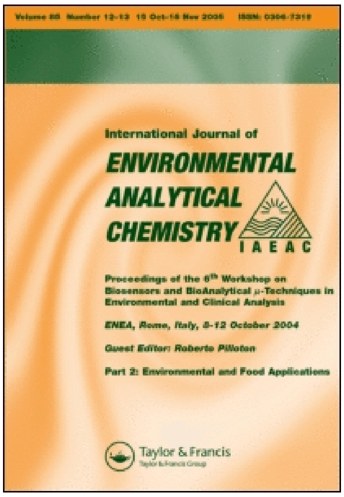

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ACID LEACHING/SOLVENT EXTRACTION TREATMENT OF SEDIMENT SAMPLES FOR ORGANOTIN SPECIATION

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A method is described for leaching of nanogram amounts of monobutylin (MBT), dibutyltin (DBT) and tributyltin (TBT) and monophenyltin (MPT), diphenyltin (DPT) and triphenyltin (TPT) from sediments. The procedure is based on soaking the sediments in water-hydrogen bromide mixture (1 : 1) with magnetic stirring for 30 min followed by extraction with 0.04% (w/v) tropolone solution in dichloromethane for 2 h. Organotins are determined by gas chromatography with a flame photometric detector (GC-FPD) after cleanup through a Florisil column and derivatization by Grignard pentylation. The method has been applied to the study of water and sediments in different areas of the south-west Spain. Predominant species are butyltins, especially TBT which rise critical levels in waters and sediments of fishering harbours. In this study it has been found a direct relation between organotin levels and distance to potential sources determined by boating activities. In addition, it has been verified the relative occurrence of DBT and MBT together with TBT, possibly as a result of a degradation process, and the influence of sediment grain size and organic matter content on organotins accumulation.

Keywords: Tributyltin; triphenyltin; organotin; speciation; sediments; gas chromatography; south-west Spain

INTRODUCTION

The frequent and wide use of organotin compounds for industrial and biocidal purposes makes necessary the development of suitable analytical methods for simultaneous speciation of the most usual components in formulations such as TBT and TPT, as well as other compounds formed by environmental degrada-

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tion. Due to its toxicity, TBT can induce harmful effects on non-target organisms, some of which are very important from an economical point of view[1–3]. As a consequence, the environmental quality standard value (EQS) for TBT was set at 20 ng dm^{-3} in UK in 1987 and lately re-set at 2 ng dm^{-3} in order to achieve complete protection of marine life[4]. This measure has produced a clear reduction of TBT concentrations in UK estuaries[4,5].

Analytical speciation techniques for organotin compounds in sedimentary samples are more complex than those for waters[6]. This makes necessary to pay special attention to sample preparation, as well as species extraction and preconcentration.

Organotins extraction from sediments generally involve leaching of the species with acidic solutions. Tugrul *et al.*[7] sonicate 0.5–1 g of dry ground polluted sediment for 1 h in 40 ml of 0.1M hydrochloric acid, Seidel *et al.*[8] use 0.3M hydrochloric acid leaching to extract tin and organotin compounds from sediments and Randall *et al.*[9] use a 2.5 M calcium chloride and 2.5 M HCl extraction and analyze the tin with hydride generation atomic absorption spectrometry (HGAA). On the other hand, Astruc *et al.*[10] and Quevauviller *et al.*[11,12] extract organotins with acetic acid in two successive steps: stirring overnight and ultrasonic extraction. Other authors combine acid leaching with the extraction with a nonaqueous solvent. Tsuda *et al.*[13] propose the extraction with hexane after acid leaching with HCl, Muller[14] use a HCl and diethylether extraction followed by methylation with methylmagnesium chloride and analysis with flame photometric gas chromatography and GC-MS. Hattori *et al.*[15] use methanolic hydrochloric acid and benzene extraction and analysis with GC-ECD. Other authors propose the use of a chelating agent, generally tropolone, to enhance the organotins extraction. Maguire *et al.*[16] use HCl, tropolone and benzene, Muller[17] and Tolosa *et al.*[18] propose an acid treatment with HCl to pH 2–3 and extraction of the resulting slurry with an ethereal tropolone solution, and Batley *et al.*[19] use sonication of the sediments with concentrated HCl and methanol followed by extraction with tropolone in dichloromethane. Ashby and Craig[20] also propose a very similar procedure based on the use of HCl for leaching of tin species and extraction with tropolone in dichloromethane. Finally, Martin-Landa *et al.*[21] recommend the treatment with concentrated hydrobromic acid and extraction with tropolone in pentane.

