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File Report

LEVELS OF ORGANOTIN IN WATER, SEDIMENTS AND OYSTERS (*CRASSOSTREA GIGAS*) FROM NANOOSE BAY, B.C.

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ABSTRACT

Following observations of growth abnormalties in oysters, *Crassotrea gigas*, from Nanoose Bay, samples of sediments, water and oyster tissue were analysed for organotins. Highest concentrations of tributyltin (TBT) in both sediments and water were measured at a salmon farm, and highest concentration of TBT in oysters was measured at an oyster farm adjacent to the salmon farm. In March, 1987, Environment Canada and Agriculture Canada advised the aquaculture industry that TBT is not permitted for use as a marine growth retardant on net pens and the products are no longer available in retail outlets.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Tributlyltin- (TBT) based antifoulants are widely used in Canada to treat ship hulls at maintenance facilities, where levels in the several parts per million range (ppm) are found in marine sediments (McGuire et al., 1985). A more recent use has been the application of TBT-based marine growth retardants to pen nets at salmon farms. The number of salmon farm licences issued for B.C. marine waters rose from none in 1983 to 15 in 1984, 30 in 1985, 91 in 1986 and 108 in 1987. The B.C. Salmon Farmers' Association listed 78 operational farms in the province in late 1987. Many used TBT-based growth retardants. Some of these new farms are located near previously existing oyster (Crassostrea gigas) farms, and indeed a few included co-location of oyster farms on the same foreshore lease.

One such salmon farm was licenced in May, 1985, in Nanoose Bay, where two oyster farms already existed. Almost immediately upon installation of the treated net pens, growth abnormalities were noticed at an adjacent oyster farm; within a year, similar effects were seen at the other oyster farm 3 km away (P. McLellan and A. Vieaux, pers. comm.). Abnormalities included vacuolization of the shell, reducted growth, poor condition of the soft tissues, and mortality: classic symptoms of organotin poisoning (Alzieu 1986; Stephenson et al., 1986). Two and three year old, cultured oysters from the nearest oyster farm which were examined by the authors were 5.7 cm and 7.0 cm long, respectively, approximately 30% of the length of normal oysters of the same ages, and were heavily layered and chambered.
In March, 1987, based on these reports to Environment Canada, Agriculture Canada removed marine growth retardants containing TBT intended for net pen application from Vancouver-area retail outlets. Although TBT-based antifoulants were permitted for use on ship hulls, they were not registered for net pen application. The purpose of this study was to determine the levels of organotins in water, oysters and sediments near two potential sources in Nanoose Bay: a military ship wharf and a salmon farm where TBT-treated nets had been used.

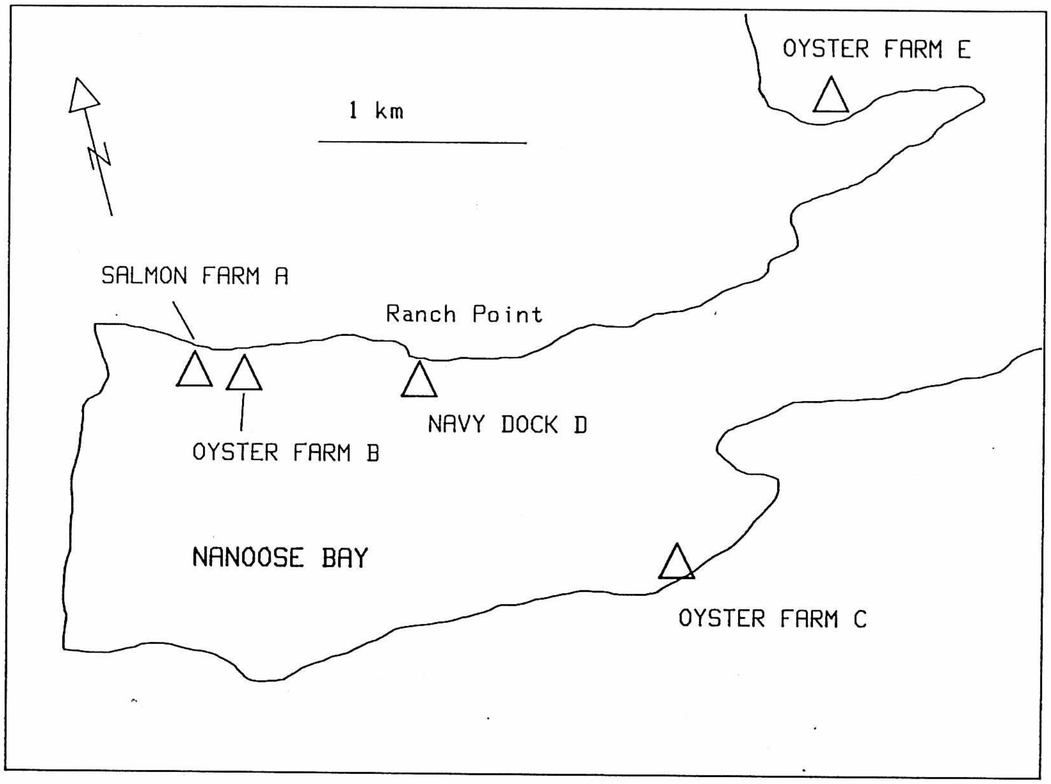

Fig. 1. Location of sampling stations in Nanoose Bay, B.C., February, 1987.

