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Organolead Compounds in Mussels (*Mytilus galloprovincialis*) from the Eastern Adriatic Coast

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Mussels (*Mytilus galloprovincialis*) and surrounding seawater were collected from various sites on the eastern Adriatic coast and examined for the presence of alkyllead compounds and the total lead content. Organoleads were quantified by gas chromatography-atomic absorption spectrometry, and total lead was quantified by differential pulse anodic stripping voltammetry. The presence of all alkyllead species in mussel tissues was established (in nanograms/gram of wet weight): tetraalkyl (<0.2-43.6), trialkyl (<0.1-31.8), and dialkyl (<0.1-9.2), with a dominance of ethyl derivatives. The organolead level in mussels is shown to be a better indicator of pollution with organic lead than that in seawater, whereas the total lead level cannot serve this purpose as it comes from other sources. Trimethyllead amounts in mussels and seawater are highly correlated; thus, mussels provide a good bioindicator for this chemical species. Correlation between alkyllead levels suggests the possible environmental methylation of lead. Bioconcentration factors between mussels and water for individual alkyllead compounds are, on average, lower than those for total lead, indicating less efficient bioaccumulation of organic lead.

Introduction

Organolead compounds are widespread in the environment as a result of their use as an antiknock additive in gasoline (1, 2). Despite a virtual phase-out of use in North America, a substantial proportion of gasoline sold within Europe still contains lead additives, and in the developing world, levels of lead in gasoline are still high. Since the 1970s when it was recognized that organolead compounds, in addition to inorganic lead, are emitted from motor vehicles, much work has been done on the environmental cycling of organic lead. Vehicular emissions include both tetra-

alkyllead compounds and the ionic tri- and dialkylleads. Under environmental conditions, dealkylation occurs to produce less alkylated forms, although there is limited evidence that environmental methylation of lead can occur to increase the degree of alkylation under some circumstances.

The presence of organolead compounds has been established in a wide range of environmental media, including air (3, 4), rainwater (5-7), surface waters (8, 9), street dust (10), sediment and soil (9, 11), aquatic organisms (12-15), birds (16, 17) and human brain (18). Most published studies have dealt with abiotic compartments such as air and rainwater in which organolead compounds can exist in appreciable concentrations. The equivalent data on the concentrations of these compounds in aquatic organisms are very few, although there is evidence that alkyllead can be appreciably more toxic to organisms than inorganic lead (19, 20). An extensive study has been carried out in an aquatic environment polluted by the manufacture of alkyllead (21), where it was shown that tetra-, tri-, and dialkylleads can be accumulated from water by fish, which contained 50-75% of their total lead as alkyllead. However, comparable data from areas polluted only by the routine use of leaded gasoline are very few. It has been shown that aquatic organisms such as salt-marsh snails (12) and freshwater and marine fish (13-15) can accumulate low levels of tetraalkyllead and/or ionic alkyllead compounds. No data are available in the literature on the concentrations of organolead compounds in mussels of the *Mytilus* species, which have been widely used as indicator organisms for heavy metal pollution in the marine environment (22). Bioconcentration factors, defined as the ratio of the concentration of a compound in an aquatic organism to that in the aquatic environment in which it lives, express the efficiency of uptake of a compound from the environment. Data for organolead compounds are very few, and those that do exist are mostly derived from laboratory experiments in which an abnormally high concentration of organolead compounds in water was used (23).

The present study was conducted with two objectives: firstly, to establish the level of alkyllead compounds in mussels, *Mytilus galloprovincialis* from the coastal region of the eastern Adriatic, and secondly, to investigate the bio-concentration of different alkyllead compounds from seawater to mussels in their natural habitat.

Experimental Section

Sample Collection and Pretreatment. Samples of mussels and seawater were collected at several sites along the eastern Adriatic coast. Sampling locations were chosen so as to reflect the influence of maritime activities and gasoline stations located on the coast. Larger coastal towns (from north to south: Rovinj, Rijeka, Zadar, Šibenik, and Split; Figure 1) were selected for this purpose. In each of them, if possible, mussels and water samples were taken in front of the gasoline station, in the harbor area, and in an area far from maritime activities (reference area). Sampling was performed on several occasions between February 1992 and June 1994. If possible, mussels were collected at a depth of 0.5 m, although sometimes (sampling in September 1993 and April and June 1994 in the Šibenik area) samples

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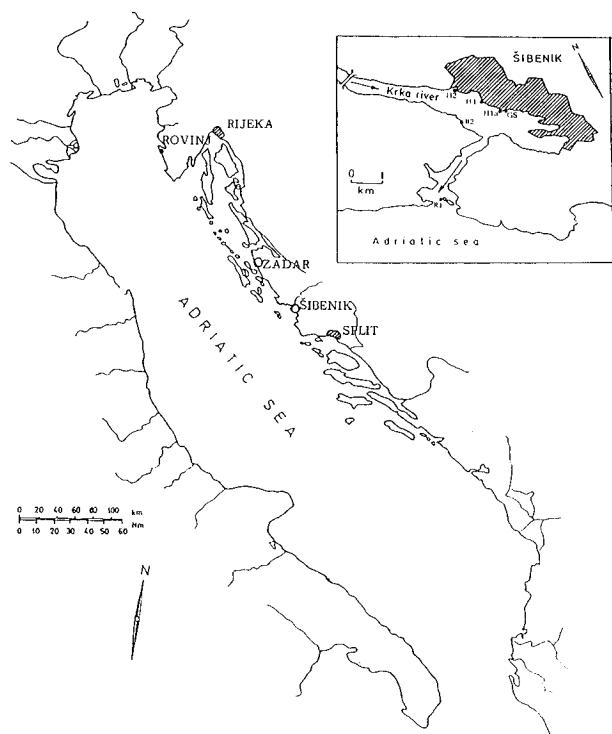


