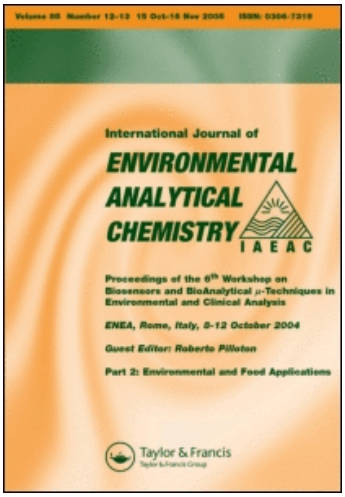

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Critical evaluation of various extraction procedures for the speciation of butyltin compounds in sediments

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Critical evaluation of various extraction procedures for the speciation of butyltin compounds in sediments

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The efficiency of different extraction procedures for the simultaneous determination of butyltin compounds in marine sediments by gas chromatography–mass spectrometry (GC–MS) was critically evaluated in the present work. Three different polar solvents (acetic acid, a mixture of acetic acid with methanol, and a mixture of acetic acid, methanol, and water) and three different extraction approaches (mechanical shaking, ultrasonic, and microwave-assisted extraction) were used for the extraction of butyltin compounds from PACS-2 certified marine sediment reference material. Before determination by GC–MS, extracted butyltin species were derivatized with sodium tetraethyl borate and extracted into iso-octane. The results indicated that 30-min ultrasonic extraction with 100% acetic acid provided satisfactory recoveries for all certified butyltins. The developed analytical method was successfully applied for determination of butyltin compounds in coastal sediments of the Northern Adriatic Sea. The results demonstrated that butyltins were present in all sediments analysed.

Keywords: Butyltin compounds; Extraction procedures; GC–MS

1. Introduction

Widespread use of organotin compounds (OTC) [1–5] has created great concern about their potential effects and toxicity in the environment [6]. Trisubstituted OTC, especially tributytin (TBT) and triphenyltin (TPhT), are among the most hazardous pollutants encountered so far in aquatic systems [1, 7, 8]. Because of their toxic effects to non-target aquatic living organisms, the European Commission banned the use of TBT-containing antifouling paints on the hulls of boats smaller than 26 M and vessels of any length used predominantly on inland waters [9]. TBT were included to the list of priority pollutants in the field of water policy in the EU Water Framework

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Directive – integrated river-basin management for Europe [10]. From 1 January 2008, any OTC should be removed from the surfaces of ships, or efficient sealing should be performed to prevent OTC leaching into the water [11]. OTC in the marine environment undergo microbial and UV degradation [5]. The degradation of trisubstituted OTC follows a stepwise debutylation to inorganic tin, which is practically non-toxic to living organisms. This can be considered as a mechanism of detoxification [8]. Half-lives of OTC in waters are in the order of weeks, and in sediments in the order of several months to several years [3].

The toxicity of OTC depends on the number and nature of their alkyl substituents. Therefore, individual OTC must be determined simultaneously in different environmental and biological samples by accurate and sensitive analytical methods [1]. Shortly, these methods typically comprise the following steps: extraction from the sample matrix, derivatization in the case of gas chromatographic separation, chromatographic separation, and selective detection [2]. For separation and detection of OTC, gas (GC), or liquid chromatography (LC) coupled with a sensitive and element or molecule-selective detection method, such as atomic absorption spectrometry [12], mass spectrometry [13, 14], inductively coupled mass spectrometry [15, 16] or pulsed flame photometric detection [17–19] has been commonly used. GC separation has the high resolution which is needed for simultaneous determination of all OTC in different samples analysed [20]. Prior to GC separation, the extracted OTC must be derivatized, usually by alkylation with Grignard reagents or sodium tetraethyl borate ($NaBEt_4$).

