Acta Adriat., 23 (1/2): 307—312 (1982) YU ISSN: 0001—5113
AADRAY

FATE AND DISTRIBUTION OF TOXIC HEAVY METALS IN SEDIMENTS AND ORGANISMS OF THE KAŠTELA BAY

SUDBINA I RASPODJELA TEŠKIH METALA U SEDIMENTIMA I ORGANIZMIMA KAŠTELANSKOG ZALJEVA

Ilija Vukadin, Petar Stegnar* and Borut Smodiš*

Institute of Oceanography and Fisheries, Split
** Institute »Jože Stefan«, Ljubljana*

Sample of sediments and marine organisms from different sampling points of Kaštela Bay were analysed on several toxic heavy metals. This Bay is probably the most polluted area of Dalmatia.

The results obtained by two different analytical technicques, NAA, and AAS, show extremly high concentrations toxic trace elements in upper levels of sediments as a consequence of pollution from different industrial plants located on the coast of the Bay.

Extremely high mercury concentrations were recorded in *Mytilus galloprovincialis* (up to 17 ppm FW) at the stations near PVC and chloralkaly industry. These concentrations considerably exceed these values in organisms from any other region of the Adriatic.

INTRODUCTION

Fate and characterization of heavy metals and their compounds in an ecosystem have recently become the subject of a large number of meetings and discussions. A large number of heavy metals are toxic and dangerous for human health. They are therefore taken as a good indicator of the quality of waste waters. Their very long resindence time and accumulation in sediment is another reason for their detailed studies.

On this basis we started our researches on this matter aiming to carry out an ecological study of the Kaštela Bay, one of the most thereatend areas in the central Adriatic due to the discharge of the large quantities of unpurified domestic sewage and industrial effluents from the nearby land.

METHODS

Sampling. Sediment and marine organisms were sampled by the m/v »Bios« in May 1979. Sediment was collected by a probe with a 35 mm diameter plastic corer of about 20—30 cm length. Sediment was disaggregated imme-

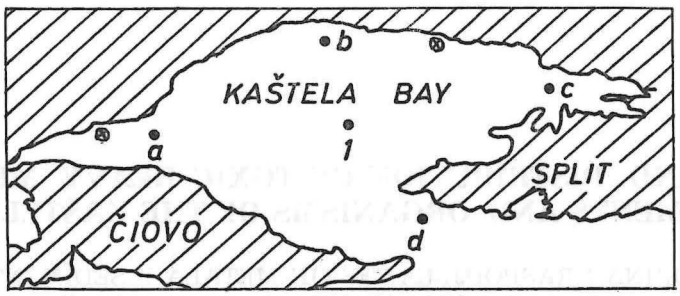

Fig. 1. Sampling locations (●) of sediments and (×) marine organisms in the Kaštela Bay

diately upon sampling and 5,0 cm pieces kept in deep freezer unitil the analysis. Sediment samples were oven-dried at 105°C and passed through a 0.1 mm pore size nylon sieve. Edible mussel (Mytilus galloprovincials) tissues were analysed.

ANALYSES

The analyses of sediment and organism samples were carried out on a NAA in a TRIGA Mark II reactor at the »Jože Štefan« Institute in Ljubljana.

Irradiations of 15—20 hours at a flux of 2×10^{12} n cm^{-2} sec^{-1} were used for As, Cd, Co, Cu, Hg, Sb, Se and Zn. For marcury analyses samples were sealed in quarz ampules, otherwise sealed polythene vials were used.

^{197}Hg and ^{75}Se were isolated from irradiated samples by volatilization technique. As and Sb were separated as ^{76}As and ^{122}Sb by iodide extraction with toluene. Zn, Cd, Cu and Co were isolated as ^{69m}Zn, ^{115}Cd — ^{115m}In, ^{64}Cu and ^{60}Co, by NaDDTC extraction, following wet ashing. Manganese and iron were determined spectrophotometrically by the classical periodate and α α' — dipyridyl methods, respectively. Pb was determined after complete digestion of the sample by flame AAS using a Varian AA5 apparatus.

