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Organotin concentrations in the Rivers Bure and Yare, Norfolk Broads, England

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Butyltin concentrations have been measured at eight freshwater sites (rivers and lakes) in the Norfolk Broads, UK, during 1986 and 1987. Tributyltin (TBT) was found in water samples from seven of the sites. Wherever TBT was present, dibutyltin and (usually) monobutyltin occurred. Levels of TBT exceeded 100 ng dm^{-3} in open stretches of both the Rivers Bure and Yare in 1986 and 1987. The highest concentration of TBT recorded for Wroxham Broad (a shallow lake) was 898 ng dm^{-3}. Values of up to 3.26 μg dm^{-3} were measured in water samples taken from a marina. A depth profile for Wroxham Broad showed TBT to be uniformly distributed throughout the shallow water column. The results are discussed in relation to toxicity of TBT to freshwater organisms. Laboratory measurements of the degradation of TBT in freshwater from a marina gave a half-life of six days at 20°C in the light.

Keywords: Organotin, tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), environmental, freshwater, monitoring, toxicity, degradation, half-life

INTRODUCTION

During the last six years, the Ministry of Agriculture, Fisheries and Food (MAFF), UK, Fisheries Laboratory at Burnham-on-Crouch has been monitoring estuarine waters for concentrations of organotin compounds, derived from the tributyltin (TBT)-based antifouling paints commonly applied to yachts and other pleasure craft.[1–3] In laboratory studies adverse biological effects were shown to occur in a variety of marine species at low, sub-part per billion (μg dm^{-3}), concentrations of TBT. Additionally, field experiments showed that growth and reproduction in several species of bivalve molluscs were impaired at concentrations of TBT found in many UK estuaries.[4–6]

Concentrations of TBT similar to those found in the marine environment also occur in freshwaters in Switzerland[7,8] and in the Great Lakes region of North America.[9–11]

An investigation into the concentrations of organotins found in the Norfolk Broads (a system of rivers and lakes) was requested by the Secretary of State for the Environment, UK. This study was carried out as part of an assessment of the impact of TBT on the aquatic environment, following initial Government action to regulate the use of TBT-based antifouling paints.[12] Since 1987 the sale and use of TBT has been controlled under the provisions of the Food and Environment Protection Act (1985). The Rivers Bure and Yare, which feed a number of the shallow lakes known as broads, were chosen as sites for initial investigation (Fig. 1). Studies centred on Wroxham, a popular area for pleasure craft activity. A survey of local chandlers suggested that TBT-based copolymer paints were commonly used on boats in the area. This was borne out by the concentrations of organotins found in the water samples from the Norfolk Broads area reported here.

Preliminary results for degradation studies of TBT in water are also presented to give an indication of the persistence of the biocide in freshwaters. The results are discussed in the context of the few toxicity test data available.

MATERIALS AND METHODS

The number of boats on the Rivers Bure and Yare in August 1986 was determined from aerial photographs, taken by the MAFF aerial survey department.