Extraction of OTC from solid samples, such as sediment, soil, sewage sludge, and biological samples is the most difficult step in OTC speciation analysis, due to the limited stability of the analyte and the strong interactions between the analyte and matrices [20]. Various extractants have been used for extraction of OTC from environmental samples. They can be categorized according to solvent polarity, sample acidification and the use of enzymatic hydrolysis for biological samples [21]. Acidic extractants have been used to enhance the solubility of ionic OTC [20, 21]. Extraction has been performed by mechanical shaking [22], ultrasonic extraction [20, 22], microwave extraction [20, 21, 23, 24], supercritical fluid extraction [25], and solid-phase microextraction as an alternative method to liquid–liquid extraction [26, 27].

There are some publications comparing extractions [20, 21, 28], derivatizations [20, 29] or analytical methods [20, 30, 31] for speciation of OTC in sediments [32], water [33], and biological samples [22].

Extraction is one of the major sources of error in the speciation of OTC in sediments [2]. From all OTC, butyltins are most frequently present in the environment [1]. Therefore, the aim of our work was to optimize and critically evaluate different extraction procedures for the speciation of butyltins in marine sediments by gas chromatography–mass spectrometry (GC–MS). For this purpose, three different polar extraction solvents (acetic acid, a mixture of acetic acid with methanol and a mixture of acetic acid, methanol and water) and three different modes of extraction (mechanical shaking, ultrasonic, and microwave-assisted extractions) were compared. An accurate and reliable analytical method for speciation of butyltins by GC–MS, developed on PACS 2, harbour sediment (National Research Council of Canada, NRCC, Ottawa, Canada) certified reference material, was then applied for the analyses of sediments from the Slovenian costal area of the Northern Adriatic Sea.

2. Experimental

2.1 *Apparatus*

In the extraction procedures applied, a mechanical shaker (Vibromax 40, Tehtnica Železniki, Slovenia), an ultrasonic bath (VWR, Model 550D, VWR International, West Chester, PA), and a microwave digestion system (MARS X, CEM Corporation, Mathews, NC) were used. Butyltin speciation analyses of sediments were carried out on a Hewlett-Packard 6890 gas chromatograph (Hewlett-Packard, Waldbronn, Germany) equipped with an HP6890 series automatic injector and connected to an HP5972A MSD mass selective detector. The GC was fitted with a HP-MS5 capillary column (30 m × 0.25 mm × 0.25 μm). The injection port, transfer line, and detector temperatures were maintained at 240, 280, and 180°C, respectively [14]. For the separation of butyltins, the following temperature programme was applied: for the first minute, the column temperature was held at 90°C, raised to 170°C at a heating rate of 10°C min^{-1}, held there for 2 min, raised to 220°C at a heating rate of 20°C min^{-1}, held there for 1 min, raised to 270°C at a heating rate of 30°C min^{-1}, and held at the final temperature for 6 min. The injection volume in the splitless injection mode was 1 μL. As a carrier gas, helium at a flow rate of 1 mL min^{-1} was used. For MSD electron impact (70 eV), ionization was used. The MSD was operated in the selected ion monitoring (SIM) mode where the three most abundant tin isotopes of the first fragment ion were measured [34]. Confirming ions are presented in table 1.

2.2 *Standards and reagents*

Monobutyltin trichloride ($MBTCl_3$, 95%), monophenyltin trichloride ($MPhTCl_3$, 98%), and diphenyltin dichloride ($DPhTCl_2$, 96%) were purchased from Aldrich (Milwaukee, WI). Dibutyltin dichloride ($DBTCl_2$, 97%), tributyltin chloride (TBTCl, 96%), triphenyltin chloride (TPhTCl, 95%), and tripropyltin chloride (TPrTCl, 98%) were obtained from Merck (Darmstadt, Germany). Monooctyltin trichloride ($MOcTCl_3$, 98%) and dioctyltin dichloride ($DOcTCl_2$, 98%) were purchased from LGC Promochem (Wesel, Germany) and trioctyltin chloride (TOcTCl, 95%) from Fluka (Buchs, Switzerland). Butyltin standard stock solutions containing 1000 mg (expressed as Sn)/L were prepared in methanol. Fresh standard stock solutions were made every 6 months. Working butyltin standard solutions were prepared weekly (10 mg Sn L^{-1}) or daily (100 μg Sn L^{-1} and lower). All the standards were stored in the dark at 4°C.