FIGURE 1. Map of towns and sites on the eastern Adriatic coast where mussels and seawater samples were collected.

had to be collected at greater depths (2–3 m) due to a deficiency of mussels at the depth of 0.5 m (in autumn and winter 1993, a very low salinity of the surface layer of the stratified Krka River estuary caused high mussel mortality). Mussels were collected manually and selected according to their lengths in two categories. In each category, 20–40 specimens were dissected by precleaned quartz tools, and whole soft tissues were homogenized in a mixer and stored in plastic bags at -20°C until analysis. Water was collected manually into 2.5 L dark glass bottles for organolead analysis and into acid-precleaned 0.5 L plastic bottles for total lead analysis. Water samples were stored in the dark at 4°C .

Analytical Methods. (a) *Chemicals.* Trialkyllead chlorides were obtained from Alfa-Ventron. Dialkyllead compounds were prepared from the corresponding trialkyllead standards by reaction with iodine monochloride (24). A tetraalkyllead mixture containing Me_4Pb , Me_3EtPb , $\text{Me}_2\text{Et}_2\text{Pb}$, and Et_4Pb was prepared in *n*-hexane. Standard solutions of ionic alkyllead compounds (IAL) were prepared in tetradistilled water and stored in the dark. Propylated IAL compounds in hexane were prepared by the same procedure used for the extraction of water samples. The inorganic lead standard was from Merck. Other chemicals were of analytical reagent grade, except nitric acid, which was tetradistilled.

(b) *Determination of Alkyllead Compounds.* Mussel homogenate (5 g) was solubilized in 10 mL of TMAH (tetramethylammonium hydroxide, 25% solution in water) at room temperature overnight in closed dark glass bottles. The solution was then diluted to 200 mL with Milli-Q (MQ) water, the pH was adjusted to about 8 by 50% hydrochloric acid, and then the extraction of organolead compounds was performed. For the extraction of ionic alkyllead compounds, 5 g of NaCl and 5 mL of 0.25 M NaDDC (sodium diethyldithiocarbamate) were added, and double extraction with 10 + 10 mL of hexane was performed. The hexane layer was separated from the emulsion by centrifugation

combined with Na_2SO_4 drying and evaporated under nitrogen flow at room temperature to a volume of 500 μL . Propylation of ionic alkyllead compounds was performed by the addition of 300 μL of propylmagnesium chloride (Grignard reagent), the excess of which was destroyed with 5 mL of 0.5 M H_2SO_4 (25). To prevent clogging of the GC column and interface line, extracts were cleaned up on a miniature silica column (Altech, 500 mg Si column) and gently evaporated to a final volume of 200 μL . Quantification was made by comparison with external calibration, which was run each day. For tetraalkyllead analysis, TMAH solution was extracted with 10 mL of hexane, which was separated by centrifugation, evaporated to 500 μL , cleaned by the silica column, and analyzed by GC–AAS. The whole procedure for the determination of different alkyllead species in mussel tissue will be described in full detail elsewhere (in preparation). The detection limit (from 5 g of mussels and a 100 μL injection volume) was 0.1 ng/g for IAL compounds, 0.2 ng/g for Et_4Pb , and 0.5 ng/g for Me_4Pb . Some of the higher concentration samples were also analyzed by GCMS to confirm peak identity.

For water analysis essentially the same procedure was applied. Tetraalkyllead (TAL) determination was not performed on water samples, as analyses could not be performed immediately after sampling. It is known that tetraalkyllead compounds in water are quickly decomposed, so that samples should be analyzed within 48 h after sampling (7). Literature data show that tetraalkylleads are not generally found in natural waters (2), which may be a consequence of their hydrophobicity and/or lack of stability in the collected water sample. However, as tetraalkyllead is converted to trialkyllead (7), the concentration of ionic alkylleads in the sample corresponds to the total organic lead. For the ionic alkyllead determination, seawater samples (2.5 L) were extracted in the same bottles in which samples were collected. After the addition of 12 mL of 0.25 M NaDDC, a double extraction with 20 + 10 mL hexane was performed. The hexane extract was then treated as in the case of mussel analysis. Some samples were also analyzed by an electrochemical method, based on the reextraction of IAL from carbamate complexes to an acid aqueous solution and DPASV determination (26). The detection limit (from 2.5 L of water) was 0.5 ng/L for both GC–AAS (100 μL injection volume) and the electrochemical method.

(c) *Determination of Total Lead.* For analysis of the total lead in mussels, about 0.5 g of tissue was digested in a quartz vessel by a mixture of HNO_3 and HClO_4 (3 + 0.5 mL). A white residue was dissolved in acidified, redistilled water (0.5 mL of HNO_3 /50 mL), and the lead concentration was determined by DPASV (at a deposition potential of -0.85 V vs Ag/AgCl) using a standard addition method. The method was tested on Standard Reference Material FISH MA-B-3/TM and was found satisfactory. For water analysis, unfiltered samples were acidified to pH 2 (100 μL of HNO_3 /25 mL) and UV irradiated (150 W lamp) for 24 h prior to the lead analysis.