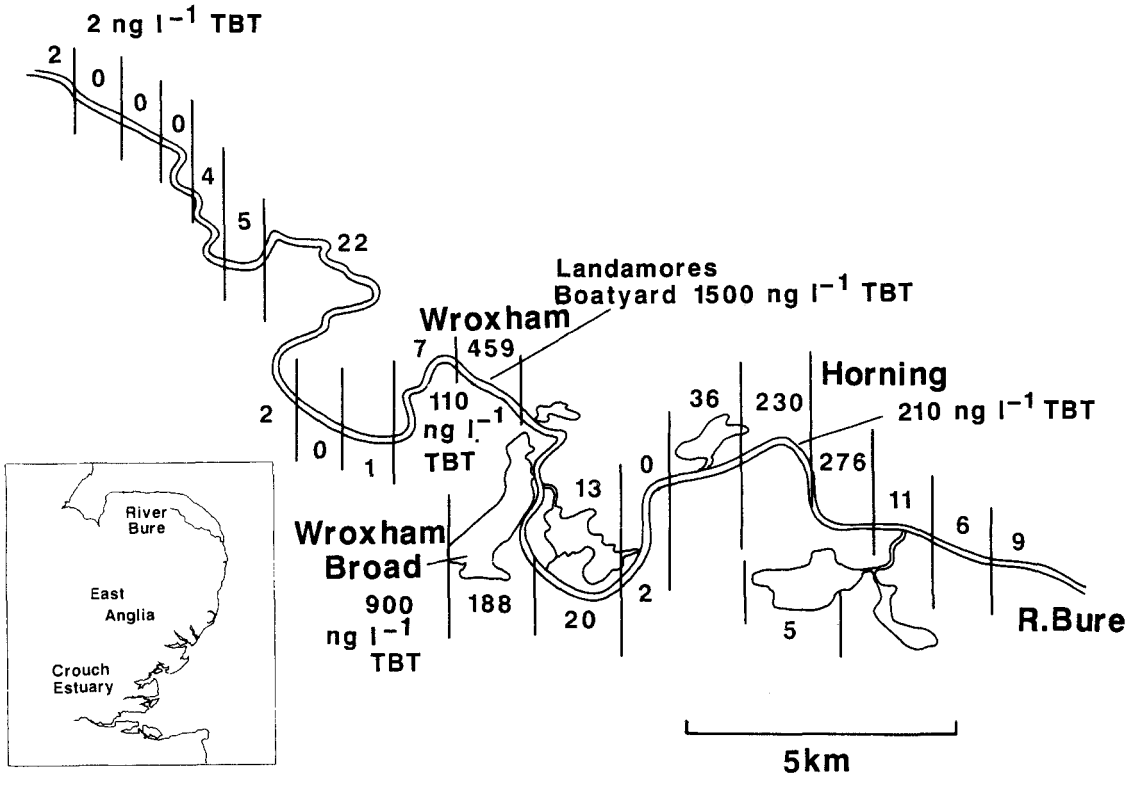

Figure 1 Number of boats and maximum TBT concentrations in the River Bure, Norfolk Broads, during 1986.

Water samples

Sub-surface (10 cm deep) water samples of two litres (2 dm^3) were taken by hand in calibrated 2.7 dm^3 glass bottles with PTFE-lined screw caps. Depth profiles were obtained using a stainless-steel and PTFE bottle holder. Samples were taken at monthly intervals from June to December 1986 and in March, June and September 1987 at six sites in the Bure (Fig. 1) and two sites on the Yare. Organotin concentrations were measured using the method developed by Matthias *et al.*[13] in which alkyltin compounds are reduced to the hydride form and simultaneously extracted into dichloromethane; the extract is then reduced in volume and injected into a gas chromatograph fitted with a flame photometric detector. The limit of detection for TBT compounds is approximately 1 ng dm^{-3}. Details of the technique as used in this study are as follows: to each 2 dm^3 water sample an appropriate amount of internal standard (tripropyltin chloride, TPTCl) in dichloromethane was added, 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 centrifuge tube, and centrifuged at 1000 *g* 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. Gas chromatography (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. Alkyltins were separated on a 25 m × 0.3 mm i.d. fused-silica capillary column coated with a crosslinked 5% phenyl methyl silicone fluid with a film thickness of 0.52 μm.

Degradation studies

Water samples for degradation studies were collected from St Ives Marina on the Great Ouse, Cambridgeshire (the initial concentration of TBT was approximately

1.5 μg dm^{-3}). Two experimental approaches to the study were adopted.

(1) In order to ensure homogeneity of the sample 20 dm^3 of water were collected in a clear glass aspirator. The sample was continuously stirred with a magnetic spin bar, maintained at 20 ± 1°C and exposed to a continuous light regime. Two 750 cm^3 subsamples were taken on day 0 and at intervals over a period of 55 days. These subsamples were analysed for mono-, di- and tri-butyltin (MBT, DBT, TBT) by the method described above. On day 0 and day 55 two additional 750 cm^3 aliquots were taken and total tin determined by toluene/tropolone extraction and measurement by electrothermal atomic absorption spectrophotometry.[1]

(2) In a second experiment two 20 dm^3 samples of marina water (A and B) were divided into 750 cm^3 aliquots and placed in 1 dm^3 amber glass bottles. In order to keep the water well mixed, glass marbles were introduced into each bottle (the bottle then being capped with aluminium foil) and the contents continually agitated on an orbital shaker, for the duration of the experiment. The subsamples were held under the same light and temperature regime as previously described, but received light of a lower intensity because of the amber colour of the bottles. Two subsamples were analysed for MBT, DBT, and TBT by in-bottle extraction, using the above method, at day 0 and at intervals over a period of 55 days. On day 55 two additional aliquots were taken for determination of total tin concentrations. Since TBT is known to adsorb to glass surfaces,[14] this second experiment, using in-bottle extraction, ensured that both dissolved TBT and TBT which had adsorbed to the walls of the bottle were measured. In the first experiment water samples were taken from the glass aspirator and then extracted, so that any TBT adsorbed to the walls of the aspirator was not accounted for.