Acetic acid, hydrochloric acid, nitric acid, iso-octane, methanol, sodium acetate trihydrate, and ammonia were obtained from Merck (Darmstadt, Germany).

Table 1. Confirming ions for monitoring of butyltins.

Compound	Starting time (min)	*m/z*
MBT	4.0	231, 233, 235
TPrT	6.0	245, 247, 249
DBT	7.1	259, 261, 263
TBT	9.3	287, 289, 291

Sodium hydroxide was purchased from Carlo Erba (Milan, Italy) and sodium tetraethyl borate ($NaBEt_4$) from Galab products (Geesthacht, Germany). All water used was Milli-Q water (18.2 MΩ) (Millipore, Bedford, MA).

Acetate buffer (0.4 mol L^{-1}) was prepared weekly and an aqueous solution of $NaBEt_4$ (2% (w/v)) daily.

2.3 *Cleaning*

To avoid contamination, laboratory ware was rinsed throughout with tap water, put into a polyethylene container with 10% nitric acid, and left for 48 h. It was then rinsed twice with tap water and three times with Milli-Q water.

2.4 *Reference material*

To evaluate the accuracy of various extraction procedures for the speciation of butyltins in sediments by GS–MS, the certified reference material PACS 2, harbour sediment from the National Research Council of Canada, was used. PACS-2 is certified for TBT and DBT content, while for MBT an indicative value is given.

2.5 *Sampling and sample preparation*

Coastal sediment samples were collected from the Slovenian part of the Adriatic Sea at five sampling sites in July 2005. The sampling sites shown on figure 1 were as follows: Debeli Rtič (DR), Koper (KO), Izola dockyard (IL), Izola marina (IM), and Bele skale beach (BS). The top 5-cm surface sediments were collected with a Plexiglass tube with an inner diameter of 6 cm and immediately transported to the laboratory. They were wet-sieved through a 63-μm sieve (Retsch, GmbH, Haan, Germany) and air-dried. Before analysis, they were stored in glass containers in the dark at 4°C.

2.6 *Analytical method*

The analytical method for the speciation of butyltins by GC–MS can be divided into the following steps: extraction, derivatization, separation, and detection. In our work, extraction procedures involving the use of three different extraction solvents and modes of extraction were compared and critically evaluated from the results of analyses of PACS-2 certified reference material. All samples were analysed in three parallel determinations. Approximately 0.5–2 g of sample was weighed into a 50-mL polypropylene centrifuge tube (Nalgen International, Rochester, NY). To the sample, 20 mL of selected extraction solvent and TPrT (for PACS-2 in a concentration of 300 ng Sn g^{-1} and for samples from 140 to 300 ng Sn g^{-1}) as an internal standard were added. After the different extraction procedures described later, samples were centrifuged for 5 min at 4000 rpm (Centrifuge LC-320, Tehtnica, Železniki, Slovenia). Two millilitres of extract was then added in a glass flask containing 100 mL of 0.4 mol L^{-1} acetate buffer. pH was adjusted to 4.8 ± 0.2 with glacial acetic acid or a 25% water solution of NH_3 [20]. For the standard addition method, appropriate