(d) *Analysis by GC–AAS.* For the GC separation of alkyllead species, a glass column (1.2 m \times 6 mm o.d. \times 3 mm i.d.) packed with 10% OV-101 on Chromosorb W (80–100 mesh) was used (27). The injection temperature was set at 150°C , and an oven temperature program of 80 – 180°C ($20^{\circ}\text{C}/\text{min}$) was applied. The transfer line from the GC to the AAS was a PTFE tube (0.75 m \times 1.6 mm i.d.), which

TABLE 1

Average Recovery for Determination of Different Alkyllead Species in Mussels and Water

	TAL recovery (%)			
	Me ₄ Pb	Me ₃ EtPb	Me ₂ Et ₂ Pb	Et ₄ Pb
mussels/I ^a	21	35	38	50
mussels/II	5	17	21	39

	IAL recovery (%)			
	Me ₃ Pb ⁺	Me ₂ Pb ²⁺	Et ₃ Pb ⁺	Et ₂ Pb ²⁺
mussels	88	72	92	99
water	91	81	95	92

^a I: separate extraction with hexane. II: extraction and determination with IAL.

was kept at 160 °C. The atomization cell was a silica tube (16 cm × 1.5 cm o.d.) heated at 950 °C.

(e) **Analysis by DPASV.** A Princeton Applied Research (PAR) 174A polarographic analyzer with an HP-7045A x-y recorder was used for differential pulse anodic stripping voltammetry (DPASV) measurements. The working electrode was a hanging mercury drop electrode (Metrohm E-290), the auxiliary electrode was a platinum wire, and the reference electrode was saturated Ag/AgCl. The conditions for DPASV were as follows: pulse amplitude, 50 mV; pulse frequency, 2 s⁻¹; scan rate, 5 mV/s.

Results and Discussion

Recovery. Mean recoveries of tetra-, tri-, and dialkyllead compounds in mussels and water are given in Table 1. Tetraalkylleads can be measured by two methods: separately by the hexane extraction (I) and together with ionic alkyllead (IAL) compounds (II). For tetraethyllead it is possible to use both methods, but more volatile methyl derivatives, especially tetramethyllead, are almost completely lost in method II, probably during the propylation step. Additionally, in the blank of propylated samples, some peaks may appear that can interfere with the determination of tetraalkylleads. For these reasons, tetraalkylleads are measured separately in all mussels samples. In some samples where higher concentrations of IAL or TAL were obtained (SI/GS/92 or RO/GS/94), confirmation by standard addition of the detected species to a final hexane extract was carried out.

Distribution in Mussels. Given in Table 2 are the results of analyses of soft mussel tissues for their organic and total lead contents. In all samples except one (at one reference station), some alkyllead compounds were detected. Both tetra- and ionic alkyllead compounds were found. About half of the samples (45%) contained tetraethyllead, but only one contained tetramethyllead. Mixed tetraalkyllead species are not found. Of the seven ionic alkylleads that had been reported in environmental samples, neither dimethyllead nor mixed methylethyl species were detected in any of the mussel samples. Trimethyllead appeared the most frequently (in 97% of samples), followed by triethyllead (in 74% of samples) and diethyllead (in 52% of samples). The highest individual concentration was found for tetraethyllead. Generally, ethyl species show a wider range of concentrations than trimethyllead, whose concentration is more uniform.

Due to a few rather high concentrations, which significantly influence the arithmetic mean values (Table 2),

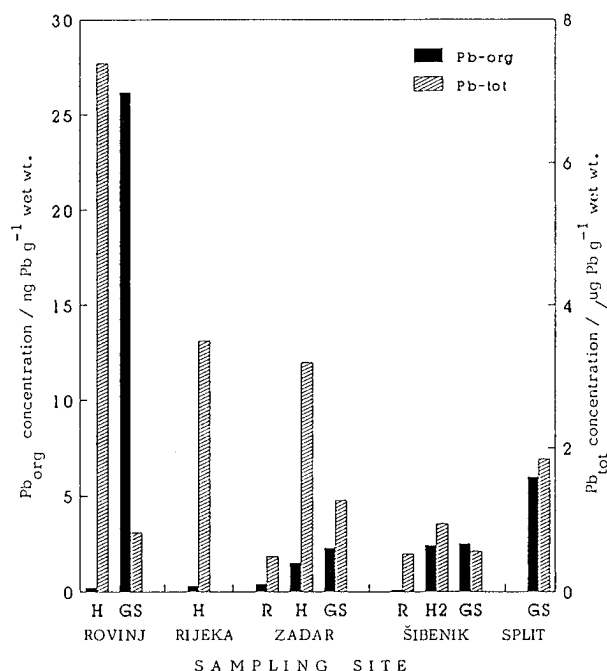


FIGURE 2. Comparison of organic and total lead concentrations in mussels sampled in April–May 1994 at different sites along the Eastern Adriatic Coast.

geometric means, which are closer to the median values (Table 2), were considered to more reliably represent the average concentrations of particular lead species. Wong et al. (21) also used geometric means for comparison of alkyllead levels in fish and other biological samples from rivers in Canada contaminated with organolead compounds. A few conclusions can be drawn from these data: ethyllead species (sum of tetra-, tri-, and dialkylleads) are more abundant than methyllead species; trialkyl compounds are the dominant alkyllead species; the relative concentrations of Et₄Pb, Et₃Pb⁺, Me₃Pb⁺, and Et₂Pb²⁺ roughly correspond to 2:2:2:1 (Me₄Pb was not taken into account because it is not generally present in mussels).

