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Stir bar sorptive extraction of parabens, triclosan and methyl triclosan from soil, sediment and sludge with *in situ* derivatization and determination by gas chromatography–mass spectrometry

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ABSTRACT

The aim of this research work was the evaluation of stir-bar sorptive extraction (SBSE) in combination with an *in situ* derivatization to determine parabens (methylparaben, isopropylparaben, n-propylparaben, butylparaben and benzylparaben), triclosan and methyltriclosan in soil samples. This is the first time that this approach has been applied to the determination of these compounds in soil samples, providing important advantages over conventional extraction techniques, such as minimization of sampling handling, complete elimination of the use of organic solvents and simplification of the analytical procedure with reduced time consumption. The enriched target analytes were desorbed thermally using a thermodesorption system coupled to a gas chromatograph and a mass spectrometer. The optimized derivatization and SBSE extraction conditions, as well as the analytical characteristics of the method were obtained using spiked soil samples. The proposed methodology proved to be easy to use and sensitive, with limits of detection between 80 ng/kg and 1.06 μg/kg, and reproducibility values below 13%. The accuracy of the method was evaluated at two concentration levels, obtaining apparent recoveries between 91% and 110%. The matrix composition significantly influenced the extraction procedure, and a need to adopt a standard additions protocol is apparent. The analytes assayed were determined successfully in different environmental soil samples.

1. Introduction

Stir bar sorptive extraction (SBSE) is a solventless sampling technique introduced by Baltussen et al. [1] to extract organic analytes from environmental samples by sorption onto polydimethylsiloxane (PDMS) coated stir bars (so-called twisters™) [2]. The analytes are recovered thermally and analyzed on-line by gas chromatography (GC) [3]. Additionally liquid desorption can be combined with classical GC and liquid chromatography (LC) [4]. Large volume injection is often applied in order to obtain the highest possible sensitivity [4]. For complete transfer of the sorbed fraction into the analytical system, thermal desorption is preferred.

SBSE has mainly been used for the analysis of different types of contaminants in aqueous samples, with hundreds of applications in the literature [5–10], and it is also possible to find applications for the determination of organic compounds in biological fluids [11–15] and in food matrices [16–19].

For the analysis of soil samples with SBSE, most applications reported require a previous extraction step with techniques such as ultrasonic solvent extraction (USE) [20,21], pressurized liquid extraction (PLE) [22], or pressurized subcritical water extraction (PSWE) [23]. The extract, previously diluted in water, is subjected to the SBSE extraction process. Few references are available concerning the extraction of pollutants by the twister directly in the soil sample. To the best of our knowledge, only Tan et al. [24] have analyzed a range of endocrine disrupting compounds (EDCs) in biosolids and sludge samples, using SBSE directly in solid samples.

Esters of p-hydroxybenzoic acid (parabens) and 2-(2,4-dichlorophenoxy)-5-chlorophenol (triclosan) are compounds with bactericidal and antimicrobial properties and are mainly employed in the formulation of personal care products (PCPs) such as toothpaste, deodorants, beauty creams, solar filters, and bath gels [25]. In addition, parabens are added to canned foods and beverages as preservatives. Triclosan is also incorporated as a biocide in sports clothes, footwear, carpets, plastic toys and kitchenware [26]. Methyl triclosan is a transformation product of triclosan formed for instance during wastewater treatment [27]. These compounds are known as endocrine disrupting contaminants (EDCs), and several authors have reported their estrogenic activity [28–31].

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Few works have addressed the analysis of these compounds in environmental matrices. Their presence has been confirmed in aqueous matrices [32–34], although there are also publications dealing with air [35] and dust [36] samples.

Considering that wastewater is increasingly being reused for irrigation, reliable methods for their analysis in soils are required. Nuñez et al. have proposed the analysis of parabens using ultrasonic-assisted extraction [37] or molecularly imprinted polymer solid-phase extraction [38]. Nieto et al. [39] used pressurized liquid extraction for the analysis of parabens in sewage sludge. Regarding the determination of triclosan in soil samples, the techniques that have been reported previously are microwave-assisted solvent extraction (MASE) [40], ultrasonic solvent extraction (USE) [41] and pressurized liquid extraction (PLE) [42–44], all of them techniques that require the use of organic solvents and all of them time-consuming. Sánchez-Brunete et al. and González-Mariño et al. have proposed the determination of triclosan and methyl triclosan in soils and sludge samples by matrix-solid-phase dispersion (MSPD) [45,46].

