Applied Organometallic Chemistry (1987) 1 287–301
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0268–2605/87/01401287/$03.50

The distribution and potential toxic effects of TBT in UK estuaries during 1986

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Received 4 April 1987 Accepted 24 April 1987

The concentrations of butyltin compounds in seawater were measured at nine sites in the UK during 1986. In popular yachting centres concentrations of tributyltin (TBT) ranged from less than detectable (<1 ng dm^{-3}) in the winter, up to 1500 ng dm^{-3} in marinas in the summer. Measurements of wastewater generated by high-pressure hosing of yachts demonstrated that even higher environmental concentrations of TBT resulted from the procedure. The results of the monitoring programme are discussed in relation to the toxicity of TBT and recent government legislative actions.

Keywords: Butyltin species, environmental concentrations, seawater, analysis, toxicity

INTRODUCTION

The deleterious effects of tributyltin (TBT) leached from antifouling formulations to the marine environment have been the subject of increasingly extensive studies during the last six years (see reviews in the *Proceedings* of the Oceans 86 symposium[1]). From these studies it has become apparent that certain uses of TBT result in unacceptable environmental harm, and unregulated use of the compound can lead to catastrophic damage to sensitive stages of a variety of aquatic organisms, and especially molluscan species. Attention has focused particularly on the contribution of leachates from yacht antifoulings to local environmental contamination, since small boats are often moored in shallow enclosed estuaries. Such areas historically have also been the major sites for shellfish production in the UK, as well as nursery grounds for commercially important fish species, and conservation areas. During 1985 the UK Government took action under the Control of Pollution Act (1974)[2] to regulate the sale of TBT-based antifouling paints for use on small vessels. A package of measures was introduced including: (i) regulations to control retail sale of the paints; (ii) a voluntary notification scheme for new antifouling paints; (iii) guidelines for handling paints; (iv) coordination of research; (v) establishment of an environmental quality target (EQT) concentration. Details of the control measures are described in the UK Department of the Environment Pollution Paper 25.[3]

Subsequently, regulations were made to control the amount of organotin allowed in the dry film of the formulation when applied to a hull. After 13 January 1986, retail sale was restricted to paints containing less than 7.5% tin in copolymer and 2.5% in free association paints respectively.

In 1985 the EQT was set at a water concentration of TBT of 20 ng dm^{-3}, a level which at the time was thought would give adequate protection to marine organisms. This value was not proposed as a standard because the toxicological evidence was based on a few commercially-important species, and did not take into account effects on other more sensitive organisms. It was in effect a target concentration which paint manufacturers could use to demonstrate that the latest generation of TBT-based paints could be environmentally acceptable. The target was set for TBT, since within the range of organotin compounds used in paint formulations TBT was the most common and most potent biocide, being some 10 to 100 times more toxic than dibutyltin (DBT).[4–7]

At that time few analytical procedures were capable of speciating the various organotin compounds below the 20 ng dm^{-3} level. Hence, in order to gauge the efficacy of the action, the UK Department of the Environment commissioned a research and monitoring programme, a large part of which was carried out by the Ministry of Agriculture, Fisheries and Food at Burnham-on-Crouch. As part of the programme, analytical methods were adopted and developed to speciate and measure TBT in seawater, in order to ascertain whether or not the EQT was likely to be achieved. This paper presents a summary of the concentrations of organotin compounds found in UK estuaries in 1986, and results are discussed in the context of the present knowledge of TBT toxicity to marine organisms.

MATERIALS AND METHODS

Water samples were taken from 40 stations around the UK during 1986, but monitoring effort was concentrated at nine sites: one enclosed bay, one open coastal site, and seven estuarine sites, all of which traditionally supported shellfisheries, and six of which were popular yachting centres. Within each estuary at least three stations were monitored, chosen where possible to represent: (a) a location high in the estuary to reflect the quality of water flowing into the estuary; (b) a location supporting shellfish culture (at these sites oysters and mussels were relaid as indicator species and results are to be presented elsewhere); (c) a harbour or marina area where concentrations were likely to be highest within the estuary. The frequency of sampling varied from site to site, but was generally monthly. In the Crouch estuary 13 stations were monitored monthly and samples from a station close to the MAFF laboratory were collected at least fortnightly. Sampling sites are listed in Table 1 and shown in Fig. 1. Usually, single samples of whole water column were collected and, wherever possible, water samples were collected at slack water low tide.

In addition to the above sampling regime, depth and tidal profiles of concentration were measured at some stations during the yachting season. Water samples were also taken to identify 'hot spots', by measuring the contribution to the surrounding water of leachates from hosed yachts, newly painted yachts and contaminated sediments. Concentrations of organotin in the samples were measured using the method developed by Matthias et al. (1986).[8] Alkyltin compounds are reduced to the hydride form and simultaneously extracted into dichloromethane. The extract is reduced in volume and injected into a gas chromatograph with a flame photometric detector. The limit of detection for TBT compounds is approximately 1 ng dm^{-3}. The method allows the unambiguous identification of mono-, di-, and tri-alkyltin compounds.

Two-litre water samples were collected in calibrated 2.7-litre glass bottles with Teflon-lined, screw-capped lids. The majority of samples were collected by hand at a depth of approximately 10 cm below the water surface (sub-surface). Deeper water samples were collected at some sites using a PTFE and stainless-steel bottle

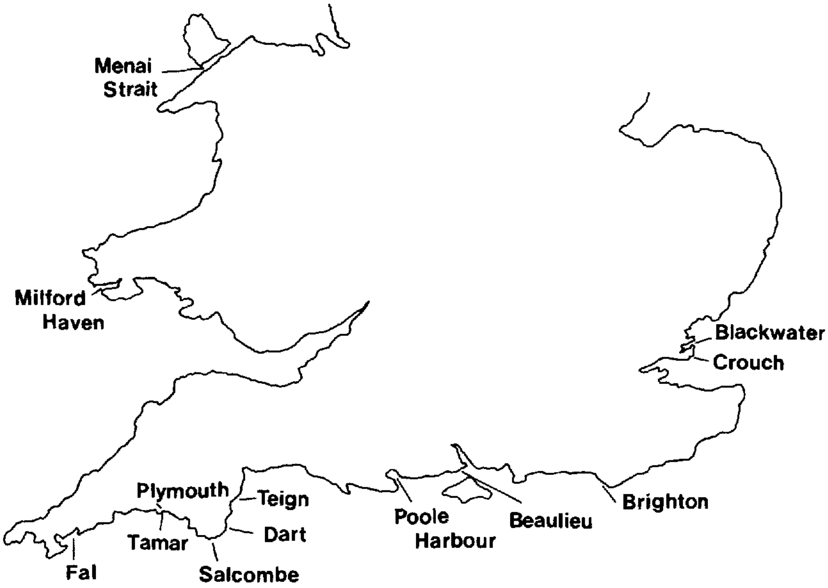


Figure 1 Sampling sites.

holder. An appropriate amount of internal standard (tripropyltin chloride, TPTCl) in dichloromethane was added to the water sample followed by a sodium borohydride pellet (0.25 g) and 40 cm^3 of dichloromethane. The bottle was capped and shaken on an orbital shaker for 15 min, and then allowed to stand while the solvent phase separated out. The dichloromethane was then drawn off into a capped, glass centrifuge tube, and centrifuged at 1000 rpm for 10 min. Any water in the tube was removed using a Pasteur pipette and the extract blown down to approximately 3 cm^3 using a gentle stream of compressed air at ambient temperature. The extract was then transferred to a 'reactivial' and blown down to approximately 200 μl. Although dichloromethane is reasonably soluble in water and only about 15 cm^3 of solvent was recovered using a single extraction, the ratio of TBT to internal standard recovered was constant. At the 50 ng dm^{-3} level, the mean recovery for TBTO was 88% (SD = 15, $n = 12$).

