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The analyses of alkyllead compounds in fish and environmental samples in Ontario, Canada (1981–1987)

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Analyses of fish and other environmental samples (clams, macrophytes, sediments and waters) from areas upstream and downstream from two alkyllead manufactures beside the St Lawrence and St Clair Rivers, Ontario, show a clear indication of elevated alkyllead levels in samples near the industries. Most species of fish contained alkyllead compounds with tetraethyllead and triethyllead as the predominant forms. Most fish from the contaminated areas contained 50–75% of total lead as alkylleads. Carp, yellow perch and white sucker were generally the most contaminated species while pike, alewife and rock bass were the least contaminated. Average alkyllead levels varied from year to year but declined steadily after 1981. For example, the geometric mean of alkyllead compounds in carp from the St Lawrence River decreased from 4207 μg kg^{-1} in 1981 to 2000 μg kg^{-1} in 1982 and to 49 μg kg^{-1} in 1987, reflecting the reduction of alkylleads in the effluents and the closure of one of the manufactures in 1985. Alkyllead levels were consistently lower in muscle and carcass samples in comparison with whole fish containing fatty intestines. However, muscle levels were generally equal to carcass levels.

The concentrations of alkyllead compounds were generally low in clams, macrophytes, sediments and waters except from the immediate vicinity of the manufactures' final effluent discharges.

Keywords: Environmental analysis, alkyllead, tetraethyllead, triethyllead, lead, fish, clam, macrophyte, sediment, water

INTRODUCTION

Lead exists in two valence states: lead(II) in inorganic forms such as lead chloride and lead sulphate and lead(IV) in organic forms such as triethyllead and tetraethyllead. Lead contamination of the environment is usually measured as inorganic lead(II). The occurrence of organic lead(IV) in the environment was rarely reported, probably because of the lack of suitable analytical techniques specific for these compounds at very low levels of sensitivity.[1] During the last decade, great advances have been made in the development of speciation techniques. As a result, organic lead can now be speciated to its molecular forms at environmental concentratons.[2]

There are two types of organolead compounds of environmental concern. One is tetraalkyllead (R_4Pb) compounds which are volatile and water-insoluble; their presence in water is only transient. They will be partitioned into the lipids of living organisms, adsorbed onto particulates or volatilized to the atmosphere. They include tetraethyllead (Et_4Pb) and tetramethyllead (Me_4Pb). The second type is water-soluble and includes trialkyllead (R_3Pb^+) and dialkyllead (R_2Pb^{2+}) compounds. Monoalkyllead (RPb^{3+}) compounds are extremely unstable and their existence has not been established in the environment.

The dominant use of organolead compounds since 1923 has been antiknock additives to gasoline (R_4Pb). Tetraethyllead has been the principal additive in Canadian gasoline since 1926. Consumption of Et_4Pb in Canada has declined from 16 000 tons in 1975 to 9100 tons in 1982 as a result of a 1974 federal standard of 0.77 g dm^{-3} for lead in gasoline and an increasing

number of automobiles designed for non-leaded gasoline.[3] About 1% of R_4Pb in gasoline is emitted into the atmosphere via automobile exhaust and further emissions are caused by evaporative losses of fuel from fuel tanks, carburettors and spillage during the production and transfer of antiknock compounds.[4] In addition to their use as gasoline additives, alkyllead compounds also have minor industrial and commercial applications in the manufacturing agents and polyurethane foam catalysts.[5] Significant anthropogenic inputs of R_4Pb to the environment may be compounded by a natural methylation of lead compounds.[6]

After entry into the environment, tetraalkyllead compounds decompose to trialkyllead, dialkyllead and inorganic lead species. The rates of photolysis for Me_4Pb and Et_4Pb range from 8% and 26% per hour respectively in bright summer sunlight to 0.2% and 0.7% per hour respectively in the dark.[7] Tetraalkyllead compounds also decompose in aqueous systems, forming primarily trialkyllead species. Jarvie *et al.*[8] reported that Et_4Pb was very stable in water in the dark with only 2% decomposition after 77 days. When exposed to sunlight, almost 100% of Et_4Pb was decomposed after 15 days. Trialkyllead compounds are very stable in water with virtually no decomposition for up to six months.

To date, few measurements have been made of alkyllead compounds in the environment. Rainwater samples at six locations in or near Antwerp, Belgium, contained 28–330 ng dm^{-3} R_3Pb^+ with an apparent correlation with local traffic density.[9] Et_4Pb was detected in several samples of surface microlayer of the St Clair River but not in the water.[10] Due to high vapour pressures and lipophilicity, R_4Pb tends to bind to the hydrophobic surface microlayer and lipid fraction in fish.

The presence of R_4Pb compounds in fish was first reported by Sirota and Uthe,[11] who found high ratios of alkyllead to total lead in several fishery products in Halifax, Nova Scotia. The source of alkyllead was not known; however, the possibility of environmental methylation of lead compounds was suggested. Mor and Beccaria[12] reported high concentrations of R_4Pb in mussels collected in the Adriatic Sea near the *SS Cavtat*, a ship that sank with a load of 200 tons of R_4Pb. Chau *et al.*,[1] in an extensive survey of lakes and rivers in Ontario, found that 17 of 107 fish samples contained R_4Pb. No detectable amount of R_4Pb was found in the water, macrophytes and sediments. Unfortunately, analysis of other forms of organic lead was not carried out in this survey.

