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WATER POLLUTION RESEARCH REPORTS

TRIBUTYLTIN IN THE ENVIRONMENT
SOURCES, FATE AND DETERMINATION

Report

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WATER POLLUTION RESEARCH REPORT 8

TRIBUTYLTIN IN THE ENVIRONMENT SOURCES, FATE AND DETERMINATION

An assessment of present status and research needs
1988
COST 641 — Organic Micropollutants in the Aquatic Environment

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SUMMARY

The aim of this report is to assess the present status and the need for further research on toxicity, sources, fate and determination of tributyltin (TBT) in the environment. The emphasis of the present report has been on information which may have an impact on the regulation concerning the use of TBT. The evaluation of available data show that the toxicity of TBT towards aquatic organisms, which tend to be the most exposed and sensitive, is well documented. The main release of TBT progresses into the aquatic environment. No significant reduction of TBT levels in the technosphere (eg sewage treatment plants) is supposed to occur. Degradation of TBT in the aquatic environment is a slow process. Half-lives range from 1 to 3 weeks under optimal conditions to several years under anaerobic conditions. TBT accumulates in sewage sludges, sediment and biota. High residue levels in sewage sludge indicate sources other than antifouling paints.

The present situation of TBT pollution in the aquatic environment is reflected in several recent publications. Levels of TBT determined in surface water are often higher than the no observed effect levels for sensitive stages of aquatic organisms.

The publications show that there is still a lack of knowledge of TBT levels in most compartments of the environment. Analytical methods are available for the determination of TBT and its degradation products at trace levels. A preferred method is gas chromatography combined with a highly specific and sensitive detector. In this respect, interlaboratory comparisons and quality assurance programmes are recommended.

Areas of future research which have been identified include:

- Assessment of sources other than antifouling paints
- Fate of TBT in sewage treatment plants
- Improvement of the database on residue levels of TBT in different compartments
- Impact of TBT released from sewage sludge and dredged sediments

1. INTRODUCTION

The present report deals with various aspects of the impact on the environment by the use of tributyltin (TBT). The main sections give an overview on use, emission, toxicity and environmental fate of TBT, butyltin speciation at trace levels and conclusions and recommendations for future research. The report was prepared by a TBT task group for the Directorate General XII of the Commission of European Community. The report gives detailed conclusions and recommendations for further research activities within the EC.

The first meeting was held in Rome on October 22, 1987, and the drafts were prepared by and distributed to the members of the task force. The contributions were revised and edited in the course of two meetings (Zürich, December 20th, 1987, and Oslo, January 7th, 1988). The final document was prepared at a meeting in Frankfurt on January 25th, 1988. While every effort has been made to present information as accurately and complete as possible without unduly delaying the finalization of the report, omissions may have occurred due to the short preparation time. Nevertheless, we feel that the present paper is a valuable contribution concerning the status of environmental research on TBT.

2. BACKGROUND

The element tin, belonging to the IV-group elements in the periodic table of the elements, forms stable, covalent tin-carbon bonds. Organotin compounds contain the element tin in its +4-oxidation state, which may have one to four organic side chains attached.

The physico-chemical properties of organotin compounds may range from the monobutyl tin ion, which resembles the inorganic tin(IV) ion[1] to the neutral, lipophilic substance Bu_4Sn. Mono- to tri-substituted organotins carry a nominal charge of +3, +2 or +1, respectively; the counterions attached may contribute significantly to the properties of the substance (e.g. in heat stabilizers for synthetic polymers [Blunden and Chapman 1986, Gächter and Müller 1979, Zuckerman et al. 1978]). The polarities of these bonds may range from nearly ionic to covalent-similar nature [Cotton and Wilkinson 1974]. Depending on environmental conditions, these anions may be exchanged fairly easily [Laughlin et al. 1984].

The first commercial organotin compound to be introduced into the market in 1936 was dibutyltin dilaurate, which was used as heat stabilizer for synthetic polymers [Zuckerman et al. 1978]. Since then, a still increasing number of organotin compounds is produced for very different purposes: methyl- and ethyltins are used as stabilizers for PVC, dibutyltins are catalysts in polyurethane foams and stabilizers in PVC, tributyltins are used as biocides, and tricyclohexyl-, phenylneopentyl- and phenyltins have found widespread applications as agrochemicals and biocides [Zuckerman et al. 1978, WHO 1980, Worthing 1987]. Tributyltins are not used deliberately in agriculture, as they show pronounced phytotoxicity and persistence in soil. Tetrabutyltin is used only as an intermediate and is not a technical product.

Annual world consumption of organotin compounds was estimated to be 33 000 tons in 1983 [Stewart 1980, Blunden and Chapman 1986]; butyltins, mostly in the form of dibutyltin and tributyltin, account for about 5000 tons per year [Laughlin et al. 1984].

As tributyltin, together with the methyltins and phenyltins, belongs to the most toxic organotin compounds [WHO 1980, Chliamovitch 1984], the use and disposal of butyltins has raised

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[1]Abbreviations used for butyltins in this review: $Bu_xSn_{z}^{n+}$ with $x + z = 4$ and $n = 4 - x$ designates a butyltin species with x butyl groups attached. Alkyl groups are abbreviated with: Me Methyl, Et Ethyl, Pr Propyl, Bu n-Butyl, Hex n-Hexyl, Phe Phenyl; H hydrogen. Bu_3Sn^+ is also abbreviated by the term TBT (for tributyltin). The charge of the ion does not imply the presence of true ionized species. Counterions (anions, e.g. halogenides) are designated by the sign X. TBTO is the abbreviation of tributyltinoxide.

growing concern regarding the impact on the environment [Jones and Millson 1984]. A series of studies, which have been reviewed [Chliamowitch 1984, WHO 1980], demonstrate that low concentrations (ppt or ng/L) of tributyltin in aqueous environments may have adverse effects on sensitive stages of invertebrates as well as vertebrates.

Consequently, the use or emissions of tributyltins have been the subject of regulations in several countries, such as the UK, France, Switzerland and the USA. Concurrently, analytical methods for the specific and sensitive assays of tributyltin and its degradation products in environmental samples were developed.

ENVIRONMENTAL TOXICOLOGY

.butyltin is one of the few chemicals known to produce
:cific adverse effects on nontarget marine invertebrates.
:ause TBT is a slow-acting toxic compound, early toxicity
:ting based on standard protocols of short duration tests
.led to indicate these effects [Laughlin and Lindén 1987].
rever, since French and English biologists discovered the
)logical effects of TBT on the oyster fisheries close to yacht
:bours, toxicological studies on a variety of organisms have
:n carried out. It has been demonstrated that TBT, together
:h the methyltins and phenyltins, belongs to the most toxic
ranotin compounds [WHO 1980].

:eries of studies, which have recently been reviewed
ıliamovitch 1984, WHO 1980], demonstrate that low
ıcentrations [ppt or ng/L levels] of TBT in aqueous
'ironments may have adverse effects on sensitive stages of
'ertebrates as well as vertebrates. Laboratory as well as field
)eriments have shown that TBT is toxic towards protozoae
)shioka 1986], bacteria [Steinhäuser et al 1985; Augustin et al
)2; Argaman et al 1984] and algae [Blank et al 1984;
:inhäuser et al 1985; Walsh et al 1985; DOE 1986] down to
ıcentrations well below 100 ng/L.

a recent report to the EC [Meinema et al 1986] on evaluation
the impact of organotin compounds on the aquatic environment
was concluded that TBT and tributyltinoxide (TBTO] are toxic
a large variety of microorganisms, algae and plankton,
lluscs and crustaceans. The observed nontoxic level is
ıerally below 1 ug/L.

has also been reported that TBTO is toxic to fish. Generally,
TO shows a high toxicity to several freshwater and marine fish
:cies [Meinema et al 1986]. These include rainbow trout (Salmo
irdneri), bluegill (Lepomis macrochirus), guppy (Lebistes
:iculatus), goldfish (Carassius auratus), cichlids (Tilapia
lotica), striped bass (Morone saxatilis), atlantic menhaden
:evoortia tyrannus), mummichog (Fundulus heteroclitus), poacher
ıonus catophractus), sole (Solea solea), sheepshead minnow
/prinodon variegatus), bleak (Alburnus alburnus) and flatfish
itharichthys stigmareus). For example, the no-observed effect-
ıcentration (NOEC) for Salmo gairdneri is reported to be
.2 ug/L, the larval stadium being particularly sensitive.