The total alkyllead burden on average accounts for less than 1% of the total lead burden in these samples (Table 2). However, this percentage is quite variable, ranging over 3 orders of magnitude (0.01–6.6%). Such a wide range is due to different spatial trends of organic and total lead regarding the three typical sampling sites chosen in this study (R, reference; H, harbor; GS, gasoline station). From Figure 2, it can be seen that the highest concentrations of organic lead are found in samples collected in front of gasoline stations, whereas the highest concentrations of total lead are found in mussels from the harbor areas. Sometimes the total lead in mussels from gas stations is not much higher than that from the reference areas. This results in a very low alkyllead percentage in mussels from harbors and a relatively high percentage in mussels sampled near gasoline stations. Such results indicate a difference in the origins of total and organic lead in mussels. In the harbor, in addition to the lead coming from leaded gasoline, inorganic lead comes from waste waters and other sources, and the concentration of total lead is not connected with local pollution coming from leaded gasoline. The same conclusion was reached from a study of alkyllead burden in marine snails (12), where the fraction of alkyllead decreased with decreasing apparent pollution stress of the sites, but the total lead burden did not appear to be related

TABLE 2

Concentrations of Alkyllead and Total Lead in Edible Parts of the Mussels *Mytilus galloprovincialis* from the Eastern Adriatic Coast

collection site, date ^a	mussel length (cm)	concentration (ng of Pb/g of wet wt)						%Pb _{org}
		Et ₄ Pb	Et ₃ Pb ⁺	Et ₂ Pb ²⁺	Me ₄ Pb	Me ₃ Pb ⁺	Pb _{tot}	
Šibenik/February 1992								
R1	4–5	<0.2	0.8	<0.1	<0.5	0.6	340	0.41
R2	5–6	<0.2	0.4	<0.1	<0.5	0.6	590	0.17
H1	3–4	1.3	3.0	2.5	<0.5	0.5	640	1.14
H1a	3–4	1.3	1.3	<0.1	<0.5	0.9	920	0.38
H2	3–4	3.5	4.8	2.7	<0.5	1.0	690	1.74
GS	3–4	3.0	16.6	9.2	<0.5	15.2	800	5.50
September 1993								
R2	4–5	<0.2	<0.1	<0.1	<0.5	<0.1	504	
H1/I	5	<0.2	1.1	<0.1	<0.5	0.3	690	0.20
H1/II	4	<0.2	1.0	<0.1	<0.5	0.3	650	0.20
H2/I	5–6	<0.2	0.7	<0.1	<0.5	0.1	770	0.10
H2/II	3–4	<0.2	0.6	<0.1	<0.5	0.3	930	0.10
GS/I	5–6	<0.2	0.4	<0.1	<0.5	0.2	760	0.08
GS/II	3–4	<0.2	0.3	<0.1	<0.5	0.2	590	0.08
April 1994								
R2	4–6	<0.2	<0.1	<0.1	<0.5	0.1	520	0.02
H1/I	5–6	0.2	0.5	0.3	<0.5	0.6	420	0.38
H1/II	3–4	0.3	0.1	0.1	<0.5	0.5	460	0.22
H2/I	5–6	0.4	1.2	0.3	<0.5	0.5	940	0.26
H2/II	4–5	0.5	1.2	0.3	<0.5	0.5	750	0.33
GS/I	5–6	1.2	0.8	0.1	<0.5	0.4	560	0.45
GS/II	4–5	<0.2	0.7	0.1	<0.5	0.4	360	0.33
June 1994								
GS/I	5–6	<0.2	0.7	0.3	<0.5	0.3	530	0.25
GS/II	4–5	0.4	0.1	<0.1	<0.5	0.2	590	0.12
split/April 1994								
GS/I	4–5	2.0	2.4	1.0	<0.5	0.6	1850	0.32
GS/II	3–4	2.0	1.6	0.3	<0.5	0.3	1200	0.35
Zadar/April 1994								
R/I	4–5	<0.2	<0.1	<0.1	<0.5	0.4	490	0.10
R/II	3–4	<0.2	<0.1	<0.1	<0.5	0.3	516	0.06
H/I	4–5	<0.2	0.6	0.3	<0.5	0.6	3200	0.05
H/II	3–4	0.6	0.6	0.3	<0.5	0.7	3330	0.07
GS1/I	4–5	0.7	0.6	0.5	<0.5	0.5	1270	0.18
GS1/II	3–4	0.7	0.6	0.5	<0.5	0.8	1180	0.22
GS2/I	6–7	<0.2	<0.1	0.5	<0.5	0.5	1340	0.07
GS2/II	5–6	<0.2	<0.1	0.5	<0.5	0.5	2260	0.04
Rijeka/April 1994								
H/I	5–7	<0.2	<0.1	<0.1	<0.5	0.3	3500	0.01
H/II	3–4	<0.2	<0.1	<0.1	<0.5	0.3	2600	0.01
Rovinj/May 1994								
H/I	4–5	<0.2	<0.1	<0.1	<0.5	0.2	7390	0.01
H/II	3–4	<0.2	<0.1	<0.1	<0.5	0.2	6270	0.01
GS/I	4–5	20.0	4.2	1.0	0.7	0.3	820	3.19
GS/II	3–4	42.6	4.2	4.1	1.0	0.6	800	6.56
summarizing statistics								
mean		2.1	1.3	0.8	0.04	0.8	1369	0.64
SD		7.5	2.8	1.8	0.2	2.4	1553	1.44
X _G		0.5	0.5	0.2	0.5	0.4	953	0.15
σ _G		3.8	3.9	3.4	1.1	2.3	2	5.8
median		<0.2	0.6	0.1	<0.5	0.5	760	0.2

^a R, reference station; H, harbor; GS, gasoline station. Values <DL were calculated as 0 for the arithmetic mean and DL value for the geometric mean.

to the anticipated pollution stress. The percentage of organic lead in mussels is comparable with that obtained in snails (12) and freshwater fish (14), but is significantly higher than that in marine fish (15), in which only tetraalkyllead compounds were detected.