RESULTS

1986–1987 survey of the Rivers Bure and Yare

The results of the 1986 and 1987 survey are shown in Table 1. The sites at Ingworth and Buxton are upstream of the majority of moorings, and showed non-detectable and low concentrations of TBT respectively. Trace amounts of MBT and DBT were also shown to be present at these sites. Further downstream at Wroxham there is a marked increase in concentrations of TBT (>120 ng dm^{-3}) and breakdown products. Landamore's Yard is a boat building and repair yard in a backwater at Wroxham, and reflects the highest inputs likely to occur in the area. A maximum concentration of 1.54 μg dm^{-3} was measured in water samples taken close to the boatyard in June 1986. Some extremely high concentrations of TBT (898 ng dm^{-3} and 458 ng dm^{-3}) were also found in samples collected in Wroxham Broad in July and September 1986; the samples were taken near the jetty of a yacht club where localized inputs may have occurred. In October 1986 water samples for a depth profile were taken some 50 m from the shore. TBT concentrations were found to be uniformly distributed throughout the shallow water column (Table 2), and even in late October, when most boating activity has ceased, were around 20 ng dm^{-3}. At Horning, another centre of boating activity, TBT concentrations exceeded 200 ng dm^{-3}.

In the River Yare even higher concentrations of TBT were found than for the River Bure. In June 1986 the level of TBT was 370 ng dm^{-3} in an open stretch of the river at Brundall, while in the same month at one of the marinas in Brundall the TBT concentration exceeded 3.2 μg dm^{-3}.

Degradation studies

The total tin concentration measured in the marina water at the start of the degradation experiment was 0.7 μgSn dm^{-3}. At the end of 55 days the concentration of total tin in the water from both the glass aspirator and from the amber bottles was 0.8μg dm^{-3}, indicating no loss of tin from the system due to adsorption to glassware; i.e. the samples were approximately the same at the beginning and end of the experiment.

Figure 2 shows that the *half-life* for TBT both in light and under low light conditions was six days although the subsequent rates of degradation differed. Under light conditions the rate of TBT degradation had decreased considerably by day 14, when TBT levels had fallen from 1.5 μg TBT dm^{-3} to 200 ng TBT dm^{-3}, and by the end of the experiment only 2% of the initial TBT concentration remained. In contrast, under low light conditions the subsequent rate of TBT degradation was slower; even by day 14 TBT concentrations had only fallen to 400 ng TBT dm^{-3}, and at

Table 1 Concentrations (ng dm^{-3}) of butyltin compounds in the Rivers Bure and Yare during 1986 and 1987

Location	June 1986				July 1986				August 1986				September 1986			
	MBT	DBT	TBT	ΣOT[a]	MBT	DBT	TBT	ΣOT	MBT	DBT	TBT	ΣOT	MBT	DBT	TBT	ΣOT
R. Bure																
Ingworth	—[b]	—	—	—	<1	1	<1	1	<1	3	<1	3	<1	2	<1	2
Buxton	—	—	—	—	<1	2	2	4	ND	7	2	9	<1	2	<1	2
Wroxham	ND[c]	14	105	119	ND	20	112	132	3	13	9	25	<1	11	75	86
Wroxham Broad	4	50	25	79	ND	98	898	996	6	48	55	109	4	34	458	496
Landamore's Yard	ND	221	1540	1761	2	154	232	388	17	109	83	209	1	79	691	771
Horning	4	31	50	85	1	32	70	103	9	21	53	83	17	65	213	295
R. Yare																
Brundall	33	30	371	434	<1	14	83	97	3	12	7	22	2	14	130	146
Brundall Marina	7	95	3260	3362	<1	18	132	150	8	33	46	87	3	23	100	126

[a]ΣOT, total organotin. [b]—, Not sampled. [c]ND, not determined.