:a also exist for toxicity of TBT to other aquatic animals.
gs and tadpoles of the frog Rana temporaria are sensitive to
TO. Furthermore, toxicity of TBTO to a polychaete worm and to
a urchin has been reported [Meinema et al 1986].

extensive review of the toxicity of TBT on mammalian animals
s given at a recent ORTEPA workshop [ORTEPA 1986, the
formation presented on that occasion will be published in the
ar future]. It is clear, however, that TBT exhibit moderate
xicity in acute and subchronic tests and that sublethal effects

may occur at low dietary levels. The acute oral LD50 for TBTO in rat applied in the diet or in vegetable oils is in the order of 150 to 250 mg/kg percutaneously [Duncan 1980]. A delayed toxic effect is reported in acute tests with many animals dying after a considerable loss of weight [Truhaut et al 1976]. TBTO aerosol inhalation causes death in guinea pigs within one hour at concentrations of 0.2 mg TBTO/L air [Meinema et al 1986].

Other toxic effects of TBT include atrophy of the thymus and peripheral lymphoid organs, depletion of splenic iron stores, erythrocyte rosettes in mesenteric lymph nodes, decreased pituitary-thyroid axis and increased LG immunoreactivity and secretion [Kranje et al 1984; Vos et al 1984]. Inhibition of neutrophil chemotaxis, inhibition of glutathione-S-aryltransferase from rat liver, inhibition of glucose-6-phosphate dehydrogenase, cell detachment of hamster kidney cells and brain ATPase [Meinema et al 1986, and references cited therein].

To the best of our knowledge, there is no conclusive evidence for mutagenic or carcinogenic action of TBT either by direct contact or via food, nor in relation with the presence of these compounds in water.

4. ENVIRONMENTAL FATE

4.1 Use pattern and releases into the environment (pathways and relative amounts)

One of the major pathways concerning the input of tributyltin compounds into the water is their use as biocide in antifouling paints. To be effective, continuous release of small amounts of tributyltin is necessary. To diminish the input of these substances into the environment, actions have been taken in several EC member states:

- antifouling paints have been modified so that the tributyltin compounds (TBT) are covalently bound; the release mechanism from these polymers is completely different (abrasion instead of leaching), thus the release on a mass versus time scale is no longer exponential but linear

- production or use restrictions

- deliberate renunciation by the formulating industry concerning the use of tributyltin monomers and the amounts of the copolymers in antifouling paints

Other uses of TBT as biocides which have not been considered as much until now are:

- in wood preservatives
- as bactericide in hospitals and stables
- as general biocide

The latter uses more or less result in emissions into the air during application or from treated surfaces despite the relatively low vapour pressures of TBT compounds (TBTO at 20°C $85 \cdot 10^{-6}$ Pa, Maguire et al 1983).

Since photochemical reactions are reported to be relatively fast, it is believed, however, that these will diminish the concentration of TBT in air appreciably. Additionally, airborne TBT can be washed out by precipitation processes, although TBT could not be measured in two rainwater samples from Switzerland at levels of 1 ng/l [Müller 1987a]. Thus, presence of TBT in air will be only of local interest.

There are no known uses of TBT resulting in a deliberate release to soil.

By far the largest amount of TBT used in the technosphere is released chemically unaltered into surface waters.

4.2 Reduction by sewage treatment

If the TBT released into water is subject to biological sewage purification (which only applies to most of the amount not used in antifouling paints), there is the chance for concentration reduction by adsorption or degradation. Due to the very low volatility of TBT compounds which is significantly smaller than that of water [Maguire et al 1983], stripping is of no relevance.

Adsorption of TBT onto surfaces eg onto activated sewage sludge is significant. Several literature values of measured n-octanol/water partition coefficients for tributyltin oxide and chloride are in the range between 1200 and 8000 [Maguire et al 1983; Laughlin et al 1986; Laughlin and Lindén 1987]. Therefore, TBT is expected to be enriched in sewage sludge, especially because degradation processes are slower under anaerobic than under aerobic conditions [WHO 1980].

Concentrations in activated sludges of two sewage treatment plants in Switzerland were in the range of 1 mg/kg dry weight, which is surprisingly high, a pooled sample of digested sludge contained about 0,2 mg/kg dry weight [Zingg 1985]. In industrial areas, the concentrations in sewage sludges may be even higher, the highest value being 6 mg/kg dry weight [Müller 1987a]. If polluted sludges are applied to soil, contamination problems have to be taken into account on a longer time scale, since TBT is extremely toxic to several classes of organisms which are essential for soil biocenoses and since the half-life in non-sterile soils is reported to be more than 100 days [Walsh et al 1985]. Furthermore, bound residues of TBT could be solved by complexing agents and reach the groundwater. Therefore, further research concerning this problem is urgently required.

Despite the relatively strong adsorption onto sewage sludge, a major reduction of TBT amounts in the sewage waters is not to be expected, since the mass of the solid phases is too low compared to the water phase.

Degradation of TBT in sewage plants takes place, but there is some doubt if the responsible processes will result in a significant reduction of TBT concentrations during normal operation conditions. While there is information that the degradation of other compounds is not inhibited below concentrations of 1 to 5 mg/l TBT [Augustin et al 1982], transformation of TBT was first observed after 290 days [Walsh et al 1985]. Conservatively ("on the safe side"), no significant degradation should be expected at all.

In summary, adsorption or degradation processes should not result in a significant decrease of TBT concentrations during sewage treatment.

Measurements at two Swiss sewage plants, where influent and effluent samples were taken at the same time (without a time-lag corresponding to the sewage residence times), showed influent to

luent ratios of 1.0 to 5.4 [Zingg 1985], which indicates th
hing to up to 80 percent of the TBT in the sewage is somehow
minated from the water phase during treatment, provided t
centrations do not change during the day, an assumption which
obviously not true. Therefore, no conclusions can be drawn
m these few measurements. Additional measurements are
essary to study the fate of TBT during sewage treatment.

Fate of TBT in the aqueous environment

.1 Concentrations in water

mentioned in chapter 4.2, TBT compounds are almost non-
atile from aqueous solutions, so that the environmental impact
restricted mainly to water, sediment and soil. Up to now,
re are not enough monitoring data to allow a Europe-wide
vey, but present data suggest that the mobility of these
stances in surface waters is sufficient to result not only in
al but in regional problems. According to the few data which
e been published yet, several surface waters in Switzerland
tain TBT in concentrations between 1 and 50 ng/l [Zingg 1985;
ler 1984; Müller 1987a], the higher values being in the range
sured for sewage plant effluents (20 to 64 ng/l [Zingg 1985;
ler 1987a]. Most of the coastal waters of Southwest England
o contain TBT at levels below 100 ng/l [Cleary and Stebbing
5]. In marinas and harbours of England and Denmark, however,
ıcentrations of up to 3000 ng/l have been measured [Cleary and
ıbbing 1985; Laughlin and Lindén 1987]; most of the values were
.ween 100 and 1000 ng/l [Laughlin and Lindén 1987]. These
'els often exceed the concentrations which have been found to
toxic towards aquatic organisms (10 to 1000 ng/l).

ı water solubilities of TBT compounds as they were determined
the laboratory strongly depend on pH values; at about pH 6,
ı lowest solubilities were measured (about 1 mg/l for TBTO and
'Cl), at pH 3 to 4 they increase to about 2 mg/l TBTCl and 10
'l TBTO, respectively [Maguire et al 1983]. At pH 8 to 10,
.ues of about 6 mg/l (TBTCl) and 15 to 30 mg/l (TBTO) are
›orted [Maguire 1983]. Thus, water solubilities of TBT
ıpounds are 3 to 5 orders of magnitude higher than toxic
ıcentrations.

general, the following mechanisms govern TBT levels in surface
:ers:

›hotolysis
legradation by microorganisms and algae
legradation by organisms of higher trophic levels
ıdsorption onto suspended solids and sediment

4.3.2 Photolysis and biological degradation

Photolysis is reported to be a major degradation pathway of TBT compounds. The transformation products are dibutyl- and monobutyltin as well as inorganic tin [Augustin et al 1982]. In seawater and estuaries, methyltin compounds are also reported to be formed.

When comparing laboratory studies with real field behaviour, one has to bear in mind that

- at a wavelength of 300 nm the intensity of sunlight is comparatively small, so that a half-life of about 1 day reported for the photolysis of TBTCl at this wavelength [Maguire et al 1983] is not representative.

- fulvic acids which are present in most surface waters enhance the photolysis rate at 300 nm and at 350 nm by a factor of 2 to 3.