Relationships between different lead species can indicate the origins of these species. Correlation coefficients for different analytes in mussels, in water, and between mussels and water are given in Table 3. To determine an influence of sampling site and time, samples were divided into three groups: all samples (A), all samples in the Šibenik area (B), which excludes the influence of site, and all samples from

the year 1994 (C), which excludes the influence of time. The absence of a correlation between organic and total lead in all groups supports the conclusion of a different origin for these lead compounds. Correlations between individual ethyl species and between each of them and total organic lead are highly significant for groups B and C, indicating a common origin of these species. The lack of correlation when all samples are taken shows that time and site influence the level of ethylleads in mussels. Correlations of trimethyllead with different ethyl species and the total organic lead in groups B and C are much weaker and quite variable. This means that a separate

TABLE 3

Correlation Coefficients between Different Alkyllead Species, Organic and Total Lead in Analyzed Samples

		Et ₃ Pb ⁺	Et ₂ Pb ²⁺	Me ₃ Pb ⁺	Pb _{org}	Pb _{tot}	CORRELATION IN MUSSELS
Et ₄ Pb	A	0.200(17)	0.300(15)	-0.045(17)	0.798(17)	-0.106(17)	
	B	0.738(10)	0.739(8)	0.571(10)	0.728(10)	0.286(10)	
	C	0.846(13)	0.944(12)	0.007(13)	0.999(13)	0.138(13)	
Et ₃ Pb ⁺	A	-0.500(6)	0.962(18)	0.923(28)	0.773(28)	-0.052(28)	
	B	-0.684(4)	0.992(10)	0.965(20)	0.998(20)	0.242(20)	
	C	0.911(5)	0.770(15)	-0.074(19)	0.875(16)	0.055(16)	
Et ₂ Pb ²⁺	A	0.011(4)	-0.479(4)	0.880(20)	0.819(20)	-0.546(20)	
	B		1.000(2)	0.182(17)	0.991(10)	0.420(10)	
	C		-0.479(4)	0.945(10)	0.944(17)	-0.067(17)	
Me ₃ Pb ⁺	A	-0.503(6)	-0.808(4)	0.942(8)	0.587(37)	-0.077(37)	
	B			0.984(5)	0.970(21)	0.209(21)	
	C			0.592(7)	0.188(25)	0.202(25)	
Pb _{org}	A	0.555(6)	0.341(4)	0.435(8)	-0.055(8)	-0.143(37)	
	B				0.309(5)	0.243(21)	
	C				-0.434(7)	0.152(25)	
Pb _{tot}	A	0.711 (6)	-0.554(4)	0.113(8)	0.344(8)	0.126(16)	
	B					0.064(10)	
	C					0.060(11)	
CORRELATION IN SEAWATER							Correlation mussel/water

^a Number of samples is given in parentheses. A, 1992–1994; B, Šil/1992–1994; C, 1994.

source of methyllead, other than directly from the demethylation of Me₄Pb gasoline additive, may exist. It could be, as was suggested in the study on the alkyllead distribution in marine snails (12), due to environmental methylation. Such a conclusion is also supported by the more constant trimethyllead level in mussels, as well as by their appearance at all reference sites. The evidence for environmental methylation of lead is currently weak; if the process occurs, it is of low efficiency (4). Differing breakdown rates for methyl- and ethyllead compounds may also be important.

Apart from the different trends of total and organic lead between R, H, and GS (Figure 2), few other statements can be made about the distribution of individual alkyllead species at these typical sites. At the reference stations, with the exception of February 1992 in Šibenik, when ethyllead

species were also detected, mussels contained only trimethyllead. In harbor areas, both ethyl and methyl species were present. For mussels living in front of gasoline stations, occasional occurrences of very high (compared with other locations) concentrations of alkylleads, especially tetraethyllead, were characteristic. The measured concentrations of tetraethyllead are the highest ever obtained in marine organisms from areas polluted by the use of leaded gasoline (Table 4). The only study dealing with organisms on the lower food chain level (12) showed that concentrations of IAL compounds for marine snail and mussels are comparable, but unfortunately, there are no data on the tetraalkyllead levels in the snails. Measurements in different freshwater organisms from rivers polluted with tetraethyllead from manufacturing operations (21) proved that fish efficiently accumulate both tetra- and triethylleads. In fish

TABLE 4

Literature Data on Organic and Total Lead Concentrations in Aquatic Organisms from Areas Polluted by the Use of Leaded Gasoline

species	lead compd	concn range (ng of Pb/ g of wet wt)	Pb _{org} (%)	ref
marine snail	R ₃ Pb ⁺	1.0–12.4	0.04–0.95	12
	R ₂ Pb ²⁺	<0.2–8.5		
	Pb _{tot}	1290–4140		
marine fish	Me ₃ Pb ⁺	0.8–1.6	1.6–16.6	13
freshwater fish	Me ₃ Pb ⁺	<0.08–2.1		14
	Et ₃ Pb ⁺	<0.08–1.1		
	Et ₄ Pb	<0.1–1.3		
	Pb _{tot}	<1.8–96.7		
marine and freshwater fish	R ₄ Pb	0.06–1.3	0.005–0.01	15
	Pb _{tot}	0.3–4.1		