In 1979, surveys were initiated in our laboratory to study the degree of lead contamination in several fish species in the lower Great Lakes. Several sites were monitored, ranging from Sarnia on the St Clair River to Maitland on the St Lawrence River. Blood lead concentrations in fish increased from a geometric mean of 59 $\mu g\ dm^{-3}$ at Sarnia to a high of 456 $\mu g\ dm^{-3}$ at Maitland.[13] The erythrocyte enzyme δ-aminolevulinic acid dehydratase (ALA-D) was only marginally inhibited in the high-lead-containing fish. Published information indicates that ALA-D is only sensitive to inorganic lead and insensitive to alkyllead compounds. Hence an investigation was carried out to analyse both total lead and alkylleads in fish, particularly fish from areas where alkyllead compounds were produced.

In 1981, there were two alkyllead manufacturers in Ontario: at Maitland by the St Lawrence River and at Corunna by the St Clair River. Plant A is located approximately 2 km east of Maitland. It produced Et_4Pb, nylon intermediates, chlorinated fluorocarbons and spandex fibres. Effluent from Et_4Pb production was filtered and settled before being discharged to the St Lawrence River via two submerged 48-inch diameter outfalls. Plant B, just upstream of Corunna, released an effluent containing inorganic and organic lead compounds. However, the St Clair River has a higher velocity water-flow rate at Corunna than does the St Lawrence River at Maitland so that sediments are coarser and the lead compounds are more rapidly dispersed.

In this report, we present data on the occurrence of various alkyllead compounds in samples mainly of fish but also of clams, macrophytes, sediments and water from the St Lawrence and St Clair Rivers between 1981 and 1987. Figure 1 shows a map of the region.

MATERIALS AND METHODS

Fish, clams, macrophytes, sediments and water were collected from the St Lawrence River, upstream and downstream from Maitland and from the St Clair River, upstream and downstream from Corunna. Surface microlayer samples were obtained by the dipping glass plate technique.[14] Subsurface water samples were taken with 4 dm^{-3} Winchester bottles just below the surface. Sediments were obtained by means

