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Use of Cartridges for Speciation of Organotin Compounds in Environmental Samples

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The performance of cartridges with different polar and non-polar stationary phases (C_{18}, C_8, C_2, phenyl) has been investigated for the quantitative separation of butyltin and phenyltin species (TBT, DBT, MBT, MPT, DPT, TPT), and conditions have been established to optimize the separation, using gas chromatography with a flame photometric detector, to characterize the different organotin species. Optimum separation and preconcentration of organotins is based on retention in a C_{18} cartridge and elution with 2 cm^3 of 1% (v/v) HBr and 0.1% tropolone solution in methanol, being successfully applied to seawater. Finally, the possibilities of the cartridges for selective elution and their use in direct non-chromatographic speciation are discussed.

Keywords: Tributyltin, dibutyltin, monobutyltin, triphenyltin, diphenyltin, monophenyltin, speciation, C_{18} cartridges, C_8 cartridges, preconcentration, water

INTRODUCTION

Organotin compounds, specially tributyltin (TBT) and the species formed from it by degradation, i.e. dibutyltin (DBT) and monobutyltin (MBT), are an important environmental concern because of their high toxicity. The TBT is mainly introduced into the marine environment in antifouling paints and can induce deleterious effects on non-target organisms, some of which have an important economical significance, such as mussels, crabs, clams and oysters. On the other hand, tri-, di- and mono-phenyltin compounds (TPT, DPT and MPT) can also be found in aquatic media because of their use as agricultural fungicides and paint biocides.

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Many methods have been developed for analytical speciation of butyl- and pheny-tin compounds at the part per thousand (ppt) levels,[1] as (for example) the UK environmental quality target value was set at 20 ng dm^{-3} in 1987.[2] However, most of these methods need a previous step to separate tin species from the matrix and to concentrate them. Liquid–liquid extraction has been used for this purpose with good recoveries and enrichment factors, but this preconcentration procedure is time-consuming, involves the use of large volumes of organic solvents, and is not applicable in field sampling manipulations.

Recently, adsorption of organotin compounds (monomethyltin, dimethyltin, trimethyltin, monobutyltin, dibutyltin, tributyltin, diphenyltin and triphenyltin) has been studied by Kadokami *et al.*,[3] by passing a water sample through a silica-gel C_{18} disposable column. The species were later recovered with tetrahydrofuran–acetic acid containing 0.5% (m/v) tropolone for determination by HPLC–AA. Junk and Richard,[4,5] and Evans *et al.*,[6] have reported the possibilities of liquid–solid extraction (LSE) of TBT based on the use of C_{18} discs noting their advantages against LSE with column or cartridge housings. Morabito and coworkers[7] have proposed the use of three solid phases (Carbopack, C_8, and C_{18}) and different eluting agents (methanol–tropolone, methanol, dichloromethane, hexane, and diethyl ether) for extraction/elution of TBT, DBT and MBT from seawater. These authors propose the use of Carbopack or C_{18} phases for the separation of TBT from DBT and MBT, performing the elution in two steps with methanol and methanol–tropolone. Finally, Compañó *et al.*[8] have reported the LSE of triphenyltin from seawater with C_{18} cartridges, eluting with methanol and 3-hydroxyflavone in methanol: levels of triphenyltin were evaluated by fluorimetry with 3-hydroxyflavone in micellar media.

In this work, different non-polar stationary

phases, C_{18}, C_8, C_2 and phenyl, have been tested for the quantitative LSE of monobutyltin, dibutyltin, tributyltin, monophenyltin, diphenyltin and triphenyltin from water samples, and performance of these cartridges has been evaluated. In addition, the use of the cartridges for direct non-chromatographic speciation of organotin compounds, in combination with some atomic detection technique, which could eliminate the gas or liquid chromatographic step, is discussed.

EXPERIMENTAL

Reagents

All organic solvents were HPLC grade; organotin standards were obtained from Aldrich and were used without further purification, but analysis did not reveal any detectable impurities. The other chemicals were analytical reagent grade. Water used in all the experiments was distilled and deionized and gave blank readings in all analyses.