GC analysis was carried out using a Carlo Erba 4160 GC equipped with a flame photometric detector and linked to a Hewlett Packard 1000 minicomputer. Organotins were separated on a 25 m × 0.3 mm ID fused silica capillary column coated with a crosslinked 5% phenylmethylsilicone fluid with a film thickness of 0.52 μm. Using a carrier gas flow rate of 2 cm^3 min^{-1}, and temperature programme; initial 40°C, increasing at 15°C min^{-1} to 200°C, the retention times of MBT, DBT were 2.25, 6.92 and 10.33 min respectively.

Organotin concentrations in wastewater collected during hosing operations on yachts treated with TBT were measured using toluene extraction and electrothermal atomic absorption spectrophotometry.[9] The EAAS method was used for convenience, in order to keep separate the highly contaminated samples from those used for trace analysis. Further details of the sampling strategy, exact site locations, numbers and distribution of boats present and concentrations of TBT in indicator species are in preparation.

RESULTS

Results are expressed as concentrations of alkyltin cation in the sample; in the case of TBT these are 2.5 times Sn concentrations. Monthly survey data are listed in Table 1. Results are shown for tributyltin, and breakdown products di- and mono-butyltin. Total organotin loading of the water column is presented for comparisons with earlier data.[1,9] At the three sites where water samples could be taken at the riverine end of the estuary above the influence of yachts, only low levels of organotins were detected in the water. TBT concentrations were barely above detection limits at station 1 in the Beaulieu, Teign and Dart sites, suggesting that no significant inputs of TBT were entering the estuaries from the riverine end. Despite the inclusion of these values in the data set, concentrations of TBT found in almost half of the 250 samples taken from April to December 1986 were equal to or in excess of the EQT (20 ng dm^{-3}) for TBT. Harbours and marinas invariably showed the highest concentrations of TBT in the water and values reflected the degree of flushing; for example in Sutton marina, Plymouth, which is enclosed and has poor water exchange, concentrations exceeded 1000 ng dm^{-3} from May to September, up to 75 times the EQT. The Dart marina is well flushed and water concentrations did not rise above 200 ng dm^{-3}.

Concentrations of TBT in open estuarine locations exceeded the EQT in six of the nine sites studied; by up to three or four times in the Dart, Crouch, Blackwater and Poole Harbour, and by up to ten times at Salcombe and Beaulieu. All six are popular yachting estuaries. Samples from the Teign, Menai Strait and Milford Haven contained low but often detectable concentrations of organotins, and in one sample from the Teign in September concentrations were just above the EQT. Samples from the Menai Strait showed unusually high concentrations of DBT compared with TBT, but few boats were present near the site, and it seems improbable that the DBT arose from yacht antifouling agents.

The ratios of tri- to di- and mono-butyltins were variable. In marinas, where there were constant inputs of TBT from leachates, TBT predominated. At sites remote from boats, TBT levels were around half the total organotin content, with a corresponding increase in DBT. Monobutyltin (MBT) concentrations were generally low.

Table 2 shows concentrations of organotin compounds found in water outside the Burnham laboratory at weekly or fortnightly intervals. Mean values for each month are displayed in Fig. 2. It can be seen that concentrations rose rapidly in the spring at the time of launching,

Table 1 Concentrations of organotin compounds in marine and estuarine waters around the UK during 1986 (ng dm^{-3})

		April				May				June				July			
Site	Station	MBT	DBT	TBT	$\sum$OT	MBT	DBT	TBT	$\sum$OT	MBT	DBT	TBT	$\sum$OT	MBT	DBT	TBT	$\sum$OT
Crouch	(1) Woodham Ferrers	—				—	—	—	—	—	—	—	—	5	24	9	38
	(2) Fambridge Marina				—	—	—	—	—	6	141	336	483	23	137	425	585
	(3) Fambridge	7	24	23	54	nd	nd	18	18	6	15	13	34	2	29	23	54
	(4) Bridgemarsh	nd	74	22	96	nd	nd	24	24	6	32	19	57	2	20	9	31
	(5) Creeksea	nd	30	28	58	nd	65	19	84	3	28	17	48	3	30	28	61
	(6) Essex Marina	nd	111	158	269	5	36	44	85	4	26	20	50	10	41	52	103
	(7) End Moorings	nd	41	40	81	4	43	50	97	—	—	—	—	—	—	—	—
	(8) MAFF Laboratory	nd	25	32	57	nd	113	70	183	9	40	28	77	2	41	61	103
	(9) End Moorings	nd	40	39	79	—	—	—	—	—	—	—	—	—	—	—	—
	(10) Bush Shore	—	—	—	—	2	29	39	70	2	23	24	49	2	8	18	28
	(11) Roach Mouth	nd	23	13	36	6	30	20	56	5	31	18	54	3	40	20	63
	(12) Holliwell Buoy	nd	10	<1	10	—	—	—	—	3	23	16	42	2	19	10	31
	(13) Holliwell Point	nd	16	8	24	nd	7	25	32	5	7	7	19	—	—	—	—
Blackwater	(1) Goldhanger	nd	5	<1	5	32	29	3	64	8	17	7	32	1	7	2	10
	(2) West Mersea	nd	9	10	19	nd	18	37	55	8	34	46	88	1	27	70	98
	(3) Blackwater Marina	—	—	—	—	—	—	—	—	nd	67	351	418	nd	108	831	939
Beaulieu	(1) Leygreen Farm	nd	7	<1	7	nd	<1	<1	<1	6	6	4	16	3	4	<1	7
	(2) Bucklers Hard	nd	22	45	67	nd	29	50	79	10	83	107	200	14	52	44	110
Poole Harbour	(1) Sandbanks	21	88	17	136	—	—		—	—							
	(2) Commercial Dock	5	17	8	30	—						—	—	—	—	—	—
	(3) Mid-Harbour	4	9	<1	13	7	26	45	78	5	28	6	39	4	26	19	49
	(4) Harbour Entrance	<1	5	<1	5	—	—	—	—	—	—	—	—	—	—	—	—
	(5) Cobbs Quay Marina	nd	72	282	354	nd	245	331	576	24	299	1520	1840	12	221	1190	1420
Teign	(1) Newton Abbot	—	—			nd	2	<1	2	<1	2	1	3	3	<1	<1	3
	(2) Archbrook	—	—	—	—	nd	<1	<1	<1	nd	10	15	25	3	9	4	16
	(3) Teignmouth Harbour	—	—	—	—	—				nd	3	8	11	3	11	5	19
Dart	(1) Caddaford	nd	<1	<1	<1	nd	<1	<1	<1	<1	<1	2	2	5	<1	<1	5
	(2) Blackness Point	nd	<1	<10	<10	nd	<1	1	1	nd	7	40	47	2	5	56	63
	(3) Dartmouth Marina	nd	9	4	13	6	29	48	83	nd	12	109	121	21	23	106	150
Salcombe	(1) Kingsbridge	—	—	—	—	<1	<1	<1	<1	nd	14	29	43	17	16	29	62
	(2) Frogmore Creek	—	—	—	—	8	33	16	57	nd	15	23	38	25	16	17	58
	(3) Salcombe Harbour	nd	11	36	47	nd	nd	80	80	nd	9	60	69	26	29	264	319
Milford Haven	(1) West Williamson	<1	6	<1	6	13	4	2	19	<1	4	10	14	2	2	1	5
	(2) Cosheston Point	<1	<1	<1	<1	<1	3	3	6	<1	4	10	14	<1	2	4	6
	(3) Brunnel Quay Marina	4	10	17	31	<1	35	221	256	2	17	80	99	3	34	290	327
Menai Strait	(1) Tal-y-Foel	—	—	—	—	—	—	—	—	—	—			5	17	<1	22
Conwy	Conwy Town	—	—	—			—	—	—	—	—	—	—	3	1	3	7
Plymouth	Sutton Marina	nd	286	398	684	5	112	1070	1190	193	150	1210	1550	26	45	1090	1160
Brighton	Brighton Marina	nd	25	57	82	nd	nd	101	101	29	231	573	833	48	141	879	1070

