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The Performance of an Analytical Method for Determination of TBT During a Six-Year Monitoring Programme

M. J. Waldock and M. E. Waite*
Ministry of Agriculture, Fisheries and Food, Fisheries Laboratory, Remembrance Avenue, Burnham on Crouch, Essex CM0 8HA, UK

Tributyltin (TBT) concentrations have been measured in UK waters, shellfish and sediments during the period 1986–1992. The methodology was based on conversion of alkyltin compounds to hydrides following extraction, and then measurement by gas chromatography with flame photometric detection. The collection of a large set of data to assess changes in environmental concentrations of organotins required use of good analytical quality control procedures at a time when no reference materials were available. An analytical quality control (AQC) system based on in-house quality control materials was devised and the performance of the method independently assessed by periodic participation in intercalibration exercises with other expert laboratories.

Keywords: Butyltin, analysis, shellfish, waters, sediments, environment

1 INTRODUCTION

Controls on the use of TBT-based antifouling paints were introduced in the UK in 1985, at a time when there were no well-established and robust methods for the trace determination of TBT in water, sediments and animal tissues. The UK legislation established an Environmental Quality Standard of 2 ng l^{-1} in seawater for the protection of marine life, and required the provision of a monitoring programme in order to establish whether or not the control measures would result in substantial reductions of TBT concentrations. The MAFF Burnham on Crouch laboratory was given the task of developing methods for analysis of TBT at trace concentrations in water (1 ng l^{-1}), and in sediment and shellfish tissue (0.01 μg g^{-1}), and establishing a monitoring programme based on analysis of oysters, mussels, sediment and water samples from 13 sites in the UK. Since 1986 over 5000 samples have been analysed using the methods described here. No certified reference materials were available when the programme began and the AQC programme was developed using 'in-house' laboratory-produced reference materials. The performance of the methods was established by participation in a series of intercalibration exercises.

* Present address: NRA South Western Region, Manley House, Kestrel Way, Exeter, UK.

2 METHODOLOGY

2.1 Water samples

The principle of the method is that organotin compounds are reduced using sodium borohydride to the hydride form (to improve compatibility with capillary GC analysis) and simultaneously extracted into dichloromethane. The extract is 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 l^{-1}. The method was developed by Matthias *et al.*[1] and subsequently modified as described by Waldock *et al.* in 1989.[2]

The reagents used were 0.25 g sodium borohydride pellets, atomic absorption spectroscopic grade (e.g. SpectrosoL); dichloromethane (glass-distilled grade); and as standards, butyltin trichloride, dibutyltin dioxide, bis(tributyltin) oxide and tripropyltin chloride (internal standard).

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Stock solutions of monobutyltin and dibutyltin compounds were prepared by dissolution in methanol, and those of tributyltin compounds by dissolution in dichloromethane. Individual stock solutions of standards were prepared by dissolving 60 mg of each compound in 100 ml of solvent to produce a solution containing 0.6 mg ml^{-1} of each compound. Individual working solutions were prepared by dissolving 0.5 ml of stock solution in 50 ml of dichloromethane to give 6 μg ml^{-1}.

A composite working solution was prepared by mixing mono-, di- and tri-organotin species (including internal standard) and diluting with dichloromethane to give an approximate concentration of 0.25 μg ml^{-1}. The composite standard was derivatized by mixing approximately 0.5 ml of standard with 2 ml of distilled water plus approx. 50 mg of sodium borohydride powder in a vial, which was then capped and shaken for 10–15 min. The composite standard was used to assess the relative response factors for each compound measured by the flame photometric detector.

The combined recovery and response factor for each individual organotin compound (i.e. MBT, DBT and TBT) was assessed by spiking a 2 l sample of water (either filtered laboratory seawater or distilled water) with either MBT, DBT or TBT together with internal standard which was then derivatized by the extraction method listed below.

Samples of water (2 l) were collected in calibrated 2.7 l glass bottles and were not filtered before analysis. A sodium borohydride pellet (0.25 g) and 40 ml of dichloromethane were added to each sample, followed by an appropriate amount of internal standard (20 μl for samples containing 1–100 ng l^{-1} TBT). The bottles were capped and shaken by hand for a few seconds. Internal pressure was then released and the bottle was shaken on an orbital shaker for 15 min. The pressure was released and the bottle allowed to stand while the solvent phase separated out. The cap of the bottle was then replaced with a PFTE tap, the bottle was inverted, and the dichloromethane drawn off into a centrifuge tube and centrifuged at 2500 rpm for 5 min. Any water in the tube was removed using a Pasteur pipette, and the extract was blown down to approx 3 ml using a gentle stream of compressed air at ambient temperature. The extract was then transferred to a 5 ml capacity tapered vial and blown down to approximately 100–200 μl; 1 μl of the extract was then introduced to the GC system.