Apparatus

A gas chromatograph (Perkin–Elmer model 8140; Perkin–Elmer Hispania, Madrid) fitted with a split–splitless injector, a glass capillary column (SPB-1; Supelco; Bellefonte, PA, USA) 15 m long, 0.53 mm i.d. and a film thickness of 1.5 μ and a flame photometric detector were used. The detector was operated with a 610 nm filter.

Liquid–liquid extraction

Previous procedures reported by the authors[9] were used; these make possible recoveries of organotins of about 100%: a 1000-cm^3 portion of water sample containing the organotin species acidified with 10 cm^3 of HBr (Merck) was extracted by shaking vigorously in darkness with 300 cm^3 of 0.07% (w/v) solution of tropolone (Aldrich) in pentane for 10 min; the tropolone concentration was optimized to prevent dismutation.[11] The organic extract was dried with anhydrous Na_2SO_4 and reduced in volume to 0.5 cm^3 in a rotary evaporator. Then the extract was derivatized by pentylation, to be analysed by GC.

Solid–liquid extraction

Cartridges

Reverse-phase Waters Sep-Pak Classic cartridges (Millipore Co.) with octadecyl (C_{18}), and Maxi-Clean™ cartridges (Alltech) with octyl (C_8), ethyl (C_2), and phenyl packing material, suitable for manual operation, were used in the different tests. The averaged weight of packing material was about 360 mg/cartridge for C_{18} and 300 mg/cartridge for C_8, C_2 and phenyl sorbents. The possible use of the cartridge for water samples containing organotin species from the detection limit to 5000 ng has been tested although no experiments have been developed to check the total adsorption capacity of the cartridge. However, this capacity depends on the presence of other substances in the sample (hydrocarbons, fats, etc) which can also be adsorbed on the cartridge.

Cartridge conditioning

With the aid of a vacuum pump, 10 cm^3 of the solvent under study was passed through the cartridge using a flow rate of 5 cm^3 min^{-1}. With the same flow rate 10 cm^3 of methanol was then passed, followed by 10 cm^3 of distilled water.

Sample loading

The water sample (100 to 5000 cm^3) was passed through the cartridge, conditioned as above, with a flow rate of 8 cm^3 min^{-1}. Then the cartridge was dried under a nitrogen stream for 5 min.

Elution

Elution was developed without significant losses of analyte, using the following procedure: a suitable volume of solvent was passed with a syringe (flow rate 1 cm^3 min^{-1}). The solvent was collected and concentrated to 0.5 cm^3 with a rotary evaporator. When ether or pentane were used as eluent the extract was directly derivatized for GC analysis, but if dichloromethane or methanol were the eluents it was necessary to eliminate them to avoid their reaction with the Grignard reagent used for derivatization. In this case 10 cm^3 of hexane was added and the solution was concentrated again to 0.5 cm^3 prior to the derivatization step.

Analytical method

Derivatization

Preparation of Grignard reagent

This reagent was prepared according to standard

synthetic methods: 25 cm^3 of 16% (v/v) pentyl bromide solution in ether was added dropwise to 0.8 g of magnesium (0.03 mol), which had previously been heated with a small amount of iodine as catalyst. The mixture was then refluxed with continuous stirring at 40 °C for 1 h.

Derivatization

The pentane extract containing the organotin species was added to 4 cm^3 of 1 M pentylmagnesium bromide solution in ether (Grignard reagent, prepared as above) and the mixture held for 1 h in a sealed device, at room temperature.

Clean-up

The excess of Gignard reagent was removed with 0.5 M sulphuric acid, the organic extract was reduced to 1 cm^3, and then purified by chromatography on a 7 cm × 1 cm i.d. column of Florisil (Merck); 10 cm^3 of pentane was used as the eluent. This pentane extract was then reduced to 2 cm^3 and transferred into a microevaporator together with the internal standard (dimethyldipentyltin) and concentrated to 0.5 or 0.2 cm^3 under a nitrogen stream.