Measured half-lives of TBTCl under artificial UV light range from 0.6 days at 300 nm in the presence of fulvic acids [Maguire et al 1983] to more than 18 days at 350 nm and 6 days in the presence of fulvic acids at the same wavelength, respectively [Maguire et al 1983]. In another study, the photochemical degradation rate of TBT under strong UV light is reported to be 7 days [WHO 1980].

TBT in natural and distilled waters irradiated by sunlight during summer (Burlington, Canada) [Maguire et al 1983; Walsh et al 1985; WHO 1980; Maguire and Tkacz 1985] was only slowly degraded with half-lives of up to 120 days. Other laboratory experiments irradiating TBT at concentrations in the ug/l-range in estuarine waters with sunlight resulted in half-life values of 4 to 15 days [Seligman et al 1986a,b; Lee et al 1987]. Similar half-lives of 5 to 19 days have been estimated for the degradation of TBT in an enclosed coastal ecosystem [Hinga et al 1987]. It has been shown that the biodegradation of TBT in estuarine waters at temperatures corresponding to winter conditions is slow (half-life <30 days), while at 23 °C the half-lives where in the range of two to four weeks in the dark and one to two weeks under artificial light [Olson and Brinckman 1986].

When data from laboratory experiments are extrapolated to naturally occurring photolytic or photochemical processes, it should be realized that these reactions can only occur within the upper 2 m of water. Below that limit, the light intensity is too low. Degradation processes of organic substances in river waters mainly take place at the so-called "Aufwuchs", i.e. a litoral zone on the banks where the abundance of degrading organisms is greatest.

Thus, transformation by microorganisms in estuarine and coastal waters is possible, but occurs only with moderate to slow rates, at least at low temperatures like in winter. The degradation is

accelerated by the influence of light. The degradation half lives are in the range of some weeks and hence may often not compete with adsorption.

The transformation of TBT by large numbers of algae seems also to be an effective biodegradation process [Maguire et al 1984; Lee et al 1987], with a half-life reported to be 25 days [Maguire et al 1984], resulting mainly in dibutyltin . Degradation by organisms of a higher trophic level are not believed to play an important role due to their relatively low abundance in natural waters.

4.3.3 Adsorption and Accumulation

Due to the medium range water solubility and the tendency of TBT compounds to adsorb onto solid surfaces (see chapter 4.2), these substances will be found in the solubilized form as well as adsorbed onto suspended particles. They tend to settle with these particles resulting in enhanced sediment concentrations.

The degradation of TBT compounds in the partly anaerobic sediment is believed to be negligible since transformation processes under such conditions are reported to be even slower than aerobic transformation processes [Blunden and Chapman 1982]. The biological degradation of TBT by oligochaetes [Maguire and Tkacz 1985] cannot account for a quantitatively relevant amount. In accordance with this, concentrations up to several mg per sediment have been reported in yacht habours, where usually TBT containing antifouling paints are used, and in adjacent estuaries. Concentrations in adjacent or remote areas of Swiss lakes are reported to range between 0.002 and 0.28 mg/kg dry weight [Müller 1984, 1987a].

The most polluted areas, i.e. estuaries, are in particular those places where most of the millions of tons of dredged material are dredged and to a major part again released to the water or banks nearby. The dredging is necessary to keep the waterways clear from settled sand and sediment, and, for economical reasons, this material is only partly deposited on land. The possible remobilisation of TBT during the dredging operations and subsequent damage of aquatic organisms has to be regarded carefully, especially when the extreme toxicity is taken into account. Monitoring of sediments to be dredged, especially of the small particle fractions, is therefore strongly advised.

If the dredged material is disposed of on land, its agricultural use may be limited - among others - by the concentration level of TBT.

Bioaconcentration of TBT has been shown for several aquatic species. Measured values are much higher than calculated from the octanol/water partition coefficient. They range from 1000 to above 10 000 for macroorganisms [Laughlin and Lindén 1987] and 30 000 for algae and bacteria [Laughlin and Lindén 1987]. These

high concentration factors may result in bioaccumulation along the food chain.

4.4 Conclusions

In summary, the reduction of TBT levels in sewage plants is not well documented; high levels in some sewage sludges indicate that biological degradation is of minor importance.

Concentrations of TBT in surface waters are often higher than concentrations which have been shown to be toxic to aquatic organisms.

The overall photochemical and biological degradation half-lives of TBT compounds in the environment can be given by one to three weeks under optimum conditions (upper 2 m sunlight, near Aufwuchs, no sedimentation).

This means that TBT once released to surface waters is either buried in the sediment until it happens to be remobilized by dredging or high water, or the major portion is washed to the sea before it can be degraded (travel time down the Rhine river, e.g., one to three weeks), or it is released directly into the sea from antifouling paints.

Areas of concern are

- sewage treatment
- soils applied with contaminated sewage sludges
- freshwater and estuarine water near point releases like sewage plant outlets, if TBT compounds are released by uses other than antifouling paints for marine ships
- freshwater and estuarine sediments (condition like above), especially before dredging
- seawater
- marine and coastal sediments

5. DETERMINATION OF BUTYLTIN COMPOUNDS IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES

5.1 Introduction

The progress made in this field is reflected in the growing number of references contained in review papers which appeared in the last few years [Chapman 1983, Mushak 1984, Riggle et al 1978, Blunden 1986]. The toxicity and environmental behaviour of the various butyltins is drastically different- tributyltin is the most toxic to aquatic organisms and inorganic tin(IV) has low toxicity [Chliamovitch 1984, WHO 1980]. Therefore, the ecotoxicological risk assessment and the search for sources of pollution etc. have to rely on data of trace level concentrations of specific butyl tin compounds (butyltin speciation). Non specific data, e.g. on total organic bound tin, are not adequate for this purpose.

There is now a range of methods for specific and sensitive butyltin speciation available. Interlaboratory comparisons have shown that several approaches may be used [Blair et al 1986, Stephenson et al 1987], and that each method has to be carefully checked and evaluated with respect to its drawbacks and shortcomings. Nevertheless, there seems to be a general agreement on implementing an efficient chromatographic separation step in combination with a specific and sensitive detection method into the procedure.

The methods of choice are in general gas chromatography (GC, preferably high resolution capillary GC, HRGC) or high performance liquid chromatography (HPLC). These separation techniques usually define sample preparation (by the mode of sample introduction) as well as the choice of detection methods available. Therefore, methods will be grouped into sections concerning procedures using GC, HPLC, and others (low resolution or non-chromatographic methods such as hydride generation with purge and trap).

5.2 Butyltin specification using gas chromatography

This section is grouped into subsections on sample preparation, derivatization and detection. All papers from this section are summarized in Table 1.

5.2.1 Liquid and solid phase extraction

In trace level determination of butyltin species using GC, a separation of the compounds of interest from the matrix, concentration and in most cases also a derivatization is required.

TABLE 1. Butyltin speciation using gas chromatography

Butyltins determined[a]	Matrix	Method[b]	LOD[c]	Reference
Bu_1 - Bu_2 - Bu_3Sn^+	Fresh sea water	Hydride generation purge LRGC-AAS	0.1-2 ppb	Donard 1986
Bu_2Sn - Bu_3Sn^+	Sea watersediment	Acid extraction followed by hydride form. LRGC-ECD	400 ppt	Hattori
Bu_2 - Bu_3Sn+ - Bu_4Sn	Sea water	Hydride formation extraction LRGC-FPD	20-30 ppt	Hall 1987
Bu_3SN^+	Sea water	Solid phase extraction HRGC-ECD		Junk 1987
Bu_1Bu_2 - Bu_3Sn^+	Sea water, sedim.	Extraction pentylation GC-PFD	4 ppt (as Sn)	Maguire 1986 (1981-1986)
Bu_1Bu_2 - Bu_3Sn^+	Water, sediment	Extraction-hydride generation LRGC-FPD	5 ppt	Matthias 1987
Bu_1Bu_2 - Bu_3Sn^+	Sea water	Extraction-methylation, LRGC-MS	10 ppt	Meinema 1978
Bu_1Bu_2 - Bu_3Sn^+	Sea water	Autom. hydride gener. purge/trap PRGC-AAS	low ppt	Michel 1987
Bu_3Sn^+	Biota	Acid extr., alumina clean-up LRGC-ECD	50 ppb	Moriyama 1986
Bu_1Bu_2 - Bu_3Sn^+	Fresh water, sew. sludge, sediment	Extraction, ethylation HRGC-FPD, GC-PCI-MS	1 ppt	Müller 1987
Bu_3Sn^+	Sea water, sedim.	Acid extraction, LRGC-ECD	100 ppt	Takahashi 1987
Bu_2 - Bu_3Sn^+	Biota	Cation exchange solid phase extr. hydride gener. GC-ECD	8 ppb	Takami 1987
Bu_3Sn^+	Biota	Acid extraction LRGC-ECD after Florisil clean-up	0.5 ppb	Takeuchi 1987
Bu_3Sn^+	Biota	Acid extraction, LRGC-ECD	10 ppb	Tsuda 1987
Bu_2 - Bu_3Sn^+	Sea water	Extraction, hexylation, HRGC-AAS	5 ppt	Unger 1986
Bu_2 - Bu_3Sn^+	Sea water	Hydride generation purge/trap LRGC-AAS	5 ppt	Valkirs 1987
Bu_2 - Bu_3Sn^+	Water	Hydride generation HRGC-AAS	10 ppb	Woolins 1984
Bu_2 - Bu_3Sn^+	Waste water	Extraction, methylation HRGC-EI MS	100 ppt	Zuetz 1987

[a] Bu- means $BuSn^{3+}$, Bu_2- Bu_2Sn^{2+}; [b] for abbreviations cf. section 3.
[c] values are in general given for Bu_3Sn^+-determination in water unless stated otherwise.