2.2 Tissues and sediments

The principle of the method is that alkyltin compounds are extracted from animal tissues or sediments by sodium hydroxide and methanol, converted to hydrides and partitioned into hexane. The derivatives are then analysed by gas chromatography with flame photometric detection. The method was developed by Waldock *et al.*[2]

The reagents consist of sodium borohydride powder (purity 96% or better); hexane (glass-distilled grade); double-distilled water; sodium hydroxide/methanol reagent, prepared by dissolving 1 g sodium hydroxide (98% pure or better, e.g. AnalaR) in 1 l of methanol (99.8% pure or better, e.g. AnalaR) to give a 1% solution; and as standards, butyltin trichloride, dibutyltin dioxide, bis(tributyltin) oxide and tripropyltin chloride (internal standard).

Individual stock solutions of standards were prepared by dissolving 0.1 g of each compound in 100 ml of methanol to produce a solution containing 1 mg ml^{-1} of each compound. Individual working solutions were prepared by dissolving 0.5 ml of stock solution in 50 ml of methanol to provide a 10 μg ml^{-1} solution. A composite working standard was prepared by adding 50 μl of each working standard to a centrifuge tube containing 2 ml of distilled water, 8 ml of sodium hydroxide/methanol reagent, 100 mg of sodium borohydride and 2 ml of hexane. The tube was then shaken for 15 min, and centrifuged at 2500 rpm.

Samples were prepared as follows. Subsamples of 4 g of sediment were oven-dried to constant weight at 105 °C to determine moisture content. Extraction of alkyltin was then carried out on up to 4 g of wet sediment sample, ensuring that there was at least 2 ml of water (either natural or added) in the sample. Animal tissues (shellfish) were removed from their shells, drained, and the meat was weighed. The tissue was then homogenized in a glass jar and 4 g of the homogenate was used for each analysis.

An appropriate amount of internal standard, tripropyltin chloride, was added to the sediment or tissue in a PTFE centrifuge tube, e.g. 50 μl for samples containing 0.01–1 μg TBT g^{-1}. Double-distilled water was added to the sediment sample if necessary (see above). Sufficient 0.1% sodium hydroxide in methanol was then added to the sample to obtain a 4:1 methanol/water (v/v) ratio. The minimum volume of methanol reagent was therefore 8 ml and the maximum below 16 ml

for sediment samples. For shellfish, 10 ml of sodium hydroxide/methanol reagent was added for wet samples. The tube was capped and shaken for 45 min, then 2 ml of hexane and approximately 100 mg of sodium borohydride were added, and the sample shaken for a further 15 min. After centrifugation (4000 rpm for 20 min), the hexane phase was pipetted into an autosampler vial and 1 µl was analysed by GC FPD. The method does not employ a clean-up procedure, and therefore it is rapid and suitable for high throughput of monitoring samples. Residues of extracted organic material do however tend to accumulate at the injection end of the analytical column and retention gap, and degrade the performance of the capillary columns. The retention gap was frequently changed and 15 cm of fused silica was periodically removed from the injection end of the analytical column.

Extracts may be stored at −20 °C for several weeks. However, on storage in dichloromethane the hydrides revert to alkyltin chlorides within hours of preparation. The hydrides may be reformed by shaking extracts with 300 µl of 5% aqueous sodium borohydride.

Determination of alkyltins was carried out on a number of capillary column GCs with temperature programming and flame photometric detection. Each was fitted with a 25 m × 0.32 mm i.d. fused silica capillary column, coated with a cross-linked 5% phenyl methyl silicone fluid with a film thickness of 0.52 µm. A retention gap consisting of 1 m of deactivated, uncoated fused silica 0.53 mm i.d.) was attached to the injection end of the analytical column in order to allow on-column injection and better chromatographic resolution. The sulphur filter in the detector was removed and replaced by a narrow band filter of 610 ± 10 nm. Pure oxygen was not required for the flame, which was hydrogen-rich. As a general rule, flows of around 160 ml min^{-1} hydrogen, and 90 ml min^{-1} air were found to be satisfactory. Nitrogen was used as a make-up gas at 20 ml min^{-1}. Both direct on-column and splitless injections have been used successfully. Hydrogen at approx. 2 ml min^{-1} was used as carrier gas. The usual oven programme was 40–200 °C at 15 °C min^{-1}, with the detector set at 225 °C. Hewlett–Packard 5890 FPD systems were used most frequently and showed a linear response for concentrations of 50–900 pg alkyltin compounds on-column (Fig. 1).