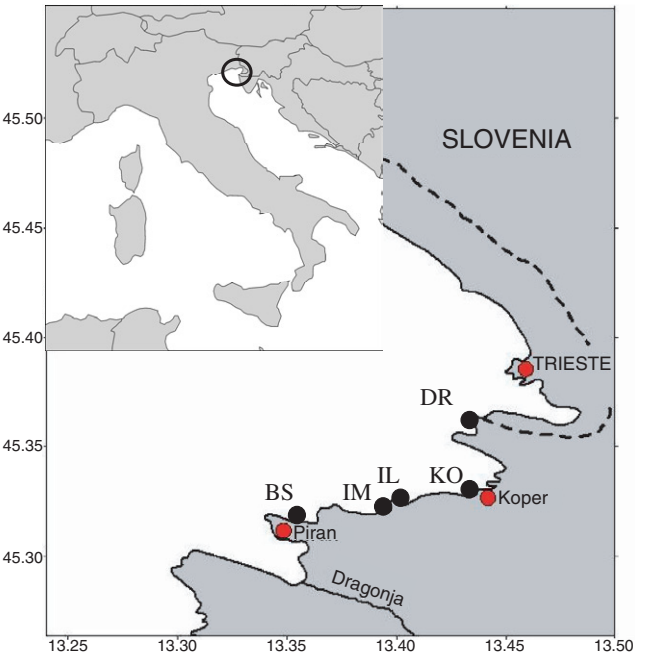

Figure 1. Locations of sampling sites: Debeli Rtič (DR), Koper (KO), Izola dockyard (IL), Izola marina (IM), and Bele skale beach (BS).

amounts of diluted butyltin stock solutions were added. Standard addition was carried out at three different butyltin levels [35]. For derivatization, 0.5 mL of 2% $NaBEt_4$ was added to the extract, followed by the addition of 1 mL of iso-octane. The sample was shaken for 45 min on a mechanical shaker at 300 rpm (Vibromax 40, Tehtnica, Železniki, Slovenia). The iso-octane extract was directly injected into the GC–MS. The concentration of butyltins in sediment samples was calculated on a peak area basis using the standard addition method.

2.6.1 Extraction procedure. For extraction of butyltins from sediments, the most frequently used solvents are different mixtures of acetic acid, methanol, and water [20]. However, there is a lack of data on the comparison of the efficiencies of extractions of butyltins from sediments using the latter solvents. Therefore, to optimize and evaluate the extraction step in speciation analysis of butyltins in sediments, three extraction solvents and modes of extraction were compared. The extraction solvents were 100% acetic acid (solvent A), a mixture of acetic acid and methanol (3 : 1, solvent B), and a mixture of acetic acid, methanol, and water (1 : 1 : 1, solvent C), while extraction was performed by mechanical shaking, ultrasonically, or by closed vessel microwave-assisted extraction. Mechanical shaking was performed at room temperature for 8 or 16 h. Ultrasonic and microwave-assisted extractions were carried out at 50°C for 0.5, 1, or 3 h and for 3, 6, or 10 min, respectively. Comparison of different extraction procedures is schematically presented in table 2.

Table 2. Scheme of different extraction procedures applied for butyltin speciation in PACS-2 by GC–MS.[a]

Mode of extraction	Solvent[a]	Extraction time
Mechanical shaking (20°C, 300 rpm)	A	8, 16 h
	B	8, 16 h
	C	8, 16 h
Ultrasonic extraction (50°C, 700 W)	A	0.5, 1, 3 h
	B	0.5, 1, 3 h
	C	0.5, 1, 3 h
Microwave-assisted extraction (1200 W, ramp to 50°C for 1 min, holding for 2, 4, or 9 min at 50°C)	A	3, 6, 10 min
	B	3, 6, 10 min
	C	3, 6, 10 min

[a] A: 100% acetic acid. B: mixture of acetic acid and methanol (3 : 1). C: mixture of acetic acid, methanol, and water (1 : 1 : 1).