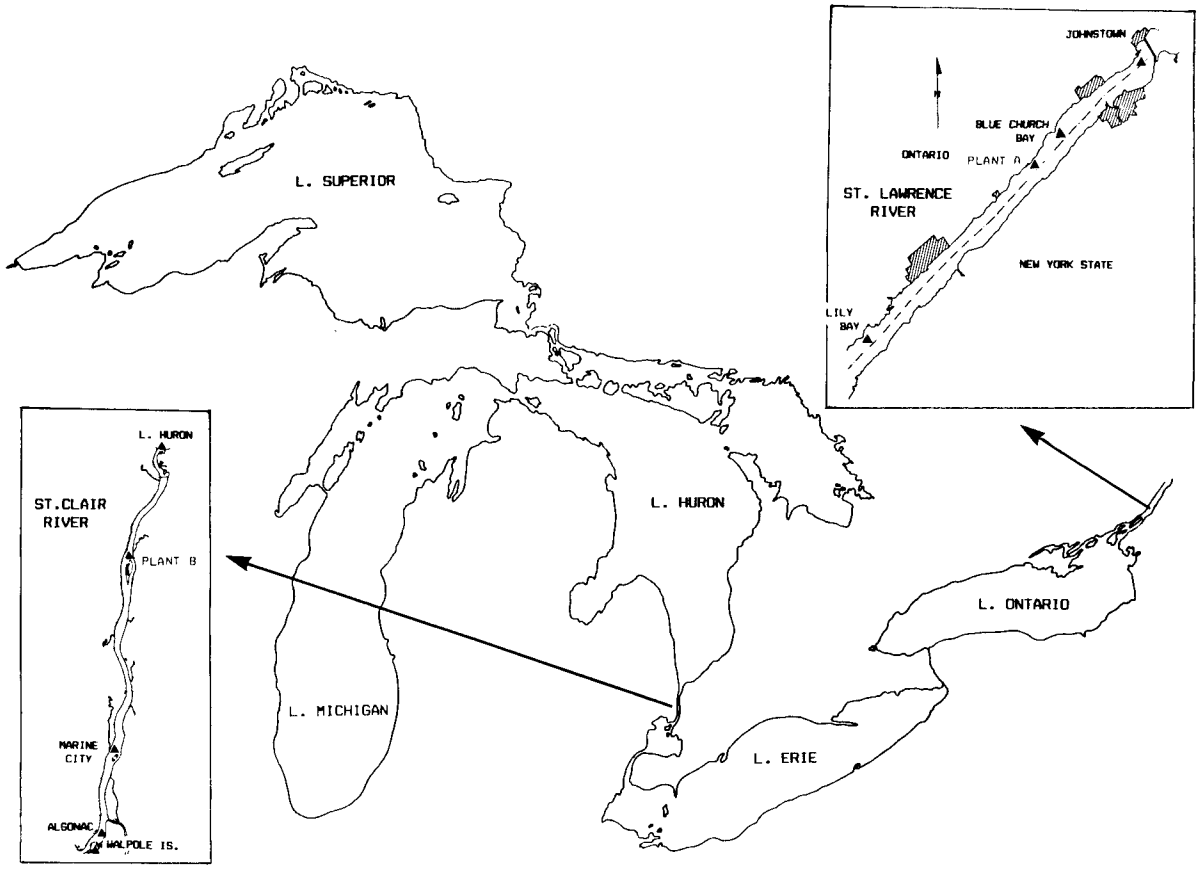

Figure 1 Map of the St Lawrence River and the St Clair River sampling sites.

of an Ekman grab sampler or scoop. Fish were caught by gill net. Clams and macrophytes were collected by Scuba divers.

Water samples were untreated and stored in dark bottles at 4°C until analysis. Fish samples were homogenized in a meat grinder and frozen. Sediments, clams and macrophytes were frozen immediately after collection.

Sampling sites (Fig. 1)

(1) Maitland: 0–2 km downstream of the discharge; Lily Bay, 20 km upstream; Blue Church Bay, 2 km downstream; and Johnstown, 10 km downstream respectively from Plant A.

(2) Corunna: 0–2 km downstream; Lake Huron, 13 km upstream; Marine City, Algonac and Walpole Island, 16, 26 and 27 km downstream respectively from Plant B.

Chemicals

Trimethyllead acetate (Me_3PbOAc), triethyllead acetate (Et_3PbOAc), tetramethyllead (Me_4Pb) and tetraethyllead (Et_4Pb) were obtained from Alfa Chemicals (Danvers, MA, USA). Dimethyllead dichloride (Me_2PbCl_2) and diethyllead dichloride (Et_2PbCl_2) were gifts from Associated Octel Co. (S. Wirral, UK). Tetramethylammonium hydroxide (TMAH) was from Fisher Chemicals; sodium diethyldithiocarbamate (NaDDTC) from Baker Co.; n-butyl Grignard reagent in tetrahydrofuran from Alfa Co. All other reagents and solvents were commercially available in high-purity grade.

Procedures

Determination of alkyllead and lead species in water

Water samples (1 dm^3) were extracted with 50 cm^3 of 0.5 mol dm^{-3} NaDDTC, 50 g of sodium chloride

(NaCl) and 50 cm^3 of benzene for 30 min. The benzene phase was carefully evaporated in a rotary evaporator to 1 cm^3 in a 15 cm centrifuge tube to which 0.2 cm^3 of n-butyl Grignard reagent was added. The mixture was gently mixed for 1 min and washed with 2 cm^3 of 0.5 mol dm^{-3} sulphuric acid (H_2SO_4). The organic phase was dried in anhydrous sodium sulphate. Appropriate amounts (10–20 μL) were injected into the GC–AA system for analysis. Detection limit for water was 8 ng dm^{-3}.

Determination of alkyllead and lead species in fish, clams and macrophytes

Homogenized fish samples (2 g), whole clams (1–2 g) or shredded pieces of macrophytes (2 g) were first digested with 5 cm^3 of TMAH (20%) in a hot water bath at 60°C for 1–2 h or until the tissue was dissolved. After cooling, the mixture was neutralized with 50% hydrochloric acid to pH 6–8 and extracted with 5 cm^3 benzene, 2 g of NaCl and 3 cm^3 of 0.5 mol dm^{-3} NaDDTC solution. The mixture was centrifuged and 2 cm^3 of the benzene phase was transferred to a glass-stoppered vial for butylation with 0.2 cm^3 of n-butyl Grignard reagent, followed by shaking with 3 cm^3 of 0.5 mol dm^{-3} H_2SO_4 to destroy the excess Grignard reagent. A 1 cm^3 aliquot of the benzene phase was loaded onto the silica gel column for 'clean-up' as described in the following section. The detection limit for fish, clams and macrophytes was 8 μg kg^{-1}.

Determination of alkyllead and lead species in sediments

Dried (1–2 g) or wet (5 g) sediment samples were extracted in a capped vial with 3 cm^3 of benzene after adding 10 cm^3 H_2O, 6 g NaCl, 1 g potassium iodide (KI), 2 g sodium benzoate, 3 cm^3 0.5 mol dm^{-3} NaDDTC and 2 g coarse glass beads (20–40 mesh) for 2 h on a mechanical shaker. After centrifugation, a measured aliquot (1 cm^3) of the benzene layer was withdrawn for butylation as described. Detection limit for sediment was 15 μg kg^{-1}.

Clean-up procedures for fish and clam samples

Fish and clam homogenates required 'clean-up' on a silica gel column prior to analyses because of their high protein and lipid contents which might clog the GC as well as the transfer line from the GC to AA.