Butyltins may be extracted out of environmental samples (water, sediment, sludge, biota) using appropriate solvents or solid-phase extraction. Silica material modified with C_{18} groups was used alone [Matthias and Bellama 1987, Junk and Richard 1987] or loaded with a complexing agent [Müller 1987a] and was found to be well suited for aqueous samples. A cation exchange material containing sulfonyl groups was used to adsorb butyltin residues contained in digested fish tissue [Takami et al 1987], followed by hydride forming. Poropak was used to sample butyltins in air, followed by elution and methylation [Zimmerli and Zimmermann 1980].

The extraction behaviour of the ionic butyltins and inorganic tin(IV) was investigated by the group of Meinema and his colleagues [Meinema et al 1978]. They used various organic solvents, which do not mix with water, with the addition of mineral acid and complexing agents to extract butyltins fromaqueous solutions and found tropolone (a hydroxy-cycloheptatrienone) to be best suited for extraction of all butyltins, combined with methylation by the Grignard reagent MeMgBr and GC/MS analysis. In this way, mono- to trisubsti- tuted butyltins and inorganic tin(IV) can be determined simultaneously. This extraction has in the meantime been used and successfully evaluated by several groups [Maguire et al 1981, 1982, 1983, 1984, 1985, 1986, Müller 1987a, Unger et al 1986, Zingg 1985, Zietz and Haag 1987].

5.2.2 Derivatization by alkylation vs. GC of free halogenides

The extraction step after addition of hydrobromic or hydrochloric acid leads to an a organic solution of butyltins as their halogenides. Whereas Bu_2SnX2 and Bu_3SnX (X: bromide or chloride) are sufficiently volatile for GC-determination, Bu_2SnX2 and BuSnX3 show pronounced adsorption and reactivity in the GC system and are therefore difficult to be determined.

Nevertheless, a series of papers, mainly from japanese authors, report (partly in japanese) on tributyltin detection as free halogenides (sea water [Junk and Richard 1987, Takashi 1987] sediment and biota [Tsuda 1986, Takeushi 1987, Moriyama 1986, Tsuda 1987]). The procedures suggested base mainly on acid/base treatment of the matrix, extraction of TBT as chloride and clean up via acid treated adsorption material. Determination is by packed column GC with electron capture detection (ECD). In general, this method is adequate for TBT-residue determination in biota, but limits of detection are rather high (cf. also section 4.2.4 Specific detectors). As the chromatographic resolution achieved with the free halogenides on packed columns is poor and interferences from coextracted material were observed even on capillary columns [Junk and Richard 1987], this approach seems to be less favorable.

The butyltin halogenides, present in an organic solvent, are easily converted into the corresponding tetrasubstituted

butylalkyltin compounds by means of either a Grignard reagent or an alkyllithium compound [Coates and Wade 1980]. The alkylation reaction proceeds smoothly and goes to completion when carried out in a suitable solvent, e.g. diethylether or tetrahydrofuran. Tetraalkyltins are much easier to handle with respect of sample clean up and GC determination than the respective halogenides. This approach was used in a series of papers with various alkylating agents.

Methylation was used by various groups [Meinema 1978, Zimmerli 1980, Müller 1984, Zingg 1985, Zietz 1987], ethylation [Müller 1987a], pentylation [Maguire 1981 - 1986] and hexylation [Unger 1986] were used as well. The choice of the alkyl group to be introduced is not very critical. Butylation is excluded, as the alkyl group introduced must be different from those already present at the tin atom. The size of the alkyl group introduced defines the volatility of the derivatives. Methylation is not advisable when environmental methylation of butyltins has also to be taken into account [Tugrul et al 1983]; larger alkylgroups than butyl invert the order of elution in GC (e.g. $BuSnHex_3$ elutes latest, Bu_3SnHex elutes first) which in some cases may not be desirable.

5.2.3 Hydride generation prior or after extraction

Tin and alkyltin compounds readily form the respective hydrides [Cotton and Wilkinson 1974]. The reaction proceeds in aqueous solution with sodium borohydride as reagent and leads to neutral, apolar and volatile tinhydride species. These compounds can be extracted from the reaction solution and analyzed by GC using various detector systems (cf. section 4.2.4).

Similar to the halogenides, the hydrides show a sufficient response with the ECD [Hattori et al 1984, Tsuda et al 1986]. The method was modified and applied by several groups [Valkirs et al 1986, Valkirs et al 1987, Donard et al 1986, Hall et al 1987, Takami et al 1987] for the examination of residues in sea water, sediment and biota.

Some methods are based on hydride formation in the extract [Tsuda 1986, Matthias and Bellama 1987] or in the solid phase extraction material [Takami et al 1987]. The advantage of the in situ derivatization is that extraction of the butyltins, which may be critical, is circumvented. The method works well for surface water samples, but requires careful sample pretreatment, when sediment or sewage sludge samples are to be analysed [Hattori 1984] due to strongly adsorbed butyltin species.

This problem exists also in surface water samples, where there is a part of butyltins present which is not converted to hydrides [Tsuda et al 1986]. This is explained by butyltins adsorbed on particles, thus shielding the organotins from being converted. This is less encountered when organic solvents or solid phase extraction is used, as the particles are also extracted either by

the organic solvent in the aqueous phase or on the adsorption material. Therefore, filtering off the particles before water analysis is rarely reported.

Butyltin hydrides are considered to be less stable than the tetraalkyltins because they possess reducing properties [Cotton 1974, Unger 1986]. This may be a drawback when clean up or repeated injections (e.g. using different detection systems) are to be carried out. The volatilities of these compounds are considerably higher as compared to e.g. the ethylation product of $BuSn_3^+$, $BuSnEt_3$, so that losses in evaporation steps may occur.

Hydride generation seems to be a highly attractive method for butyltin speciation in surface water samples, allowing simultaneous determination of all butyltins. Furthermore, this method may easily be automatized for routine monitoring of environmental pollution [Michel 1987].

5.2.4 Gas chromatography with specific detectors

The use of the flame photometric detector (FPD) for the sensitive and specific determination of organotin compounds in a hydrogen rich flame has been described by Aue and Flinn [1977]. The detector performance (sensitivity, chromatographic signal shape) is strongly dependent on gas flows, which have to be carefully optimized [Müller 1987a]. A series of publications make use of this relatively inexpensive and simple detector, also in combination with other detection methods (cf. Table 1).

Interfering signals in the gas chromatogram, presumably from coextracted organic phosphates, can be circumvented by the use of an optical filter positioned between the detector cell and the multiplier; however these filters (if available) reduce sensitivity from typically low pg to ng-range [Zimmerli and Zimmermannn 1980]. The dynamic range is good to excellent, but the system is sensitive to injections of high amounts (ng or more) of organotins. A decrease in detector performance ("poisoning") is then observed; a phenomenon which occurs also in the optical cell of a GC/atomic absorbtion spectrometer (GC/AAS) combination [Maguire 1983] and which requires comparably frequent cleaning.