3. Results and discussion

3.1 *Evaluation of the extraction efficiencies*

The efficiencies of different extraction procedures for the determination of butyltins in marine sediments by GC–MS were evaluated by analyses of the certified reference material PACS-2. The use of a reference material ensured that differences between results are not caused by poor homogeneity of the analysed sample [22]. Certified values for TBT and DBT in PACS-2 reference material are 890 ± 105 and 1047 ± 64 ng Sn g^{-1}, respectively. The value 600 ng Sn g^{-1} for MBT is indicative. Recoveries were calculated from the results of analyses of PACS-2 obtained with different extraction procedures (see scheme presented in table 2). They represent the ratio of the analyte content found to the certified value [35]. The differences between recoveries depend only on the differences in extraction procedure, as the post-extraction steps in the analytical method remained the same.

Extraction recoveries for mechanical shaking are presented in table 3. It can be seen from these data that after 8 h, TBT was efficiently extracted (approximately 100% recoveries) from the sample matrix by all three solvents applied. Extraction was less efficient for DBT and MBT, where recoveries depended upon extraction solvent and lay from 68 to 84% and 40 to 69%, respectively. It is also evident that a longer extraction time (16 h) is needed in order to improve the extraction efficiency for DBT and MBT. It was experimentally proven that further prolongation of the extraction time had no influence on the extraction efficiency of mechanical shaking.

In order to ensure a more efficient and accelerated ultrasonic extraction of butyltin species from the sample matrix, the temperature was kept at 50°C [20]. Recoveries calculated for ultrasonic extraction are presented in table 4. These results show that recoveries for TBT were between 95 and 110% for all extraction solvents applied. Convenient recoveries were also obtained with all extraction solvents for DBT (values between 89 and 110%). Solvents A (acetic acid) and B (mixture of acetic acid and methanol) almost quantitatively extracted MBT (recoveries from 91 to 105%), while solvent C (mixture of acetic acid, methanol and water) extracted approximately half of its content from sample matrix. No degradation of butyltin species was observed over the time (up to 3 h); neither prolonged time of extraction had the observable influence on extraction efficiency.

Table 3. Extraction recoveries for mechanical shaking.

Solvent[a]		Recovery (%) 8 h	16 h
A	MBT	63 ± 4	70 ± 4
	DBT	68 ± 9	79 ± 4
	TBT	103 ± 1	109 ± 7
B	MBT	69 ± 4	85 ± 15
	DBT	80 ± 3	88 ± 4
	TBT	117 ± 6	103 ± 3
C	MBT	40 ± 4	46 ± 2
	DBT	84 ± 2	94 ± 1
	TBT	101 ± 4	101 ± 5

[a]A: 100% acetic acid. B: mixture of acetic acid and methanol (3 : 1). C: mixture of acetic acid, methanol, and water (1 : 1 : 1).

Table 4. Extraction recoveries for ultrasonic extraction.

Solvent[a]		Recovery (%) 0.5 h	1 h	3 h
A	MBT	100 ± 4	98 ± 3	105 ± 3
	DBT	94 ± 5	99 ± 9	98 ± 5
	TBT	101 ± 6	92 ± 8	94 ± 9
B	MBT	91 ± 5	109 ± 5	91 ± 9
	DBT	89 ± 5	91 ± 2	89 ± 4
	TBT	117 ± 3	117 ± 11	107 ± 3
C	MBT	54 ± 17	75 ± 11	54 ± 17
	DBT	99 ± 3	110 ± 5	98 ± 3
	TBT	118 ± 2	117 ± 5	118 ± 2

[a]A: 100% acetic acid. B: mixture of acetic acid and methanol (3 : 1). C: mixture of acetic acid, methanol, and water (1 : 1 : 1).

