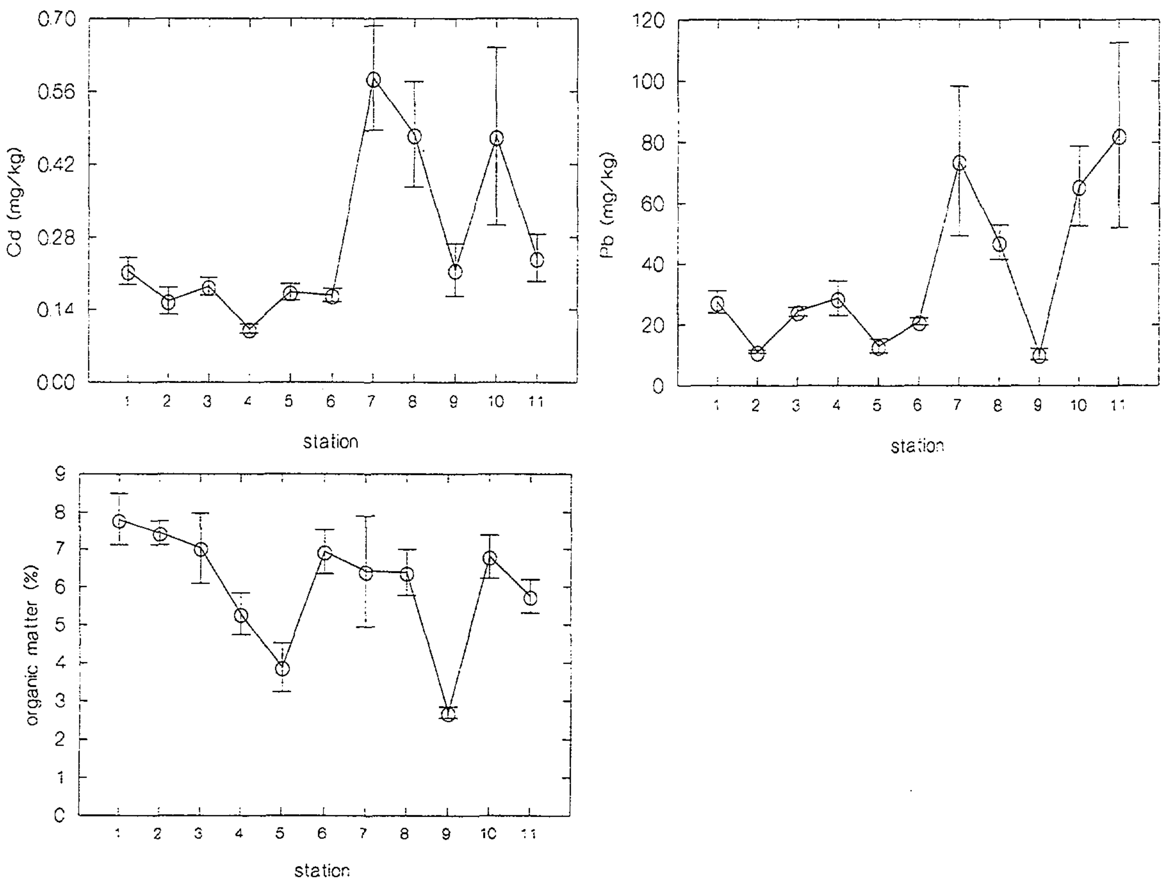

FIG. 2. Trace metal distribution and organic matter content in the sediment (upper 5cm) from 11 station from the coastal Adriatic Sea (Croatia).

The distribution pattern of organic matter differs from those for the trace metals (Fig. 2). While trace metal concentrations were much higher in the southern coastal area, particularly near industrial zones (stations 7, 8), the organic matter content in the most northern area is a little higher than in the other areas (Table 1). The high organic matter content may be related to the high input of suspended organic material from land based sources: rivers (stations 2, 7, 10) and urban waste outlets (stations 1, 8). The lowest content of organic matter was observed at stations 5 and 9, which are located far away from land based sources of organic matter. The sediment samples at these two stations are coarse- grained indicating the absence of organic matter, while at the other stations they are fine grained. Despite the fact that the organic matter content in sediment samples from stations 1-5 is high, the trace metal concentration at same stations are relatively low. This may be explained by the absence of a significant input of trace metals into the marine environment.

Figure 3 shows Pb concentrations in long sediment cores sampled at stations 1, 3 and 7. At stations 1 (nearby the town of Rijeka), 3 (island Rab) and 7 (Šibenik, the river Krka station) the increased Pb concentration in the 10 cm surface sediment layer may indicate an anthropogenic influence. The average Pb concentration in all samples was approx. 15 mg/kg, except at stations 1 and 7, where the average concentration was 22 mg/kg. The Pb concentration increase in the upper layers is not accompanied by an increase of organic matter content (Fig. 3). Organic matter content, in general, is higher in the upper part of the core. The average organic matter content in deeper layers is 5 %, while at the surface it reaches 8 %.