August				September				October				November				December			
MBT	DBT	TBT	∑OT	MBT	DBT	TBT	∑OT	MBT	DBT	TBT	∑OT	MBT	DBT	TBT	∑OT	MBT	DBT	TBT	∑OT
—	—	—	—	2	19	18	39	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	4	91	525	620	—	—	—	—	—	—	—	—	—	—	—	—
<1	2	4	6	—	—	—	—	4	15	7	26	4	16	19	39	3	8	3	14
4	34	37	75	—	—	—	—	3	18	7	28	3	14	20	37	6	13	6	25
2	24	47	73	—	—	—	—	3	19	18	40	3	15	16	33	2	6	3	11
—	—	—		—	—	—	—	—	—	—	—	2	10	49	61	18	26	37	81
1	22	32	55	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
31	32	76	139	2	25	44	71	3	20	24	47	4	20	24	48	9	26	32	67
—	—	—	—	—	—	—	—	—	—		—	—	—	—	—	—	—	—	—
1	11	24	36	—	—	—	—	—	—	—	—	2	8	9	19	7	26	129	162
3	30	44	77	—	—	—	—	—	—	—	—	2	10	20	32	2	11	9	22
2	13	8	23	—	—	—	—	—	—	—	—	2	9	14	25	4	8	<1	12
—	—	—	—	—	—	—	—	—	—	—	—	1	9	16	26	4	9	2	15
nd	<1	4	4	<1	4	4	8	<1	13	2	15	nd	7	4	11	5	4	<1	9
<1	3	16	19	1	16	22	39	3	21	76	100	—	—	—	—	<1	4	2	6
2	81	700	783	1	55	652	708	—	—	—	—	9	30	206	245	8	145	60	213
<1	2	5	7	<1	<1	1	1	3	4	<1	7	1	3	<1	4	6	2	<1	8
3	26	146	175	3	34	120	157	2	23	34	59	3	<1	21	24	5	6	4	15
—	—	—	—	—	—	—	—	—	—	—	—	—		—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5	72	59	136	1	5	6	12	<1	8	5	13	2	4	5	11	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12	415	315	742	4	92	686	782	5	73	192	270	6	39	113	158	—	—	—	—
<1	24	2	26	<1	2	1	3	3	5	1	9	3	6	1	10	3	3	2	8
3	6	13	22	<1	<1	26	26	<1	3	1	4	3	4	<1	7	4	13	4	21
4	15	16	35	<1	15	57	72	1	7	4	12	2	4	4	10	10	49	41	100
1	2	2	5	2	1	1	4	1	2	<1	3	nd	6	<1	6	4	2	<1	6
2	6	10	18	<1	2	81	83	1	5	5	11	4	3	8	15	1	4	13	18
4	16	20	40	2	21	191	214	1	10	30	41	nd	5	8	13	2	9	18	29
3	11	25	39	4	36	238	278	1	8	9	18	4	<1	10	14	3	7	5	15
2	8	8	18	1	13	10	24	1	9	7	17	3	4	4	11	5	5	11	21
4	17	103	124	2	27	78	107	1	4	75	80	26	42	243	311	2	9	46	57
<1	1	4	5	1	1	3	5	<1	11	4	15	2	4	1	7	—	—	—	—
<1	4	5	9	<1	4	5	9	1	<1	7	8	2	<1	1	3	—	—	—	—
<1	12	111	124	<1	4	56	60	<1	7	27	34	—	—	—	—	—	—	—	—
3	51	2	56	<1	20	<1	20	4	55	<1	59	3	3	3	9	—	—	—	—
<1	3	3	6	<1	3	9	12	1	2	1	4	<1	2	1	3	—	—	—	—
6	165	1140	1310	3	121	1270	1400	4	121	667	792	3	31	157	191	2	14	83	99
9	200	389	598	1	13	132	146	1	39	285	325	2	32	178	212	5	25	27	57

Abbreviations: nd, not determined; ∑OT, total organic tin.

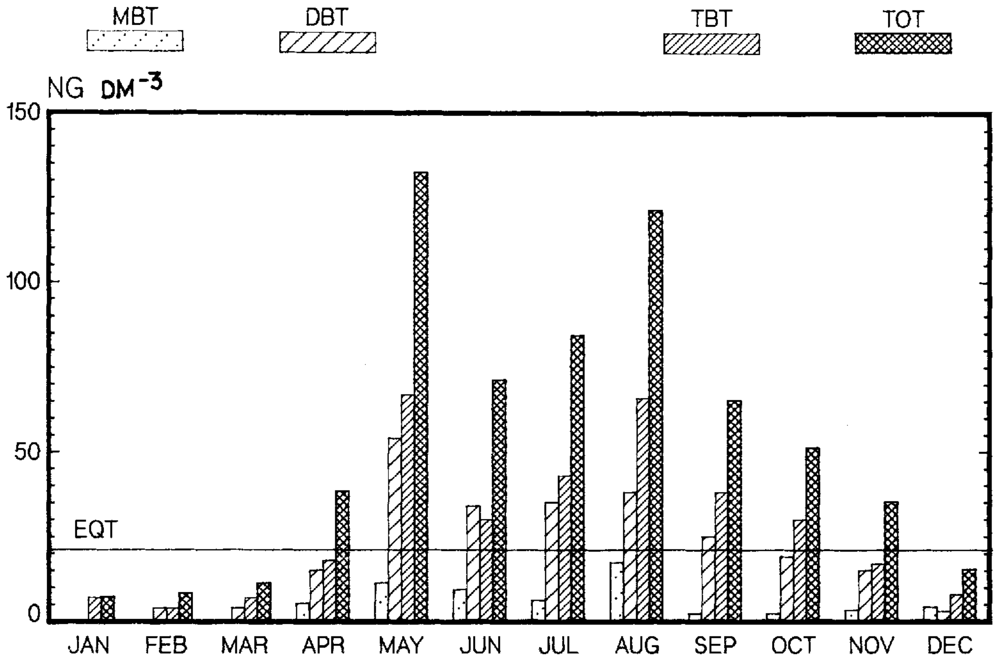


Figure 2 Concentrations of organotin in water at Burnham-on-Crouch during 1986 (ng dm^{-3}). (TOT = total organotin).

Table 2 Concentrations of organotin in sub-surface samples of water at Burnham during 1986 (ng dm^{-3})

Date (1986)	MBT	DBT	TBT	∑OT
28 Jan.	nd	nd	7	7
10 Feb.	nd	4	4	8
14 Mar.	nd	4	7	11
2 Apr.	nd	4	9	13
8 Apr.	6	17	32	55
28 Apr.	10	23	12	45
16 May	11	29	68	108
27 May	nd	79	66	145
10 Jun.	9	28	33	70
25 Jun.	9	40	28	77
8 July	8	34	34	76
15 July	4	36	36	76
16 July	21	40	32	93
28 July	2	41	61	104
6 Aug.	4	42	56	102
21 Aug.	31	32	76	139
4 Sept.	<1	22	36	58
11 Sept.	2	25	44	71
22 Sept.	2	21	21	44
29 Sept.	5	31	45	81
7 Oct.	2	19	30	51
10 Oct.	<1	12	14	26
24 Oct.	3	20	24	47
5 Nov.	4	20	28	52
13 Nov.	4	16	18	38
21 Nov.	2	9	6	17
28 Nov.	4	19	12	35
12 Dec.	3	7	3	13
19 Dec.	5	nd	14	19

Abbreviations: nd, not determined; ∑OT, total organic tin.

reduced slightly in mid-summer, and there was then a second peak in the late summer. The second peak has in the past been attributed to hosing down and repainting of yachts for Burnham Regatta week in August. Mid-season cleaning and/or repainting and late-season scrubbing off directly into the estuary were common practices in all of the estuaries under study, and a similar late-season peak was often observed.