This paper considers the use of HBr/dichloromethane and HCl/dichloromethane as leaching systems for butyltin and phenyltin species in sediment samples. These methods are applied to assess the occurrence of these species in waters and sediments of the Huelva coast (southwest Spain).

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 analysis.

Water Extraction Procedure

A 1000-cm^3 portion of the unfiltered water sample was acidified with 10 cm^3 of HBr (Merck) and extracted by shaking vigorously in darkness with 300 cm^3 of 0.07% (w/v) solution of tropolone (Aldrich) in dichloromethane for 10 min. Tropolone concentration was optimized to prevent dismutation[22]. The organic extract was dried with anhydrous Na_2SO_4 and reduced in volume to 0.5 cm^3 in a rotatory evaporator.

Sediment Chemical Treatment/Extraction Procedure

A suitable weight of wet homogenized sediment (about 20 g) was placed in a 250 ml flask with a PTFE screw closure and treated with 50 ml of a water-hydrogen bromide mixture (1:1) with magnetic stirring for 30 min. Then, the mixture was extracted with 50 ml of 0.04% (w/v) tropolone solution in dichloromethane for 2 h. The phases were separated in 50 ml Teflon tubes by centrifugation at 10000 rpm for 10 min and both the aqueous and organic phases were transferred to a separating funnel, in which the organic phase was separated and dried with anhydrous sodium sulphate. The resulting extract was reduced in volume about 1.0 cm^3 by rotatory evaporation. The solid residue remaining in the centrifuge tubes was shaked again for 5 min with 5 ml of hexane and centrifuged. The resulting organic phase was used to reextract the former aqueous phase for 3 min, and the hexane extract was dried and added to the concentrated dichloromethane extract. The mixture was reduced again in volume to 1 ml by rotatory evaporation.

Analytical Method

Derivatization

The dichloromethane extract was treated with 4 ml of 1M pentylmagnesium bromide solution in ether for 1 h in a sealed device, at room temperature.

The excess of reagent was removed with 1N sulfuric acid and the organic extract was reduced to 1 ml, then purified by passing through a 7 × 1 cm i.d. column of Florisil (Merck) using 10 ml of pentane as eluent. This pentane extract was then reduced to 2 ml and transferred into a microevaporator together with the internal standard (dimethyldipentyltin) and concentrated to 0.5 or 0.2 cm^3 under a gentle stream of nitrogen.

Measurement of organotin concentrations

Organotin species were determined using a GC-FPD system, following a procedure reported previously.[23,24] A Perkin-Elmer 8140 gas chromatograph fitted with a split/splitless injector, 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. 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 not directly carried out on sediments or waters. Calibration curves were linear for Sn amounts lower 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.

Quality control of results was monitored by preparing a calibration graph per week and injecting a derivatized standard with all tin species every day to test the instrument signal. Absolute limits of Sn able to be detected for the instrument evaluated as 3 times the blank signal were about 0.3 ng for butyltins and

0.5 ng for phenyltin species. The detection limits in water and sediment analysis (including the extraction step) are the following: **water** (ng l^{-1}): TBT 4.6, DBT 5.3, MBT 5.3, MPT 12, DPT 12 and TPT 11; **sediment** (ng g^{-1}): TBT 0.61, DBT 0.75, MBT 0.76, MPT 2.8, DPT 3.2 and TPT 2.7.

Both water and sediment samples were analysed at least 5 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 the peak height was used throughout.