MATERIALS AND METHODS

Triplicates of water samples were collected in February, 1987 at Salmon Farm (A), Oyster Farm (B), Oyster Farm (C), Ranch Point Navy Dock (D) and a reference site, Oyster Farm (E) (Figure 1). Triplicate oyster samples were also taken at Oyster Farm (C). Oyster samples were provided by the growers and shucked into glass jars supplied by the laboratory. Each water sample consisted of a pair of 4 litres samples (8 litres total), and were collected by divers at 3 m depth with bottles supplied by the laboratory.

Replicate sediment samples were taken by SCUBA diver in an equilateral triangle of 10 m per side, using a stainless steel spoon, sampling the top two cm of sediment. This sediment was stored in glass jars provided by the laboratory.

Samples were analysed by Seakem Oceanography Ltd. Tissue samples were extracted by a method based closely on that of Chau et al (1984). Sediment, tissue and water samples were analyzed according to methods of Humphries and Hope (1987).

The samples were analysed using a Finnigan 9500/3200 gas chromatograph/mass spectrometer with a Finnigan 3100 interactive data system. Butyltin compounds present as the pentylderivatives were detected using the selected ion monitoring (SIM) mode, set to monitor three abundant and characteristic ions of the butylpentyltins (235+, 249+, and 305+ for tri- and dibutyltin; 249+, 263+, 319+ for monobutyltin). The characteristic ions of the internal standards dipropyltin (at 249+ and 305+), d 10anthracene (at 188+) and d 10pyrene (at 212+) were also monitored.

The GC/MS retention time and response of the pentyltin derivatives relative to the predeuterated internal standards were determined using a calibration standard containing the derivatized organotin compounds of interest. The mass chromatogram peak areas of the internal standards and the characteristic ions of the organotins were determined on the 6100 data system by manually controlled integration at the appropriate retention time window. The quantification is based on the ratio of the 135+, 249+ and 305+ ion peak areas to the 305+ ion peak area for monobutyltin. The deuterated internal standards were only used to confirm concentrations. In conjunction, retention times and relative ratios of the characteristic ions were used as a confirmation of the assignment of the compound. Tissue and sediment concentrations are calculated on a dry weight basis as ng/g tin. Water concentrations are calculated as ng/L tin.

Instrument calibration was replicated before and after sample analysis. Linearity of GC/MS response was confirmed over three orders of magnitute including the concentration range encountered in these samples. The identities of the derivatized organotins were confirmed by continuous scan GC/MS. Relative retention time of inferred organotin peaks was within $\pm 1\%$ of that expected from the authentic material standards. Relative intensity ratios of the characteristic ions of each compound was within 20% of the mean found for the authentic compound in the calibration standard. Detection limits are shown in Table 1 and results of spike sample analyses are shown in Table 2. Four procedural blanks were also analysed; results were negative for butyltins.

Table 1: Detection Limits (ng/L as Sn)

	Water	Sediment	Tissue
Tributyltin	0.1	.07	1.0
Dibutyltin	0.2	---	---
Monobutyltin	0.1	---	---

Table 2: Results of Spike Sample Anaysis

	TBT	DBT	BT
Tissue 1			
Spike	220	52	24
Recovery a	260	56	12
Std. Dev. (%)	6	9	18
Tissue 2			
Spike	840	200	95
Recovery b	750	185	53

a. triplicate analysis

b. duplicate analysis

RESULTS AND DISCUSSION

Table 3 gives results of water analyses for organotins in Nanoose Bay and the reference site (E, Figure 1) in Georgia Strait. Table 4 gives results of oyster tissue analyses and Table 5 gives results of sediment analyses.

Table 3. Results Of Triplicate Water Analyses For Tributyltin (TBT), Dibutyltin (DBT) And Monobutyltin (MBT) At A Salmon Farm And Naval Base In Nanoose Bay, And a Reference Site In Georgia Strait, British Columbia (ng/L as Sn).

Sample Site	TBT	DBT	MBT
Salmon Farm (A)	6.6	6.6	7.6
	4.7	4.7	3.6
	6.2	7.2	8.4
Mean	5.8	6.2	6.5
Naval Base (D)	3.7	1.2	<0.1
	5.7	2.0	1.1
	5.1	1.0	0.8
Mean	4.8	1.4	0.9
Reference Site (E)	1.6	1.0	2.8
	2.9	<0.2	4.1
	2.1	2.1	4.8
Mean	2.2	1.5	3.9

These results confirm the presence of organotins, and particularly tributyltin, in waters and sediments where oyster growth abnormalities were observed. The levels measured in the water were less than the levels previously considered safe: 20 ng/L by Great Britain (Abel et al 1986) and 50 ng/L in the U.S. (Henderson 1986). It is not known, however, what the concentrations in water were when the freshly treated salmon nets were installed in about May, 1985; they could have been much higher. The levels measured at the control site, far from either potential source of organotins, are surprising, and suggest very broad distribution by diffusive and advective processes (samples were taken within 1 h of a high slack tide).