Table 3 shows concentrations of organotins measured during tidal cycles and at various depths in estuaries of the Crouch, Fal and Tamar. Data are shown for Sutton marina, Plymouth (an enclosed marina site), and for Essex marina in the Crouch (open to the estuary). Organotins were well mixed throughout the water column at open estuarine locations, but a marked gradient with depth was seen in the enclosed marina at Sutton harbour. Samples taken from the surface microlayer at the same locations showed higher concentrations of organotins.[10]

Table 4 shows concentrations of organotins measured in the vicinity of hosed and recently repainted yachts. Wastewater after exposure of boats to high-pressure hoses was collected and analysed, and the TBT content determined. Hard, free association formulations released 0.1–0.7 g of organotin per boat, whereas softer, copolymer formulations released 1–6 g on hosing (Table 4a). Where yachts were hosed on the foreshore at low tide, samples of sub-surface water in the general

Table 3a Depth profiles of organotin concentrations in the Crouch, Fal and Tamar during 1986 (ng dm^{-3})

Site	Station	Date	Depth	MBT	DBT	TBT	∑OT
Crouch	(7) End Moorings	May	1 cm	4	62	43	109
			10 cm	4	43	50	97
			1 m	3	40	62	105
			5 m	2	21	80	103
			10 m	6	16	48	70
Crouch	(5) Creeksea	July	1 cm	18	38	37	93
			10 cm	13	40	37	90
			1 m	13	35	43	91
			2 m	33	38	30	101
			3 m	28	36	29	93
			3.5 m	14	42	26	82
Crouch	(8) Burnham	July	1 cm	19	38	36	93
			10 cm	21	40	32	93
			1 m	13	36	30	79
			2 m	21	37	28	86
			3 m	10	35	41	86
			4 m	20	33	21	74
			5 m	22	36	24	82
			6 m	11	35	35	81
Fal	King Harry Ferry	Sept.	1 cm	1	5	11	17
			10 cm	1	6	17	24
			1 m	1	7	15	23
			5 m	<1	3	15	18
			10 m	1	3	6	10
Crouch	(7) End Moorings	Aug.	1 cm	2	14	33	49
			10 cm	1	22	32	55
			1 m	1	18	33	52
			5 m	2	16	44	62
			7.5 m	1	18	33	52
Crouch	(5) Creeksea	Aug.	1 cm	1	19	11	31
			10 cm	1	21	60	82
			1 m	1	15	23	39
			2 m	1	24	42	67
			4 m	1	12	13	26
Crouch	(6) Essex Marina	May	1 cm	5	31	73	109
			10 cm	5	36	44	85
			1 m	6	35	82	123
			5 m	3	32	56	91
			7 m	11	31	35	77
Plymouth	Sutton Marina	Sept.	10 cm	3	121	1270	1400
			1 m	1	33	170	204
			5 m	1	4	11	16
Tamar	Devonport	Sept.	1 cm	<1	3	4	7
			10 cm	1	4	5	10
			1 m	<1	4	9	13
			5 m	1	9	17	27
			10 m	<1	1	18	19

Table 3b Organotin concentrations during a tidal cycle in the Crouch (ng dm^{-3})

Site	Station	Time	Tide	MBT	DBT	TBT	∑OT
Crouch	(8) Burnham	8.40	Ebb	4	32	44	80
		10.20	Slack low	5	25	43	73
		11.45	1/3 Flood	5	37	36	78
		13.45	Flood	4	42	46	92
		15.45	Slack high	5	31	60	96
		17.40	2 h Ebb	13	42	67	122

Table 4a Concentrations of organotins in the Crouch at sites of hosing and repainting yachts during 1986—wastewater from hosing of yachts 7 to 8 m long

Formulation	Washwater (mg dm^{-3})	Calculated amount of organotin removed from hull (g)
Free association	0.5	0.1
	1.4	0.4
	2.3	0.7
Copolymer	4.0	1
	7.0	2
	14.3	4
	15.3	5
	19.3	6

Table 4b Estuarine water in the vicinity of hosing operations (sample taken on rising tide after hosing) (ng dm^{-3})

		MBT	DBT	TBT	∑OT
Sample	(1)	80	1630	7080	8790
	(2)	34	1740	6540	8310

Table 4c Release of organotin from contaminated sediments on the foreshore (ng dm^{-3})

	MBT	DBT	TBT	∑OT
Whole water column	98	192	502	792
Centrifuged water	24	80	134	238
Offshore whole water column	2	41	61	104

Table 4d Sub-surface water in the vicinity of a yacht newly painted with a copolymer formulation (ng dm^{-3})

Distance from yacht	MBT	DBT	TBT	∑OT
5 cm	7	142	1230	1380
30 cm	6	83	257	326
1 m	6	55	50	111

vicinity were taken once the tide had come in (water depth approximately 2 m). Concentrations of TBT in sub-surface waters were approximately 7 μg dm^{-3} (Table 4b).

To measure the release of TBT from contaminated muds, water samples containing high levels of suspended particulates were taken from the water/foreshore interface (water depth approximately 30 cm) outside a local boatyard. TBT at 500 ng dm^{-3} was found in the whole water column and, after centrifugation, over 130 ng dm^{-3} was found in solution. Further from the shore, concentrations of TBT were 60 ng dm^{-3} in the whole water column (Table 4c).

Sub-surface samples were also taken close to the hull of a newly painted 8 m yacht. A gradient of TBT was found away from the hull (Table 4d).

DISCUSSION

Inevitably, when designing a monitoring strategy it is difficult to select sites typical for the whole country, and one or a few stations which are truly representative of each estuary. Upper estuarine stations were chosen to confirm that inputs of TBT other than from boats were unlikely to occur, and estuaries with few moored yachts were selected to demonstrate that environmental problems with TBT are specifically related to small boats. Clearly, these results are atypical of the majority of enclosed estuaries with large numbers of pleasure craft. Furthermore, even in estuaries with large numbers of moored boats, stations were selected to be representative of those used for mariculture; for example at Salcombe, Dart and Poole, stations were several kilometres from the nearest important mooring areas. Samples were also taken before the yachting season began in April and long after boating activity had ceased in November and December.

All of these factors suggest that the data set presented here was biased to underestimate the contaminant concentrations in the estuaries as a whole. The point is further illustrated by the more detailed study of the Crouch estuary. Spatial, temporal and depth information for the estuary demonstrated that concentrations were highest in mid-estuary close to swinging moorings (stations 6 to 9 in Table 1) in the summer, were evenly distributed throughout the water column, and were lower at slack water low tide than during the rest of the tidal cycle. Hence, sub-surface samples taken at slack water at stations remote from moorings at other sites would not represent maximum concentrations of TBT in the estuary.

Despite the bias towards underestimation, during the summer concentrations of TBT in open estuarine locations at all six estuaries with significant yachting activity were at least three or four times the EQT. Concentrations of TBT in marinas and harbours were 10 to 50 times higher than the EQT, and such sites, clearly, act as a major input of the toxin. The significance of the sink for TBT in heavily-contaminated marina sediments is currently under investigation.