4. DISCUSSION

The coastal area, where the studied sediment samples were taken from, is very specific in terms of local oceanographic characteristics and due to fresh water influences. Sediment samples differ in their origin in prevailing sediment type and organic matter content as the result of the surrounding lithology, and local oceanographic characteristics. Sediment from station 3 and 4 are of biogenic origin, while stations 1, 2 and 5 are of terigenic origin. Cretaceous limestone and Eocene flysch are predominant in the entire coastal area, while alluvial sediments are rare, found mainly at river mouth (in the vicinity stations 2 and 10). In the non-polluted areas, the weathering process of land-based material is the main source of particles sinking on the seabed and forming marine sediments. Flysch is the main source of fine-grain clay particles, while coarse-grained sediment represents mainly preholocene and/or particles of recent marine biogenic origin. At stations that are not located in the immediate vicinity of the coast the predominant sediment types are silt (station 3), sandy silt (station 5), silty sand (station 4) or sand (station 9). Clayey silt type of sediment, with clay content between 19 and 46 %, is present at other stations. The highest content, found at station 11, is most likely caused by the discharge of fresh water from a nearby hydroelectric power plant, using the fresh water from the hinterland river Trebišnjica. It is confirmed by the lowest carbonate content (21 %), while at the other stations, the carbonate content varied between 35 and 73 % (Table I). The former indicates that the particles originated from a remote source area, are not primarily of carbonate composition, while the high carbonate contents at the other stations indicate the nearby origin of sediment particles. Organic matter contained in the marine sediment may be originated either from the sea or from the land (anthropogenic and/or natural source) [12]. The lowest organic matter content (2.6 %) was recorded at station 9, which is under the influence of open sea waters. Station 11 is also under the influence of open sea waters, but at this station the organic matter content is twice as high as at station 9. This is the consequence of the impact of the already mentioned nearby fresh water discharge. The highest values (6.3-7.8 %) was found in polluted bays and channels (stations 1, 6), in areas under freshwater influence (stations 2, 7, 8, 10) and indicate a land-based source of organic matter. By plotting the relation of organic matter with clay fraction content (Figure 4), stations can be separated into two groups; the first one containing stations that are not under the influence of freshwater, and the second one containing stations located in the vicinity of freshwater sources. The first group of stations, the organic matter content is linearly dependent on the clay particle content ($r=0.923$, $P=0.009$, $b=2.049$). The percentage of organic matter in the second group of station is lower than expected, which means that clay particles are primarily consisted of non-organic (mineral) matter, while at the first group the small size particles are of organic origin. Trace metals contained in marine sediments may be of natural and of anthropogenic origin. A question that should be answered is what is the natural background and what is the contribution of anthropogenic activities? Discharge of the trace metals either by rivers or directly into the sea would result in metal accumulation in marine sediments. In fresh and marine waters metals are adsorbing onto clay minerals and/or are bonding to organic matter. Flocculation and sedimentation of particle clay minerals trap organic matter, and trace metals remain trapped in the marine sediments. Primarily both high clay and moderate organic matter