Measurement of organotin concentrations

Organotin species were determined using a GC FPD system, following a procedure reported previously.[10,12] A Perkin–Elmer 8140 gas chromatograph fitted with a split–splitless injector, a glass capillary column (Supelco, SPB-1 15 m in length, 0.53 mm i.d., film thickness 1.5 μm) and a flame photometric detector was used. The detector was operated with a 610-nm cut-off interference filter, at a temperature of 250 °C, using hydrogen and air flow rates of 46.5 and 88.0 cm^3 min^{-1}, respectively. The injector temperature was set at 250 °C and helium (9.5 cm^3 min^{-1}) served as carrier gas using a split ratio of 3.8 to 1. Sample aliquots of 5–10 μl were injected and the compounds of interest were eluted with the following temperature programme: initial column temperature 50 °C, heating to 250 °C at 10 °C min^{-1} and isothermal at this temperature for 7 min.

Calibration and analytical quality control

Organotin concentrations were deduced from calibration curves derived from derivatized standard solutions using peak heights. Calibration experiments were performed directly on sediments or waters. Calibration curves were linear for tin amounts less than 40 ng; this limit increased to 55 ng and 60 ng for DPT and TPT, respectively. The determinations were carried out using Me_2SnPe_2 as internal standard which improved the precision.

Quality control of results was monitored by preparing a calibration graph each week and injecting a derivatized standard with all the tin species every day to test the instrument signal. The absolute limit of tin able to be detected by the instrument, evalulated as three times the standard deviation of blank, was in the range of about 0.3 ng for butyltins and 0.5 ng for phenyltin species. The detection limits in water analysis (including the solid–liquid extraction step) for 5000 cm^3 samples are the following: 2.0 ng dm^{-3} (TBT), 1.5 ng dm^{-3} (DBT), 2.2 ng dm^{-3} (MBT), 10 ng dm^{-3} (MPT), 12 ng dm^{-3} (DPT), 11 ng dm^{-3} (TPT).

Water samples were analysed at least five times with relative standard deviations in the range 4–10% when peak height was used. The precision of the detector response using the area peak decreases: for this reason, peak height was used throughout.

RESULTS AND DISCUSSION

The use of cartridges for organotin extraction: general considerations

The use of cartridges for solid extraction of organotin species has undoubted advantages:

(1) it requires less volume of solvent than traditional liquid–liquid extraction;
(2) it involves simple manipulations which are not time-consuming and make possible *in situ* treatment of samples;
(3) the cartridges can be used for storage of organotins;
(4) it is possible to extract greater volumes of sample if the cartridge capacity is not overloaded.

Interactions between the cartridge packing material and the aqueous matrix (which contains organotins) are complex, involving forces very different in character, i.e. polar, non-polar, chemical bond and ion exchange. In addition, the interactions between aqueous matrix and analyte also affect the retention of the latter in the cartridges, it being necessary to consider the solubility of the species, dissociation constants of ionic

groups and possible adsorption of the analyte on suspended solids, which are usually retained by the cartridge filter, giving low recovery values.

Organotins are easily retained in reverse-phase cartridges due to the presence of organic groups that determine strong non-polar interactions. However the tin atom is polar in character and influences the final polarity of these compounds. Generally the overall polarity of the molecules increases in the order trialkyltin < dialkyltin < monoalkyltin and this fact determines the elution of these compounds from the cartridges due to secondary interactions with the polar silica and silanol groups of the packing substrate. As a consequence a few weakly held polar components (TBT and TPT) can be eluted with polar solvents such as methanol, while more tightly bound components (DBT, DPT, MBT, MPT) need progressively increased polarity of the solvent by addition of HBr for elution.