The use of a mass spectrometer as a selective detector for GC (either packed column or capillary column) has been applied to the detemination of butyltins. Both electron impact (EI) ionization [Meinema 1978 et al, Zietz and Haag 1987] and positive ion chemical ionization (PCI) [Müller 1987a, Unger et al 1986] have utilised. As butyltins undergo extensive fragmentation under EI-conditions [Gielen and Mayence 1972] and the ion current distributes on the complex tin isotopic cluster, EI-MS seems to be less favorable and more prone to interferences than the FPD or AAS. PCI with methane as reactant gas was found to be more sensitive and yielding simpler mass spectra for organotin compounds [Fish et al 1974]. Furthermore, numerous coeluting

compounds are virtually transparent under CI-conditions, thus enhancing butyltin detection. In multiple ion detection (MID) either in the EI or CI mode, one has to consider the complex isotopic pattern of tin. As in the mass range of interest (200 - 400 amu, depending on the alkyl group or hydrogen introduced in the derivatization step) numerous substances may interfere, at least three signals in the ion cluster of each fragment of interest have to be observed for confirmation purposes. This leads to a significant reduction in the inherent high sensitivity of MS/ MID detection. Nevertheless, MS is a valuable tool in the identification and confirmation of organotin compounds detected in environmental sample extracts.

Atomic absorption spectrometry (AAS) has proved to be a very sensitive and specific detection method for organotins. It may be regarded as a drawback that no commercial interface exists for the combination of the GC with the AAS [Forsyth 1987]. This interfacing has to be done very carefully in order to fully maintain the high separation power of HRGC, because the optical cell in the spectrometer may contribute significantly to chromatographic signal broadening.The excellent detection limits, large dynamic range and chromatograms free of interfering signals are highly attractive features of a GC-AAS combination [Maguire et al 1983].

Electron capture detection (ECD) was used for detection of free halogenides [Junk and Richard 1987, Takeushi et al 1987, Moriyama et al 1986] and hydrides of the butyltins [Takami et al 1987]. This detector possesses sufficient sensitivity, is easy to handle, but offers insufficient specificity for the organotins in the trace level concentration range as compared to the FPD, AAS or MS. The occurrence of interfering signals in the gas chromatogram is highly expectable due to coextracted material with strong ECD-response. Tetraalkyltins cannot be detected using the ECD [Müller 1987b].

Beside AAS, inductively coupled plasma emission (ICP) was used in combination with GC [Deubelbeis et al 1986]. ICP offers high sensitivity together with multi-element capability, but instrument costs are considerably higher than for AAS. Whereas flame ionization detection is not sensitive and rather unspecific for organotins, the quenching of an FID was used for detection of alkyltins [Hansen et al 1985]. Experiences using this detection technique are too sparse to make a judgement.

5.3 High performance liquid chromatographic methods

HPLC methods offer the advantage of the separation of underivatized butyltins, but suffers from a lack of established, sensitive and specific detection techniques which are available for GC. These techniques (AAS, FPD, MS) are predominantly gas phase methods and are easily coupled with gas chromatography. The liquid effluent of a HPLC column has to be modified by more or

less sophisticated procedures to b ompatib with th techniques. Unfortunately, minimal detectable amounts for such combinations as reported for a HPLC-AAS interface [Burns et al 1981] are higher by several orders of magnitude as compared to the combination GC-AAS or GC-FPD [Maguire et al 1983b]. Direct coupling of an ion-exchange HPLC with a graphite furnace AAS in a non-continuous mode [Jewett and Brinckman 1981] showed a comparably low resolution and sensitivity.

As the low UV-absorbance of butyltins prevents their direct photometric detection, HPLC methods have to rely on pre- or postcolumn reaction.

Morin, a hydroxyflavone, forms fluorescent derivatives with ionic alkyl- and phenyltins in postcolumn reaction, rendering these compounds detectable at the low pg-level [Blair et al 1987, Yu and Arakawa 1983; Langseth 1984].

HPLC using a post-column reaction with oxin and photometric detection [Lakata et al 1984] was described. But up to now, these techniques have not been adapted for routine analysis of butyltins in environmental samples. This may be due to the fact, that these sensitive HPLC methods require careful sample preparation procedures to maintain the optimal conditions for pre- or postcolumn reaction with the chromophore. One can therefore conclude that HPLC can separate and detect butyltin species with sufficient sensitivity and specificity, but sample preparation and detection methods are tedious and require careful adaptation to make them work with real environmental samples. The HPLC methods seem to be well suited for special applications, e.g. organotin determinations in toxicological experiments [Yu and Arakawa 1983] or assays of organotin stabilizer migrations [Koch and Figge 1975]. However, at present they seem less adequate for trace level detection of butyltins in environmental samples.

A recent publication [Irth et al 1987] on a sensitive and specific HPLC method based on a pre-column adsorption of trace metals in water samples as carbamates followed by chromatographic separation indicates that the potentialities of LC methods are not yet fully exploited. Liquid chromatography may also be a valuable tool in the investigation of the various forms of butyltins in the environment: Laughlin followed the conversion of Bu_3Sn^+ into sulfides and oxides using HPLC [Laughlin et al 1986].

5.4 Other methods

Thin-layer chromatographic methods were, from a historical point of view, the first steps towards butyltin speciation. As the separation efficiency is relatively low (typically 1 000 plates) compared with HPLC (typically 10 000 plates; HRGC: 50 - 100 000 effective plates), Therefore, sensitivity and specificity are

considered to be insufficient for trace analysis of butyltins [Meinema et al 1978, Koch and Figge 1975].

Hydride generation in aqueous solution followed by purge and trap was used for methyl- and butyltin determination [Hodge et al 1979, Donard et al 1986, Randall and Weber 1986]. The method is well suited for determination of methyltins, but of limited value for butyltins. $BuSnH_3$ is sufficiently volatile for being purged out of an aqueous solution, but the purging efficiency decreases further from Bu_2SnH_2 to Bu_3SnH. The hydrides evaporate from the cold trap (after removal of the liquid nitrogen) into the optical path of an AAS system. This distillation provides an insufficient time resolution of the butyltin hydrides. Hydride generation followed by liquid extraction (cf. section 5.2.) is therefore to be preferred.

A series of papers dealing with the non-chromatographic determination of single butyltins have also been published. In most cases, combinations of various extraction and liquid/liquid partition steps together with a fluorometric [Arakawa et al 1983] or AAS detection steps [Apte and Gardner 1987, Pinel et al 1986, Parks et al 1985] were used. Limits of detection achieved range from ppm to ppb-range , but in most cases interferences from closely related organotins or other coextracted material seem to be insufficiently checked. This holds also for single-species electrochemical methods such as anodic stripping voltammetry [Kenis and Zirino 1983], where other organotin compounds may have similar electrochemical potentials. Nevertheless, these methods may be valuable in combination with specific methods, as they are fast, inexpensive and usually require minimal sample preparation. Total tin methods [Short and Thrower 1986] also belong to this category of methods, which do not meet the requirements for butyltin speciation.

5.5 Limits of detection precision and accuracy, intercalibration tests, standard materials.

5.5.1 Limits of detection, precision and accuracy

As in general, limits of detection (LOD) of the methods summarized in section 3.2. and 3.3 and Table 1 are defined by
- the absolute sensitivity of the detection system

- the aliquot of sample which can be introduced into the separation system.

- eventual chemical interferences which limit quantitation (or the specificity of the detection system)

LODs have to be distinctly lower than no-adverse-effect- levels of Bu_3Sn^+ for aquatic organisms [Chliamovitch 1984], if possible low enough to determine background levels for localisation of sources of pollution. This level can roughly be fixed in the low ng/l-concentration range for surface water and is met as well

using the hydride generation and extraction/ alkylation approach (cf. Table 1).

The accuracy can, of course, only be assessed using certified standard materials as distributed by the organizing laboratories of interlaboratory comparisons.

The corresponding LODs for determination of butyltins in more complex matrices (sediments, sludge of biological material) are considerably higher than in surface water samples (ppb/ppm or ppt, respectively). The residue levels generally encountered in these samples follow a similar trend [Maguire et al 1986, Müller 1987a]).

5.5.2 Accuracy, interlaboratory comparisons

Three interlaboratory tests were carried out on butyltin speciation in the last few years. The results of two tests are available. W.R. Blair at the NBS very carefully organized a test in 1984 on butyltin speciation at the 100 ppt-level without specifying a method. A total number of 27 labs cooperated. The results show that good to excellent precision and accuracy may be achieved using different approaches [Blair et al 1986].

Recently, a second test was carried out with the aim of simultaneous speciation of Bu_2Sn2+, Bu_3Sn+ and Bu_4Sn at levels of total 100 - 300 ng/l. Results of this test are expected to be available in the near future.

