DISTRIBUTION OF HG, CU, ZN, CD AND PB IN SURFACE SEDIMENTS FROM THE COASTAL REGION OF THE CENTRAL ADRIATIC

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Abstract

Surveys of Hg, Cu, Zn and Cd concentrations in surface sediment began in 1983 at six main stations along the central Adriatic coast. The results of chemical and statistical analyses for 1983-1995 show that the highest concentrations of almost all the heavy metals examined are found in the naturally enclosed areas with marginal biodegradation abilities (Kastela, Sibenik, Gruz Bays), where some heavy metals have already accumulated in edible organisms (mussels, fish) in concentrations higher than the WHO recommended values for human consumption. Although these bays are still receiving uncontrolled quantities of different pollutants, it is encouraging that owing to the semi-enclosed nature of the bays, pollution by these metals has not yet reached the open sea.

Key-words: metals, pollution, sediments, Adriatic Sea

Introduction

Since the biogeochemical cycles of individual metals could not be studied in detail, the monitoring of sediment became the principal focus based on the assumption that the history and present state of ecosystem pollution could be identified in sediments. Even though the available data give a rather rough estimate, it is sufficient to determine the intensity and the extent of anthropogenic loads in individual areas.

Materials and methods

Sampling and analytical procedures. The sediment samples were collected using a plastic gravity corer. Immediately after sampling, surfacial sediment sample (5 cm top layer) was cut from the core tube and frozen until further treatment. Before analysis the samples were defrosted at room temperature, dried at 60°C and, after cooling to room temperature, ground in a mortar. The granulometric composition of sediment was determined by sieving (> 63 μm) and areometring (Casagrande < 63 μm). The organic matter content was determined as a weight loss after H_2O_2 treatment and heating at 450°C for 6 h.

Chemical analysis. For Cu, Zn, Cd and Pb determination, 0.1-0.2 g of dry sediments were placed in a Teflon vessel and digested with a mixture of hydrofluoric (HF), nitric (HNO_3) and perchloric ($HClO_4$) acid in a microwave oven [1]. The digested samples were cooled and diluted to 25 ml with milli-Q water. The concentrations of Cu, Zn, Cd and Pb were determined by the ET-AAS method using Perkin-Elmer 1100B, equipped with a HGA 700 Graphite furnace. Each sample was analyzed at least in duplicate. The accuracy and precision of the methods were evaluated on the basis of analysis of international standard reference materials (marine sediments SD-N-1/2/TM: SD-M-2/TM-IAEA, Monaco; SRM 1646-NBS) with each batch of samples.

Total mercury values were obtained by digestion of dry sediments with HNO_3 and H_2SO_4, reduction to Hg^0 by $SnCl_2$, and detection by cold vapour atomic absorption or fluorescence spectrophotometry (CV AAS/AFS). The accuracy of the results was also checked by the analyses of SRM IAEA 356, certified for mercury [2].

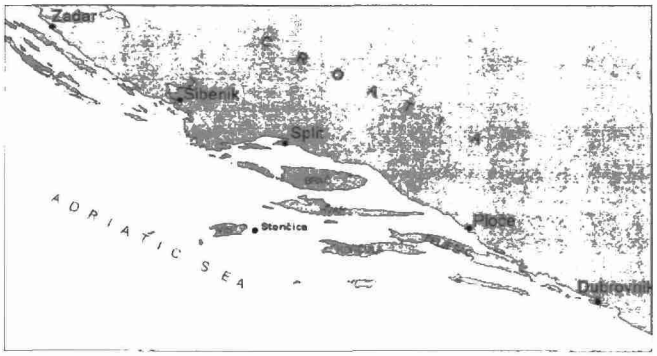

Fig. 1. Study area in the Central Adriatic.

Results and discussion

Granulometric characteristics of surface sediments from the study area, together with average percentage of organic metter, are presented in Table 1. According to the sand-silt-clay ratio [3], surface sediments (0-5 cm) in front of Zadar, Sibenik and Split were clayey silt, off Ploce and Dubrovnik sandy silt, and at the reference station Stoncica silty sand. Organic matter varied in the range from 3,65 to 8,95%. The results of the chemical analyses and statistical interpretation for the survey period (1983-1995) are given graphically and tabulated for each individual metal.

Table 1. Granulometric characteristics of sediment samples and organic matter content.

Stations	Bottom depth (m)	Sediment tipe [3]	Organic matter (%)
ZADAR	34	Clayey silt	6,97
SIBENIK	38	Clayey silt	8,84
SPLIT	34	Clayey silt	6,10
PLOCE	20	Sandy silt	7,38
DUBROVNIK	33	Sandy silt	8,95
STONCICA	103	Silty sand	3,65

Mercury (Hg). Mercury levels in sediment were considerably more than the background concentrations at almost all the stations, with the exception at Ploce and Zadar where the mercury level was slightly higher than at the reference station Stoncica (Fig. 2). Mercury content in sediment showed enhancement (positive regression coefficients b-Table 2) at almost all the stations (except in Split and Ploce). This was particularly pronounced at the stations close to Dubrovnik and Sibenik. Because Kastela Bay is rather enclosed, high mercury concentrations in its sediment (KZ_1, KZ_2) do not significantly affect mercury levels in sediment from Split, where the tendency for a decrease in mercury content was recorded.

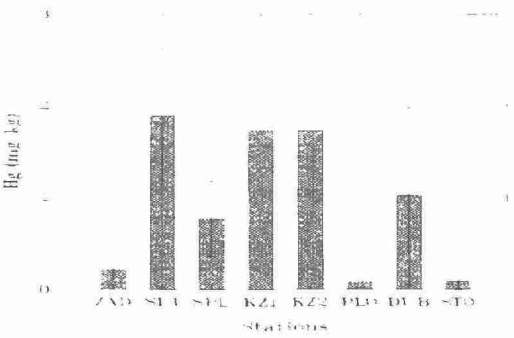

Fig. 2. Average mercury values in sediments from the study area for the study period.

Table 2. Trends of mercury level variation in sediment for the study period. N - number of sampling; b - regression coefficient.

	STATIONS							
Hg	ZADAR (ZAD)	SIBENIK (SIB)	SPLIT (SPL)	KASTELA BAY (KZ1)	(KZ2)	PLOCE (PLO)	DUBROVNIK (DUB)	STONCICA (STO)
N	10	10	10			9	10	6
b	0.013	0.072	-0.067			-0.008	0.132	0.016

Copper (Cu). Copper concentrations in sediment from Sibenik, Split and Dubrovnik stations differed considerably from the level in sediments from the reference station Stoncica (Fig. 3). However, copper level in sediment of Kastela Bay was lower than at the station off Split. It should be pointed out that a tendency for a reduction in copper content (Table 3) was recorded in the sediments of Split, Stoncica and Sibenik during the study period. This tendency was also noted at the central Kastela Bay station (KZ_2).