(1) Column preparation Glass wool was placed in the bottom of a 50 cm^3 burette (1.5 cm i.d.) followed by 1 cm layer of anhydrous sodium sulphate. A slurry mixture of pentane and kiesel-gel 60 was poured into the column, aided by a vibrator against the sides of the burette to pack tightly. Silica gel was about 48 cm deep. The packing was sealed with 1 cm of anhydrous sodium sulphate.

(2) Sample loading The level of pentane was drained to the top of the packing in the column. Exactly 1 cm^3 of the butylated sample in benzene was added to the top of the column. The sample level was drained to the top of the sulphate layer and the interior walls of the column were rinsed with a few drops of pentane. The rinse pentane was drained to the top of the sulphate layer and the stopcock was closed. A 3–4 cm^3 aliquot of pentane was slowly drained into the column from the reservoir (separatory funnel) containing 60 cm^3 of pentane. A 100 cm^3 round-bottom flask was placed under the column and the flow of pentane through the column was adjusted to one drop every 2 s. The reservoir opening and the round-bottom flask were covered with aluminium foil. When about 55 cm^3 of pentane had been eluted through the column, the stopcock was closed.

(3) Volume reduction Iso-octane 600 μL was added to each sample to prevent the volatilization of the alkyllead compounds during volume reduction. The sample was concentrated in a rotary evaporator at 20°C to about 2 cm^3 and transferred to a 15 cm^3 graduated centrifuge tube. The sample was vortexed and evaporated on an unheated sample block to exactly 1 cm^3 and placed in a small vial that was sealed tightly. A syringe was used to inject the sample into the GC–AA.

The gas chromatography–atomic absorption (GC–AA) system

The GC–AA system has been described in a previous publication.[15] The butylated sample was injected directly into the chromatographic column by a syringe. The chromatographic column was of glass, 1.8 m long, 6 mm diameter, packed with 10% OV-1 on Chromosorb W (80–100 mesh) with a nitrogen carrier gas flow rate of 65 cm^3 min^{-1}. Temperatures of the injection port and transfer line were 150 and 160°C, respectively. The column was programmed from 80 to 200°C at a rate of 5°C min^{-1}. In the AA, a quartz furnace electrically heated at 900°C with hydrogen gas flowing at 85 cm^3 min^{-1} was used for atomization. The 217-nm lead line from a lead electrodeless discharge lamp at 10 W was used. Deuterium

background correction was used. Peak areas were recorded with an HP 3392A integrator. The sum of total lead was determined by adding the concentrations of individual alkylleads and inorganic lead.

Accuracy, precision and interferences

The recoveries of dialkylleads and trialkylleads from biological (fish, clams and macrophytes), sediment and water samples were evaluated by spiking various levels (1–20 μg) of the lead compounds to the samples and extracting the samples with the above procedures. The average recovery varied from 71% for Me_2Pb^{2+} to 101% for Et_2Pb^{2+} in the biological samples, 94% for Et_3Pb^+ to 111% for Me_3Pb^+ in sediments and 94% for Et_3Pb^+ to 106% for Me_3Pb^+ in water. Recoveries were evaluated by comparing values from alkyllead standards with and without spiked samples. The results indicated that there were no serious sample matrix interferences.

The precision of the method was also evaluated by replicate analyses ($n=6$) of biological (fillet, clams and macrophytes) and sediment samples spiked with 5 μg of each of the alkylleads. For biological samples the reproducibility varied from 6.5% for Et_3Pb^+ to 20% for Et_2Pb^{2+} expressed in relative standard deviation at this level. Better reproducibility was obtained for sediment analysis. Replicated analysis ($n=6$) showed an average standard deviation of 4% for Me_3Pb^+ and Et_3Pb^+ and up to 15% for the dialkyllead compounds. The precision of the water analyses was evaluated by determining 10 replicate samples from 100 cm^3 of Lake Ontario water enriched with 10 μg of each of the alkyllead and lead species. The relative standard deviation for the four alkyllead and lead compounds at this level varied from 5.4% for Me_3Pb^+ to 9.5% for lead species.

Of all the alkyllead compounds, Me_3Pb^+ and Et_3Pb^+ were the most stable. Since equal quantities of all the alkyllead species gave equal peak areas, Me_3Pb^+ and Et_3Pb^+ were used as internal standards for other lead compounds.

RESULTS AND DISCUSSION

Between 1981 and 1987, we collected and analysed about 700 samples of fish, clams, macrophytes, sediments and water for alkyllead contamination in areas upstream and downstream of two alkyllead manufactures in St Lawrence and St Clair Rivers, Ontario. Detailed results have been published in a technical report[16] and this paper will discuss some of the main features.