October 1986				November 1986				March 1987				June 1987				September 1987			
MBT	DBT	TBT	ΣOT	MBT	DBT	TBT	ΣOT	MBT	DBT	TBT	ΣOT	MBT	DBT	TBT	ΣOT	MBT	DBT	TBT	ΣOT
2	3	<1	5	1	1	<1	2	—	—	—	—	1	1	<1	2	<1	<1	<1	<1
<1	3	<1	3	2	2	1	5	—	—	—	—	1	3	<1	4	<1	9	<1	9
<1	11	7	18	6	24	84	114	3	10	102	115	13	81	121	215	<1	5	32	37
10	16	17	43	4	9	27	40	5	8	12	25	16	27	44	87	3	41	136	180
29	104	180	313	18	88	346	452	—	—	—	—	113	201	336	650	4	71	385	460
7	16	11	34	2	6	6	14	3	7	20	30	8	28	112	148	—	—	—	—
9	13	42	64	5	9	9	23	<1	2	28	30	16	51	235	302	<1	<1	47	47
11	32	61	104	6	19	22	47	4	13	142	159	13	47	202	262	3	25	162	190

Table 2 Depth profile of butyltin concentrations (ng dm^{-3}) in Wroxham Broad (October 1986)

Depth (m)	MBT	DBT	TBT	ΣOT[a]
0.1	10	16	17	43
0.5	20	16	18	54
1.0	8	11	25	44
1.5	5	11	19	35

[a]ΣOT = total organotin.

the end of the experiment 15–20% of initial TBT concentrations remained.

DISCUSSION

Environmental concentrations

The aerial survey in August 1986 showed that there were more than 1400 boats on the River Bure, the highest densities being around Wroxham and Horning. Boats on the lower river could not get above a lock system at Coltishall and there were few boats at the upper river site of Buxton, and none at the furthest upstream site of Ingworth (Fig. 1). Only MBT and DBT were found in the samples from Ingworth: these organotins may have been derived from metabolism or degradation of TBT, but diffuse contamination from the use of diorganotin catalysts and stabilizers in the plastics industry cannot be ruled out.

A simple model was devised for TBT contamination at Wroxham. It was calculated that the total immersed hull area for 200 boats was approximately 1400 m^2. Assuming that all of the boats used TBT antifouling paints, with a release rate of approximately 4 μg cm^{-2} day^{-1} (Waldock and Thain, unpublished data; Refs 12, 15), and with a mean volumetric flow for the River Bure of 282 000 m^3 day (Anglian Water Authority, personal communication), then the theoretical concentration of TBT at the sampling station at Wroxham would be approximately 200 ng dm^{-3}. The concentrations recorded in 1986 rose to 112 ng dm^{-3},