All results produced in the programme are expressed as cation equivalents; they are in ng l^{-1} for water; µg g^{-1} dry weight for sediments and µg g^{-1} wet weight for animal tissues.

3 PRECISION AND ACCURACY

3.1 Water samples

The tripropyltin internal standard behaves very much like the TBT naturally occuring in the sample, and therefore loss of some of the sample on extraction and derivatization may be tolerated without compromising the precision and accuracy of the final determination. Hence only a one-step dichloromethane extraction was employed, rather than sequential extraction steps. At the 50 ng l^{-1} level the mean recovery for TBT relative to TPT was found to be 88% initially (SD = 15, $n = 12$); for DBT 88% (SD = 5.8, $n = 8$); and for MBT 84% (SD = 5.3, $n = 8$). As analysis progressed the RSD for successive TBT and DBT determinations was found to be consistently around 15% MBT values were more variable and the analysis could not be held within AQC control limits.

3.2 Tissue and sediment

The recovery of tributyltin was determined by standard additions of tributyltin hydride to samples previously spiked with TBTO, and comparison of the resultant GC peak areas over a range of spiked concentrations. The calculated recovery ranged from 90 to 97% (mean 93%) for sediment and 95 to 104% (mean 98%) for shellfish tissue. However, the use of an internal standard, tripropyltin chloride, which behaves in a similar way to TBT, allows for loss of sample without compromising the precision and accuracy of the determination. The recovery for each of TBT, DBT and MBT relative to the internal standard was close to 100%. The detection limit for the method was 0.005 µg g^{-1} for TBT, 0.010 µg g^{-1} for DBT and 0.02 µg g^{-1} for MBT. These limits may be reduced by concentration of the hexane extracts before GC analysis; however, since a clean-up procedure was not employed, concentrated samples degrade the performance of the capillary column more rapidly.

4 QUALITY ASSURANCE

4.1 Water samples

The use of a relatively large volume of water (2 l) prohibits the storage of a quality control sample.

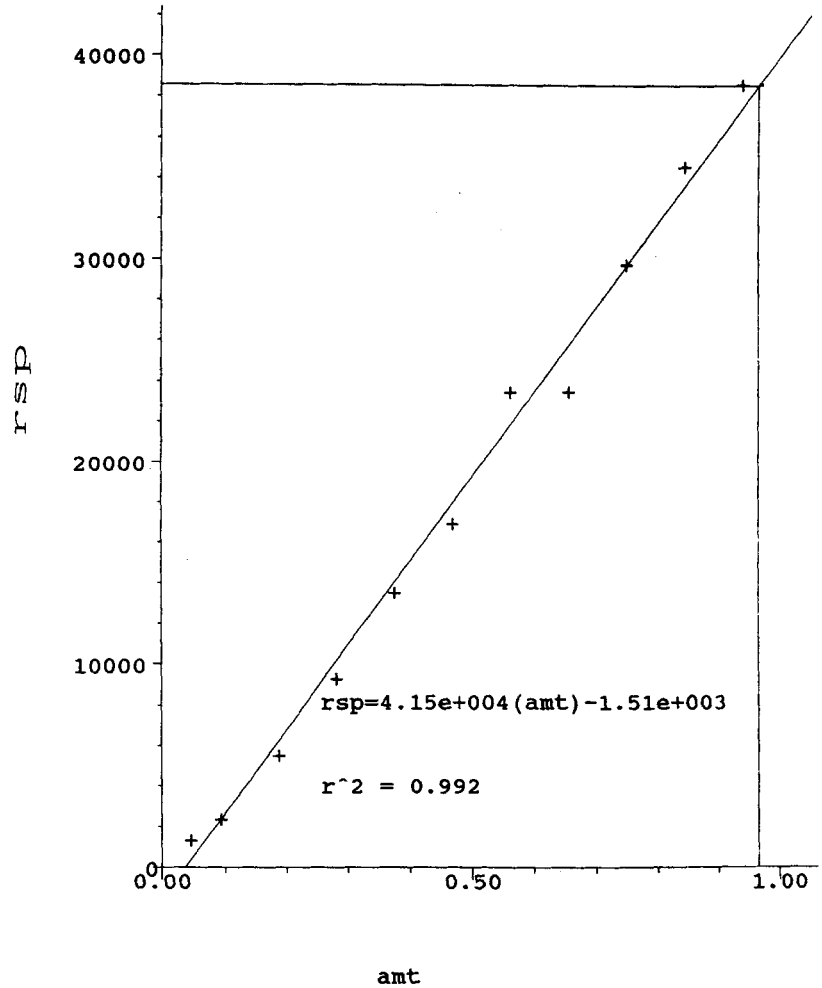

Figure 1 Calibration curve to show the linearity of the FPD. The detector showed a linear response from 50 to 900 pg TBT hydride loaded on the column.

