

# DISTRIBUTION OF ORGANOLEAD COMPOUNDS IN THE ADRIATIC COASTAL MARINE ENVIRONMENT

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## Abstract

The distribution of alkyllead compounds, originating from leaded gasoline, between different marine compartments was studied. The following concentration ranges of organic lead in samples collected in the eastern Adriatic coast during period 1994-1995 were obtained: water 7-7.8 ng/l, mussels 1-3.9 ng/g, fish 0.2-2.7 ng/g and sediment 0.04-0.42 ng/g. The percentage of organic lead was found to decrease going from water (2.7-16%) to mussels (0.3-1%), fish (0.4-1.6%) and sediments (0.0006-0.001%). Evidently, organolead compounds are not accumulated in sediment, but they could be accumulated from water into living organisms. Biomagnification in the marine food chain most probably does not take place. This study confirms the limited extent of organolead pollution in the Adriatic marine environment.

**Key-words:** lead, mollusca, Adriatic sea

## Introduction

Organolead compounds are introduced into the environment by their use as an antiknock additive in gasoline. It is estimated that about 1% of lead in gasoline is emitted from vehicles in the form of tetra- and ionic alkyllead compounds (TAL and IAL). The presence of alkyllead compounds has been established in different kinds of environmental samples, mostly abiotic compartments such as air and rainwater, in which organolead compounds exist in appreciable concentrations (1). The fate of organolead compounds in aquatic organisms and especially in the marine environment is still not well known, although there is evidence that alkyllead is appreciably more toxic than inorganic lead. Our previous study has shown that alkyllead compounds are readily accumulated in sedentary organisms such as the mussel *Mytilus galloprovincialis* (2) which has been widely used as an indicator organism for heavy metal pollution in the marine environment. The aim of this work was to establish the distribution of alkyllead compounds introduced into the Adriatic marine environment from local sources (coastal gasoline stations and navigation) between different marine compartments, and to study in more detail the uptake of these compounds in the mussel *Mytilus galloprovincialis*.

## Methods

Samples of subsurface seawater, surface microlayer, sediment, various fish species and the mussel *Mytilus galloprovincialis* were collected in July 1995 from the Sibenik area in the central part of the eastern Adriatic coast. Mussels and water samples were also collected in front of gasoline stations in the towns of Split (July 1995) and Rovinj (October 1994 and September 1995). Organolead compounds were extracted from water, sediment and biota (after tissue digestion by tetramethylammonium hydroxide) into hexane (TAL directly, IAL after complexation with carbamate), evaporated to smaller volume, cleaned by passing through a silica column and after propylation analysed by GC AAS (gas chromatography/atomic absorption spectrometry). Total lead was measured by DPASV (differential pulse anodic stripping voltammetry) after UV irradiation of unfiltered water samples or acid digestion in the case of sediments and organisms. Analytical methods are described in more detail elsewhere (3,4).

## Results and discussion

**Distribution between different compartments.** Previous studies of the organolead distribution in the marine environment of the Adriatic sea have shown that gasoline stations represent a continuous source of organolead compounds as demonstrated by both contamination of seawater (4,5,6) and mussels (2). In July 1995 in addition to seawater and mussels, samples of microlayer, sediment and fish were also collected from Sibenik Bay, in order to see how organolead contamination is reflected in other marine compartments (Table 1).

Table 1. Concentration ranges of organolead compounds and total lead in different marine compartments of Sibenik Bay in July 1995.