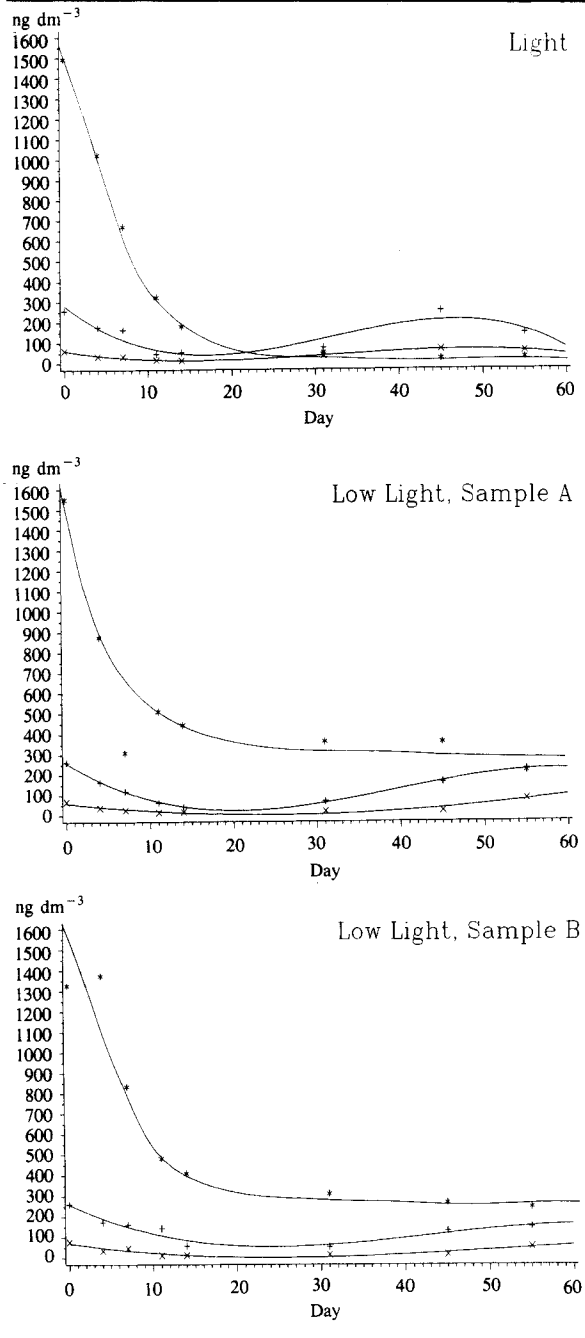

Figure 2 Degradation of TBT in freshwater at 20°C. X, MBT; +, DBT; *, TBT.

suggesting that the predicted environmental concentration from input estimates is close to the concentrations measured.

In the enclosed waters of Wroxham Broad the potential for build-up of TBT is clearly much greater than in the open river and this is confirmed by the very high concentrations found close to one yacht club in July (>800 ng dm^{-3}) and September (>400 ng dm^{-3}) 1986. Cleary and Stebbing[16] found levels of over 50 ng Sn dm^{-3} organotin (TBT and DBT) in Wroxham Broad even in March when boating activity was reduced.

The levels of TBT recorded in the River Yare at Brundall exceeded 370 ng dm^{-3} in June 1986 and 230 ng dm^{-3} in June 1987, indicating that the River Yare was even more contaminated than open stretches of the River Bure. In the enclosed waters of Brundall Marina the level of TBT reached the extremely high value of 3.26 μg dm^{-3} compared with the highest value recorded on the River Bure of 1.50 μg dm^{-3} at Landamore's Yard. A winter value for organotin (TBT and DBT) of 180 ng Sn dm^{-3} at Brundall Marina was measured by Cleary and Stebbing.[16]

These levels can be compared with tributyltin values of 10 ng dm^{-3} to 5.7 μg dm^{-3} which have been recorded in freshwater systems in Canada.[9–11,17] The only other documented measurement of TBT in freshwater is in Switzerland where relatively low concentrations, 13 ng dm^{-3}, were found.[7,8] Also, Linden[18] has reported the presence of TBT in the tissues of freshwater molluscs from Lake Malaren, a popular boating centre in Sweden.

The depth profile study of Wroxham Broad showed that TBT was fairly uniformly distributed throughout the water column; however, the concentration of TBT in the surface microlayer was not measured, and this could well have been higher. Cleary and Stebbing[16] found enhanced levels of organotin in the surface microlayer of Wroxham Broad and at several other sites on the Broads. Extremely high concentrations of TBT (61 μg dm^{-3} to >1 mg dm^{-3}) occur in the surface microlayer of certain Canadian lakes and rivers.[9,19] Elevated levels of organotin in the surface microlayer have also been reported in marine systems.[16,20]

TBT degradation

Since the broads (i.e. shallow lakes) are not well flushed, loss of TBT is more likely to occur from degradation rather than dilution. The main processes responsible for the breakdown of organotins in the environment are UV irradiation and biological degradation,[21] with biological degradation being the most important.[22–24] The degradation of TBT occurs by

stepwise dealkylation to inorganic tin, with the formation of DBT and MBT as intermediates.[21] Wherever TBT occurred in the Rivers Bure and Yare, DBT was also found.

The half-life values for TBT recorded in the literature show a wide variation depending on the conditions under which they were measured. The shortest half-life so far reported is 3.5 days for an enclosed ecosystem.[25] Conversely, Maguire *et al.*[26] found that direct photolysis of TBT, in distilled water and water from a freshwater harbour, was slow with a half-life of more than 89 days. Half-lives of between six weeks and five months have also been reported for freshwater at 20°C, where biological degradation appears to be the rate-limiting factor which determines the persistence of TBT.[17,22]

TBT half-lives are shorter under light conditions than dark; this is not due simply to photolysis, but also to the fact that many photosynthetic micro-organisms are involved in the breakdown of TBT to DBT and MBT.[25,27,28] Although microbial degradation appears to be of primary importance in the breakdown of TBT,[24,27] microalgae may play a significant role when present in high numbers.[24] It has been shown experimentally that the freshwater alga, *Ankistrodesmus falcatus*, is able to metabolize TBT to DBT, MBT and inorganic tin.[29] Temperature also governs degradation rate: Thain *et al.*[30] estimated the half-life of TBT in seawater at 5°C to be approximately 60 days in the light, whilst Olson and Brinckman[28] reported no biodegradation of TBT after two weeks at 5°C in the dark.