Even higher concentrations of TBT (some 350 times the EQT) were detected in sub-surface waters above sediments contaminated by hosing operations on the previous tide. The significance of such situations is difficult to quantify, but plumes of contaminated water from this source are certainly present in the Crouch. Measurements of wastewaters from hosing operations give a better perspective of the degree of potential environmental damage, e.g. up to 6 g of TBT was hosed from an 8 m yacht previously coated with a TBT-based copolymer formulation. This would require dilution with over $300000\,m^3$ of water to achieve the EQT.

Figure 3 shows results of monitoring for organotin concentrations in water from the Crouch from 1982 to 1986. The data recorded before 1986 suffered from the higher detection limit of $100\,ng\,dm^{-3}$ available at that time. However, in each year, organotin concentrations increased in the spring with the launching of yachts, usually followed by a secondary peak in later summer or autumn associated with repainting or hosing off activities, and concentrations fell away during the winter. During the period of study there was a gradual decrease in environmental concentrations probably associated with a change in the composition of the paints, as free association products gave way to copolymer formulations. No marked decrease in the concentrations of organotins occurred in 1986 following restrictions under the Control of Pollution Act.[2]

Table 5 summarizes the toxicological information currently available for tributyltin compounds, and shows concentrations of organotins found during the last five years in open estuarine and marina locations.[1,3] The marked overlap between observed concentrations and effect data leaves little doubt that a variety of marine organisms have been killed or debilitated by the use of potent TBT biocides. At first sight, Table 5 appears to suggest that fish and crustaceans were less sensitive than most other phyla. However, most research has centred on lethal effects and there is little information on long-term, sub-lethal responses. Fish and crustaceans have been demonstrated to have a greater ability to metabolize TBT than molluscs,[65] but until long-term tests are completed conclusions must be guarded.

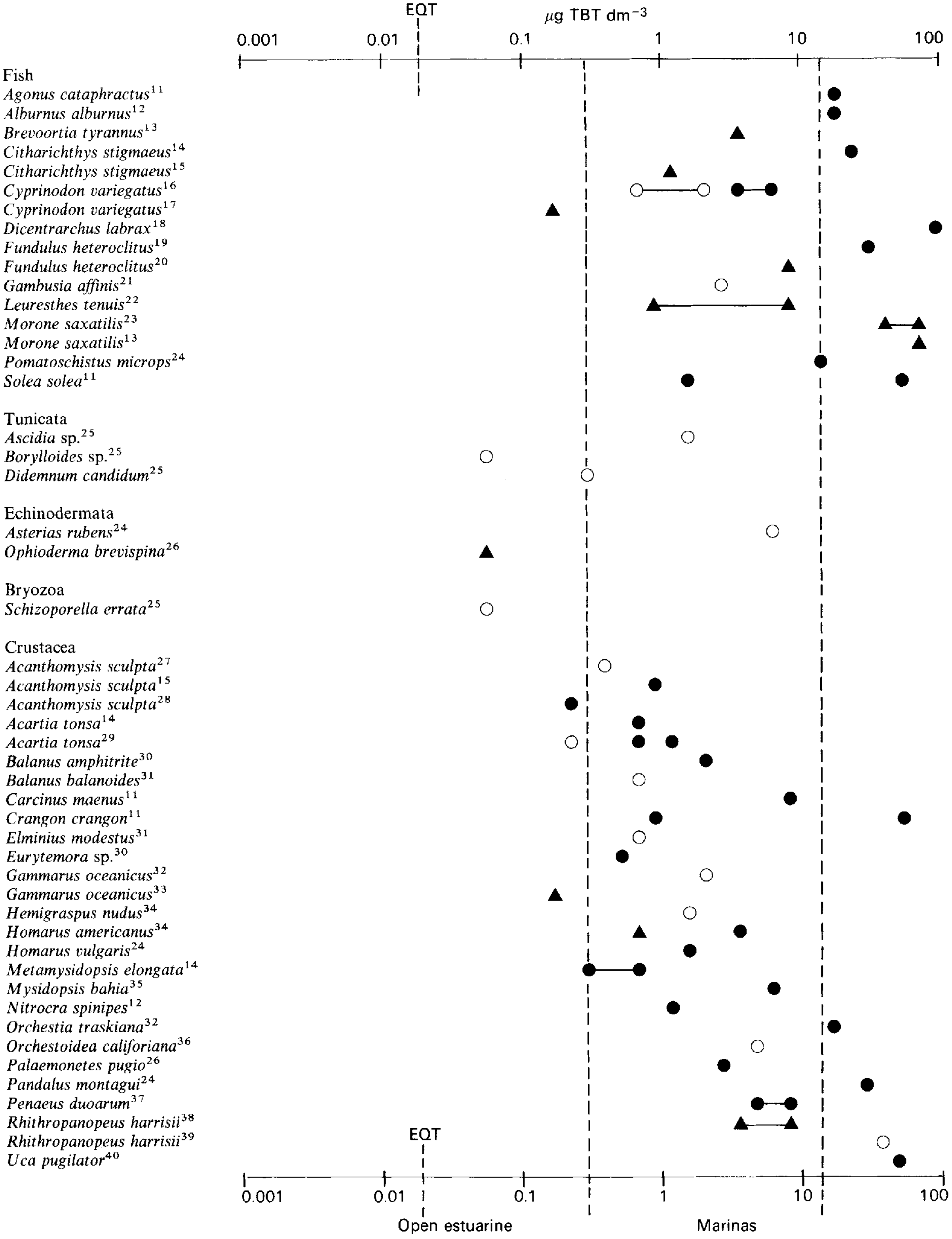
On the basis of chronic exposure data, molluscs and algae exhibit extreme sensitivity to TBT. Gross abnormalities, shell thickening and chambering in Pacific oysters (*Crassostrea gigas*) occurred at $50\,ng\,dm^{-3}$, a concentration at which larval growth was also inhibited.[46] Growth and survival was normal at $20\,ng\,dm^{-3}$. Growth of recently metamorphosed European flat oysters (*Ostrea edulis*) was reduced at $60\,ng\,dm^{-3}$, and marginally so at $20\,ng\,dm^{-3}$.[53] However, the growth of spat (juveniles) of *C. gigas*, the mussel (*Mytilus edulis*) and the clam (*Venerupis semidecussata*) was severely reduced at $240\,ng\,dm^{-3}$, although not that of large *O. edulis* spat, and the inference is that the latter is more resistant. Tests on the veliger larvae of *M. edulis*[52] exposed to $100\,ng\,dm^{-3}$ showed that there was a 50% mortality by 15 days, and many of the survivors were moribund and their growth rate was reduced; lower concentrations were not tested.

One of the effects noted with gastropod molluscs exposed to TBT compounds was the development of 'imposex'—the development of male sex characteristics in the female—leading to impairment of reproduction. Bryan et al. (1986)[55] showed that this effect was produced in the common dogwhelk (*Nucella lapillus*) exposed to $50\,ng\,dm^{-3}$ TBT under laboratory conditions, and a comparison between the tissue concentration of TBT associated with imposex in this experiment and concentrations found in *N. lapillus* from coastal areas of SW England, where populations were similarly affected, indicated that water concentrations as low as $2.5\,ng\,dm^{-3}$ TBT may give rise to the effect. This and other evidence suggests that the decline in the common dogwhelk in and around the UK estuaries may be caused by the lower reproductive capacity induced by TBT, rather than by mortality.

From consideration of the most recently published data, it would appear that the EQT was set at too high a level to safeguard all sensitive marine species.