Complete adsorption of organotins on the cartridges has been verified by the absence of these species in the aqueous phase eluted from them during the loading step. Also, experience based on spiked aqueous samples shows good recoveries of organotin concentrations during cartridge extraction and elution, which exclude both the occurrence of blockage processes and the possible dismutation of tin species described in the literature.[4]

The elution of organotins from the cartridges has special characteristics because the separation step is usually combined with the chromatographic determination of these compounds. The elution volume is not a determining factor, since the extract has to be derivatized with a Grignard reagent to obtain volatile species for the GC device, which involves the final reduction of solvent volume. The purity of the solvent is not decisive because the derivatized extract undergoes a clean-up treatment through a Florisil column. Finally, derivatization establishes restrictions in the eluent choice, because it must not react with the Grignard reagent or be volatile enough for easy elimination in a rotary evaporator.

Discussion of experimental work

Cartridges with different non-polar stationary phases were tested: octadecyl (C_{18}), octyl (C_8), ethyl (C_2), phenyl, and solvents that do not react with the pentylmagnesium bromide (used as derivatizing reagent) such as pentane and ethyl ether. Other experiments have been developed with more polar solvents such as dichloromethane or methanol with boiling points of 40 °C and 65 °C, respectively, which makes possible their later elimination by addition of hexane (b.p. 69 °C) and concentration of the mixture in the rotary evaporator.

The retention/elution experiments have been carried out on seawater in which the absence of organotin species was proved, applying the speciation procedure previously reported.[9,10] The water has been filtered through a 0.45-μm filter to eliminate suspended solids and doped at the appropriate levels with TBT, DBT, MBT, TPT, DPT and MPT.

Influence of pH on retention

Loading of organotins in the different cartridges has been studied using aqueous solutions of these compounds at different pH values (3.0, 6.0 and 8.5). For this purpose, 100 cm^3 of spiked seawater, in which the pH was fixed using HCl and NaOH solutions, was extracted with C_{18}, C_8, C_2 and phenyl cartridges, and the presence of tin species in the aqueous eluent was evaluated by liquid–liquid extraction and GC FPD determination. In all cases the species were retained in the cartridges.

Elution with non-aqueous solvents

The retention properties of cartridges are basically due to the functional groups bonded to the silica structure, although secondary interactions, due to both the polar character of the silica substrate and the silanol groups on the particle surface, are also present. Elution has been carried out manually with a syringe, collecting separately three successive fractions of 2, 3 and 5 cm^3, in which organotins were analysed. The polarity of the solvent controls the elution of the different species, so with a non-polar solvent such as pentane it is not possible to elute any organotins, regardless of the type of cartridge packing. Elution starts with progressively more polar solvents ethyl ether partially elutes TBT and TPT using a C_{18} cartridge and dichloromethane but methanol especially gives quantitative recoveries for TBT and TPT using C_{18} and C_8 cartridges (Fig. 1). On the other hand, when the polarity of the packing increases, the recoveries decrease (Fig. 2). These results suggest that non-polar interactions are the determinant factor during the retention step, causing species adsorption from the aqueous solution; however, secondary polar

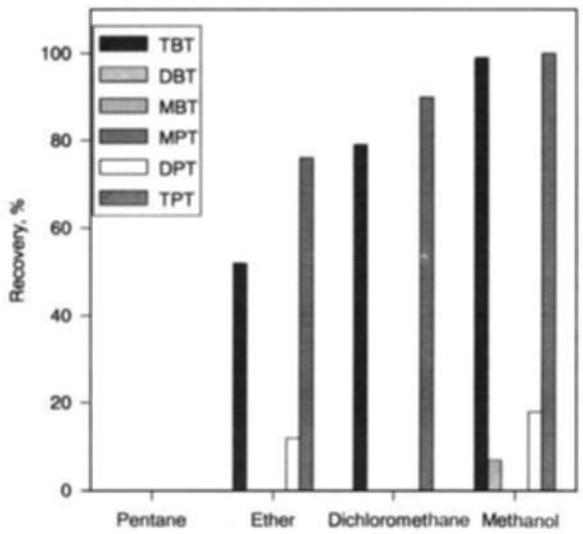

Figure 1 Recoveries of organotins obtained with 5 cm^3 of different eluents, using C_{18} cartridges for the liquid–solid extraction of 100 cm^3 of spiked water samples.

interactions become important in the elution, which determines the use of polar solvents in this step.