Area of Study

The presence of organotin compounds was studied in waters and sediments of the Huelva coast (southwest Spain) (Figure 1) in which levels of TBT were previously checked in waters[24]. This area has a remarkable ecological importance because it is a feeding ground of international importance for migratory birds (*Odiel Marshes Natural Park*). Sampling sites were selected in relation to the suspected presence of organotins caused by the boating activity in wharves, docks, shipyards, etc.

Three locations were studied: *(a) Ayamonte-Isla Cristina area* (Figure 1b), a marshes area between two rivers (*Guadiana* and *Carreras*), with small fishering harbours and shell-fish farms; *(b) Piedras River* (Figure 1c), with a long sandy bar in the mouth that causes strong enclosure of waters; and *(c) Huelva city area* (Figure 1d), including Huelva city and Punta Umbria village with a very complex hydrodynamic characteristics.

Sample Collection

All the samples were collected during January and February 1992, and analysed in seven days after sampling.

Water samples were collected in 2.5 l polycarbonate bottles. Where possible, samples were collected from land, if not they were collected from a boat. All of the samples were manually collected from just beneath the surface. To avoid microlayer contamination the bottle cap was carefully removed under the water surface. The samples were then stored at 4°C in the refrigerator.

Sediment samples were collected at the surface taking aliquots of about 10 cm depth, which were carefully homogenized. The aliquots from each sampling point were mixed to get composite samples using 4 crossed sites spaced out 2 m, then homogeneized and placed in polyethylene bottles for freezing and storage.

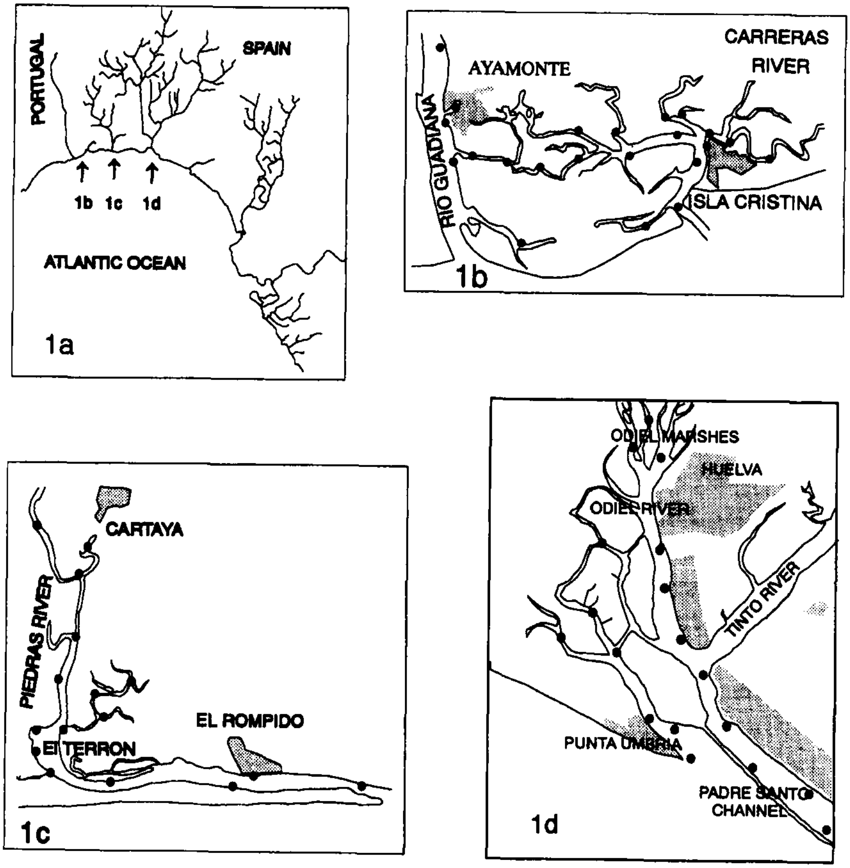

FIGURE 1 (a) Area of study in the Huelva coast (southwest Spain); (b) Sampling sites in Ayamonte-Isla Cristina area; (c) Details of sampling locations in the Piedras river; (d) Sampling points locations in the Huelva city area (Odiel marshes, Padre Santo channel and Punta Umbría beach)

RESULTS AND DISCUSSION

Extraction of the different organotins from the sediments is a decisive step for their analytical characterization. For this purpose a double treatment is usually necessary: acid treatment (leaching) followed by extraction in a non-aqueous solvent for later derivatization and analysis.

