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TOTAL MERCURY, CADMIUM, COPPER, ZINC AND ARSENIC CONTENTS IN SURFACE SEDIMENTS FROM THE COASTAL REGION OF THE CENTRAL ADRIATIC*

SADRŽAJ UKUPNE ŽIVE, KADMIJA, BAKRA, CINKA I ARSENA U POVRŠINSKIM SEDIMENTIMA PRIOBALNOG PODRUČJA SREDNJEG JADRANA

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In the framework of the Long-term Programme for Pollution Monitoring MED POL Phase II, the Institute of Oceanography and Fisheries in collaboration with the »J. Stefan« Institute, has analysed total Hg, Cd, Cu, Zn and As contents by neutron activation analysis (NAA) in surface sediments sampled during 1985 and 1986 in the vicinity of industrial and urban centres located over the wider territory of the central and southern Adriatic coast. Results obtained show that the highest values for most elements were recorded from stations in the vicinity of Šibenik and Split, suggesting the influence of industrial and urban effluents from these two largest central Adriatic towns.

INTRODUCTION

Heavy metals enter the marine environment through different routes (surface runoff, domestic and industrial effluents disposed through outfalls, and the atmosphere). Various anthropogenic activities (such as agriculture, mining, industrial processing of metals, as well as the use of metals and metal components) have resulted in increased inputs of heavy metals into marine ecosystems.

The release of heavy metals into the aquatic environment (particularly the toxic ones) has long been recognized as a major treat to aquatic fauna and human health.

A particularly serious situation was observed in the vicinity of industrial and urban centres, since industry is the principal source of pollution by these microelements.

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Since sedimentation processes, especially in areas receiving large amounts of terrigeneous and biogenic material, seems to be the major mechanism responsible for removing heavy metals to the sea bottom (UNEP, 1986.), the determination of the heavy metal contents of sediments is one of the first steps in the assessment of the degree of heavy metal pollution of an exposed area.

Therefore, the present work is an attempt to assess total Hg, Cd, Cu, Zn and As contents in surface sediments, sampled in the vicinity of industrial and urban centres located along the coastal region of the central and southern Adriatic, as a relevant contribution to the important problems of locally polluted marine environments.

MATERIALS AND METHODS

Sampling

Our investigations included the coastal area in the vicinity of five Adriatic towns (Zadar, Šibenik, Split, Kardeljevo, Dubrovnik) and an open sea station (middle Adriatic) as a reference station (Fig. 1).

Sediment samples were collected by gravity corer in perspex tubes from the r/v »BIOS«. The surface sediment layer (0—5 cm) was sampled. All samples were frozen and stored in polythene bags before analysis.

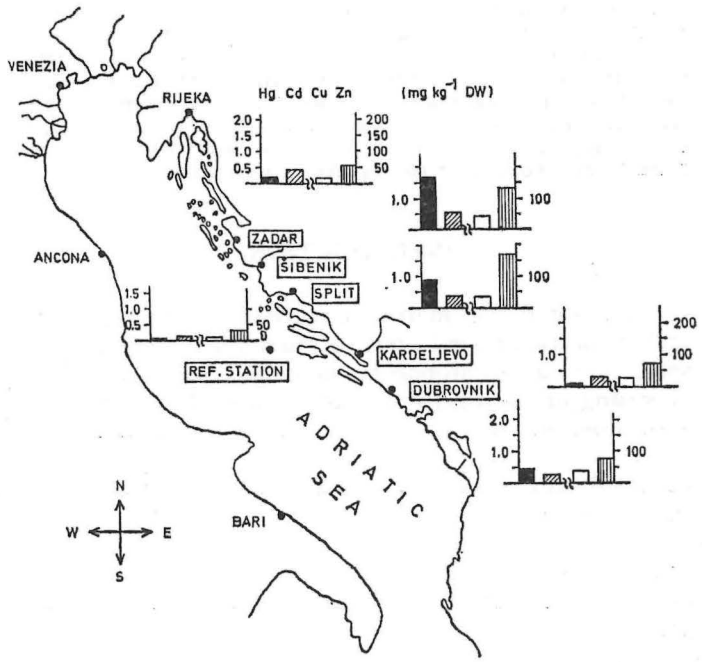

Fig. 1. Sampling locations with corresponding histograms of mean concentrations for the 1980—1985 period.

Analysis

All samples were prepared in the Department for Nuclear Chemistry at the »J. Stefan« Institute in Ljubljana following recommended procedures (UNEP/FAO/IAEA, 1983).