Sample type (number of data analyzed)	Concentration range (ng/l for water or ng/g w.w. for solid samples)					
	Et <sub>4</sub> Pb	Et <sub>3</sub> Pb <sup>+</sup>	Me <sub>3</sub> Pb <sup>+</sup>	Pb <sub>org</sub>	Pb <sub>tot</sub>	%Pb <sub>org</sub>
Water (20)	<0.5-1.1	1.0-2.9	2.0-4.9	4-7.8	132-220	2.7-4.3
Microlayer (5)	<1.0	<0.5-3.3	2.9-8.4	8.5-11.7	2700-3400	0.3-0.4
Sediment (5)	<0.2	<0.02-0.3	0.04-0.12	0.04-0.42	6800-44800	0.0006-0.001
Mussels (20)	<0.2-1.5	<0.2-1.4	1.0-1.2	1.0-3.9	210-530	0.3-1.0
Fish-muscle (10)*	<0.2-1.0	<0.2-1.3	0.2-0.5	0.2-2.7	20-112	0.4-1.6
Fish-intestine (5)	<0.2-1.2	<0.2-1.4	0.3-0.5	0.4-2.9	144-3400	0.04-0.1

\* Species of fish are given in Fig 2.

A decrease of organolead concentration and percentage going from water to sediments (Table 1) indicates insignificant settling of organic lead into sediments. However, few times higher concentrations of ethyllead derivatives were observed in the immediate vicinity of the pollution source (gasoline station-GS, Fig. 1) in comparison with a 200 m distant location (center of the Bay-C, Fig. 1). The concentration of trimethyllead was lower and comparable at these two locations (Fig. 1). A low organolead percentage in sediment could be a consequence of decomposition (photolysis) of alkyllead compounds in the photic layer of the water column (1,7) or their elimination by accumulation into biota (1,2). Contrary to the organic lead, the distribution of total (inorganic) lead demonstrates that sediment represents a sink for inorganic lead (Table 1), an observation that is in agreement with a much higher affinity of inorganic lead for particulate matter than the organic form (5,8). The extent of such pollution is also limited, since the concentration of the total lead is an order of magnitude higher in front of the gasoline station (30-45 μg/g) than in the centre of the bay (6-8 μg/g).

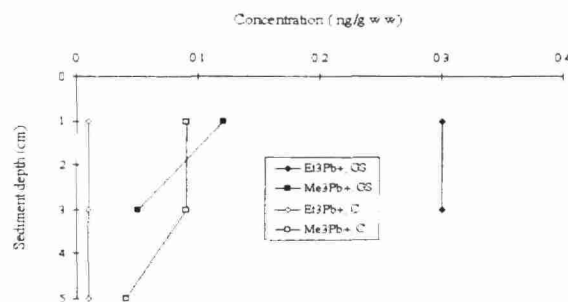


Fig. 1. Alkyllead compounds (triethyllead-Et<sub>3</sub>Pb<sup>+</sup>; trimethyllead-Me<sub>3</sub>Pb<sup>+</sup>) in sediments of Sibenik Bay (GS = gasoline station; C = center of the bay) in July 1995.

The concentration of lead species in mussels obtained in July 1995 are comparable with the levels obtained earlier in the same area (2). The previous study confirmed that such organisms could serve as a good indicator of the environmental organolead level (2). A similar organolead concentration is obtained in fish samples (Table 1), indicating that these compounds are not biomagnified in the marine food chain. Bioconcentration factors (BF) for organic lead are of the same order of magnitude for mussels (about 200-500) as fish muscle (50-300). A difference in the internal distribution of organic and the total lead in fish is evident, as organic lead is more equally distributed in the whole organism (Fig. 2), compared to the total lead which is accumulated primarily in the intestine (Table 1). The concentration of trimethyllead is less variable than those of ethyllead derivatives (Fig 2), similar to that found for the mussel *Mytilus galloprovincialis* from the eastern Adriatic (2). This seems to be a general trend in biological samples and could be related to either higher stability of methyl derivatives or their formation by biomethylation.

**Uptake into mussels.** In order to learn more about the uptake of organolead compounds into mussels, the tissue distribution of these compounds was determined in samples containing different organolead levels (Figs. 3 and 4). Samples collected from Sibenik and Split (SI/GS, ST/GS, Figs. 3a and 4 a,b) were within the concentration range of 0.1-10 ng/g, established as a common organolead level in mussels polluted by leaded gasoline (2). Samples collected from