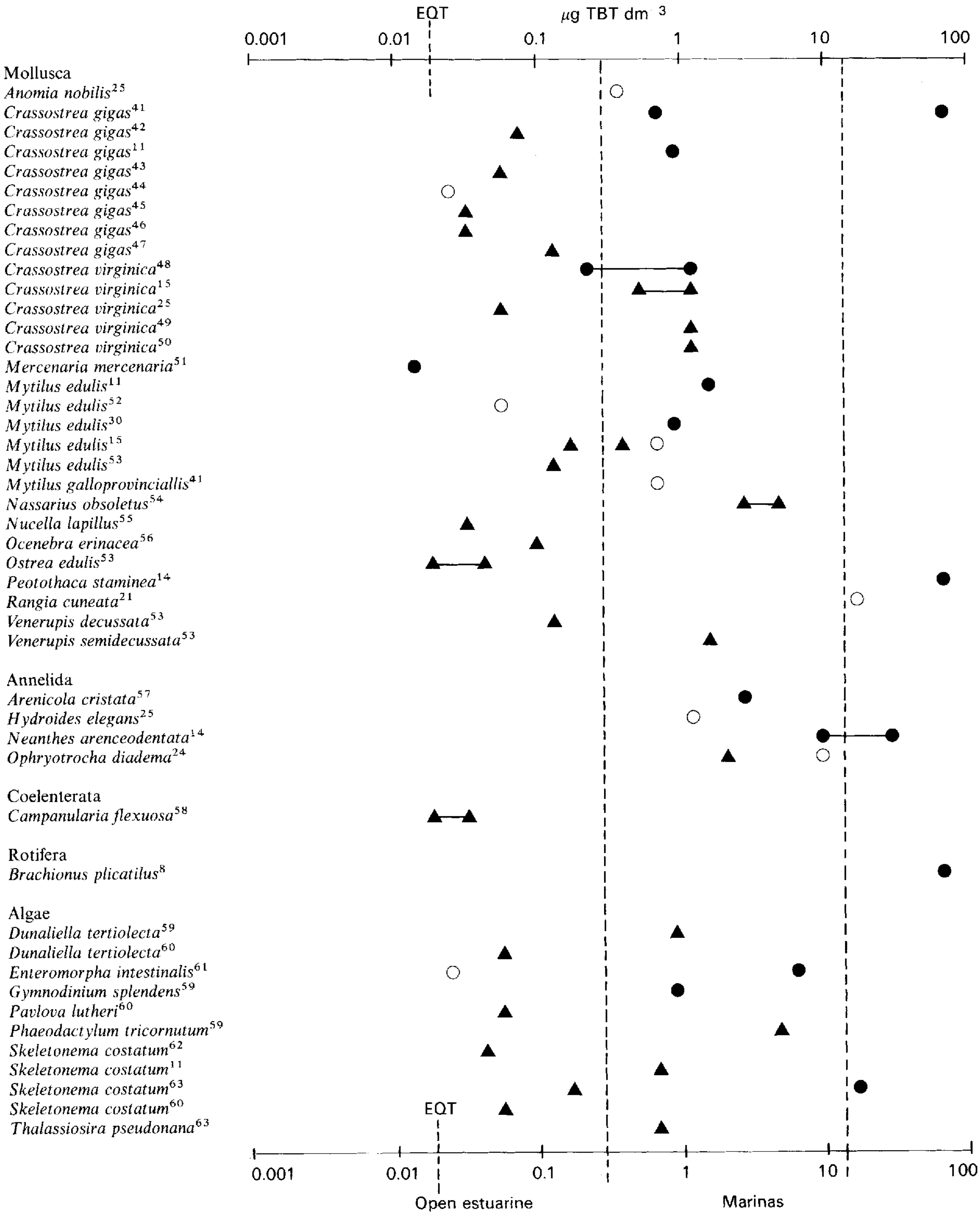
Current information suggests that to achieve environmental protection, the EQT would have to be reduced by at least a factor of ten. Although the control measures taken on 13 January 1986 may have brought about some reduction in environmental concentrations, they were not effective in reducing contamination to a now-acceptable level.

Table 5 Toxicity of TBT to marine organisms



Significant mortality, ● ≤96 h; ○ >96 h. Sublethal effects, ▲.

Table 5 Continued



Significant mortality, ● ≦96 h; ○ >96 h. Sublethal effects, ▲.

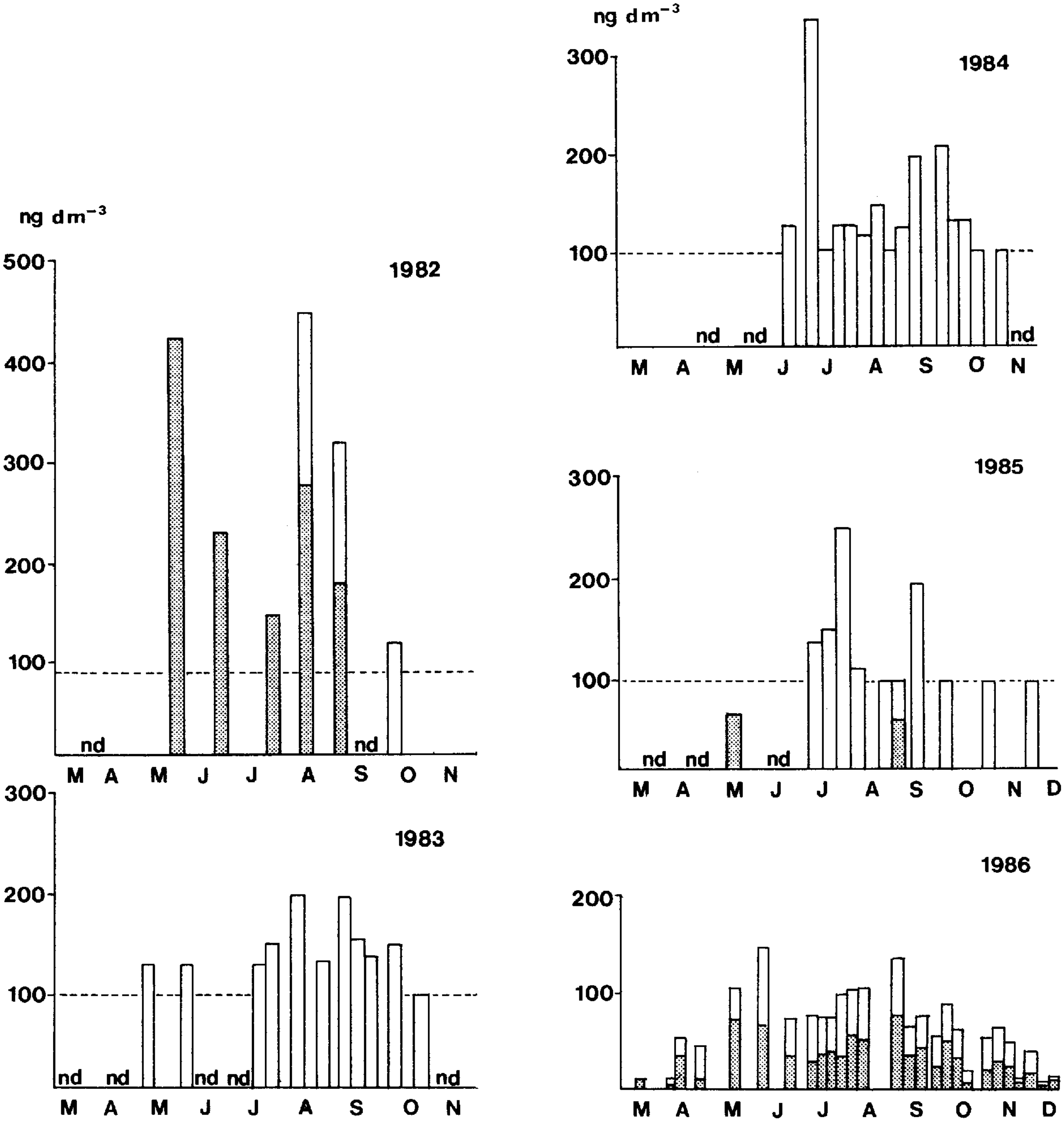


Figure 3 Concentrations of organotin and tributyltin in water at Burnham-on-Crouch 1982–1986. □, Toluene-extractable organotin; ▨, tributyltin (ng dm^{-3}), nd = not detected.