The concentrations of alkylleads in fish from alkyllead-contaminated area in Maitland, St Lawrence River were highest in 1981, with carp containing much higher levels than white sucker and northern pike (Table 1). One carp contained 139 mg of alkylleads per kg wet weight, a value representing the highest concentration of either alkyllead or inorganic lead ever reported in fish. A previous survey of 'total lead' in Great Lakes fish from areas with no direct lead contamination generally showed residues less than 0.1 mg kg^{-1} and maximum values rarely exceeded 0.5 mg kg^{-1}.[17] Even various marine fish species (cod, lobster and mackerel) from alkyllead-contaminated areas contained much lower alkyllead levels, from 0.1 to 4.8 mg kg^{-1}.[11] Fish exposed to

Table 1 Alkylleads in whole fish (minus intestine) and intestine from Maitland area (1981)

	Whole fish (minus intestine)			Intestine		
		Alkyllead (μg kg^{-1})			Alkyllead (μg kg^{-1})	
Fish species	N_1/N_2[a]	G. mean[b]	Range	N_1/N_2[a]	G. mean[b]	Range
Carp	12/12	4207	190–138999	11/12	2919	100–100644
White sucker	8/10	218	24–1221	9/10	1009	236–3447
Northern pike	5/6	173	30–1384	5/6	2248	1360–4454

[a] Number of fish samples with alkyllead conc > 8 μg kg^{-1} over number of fish samples analysed. [b] Geometric mean was calculated from samples with alkyllead conc > 8 μg kg^{-1}.

inorganic lead in the laboratory generally contained less than 6 mg kg^{-1},[18] whilst fish sampled from a river polluted by lead mines contained up to 18 mg kg^{-1}.[19] There was no direct relationship between fish size and alkyllead level, as would be expected if fish accumulated alkyllead from the food chain. In other words, the lead was possibly taken up directly from water. Except for carp, most of the alkylleads were found in fish intestines (Table 1). This is not too surprising since alkylleads are lipophilic and accumulate in the lipid layer of the intestine. Rainbow trout exposed to waterborne tetramethyllead in the laboratory also accumulated the compound mainly in the lipid layer of the intestine.

Analyses of alkyllead species indicated that the majority was in the form of Et_4Pb and its degradation products of Et_3Pb^+ and Et_2Pb^{2+} (Table 2). The occurrence of the degradation products in fish could be derived from the metabolism of Et_4Pb accumulated by fish or from direct concentration of these compounds from water. Methylated forms of the degradation products were also detected, suggesting the possible methylation of the lead compounds either in the environment or in the fish. Lead methylation was first reported by Wong *et al.*[6] and was subsequently confirmed by other workers.[21,22]

Concentration of alkylleads in fish vary with fish species. Yellow perch, carp, smallmouth bass and

Table 2 Percentage of alkyllead species distribution in whole fish (minus intestine) and intestine from Maitland area (1981)

		Alkyllead species (%)				
Fish species	N_1/N_2[a]	Et_4Pb	Et_3Pb^+	Et_2Pb^{2+}	$MeEt_3Pb^+$	Me_2Et_2Pb
(A) Whole fish (minus intestine)						
Carp	12/12	55	39	1	4	1
White sucker	8/10	47	51	0	2	0
Northern pike	5/6	0	40	39	21	0
(B) Intestine						
Carp	11/12	32	54	11	2	1
White sucker	9/10	27	52	18	2	1
Northern pike	5/6	46	28	16	8	2

[a] Number of fish samples with alkyllead conc > 8 $\mu g\ kg^{-1}$ over number of fish samples analysed.

Table 3 Species variation in the contamination of whole fish (minus intestine) and fish intestine by alkylleads
The fish were from the Maitland area (1982)

	Whole fish (minus intestine)			Intestine		
		Akyllead ($\mu g\ kg^{-1}$)			Alkyllead ($\mu g\ kg^{-1}$)	
Fish species	N_1/N_2[a]	G. mean[b]	Range	N_1/N_2[a]	G. mean[b]	Range
Yellow perch	5/5	1994	912–5415		No sample	
Carp	5/6	1976	102–61713	6/6	1606	159–30608
Smallmouth bass	4/4	1972	890–3115	3/3	3198	1955–5079
White sucker	3/5	1747	717–3187	3/5	6336	2767–12085
Brown bullhead	2/3	1135	553–2329	2/3	587	328–1052
Redhorse sucker	5/5	721	189–2042	5/5	1486	350–4857
Pumpkinseed	3/5	567	89–1882		No sample	
Pike	4/5	287	55–1324	5/5	981	411–2063
Alewife	2/5	244	209–285		No sample	
Rock bass	0/2	< 8		0/2	< 8	

[a] Number of fish samples with alkyllead conc > 8 $\mu g\ kg^{-1}$ over number of fish samples analysed. [b] Geometric mean was calculated from samples with alkyllead conc > 8 $\mu g\ kg^{-1}$.

white sucker had higher alkylleads than pike, alewife and rock bass (Table 3). The feeding habit, the lipid content of the fish, and the location where the fish were caught probably would account for the differences. Results in Table 3 also reveal the decrease in levels of alkylleads in fish from 1981. The geometric mean levels of alkylleads in whole (without intestine) yellow perch and carp were less than 2 mg kg^{-1}, as compared with 4.2 mg kg^{-1} in carp in 1981. However, the majority of alkylleads was still found in the intestinal layer.

