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Occurrence of Tetraalkyllead Compounds in the Aquatic Environment

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Organolead compounds are in general more toxic than the inorganic lead compounds (WONG et al. 1978). In a study of the acute toxicity of alkyllead compounds to three marine species; namely, mussel (Mytilus edulis), shrimp (Crangon crangon) and plaice (Pleuronectes platessa), it was found that ethyl derivatives were more toxic than methyl derivatives, and that the toxicity increased with the increasing degree of alkylation, with tetraalkyllead being the most toxic (MUDDOCK & TAYLOR 1977). For microorganisms, it was also found that algae after exposure to tetramethyllead suffered severe damage and alterations in cell fine-structure with lead granules deposited in concentration bodies (SILVERBERG et al. 1977). The primary productivity and cell growth of Scenedesmus quadricauda were observed to decrease by 85% and 32%, respectively.

The occurrence of tetraalkyllead in environmental samples has been rarely reported in the literature probably because of the lack of suitable analytical techniques specific for these compounds at very low concentration level. Interest in the environmental methylation of lead was rekindled by the recent findings (HARRISON & LAXEN 1978) of the presence of excess alkyllead in the air over mudflats in Morecambe Bay, England, and the attribution of such excess to a natural conversion process of inorganic to methyl lead. The presence of tetraalkyllead compounds in fish was first reported by SIROTA and UTHE (1977) who found high ratios of alkyllead to total lead in several fishery products in Halifax, Canada. The source of alkyllead was not known; however, the possibility of environmental or in vivo methylation of lead compounds was suggested. MOR and BECCARIA (1977) reported high concentrations of tetraalkyllead in mussels collected at a marking buoy near the "SS Cavtat" incident (HARRISON 1977) in the Adriatic Sea where a shipload of antiknocking compounds (ca. 200 tons) was sunk. High organolead concentrations, mainly of tetraethyllead were also found in mussels in the adjacent Italian Seas. These workers suggested that tetraalkyllead compounds were not readily metabolized by aquatic animals, and might remain in their original forms for a long time. It has been shown in a previous study (CHAU et al. 1979) that tetraalkyllead can be concentrated by fish. Consequently, an extensive survey of environmental samples (fish, vegetation, sediment and water) for the presence of tetraalkyllead compounds was carried out. The present study presents results of the

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study. The survey included fish (107 samples), water (32), vegetation, algae and weeds (44) and sediment (50) taken from various lakes and rivers in Ontario. Only fish samples were found to contain these compounds.

MATERIALS AND METHODS

Volatile lead compounds. Fish, sediment and vegetation samples were first screened for the presence of volatile lead compounds by heating the sample (2 g wet weight) in a glass "U" tube closed at both ends for 15 min at 100°C. The tube was then connected to the atomic absorption spectrophotometer. The volatile material was swept into the AA atomizer in a stream of methanol-saturated nitrogen. Methanol was used to prevent the possible deposition of metallic lead in the heated part of the transfer line near the burner. The AA atomizer was a stainless steel "T" tube mounted on top of, and heated by, the AA burner of air-acetylene flame (RADZIUK et al.1979). Only those samples giving positive results were then further analyzed for tetraalkyllead. This volatile lead fraction represents tetraalkyllead and possible other lead compounds of organic nature. The method was standardized by injecting a known amount of trimethylethyllead into the sample tube containing the spent sample and repeating the procedure.

Tetraalkyllead. Tetraalkyllead in fish, sediment, and vegetation was determined by heating a sample (1 g wet weight) in a glass "U" tube to 100°C for 20 min. While heating, air was sucked at 70 ml/min through the "U" tube into a moisture trap (empty U tube) and a sample trap (U tube packed with 3% OV-1 on Chromosorb W) both immersed in a dry ice-methanol bath. The sample trap was removed from the sampling line and connected to the gas chromatograph-atomic absorption spectrophotometer system for the analysis of individual tetraalkyllead compounds (CHAU et al. 1976). Standardization was carried out by injecting a known amount of a tetraalkyllead compound to the sample trap and carrying through the procedure. Tetraalkyllead in water was extracted by hexane and determined by the GC-AA method (CHAU et al. 1979). The hexane extract was further analyzed for total lead which represents hexane extractable lead in water.

Hexane extractable lead. Hexane extractable lead was determined by extracting 1 g wet weight of sample (fish, sediment or vegetation) with 2 ml of hexane in a capped test tube immersed in a sonic bath for 15 sec. followed by mechanical shaking for 1 min and settling overnight. The hexane layer was analyzed for total lead using the graphite furnace of the AAS as for total lead analysis. Hexane extractable lead includes all tetraalkyllead compounds and other organic lead compounds. An organic lead compound (tetraalkyllead) was compared with inorganic lead for standardization. There was no appreciable difference and hence aqueous inorganic lead standards were employed for standardization.