Another interlaboratory comparison for butyltin speciation in sediment material and mussel tissue with 7 laboratories cooperating was organized by the group of M. Stephenson [Stephenson et al 1987]. Data reported agree within a factor of 2 to 3 for Bu_3Sn+ determinations (at levels of several hundred ppb for sediment and a few ppm for mussel tissue). Standard deviations for Bu_2Sn2+ were, if reported, considerably higher.

5.5.3 Standard Material

There is still a lack of high purity standard material (99.9% or better) of butyltin compounds. In most cases, purity is determined by AAS and does not exceed 95 %.

Whereas many authors report on methods and data relying on external standardisation, there is a growing interest in the use of internal standards. Pe_3Sn+ [Unger et al 1986] and $HexBu_2Sn+$ [Müller 1984, 1987a] were used as internal standards, added prior to sample preparation. Internal standards are usually homologues of Bu_3Sn3+, which is the most toxic of the butyltins. If detection of all ionic butyltins is required, the addition of corresponding homologues (e.g. $PrSn_3+$, Pr_2Sn2+ and Pr_3Sn+) would be advisable.

The possibilities of using stable, labelled compounds as surrogates for butyltins are rather limited, as they would require the use of a mass spectrometer for detection. Furthermore, possible mass spectral interferences have to be carefully considered. The complex isotopic pattern of tin (m/z 116 to 126) requires the complete separation of the strategic mass spectral fragments produced by the labeled surrogate from those of the native compound. This can not be achieved by using a labeled tin, as there exists no stable tin isotope with a mass higher than 124 amu [Weast 1979].

The radioactive isotop ^{113}Sn was used for elucidation of the environmental fate of TBT in an enclosed ecosystem [Hinga et al 1987]. Its use for routine analysis can, of course, not be recommended, as butyltin speciation calls for detection of specific butyltin compounds.

5.6 Conclusions

Butyltin speciation means determination of specific butyltin compounds in environmental samples or biota. It can be carried out by separation of the butyltins from the matrix and separation of the various butyltin species using an efficient chromatographic step and specific detection.

The methods of choice are either extraction/alkylation or hydride generation/extraction followed by high resolution GC. Detection methods are either AAS, FPD or MS in the PCI-mode. These methods are shown to be adequate in terms of specificity, limits of detection, as well as of precision and accuracy.

Butyltin speciation at trace levels is, however, a demanding task calling for specialized, experienced laboratories with skilled personnel and good equipment. There are several laboratories which carry out butyltin determinations on a routine base [Blair et al 1986]. The two main approaches (extraction/alkylation or hydride generation) seem to be more or less equivalent in their performance. Extraction/alkylation is more universally applicable than hydride generation and may therefore be considered as more favorable for a monitoring programme covering a wide range of matrices.

CONCLUSIONS AND RECOMMENDATIONS

The high toxicity of TBT towards aquatic organisms is well documented. As far as environmental regulations are concerned further toxicity testing is presently not required.

Triphenyltin is used as a substitute for TBT in several applications. The toxicity of triphenyltin is also well documented and comparable to that of TBT. Its use should therefore also be restricted.

Data indicate that there are differences in the use patterns between various countries. To provide a basis for regulations, country specific assessments of sources other than antifouling paints are therefore recommended.

The few data available on TBT residues in sewage sludge indicate a high degree of contamination. Further studies on levels, fate and ultimate degradation in sewage treatment plants are recommended.

The environmental impact of using TBT contaminated sludge in soil amendment should be studied.

There is a lack of knowledge concerning TBT levels in fresh waters, estuaries, river water, and sediment and biota in contact with these waters. Measurements are strongly recommended in order to determine the present environmental concentrations, to study changes in concentration with time and for identification of potential new sources of TBT.

TBT has a long half-life time under anaerobic conditions in sediments (months to years). However, TBT may be remobilized when sediments are dredged. The environmental impact of such remobilization should be studied.

Degradation pathways of TBT in the aquatic environment are well known. Properties of degradation products, e.g. toxicity and physico-chemical data are sufficiently established. Further studies on degradation in the aquatic environment are presently not recommended.

Volatilization of TBT from water is negligible. Photolytic degradation in the atmosphere is rapid. This indicates that air is not an important vector for TBT distribution in the environment. Further studies are not recommended.

TBT and other organotin compounds are bioavailable. Observed bioconcentration factors (~ 10 000) are higher than estimated from octanol/water partition coefficients. Bioconcentration should be considered when evaluating the environmental hazards for higher trophic levels.

11. Analytical methods are available for the determination of TBT and its degradation products at trace levels. The preferred method is presently gas chromatography combined with a highly sensitive and specific detector. Further research is not recommended.

12. Laboratories determining TBT and other organotin compounds should have quality assurance of their methods, e.g. participation in interlaboratory tests.

13. When TBT is determined it is recommended also to include determination of its degradation products and other organotin compounds, e.g. triphenyltin whenever possible.

7. REFERENCES

Apte S.C.; Gardner M.J.: Determination of organotins in natural waters by toulene extraction graphite furnace. Report PRU 1577-M, Water Research Center, GB (1987).

Arakawa Y.; Wada O.; Manabe M.: Extraction and Fluorometric Determination of Organotin Compounds With Morin. Anal. Chem. 55 (1983) 1901 - 1904.

Argaman Y.; Hucks C.E.; Shelby S.E.Jr.: The Effects of Organotin on the Activated Sludge Process. Water Res. 18 (1984) 535.

Aue A.W.; Flinn C.G.: A Photometric Tin Detector for Gas Chromatography. J. Chromatogr. 142 (1977) 145 - 154.

Augustin Bauer U. Bessems Bestmann, Botzenhart, Dietz, Genth, Gerike, Jung: Mikrobiozide Wirkstoffe als belastende Verbindungen im Wasser. Vom Wasser 58 (1982) 297.

Barug D.; Vonk J.W.: Studies on the Degradation of Bis(tributyltin) Oxide in Soil. Pestic. Sci. 11 (1980) 77-82.

Blair W.R.; Olson G.J.; Brinckman F.E.; Paule R.C.; Becker D.A.: "An International Butyltin Measurement Methods Intercomparison, Sample Preparation and Results of Analyses" U.S: Nat. Bureau of Standards, NBSIR 86-3321, 1986.

Blair E.J.; Parks E.J.; Olson G.J.; Brinckman F.E.: Characterizaton of Organotin Species using Microbore and Capillary Liquid Chromatographic Techniques with an Epifluorescence Microscope as a Novel Imaging Detector. J. Chromatogr. 410(1087) 383-394.

Blanck H.; Wallin G.; Wängberg S.-A.: Species-Dependent Variation in Algal Sensitivity to Chemical Compounds. Ecotox. Environ. Safety 8 (1984) 339.

Blunden S.J.; Chapman A.H.: The Environmental Degradation of Organotin Compounds - A Review. Environ. Technol. Lett. 3 (1982) 267-272.

Blunden S.J.; Chapman A.: "Organotin Compounds in the Environment", in Organometallic Compounds in the Environment", 1986 Longman, p. 111 - 159.

Burns D.T.; Glockling F.; Harriott M.: Investigation of the Determination of Tin Tetraalkyls and Alkyltin Chlorides by Atomic-Adsorption Spectrometry After Separation by Gas-Liquid or High-Performance Liquid-Liquid Chromatography. Analyst 106 (1981) 921 - 930.

Chapman A.H: Determination of organotin compounds in waterways and seaways. Anal. Proc. 20 (1983) 210 - 212.

Chliamovitch Y.P.: L'Etain, les Organo.tains et l'Environnement (1984) Travail Bibliographique, Fed. Office for Environmental Protection (OPFE) Berne.

Cleary J.J.; Stebbing A.R.D.: Organotin and Total Tin in Coastal Waters of Southwest England. Marine Pollut. Bull. 16 (1985) 350.

Coates G.E.; Wade K.: "The main group elements" in "Organometallic Compounds", (Coates G.E.; Green M.L.H.H.; Wade K. Eds), Methuen, London, 1980, p. 413 - 482.

Cotton A.F.; Wilkinson G.: Advanced Inorganic Chemistry, John Wiley, (1974) p. 309.

Department of the Environment (DOE) - Central Directorate of Environmental Protection: Organotin in Antifouling Paints - Environmental Considerations. Pollution Paper No. 25. Publisher: Her Majesty's Stationery Office, London (1986).

Deubelbeis D.O.; Kapila S.; Yates D.E.; Manahan S.E.: Gas chromatographic-inductively coupled plasma emission spectrometric determination of volatile organometallic species. J. Chromatogr. 351 (1986) 465 - 473.