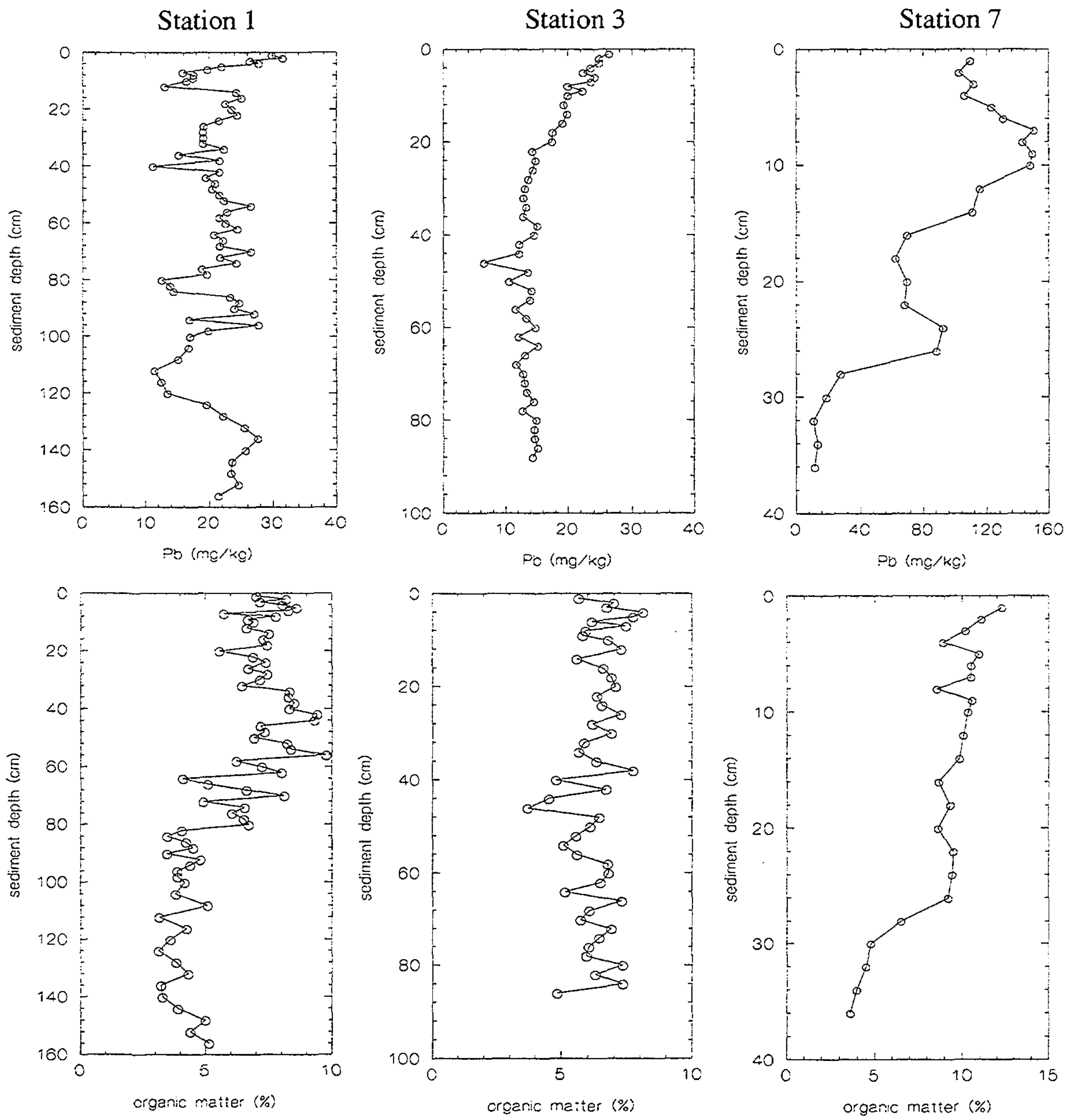

FIG. 3. Lead and organic matter distribution along the sediment cores from stations 1, 3 and 7.

content may explain relatively high concentration of trace metals at station 11. Such high metal concentrations suggest that all metals are of anthropogenic origin collected over the very wide drainage area of the Trebišnjica River. The highest trace metal concentrations, recorded at station 7 are the result of the above mentioned sources of pollution, but they are also the result of specific local hydrodynamic characteristics of the Krka River estuary. Namely, a relative thick surface layer of fresh water is discharging through a narrow channel into the open sea, while the majority of marine water remains in the station area. Unexpectedly low concentrations of all trace metals were found at station 1, probably due to predominant current carrying discharged matter opposite to the station.

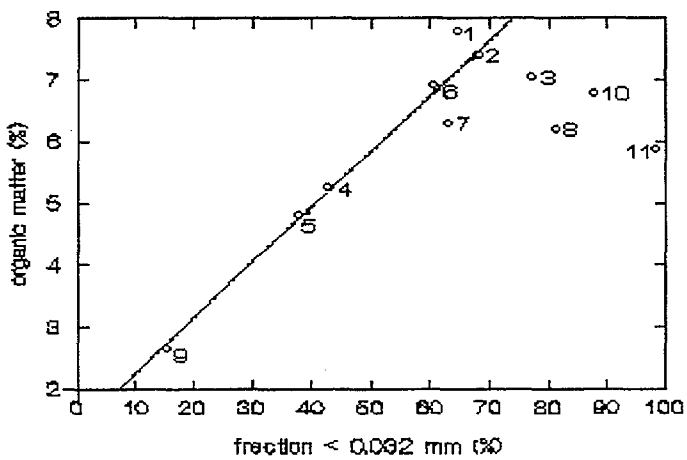

FIG. 4. Linear relationship between organic matter content and percentage of <0,032 mm sediment fraction.

Lead concentration in the long sediment core at station 1 clearly indicates the concentration increase in the top twelve centimetres (Fig.3). Taking the yearly estimated sedimentation rate of 1.7 mm [Juračić, unpublished data] this depth corresponds to the period of 70 years. Cs ^{137} measurements on the sediment sample indicated that the sedimentation rate is not higher than 3.2 mm/yr. [Barišić, unpublished data]. A similar concentration increases were found at station 3 where the sedimentation rate is higher due to river contribution; the concentration increase is visible in deeper layers similar as those at station 7. The background Pb concentration at station 1 is approximately 22 mg/kg, while at the two other stations the concentration is approximately 15 mg/kg, which is the result of the geochemistry of source material. The small decrease in the surface layer at station 7 is probably the result of a drastic reduction of all economic activities in the region that has occurred over the last 10 years. Variations in concentrations of Pb, particularly from stations very close to seashore, could be the consequence of temporal variations in precipitation and suspended matter input.

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