OCCURENCE OF DIMETHYLMERCURY IN THE POLLUTED PART OF KASTELA BAY (EASTERN ADRIATIC COAST)

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Abstract

Dimethylmercury (CH₃)₂Hg, a highly volatile mercury compound, was initially detected in sediments and seawater samples of the Kastela Bay (Eastern Adriatic coast) in the vicinity of a chlor-alkali plant. An adequate sampling procedure followed by immediate measurements enabled the detection of dimethylmercury. Prior to measurements by a cold vapour atomic absorption spectrometry, the dimethylmercury (CH₃)₂Hg was preconcentrated in a cryogenic trap, eluated and pyrolitically decomposed on a gold wire, with the detection limits of 0.005 ng L-1 and 0.002 ng g-1 in seawater (1000 ml of the water sample) and sediment (10 g of the sediment sample), respectively. The dimethylmercury was found in sediment and seawater samples between 0.01 and 0.15 ng g^{-1} and 0.02 and 0.12 ng L^{-1} , respectively, only in a very limited area of the Kastela Bay. The results obtained indicate that dimethylmercury occurs under very specific biogeochemical redox conditions which probably lead to a decrease of a high content of total mercury from the sediments which has been accumulating for years in such a highly polluted area of the Adriatic Sea.

Key words: mercury, sediments, sea water, Adriatic Sea

Study area

Kastela Bay is situated in the central part of the eastern Adriatic coast in the vicinity of the town of Split (Fig.1). It is the largest bay in central Dalmatia with the surface of 61x10⁶ m (14.8 km in length and 6.6 km in width) and the volume of 1400x10⁶ m³. The contamination with mercury discharged from a PVC plant endangered this aquatorium for 40 years (the plant was shut down in 1990) (1).



Figure 1. Map of sampling area

Sampling and analysis

The sediment and water samples were collected by a diver using an acrylic glass tube (20 cm long and 6 cm i.d.) and one-liter Pyrex glass bottles, respectively. The analyses were performed 2 to 3 hours after the sampling (2-4).

Dimethylmercury was analysed in unfiltered seawater samples and in wet and total sediment samples collected from the surface (0 cm) and a depth of 10 cm in the sediment column. After the separation from liquid and solid samples, preconcentration in a cryogenic trap, elution and pyrolitical decomposition on a gold wire, dimethylmercury was measured using a cold vapour atomic absorption spectrometry (5, 6). In each sample a known amount of a standard dimethylmercury solution was added for the calibration purposes.

Results and discussion

Fig.1 illustrates that dimethylmercury was detected only in a very restricted area of the Kastela Bay (about 400 m from the coast) in the vicinity of the outlet of the chlor alkali plant which was shut down in 1990. Dimethylmercury in water was detected at sites 1 and 4, whereas in sediments, mostly it was found at site 1. The only exception was site 4 (shallow waters), where, the highest concentration of total mercury was found in sediments (up to 85 mg kg-1).

The concentrations of dimethylmercury and monomethyl mercuy in water were in the range between 0.02 and 0.120 ng L^{-1} and 1 and 4 ng L^{-1} , respectively. The concentration of total mercury at the same locations ranged between 200 and 400 ng L⁻¹. However in unpolluted waters of the Adriatic Sea normally range between 0.05 and 5 ng L-1. Recovery efficiency of dimethylmercury for brackish and seawater is between 94 and 106%.Dimethylmercury concentrations in the sediment column (0 cm and 10 cm) are in the range between 0.02 and 0.150 ng g⁻¹. The values are significantly higher at the surface (several orders of magnitude) than those at a depth of 10 cm. At the same locations the concentrations of total mercury in sediments are in the range from 10 000 ng g-1 (location 1) to 85 000 ng g⁻¹ (location 4). The concentrations of monomethyl mercury in sediments ranged between 5 and 18 ng g⁻¹ (location 1).

Table 1. Dimethylmercu	y concentration in	n the	seawater	(ng L	1)	۱
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	Date of sa	mpling and de	termination		
Position	6.05.1997.	7.07.1997.	10.07.1997.	25.07.1998 N.D.	
1a	N.D.	N.D.	N.D.		
1b	N.D.	N.D. N.D.		N.D.	
1	0.04 0.04	0.03 0.03	0.04 0.04	0.05 0.04	
2	0.050 0.04	0.02 0.02	0.04 0.06	N.D.	
3	0.120 0.100	0.02 0.04	0.04 0.05	0.03 0.03	
4	N.M.	N.M.	0.05 0.05	0.06 0.06	

N.D. not detected; N.M. not measured

Table 2. Dimethylmercury concentration in the sediment (ng g⁻¹)

	Da	te of sai	mpling	and det	ermina	tion		
6.05.1997.	7.07.1997.		10.07.1997.		25.07.1998.			
Position	(0 cm	10 cm)	(0 cm	10 cm)	(0 cm	10 cm)	(0 cm	10 cm)
1a	N.D.		N.D.		N.D.		N.D.	
1b	0.02	0.003	0.01	0.005	0.03	0.006	0.005	N.D.
1	0.14	0.030	0.0	8 0.01	0.150	0.007	0.005	N.D.
2	N.D.		N.D.		N.D.		N.D.	
3	N	.D.	N.D.		N.D.		N.D.	
4	Ν	.D.	N.D.		N.D.		0.002	N.D.

N.D. not detected

Conclusion

The modified method for the determination of highly volatile mercury compounds in the pico and femto concentration range has successfully been tested on natural water and sediment samples. The presence of harmless, volatile and hydrophobic dimethylmercury in the sediments and water column of Kastela Bay, leads to the natural removal of the total of mercury and consequently selfpurification of the polluted part of the Bay.

References

1. Zvonaric T., 1991. The cycling of mercury through the marine environment of Kastela Bay, MAP Technical Reports Series No. 59, UNEP, Athens, 369-381. 2. Martincic D., Kwokal Z., Stoeppler M., Branica M., 1989. Trace metals in sediments from the Adriatc Sea , *Sci. Tot. Environ.* 84: 135-147. 3. Kwokal Z., May K., Branica M., 1994. "On spot" collection of reactive mercury onto gold wire from aquatic envirinment, Sci. Tot. Environ. 154: 63-69.

Kniewald G., Kwokal Z., Branica M., 1987. Marine sempling by scuba diving.
Sampling procedure for measurment of mercury concentrations in estuarine

waters and seawater. Mar. Chem., 22: 343-352.

5. Fisher R., Rapsomanikis S., Andreae M.O., 1993. Determination of methylmercury in fish samples using GC/AA and sodium tetraethylborate derivatization, *Anal. Chem.*, 65 (6): 763-766.

6. Kwokal Z., Branica M., 2000. Determination of dissolved

monomethylmercury in saline, estuarine and fresh waters of Croatia, *Croat. Chim. Acta*, 73 (1): 97-109.