Donard O.F.X.; Rapsomanikis S.; Weber J.H.: Speciation of inorganic tin and alkyltin compounds by atomic absorption spectrometry using electrothermal quartz furnace after hydride generation. Anal. Chem. 54 1986 777-781.

Duhamel K; Blanchard G.; Dorange G.; Martin G.: Etude systematique des produits de degradation photolytique des composes du tributyletain. Appl. Organometall. Chem. 1 (1987) 133-142.

Duncan J: The toxicology of molluscicides. The organotins. Pharmacol. Ther. 10 (1980) 407-429.

Fish R.H.; Holmstead R.L.; Casida J.E.: Chemical ionization mass spectrometry of organotin compounds. Tetrahedron Letters 14 (1974) 1303 - 1306.

Forsyth D.S.: Design and evaluation of a capillary gas chromatography-atomic absorption spectrometer interface. Anal. Chem. 59 (1987) 1742.

Gielen M.; Mayence G.: Organometallic compounds. XXXVII*. Mass spectra of mixed tetraalkyltins and of trimethyltin halides. J. Organomet. Chemistry 46 (1972) 281 - 288.

Gächter R.; Müller H.: Taschenbuch der Kunststoff-Additive, Stabilisatoren, Hilfsstoffe, Weichmacher, Füllstoffe, Verstärkungsmittel. Carl Hanser Verlag München Wien, 1979.

Hall L.W.Jr.; Lenkevich M.J.; Hall W.S.; Pinkney A.E.; Bushong S.J.: Evaluation of butyltin compounds in Maryland waters of Chesapeake Bay. Mar. Poll. Bull. 18 (1987) 78 - 83.

Hansen D.R.; Lillie C.H.; Hill H.H. Jr.: Detection of organotins after gas chromatography by flame ionization-quenching. J. Chromatogr. Science 23 (1985) 208 - 213.

Hattori Y.; Kobayashi A.; Takemoto S.; Takami K.; Kuge Y.; Sugimae A.; Nakamoto M. J.: Determination of trialkyltin, dialkyltin, and triphenyltin compounds in environmental waters and sediment. Chromatogr. 315 (1984) 341 - 349.

Hinga K.R.; Adelman D.; Pilson M.E.O.: Radiolabeled Butyl Tin Studies in the MERL Enclosed Ecosystems. Oceans 87 Proc.: The Ocean - An International Workplace. Vol. 4: Int. Organotin Symp., Halifax, Nova Scotia, Canada, Sept. 28 - Oct. 1 (1987) 1416-1419.

Hodge V.F.; Seidel S.L.; Goldberg E.D.: Determination of tin (IV) and organotin compounds in natural waters, coastal sediments and macro algae by atomic absorption spectrometry. Anal. Chem. 51 (1979) 1256 - 1259.

Irth H.; de Jong G.J.; Brinkman U.A.Th.; Frei R.W.: Anal. Chem. 59 (1987) 98 - 101.

Jewett K.L.; Brinckman F.E.: Speciation of trace di- and triorganotins in water by ion-exchange HPLC-GFAA. J. Chromatogr. Sci. 19 (1981) 583 - 593.

Jones P.A.; Millson M.F.: Organotins in the Canadian Environment: A Synopsis, Environment Canada (1984).

Junk G.A.; Richard J.J: Solid phase extraction, GC separation and EC detection of tributyltin chloride. Chemosphere 16 (1987) 61 - 68.

Kenis P.; Zirino A.: Quantitative measurement of tributyltin oxide in sea water by differential pulse anodic stripping voltammetry. Anal. Chimica Acta 149 (1983) 157 - 166.

Koch J.; Figge K.: Zur analytik von methylzinnstabilisatoren. J. Chromatog. 109 (1975) 89 - 100.

Kraine E.I.; Wester P.W.; Loeber J.G.; vanLeeuwen F.X.R.; Vos J.G.; Vaessen H.A.M.G.; van der Heijden C.A.: Toxicity of bis(tri-n-butyltin)oxide in the rat. I. Short-term effects on general parameters and on the endocrine and lymphoid systems. Toxicol. Appl. Pharmacol. 75 (1984) 363-386.

Lakata W.G.; Lankmayr E.P.; Müller K.: Speciation of organotin compounds by complex chromatography and reaction detection. Z. Anal. Chemie 319 (1984) 563 - 568.

Langseth W.: Determination of diphenyltin and dialkyltin homologues by HPLC with morin in the eluent. Talanta 31 (1984) 975 - 978.

Laughlin R.B.Jr.; French W; Johannesen R.B.; Guard H.E.; Brinckman F.E.: Predicting toxicity using computed molecular topologies: the example of triorganotin compounds. Chemosphere 13 (1984) 575-584.

Laughlin R.B.Jr.; Guard H.E.; Coleman W.M.III.: Tributyltin in Seawater: Speciation and Octanol-Water Partition Coefficient. Environ. Sci. Technol. 20 (1986) 201-204.

Laughlin R.B.Jr.; Linden O.: Tributyltin - Contemporary Environmental Issues. Ambio 16 (1987) 252-256

Lawler I.F.; Aldrich J.C.: Sublethal Effects of Bis(Tri-N-Butyltin)Oxide on Crassostrea gigas Spat. Mar. Pollut. Bull. 18 (1987) 274-278.

Lee R.F.; Valkirs A.O.; Seligman P.F.: Fate of Tributyltin in Estuarine Waters. Oceans 87 Proc.: The Ocean - An International Workplace. Vol. 4: Int. Organotin Symp., Halifax, Nova Scotia, Canada, Sept. 28 n- Oct. 1 (1987) 1411-1415.

Maguire R.J.; Huneault H.: Determination of butyltin species in water by gas chromatography with flame photometric detection. J. Chromatogr. 209 (1981) 458-462.

Maguire R.J.; Chau Y.K.; Bengert G.A.; Hale E.J.; Wong T.S.; Kramar O.: Occurrence of organotin compounds in Ontario lakes and rivers. Environ. Sci. Technol. 16 (1982) 698-702.

Maguire R.J.; Carey J.H.; Hale E.J.: Degradation of the Tri-n-Butyltin Species in Water. J. Agric. Food Chem. 31 (1983a) 1060.

Maguire R.J.; Tkacz R.J.: Analysis of butyltin compounds by gas chromatography. Comparison of flame photometric and atomic absorption spectrophotometric detectors. J. Chromatogr. 268 (1983b) 99-101.

Maguire R.J.: Butyltin compounds and inorganic tin in sediments in Ontario. Environ. Sci. Technol. 18 (1984) 291-294.

Maguire R.J.; Wong P.T.S.; Rhamey J.S.: Accumulation and Metabolism of Tri-n-butyltin Cation by a Green Alga, Ankistrodesmus falcatus. Can. J. Fish. Aquat. Sci. (1984).

Maguire R.J.; Tkacz J.: Degradation of the Tri-n-butyltin Species in Water and Sediment From Toronto Harbor. J. Agr. Food Chem. 33 (1985) 947-953.

Maguire R.J.; Tkacz R.J.; Sartor D.L.: Butyltin species and inorganic tin in water and sediment of the Detroit and St Clair rivers. J. Great Lakes Res. 11 (1985) 320-327.

Maguire R.J.; Tkacz R.J.; Chau Y.K.; Bengert G.A.; Wong P.T.S.: Occurrence of Organotin Compounds in Water and Sediment in Canada. Chemosphere 15 (1986) 253-274.

Matthias C.L.; Bellama J.M.; Olson G.J.; Brinckman F.E.: Comprehensive method for determination of aquatic butyltin and butylmethyltin species at ultratrace levels using simultaneous hydridization/extraction with gas chromatography-flame photometric detection. Environ. Sci. Technol. 20 (1986) 609-615.

Matthias C.L.; Bellama J.M. Oceans '87, Proc: Int. Organotin Symposium Halifax, (1987) p. 1344 - 1347.

Meinema H.A.; Burger-Wiersma T.; Versluis-de Haan G.; Gevers E.: Determination of trace amounts of butyltin compounds in aqueous systems by gas chromatography/mass spectrometry. Environ. Sci. Technol. 12 (1978) 288-293.

Meinema H.A.; van Dam-Meerbeek T.G.; Vonk J.W.: Evaluation of the Impact of Organotin Compounds on the Aquatic Environment. Final Report of TNO, Utrecht, to EEC, Contract No. 85/B/6600/11/007/11/N (1986)

Michel P.: Ocean 87'Proc.: Int. Organotin Conference Halifax (1987) p.1340-1343.

Moriyama H.; Koide K.; Tsuij I.: Kumamoto ken Eisei Kogai Kenkuyoshoho 15 (1986) 28-29.