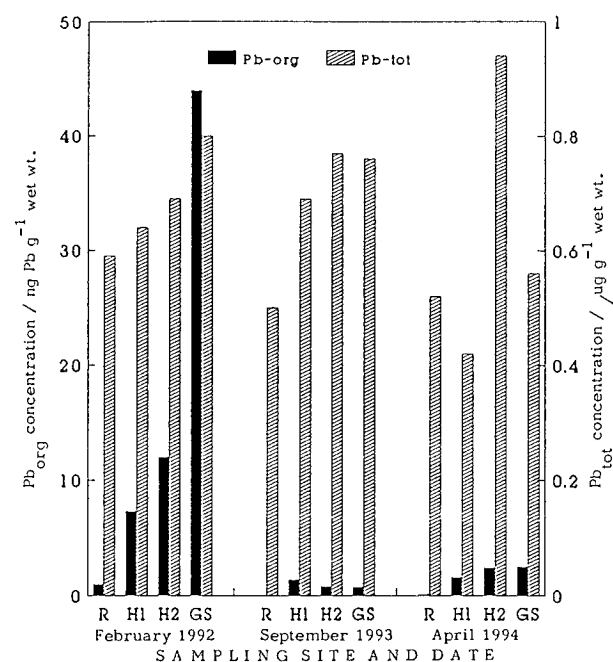


FIGURE 3. Temporal trend of organic and total lead concentrations in mussels from the Šibenik area.

from freshwater and coastal areas polluted by the use of leaded gasoline, TAL levels have never exceeded a few nanograms/gram (13–15). Laboratory experiments had shown (28) that the accumulation of tetraalkylleads into *Mytilus galloprovincialis* mussels was about 10 times more efficient than that for trialkyl species. Therefore, the presence of some high tetraethyllead levels in mussels is not surprising.

It seems that mussels living in front of gasoline stations do not contain a permanently increased level of organic lead. The temporal trend obtained in mussels from the Šibenik area (Figure 3) indicates such a conclusion. From four samplings, only once (in February 1992) were relatively high concentrations observed. First we suspected that it was a consequence of different gasoline consumption, but this was not the case, as gasoline consumption was similar in all of the sampling periods (ranging from 94×10^3 to 119×10^3 L of the high-octane gasoline, which contains 0.6 g of Pb/L as TAL, and from 16×10^3 to 22×10^3 L for low-octane gasoline containing about 0.4 g of Pb/L as TAL; from both of them about one-third is used for boat traffic). High concentrations may be a consequence of the occasional

spillage of gasoline, from which tetraalkylleads obviously are readily accumulated into these sedentary, filter-feeding organisms. However, as tetraalkyllead is not permanently present in mussels, it also must be efficiently eliminated from them. It was reported by Maddock et al. (28) that the half-life of trialkyllead in mussels is very short (3 days), compared with that for inorganic lead (30–300 days). From Figure 3 it is clear that, whereas the content of organic lead is changing considerably, the total lead concentration is fairly constant, confirming our earlier conclusion on the different origins of organic and total lead in mussels.

To determine whether the concentration of alkyllead compounds is influenced by mussel age, we divided samples into two groups according to their length (Table 2). Concentrations of different analytes (including the total lead) were compared in 15 pairs of samples. For different IAL compounds and total lead, it was found that bigger mussels mostly had comparable (in 36–56% of pairs) or higher (in 33–64% of pairs) levels than smaller ones, i.e., in 80–100% of pairs the concentration was equal in both groups or higher in bigger mussels. Only for tetraethyllead in 56% of pairs was the concentration higher in smaller mussels. Mussels in the investigated areas do not necessarily accumulate organic and inorganic lead with age. For *Mytilus edulis* species, the relationship between lead concentration and mussel size/age was found to be negative (29), not discernible (30), or complicated, e.g., dependent on the sexual maturity of mussels (31). Generally, it is accepted that a size effect does not influence the total lead concentration in mussels to a great extent (31), which also appears to be the case for organic lead.

Distribution in Water. Concentrations of alkylleads and total lead in seawater are presented in Table 5. Only half of the samples contained measurable alkyllead compounds. The most frequent species were trimethyllead (in 53% of samples) and triethyllead (in 40% of samples), followed by diethyllead (in 27% of samples). Neither dimethyllead nor mixed methylethyl species were found in seawater. The detection limit for the extraction of 2.5 L of seawater is 0.5 ng L⁻¹. The absence of mixed ethylmethyl derivatives is not surprising as no mixed alkyls are used locally in gasoline, and transmethylation reactions are unlikely at the low concentrations in seawater. The absence of dimethyllead may reflect the greater stability of trimethyllead or its breakdown directly to inorganic lead, as some workers have failed to identify dimethyllead among its breakdown products. Statistical evaluation (Table 5) shows that ethyl species are more abundant than methyl, that trialkylleads are the dominant species, and that relative concentrations of Et₃Pb⁺, Me₃Pb⁺, and Et₂Pb²⁺ roughly correspond to 1:1:1. The percentage of organic lead varies between 0.09 and 2.63%. At the reference stations, organic lead is not measureable in the water. There is no consistent difference between H and GS sites of the kind that exists for mussels, and concentrations in harbors are sometimes higher than in front of gasoline stations. Data are comparable with those obtained in the seawater of the Šibenik area in the period 1987–1988 (32, 33). Although the maximal concentrations of trialkyllead found in front of GS in Šibenik during 1987–1988 are higher (up to 12.5 ng/L) than the maximal concentrations obtained in 1992–1994 (Table 5), the average concentrations are similar. This might be expected, as the level of organolead compounds in gasoline has not changed since 1987. The absence of a correlation between different analytes in water (calculated only for the