Analytical quality control was monitored by the addition of a standard (50 ng l^{-1} DBTO or TBTO) to either 0.43 μm filtered seawater, or to tap water, for salt and freshwater samples respectively. Three spiked samples were analysed with each batch of environmental samples (usually ten per batch). A single blank sample of water from the same source was analysed with each batch of environmental samples. Figure 2 shows the recovery of DBT and TBT cations relative to the internal standard TPT cation during 95 consecutive analyses of standards spiked into seawater over a period of one year. All results are for the same GC (Hewlett–Packard 5890 series II), but generated by three different analysts. The overall RSD for both compounds was 16%.

Rejection thresholds for analytical samples were set at 3σ of means generated for the first 10–15 samples, and warning limits set at 2σ. In effect, batches of water samples with values derived for added standards that were more than approximately 45% from the initial mean were rejected.

4.2 Tissues and sediments

At the start of the analytical programme no standard reference mateials were available. Tissues for in-house reference materials were prepared by bulking and homogenizing several hundred juvenile oysters obtained from TBT-contaminated sites. Similarly sediments were either taken from naturally contaminated sites or, in order to provide a highly contaminated

material free from paint chippings, they were artificially contaminated in the laboratory. TBT dissolved in glacial acetic acid was added to a small amount of sediment (estuarine mud) slurry in a concrete mixer and diluted with TBT-free sediment during mixing. A single sample of quality control sediment or tissue was analysed with each batch of environmental samples (usually 12 per batch). Figures 3 and 4 show typical quality control diagrams.

Rejection thresholds for analytical samples were set at 3σ of means generated for the first 10–15 samples, and warning limits set at 2σ. For tissues, values more than approximately 25% away from mean QC material values were rejected. For sediments, the rejection value was approximately 45% from the mean.

5 INTERCALIBRATION PERFORMANCE

In order to demonstrate that the methods employed were also consistent with those of other researchers, the laboratory embarked upon a series of intercalibration exercises with other laboratories.

5.1 Water samples

5.1.1 BCR water intercalibration, 1988

In 1988 the BCR (EC Bureau of reference, Brussels) organized an intercalibration on the determination of TBT in water. Four different solutions were analysed, each at two different concentrations. Solution A contained tributyltin; solution B, tributyltin and inorganic tin; solution