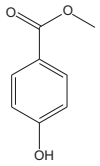
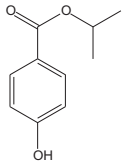
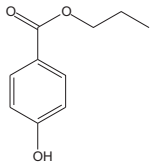
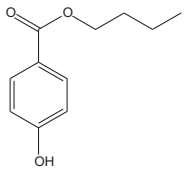
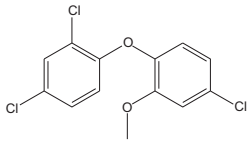
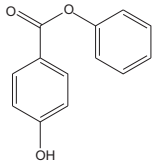
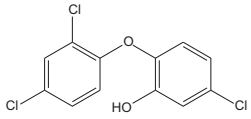
Direct extraction of parabens, triclosan and methyl triclosan from soils using the SBSE method has not been reported in any previously published work. The aim of this study was to evaluate whether stir bar sorptive extraction with an *in situ* derivatization reaction can be applied successfully for the extraction and determination of these analytes directly from soils without any organic solvent. This method has the potential to reduce the sample preparation and analysis time to a considerable extent in comparison with the usual solid–liquid extractions combined with solid phase extraction (SPE) or liquid–liquid extraction (LLE) methods. Since the acetylation with acetic anhydride is used frequently for the derivatization of phenols, it was selected as *in situ* reaction for the determination of the phenolic target analytes in soil slurry [34,47,48]. Optimization of the derivatization reaction and the extraction step from soils was accomplished in order to obtain the best conditions. The enriched target analytes were desorbed thermally using a thermodesorption system coupled to gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Chemicals

Isopropylparaben (iPrP) was supplied by TCI Europe (Zwijndrecht, Belgium). The other parabens (methylparaben (MeP), n-propylparaben (nPrP), n-butylparaben (BuP) and benzylparaben (BzP)), triclosan (TCS) and methyl triclosan (MeTCS) were supplied by Sigma–Aldrich (Steinheim, Germany). Analytical grade methanol, acetonitrile, sodium chloride as well as $NaHCO_3$ buffer salt were supplied by Merck (Darmstadt, Germany). Acetic anhydride (ReagentPlus®) was delivered by Sigma–Aldrich (Munich, Germany). The chemical structure and the octanol/water coefficients of the compounds and the retention times corresponding to the chromatographic method used are shown in Table 1.

Table 1
Structural formulas, logarithm of the octanol/water coefficient, and retention times of the compounds studied.

Name	Structure	Log K_{ow}	t_R (min)[a]
Methylparaben		1.96	5.155
Iso-propylparaben		3.04	5.559
n-propylparaben		3.04	5.899
Butylparaben		3.81	6.521
Methyl triclosan		5.15	8.279
Benzylparaben		3.59	8.40
Triclosan		4.76	8.461

[a] Derivatized compounds.

2.2. Standard solutions and soils

2.2.1. Standard solutions

Stock solutions of all the analytes (500 mg/L in methanol) were prepared and stored at 4 °C in the refrigerator. Working solutions containing the compounds were prepared by dilution with acetone at the appropriate concentrations prior spiking the soil samples. Optimization experiments were performed using 0.5 g of soil spiked with the analytes at 100 μg/kg.

2.2.2. Soil samples

Soil matrices were used to optimize the derivatization and extraction conditions and to determine the analytical characteristics of the method. Three different types of soil were chosen for the experiments: a river sediment (Leipzig, Germany), a garden soil (Norway) and a sandy soil (Leipzig, Germany). The study also included a sludge collected from a wastewater treatment plant in Leipzig, a town with about 500,000 inhabitants. The sludge was dried, sieved, and the fraction below 1 mm was collected and stored in an amber vial at 4 °C in the refrigerator until analysis. The total organic carbon (TOC), total inorganic carbon (TIC) and total carbon (TC) values shown in Table 2 of the soils and the sludge were measured using a "HighTOC II" analyser (elementar Analysensysteme, Hanau, Germany).

The spiked soil samples were prepared by adding 75 mL of a stock solution of parabens, triclosan and methyl triclosan standards

Table 2
Characteristics of the soils studied. TOC, total organic carbon; TIC, total inorganic carbon; TC, total carbon.

Soil	TOC (%)	TIC (%)	TC (%)
River sediment	5.51	0.21	5.73
Garden soil	1.55	0.03	1.58
Sandy soil	7.11	0.03	7.14
Sludge	24.2	0.28	24.5

in acetone to 50 g of soil. Subsequently, the solvent was let to evaporate at room temperature under frequent homogenization. The spiked soils were stored at 4 °C under darkness to prevent the compounds from degrading. In all cases, concentrations of the analytes in the soils were referred to dry weight.

The methods of optimization and evaluation were performed using fractions of 0.5 g of river sediment spiked at the concentration level required in each case. The absence of the analytes was confirmed by subjecting a portion of soil to the extraction procedure and to the ensuing instrumental analysis. Each level was analyzed in triplicate.