The selective elution of TPT and TBT previously described could be used for quantitative separation of these species from other organotins usually present in environmental samples as a consequence of degradation processes.

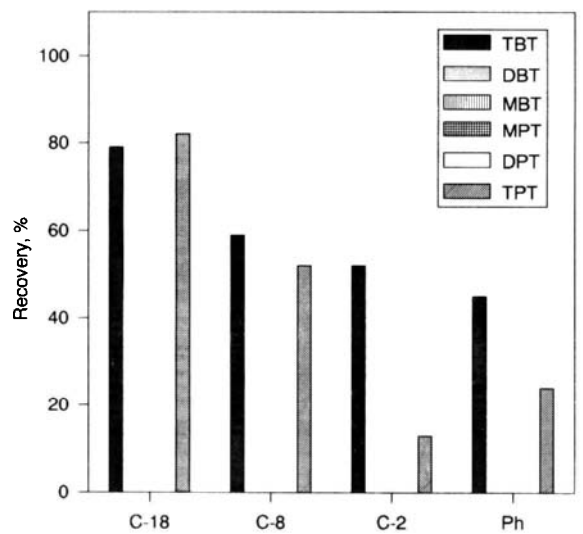

Figure 2 Recoveries of organotins from 100 cm^3 of spiked water samples, using cartridges with different reverse-phase packings: octadecyl (C_{18}), octyl (C_8), ethyl (C_2), and phenyl (Ph). Eluent: 2 cm^3 of methanol.

Influence of tropolone and HBr

The use of a tin-chelating agent such as tropolone can modify the elution properties of solvents, since the reagent reduces the polarity of organotin species when they form the corresponding complexes. Experiments on the elution of the six organotins under study have been carried out, using fresh 0.1% (w/v) solutions of tropolone in the four solvents tested: pentane, ethyl ether, dichloromethane and methanol. Tropolone has a decisive influence on the quantitative elution of all the species which can be completely recovered using non-polar cartridges such as C_{18} and C_8 and any of the solvents tested, with the exception of pentane.

The acidification of the eluent can affect the recoveries of the organotins from the cartridges. With this purpose the elution of all the species has been studied with 1% (v/v) HBr solution in the different solvents under consideration. The best results are obtained with methanol which gives quantitative elutions of all the species with C_{18} and C_8 cartridges. With ethyl ether and dichloromethane quantitative recoveries are possible only when using C_{18} packing. With pentane, elution was unsuccessful.

Finally, if both tropolone and HBr are added simultaneously to the eluent, it is possible to obtain a general improvement of the recoveries from the cartridges, except for pentane. The best results have been obtained in the following cases:

(1) Eluting organotins with 2 cm^3 of methanol from a C_{18} or C_8 cartridge;
(2) With 2 cm^3 of ethyl ether and a C_{18} cartridge;
(3) Using two fractions of 2 and 3 cm^3, respectively, of dichloromethane and C_{18};
(4) Using two fractions of 2 and 3 cm^3 of ethyl ether with a C_8 cartridge.

Selective elution of organotins

Solvents of different strength can be used for selective or successive elution of all the organotins under study. For this purpose it is possible to classify the species in three groups:

(1) TBT, TPT;
(2) DBT, DPT;
(3) MBT, MPT.

Their increasing polarity determines their different behaviour in the eluting process.