The concentration of TBT in the environment may play a key role in the rate of degradation. Seligman *et al.*[27] found that TBT at a concentration of 744 μg dm^{-3} was not degraded over the 144 days of their experiment. Long half-lives may be a result of the toxicity of TBT to micro-organisms, so causing inhibition of biodegradation. Although microbial degradation of organic compounds may proceed at low concentrations, at high concentrations degradation is reduced.[31] It seems unlikely that inhibition of biological degradation would occur in the Norfolk Broads as TBT levels are generally below 1.00 μg dm^{-3} and the only time this value was exceeded was in June 1986 at Landamore's Yard (approximately 1.5 μg dm^{-3}) and at Brundall Marina (approximately 3.3 μg dm^{-3}).

The half-life of 6 days for TBT in the present study is in agreement with Seligman *et al.*,[32] who recorded a half-life of 7 days for TBT in marina water held under similar conditions and with an initial TBT concentration of 530 ng dm^{-3}.

The results of the degradation experiments show that the initial breakdown of TBT is rapid, so that under ideal conditions the very high concentrations of TBT (>1.0 μg dm^{-3}) which occurred in certain areas of the Norfolk Broads may not have been long-lived. However, this is probably an over-estimate of the breakdown rate of TBT in the Broads, as the experiments were carried out at a relatively high temperature of 20°C (such a temperature only occurs for a short while during the summer in the Broads) and used marina water containing micro-organisms which were presumably tolerant to high levels of TBT. Seligman *et al.*[27] and Lee *et al.*[24] found that when TBT was spiked into water with a high ambient TBT concentration it degraded more rapidly than when spiked into water with a low ambient concentration. They speculate that microbes capable of degrading TBT were present in greater numbers in the water with the high ambient TBT concentration, and that these microbes were adapted to high levels of TBT. However, work on phytoplankton has not indicated any adaptation to TBT after 12 weeks' exposure.[33]

Potential environmental impact

The currently available data on the toxicity of TBT to freshwater organisms are shown in Fig. 3. The concentrations of TBT found in the Rivers Bure and Yare are sufficiently high to cause at least localized environmental damage. Certain boatyards and marinas on the Broads had TBT water concentrations of 1–3 μg dm^{-3}, which are similar to the LC_{50} values for the crustacean *Daphnia magna*, and only just below the LC_{50} values for the fish *Alburnus alburnus*, *Lebistes reticulatus*, *Lepomis macrochirus* and *Salmo gairdneri* (see Fig. 3). In contrast, the frog *Rana temporaria*, and the few insect species tested, appear to be much less sensitive to TBT.

In both 1986 and 1987, TBT concentrations in open stretches of the Rivers Bure and Yare exceeded 100 ng dm^{-3}, which could have had sublethal effects on a variety of organisms. Seinen *et al.*[47] showed that 290 ng dm^{-3} TBT has a sublethal effect on the yolk sac fry of *S. gairdneri*. In the freshwater snail, *Biomphalaria galbrata*, egg laying is reduced at TBT concentrations as low as 1 ng dm^{-3}; marine molluscs (bivalves and gastropods) are also particularly sensitive to TBT.[3,58]