Microwaves were initially used for the mineralization of samples. In recent years, numerous organometallic compounds have been extracted by microwave-assisted extraction from different environmental samples [24]. Microwave-assisted extraction requires the optimization of temperature, time, and power of microwave energy of microwave system [23]. Results of extraction efficiency for microwave-assisted extraction applied (see table 2) are presented in table 5. In this mode of extraction, TBT was quantitatively extracted with solvent A when extraction was carried out for 3 min and with solvent C regardless of the time applied for extraction. Recoveries close to 100% were achieved for DBT with solvent C, while extraction with solvent A and B was incomplete (recoveries between 54 and 73%). Poor extraction recoveries were obtained for MBT (approximately half of its content was recovered from the sample matrix) by applied microwave extraction conditions.

From the results presented in tables 3–5, it can be concluded that, with the respect to extraction efficiency, 30-min ultrasonic extraction by the use of 100% acetic acid as extraction solvent provided satisfactory recoveries for all butyltins certified in PACS-2.

Table 5. Extraction recoveries for microwave-assisted extraction.

Solvent[a]		Recovery (%) 3 min	6 min	10 min
A	MBT	41 ± 16	48 ± 1	64 ± 4
	DBT	68 ± 6	45 ± 14	60 ± 4
	TBT	102 ± 6	72 ± 18	72 ± 5
B	MBT	41 ± 2	44 ± 18	57 ± 17
	DBT	73 ± 2	58 ± 6	63 ± 3
	TBT	80 ± 6	67 ± 3	65 ± 9
C	MBT	58 ± 8	85 ± 5	58 ± 8
	DBT	94 ± 3	108 ± 1	94 ± 3
	TBT	97 ± 5	114 ± 2	97 ± 5

[a]A: 100% acetic acid. B: mixture of acetic acid and methanol (3 : 1). C: mixture of acetic acid, methanol, and water (1 : 1 : 1).

Table 6. Limit of detection (LOD), repeatability, and reproducibility of measurements for butyltins in sediment samples.

Parameter	MBT	DBT	TBT
LOD (ng Sn g^{-1})	1.6	1.6	2.5
Repeatability RSD (%)	8	8	3
Reproducibility RSD (%)	8	8	8

This extraction approach had additional advantages to shorten the duration of extraction time in comparison with mechanical shaking and sample handling and manipulation in comparison with microwave-assisted extraction.

3.2 *Analytical performances*

Linearity of measurement was obtained over a concentration range from 8 to 500 ng Sn mL^{-1} for all butyltins. The correlation coefficients were better than 0.998. The limits of detection (LOD) for butyltins calculated on a 3s basis (three times the SD of the blank) are presented in table 6.

The repeatability of measurement was evaluated by the relative standard deviation (RSD) of six consecutive determinations of a sediment sample with a concentration similar to that of PACS-2 reference material. Analyses were performed by applying optimal extraction procedure (30 min of ultrasonic extraction by the use of 100% acetic acid as extraction solvent). Data are given in table 6.

The reproducibility of measurement was checked from a set of 12 analysis of the same sample over a period of 30 days. As for evaluation of the repeatability of measurement, analyses were performed by applying optimal extraction procedure. The RSDs are presented in table 6.

3.3 *Speciation of butyltins in sediments*

Chemical analysis of surface sediment samples provides an assessment of present levels of contamination by various pollutants [36]. In the present work, the level of pollution

Table 7. Butyltin concentrations (ng Sn g^{-1}) in marine sediment samples determined by GC–MS.

Location	MBT	DBT	TBT
DR	3 ± 1	3 ± 1	8 ± 1
KO	29 ± 7	138 ± 5	763 ± 21
IL	51 ± 1	57 ± 2	171 ± 7
IM	934 ± 62	434 ± 29	1215 ± 115
BS	2 ± 1	3 ± 1	7 ± 1