2.3. Derivatization and SBSE procedure

0.5 g of spiked soil was placed in a 10-mL headspace vial. Then, 5 mL of an aqueous solution of $NaHCO_3$ 0.4 M was added. The stir bar (Twister; Gerstel, Müllheim a/d Ruhr; Germany) containing a polydimethylsiloxane (PDMS) coating film (0.5 mm thick; 10 mm long, 24 μL) was inserted into the mixture, followed by the addition of 400 μL of acetic acid anhydride. The vial was sealed with a Teflon-covered silicone septum and the mixture was stirred for 60 min at 1000 rpm (Variomag Multipoint 6/15, H+PLabortechnik, Oberschleissheim, München, Germany) at room temperature. After the extraction, the twister was removed, rinsed with bidistilled water and dried with lint-free tissue. The stir bar was then placed in a glass thermal desorption (TD) tube and desorbed in the TD system for delivery to the gas chromatography–mass spectrometry (GC–MS) system.

2.4. Instrumentation

TD-GC–MS analysis was performed on an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled to a Gerstel thermodesorption system (TDS A). All experiments were carried out with a programmed temperature vaporizer (PTV) inlet (CIS-4), with an empty liner for cryofocusing the analytes prior to introduction into the capillary column. Cooling was accomplished with liquid nitrogen. The detector was a quadrupole mass spectrometer (HP 5973N).

2.5. TD-GC–MS conditions

The optimized conditions used for the thermodesorption system were set referring to our previous work [34]. Briefly, these were: desorption temperature, 275 °C; desorption time, 6 min and helium flow rate (desorption flow) 100 mL/min. During the desorption step, the PTV temperature was set at −10 °C (solvent-vent mode). After the desorption, the PTV temperature was programmed to increase from −10 to 280 °C at 720 K/min (held for 5 min) to transfer the analytes to the chromatographic system. The injection was performed in splitless mode at 280 °C with a splitless time of 2 min.

To perform the gas chromatographic measurements, a HP-5MS capillary column (30 m × 250 μm i.d., 0.25 μm film thickness) was used. The carrier gas used was helium at a flow rate of 1.2 mL/min. The column oven temperature program involved an initial temperature of 60 °C for 2 min; an increase at 65 K/min to 175 °C; then an increase at 45 K/min to 200 °C (held 2 min), and an increase at 40 K/min to 280 °C, then holding for 1 min. The mass spectrometer was operated in full scan mode (optimization studies) and selected ion monitoring mode (SIM) (calibration and prediction) for mass analysis after electron impact ionization (70 eV). A solvent delay of 4.5 min was established. The mass range from 50 to 350 amu was considered in full scan analysis. The substance typical target ions used for SIM analysis are listed in Table 3.

2.6. Validation of the method

All the analytes tested showed good linearity in the ranges studied, with good regression coefficients. The limits of detection obtained in SIM mode ranged between 0.08 and 1.06 μg/kg. The limits of quantification were within the 0.24–3.22 μg/kg range.

Reproducibility and repeatability, expressed as coefficients of variation, had satisfactory values (<13%). The accuracy of the method was evaluated by spiking the samples at two concentration levels and apparent recoveries between 91% and 110% were obtained.

3. Results and discussion

3.1. Derivatization reaction

Acetylation is a common reaction widely used for the derivatization of phenolic compounds in aqueous matrices. Fig. 1 compares the signals obtained with and without compound derivatization. A noticeable increase in the signals of the compounds was seen when derivatization took place. In the case of methyl triclosan, the signal remained constant, indicating that the compound was stable under the derivatization conditions.

In order to optimize the derivatization step, the relationship between the base concentration and acid volume was studied. The ranges studied were 0.1–0.4 M for the base concentration ($NaHCO_3$), and 50–400 μL for the acetic anhydride volume. Fig. 2 shows the results obtained for three of the compounds studied (MePA, BuPA and TCSA) that are representative of the observed behaviour. As the volume of acetic anhydride increased, so did the analytical signal of most of the compounds, with the exception

Table 3
Analytical characteristics of the proposed method.

Compound	*m/z*		Intercept	Slope	R^2	RSD (%)		LOD (μg/kg)	LOQ (μg/kg)	Recovery (%)	
	Quantitation ion	Qualifier ions				Repeatability	Reproducibility			10 μg/kg	50 μg/kg
MeP	121	152, 194	$(17 \pm 3) \times 10^4$	$(18 \pm 2) \times 10^3$	0.9968	7.12	8.3	1.06	3.22	102 ± 3	100 ± 4
iPrP	121	138, 180	$(7 \pm 8) \times 10^4$	$(38 \pm 2) \times 10^3$	0.9941	7.40	10.7	0.51	1.56	106 ± 6	106 ± 6
nPrP	138	121, 180	$(24 \pm 9) \times 10^4$	$(44 \pm 2) \times 10^3$	0.9987	7.50	10.8	0.74	2.26	110 ± 5	96 ± 5
BuP	138	121, 194	$(2 \pm 6) \times 10^4$	$(40 \pm 2) \times 10^3$	0.9986	6.80	12.3	0.08	0.24	104 ± 5	102 ± 4
MeTCS	302	304, 252	$(3 \pm 10) \times 10^3$	$(43 \pm 2) \times 10^2$	0.992	6.82	11.9	0.37	1.12	91 ± 6	95 ± 5
BzP	121	91, 65	$(6 \pm 13) \times 10^3$	$(206 \pm 4) \times 10^2$	0.9974	9.50	8.17	0.18	0.56	96 ± 2	100 ± 2
TCS	288	218, 63	$(8 \pm 7) \times 10^3$	$(55 \pm 2) \times 10^2$	0.9988	5.86	10.7	0.16	0.49	94 ± 3	98 ± 3