Successive elution has been tested using C_8 cartridges having intermediate retention power,

Table 1 Recoveries (%) of organotins in different fractions eluted from C_8 cartridges with HBr–methanol solvent

HBr (%)	Fraction (cm^3)	TBT	DBT	MBT	MPT	DPT	TPT
0	2	59	0	0	0	0	52
	5	78	0	0	0	0	100
	10	99	0	0	0	0	101
0.2	2	86	85	0	0	95	97
	5	93	94	0	0	97	99
	10	95	96	10	0	97	99
0.4	2	89	95	0	0	97	99
	5	97	97	0	0	97	100
	10	99	100	11	0	97	99
1.0	2	98	99	91	86	97	97
	5	100	99	98	85	99	99
	10	100	99	99	99	99	99
1.0 (+0.1% tropolone)	2	95	95	90	93	99	98
	5	97	98	97	98	99	98
	99	98	99	99	98	99	99

which establishes more significant differences between the behaviour of the species. In Table 1 can be seen the results obtained using as eluent methanol with different percentages of HBr, and also methanol with HBr and tropolone. The tri-derivatives are quantitatively eluted with 10 cm^3 of pure methanol, but if a 0.4% (v/v) HBr solution in methanol is used it is possible to obtain the complete recovery of tri- and di-derivatives with 5 cm^3 of this eluent. Finally, when 10 cm^3 of 1.0% (v/v) HBr solution in methanol or 5 cm^3 of a 1.0% (v/v) HBr and 0.1% (w/v) tropolone solution in methanol is used, the elution of all organotins is possible. Therefore, the six organotins considered can be eluted in couples using successively three different solvents:

(1) 10 cm^3 of methanol to elute TBT and TPT;
(2) 5 cm^3 of 0.4% (v/v) HBr solution in methanol for DBT and DPT;
(3) 5 cm^3 of 1.0% (v/v) HBr and 0.1% (w/v) tropolone solution in methanol for MBT and MPT.

To check the usefulness of this successive elution procedure, it has been applied to a spiked seawater sample and results, in Table 2, show a good agreement between added and estimated amounts of organotins.

Optimum size of samples

It is interesting to evaluate the volume of aqueous sample that can be treated with the cartridge without overloading the packing material. The experiments have been carried out on spiked samples ranging from 100 to 5000 cm^3, because organotin concentrations in water are usually very low: this makes necessary the use of large samples to load suitable amounts of tin species on the cartridges. Results can be seen in Table 3, which shows good recoveries for all the samples tested. In the study a C_{18} cartridge was used to retain the

Table 2 Speciation of organotins in spiked seawater using successive elution from C_8 cartridges

		Concentration ($\mu g\ Sn\ l^{-1}$)					
	Treatment	TBT	DBT	MBT	MPT	DPT	TPT
Organotin added	—	4.7	5.9	5.4	10.2	11.3	12.7
Organotin found	Elution with 10 cm^3 of methanol	4.6	<DL[a]	<DL	<DL	<DL	12.9
	Elution with 5 cm^3 of 0.4% HBr solution in methanol	<DL	5.8	<DL	<DL	11.2	<DL
	Elution with 5 cm^3 of 1.0% HBr and 0.1% tropolone solution in methanol	<DL	<DL	5.3	9.9	<DL	<DL

[a] DL, detection limit.

Table 3 Concentrations of organotins (ng Sn l^{-1}) eluted from cartridges after retention from different volumes of spiked samples

Volume (cm^3)		TBT	DBT	MBT	MPT	DPT	TPT
1000 (blank)	Added	<DL[a]	<DL	<DL	<DL	<DL	<DL
	Found	<DL	<DL	<DL	<DL	<DL	<DL
5000 (blank)	Added	<DL	<DL	<DL	<DL	<DL	<DL
	Found	<DL	<DL	<DL	<DL	<DL	<DL
100	Added	4789	5979	5495	10174	11327	12695
	Found	4.8×10^3	5.9×10^3	5.4×10^3	10.2×10^3	11.2×10^3	12.8×10^3
1000	Added	478.9	597.9	549.5	1017	1133	1269
	Found	4.7×10^2	5.9×10^2	5.5×10^2	10.3×10^2	11.1×10^2	12.4×10^2
2500	Added	191.6	239.2	219.8	407.0	453.1	507.8
	Found	18.6×10^1	24.4×10^1	21.0×10^1	40.3×10^1	44.4×10^1	51.6×10^1
5000	Added	95.8	119.6	109.9	203.5	226.5	253.9
	Found	9.9×10^1	11.7×10^1	10.8×10^1	21.1×10^1	22.6×10^1	24.8×10^1

[a] DL, detection limit.

organotins, which were eluted with 5 cm^3 of 1.0% (v/v) HBr and 0.1% (w/v) tropolone solution in methanol using a flux of 3 cm^3 min^{-1}. Therefore the use of cartridges makes possible the preconcentration of organotins from a large volume of water, reducing the detection limit of liquid–liquid extraction[10] five times when samples of 5000 cm^3 are studied.

