MERCURY SPECIATION IN SEDIMENTS FROM A SEWAGE-SLUDGE MARINE DISPOSAL SITE

Efrat Shoam-Frider [1], Gedalia Shelef [2] and Nurit Kress [1*]

[1] Israel Oceanographic & Limnological Res., The National Institute of Oceanography, PO. Box 8030, Tel Shikmona, Haifa, Israel 31080 - efrat@ocean.org.il - * nurit@ocean.org.il

[2] Division of Environmental Engineering and Water Resources, Faculty of Civil Engineering, Technion - Israel Institute of Technology, Technion City, Haifa 32000 Israel - Shelef@tx.technion.ac.il

Abstract

Mercury speciation in marine sediments collected at a sewage sludge disposal site showed it to be associated mainly with the organic matter fraction (amorphous organic sulfur compounds and humic acid), reducing it's availability to the marine environment. The third most prominent fraction was cinnabar. Methylmercury, the most deleterious species to human health consisted only of 0.1-0.5 % of the total mercury in the sediment sample, compared to 2.6% of the total mercury in the sewage sludge.

Keywords : mercury, speciation, sediment, sewage sludge, marine environment

Background

Mercury is a naturally occurring element that enters the environment as a result of natural (e.g., volcanoes, fires, surface emissions) and anthropogenic sources (e.g., combustion, commercial products). The biogeochemical cycle of mercury is complex and it can be found, among others, as elemental mercury vapor, gas-phase and dissolved ionic mercury, particulate bound, in organic forms and as cinnabar. Mercury is bioaccumulative and toxic impacting the environment and man (1). Of all the mercury species, methylmercury is the one that poses the higher risk to human health.

Although most of the introduction of mercury is via the atmospheric pathway, land based sources can cause local problems or "hot spots". Along the Israeli Mediterranean coast there are two areas with increased mercury in the sediments: in the northern coast, opposite a chlor alkali plant and in the southern coast, at the marine disposal site of excess (16,000 m^3 day^{-1}) sewage sludge from the Dan Region Wastewater treatment plant (2). The outfall operates since 1987 and is located 5 km offshore, at a water depth of ca. 38 m. About 60 Kg mercury $year^{-1}$ enters the marine environment with the sewage sludge (3). To date, only total mercury concentrations were measured in the area's sediments. This study aimed to determine the mercury speciation in the sediments of the outfall area to assess the possibility of mercury accumulation in the food web.

Experimental

Sediments were sampled in October 2002. The methods of sediment sampling, preservation and preparation are thoroughly described elsewhere (1). Speciation was performed using selective extractions of biogeochemically relevant fractions (4). Briefly, five fractions were determined: F1(water soluble), F2 ('human stomach acid' soluble), F3 (organic, humic acid chelated), F4 (elemental mercury and amorphous organic sulfur compounds), F5 (mercury sulfide, cinnabar). Methylmercury was determined in a separate aliquot of the sediment. Sediments cores of three stations were analyzed: one station at the outfall, one station located 1.5 km northward of the outfall and a non affected station located 5.5 km northwards of the outfall. Fresh sewage sludge was sampled from the treatment plant, dried and analyzed in the same manner as the sediment samples. QA/QC of the results was performed with certified international standards.

Results and discussion

Total mercury, methyl mercury and mercury speciation in the sediment samples and in fresh sewage sludge results are presented in Table 1. Total mercury concentration was the lowest at the natural station. At the affected stations, total mercury concentrations decreased with increased depth of the sediment. The highest total mercury concentration was found at the sewage sludge sample. Methyl mercury in the sewage sludge was 2.6% of the total mercury while in the sediment samples the percentage of methylmercury was much lower, in the range of 0.1-0.5%. Most of the mercury was found in the F4 fraction followed by the F3 fraction, ie, the mercury was associated with the organic matter fraction: amorphous organic sulfur compounds (F4) and humic acid (F3). The presence of elemental mercury in the F4 fraction was ruled out by pyrolisis analysis. The third most prominent fraction was F5, cinnabar. There was almost no mercury associated with the F1 and F2 fractions, the most accessible and bioavailable, neither in the sludge nor in the sediments. The distribution of mercury among the different fractions in the two stations affected by the sewage sludge was similar to that in the original sludge. The mercury species distribution in the natural station was slightly different with and higher relative contribution of the F3 fraction compared to the F4 fraction. This may be due to the association of mercury with natural humic acids. These results indicate that the mercury introduced to the marine environment with the sewage sludge is mainly associated with the most stable complexes of mercury, reducing it's availability in the environment.

Table 1. Total mercury, methyl mercury and speciation of mercury (in % from total mercury) in activated sewage sludge and in marine sediments at the disposal site.

Station	Sed. depth	Total Hg	Methyl Hg	% Methyl Hg
	cm	ppb	ppb	
outfall	-3	366.2	0.99	0.27
	-5	347.9	0.71	0.20
	-7	216	0.43	0.20
	-9	202.4	0.50	0.25
1.5 km N	-3	936	1.56	0.17
	-6	1274	1.20	0.09
	-8.5	403.6	1.19	0.29
	-12.5	501.7	0.72	0.14
Natural	0	34.36	0.19	0.54
Sewage sludge		1532	39.7	2.59

Station	Sed. depth	F1	F2	F3	F4	F5
	cm	%	%	%	%	%
outfall	-3	0	0	34.8	61.9	3.25
	-5	0.2	0	25.6	62.6	11.6
	-7	0.3	0	11.2	74.0	14.5
	-9	2.9	0	17.1	75.3	4.7
1.5 km N	-3	0.0	0	20.8	76.2	3.0
	-6	0.1	0	30.4	62.5	7.1
	-8.5	0.0	0	11.4	65.0	23.5
	-12.5	0.0	0	7.8	87.1	5.1
Natural	0	1.1	0	40.8	40.4	17.6
Sewage sludge		0	2.4	18.7	74.1	4.7

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