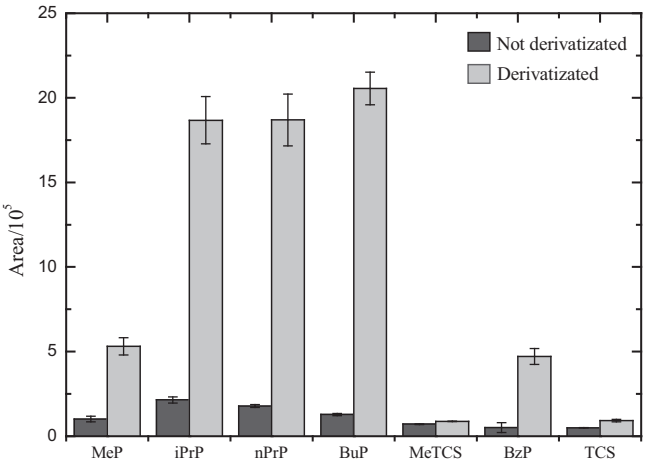


Fig. 1. Comparison of the analyte signals obtained with and without derivatization.

of the most polar ones (MePA). Accordingly, in general the best results were obtained when 400 μL of acetic anhydride was added for $NaHCO_3$ concentrations of 0.25 or 0.4 M. For the working conditions, this amount of acetic anhydride was chosen, with a $NaHCO_3$ concentration of 0.4 M, in order to ensure the buffering capacity of the medium.

3.2. Optimization of the SBSE procedure

In the proposed procedure, in which there are several phases (soil, aqueous solution and the stir-bar coating) the exogenous compounds present in the solid matrix were distributed at different proportions among the different phases of the system, as seen in the following equilibria.

$$C_{iSP} \overset{A}{\longleftrightarrow} C_{iLP} \overset{B}{\longleftrightarrow} C_{iPDMS}$$

where C_{iSP} is the concentration of the analyte in the solid phase, C_{iLP} is the concentration in the liquid phase and C_{iPDMS} is the concentration in the PDMS phase [49].

The distribution of an analyte between phases depends on its hydrophobicity. Equilibria A and B are directly related, since the analyte extracted by the PDMS phase of the aqueous phase (equilibrium B) is partially or wholly re-established by its redistribution between the solid matrix and the liquid phase (equilibrium A).

In order to modify the nature of the liquid phase, and hence its extracting capacity, a study was made concerning the influence of organic solvents and of an electrolyte added to the aqueous phase. Additionally, other variables that affect the SBSE procedure were studied, such as the amount of soil and the extraction time and temperature.

Two organic modifiers, methanol (MeOH, $\log K_{ow} = -0.63$) and acetonitrile (ACN, $\log K_{ow} = -0.15$), were tested in order to modify the extractability of the analytes. Different portions of methanol in the aqueous phase were studied: 0, 10, 30 and 50%. Acetonitrile levels (in percentages) were prepared at 10 and 30%. The results are shown in Fig. 3a. The behaviour was similar for both solvents (results only shown for MeOH), with a decrease in the signal for the parabens in parallel with an increase in the percentage of organic solvent. However, in the case of methyl triclosan and triclosan acetate, the optimum conditions would be a 30% content of organic solvent. As a compromise situation for the joint determination of all the analytes, it was decided to work without the addition of an organic modifier to the aqueous solution.

An inert salt, NaCl, was added during SBSE in order to modify the ionic strength of the liquid phase. Three amounts – 0, 1.0 and 2.5 g (supersaturation) – were added to the sample (0.5 g of soil + 5.0 mL of aqueous solution, Fig. 3b). On increasing the NaCl concentration, a decrease in signal was observed, with the exception of MePA. It was therefore decided not to add the electrolyte to the medium.