In order to set up the optimum extraction procedure for total recovery of organotin species from sediments, tests have been carried out modifying the more important experimental variables affecting the separation step.

Recoveries from Spiked Sediments

Influence of acid concentration

The action of HBr as leaching agent was tested on sediments spiked at the appropriate levels with MMT, TBT, DBT, MBT, TPT, DPT and MPT. These spiked sediments were prepared stirring overnight a free-organotin sediment (obtained from sites remote from usual organotin sources) with an aqueous solution of known concentrations of these compounds. The ratio water:sediment for these experiences was maintained at 1 : 1 value, as generally occurred in real samples. Table I shows the results obtained. The presence of a high concentration of HBr is critical for recovery of monomethyltin, possibly because it is strongly adsorbed on the sediment by its higher polarity. Recoveries are quan-

TABLE I Percentage of recovery (RSD in brackets) of organotin species in spiked sediments under different experimental conditions

% HBr	*TBT*	*DBT*	*MBT*	*MPT*	*DPT*	*TPT*	*MMT*
30	100(3.15)	98(3.23)	100(3.25)	100(4.00)	99(3.67)	98(3.53)	80(5.21)
40	99(2.99)	99(3.07)	99(3.12)	98(3.97)	97(3.54)	95(3.57)	99(3.88)
50	100(2.79)	100(2.81)	100(2.87)	99(3.02)	100(3.00)	99(2.97)	100(3.02)
60	89(4.17)	99(3.99)	99(4.03)	100(3.17)	98(3.03)	97(3.21)	99(2.87)
70	50(5.23)	64(6.45)	70(8.21)	80(7.21)	100(8.37)	85(8.41)	100(2.93)
Tropolone (%)	*TBT*	*DBT*	*MBT*	*MPT*	*DPT*	*TPT*	*MMT*
0	99(2.87)	98(2.79)	86(4.17)	85(5.15)	98(3.08)	99(3.15)	78(5.29)
0.02	98(2.73)	99(2.81)	97(3.12)	100(3.33)	98(2.95)	96(2.79)	95(3.01)
0.04	99(2.57)	100(2.77)	99(2.65)	99(2.89)	100(2.91)	99(2.83)	99(2.91)
0.1	100(2.79)	100(2.81)	100(2.87)	99(3.02)	100(3.00)	99(2.97)	100(3.02)
0.2	100(2.87)	102(2.92)	99(2.84)	97(2.97)	97(3.12)	99(3.41)	98(3.17)
Dichloromethane (ml)	*TBT*	*DBT*	*MBT*	*MPT*	*DPT*	*TPT*	*MMT*
25	98(3.21)	99(3.42)	86(3.67)	79(5.23)	99(6.17)	86(5.81)	53(7.23)
50	100(2.49)	100(2.64)	100(2.71)	99(2.90)	100(2.31)	99(2.97)	99(3.05)
100	99(2.51)	100(2.57)	100(2.83)	100(2.86)	99(2.87)	99(2.99)	98(2.99)
Time (min)	*TBT*	*DBT*	*MBT*	*MPT*	*DPT*	*TPT*	*MMT*
5	97(3.13)	95(3.37)	96(3.41)	94(3.79)	95(3.17)	97(3.86)	85(4.10)
30	98(2.55)	99(2.61)	100(2.59)	98(3.03)	100(2.89)	99(2.81)	100(2.97)
60	100(2.49)	100(2.64)	100(2.71)	99(2.90)	100(2.31)	99(2.97)	99(3.05)
Time (h)	*TBT*	*DBT*	*MBT*	*MPT*	*DPT*	*TPT*	*MMT*
0.25	55(9.37)	95(10.5)	97(8.39)	98(9.52)	75(8.88)	56(8.71)	89(7.93)
1	74(7.59)	100(6.47)	99(6.51)	99(8.11)	100(7.45)	81(7.43)	95(4.55)
2	100(2.47)	100(2.52)	100(2.49)	99(2.94)	100(2.83)	99(2.70)	100(2.87)