Most of the fish species examined in 1982 and subsequent years contained between 50 and 75% of total lead as alkylleads (Table 4). The causes of differences in alkyllead contents among fish species are not clear but could be caused by differences in the rates of uptake, depuration or metabolism of alkylleads. Concentrations of alkylleads on fish represent an equilibrium between the accumulation and depuration of these compounds in fish.[20] Several species of fish and animals have been reported to metabolize tetra-alkyllead to trialkyllead compounds.[23,24]

Table 4 Alkylleads as a percentage of total lead in whole fish (minus intestine) from Maitland area (1982)

Species	N[a]	Total lead ($\mu g\ kg^{-1}$)	Alkylleads (% of total lead)
Carp	6	2361	84
Yellow perch	5	3682	54
Rock bass	2	446	0
Smallmouth bass	4	2162	91
Pumpkinseed	5	812	70
White sucker	5	1220	74
Redhorse sucker	5	721	100
Brown bullhead	3	1135	100
Northern pike	5	1004	28
Alewife	5	308	79

[a] N = number of samples analysed.

The distribution of alkylleads in fish muscle (skinless dorsal fillet) and carcass (headless and gutted) was examined in fish from Maitland (St Lawrence River) and Algonac (St Clair River). The results (Table 5) indicate that fish muscle contained as much alkylleads as did fish carcass. In the case of yellow perch and brown bullhead, higher alkyllead levels were found in the muscle portions.

The relationship between alkyllead source and alkyllead levels in fish is demonstrated in Tables 6 and 7. There was a clear upstream and downstream distribution of alkylleads in 1983 samples of fish muscle and carcass as well as in 1984 samples of whole fish when mean levels were compared. Fish taken from Blue Church Bay, 2 km downstream from the Maitland plant, contained much higher alkyllead levels than the same fish species from Lily Bay, 20 km upstream. The alkyllead contamination in fish was detected as far as 10 km downstream at Johnstown. Similarly, fish from Marine City, 16 km downstream from the Corunna plant, had higher alklyllead levels than upstream fish from Lake Huron. Occasional high levels at upstream sites were likely due to fish migration.

Similarly to alkyllead levels in fish, water samples

Table 5 Comparison of alkylleads in muscle and carcass (whole body minus intestine) of fish from Maitland, St Lawrence River and Algonac, St Clair River (1983)

Species	N[a]	Alkylleads ($\mu g\ kg^{-1}$)		
		Muscle	Carcass	Muscle/carcass
(A) St Lawrence River				
Northern pike	15	128	279	0.46
Yellow perch	3	2434	1716	1.42
Brown bullhead	1	3585	977	3.67
Redhorse sucker	4	482	798	0.60
(B) St Clair River				
White sucker	12	62	107	0.58
Carp	7	85	138	0.62
Yellow perch	3	<8	17	—
Catfish	1	114	155	0.73

[a] N = number of samples analysed.

Table 6 Relationship between alkyllead source and alkyllead levels in fish muscle and carcass in 1983 and whole fish in 1984 from the St Lawrence River

Species	Geometric mean of alkyllead concentration ($\mu g\ kg^{-1}$)[a]		
	Lily Bay (20 km upstream)[b]	Blue Church Bay (2 km downstream)[b]	Johnstown (10 km downstream)[b]
(A) Muscle			
Brown bullhead	<8	3585	346
Yellow perch	57	2434	450
Redhorse sucker	No sample	482	No sample
Northern pike	<8	128	79
Carp	99	No sample	405
Pumpkinseed	<8	No sample	71
Smallmouth bass	19	No sample	30
(B) Carcass			
Brown bullhead	<8	977	135
Yellow perch	44	1716	379
Northern pike	<8	279	94
Carp	321	No sample	354
Pumpkinseed	247	368	112
Spottail shiner	<8	120	No sample
(C) Whole fish			
Brown bullhead	<8	294	171
Yellow perch	<8	2524	328
Pumpkinseed	<8	150	<8
Redhorse sucker	155	809	321
White sucker	150	411	495

[a] Geometric mean was calculated from samples with alkyllead conc >8 $\mu g\ kg^{-1}$. [b] Distance from Plant A, Maitland.

Table 7 Relationship between alkyllead source and alkyllead levels in fish muscle and carcass from the St Clair River (1983)

Species	Geometric mean of alkyllead concentration ($\mu g\ kg^{-1}$)[a]			
	L. Huron (13 km up)[b]	Marine City (16 km down)[b]	Algonac (26 km down)[b]	Walpole Island (27 km down)[b]
White sucker				
Muscle	31	753	33	No sample
Carcass	210	413	224	34
Carp				
Muscle	627	No sample	208	121
Carcass	323	No sample	2836	34

[a] Geometric mean was calculated from samples with alkyllead conc >8 $\mu g\ kg^{-1}$. [b] Distance upstream or downstream from Plant B, Corunna.

taken near Plant A contained much higher alkyllead and lead concentrations than did samples from upstream and downstream of the industry (Table 8). Alkyllead levels in water taken 100 m from the plant were 330 ng dm^{-3} and 900 ng dm^{-3} in subsurface and surface microlayer samples respectively. It is not too surprising that alkyllead levels were three times higher in the surface microlayer since the mircolayer contains a hydrophobic film of long-chain fatty acids, alcohols and other organic chemicals where high con-