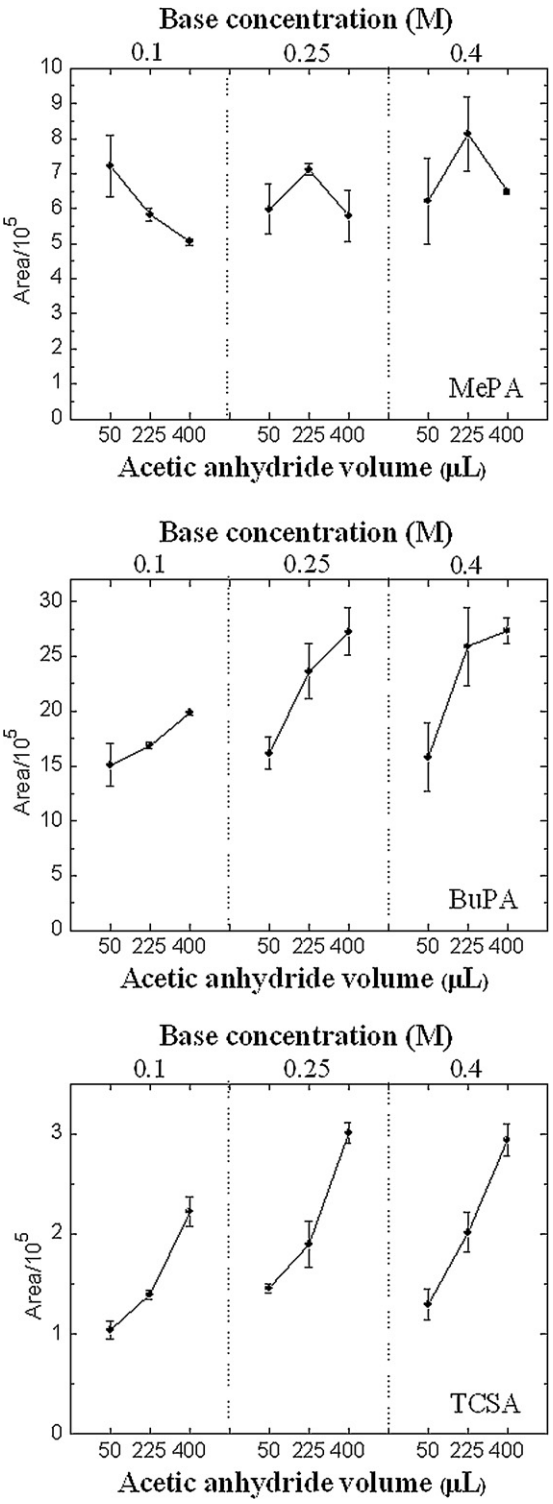


Fig. 2. Variation in the analytical signal upon the addition of different amounts of acetic anhydride and at different $NaHCO_3$ concentrations.

Next, we studied the addition of different amounts of soil. The values studied were 0.5, 1.0, 1.5, 2.0 and 2.5 g of soil. The amount of aqueous solution (5.0 mL) was held constant, although the amount of $NaHCO_3$ and acetic anhydride used to perform the *in situ* reaction was increased proportional to the amount of soil to ensure