titative using percentages of HBr higher than 30%. However, the results are not satisfactory for butyl- and phenyltin species when very high HBr concentrations (about 70%) were used, possibly due to organotin degradation.

Influence of the Tropolone and Volume of Pentane

To avoid the problems arising from the extraction of more polar organotin compounds such as MBT, MPT and MMT, the action on the process of tropolone, a complexing agent frequently recommended in the bibliography for organotin species[11,12] was tested. The results (Table I) show that at least a 0.02% of tropolone is necessary to get quantitative recoveries of monoalkyl derivatives. Therefore, 0.04% (w/v) tropolone solution in dichloromethane was used in further experiments.

The optimum volume of dichloromethane was also tested in a set of experiments and the results are also in Table I. The conclusion is that it is necessary to use a non-aqueous phase of at least 50 ml for complete recoveries.

Optimization of Both Leaching and Extraction Times

The successive application of leaching and extraction steps for the recovery of organotins from sediments makes necessary to optimize the time involved in both stages of the procedure. To optimize the leaching step, several experiments were carried out setting the extraction step at 2 h. As it is shown in Table I at least 5 min of leaching are required for quantitative results, although results are better for MMT with 30 min leaching. On the other hand, extraction step was optimized setting the leaching time at 30 min, being verified that 2 h of extraction are needed for satisfactory recoveries (see Table I), especially for tributyltin and triphenyltin derivatives.

Recoveries from Polluted Sediments

The procedure developed for the extraction of organotin species from doped sediments was checked in real sediments suffering organotins contamination, because adsorption of these species in real samples can follow different mechanisms that in doped samples. For this purpose three sediments from the SW coast of Spain (Figure 1a) receiving inputs from some boating activities (harbours, recretional boatyards, commercial wharves, fishing activities, etc) were used. Sediment samples were mechanically homogeneized for 7 h and stored in the refrigerator until use, being then manually homogeneized for 5 min.

In Table II it can be seen the influence of acid concentration (HBr) and leaching and extraction times on recoveries of organotins in the environmental samples. Results are similar to those from doped samples. HBr concentrations of 50% are optimal, therefore, a HBr-water (1 : 1) mixture was selected for extraction. The influence of digestion (leaching) and extraction times was negligible.

Occurence of Organotin Species in the Huelva Coast

Ayamonte-Isla Cristina area (Figure 1b)

Concentrations of organotin compounds in waters from this area reveal the presence of two potential organotins sources: Ayamonte and Isla Cristina harbours, decreasing the levels of these species with the distance to the focus. Generally, TBT levels were higher than other tin species, but in the secondary channels degradation causes similarities in the TBT and DBT concentrations and the absence of MBT. Phenyltin species were not detected in this area being the averaged concentration of TBT higher than 50 ng l^{-1}, a level that has subletal effects on fish and shell-fish larvaes.

Trends in sediment samples were similar to those observed in waters, high levels of TBT in harbours and the surrounding areas, decreasing rapidly with the distance to the focus, and a low presence of phenyltins, specially DPT and MPT. Concentrations of TBT in the sediments ranged from 2 to 130 μg g^{-1}, depending on their location composition (percentage of organic matter or clay with adsorptive properties). The hydrodinamic properties in the channels also have important consequences on organotin accumulation.

Piedras River (Figure 1c)

In this river very low levels of organotins were observed both in waters and sediments. Only in El Terron and El Rompido harbours significant concentrations of TBT (50 to 100 ng l^{-1}) in water and lower levels of DBT and MBT were found (phenyltins have not been detected). Levels in sediments were not significant in relation to other areas of the coast (averaged concentration of TBT was 2 ng g^{-1}, with a maximum in El Rompido, 20 ng g^{-1}). This fact is possibly due to the sandy (low adsorptive) character of these sediments.