The unfrozen sediment was sieved through a nylon net of 0.1 mm mesh size in the wet state, and a portion taken for analysis of mercury. For the other elements, the dried sediment (drying overnight at 105°C) was used for analysis.

The data were obtained by destructive neutron activation analysis in the TRIGA Mark II reactor of the Institute »J. Stefan«, with appropriate radiochemical separations.

For mercury analyses, samples were sealed in precleaned quartz ampoules, otherwise sealed polythene vials were used. A 15—20 hr irradiation at flux of 1.8×10^{12} n cm^{-2} sec^{-1} provided ample sensitivity for all determinations. Standards consisted of acidic solutions of the appropriate elements, irradiated in contact with the samples.

^{197}Hg was isolated from irradiated samples by the volatilization technique previously developed (Kosta & Byrne, 1969; Byrne & Kosta, 1974). Arsenic was separated as ^{76}As by iodide extraction with toluene (Byrne & Vakselj, 1974). Zinc, cadmium and copper were isolated as ^{69m}Zn, ^{115}Cd- ^{115m}In, and ^{64}Cu, by NaDDTC extraction, following wet ashing, as described earlier (Dermelj *et al.*, 1977; 1979).

RESULTS AND DISCUSSION

Results obtained, presented in Tables 1 and 2, represent means of seasonal samplings (4 times per year) during 1985 and 1986. Examination of the listed heavy metal values in 1985 (Table 1) shows that the highest concentrations for most elements ere recorded from the stations in the vicinity of Šibenik and Split, suggesting the influence of industrial and urban effluents from these two largest middle Adriatic towns.

Table 1. Content of total Hg, Cd, Cu, Zn and As in surface sediments (mg/kg dry weight) from the coastal region of the Central Adriatic and the reference station, determined in 1985.

Sampling area	Hg	Cd	Cu	Zn	As
ZADAR	0,18	0.25	7,9	49,6	9,6
ŠIBENIK	1.68	0.43	50.6	170,7	12.7
SPLIT	0.65	0.39	25.1	122.5	12.8
KARDELJEVO	0.10	0.25	25.1	67.6	15.8
DUBROVNIK	0.50	0.25	50.4	109.3	13.5
Refer. st.	0.02	0.10	8.6	29.0	13.9

At the same time, a comparison of these results (Table 1) with calculated means for the 1980/85 period (Table 3) shows that, except fon Cu and Zn near Šibenik and Dubrovnik, all other values are within the five year mean. However, during 1986 (Table 2) the values of almost all the metals were markedly higher, particularly in Zadar, Dubrovnik and Kardeljevo.

Table 2. Content of total Hg, Cd, Cu, Zn and As in surface sediments (mg/kg dry weight) from the coastal region of the Central Adriatic and the reference station, determined in 1986.

Sampling area	Hg	Cd	Cu	Zn	As
ZADAR	0.21	0.29	21.8	90.5	9.7
ŠIBENIK	1.10	0.52	49.0	182.6	11.4
SPLIT	0.58	0.54	31.0	125.1	11.8
KARDELJEVO	0.09	0.43	28.5	92.7	11.6
DUBROVNIK	1.37	0.63	69.5	160.0	9.5
Refer. st.	0.04	0.06	27.4	24.0	9.0

Table 3. Mean concentrations and standard deviations (in parantheses) of some heavy metals (mg/kg dry weight) in surface sediments of study area, for the 1980—1985 period.

Sampling area	Hg	Cd	Cu	Zn
ZADAR	0.18 (0.09)	0.41 (0.58)	12.4 (4.7)	51.1 (7.1)
ŠIBENIK	1.66 (0.56)	0.54 (0.20)	44.9 (8.0)	131.7 (46.8)
SPLIT	0.86 (0.49)	0.38 (0.04)	36.0 (19.7)	169.5 (100.6)
KARDELJEVO	0.10 (0.02)	0.29 (0.15)	26.4 (1.6)	72.1 (17.5)
DUBROVNIK	0.42 (0.13)	0.25 (0.05)	38.5 (24.4)	74.7 (41.7)
Refer. st.	0.03 (0.01)	010 (0.04)	10.5 (5.2)	22.4 (8.2)

Particularly surprising were very high mercury and zinc concentrations in the vicinity of Dubrovnik. This increase is very well shown by the histogram comparing results from 1986 with the mean values of the five-year monitoring (Fig. 2). This proves the fact that no efficient protection measures have been undertaken and that the situation has been growing worse in the coastal area.