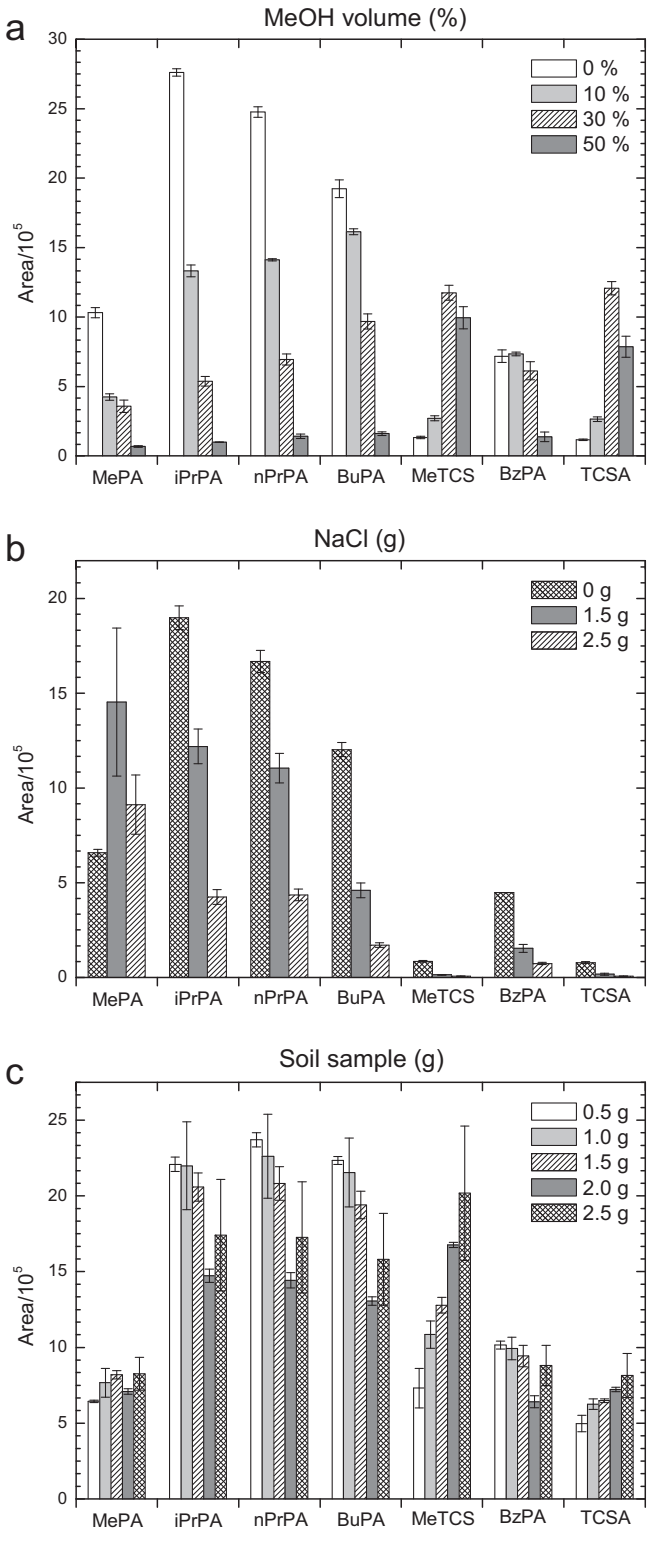


Fig. 3. Evolution of the analytical signal for the different variables studied.

the quantitative derivatization of the compounds. The extraction time was set at 240 min in order to ensure complete extraction of all the analytes. The results are shown in Fig. 3c. The increase in sample amount did not involve an increase in the analytical signal for most of the compounds (except for MeTCS and TCSA). Likewise, in general an increase in the irreproducibility of the process was observed, associated with an increase in the difficulty involved in stirring the soil–water mixture. Consequently, it was decided to work with 0.5 g of soil.

The extraction time and two different extraction temperatures (ambient temperature and 50 °C) were studied in order to obtain the optimal extraction efficiency for overall analytes. At room temperature, the time required for reaching the partition equilibrium ranged between 60 and 120 min, except for methyl triclosan and triclosan acetate, for which it was necessary to increase the extraction time to values higher than 240 min (Fig. 4). At 50 °C, the equilibrium was reached faster (30 min); longer extraction times resulted in a signal decrease in the chromatogram. However, at 50 °C most of the parabens were extracted less efficiently than at ambient temperature at equilibrium conditions. Methyl triclosan and triclosan acetate showed a different behaviour, with a very significant increase in the signal when the sample was heated. However, it was found that the lifetime of the stir bar was dramatically reduced at 50 °C. As a compromise situation it was decided to work at room temperature, setting an extraction time of 60 min since the increase in the response from 60 min to equilibrium was not very marked.

3.3. Evaluation of the SBSE-TD-GC–MS method

Linear calibration curves were obtained using the river sediment as analyte free matrix spiked at seven concentration levels ranging from 1 to 100 μg/kg (1.0, 5.0, 10, 25, 50, 75 and 100 μg/kg, dry weight). Each level was analyzed in triplicate. The analytical characteristics of the method are shown in Table 3. The calibration model displayed linear behaviour for the target analytes. The validity of the model generated was proved with good fits using ANOVA, and correlation coefficients (R^2) higher than 0.99 were obtained for overall analytes.

In order to study the repeatability and reproducibility of the process, soil samples spiked at 50 μg/kg were analyzed on the same day (six replicates) and on two different days (three replicates each day), respectively. The results, as relative standard deviations (RSD, %), are shown in Table 3, with values not higher than 13%. These results are quite good, even though no internal standard was used in the procedure.

The limits of detection (LODs) and the limits of quantification (LOQs), calculated as 3.3 and 10 times the standard deviation of a sample with an S/N ratio of 3, respectively [50], are also shown in Table 3. The limits of detection were between 0.08 μg/kg for butylparaben and 1.06 μg/kg for methylparaben. Few references are available to compare our results with others previously reported for soil samples. For parabens, Nuñez et al., using ultrasonic-assisted extraction with acetonitrile [37] or molecularly imprinted solid-phase extraction [38], obtained limits of detection between 0.04–0.14 μg/kg and 0.16–0.27 μg/kg, respectively, using 10 and 15 g of sample, respectively. In both cases, the instrumental analysis was carried out using a LC–MS/MS device.

For triclosan and the methyl triclosan, the LODs found in the literature are in the order of a few μg/kg. In all cases, the methodologies proposed involve several steps, which include an exhaustive extraction of the compounds from the soil samples, with techniques such as PLE, USE and MSPD, with later cleaning of the extract with SPE and a later analyte derivatization step [41,44,45].

The methodology proposed here offers advantages over these extraction methods, such as minimizing sample handling, the complete elimination of the use of organic solvents, and simplification of the analytical procedure, with reduced time consumption. Additionally, the use of a derivatization reaction does not complicate the process, since it occurs at the same time as extraction.