Comparison of liquid–liquid and liquid–solid extraction in environmental samples

It is interesting to compare results for organotin extraction by applying both liquid–liquid and liquid–solid procedures to waters sampled from different sources: rivers, estuaries, bays, etc. Organotins can be in two forms in waters: dissolved aqueous species or adsorbed on the solids suspended in the water. Therefore it is necessary to check whether extraction methods evaluate total amounts of organotins in water or only one form of these species (dissolved or adsorbed). For this purpose, several aliquots have been taken from the samples and organotins evaluated in the following matrix:

(1) suspended solids (retained in a 0.45-μm filter) using a previously reported procedure;[9]
(2) filtered water using liquid–liquid extraction;
(3) complete water (suspended matter + filtered fraction) using liquid–liquid extraction,
(4) complete water by liquid–solid extraction (cartridge).

Filtration was carried out not later than 48 h after sampling, and analytical determination not later than four days. Table 4 summarizes the results obtained in water samples from different points of the south-west coast of Spain. The geographical location of sites has been depicted in a previous paper,[9] but contamination characteristics of sampling points as well as data on organotin intakes, boating activity, etc, are described below.

Sample 1 Cadiz (fishing boatyard): a very enclosed place with numerous small fishing boats, and total absence of sport. Date of sampling 30 May 1992.

Sample 2 Cadiz (fishing boatyard): Date of sampling 19 June 1992.

Sample 3 Sherry Marina: Next to Puerto de Santa Maria city (Cadiz coast) with a high activity of pleasure vessels with glass-fiber hulls which usually require less protection by antifouling paints than typical fishing boats. Sampling date 19 June 1992.

Sample 4 Puerto de Santa Maria harbour (Cadiz coast): high fishing boat activity. Sampling on 19 June 1992.

Sample 5 Sevilla dock (Guadalquivir river): consisting of several small recreational boatyards and commercial wharves. Sampling 14 June 1992.

Sample 6 La Gallinera harbour (Cadiz area): it is the port of San Fernando city which receives organotin inputs from numerous small fishing boats. Sampling 9 June 1992.

Table 4 Concentrations of organotins (ng Sn l^{-1}) in natural waters using liquid–liquid and liquid–solid extraction