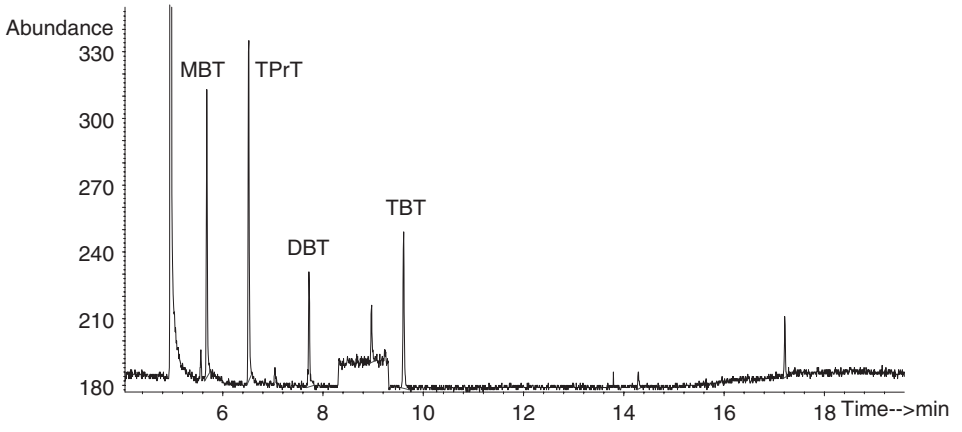

Figure 2. GC–MS spectrum of ethylated butyltins for the marine sediment sample.

with butyltins was assessed from the results of butyltin speciation in sediments that were collected in July 2005 at five representative sampling sites of the Slovenian part of the Northern Adriatic Sea. Sampling locations are presented in figure 1. Ultrasonic extraction (30 min at 50°C), using 100% acetic acid as extraction solvent (extraction method of choice, section 3.1), was applied in butyltin speciation analyses of sediments. The results for these sediment analyses (expressed on dry mass) are presented in table 7. In figure 2, a typical GC–MS spectrum of butyltins in a sediment sample is shown. As can be seen from table 7, butyltins were present in all sediments analysed with the highest concentrations of TBT, DBT, and MBT in sediments from the Izola marina (1.215, 0.43, and 0.93 μg Sn g^{-1}, respectively). An elevated concentration of TBT (about 0.8 μg Sn g^{-1}) was observed also in sediment from Koper. The butyltin concentrations in Izola marina and Koper are comparable with the concentrations reported in the literature for the sediments from some polluted marinas in Greece and Japan [37, 38]. At the Izola dockyard sampling site, moderate contamination with butyltins was observed (around 0.17 μg Sn g^{-1} for TBT and 0.05 μg Sn g^{-1} for DBT and MBT, respectively). Appreciably lower concentrations of butyltins were found in sediments of Debeli Rtič and Bele skale, presumed as non-polluted sites. These concentrations (below 0.01 μg Sn g^{-1}) were similar to the reported data for non-contaminated sites [39, 40]. The origin of butyltins in the area investigated is most likely related to the use of TBT-based antifouling paints. Since the concentrations of TBT in sediments investigated were higher than those of its degradation products, this indicates that TBT is still being introduced into the marine environment of the Northern Adriatic area.

4. Conclusion

The article presents the results of the speciation of butyltin compounds in marine sediments by GC–MS. The results of the analyses of PACS-2 certified reference material obtained after applying three different extraction solvents and three modes of extraction were critically compared. From the results described in detail in section 3.1, it can be concluded that 30 min ultrasonic extraction at 50°C using of 100% acetic acid as extraction solvent can be recommended for extraction of butyltins from marine sediments. Ultrasonic extraction provides quantitative recoveries for all butyltin species certified in PACS-2. This extraction approach has the advantage of shortening the duration of extraction in comparison with mechanical shaking, and simplifies sample handling and manipulation in comparison with microwave-assisted extraction. These findings of the presented work are in close agreement with those reported by Encinar *et al*. [32].

From the results of sediment analyses, it can be concluded that the Slovenian part of the Northern Adriatic Sea is contaminated with butyltins. Contamination is more pronounced at locations such as marinas and shipbuilding yards. Higher concentrations of TBT than those of its degradation products indicate that TBT is still being introduced into the marine environment.

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