The accuracy of the method was evaluated in terms of apparent recoveries. Two river sediment samples were spiked at two concentration levels: 10 and 50 μg/kg. The apparent recoveries (Table 3), calculated as the ratio of the measured concentration to the spiked

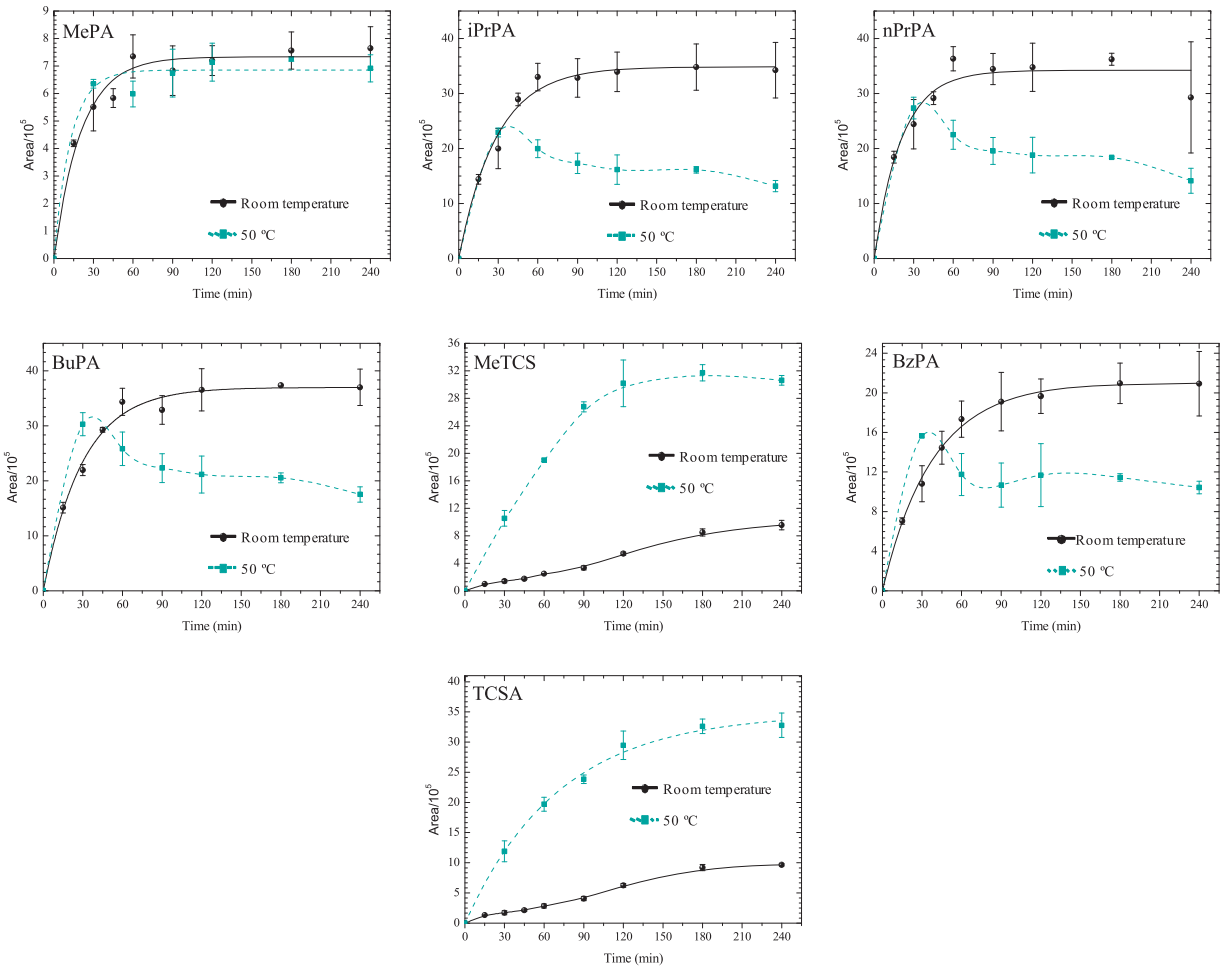


Fig. 4. Extraction curves for each of the analytes as a function of time (min) and working temperature.

concentration (expressed as percentages), were between 91% and 110%.

Absolute recoveries were calculated by comparing the GC–MS peak areas of the extracted compounds from soil samples with those of a standard solution of the completely acetylated compounds, placed on glass wool packed in a thermodesorption tube [34]. The values obtained were 13% for methylparaben, 12% for isopropylparaben, 11% for n-propylparaben, 6% for butylparaben, 3% for methyltriclosan, 4% for benzylparaben and 3% for triclosan. These values were low, showing that the extraction was not quantitative, as it occurs when using other extraction methods, such as SPME. However, it was constant along the linear range and the limits of detection and quantification of the method were satisfactory.

3.4. Environmental samples

The method developed was applied to the analysis of the parabens, triclosan and methyl triclosan in several environmental solid samples collected from different areas. Two different types of soils (a garden soil and a sandy soil) and a sludge were analyzed. The samples were not subjected to any kind of previous manipulation.

Matrix effects were investigated by comparing the signals obtained for the river sediment and those of the other types of solid matrices studied. The samples were spiked with the compounds at 50 μg/kg (Fig. 5). In all cases, non-spiked samples were also analyzed before the spiking procedure was carried out. The presence of nPrP in the garden soil and of MeTCS and TCS in the sludge was confirmed. In these cases, the peak areas obtained were subtracted from those corresponding to the spiked samples.