Sample					Content of suspended matter in water (ppm)	Volume of sample (cartridges only) (cm^3)
No.	Treatment[a]	TBT	DBT	MBT		
1	A	184	66.9	28.6	11.9	1000
	B	66.3	46	24.5	11.9	1000
	C	89	52	25.8	11.9	1000
	D	97	19.1	<DL[b]	11.9	1000
2	A	74	65	15.8	24.9	2500
	B	47	53	10.6	24.9	2500
	C	55	56	12.0	24.9	2500
	D	21	9.9	4.1	24.9	2500
3	A	66	60	<DL	25.3	2300
	B	43	44	<DL	25.3	2300
	C	46	47	1.8	25.3	2300
	D	15.9	11.1	<DL	25.3	2300
4	A	25.3	17.7	27.3	53.3	1300
	B	6.9	6.8	16.5	53.3	1300
	C	9.8	8.9	19.6	53.3	1300
	D	13.1	8.8	7.6	53.3	1300
5	A	68	49	17.4	17.4	1750
	B	20.8	27.0	11.1	17.4	1750
	C	29.8	33.4	13.8	17.4	1750
	D	38	19.1	4.7	17.4	1750
6	A	9.6	57	23.7	64.3	2500
	B	5.1	28.8	17.8	64.3	2500
	C	5.7	34	19.0	64.3	2500
	D	<DL	20.4	<DL	64.3	2500
7	A	<DL	<DL	<DL	15.8	5000
	B	<DL	<DL	<DL	15.8	5000
	C	2.1	4.0	6.8	15.8	5000
	D	<DL	<DL	<DL	15.8	5000
8	A	7.2	11.4	19.1	16.9	3700
	B	<DL	<DL	<DL	16.9	3700
	C	1.5	2.2	3.6	16.9	3700
	D	2.3	5.9	<DL	16.9	3700
9	A	21.7	5.7	14.3	39.7	2500
	B	15.6	<DL	13.6	39.7	2500
	C	14.2	<DL	13.8	39.7	2500
	D	<DL	<DL	<DL	39.7	2500
10	A	11.0	22.4	9.8	22.0	1400
	B	7.1	17.7	8.1	22.0	1400
	C	7.8	19.1	8.3	22.0	1400
	D	<DL	<DL	<DL	22.0	1400
11	A	15.3	13.8	10.3	49.0	1600
	B	6.8	14.2	10.4	49.0	1600
	C	8.4	14.1	10.5	49.0	1600
	D	6.2	<DL	<DL	49.0	1600

[a] A, liquid–liquid extraction of non-filtered water; B, liquid–liquid extraction of filtered water (0.45-μm filter); C, liquid–solid extraction of non-filtered water; D, the organotins were evaluated in the suspended matter retained in the filter. [b] DL, detection limit.

Sample 7 San Pedro river (Cadiz): with scarce boat activity but suffering the influence of Cadiz Bay and Puerto de Santa Maria harbour. Sampling 6 June 1992.

Sample 8 Caiman point (Isla Cristina village–Huelva coast). situated near open sea but the proximity of a small harbour with numerous boats represents a potential focus of pollution. Sampling 5 May 1992.

Sample 9 Pinillos channel (Carreras river Huelva coast): this place is remote from usual organotin sources; there are some oyster farms. Sampling 5 May 1992.

Sample 10 Isla Cristina harbour (Huelva coast): plentiful boat activity, both fishing and recreational. Sampling 7 July 1992.

Sample 11 Canela channel: next to Pinillos channel. Sampling 7 July 1992.

Data from Table 4 reveal that organotin concentrations estimated by liquid–liquid extraction (treatment A) are higher than those of liquid–solid extraction (treatment C). In addition, concentration values of liquid–solid extraction plus those corresponding tin species in the suspended matter present in the water (treatment D) are approximately the same as for treatment A. This means that cartridges should not be used for waters containing suspended matter, when organotin speciation has to be evaluated simultaneously both as solvated and particulate forms. However the method seems to be useful to estimate solvated organotins. Finally, the data on tin species in filtered waters (0.45-μm glass-fiber filter), treatment B, show some losses that could be attributed to adsorption processes on the glass filter attachment.

CONCLUSIONS

Comparison of liquid–liquid with liquid–solid extraction for organotins shows advantages and drawbacks in both procedures. Liquid–liquid extraction recovers quantitatively organotins present in water samples, both dissolved and adsorbed on suspended matter species. However, the extraction procedure is time-consuming and requires a large volume of non-aqueous solvent. In addition, the volume of sample is limited to 1 dm^3 and a selective extraction of species for non-chromatographic speciation is not possible.

Liquid–solid extraction involves simple handling and manipulation, the time and solvent volume necessary for the separation being small. The elimination of non-polar impurities are possible, by elution with pentane prior to the final treatment with methanol, and extraction of large-volume samples which increases the detection limit of the procedure. The sample can be extracted at the sampling point and the organotins retained are easily transported and stored. Finally, organotins can be eluted from the cartridge in couples using a C_8 packing. The principal drawback is the unsuitability of cartridges for extraction of turbid water with organotin species adsorbed on suspended solids, which are retained in the cartridge, causing losses.

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