TABLE 5

Concentrations of Ionic Alkyllead and Total Lead in Seawater from Locations Where Mussels Were Collected

sampling site and date ^a	concentration (ng of Pb/L)					%Pb _{org}
	Et ₃ Pb ⁺	Et ₂ Pb ²⁺	Me ₃ Pb ⁺	R ₃ Pb ⁺	Pb _{tot}	
Šibenik/February 1992						
H2				2*	207	0.97
GS	0.6	<0.5	3.1		307	1.21
September 1993						
H1	<0.5	<0.5	<0.5		165	
H2	<0.5	<0.5	<0.5		385	
GS	<0.5	<0.5	<0.5		119	
April 1994						
R2	<0.5	<0.5	<0.5		193	
H1	1.2	<0.5	0.6		132	1.36
H2	1.9	2.0	0.6		171	2.63
GS	1.0	1.8	1.0		160	2.38
June 1994						
GS	<0.5	<0.5	0.5		414	0.10
Split/April 1994						
GS	2.3	1.2	1.3		5200	0.09
Zadar/April 1994						
H	1.1	1.0	1.1		964	0.33
GS				<0.5*	664	
Rijeka/April 1994						
H	<0.5	<0.5	<0.5		490	
Rovinj/May 1994						
H	<0.5	<0.5	<0.5		413	
GS	<0.5	<0.5	0.5		230	0.17
summarizing statistics						
mean	0.5	0.4	0.6		1518	1.03
SD	0.8	0.7	0.8		1724	0.97
X _G	0.7	0.7	0.7		1045	0.56
σ _G	1.7	1.7	1.7		2	3.8
median	<0.5	<0.5	0.5		790	0.97

^a R, reference station; H, harbor; GS, gasoline station. Values <DL were calculated as 0 for the arithmetic mean and DL value for the geometric mean. *, measured by DPASV.

full data set, Table 3) most probably is the consequence of too few samples with concentrations above the detection limit.

Accumulation from Water into Mussels. Accumulation of lead compounds from water into mussels can be expressed by bioconcentration factors (BF). They are calculated for individual alkyllead species and for total organic lead and total lead (Table 6). The values are much more variable for ethyllead species than for trimethyllead and total lead. Mean values (calculated as geometric means) for Et₃Pb⁺, Me₃Pb⁺, and Et₂Pb²⁺ roughly correspond to 2:1.5:1. Although individual BF values can be up to 40 times higher for organic than for inorganic lead, on average for individual ionic alkylleads, they are significantly lower than for total lead, but are comparable for total organic lead and total lead (BF_{IAL} < BF_{Pborg} ≈ BF_{Pbtot}). This suggests that organic lead is accumulated into mussels at a comparable or even a lesser extent than is inorganic lead. No other data have been found on the accumulation of organolead compounds in mussels in their natural habitat that can be contrasted with the present study. In the laboratory experiment reported by Maddock (28) on the same mussel species, much lower BF factors were obtained (8–24 for TriAL, 120–170 for TAL), which were the consequence of a much higher concentration in water and a very short accumulation period (96 h). These data are not directly comparable with ours, but a general conclusion made from this experiment, that the accumulation of inorganic lead is more pronounced than that for trialkyllead, fits well with our results. Our BF values are in the same range as values obtained for other aquatic organisms in the

natural environment [TAL + IAL, 1000–35000 for freshwater fish, 3300 for freshwater mussels (21); TAL, 250–3500 for marine fish (15)]. The total lead BF values can be compared with data obtained a few years earlier in the Šibenik area on transplanted mussels (34). They varied between 5000 (in the locations situated near R sites, where BF values are comparable with our data) and 50 000 (in the coastal zone), e.g., they increased in going from a more to a less polluted environment. Such a pattern is not evident in our samples for any of the lead compounds, because BF values are calculated only for mussels from the relatively polluted environment (because of the inadequacy of data for the reference stations).

Correlation of analytes between mussels and water is consistently positive only for trimethyllead and is mostly negative for other species (Table 3). The reason for the absence of consistent correlation for ethyl species could be that the level of tri- and dialkylleads in mussels is more dependent on the in vivo transformation of tetraethyllead than on the direct uptake of these species from water. Laboratory experiments in freshwater mussels have shown that in vivo transformation is much more pronounced for ethyl than for methyl species (23).

It is interesting to look at how the ratio of ethyl and methyl species changes in going from gasoline to water and mussels. The antiknock additive used locally in gasoline is a Motor Mix consisting of PM50-CB, i.e., a physical mixture of 50:50 TEL/TML is used exclusively (information from manufacturer), and all gasoline stations investigated are supplied by the same manufacturer. The ratio of TML:TEL of 1.0 in gasoline is not preserved in water and mussels,

TABLE 6

Bioconcentration Factors (BF) between Mussels and Seawater for Lead Compounds

collection site and date ^a	BF (ng of Pb kg ⁻¹ of wet wt/ng of Pb L ⁻¹)				
	Et ₃ Pb ⁺	Et ₂ Pb ²⁺	Me ₃ Pb ⁺	Pb _{org}	Pb _{tot}
Šibenik/February 1992					
H2				6000	3333
GS	27667	> 18400	4903	11892	2606
April 1994					
H1/I	416	> 600	1000	888	3182
H1/II	83	> 200	833	555	3485
H2/I	632	150	833	533	5497
H2/II	632	150	833	555	4385
GS/I	800	56	400	658	3500
GS/II	700	56	400	316	2250
June 1994					
GS/I	> 1400	> 600	600	2600	1280
GS/II	> 200		400	1400	1425
split/April 1994					
GS/I	1043	833	462	1250	356
GS/II	686	250	231	875	231
Zadar/April 1994					
H/I	545	300	545	469	3320
H/II	545	300	636	688	3454
Rovinj					
GS/I	> 8400	> 2000	600	52400	3565
GS/II	> 8400	> 8200	1200	105000	3478
summarizing statistics					
mean	3477	2293	925	11630	2834
SD	7288	5099	1130	28045	1415
X _G	994	474	677	1826	2236
σ _G	4.5	5.4	2.0	5.7	2.4
median	696	300	600	875	3320