Table 4 shows the ratios between the signals obtained for the analytes in the different matrices studied normalized to those obtained with the river sediment (set as 1). The ratios calculated varied clearly, indicating that the matrix composition significantly influences the extraction procedure. These results emphasize that for the quantification of real samples a standard additions protocol is recommended. This type of calibration is common when working with complex matrices, such as soils, using techniques such as headspace generation [51], QuEChERS [52] or solid-phase microextraction [53]. The greatest differences were obtained for the sludge, which is logical in view of its high organic matter content (Table 2), which leads to a stronger retention of the analytes probably sorbed on the carbon rich sludge surface.

Table 4
Quotient between the signals obtained for the compounds studied in the different soils and signals obtained for the river sediment (reference in bold).

Compound	**River sediment**	Garden soil	Sandy soil	Sludge
MeP	**1**	0.40	0.31	0.31
iPrP	**1**	2.48	0.93	0.43
nPrP	**1**	2.27	0.82	0.32
BuP	**1**	4.64	1.20	0.28
MeTCS	**1**	2.21	0.53	0.17
BzP	**1**	3.31	0.55	0.28
TCS	**1**	1.81	0.33	0.14

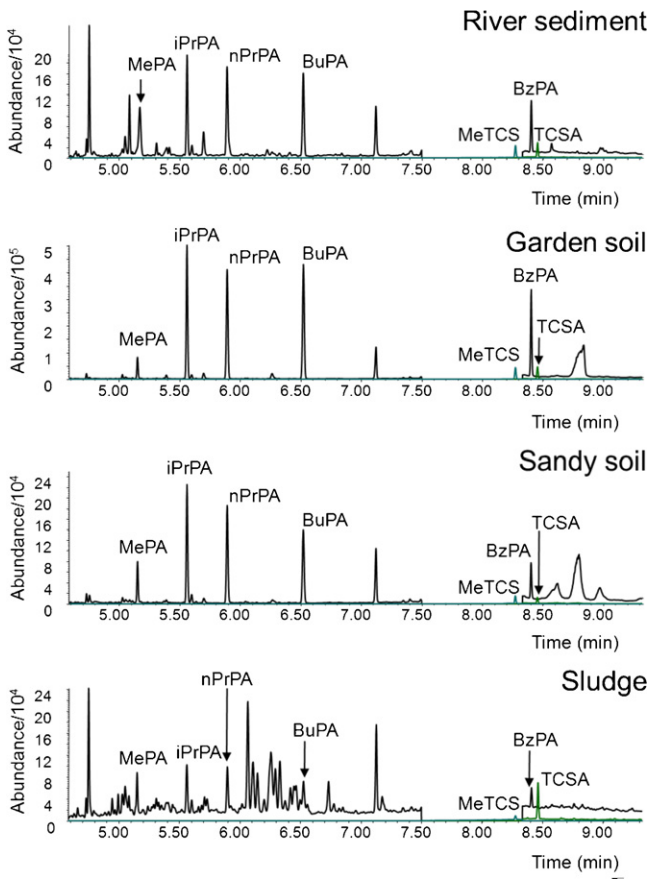


Fig. 5. Chromatograms obtained with the different soil samples studied, spiked at a concentration 50 μg/kg.

The standard additions method was used to determine the concentration levels of the analytes found in the different soil samples. In the case of the garden soil, the nPrP concentration was 1.5 μg/kg, and in the case of the sludge, MeTCS was found at a concentration of 30 μg/kg, and TCS at a concentration of 280 μg/kg.

4. Conclusions

In the present work we propose the use of stir bar sorptive extraction with an *in situ* derivatization reaction for the analysis of parabens, triclosan and methyl triclosan in soils. The literature contains few references to direct applications of extraction by SBSE in soils.

The effects of the variables affecting the derivatization reaction and the SBSE extraction were studied using spiked river sediment samples. The optimized method proved to be easy and sensitive, with detection limits ranging from 80 ng/kg to 1.06 μg/kg. It showed good linearity, with high correlation coefficients (higher than 0.99 in all cases) and no lack of fit. The reproducibility and repeatability of the method were evaluated, with the finding of values below 13%. The accuracy of the method was evaluated in terms of apparent recoveries, with values between 91% and 110%. With these characteristics, it is possible to determine these compounds in real samples, for which a standard additions protocol must be implemented.

Regarding the analytes studied, differences can be seen in behaviour between the parabens and triclosan and methyl triclosan. The working conditions chosen were compromise situations in order to create a multicomponent protocol. When focused on the determination of triclosan and methyl triclosan, other optimum conditions have to be chosen and a higher sensitivity can be achieved. Nevertheless, the LODs of overall analytes were satisfactory bearing in mind the concentration levels found in real samples.

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