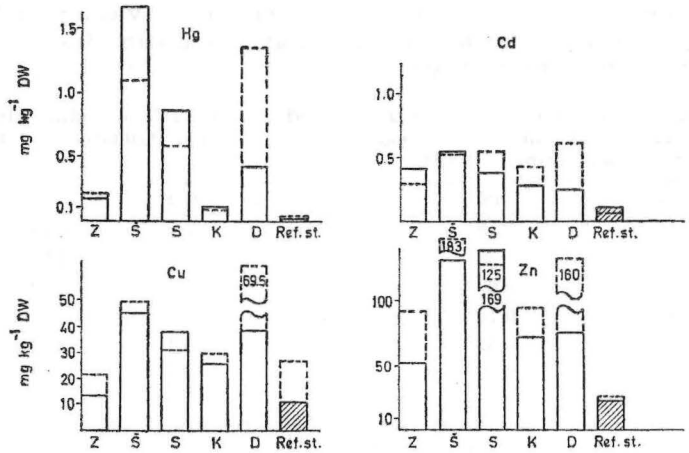

Fig. 2. Histogram of Hg, Cd, Cu and Zn contents in surface sediments of study areas determined in 1986 (— — —) and mean concentrations for the 1980—1985 period (———)

If the results of our measurements (Tables 1 and 2) are compared with the concentration ranges from other Mediterranean areas (Table 4) it appears that our coastal area is relatively uncontaminated. Namely, only zinc and mercury concentrations exceed the level of natural »background« as a consequence of anthropogenic influence.

Table 4. A probable »background« concentrations for some heavy metals in Mediterranean marine sediments (mg/kg DW) (FAO et al,, 1984., UNEP, 1985.).

Hg	Cd	Cu	Zn	As
0.01—0.2	0.1—2.5	2—52	20—78	5—15

However, this is by no means a comforting statement, since the monitoring carried out so far has shown all metal concentrations except As are increasing from one year to another.

This, in fact, means that the ecosystems in question will be threatened by most of the studied elements in the near future.

This is particularly true of mercury, one of the most toxic pollutants, which has already been incorporated into individual links of the food chain (UNEP, 1986., Zvonarić *et al.*, 1986) in concentrations exceeding or at the level of the maximum permissible limits by WHO.

A comparison with the reference area, distant from obvious pollution sources, and which should be taken as a »background« for walues from the middle Adriatic, proves the fact that considerable quantities of heavy metals have been deposited in the coastal area, mainly due to the discharges of untreated industrial effluents.

CONCLUSION

— the level of pollution of sediments by the majority of heavy metals studied shows no levelling-of, but on the contrary, a distinct increase
— the situation in areas where measurements performed few years ago showed relatively low levels of these elements, is growing worse (Zadar, Dubrovnik)
— the results undoubtedly show that nothing has been done so far to eliminate principal pollution sources, that is to say that the trend of discharging these pollutants in areas adjacent to cities has been continued.

Therefore it should be pointed out that continuous monitoring and further research appear to be called for. In the first place, studies of the ecocycles of individual toxic heavy metals (mercury, methyl-mercury, cadminum, lead), that is to say, studies of their pathways from sediments through the links of the food chain, should be continued.

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SADRŽAJ UKUPNE ŽIVE, KADMIJA, BAKRA, CINKA I ARSENA U POVRŠINSKIM SEDIMENTIMA PRIOBALNOG PODRUČJA SREDNJEG JADRANA

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KRATKI SADRŽAJ

U radu su prikazani rezultati analiza sadržaja ukupne Hg, Cd, Cu, Zn i As u površinskim sedimentima uzorkovanim tijekom 1985. i 1986. godine u blizi, ni pet industrijskih i urbanih centara priobalnog područja srednjeg i južnog Jadrana.

Izmjerene vrijednosti pokazuju da su najopterećenija područja s većinom istraživanih metala, ispred Šibenika i Splita, što je potvrdilo sumnju u nekontrolirano ispuštanje industrijskih i urbanih otpadnih voda u priležeće akvatorije.

Usporedba navedenih rezultata sa vrijednostima iz prethodnih godina pokazala je porast sadržaja većine metala i u zonama koje su do nedavno smatrane relativno nezagađenim (Zadar i Dubrovnik), što upućuje na potrebu neodložive akcije saniranja postojećeg stanja, te daljnjih istraživanja usmjerenih na proučavanje ekociklusa najtoksičnijih elemenata.