TABLE II Influence of HBr percentage and leaching and extraction times on the recovery of organotins (measured as Sn, ng g^{-1}) from polluted sediments of the southwest Spain. Dichloromethane was used as extractant. The data in brackets correspond to the standard deviation for three replicates.

Sample	*Organo tin*	*HBr (%)*			*Leaching time (h)*		*Extraction time (h)*	
		40	*60*	*80*	*1*	*3*	*2*	*3*
1	TBT	75(2.01)	78(1.58)	75(1.75)	76(0.86)	78(1.12)	76(0.93)	74(1.24)
	DBT	298(4.97)	275(4.32)	282(8.29)	271(9.42)	272(8.52)	293(7.79)	283(5.72)
	MBT	100(3.10)	94(0.42)	91(2.01)	97(1.42)	98(2.18)	93(1.42)	95(1.92)
	MPT	14.9(0.08)	16.2(0.37)	15.8(0.51)	16.3(0.24)	15.9(0.36)	14.8(0.42)	15.0(0.28)
	DPT	13.0(0.28)	14.2(0.29)	13.4(0.43)	12.8(0.08)	14.1(0.29)	13.8(0.43)	12.9(0.36)
	TPT	7.1(0.29)	6.8(0.14)	6.3(0.24)	7.2(0.24)	6.8(0.22)	6.9(0.16)	7.1(0.22)
2	TBT	156(4.08)	149(2.16)	150(2.94)	155(3.56)	145(2.94)	147(2.83)	150(1.63)
	DBT	48(0.86)	51(1.07)	48(1.20)	46(1.07)	48(1.24)	51(1.39)	51(0.85)
	MBT	28(0.43)	29(0.75)	30(0.78)	30(0.36)	27(0.92)	28(0.70)	30(0.78)
	MPT	14.3(0.43)	15.9(0.36)	16.3(0.45)	14.8(0.28)	15.6(0.36)	16.0(0.29)	15.9(0.22)
	DPT	13.2(0.22)	13.3(0.28)	11.8(0.33)	12.1(0.29)	11.7(0.42)	13.0(0.42)	12.7(0.29)
	TPT	23.1(0.50)	24.2(0.57)	22.4(0.33)	22.9(0.79)	23.8(0.36)	23.7(0.43)	24.3(0.37)
3	TBT	1.66×10^4	1.50×10^4(377)	1.65×10^4(283)	1.71×10^4(63.5)	1.66×10^4(201)	1.64×10^4(200)	1.58×10^4(210)
	DBT	1.21×10^3(11.0)	1.29×10^3(13.1)	1.26×10^3(18.8)	1.20×10^3(11.8)	1.21×10^3(17.5)	1.26×10^3(10.0)	1.28×10^3(20.8)
	MBT	533(5.66)	566(7.26)	532(6.16)	521(6.68)	574(8.83)	578(6.48)	561(6.16)
	MPT	372(6.38)	395(4.97)	401(7.48)	388(7.79)	374(5.72)	363(5.10)	367(7.12)
	DPT	180(4.97)	196(3.56)	186(3.56)	174(5.72)	185(3.56)	188(3.74)	189(5.10)
	TPT	330(5.35)	331(5.72)	309(6.38)	311(5.72)	317(6.16)	322(4.55)	332(5.10)
Blank	TBT	<DL*	<DL	<DL	<DL	<DL	<DL	<DL
	DBT	<DL	<DL	<DL	<DL	<DL	<DL	<DL
	MBT	<DL	<DL	<DL	<DL	<DL	<DL	<DL
	MPT	<DL	<DL	<DL	<DL	<DL	<DL	<DL
	DPT	<DL	<DL	<DL	<DL	<DL	<DL	<DL
	TPT	<DL	<DL	<DL	<DL	<DL	<DL	<DL

*DL, detection limit

Huelva city area (Odiel marshes, Padre Santo channel, Punta Umbría beach) (Figure 1d).