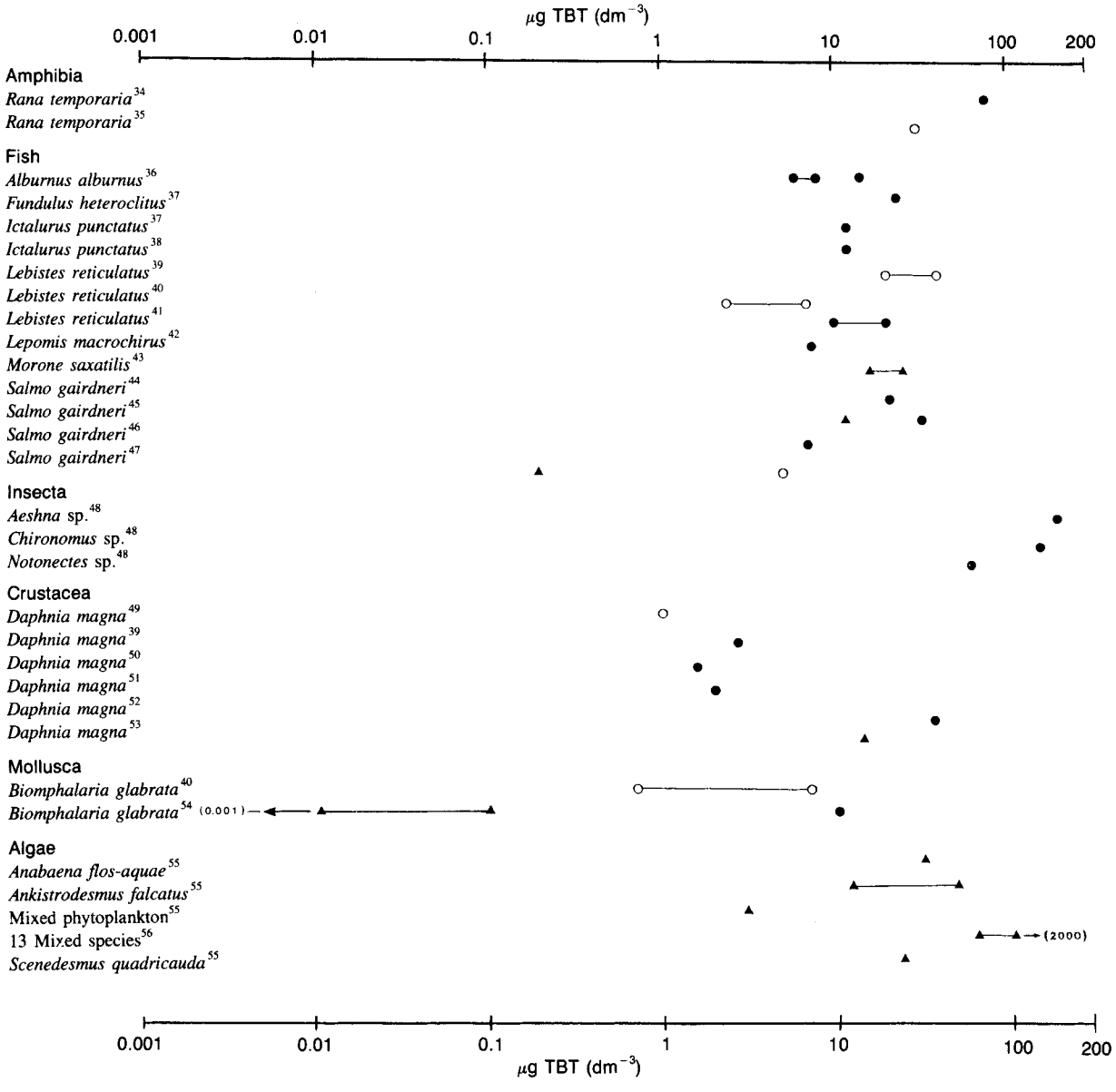

Figure 3 Toxicity of TBT to freshwater organisms. Significant mortality: ●, ≤96 h; ○, >96 h. Sublethal effects: ▲.

Micro-algal species show a wide range of tolerance to TBT. Algistatic concentrations for mixed species have been reported to be as high as 63–2000 μg dm^{-3},[56] yet 5 μg Sn dm^{-3} TBT inhibits reproduction in *Ankistrodesmus falcatus* and 100 ng Sn dm^{-3} was found to inhibit primary production of phytoplankton from Lake Ontario.[55] Moreover, some species are good accumulators of the toxin; a bioconcentration factor of 3×10^4 has been calculated for *Ankistrodesmus falcatus*.[29] The levels of TBT found in the Norfolk Broads may well have had a deleterious effect on the local phytoplankton.

The Broads area has been subject to eutrophication for a number of years[59] with abundant development of microphytes at the expense of zooplankton species. It is tempting to speculate that the imbalance in community structure has been further exacerbated by selective effects of TBT on grazing species; however,

previous studies have not shown a positive correlation between environmental impoverishment and the distribution of boats in the Norfolk Broads.[59]

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