RESULTS AND DISCUSSION

Means, standard deviation and variations in the analysed samples from the surface and subsurface layer of the Kaštela Bay sediments are given in the following tables:

Table 1. Heavy metal concentrations in the surface sediment layer of the Kaštela Bay in mg/kg DW

	Hg	Cd	Zn	Cu	Co	As	Sb	Mn	Fe	Pb	Sr
x	2.62	0.48	203	81	7.5	18.0	0.54	421	1.79	178	584
s	2.62	0.63	401	176	1.7	4.9	0.27	75	0.56	412	249
kv	1.0	1.31	1.97	2.17	0.22	0.27	0.50	0.18	0.31	2.31	0.73
sp	0.87	0.21	133	58.6	0.56	163	0.09	25	0.19	137	83

Table 2. Heavy metal concentrations in the sub-surface sediment layer of the Kaštela Bay in mg/kg DW

	Hg	Cd	Zn	Cu	Co	As	Sb	Mn	Fe	Pb	Sr
$\bar{x}$	0.07	0.19	55.0	17.0	6.3	17.8	0.29	411	1.51	35.6	587
s	0.08	0.04	18.4	6.1	3.0	4.5	0.08	62	0.38	50	208
kv	1.14	0.21	0.33	0.36	0.47	0.25	0.28	0.15	0.25	1.40	0.35
sp	0.03	0.01	6.13	2.0	1.0	1.5	0.03	20.6	0.13	16.6	69.3

Statistical analysis of the obtained data shows a considerable increase in heavy metal levels in surface sediment layer (0—5 cm). These differences are particularly great in Hg, Cd, Zn, Cu and Pb, i. e. in elements which belong to a group of great toxicity for human health. Considerable heavy metal concentrations were found in the surface sediment layer at station 1c in the vicinity of the town sewage outfall. Maximum levels of almost all of these metals were recorded from this station as well (Hg — 4.39, Cd — 3. 210, Zn — 1300, Cu — 550, Co — 10.0, As — 28.0, Sb — 0.88 and Pb 1275 mg/kg DW). This station is strongly influenced by the land effluents, particularly by the industrial ones due to a large number of industrial firms in that part of the town (Shipyard, Breaker's Yard, Clement Factory, Slaughter-house and others).

Extremely high Hg levels were recorded in the vicinity of the PVC factory »Jugovinil«, i. e. Hg — 8.51 mg/kg DW. This is directly indicative of this factory being the principal contributior of this metal in the sediments.

The industries like this one are obviously the most important marcury source in an ecosystem. Turner, R. L. and Lindberg, S. E. (1968) find mercury to be released from sediments in the vicinity of such factories even twenty years after they have ceased to work.

Different authors also calculated that in the course of production a PVC plan of medium size releses about 3 tons of Hg per year in its adjacent environment. Extermely high Hg and Se levels were recorded from marine organisms, as well. These levels were for the two orders of magnitude higher (Hg — 17.4 mg/kg FV — and Se — 1.63 mg/kg FW) in mussels (Mytilus galloprovincialis) collected from the vicinity of the above mentioned factory than in those collected from the open sea.

That high Hg levels in mussels and sediment from the vicinity of the PVC factory indicate that this factory probably makes significant inputs of these metals into the Kaštela Bay waters via effluents.

Spatial distribution of heavy metals in the Kaštela Bay is given in Figs. 2 and 3. As it may be seen, the eastern part of the Bay is under the strong influence of town outfalls and industrial effluents.

All metal concentrations in sediments are decreased with the distance of the site from the pollution sources. This is particularly applicable to the surface sediment layer. Marine sediment shows an extraordinary absorption capacity of heavy metals from a water column. In fact, sediment in itself is a heavy metal reservoir, wherefrom heavy metals may easily be released and returned in to the water column. In winter, the Kaštela Bay is under the particularly strong north wind (bora) influences. Wind causes the entire water column mixing. By this process, large quantities of heavy metals are