The results obtained in this zone reveal† the absence of phenyltins in water and the existence of high concentrations of butyltins in both the small Punta Umbria fishering harbour (50 to 100 ng l^{-1}) and the Levante wharf situated in Huelva city (82 ng l^{-1}). The levels of TBT decreases in other points, although they were still higher than 20 ng l^{-1} in the Padre Santo channel and in the marshes. The presence of butyltins in sediments show a similar trend with levels of about 100 to 200 ng g^{-1} in the focus, and about 5 to 10 ng g^{-1} in points away from the sources. Generally, concentration of organotins decreases in sandy samples or those with a low content of organic matter.

CONCLUSIONS

The use of a strong treatment is required to complete the separation of organotins from the complex matrix of the sediments for analysis, which involves both acid leaching and solvent extraction. The use of concentrated HBr and tropolone are critical for more polar organotin compounds, and the total procedure is cumbersome because it requires 2.5 h for extraction.

The appraisal carried out in the Huelva coast reveals that the presence of organotins in waters and sediments is critical, with a number of points in which levels of butyltin species in waters and sediments could have consequences on the biological quality of the ecosystem. Therefore, regulations should be established in the area under study.

The presence of organotins in harbours and sites with high boat activity has been summarized in Table III, which denotes the critical levels of TBT in the fishering dock of El Terron and in Punta Umbria fishering harbour. However, levels decrease in other similar sites of this coast, such as Ayamonte and Isla Cristina harbours and Huelva dockyard.

TABLE III Concentration of butyltin species (as ng l^{-1} of Sn) in habours of Huelva Coast

Site	*TBT*	*DBT*	*MBT*	*Total*
Ayamonte (1b)	79	20	51	150
Isla Cristina (1b)	74	9	33	119
El Rompido (1c)	53	11	<DL	64
El Terrón (1c)	101	14	10	125
Punta Umbria (1d)	100	98	44	242
Huelva (dockyard) (1d)	82	50	32	164

TABLE IV Averaged values of butyltins (as ng l^{-1} of Sn) in waters of southwest Spain

Area		*TBT*	*DBT*	*MBT*	*Total*
Ayamonte-Isla Cristina (1b)	harbour zone	65	18	38	120
	non-harbour zone	10	8	<DL	18
Piedras River (1c)	harbour zone	77	12	5	94
	non-harbour zone	10	7	7	24
Huelva (1d)	harbour zone	80	52	30	162
	non-harbour zone	20	10	9	38

There is a strong connection between the presence of organotins in the environmental components and the boat activity in the Huelva coast. Tables IV and V show the averaged organotin concentrations in waters and sediments, obtained from the data of this paper. Two subareas are established: with *high boat activity* and with *low boat activity* according to the relative presence of boats which could leach organotins from theirs hulls. However, these figures have only a relative statistical value and they do not intend to provide a global evaluation of the presence of organotins in this coast.

From the previous Tables IV and V we can establish some trends: (i) TBT is the predominant species in waters; (ii) DBT exhibits higher concentrations than MBT in harbours, but the levels of the former decrease with distance to these focus, being verified a correlative increase in MBT concentration, which can be related to natural degradation processes[25,26]; (iii) the predominance of TBT is not so marked in sediments, which show relatively high concentrations of DBT and MBT; (iv) concentrations of DBT are higher than MBT.

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TABLE V Averaged values of butyltins (as ng g^{-1} of Sn) in sediments of southwest Spain

Area		*TBT*	*DBT*	*MBT*	*Total*
Ayamonte-Isla Cristina (1b)	harbour zone	69	133	62	264
	non-harbour zone	13	25	17	55
Piedras River (1c)	harbour zone	20	32	14	66
	non-harbour zone	3	5	9	16
Huelva (1d)	harbour zone	126	94	65	285
	non-harbour zone	12	12	9	34

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