As a result of this evidence, in February 1987 the UK Government announced its intention to introduce further controls under the Control of Pollution Act (1974);[2,66] it now includes a complete ban on retail sale of paint formulations containing TBT and a ban on the wholesale and retail sale of products containing TBT used to treat fish farm cages. Regulations were laid before Parliament on 7 May 1987, and were effective from 28 May 1987. More comprehensive controls will be put in hand from 1 July 1987 when all antifoulings, whether or not they contain TBT, become subject to the provisions of the Food and Environment Protection Act (1985).[67] After that date, all formulations containing aquatic biocides will require prior approval by Ministers before they can be sold or used.

Acknowledgement This work was funded by the UK Department of the Environment. The authors gratefully acknowledge the cooperation and support of Dr R Abel and Dr T Wilkinson.

REFERENCES

1. Anon *Proceedings of Oceans 86 Conference and Exposition on Science Engineering and Adventure, Washington D.C., 23–25 Sept. 1986, Organotin Symposium*, IEEE, Piscataway, NJ, USA, and Marine Technology Society, Washington D.C., 1986, Vol 4, pp 1101–1329
2. Control of Pollution Act, 1974, Her Majesty's Stationery Office, London, UK, 1974
3. Department of the Environment, UK *Organotin in Antifouling Paints, Environmental Consideration*, Pollution Paper No 25, DOE, London, UK, 1986
4. Blunden, S J, Hobbs, L A and Smith, P J The environmental chemistry of organotin compounds. In: *Environmental Chemistry*, Bowen, H J M (ed), The Royal Society of Chemistry, London, UK, 1984, pp 49–77
5. Wong, P T S, Chan, Y K, Cramar, O and Bengert, G A *Can. J. Fish Aquat. Sci.*, 1982, 39: 483
6. Vighi, M and Calamari, D *Chemosphere*, 1985, 14(11–12): 1925
7. Thain, J E *Toxicity of Organotin Compounds to Marine Organisms*. Unpublished data, 1987. Ministry of Agriculture, Fisheries and Food, Directorate of Fisheries Research, Fisheries Laboratory, Burnham-on-Crouch, Essex, UK
8. Mathias, C L, Bellama, J M, Olson, C L and Brinckman, F E *Environ. Sci. Technol.*, 1986, 20: 609
9. Waldock, M J and Miller, D *The Determination of Tributyl Tin in Seawater and Oysters in Areas of High Pleasure Craft Activity*, International Council for the Exploration of the Sea, CM1983, E:12 (mimeo)
10. Cleary, J J and Stebbing, A R D *Mar. Pollut. Bull.*, 1987, in press.
11. Thain, J E *Acute Toxicity of Bis(tributyltin) Oxide to the Adults and Larvae of Some Marine Organisms*, International Council for the Exploration of the Sea, CM1983, E:13 (mimeo)
12. Linden, E, Bengtsson, B E, Svanberg, O and Sundstrom, G *Chemosphere*, 1979, 11/12: 843
13. Hall, L W, Pinkney, A E, Zeger, S, Burton, D T and Lenkevich, M J *Wat. Res. Bull.*, 1984, 20(2): 253
14. Anon *Effect of Organotin Antifouling Leachates in the Marine Environment*, Progress Report Code 513, Naval Ocean Systems Center, San Diego, CA, USA, 1981 (cited in ref. 30)
15. Valkirs, A, Davidson, B and Seligman, P *Sublethal Growth Effects and Mortality to Marine Bivalves and Fish from Long-Term Exposure to Tributyltin*, Technical Report 1037, Naval Ocean Systems Center, San Diego, CA, USA, 1985 (cited in ref. 64)
16. Ward, G S, Cramm, G C, Parrish, P R, Trachman, H and Slesinger, A Bioaccumulation and chronic toxicity of bis(tributyltin) oxide (TBTO): tests with a saltwater fish. In: *Aquatic Toxicology and Hazard Assessment: Fourth Conference*, Branson, D R and Dickson, K L (eds), ASTM, STP 737, Philadelphia, 1981, pp 183–200
17. Anon *Effects of Tributyltin Fluoride on Survival, Growth and Development of Sheepshead Minnow (Cyprinodon variegatus)*, Report B4-84-7, M & T Chemicals Inc., Rahway, NJ, USA, 1984
18. Saroglia, Marco G, Ambrogi, R and Scarano, G *Can. Tech. Rep. Fish. Aquat. Sci.*, 1982, 1163: 164
19. Anon *Acute Toxicity of Tri-n-butyltin Ocide to Channel Catfish (Ictalurus punctatus), the Fresh Water Clam (Elliptio complanatus), the Common Mummichog (Fundulus heteroclitus) and the American Oyster (Crassostrea virginica)*, Report submitted by EG and G, Bionomics, Wareham, MA, USA, to M and T Chemicals Inc., Rahway, NJ, USA, 1976.
20. Pinkney, A E, Hall Jr, L W, Lenkevich, M J, Burton, D T and Zeger, S *Wat. Air Soil Pollut.*, 1985, 25: 33
21. Good, M L, Dundee, D S and Swindler, G Bioassays and environmental effects of organotin marine antifoulants. In: *Controlled Release of Bioactive Materials*, Baker, R (ed), Academic Press, New York, 1980, pp 387–397
22. Newton, F A, Thum, B, Davidson, A, Valkirs, A and Seligman, P *Effects on the Growth and Survival of Eggs and Embryos of the Californian Grunion (Leuresthes tenuis) Exposed to Trace Levels of Tributyltin*, Technical Report 1040, Naval Ocean Systems Center, San Diego, CA, USA, 1985
23. Hall, L W and Pinkney, A E *Crit. Rev. Toxicol.*, 1984, 14(2): 159
24. Thain, J E Acute toxicity of tri-butyl-tin to marine organisms. Unpublished data, 1986. Ministry of Agriculture, Fisheries and Food, Directorate of Fisheries Research, Fisheries Laboratory, Burnham-on-Crouch, Essex, UK
25. Henderson, R S Effects of organotin antifouling paint leachates on Pearl Harbour organisms: A site specific flow through bioassay. In: *Proceedings of Organotin Symposium of the Oceans 86 Conference and Exposition, Washington D.C. 23–25 Sept. 1986*, IEEE, Piscataway, NJ, USA, and Marine Technology Society, Washington, D.C., 1986, Vol 4, pp 1226–1233