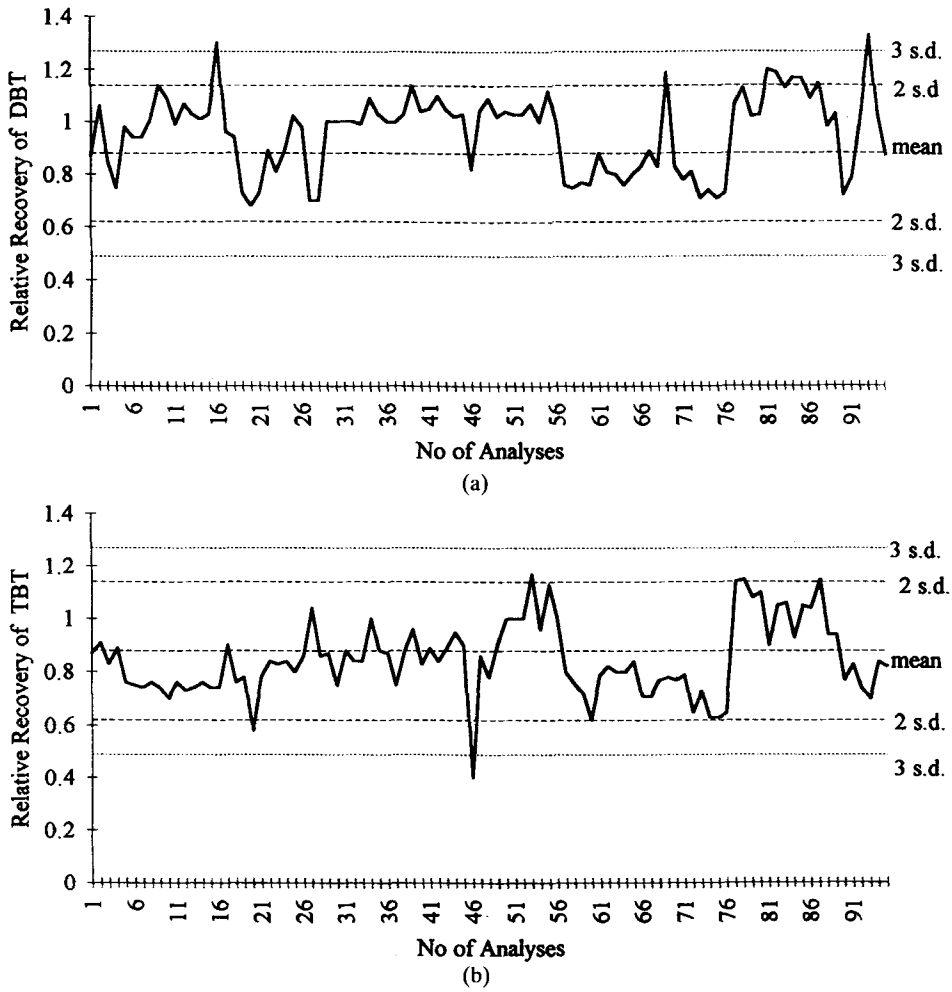

Figure 2 Recovery of (a) DBT and (b) TBT cations (TBT^+) relative to the internal standard (TPT) in 95 consecutive analyses of spiked seawater during a one-year period. Control limits on the analysis were set at 15% RSD, twice the SD giving a warning limit and three times the SD giving the rejection limit for the analysis.

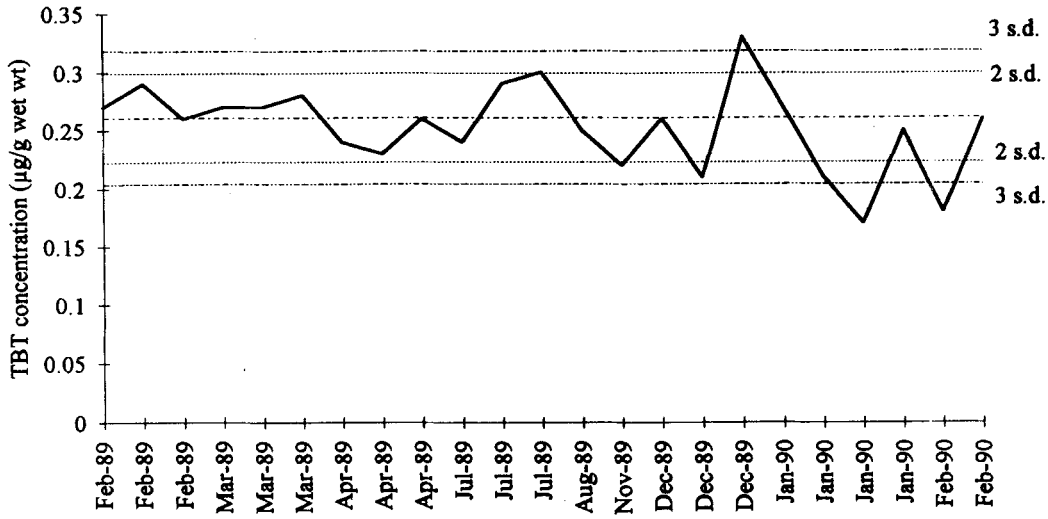

Figure 3 Concentration of TBT measured in tissue quality control material (oyster flesh) during a one-year period. Control limits on the analysis were set at 7% RSD, twice the SD giving a warning limit and three times the SD giving the rejection limit for the analysis.

C, tributyltin, dibutyltin, monobutyltin and inorganic tin; and solution D, tributyltin and triphenyltin. Each solution was diluted either ×100 or ×1000 and then analysed using the dichloromethane extraction, GC method.

Each undiluted solution supplied by the BCR had been made up to give initial concentration of 3 mg TBT acetate per litre. The mean results obtained by MAFF for each of the solutions (reported as concentrations in the initial solutions prior to dilution) were similar to the means of the results reported by all the laboratories which took part in the intercalibration. The MAFF results for samples diluted ×100 were: sample A, 2.74 ± 0.20; sample B, 2.64 ± 0.15; sample C, 3.14 ± 0.06; and sample D, 2.97 ± 0.29 mg TBT per litre as acetate (Table 1). The mean results from all the laboratories for the ×100 dilutions were: sample A, 2.83 ± 1.59; sample B, 2.39 ± 0.54; sample C, 2.54 ± 0.64; and sample D, 2.38 ± 0.56 mg l^{-1} TBT as acetate. The mean concentrations measured by MAFF for the samples A–D diluted ×1000 were: 2.96 ± 0.14; 3.00 ± 0.17; 3.04 ± 0.21; and 2.99 ± 0.12 mg l^{-1} TBT as acetate (Table 1). The overall mean results of the participating laboratories for the samples A–D diluted × 1000 were: 3.01 ± 1.07; 2.63 ± 0.81; 2.51 ± 0.79; and 2.72 ± 0.74 mg l^{-1} TBT as acetate.