Total lead analysis. Total lead content was determined by furnace AAS after acid digestion of the sample. Sample sizes were fish (1 g), vegetation (1 g), and sediment (0.25 g). Acid mixtures for digestion, HNO_3, $HClO_4$, H_2SO_4 were for fish (4:1:0.5); vegetation (4:1:1), sediment (4:1:0). NBS Bovine Liver and Orchard Leaves were used as controls with fish and vegetation. As there was no standard sediment available, Orchard Leaves were employed as control for sediment digestion. All samples were soaked overnight in the acid mixture followed by low heat digestion for 1 h, medium heat for 2-3 h, and then high heat until the solution was evaporated to fumes of SO_3. The solution was cooled and diluted to 10 ml with distilled water for analysis in the AA furnace. Water samples were directly analyzed for total lead by furnace AAS. Standard additions technique was used in the analysis.

RESULTS AND DISCUSSION

Table 1 summarizes the concentrations of several tetraalkyllead compounds in fish samples showing positive results. Of all 107 fish samples analyzed, 17 samples contained tetraalkyllead compounds. There were no detectable amounts of tetraalkyllead in water, vegetation or sediment although in some cases hexane extractable lead was present. The fish that contained tetraalkyllead also contained high total and hexane extractable lead. The areas where fish was found to contain tetraalkyllead did not have abnormally high total lead concentration in the sediment. From these results, although it is easy to account for the occurrence of tetraalkyllead in fish caught near marina areas, it is not readily understood why tetraalkyllead compounds are found in fish of other areas where gasoline is not frequently used. The possibility of environmental methylation or in vivo methylation of lead cannot be discounted.

Since tetraalkyllead compounds are sparingly soluble in water and they all have very high vapor pressure, these compounds would be expected to concentrate in the lipid tissues of aquatic organisms. This may explain why tetraalkyllead was not found in water and vegetation. Even if methylation is taking place in the sediment, the tetramethyllead so formed will be immediately volatilized through the water column. Thus it is difficult to track down the source of tetraalkyllead compounds in the environment. Despite all these uncertainties, the occurrence of tetraalkyllead compounds in fish pose immediate questions as to the validity of the allowable level of lead in food without considering its chemical forms, the possibility of bioaccumulation by fish, and the nature of the degradation products of tetraalkyllead in fish.

The findings of this investigation are: (1) there was no relationship between species and size of fish and concentration of tetraalkyllead; (2) tetraalkyllead was found in fish from various lakes and rivers in Ontario; (3) the type of tetraalkyllead varied in different locations, e.g., in Ganaraska River, trimethylethyllead;

TABLE 1. ANALYSIS OF TOTAL, HEXANE EXTRACTABLE, VOLATILE AND TETRAALKYLLEAD IN SOME FISH SAMPLES FROM ONTARIO

			ng/g wet wt.							
						Tetraalkyllead				
Location	Fish species	Wt. of fish (Kg wet wt)	Total Pb	Hexane Extract. Pb	Volatile Pb	Me_4-	Me_3Et-	Me_2Et_2-	$MeEt_3$-	Et_4-
Ganaraska R.	Rainbow Trout	0.47	95	8.4	6.8	-	2.3	-	-	-
		2.93	90	72.4	2.7	-	5.2	-	-	-
		4.09	65	23.8	9.1	-	2.7	-	-	-
Vineland Creek	Coho Salmon	1.23	75	31.0	1.5	-	4.3	2.3	2.8	-
		1.36	95	27.3	9.0	1.1	1.0	-	1.8	9.3
Bay of Quinte	White Perch	0.23	185	IS	4.3	-	-	0.2	-	0.3
	Brown Bullhead	0.42	30	IS	1.8	-	-	0.3	-	2.5
	Black Crappie	0.33	115	IS	2.7	-	-	0.5	-	1.0
	Pumpkinseed	0.14	80	IS	2.1	-	-	0.8	-	1.4
Stoco Lake	Yellow Perch	0.13	325	4.9	-	1.7	-	7.1	4.4	2.7
	Sucker	1.00	45	6.8	-	2.0	-	-	-	-
	Rock Bass	0.14	215	1.8	3.8	0.6	-	-	-	2.8
Moira Lake	Sunfish	0.13	300	3.6	6.1	0.9	-	-	2.7	1.9
	Sucker	1.00	110	6.8	3.2	1.0	-	-	-	1.9
Lake St. Clair	Smallmouth Bass	1.05	120	18.0	1.6	-	-	0.2	-	1.4
	White Bass	0.47	80	6.4	1.3	-	-	0.3	-	0.8
		0.47	75	11.2	1.1	-	-	0.3	-	1.0

Detection Limits (ng/g) - Total Pb: fish, vegetation (10), sediment (50), water (1); Hexane Extractable Pb: fish, vegetation, sediment (2), water (0.001); Volatile Pb: all samples (0.1 - 1.5), tetraalkyllead: fish, vegetation, sediment (0.1), water (0.5). IS - insufficient sample.

in Bay of Quinte and Lake St. Clair, dimethyldiethyllead and tetraethyllead were found. The reasons for the presence of certain specific alkyllead in fish are not known and are being investigated; (4) in general the concentration of tetraalkyllead is low, representing less than 10% of the total lead; (5) the values of volatile lead which should include tetraalkyllead are generally higher than that of tetraalkyllead. However, in some determinations, the values for tetraalkyllead are higher. Problems of sample homogeneity were probably the cause.

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