26. Walsh, G E Organotin toxicity studies conducted with selected marine organisms at EPA's Environmental Research Laboratory, Gulf Breeze, Florida. In: *Proceedings of Organotin Symposium of the Oceans 86 Conference and Exposition, Washington D.C., 23–25 Sept. 1986*, IEEE, Piscataway, NJ, USA and Marine Technology Society, Washington, D.C., 1986, Vol 4, pp 1210–1212
27. Salazar, M H and Salazar, S M *The Effects of Sediment on the Survival of Mysids Exposed to Organotins*, Draft Report, Naval Ocean Systems Center, San Diego, CA, USA, 1985
28. Davidson, B M, Valkirs, A O and Seligman, P F *Acute and Chronic Effects of Tributyltin on the Mysid* (*Acanthomysis sculpta*), Draft Technical Report, Naval Ocean Systems Center, San Diego, CA, USA, 1986
29. U'ren, S *Mar. Pollut. Bull.*, 1984, 14(8): 303
30. Anon *Environmental Assessment of Fleetwide Use of Organotin Antifouling Paint*, US Naval Sea Systems Command, Washington D.C., 1984, pp 1–28
31. Beaumont, A R and Newman, P B *Wat. Sci. Technol.*, 1986, 18: 299
32. Laughlin, R B Jr, Linden, O and Guard, H E *Bulletin de Liaison du Coipm.*, 1982, 13: 1
33. Laughlin, R B Jr, Nordlund, K and Linden, O *Mar. Environ. Res.*, 1984, 12: 243
34. Laughlin, R B Jr and French, W J *Contam. Toxicol.*, 1980, 25: 802
35. Anon *Acute Toxicity of BioMet 204 Red to Mysid Shrimp* (*Mysidopsis bahia*), Report BP-81-2-15 submitted by EG and G Bionomics to M & T Chemicals Inc., Rahway, NJ, USA, 1981
36. Laughlin, R B Jr and Guard, H E *Toxicity of Trialkyltin Components of Marine Antibiofouling Paints to the Amphipod Orchestoidea californiana*. Unpublished manuscript, 1981. Naval Biosciences Lab, Oakland, CA, USA (cited in ref. 30)
37. Anon *Comparative Toxicity of Tri-n-butyltin Oxide* (*TBTO*) *Produced by Two Different Chemical Processes to Pink Shrimp* (*Penaeus duoarum*), Report BP-81-4-55 submitted by EG and G Bionomics to M & T Chemicals Inc., Rahway, NJ, USA, 1981
38. Laughlin, R B Jr, French, W J and Guard, H E *Wat. Air Soil Pollut.*, 1983, 209: 69
39. Laughlin, R B Jr, Johannesen, R B, French, W, Guard, H E and Brinckman, F E *Environ. Toxicol. Chem.*, 1984, 4: 343
40. Wright, D A and Roosenburg, W H *Arch. Environ. Contam. Toxicol.*, 1982, 11: 491
41. Robert, R and His, E *Action de l'Acetate de Tributyleetain sur les Oeufs et les Larves D de Deux Mollusques d'Interet Commercial: Crassostrea gigas* (*Thunberg*) *et Mytilus galloprovincialis* (*Lmk*), International Council for the Exploration of the Sea, Comité de la Mariculture, CM1981, F:42 (mimeo)
42. Waldock, M J and Thain, J E *Mar. Pollut. Bull.*, 1983, 14(11): 411
43. Alzieu, C and Heral, M Ecotoxicological effects of organotin compounds on oyster culture. In: *Ecotoxicological Testing for the Marine Environment*, Persoone, G, Jaspers, E and Claus, C (eds), State Univ. Ghent and Inst. Mar. Scient. Res., Bredene, Belgium, 1982, Vol 2, pp 187–196
44. Anon *Acute and Chronic Toxicity of Tributyltin Fluoride to Pacific Oyster* (*Crassostrea gigas*), Report submitted by Springborn Bionomics Inc., to M & T Chemicals Inc., Rahway, NJ, USA, 1984
45. Gendron, F *Recherche sur la Toxicité des Peintures Antisalissures a Base d'Organostanniques et de l'Oxyde de Tributyetain vis-à-vis de l'Huitre Crassostrea gigas*, Thesis of Université de Droit, d'Economie et des Sciences d'Aix, Marseille, Faculté des Sciences et Techniques de Saint-Jerome, 1985
46. His, E and Robert, R *Rev. Trav. Inst. Pech. Marit.*, 1985, 47(1 and 2): 63
47. Thain, J E and Waldock, M J *The Growth of Bivalve Spat Exposed to Organotin Leachates from Antifouling Paints*, International Council for the Exploration of the Sea, Marine Environmental Quality Committee, CM1985, E:28 (mimeo)
48. Anon *Toxicity of Tri-n-butyltin Oxide* (*TBTO*) *to Embryos of Eastern Oyster* (*Crassostrea virginica*). Unpublished study, 1977. US Environmental Protection Agency, Washington D.C., Accession No 114085
49. M & T Chemicals Inc. Unpublished data, cited as personal communication by Cardwell, R D and Sheldon, A W (1986) (ref. 64)
50. Thain, J E Toxicity of TBT to bivalves: effects on reproduction, survival and growth. In: *Proceedings of Organotin Symposium of the Oceans 86 Conference and Exposition, Washington D.C., 23–25 Sept. 1986*, IEEE, Piscataway, NJ and Marine Technology Society, Washington, D.C., 1986, Vol 4, pp 1306–1313
51. Becerra-Huencho, R M *The Effect of Organotin and Copper Sulphate on the Late Development and Presettlement Behaviour of the Hard Clam* (*Mercenaria mercenaria*), Master of Science Thesis, University of Maryland, College Park, MD, USA, 1984
52. Beaumont, A R and Budd, M D *Mar. Pollut. Bull.*, 1984, 15(11): 402
53. Thain, J E and Waldock, M J *Wat. Sci. Technol.*, 1986, 18: 193
54. Smith, B S *J. Appl. Toxicol.*, 1981, 1(3): 141
55. Bryan, G W, Gibbs, P E, Hummerstone, L G and Burt, G R *J. Mar. Biol. Assoc. UK*, 1986, 66: 611
56. Feral, C and Gall, S *C. R. Acad. Sci. Paris, Ser. III*, 1982, 295: 627
57. Walsh, G E, Louie, M K, McLaughlin, L L and Lores, E M Lugworm (*Arenicola cristata*) larvae in toxicity tests: survival when exposed to organotins. *Environ. Toxicol. Chem.*, 1987, 5, in press
58. Stebbing, A R D and Brown, B E Marine ecotoxicological tests with coelenterates. In: *Ecotoxicological Testing for the Marine Environment*, Persoone, G, Jaspers, E and Claus, C (eds), State Univ. Ghent and Inst. Mar. Scient. Res., Bredene, Belgium, 1984 Vol 1, pp 307–340
59. Salazar, S M *The Effects of Bis(tri-n-butyltin) Oxide on Three Species of Marine Phytoplankton*, Technical Report 1039, Naval Ocean Systems Center, San Diego, CA, USA, 1985
60. Beaumont, A R and Newman, P B *Mar. Pollut. Bull.*, 1986, 17(10): 457

61. Davies, R J, Fletcher, R L and Furtado, S E J The effects of tributyltin compounds on spore development in the green algae *Enteromorpha intestinalis*. In: *Proc. 6th Int. Congr. Marine Corrosion and Fouling, Athens, Greece, September 1984*

62. Anon *Comparative Toxicity of Tri-n-butyltin Oxide (TBTO) Produced by Two Different Chemical Processes to the Marine Algae Skeletonema costatum*, Report BP-81-6-109, M & T Chemicals Inc., Rahway, NJ, USA, 1981

63. Walsh, G E, McLaughlin, L L, Lores, E M, Louie, M K and Deans, D H *Chemosphere*, 1985, 14(3/4): 383

64. Cardwell, R D and Sheldon, A W A risk assessment concerning the fate and effects of tributyltins in the aquatic environment. In: *Proceedings of Organotin Symposium of the Oceans 86 Conference and Exposition, Washington D.C., 23–25 Sept. 1986*, IEEE, Piscataway, NJ, USA, and Marine Technology Society, Washington D.C., 1986, Vol 4, pp 1117–1129

65. Lee, R F *Mar. Environ. Res.*, 1985, 17: 145

66. The Control of Pollution (Anti-fouling Paint and Treatment) Regulations, 1987. Statutory Instrument 783, 1987, Her Majesty's Stationery Office, London, UK, 1987

67. The Food and Environment Protection Act, 1985. Her Majesty's Stationery Office, London, UK, 1985