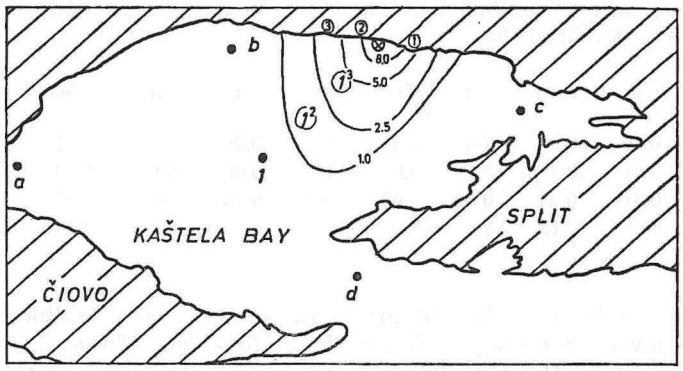

Fig. 2. Hg in surface layer (SL) of sediments near PVC--plant

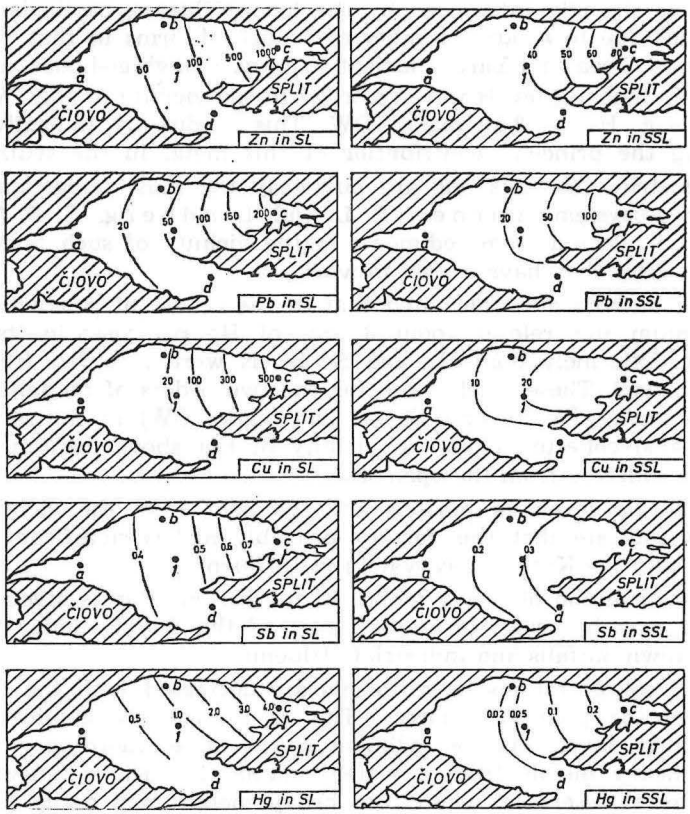

Fig. 3. Trace elements in the Kaštela Bay sediments in surface layer (SL, ie 0—5.0 cm) and subsurface layer (SSL, ie 5.0—10.0 cm) in ppm dray weight. May 1979.

released from sediments into the water column. This was proved by somewhat higher heavy metal concentrations (Zn, Cd and Cu) found in the sea water during winter (V u k a d i n, I. and Z v o n a r i ć, T., in preparation).

All of these factors indicate that the Kaštela bay is one of the most threatened areas in the eastern Adriatic. This Bay receives large quantities of unpurified effluents due to which it is continuously polluted and its ecosystem threatend.

Table 3. Trace elements in the Kaštela Bay sediments (ppm dray weight)

Stations: layer:	Cd	Hg	Pb*	Zn	As	Cu	Co	Sb	Mn	Fe (%)
1c Surface	2.10	4.39	1275	1300	28.0	550	10.0	0.88	455	2.09
Subsurface	0.23	0.23	137	85	14.0	22.0	8.5	0.36	400	2.00
1b Surface	0.22	1.07	21.0	72	19.0	18.0	6.0	0.39	470	1.97
Subsurface	0.20	0.02	11.8	33	23.0	17.0	5.2	0.21	370	1.36
1a Surface	0.13	0.38	22.0	55	18.0	13.0	6.5	0.30	420	1.60
Subsurface	0.13	0.01	12.0	38	21.5	6.5	0.6	0.18	315	1.00
1d Surface	0.16	0.07	16.5	70	17.5	18.0	6.5	0.50	540	2.00
Subsurface	0.19	0.02	14.1	55	20.0	14.0	8.0	0.31	450	1.85
1 Surface	0.14	0.78	69.1	75	16.0	21.0	6.0	0.44	420	2.40
Subsurface	0.25	0.06	23.6	60	11.5	20.0	7.5	0.30	480	1.60
In the vicinity	0.37	8.51	47.2	63	19.5	26.0	7.2	0.46	325	1.00
of PVC-fatory	0.74	2.73	21.7	53	11.5	42.0	10.6	1.12	370	0.98

Methods: NNA
* AAS

Nevertheless preliminary for this area, this study underlines the importance of a continuous sampling programme to adequately monitor and prevent and uncontrolled impact of man on this ecosystem.