5.1.2 Intercalibration of TBT in water from Mersin Harbour, 1988

Also in 1988, MAFF participated in an intercalibration with four other laboratories analysing water samples from Mersin Harbour, Turkey. MAFF found that the concentration of TBT in the harbour sample was 176 ng l^{-1}. Results from all five laboratories were in the range 18–226 ng l^{-1}, and the mean was 104 ± 89 ng l^{-1}.

5.1.3 NIST water intercalibration, 1990

In February 1990, MAFF submitted results of the analysis of ten solutions of TBT to the National Institute of Standards and Technology, USA (Table 2). The mean of the results was 6.6 ± 0.8 ng l^{-1} which was close to the mean of the results submitted by all of the participating laboratories 6.2 ng l^{-1}.[3]

5.1.4 IAEA water intercalibration, 1990

The International Atomic Energy Agency (IAEA), Monaco, organized an intercalibration between seven laboratories in April 1990. Each laboratory received three water samples for analysis: solution A was a coastal offshore seawater sample, solution B was a subsample of solution A which was spiked with tributyltin acetate to give a spike concentration of 175 ng TBT l^{-1}, solution C was a subsurface seawater sample from a harbour. MAFF's results for solutions A, B and C were 5, 175 and 370 ng l^{-1} respectively. These results were very close to the mean of the results of all the other participating laboratories: solution A, 9 ± 7 ng l^{-1}, solution B, 178 ± 26 ng l^{-1} and solution C, 366 ± 93 ng l^{-1}.

5.2 Animal tissues

5.2.1 Intercalibration on mussel tissue with Plymouth Marine Laboratory, 1988

In 1988 MAFF took part in an intercalibration of *Mytilus edulis* tissue with the Plymouth Marine Laboratory (Dr D. Page). Two mussel; samples, one from Arch Brook on the River Teign, and one from Bush Shore on the River Crouch, were analysed for DBT and TBT. The results of the intercalibration are shown in Table 3. MAFF found that the concentrations of TBT in the mussels from Arch Brook and Bush Shore were 1.01 and 6.86 $\mu g\ g^{-1}$ dry wt respectively, while PML reported values of 1.43 and 8.76 $\mu g\ g^{-1}$ dry wt.

5.3 Sediments

5.3.1 BCR sediment intercalibration, 1989

In 1989, MAFF analysed two sediment samples supplied by the Community Bureau of Reference (BCR), Brussels, as part of an intercalibration exercise involving 19 other laboratories. MAFF