Table 8 Relationship between alkyllead source and alkyllead and total lead levels in water from the St Lawrence River (1983)

Location	Water sample	Alkyllead (ng dm^{-3})			Total lead (ng dm^{-3})		
		N_1/N_2[a]	G. mean[b]	Range	N_1/N_2[a]	G. mean[b]	Range
Lily Bay (20 km upstream)	Subsurface	0/1	<8		1/1	1740	
Plant A, Maitland	Subsurface	3/3	330	200–470	3/3	2330	1760–2950
	Surface microlayer	3/3	900	430–1910	3/3	6770	3790–9390
Blue Church Bay (2 km downstream)	Subsurface	3/3	90	80–120	3/3	1820	1380–3140
	Surface microlayer	1/1	80		1/1	3550	

[a] Number of samples with alkyllead or total lead conc > 8 ng dm^{-3} over number of samples analysed. [b] Geometric mean was calculated from samples with alkyllead or total lead conc > 8 ng dm^{-3}

centrations of contaminants accumulate.[25] The alkyllead levels decreased to 90 ng dm^{-3} in subsurface and 80 ng dm^{-3} in surface microlayer samples from Blue Church Bay, 2 km downstream from Plant A and to less than the detection limit of 8 ng dm^{-3} in subsurface sample from Lily Bay (20 km upstream). Speciation of alkylleads in water samples showed no tetraethyllead. Triethyllead accounted for 84–100% with the remainder as diethyllead (Table 9). Since tetraalkylleads have high vapour pressure and are only sparingly soluble in water, their presence in water is only transient. The ionic alkyllead species, tri- and dialkyllead compounds are more stable and can exist in water for a longer period of time. Total lead levels were also higher near the alkyllead source (Table 8) and represent almost 100% of lead in samples with low alkyllead level and as low as 86% in samples with higher alkyllead levels (Table 8).

Total lead and alkyllead concentrations were high in both surface microlayer and subsurface waters, and in sediment samples, from Plant B at Corunna while alkylleads were not detected in samples from several locations downstream (Table 10). Tetraalkylleads were again absent in these samples.

Sediments and macrophytes taken near Plant A also contained higher alkyllead levels (Table 11). Clams

Table 9 Percentage of alkyllead species distribution in water samples from the St Lawrence River (1983)

Location	Water samples	N_1/N_2[a]	Alkyllead species (%)		
			Et_4Pb	Et_3Pb^+	Et_2Pb^{2+}
Lily Bay	Subsurface	0/1	—	—	—
Plant A, Maitland	Subsurface	3/3	0	84	16
	Surface microlayer	3/3	0	89	11
Blue Church Bay	Subsurface	3/3	0	89	11
	Surface microlayer	1/1	0	100	0

[a] Number of samples with alklyllead conc > 8 ng dm^{-3} over number of samples analysed.

Table 10 Relationship between alkyllead source and alkyllead and inorganic lead levels in water and sediment samples from the St Clair River (1983)

	Surface microlayer ($\mu g\ dm^{-3}$)			Subsurface water ($\mu g\ dm^{-3}$)			Sediment ($mg\ kg^{-1}$)
Distance (km)[a]	Et_3Pb^+	Et_2Pb^{2+}	Pb(II)	Et_3Pb^+	Et_2Pb^{2+}	Pb(II)	Total lead
0	0.54	0.14	8.54	0.34	0.08	2.25	644
0.75	—[b]	—	7.23	—	—	1.13	103
3.75	—	—	0.84	—	—	1.53	9
4.87	—	—	1.28	—	—	1.32	NS[c]
7.95	—	—	1.37	—	—	1.43	8

[a] Distance downstream from Plant B, Corunna. [b]; — Not detected. [c] NS, No sample.

Table 11 Relationship between alkyllead source and alkyllead levels in sediments, clams and macrophytes from the St Lawrence River (1983)

	Plant A			Blue Church Bay		
	Alkylleads ($\mu g\ kg^{-1}$):			Alkylleads ($\mu g\ kg^{-1}$):		
Samples	N_1/N_2[a]	G. mean[b]	Range	N_1/N_2[a]	G. mean[b]	Range
Sediment	6/6	323	152–1503	4/6	216	76–706
Clam	0/1	<8		1/1	335	
Macrophyte	2/2	2092	200–21888	0/1	<8	

[a] Number of samples with alkyllead conc. $>8\ \mu g\ kg^{-1}$ over number of samples analysed. [b] Geometric mean was calculated from samples with alkyllead conc. $>8\ \mu g\ kg^{-1}$.

were generally not found in this area. Only one clam each was obtained from the Maitland and Blue Church Bay areas, with levels less than the detection limit in the clam from Maitland and 335 $\mu g\ kg^{-1}$ in the sample from Blue Church Bay. The sample taken near Maitland may have not been directly in the effluent plume.