The orginal, major source of organotins in Nanoose Bay was undoubtedly the treated nets at the salmon farm. At the time of sampling, however, organotins could have been leaching from either the treated nets, or sediments, or both. Organotins leaching from antifouling paints at the naval base are also a possible source; however, the levels measured there could have come from the salmon farm. Indeed, the levels of TBT measured at the Ranch Point dock (mean = 4.8 ng/L) fall nearly precisely on a straight-line interpolation between the salmon farm and the reference site (Figure 2). The much higher levels of TBT in sediments at the salmon farm (mean = 264 ng/L) than the Ranch Point dock (mean = 6.3 ng/g) lend further support to the hypothesis that the major source of organotins in Nanoose Bay was the treated nets and/or sediments at the salmon farm.

Table 4: Results of Triplicate Oyster Tissue Analyses for Tributyltin (TBT) in Nanoose Bay, British Columbia (ng/g AS Sn)

Sample Site	TBT
Oyster Farm (C)	14
	26
	16
Mean	19
Oyster Farm (B) (Mar'87)	400
	750
	320
Mean	490
Reference Site (E)	<0.4
	<0.4
	60
Mean	---

Table 5: Results of Triplicate Sediment for Tributyltin (TBT) in Nanoose Bay, British Columbia (ng/g as Sn).

Sample Site	TBT
Salmon Farm (A)	550
	131
	111
Mean	264
Naval Base (D)	8.2
	1.6
	9.0
Mean	6.3
Reference Site (E)	<0.7
	<0.7
	<0.7
Mean	---

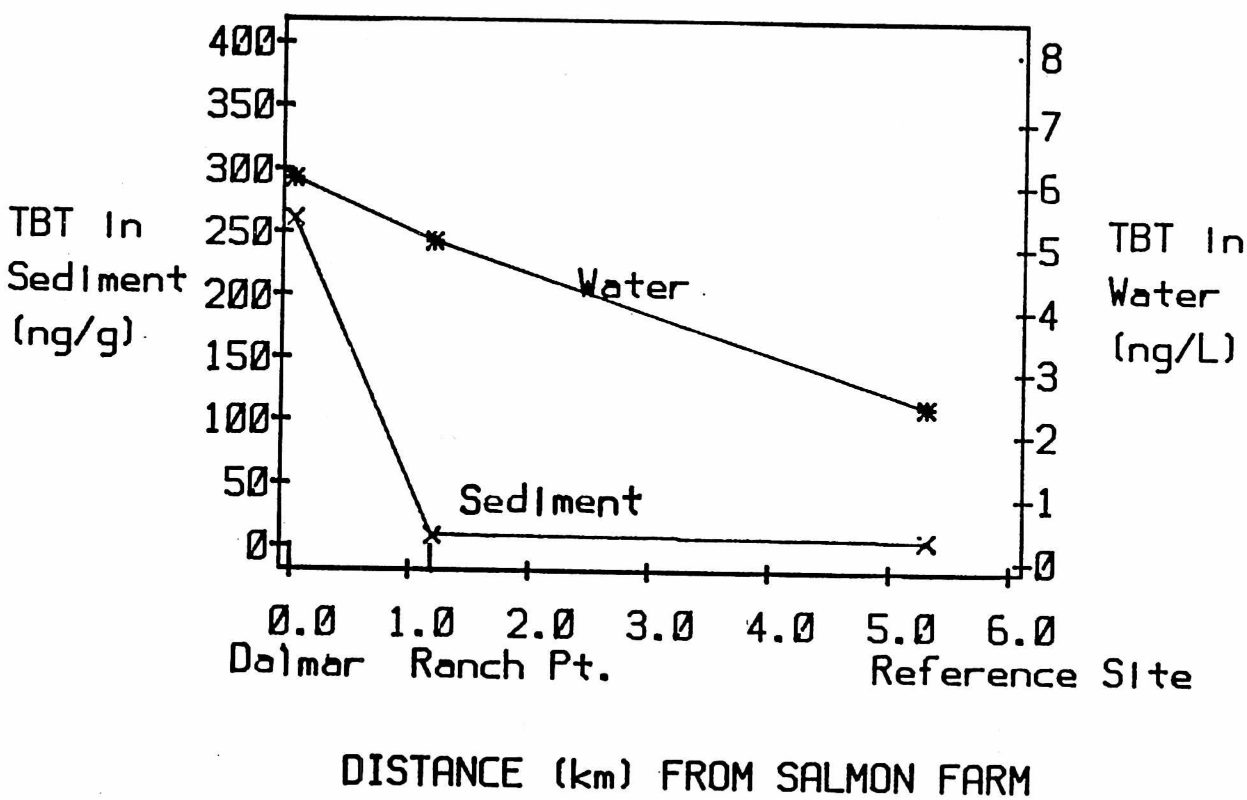

Figure 1: Mean levels of tributyltin (as Sn) in water (ng/L) and sediment (ng/g) with distance (km) from Salmon Farm (A).

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