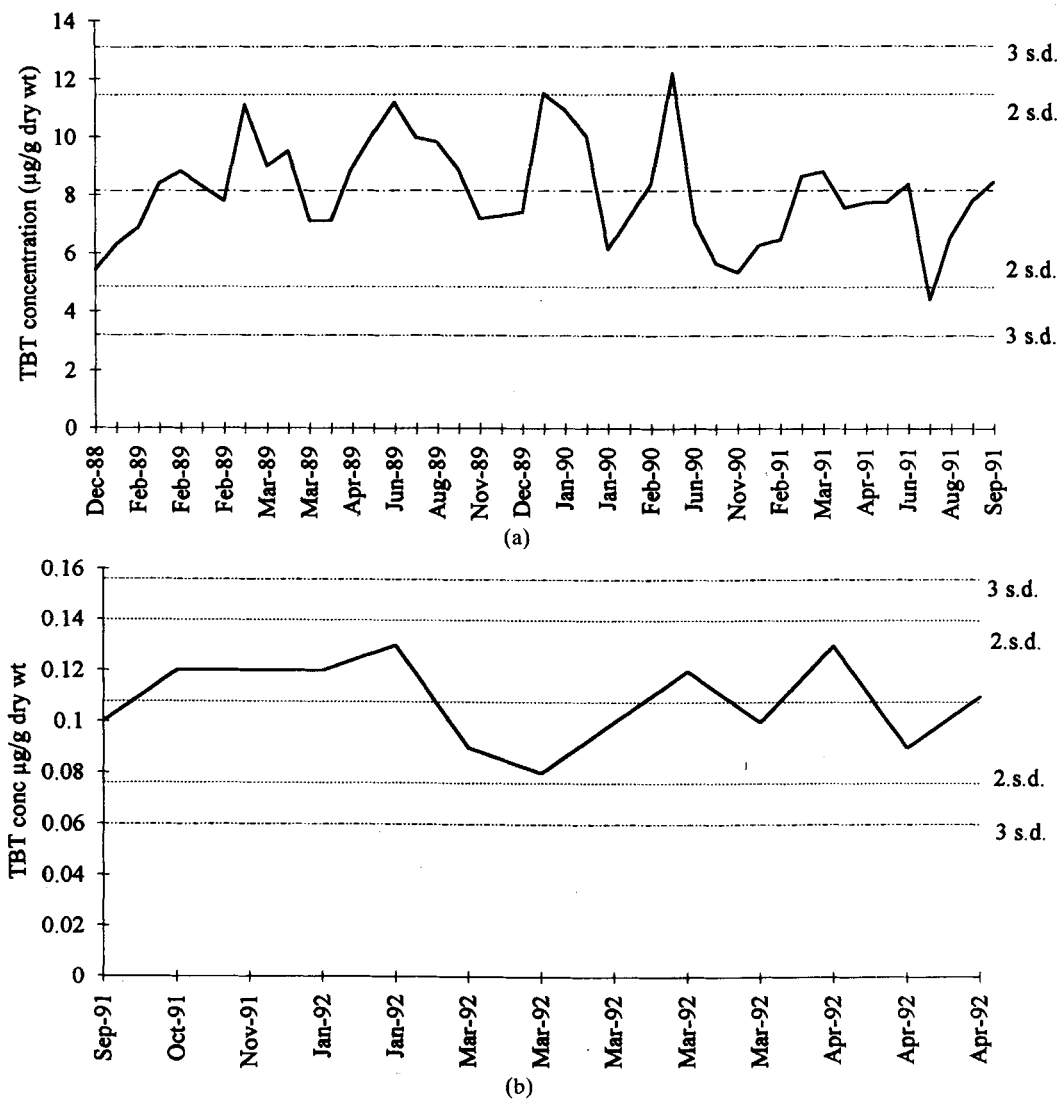

Figure 4 Concentration of TBT measured in (a) a high-level sediment quality control material (amended estuarine mud) during a 2.8-year period, and (b) a low-level sediment quality control material (marina mud) during a six-month period. Control limits on the analysis were set at 15% RSD, twice the SD giving a warning limit and three times the SD giving the rejection limit for the analysis.

Table 1 BCR TBT in water intercalibration, 1988

Concentrations of TBT acetate ($mg\,l^{-1}$) Solutions diluted × 100				Solutions diluted × 1000			
A	B	C	D	A	B	C	D
2.95	2.68	3.21	2.77	2.79	2.73	3.32	2.95
2.61	2.65	3.10	2.61	3.13	3.04	2.95	3.01
2.85	2.77	3.18	3.25	3.01	3.20	2.95	3.18
2.47	2.39	3.13	2.97	2.85	3.04	3.20	2.84
2.84	2.73	3.07	3.25	3.04	2.97	2.80	2.95
Mean (MAFF):							
2.74 ± 0.20	2.64 ± 0.15	3.14 ± 0.06	2.97 ± 0.29	2.96 ± 0.14	3.00 ± 0.17	3.04 ± 0.21	2.99 ± 0.12
Mean of all laboratories:							
2.83 ± 1.59	2.39 ± 0.54	2.54 ± 0.64	2.38 ± 0.56	3.01 ± 1.07	2.63 ± 0.81	2.51 ± 0.79	2.72 ± 0.74

reported a concentration of 0.11 ± 0.02 μg TBT as the acetate per g dry wt for sample 9A, and a concentration of 3.11 ± 0.18 $\mu g\,g^{-1}$ dry wt for sample 9B (Table 4). Sample 9A was supposedly sediment from Lake Maggiore not contaminated with TBT, and sample 9B was Lake Maggiore sediment spiked with TBT acetate to a level of 3.3 $\mu g\,g^{-1}$ dry wt. Only a few other laboratories reported the presence of TBT in sample 9A. The mean of all the individual results from the various laboratories for sample 9B was 2.80 ± 0.90 $\mu g\,g^{-1}$ dry wt.

5.3.2 BCR sediment intercalibration, 1990

In 1990 MAFF participated in a second sediment intercalibration organized by the BCR, Brussels. Five replicate analyses were made on the harbour sediment CRM 424 using the method described above. A mean value for TBT of 0.01 ± 0.00 $\mu g\,g^{-1}$ dry wt was obtained by MAFF, whilst the mean value for the results from all of the particpating laboratories was 0.09 ± 0.10 $\mu g\,g^{-1}$ dry wt. However, when data from certain labortories were rejected because of specific problems with the analysis of the sediment, or simply because the data points were deemed to be outliers, then a mean of 0.02 ± 0.01 $\mu g\,g^{-1}$ dry wt was obtained, which is close to the mean reported by MAFF.