Levels of alkylleads in fish samples have declined since our initial studies in 1981. These are summarized in Fig. 2. For example, the geometric means of alkyllead levels in carp from the Maitland area had decreased from 4207 $\mu g\ kg^{-1}$ in 1981, to 2000 $\mu g\ kg^{-1}$ in 1982, to 49 $\mu g\ kg^{-1}$ in 1987 (Fig. 2). Other fish species generally show the same trend of decline, reflecting improvements in the reduction of alkyllead compounds in the manufacturers' effluents. For example, Plant A reduced its total lead levels in its effluents to the St Lawrence River from 23 $kg\ day^{-1}$ in 1983 to 19 $kg\ day^{-1}$ in 1984 and its alkyllead production closed in 1985.[16] Plant B also decreased its lead discharge from 62 $kg\ day^{-1}$ in 1983 to 13 $kg\ day^{-1}$ in 1984.

CONCLUSIONS

These surveys have clearly demonstrated that alkyllead compounds can enter the aquatic environment in high concentrations due to manufacturing. The compounds contaminate water, accumulate in sediments and are present for a sufficiently long period to be taken up in high concentrations by benthos, plants and fish. Due to high lipid concnetrations, fish accumulate very high levels and, in the worst cases, could represent a hazard to fish consumers.

The pattern of alkyllead distribution suggests that chemical and biological transformations may be occurring in the environment after discharge. These may include hydrolysis, photolysis, biological dealkylation, methylation and transmethylation. The predominance of trialkyl forms probably reflects higher water solubility and lower volatility relative to the tetra-alkyl forms. Since the trialkyl forms are those most toxic to mammals,[24] their accumulation in fish is important.

These data suggest that stringent controls on alkyllead discharges are required if alkyllead manufac-

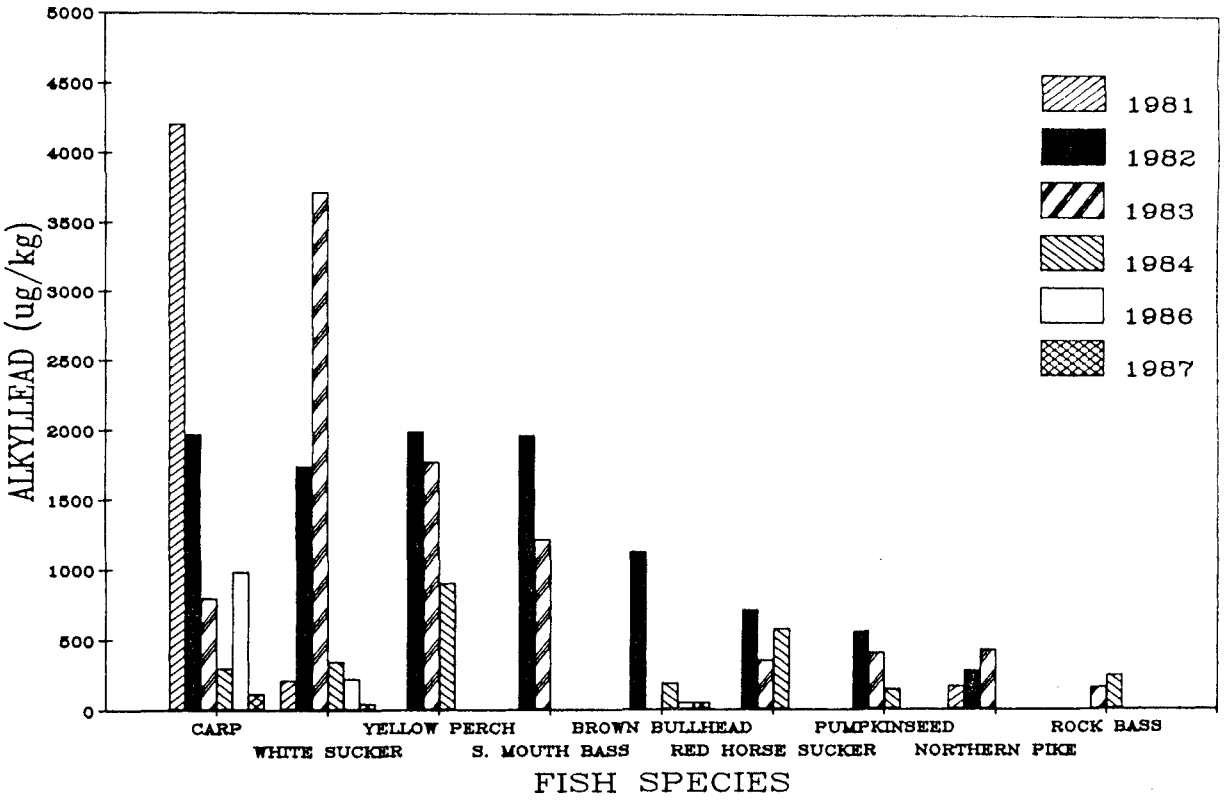

Figure 2 Summary of alkyllead concentrations in fish from St Lawrence River areas near Maitland (1981–1987).

turing is to have a minimal impact on the aquatic enviornment.

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