^a R, reference station; H, harbor; GS, gasoline station. Limiting values (>) were used for calculating both arithmetic and geometric means.

as in both media the concentrations of ethyl species are relatively increased. In water this ratio ranges from 0.2 to 6.5 (on average it is about 2). Only in sample SI/GS/1992 is the ratio less than 1, which probably does not reflect the real situation as, unlike other samples, this sample was analyzed 2 years after collection. Hence, it is highly possible that a considerable portion of tri- and diethylleads is decomposed to inorganic lead, as it is known (35) that, even in the dark, ethyl species are much more sensitive toward degradation than are methyl species (trimethyllead was found to be stable for at least 1 year). In mussels this ratio varies from <1 to 85 (on average it is about 3). Thus, it again increases on going from water to mussels. This is difficult to explain, given that ethyllead is less stable under environmental conditions. A predominance of TML over TEL in air (35) and rainwater (6) may be explained by the about 100 times higher vapor pressure of TML over TEL, which contributes an enrichment of methyl species in the atmosphere. Conversely, the evaporation of TML should cause an enrichment of ethyl species in surface waters, here in seawater. There are data for organolead levels in rainwater from the Šibenik area (37), but unfortunately an electrochemical method, capable only of discriminating between tri- and dialkylleads, was used, so that the ratio of methyl:ethyl species, which could confirm an enrichment of methyllead in rainwater, cannot be seen from these data. The absence of TML from mussels, in contrast to TEL, supports the hypothesis that TML is lost to the atmosphere. Why this ratio is even larger in mussels is difficult to explain as the long-term accumulation pattern of organoleads into mussels in their natural habitat was not studied. Short-term accumulation from water into shellfish is slightly higher for methyl than for ethyl species (23, 28). The explanation could lie in different water solubilities of TEL

(<0.1 mg/L), and TML (15 mg/l) which can cause different distributions between dissolved and particulate phases in seawater. Insoluble TEL could be more readily adsorbed by organic marine particles and, thus, more efficiently transported to mussels, who are particulate suspension feeders. Indeed, a higher affinity of ethyl derivatives for suspended particles is found in lake water, where an enrichment of triethyl- over trimethyllead in sediment compared to the aqueous phase was observed (9).

It is interesting to look more generally at the ratio of methyl to ethyl species in environmental samples. In various natural samples, a predominance of ethyl derivatives has been found [Greenland snow (38, 39); rainwater from the United Kingdom (27); lake sediment (9); grass (40); marine organisms (12, this work)]. However, in some other samples methyllead was dominant [air (36); rainwater from Belgium (7); runoff (41); wine (42, 43)]. Regarding this ratio, a clear difference between various compartments (atmospheric and terrestrial or aquatic) cannot be seen. It seems that this ratio cannot be generalized and that it is a result of the complex action of great number of factors. For example, the variations in the ethyl:methyl ratio in Greenland snow (38, 39) is interpreted in terms of backward air mass trajectories, whereas a dominance of methyllead in wine is explained by the promoted decomposition of ethyllead during fermentation (43). The following factors should be taken into account when interpreting a measured ethyl:methyl ratio: (1) source (TEL:TML ratio in gasoline) and pathway of emission [gasoline or exhaust gases, as already in the engine a rearrangement of TML and TEL occurs (44)]; (2) mode of transport (distance and transport media: gas, aerosol, and water, as different distributions of ethyl and methyl species between aerosol/gaseous or solid/aqueous phases occur); and (3) additional, specific

transformations (for example, decomposition during wine fermentation or in vivo transformations in living organisms).

Although, due to the irregular use of lead additives in gasoline, data on the ethyl:methyl ratio in different areas and matrices cannot be easily compared, it is obvious that they could not be simply connected with the relative stability of these species (derived from laboratory experiments), from which a dominance of more stable methyllead compounds could be assumed. Obviously, there are still gaps in our understanding of the environmental cycling of organic lead, in particular differences in the distribution of methyl and ethyl species.

Conclusions

It is clear that, in the part of the eastern Adriatic adjacent to urban areas from which samples were collected, pollution by alkyllead is very widespread. This is not surprising given the continued use of leaded gasoline in the area and the presence of gasoline stations adjacent to the coast. Typically, about 0.5% of the total lead in *Mytilus galloprovincialis* was in the form of alkyllead. Trialkyllead compounds are predominant, and in general, there is more ethyllead than methyllead present in the mussels. Concentrations of trimethyllead appear to be less variable than those of ethylleads, which could be a function of biomethylation or other factors. Correlations between concentrations of the alkyllead species in mussels and seawater show that trimethyllead is the only species for which consistently high correlations are observed. Mussels thus may provide a suitable bioindicator for pollution by this one alkyllead species. Organic lead and inorganic lead are not significantly correlated in seawater, mussels, or between the two, and it is thought that sources of inorganic lead other than gasoline likely are contributing to pollution locally.

Concentrations of organolead species measured in *Mytilus galloprovincialis* mussels are broadly consistent with literature data for fish and shellfish collected from other polluted locations. Bioconcentration factors between mussels and seawater have been estimated for the different forms of lead. Geometric mean values are slightly higher for inorganic lead than for organic lead, although considerable variability is seen.

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