Table 4. Mercury and Selenium in mussels (Mytilus galloprovincialis) from the Kaštela Bay (ppm FW)

Sample	Hg	Se	
1	17.40	1.56	
2	12.10	1.63	
3	15.40	0.19	In the vicinity of the PVC-
4	9.63	1.15	-factory
5	8.00	0.58	
6	4.05	0.64	In the vicinity of the PVC-
7	4.60	0.52	-factory
8	0.42	0.44	The area of relatively clean
9	0.27	0.32	sea (Trogir)

ACKNOWLEDGEMENTS

The authors is grateful to the m/v »BIOS« crew as well as to M. Obidić, M. Špenko and J. Novak for their assistance with the analytical work. Thanks are also due to all those who helped to prepare and complete this manuscript.

REFERENCES

Bilinski, H., and S. Jusufi, 1980. Model studies of the solubility of inorganic Mercury in the polluted coastal marine enviromental. Crat. Chem Acta., 53. 93—99.

Carmody, D. J., Pearce, J. B. and Yasso, W. E., 1973. Trace metals in sediments of the New York Bight. Mar. Pollut. Bull., 4 132—135.

Chester, R. 1965. Adsorption of zinc and cobalt on illife in sea water. Nature 206, 884—886.

Chester, R. and Stoner, J. H., 1974. The distribution of zinc, nikel, manganese, cadmium, copper and iron in some surface waters from the warld ocean. Mar. Chem., 2. 17—32.

Eisler, R. Lapan, R. L., Telek, G. et al. 1977. Survey of metals in sediments near Quonest Point, Rhode Island. Mar. Pollut. Bull., 8. 260—264.

Greig, A. R., Reid, R. N., and Wenzloff, R. R. 1977. Trace metal concentrations in sediments from Long Island Sound. Mar. Pollut. Bull., 8. 183—188.

Kosta, L. et al., 1978. Some trace elements in the water, marine organisms, sediments of the Adriatic by NAA J. Radional. Chem., 44. 317—332.

Skei, M. S., 1978. Serious mercury contamination of sedimenst in a Norwegian semi-enclosed Bay. Mar. Pollut. Bull., 9. 191—193.

Turner, R. R. and Lindberg, S. E., 1978. Behavior and transport of Mercury in River-reservoir system downstream of inactive Chloralkali plant. Env. Sci. & Technol., 12. 918—923.

Watling, L., Leathem, W., Kinner, P., Wethe, C., and Maurer, D., 1974. Evaluating of sludge duping of Delaware Bay. Mar. Pollut. Bull., 5. 39—42.

SUDBINA I RASPODJELA TEŠKIH METALA U SEDIMENTIMA I ORGANIZMIMA KAŠTELANSKOG ZALJEVA

Ilija Vukadin, Petar Stegnar* i Borut Smodiš*

Institut za oceanografiju i ribarstvo, Split
** Institut »Jože Štefan«, Ljubljana*

KRATKI SADRŽAJ

Uzorci sedimenata i morskih organizama sakupljeni su na nekoliko karakterističnih pozicija u Kaštelanskom zaljevu, te analiziran sadržaj teških metala. Ovaj zaljev je možda jedan od najugroženijih područja u Dalmaciji.

Rezultati dobiveni s dvije različite analitičke metode, NAA i AAS pokazali su da su vrijednosti teških metala u površinskom sloju sedimenata ekstremno visoke u blizini izljeva industrijskih postrojenja lociranih na obali samog zaljeva. Visoke vrijednosti koncentracije Hg također su nađene u morskim organizmima (Mytilus galloprovincialis) postaje u blizini PVC-industrijskih postrojenja. Ove vrijednosti su do sada najviše nađene vrijednosti u Jadranskom moru.