Table 2 NIST water intercalibration, 1990

Sample	Concentration of TBT ($ng\,l^{-1}$)
1	6.7
2	6.3
3	5.6
4	7.9
5	5.4
6	7.3
7	6.9
8	6.2
9	7.3
10	6.5
Mean (MAFF):	6.6 ± 0.8
Mean of all laboratories:	6.2

5.3.3 BCR sediment intercalibration, 1992

In 1992 MAFF participated in a third BCR sediment intercalibration. Five replicate analyses were made on the sediment CRM 462 using the GC FPD method. A mean value for DBT of 0.112 ± 0.004 $\mu g\,g^{-1}$ dry wt and for TBT of 0.064 ± 0.003 $\mu g\,g^{-1}$ dry wt was obtained by MAFF (Table 5). The mean value for the TBT results of the other participating laboratories, including MAFF, was 0.070 ± 0.018 $\mu g\,g^{-1}$ dry wt; however, this should be regarded as a preliminary value which may change after statistical analysis by the BCR has removed any outliers from the data set.

DISCUSSION

During the last 15 years a number of approaches for determination of trace quantities of organotin compounds in the environment have been developed. Extracts of the sample have been analysed directly by electrothermal atomic absorption spectroscopy (EAA),[2,4] or as volatile hydride derivatives subsequently analysed by AA.[5]

Table 3 Intercalibration of *Mytilus edulis* tissue with PML, 1988

	Concentration of DBT ($\mu g\ g^{-1}$ dry wt)	Concentration of TBT ($\mu g\ g^{-1}$ dry wt)
Arch Brook (MAFF)	0.11	1.01
Arch Brook (PML)	0.14	1.43
Bush Shore (MAFF)	0.56	6.86
Bush Shore (PML)	0.48	8.76

Alternatively, less polar derivatives of mono-, di- and tri-organotins have been produced using either a Grignard reaction or by making a hydride with final determination by GC with either MS detection or by using a flame photometric detector (FPD).[1,2,6,7]

More recently a variety of coupled techniques such as high-pressure liquid chromatography (HPLC) or GC linked to AA or even inductively coupled plasma (ICP) MS systems have been developed, all of which allow speciation of the organotins, and all of which allow detection in the nanogram to picogram per litre range (see, for example, the reviews by Donard[8] and Maguire[9]).

All of these approaches appear to be viable and there are no overwhelming reasons to recommend any particular method. Until recently the lack of available certified reference materials has prohibited systematic determination of all sources of error and bias in organotin measurements. The approach used in this study has been to ensure repeatability with a strict programme of analytical quality control, and to demonstrate accuracy by intercalibration with a number of other expert laboratories. Retrospectively the method has a proven record of success in analysis of more than 5000 samples. Rejection rates of samples falling outside control limits were approximately one batch in 20. If all blanks, standards and AQC materials and participation in intercalibration exercises are added to the overall analytical effort, the additional burden generated by the quality control programme to analysis of environmental samples was approximately 25–30%.

Table 4 BCR sediment intercalibration, 1989

Concentration of TBT ($\mu g\ g^{-1}$ dry wt)	
Sample A	Sample B
0.13	3.41
0.09	3.02
0.11	3.00
0.12	2.99
0.09	3.15
Mean (MAFF): 0.11 ± 0.02	3.11 ± 0.18
Mean of all laboratories: —	2.80 ± 0.90

Table 5 BCR sediment intercalibration, 1992

Concentration of DBT ($\mu g\ g^{-1}$ dry wt)	Concentration of TBT ($\mu g\ g^{-1}$ dry wt)
0.108	0.068
0.118	0.066
0.113	0.064
0.112	0.061
0.111	0.061
Mean (MAFF): 0.112 ± 0.004	0.064 ± 0.003
Mean of all laboratories: —	0.070 ± 0.018

During the monitoring period 1986–1992, concentrations of TBT in UK waters analysed decreased by an order of magnitude, e.g. from 60 ng l^{-1} to 6 ng l^{-1}, at sites where large numbers of pleasure craft were moored. Concentrations of TBT in oysters also decreased by an order of magnitude, e.g. 2 $\mu g\ g^{-1}$ to less than 0.2 $\mu g\ g^{-1}$. Sediment concentrations were more variable due to the fact that many sites were contaminated with paint chippings (M. J. Waldock, unpublished results). We are confident that the analytical methods employed were adequate to measure such changes, and therefore the measured decrease in environmental concentrations were real and could not be an artefact of poor analytical technique.

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