Müller M.D.: Tributyltin Detection at Trace Levels in Water and Sediments Using GC with Flame-Photometric Detection and GC-MS. Fresenius Z. Anal. Chem. 317 (1984) 32-36.

Müller M.D.: Comprehensive Trace Level Determination of Organotin Compounds in Environmental Samples Using High-Resolution Gas Chromatography with Flame Photometric Detection. Anal. Chem. 59 (1987a) 617-623.

Müller M.D.: (1987b) unpublished results.

Mushak P.: Neurotoxicology 5 (1984) 163-176.

ORTEPA (Organotin Environmental Programme Association) Symp. Toxicology and Analysis of Tributyltin, Berlin, May 15-16, 1986.

Olson G.J.; Brinckman F.E.: Biodegradation of Tributyltin by Chesapeake Bay Microorganisms. Proc. Oceans 86, Conference Record, Science-Engineering Adventure, Vol. 4 of 5: Organotin Symp., Wash., D.C., Sept. 23-25 (1986) 1196-1201.

Parks E.J.; Blair W.R.; Brinckman F.E.: GFAAS determination of ultratrace quantities of organotins in sea-water by using enhancement methods. Talanta 32 (1985) 633-639.

Pinel R.; Benabdallah M.Z.; Astruc A.; Astruc M.: Determination of inorganic tin and organotin compounds by graphite-furnace atomic absorption spectrometry with a new matrix modifier. Anal. Chimica Acta 181 (1986) 187-193.

Pinel R.; Madiec H.: Determination of "heavy" organotin pollution of water and shellfish by a modified hydride atomic absorption procedure. Intern. J. Environ. Anal. Chem. 27 (1986) 265 - 271.

Randall L.: Han J.S.; Weber J.H.: Determination of inorganic tin, methyltin, and butyltin compounds in sediments. Environm. Technol. Letters 7 (1986) 571-576.

Randall L.; Weber J.H.: Adsorptive Behaviour of Butyltin Compounds Under Simulated Estuarine Conditions. Sci. Total Environ. 57 (1986) 191-203.

Riggle C.J.; Sgontz D.L; Graffeo A.P.: The Analysis of Organotins in the Environment, in Proc.: 4th Int. Conf. Sens. Environ. Pollution, Washington, (1978), p. 761-764.

Seligman P.F.; Valkirs A.O.; Lee R.F.:
a) Degradation of Tributyltin in San Diego Bay, California, Waters. Environ. Sci. Technol. 20 (1986) 1229.
b) Degradation of Tributyltin in Marine and Estuarine Waters. Proc. Oceans 86, Conference Record, Science-Engineering Adventure, Vol. 4 of 5: Organotin Symp., Wash., D.C., Sept. 23-25, 1986, S. 1189-1195.

Short J.W.; Thrower F.P.: Accumulation of butyltins in muscle tissue of chinook salmon reared in sea pens trated with tri-n-butyltin. Mar. Poll. Bull. 17 (1986) 542-545.

Steinhäuser K.G.; Amann W.; Späth A.; Polenz A.: Untersuchungen zur Aquatischen Toxizität Zinnorganischer Verbindungen. Vom Wasser 65 (1985) 203.

Stephenson M.; Smith D.R.; Hall L.W. Jr.; Johnson W.E.; Michel P.; Short J.; Waldock M.; Huggett R.J.; Seligman P.; Kola S.: Ocean '87, Proc.: Int. Organotin Symposium Halifax, (1987) 1334-1338.

Steward T.E.; Cannizzaro R.D.:Analysis of Organotin Residues by Gas Chromatography/Mass spectrometry. ACS Symposium Series, Pesticide Analytical Methodology No 136 (1980) 367-388.

Takahashi K.; Ohyagi Y.: Bunseki Kagaku, 36 (1987) 133-137.

Takami K; Yamamoto H.; Okumura T.; Sugimae A.; Nakamoto M: Application of "Clean-up" cartridge for gas chromatographic determination of di- and tri-n-butyltin in fish. Anal. Sciences 3 (1987) 63 - 67.

Takeuchi M.; Mizuishi K.; Yamaobe H.; Watanabe Y.: Bunseki Kagaku 36 (1987) 138-142.

Truhaut R.; Channel Y.; Anger J.P.· Nguyen P.L; van der Driessche J.; Guesnier L.R., Morin N.: Contribution to the toxicological and pharmacological study of tributyltinoxide. Eur. J. Toxicol. Environ. Hyg. 9 (1) (1976) 31-40.

Tsuda T.; Nakanishi H.; Morita T.; Takebayashi J.: Simultaneous gas chromatographic determination of dibutyltin and tributyltin compounds in biological and sediment samples. J. Assoc. Off. Anal. Chem. 69 (1986) 981-984.

Tsuda T.; Nakanishi H.; Aoki S.; Takebayashi J.: J. Chromatogr. 387 (1987) 361-370.

Tugrul S.; Balkas T.I.; Goldberg E.G.: Mar. Poll. Bull. 14 (1983) 297-303.

Unger M.A.; McIntytre W.G.; Greaves J.; Huggett R.J.: GC determination of butyltins in natural waters by flame photometric detection of hexyl derivatives with mass spectrometric confirmation. Chemosphere 15 (1986) 461-470.

Valkirs A.O.; Seligman F.; Stang P.M.; Homer V.; Lieberman S.H.; Vafa G.; Dooley C.A.: Measurement of butyltin compounds in San Diego Bay. Mar. Poll. Bull. 17 (1986) 319-324.

Valkirs A.O.; Seligman F. Oslon G.J.; Brinckman F.E.; Matthias CL.; Bellama J.M.: Di- and tributyltin species in marine and estuarine waters. Inter-laboratory comparison of two ultratrace analytical methods employing hydride generation and atomic absorption or flame photometric detection. Analyst 112 (1987) 17-21.

Walsh G.E.; McLaughlan L.L.; Lores E.M.; Louie M.K.; Deans, C.H.; Effects of Organotins on Growth and Survival of Two Marine Diatoms, Skeletonema costatum and Thalassiosira pseudonana. Chemosphere 14 (1985) 383.

Weast R.C. (ed.): CRC Handbook of Chemistry and Physics, 60th ed. The CRC Press, Boca Raton 1979 , p. B 265 - B 266.

Woollins A.; Cullen W.R.: Determination of organotin compounds contained in aqueous samples using capillary gas chromatography. Analyst 109 (1984) 1527-1529.

World Health Organization (WHO): Tin and Organotin Compounds: A Preliminary Review. Environ. Health Criteria 15. Geneva (1980).

Worthing C.R. (Editor): The Pesticide Manual, The British Crop Protection Council, 1987.

Vos J.G.; deKlerk A.; Krajnc E.I.; Kruizinger W.; van Ommen B.; Rozing J.: Toxicity of bis(tri-n-butyltin)oxide in the rat. II. Suppression of thymus-dependent immune responses and of parameters of non-specific resistance after short-term exposure. Toxicol. Appl. Pharmacol. 75 (1984) 387-408.

Yoshioka Y.; Nagase H.; Ose Y.; Sato T.: Evaluation of the Test Method "Activated Sludge, Respiration Inhibition Test" Proposed by the OECD. Ecotox. Environ. Safety 12 (1986) 206.

Yu T.H.; Arakawa Y. J.: High-performance liquid chromatographic determination of dialkyltin homologues using fluorescence detection. Chromatogr. 258 (1983) 189.

Zietz E.; Haag F.: Determination of Organotin Compounds in Waste Water. Report on the Workshop "Analytical Methodologies for Selected Pollutants" within the Scope of the EC Project EG-COST 641 (Organic Micropollutants in the Aquatic Environment, 30.09./01.10. 1986, Berlin; will be published

Zimmerli B; Zimmermann H.: Gas-chromatographische Bestimmung von Spuren von n-Butylzinnverbindungen (Tetra-, Tri-, Di-) in Luft. Z. Anal. Chemie 304 (1980) 23-27.

Zingg M.: Ausmaß und Ursache der Belastung schweizerischer Oberflächengewässer mit zinnorganischen Verbindungen. Bericht des Insituts für Toxikologie der ETH und Universität Zürich für das Bundesamt für Umweltschutz, Zürich. 1985.

Zuckerman J.J.; Reisdorf P.R.; Ellis H.V. III.; Wilkinson R.R. in "Organometals and Organometalloids, Occurrene and Fate in the Environment" ACS Symposium Series, No 82. F.E Brinckman and J.M. Bellama (eds). 1978 p. 388-422.