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Journal of Chromatography A, 1022 (2004) 1–7
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of endocrine disrupting chemicals in environmental solid matrices by extraction with a non-ionic surfactant (Tween 80)

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Received 28 January 2003; received in revised form 10 July 2003; accepted 23 September 2003

Abstract

A readily applicable method based on extraction by aqueous non-ionic surfactant solutions (Tween 80) and RP-HPLC coupled to fluorescence detection, has been developed for the simultaneous determination of the phenolic endocrine disrupting chemicals (EDCs) nonylphenol (NP), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) and bisphenol A (BPA) in environmental solid matrices. Clean up of sample extracts was performed on Si-C18 solid phase extraction (SPE) cartridges. The overall Tween 80 extraction–SPE–RP-HPLC procedure was validated for accuracy and precision by analyzing sediment samples spiked with known amounts of EDCs. Recoveries for NP, NP1EO, NP2EO and BPA and limits of detection are in agreement with conventional extraction methods. The developed methodology was successfully applied to the analysis of target compounds in Italian river sediments, river suspended matter and benthonic macroinvertebrate organisms (oligochaetes *Lumbriculus variegatus*). Results confirmed that this relatively simple procedure performed satisfactorily in the determination of phenolic EDCs in environmental solid matrices of different complexity and that it can be a suitable alternative method to conventional systems even for routine analyses.

Keywords: Environmental analysis; Solid-matrix extraction; Endocrine disrupters; Alkylphenols; Bisphenol A; Tween 80

1. Introduction

There is an increasing interest in the environmental fate of a wide range of man-made chemicals because of their potential effect as endocrine disruptors (EDCs) in living organisms. Among phenolic EDCs, bisphenol A (BPA), nonylphenols (NPs) and short chain nonylphenol ethoxylates (NPEOs) have generated the most concern on the part of regulatory agencies and scientists due to their high production, widespread use and ubiquitous occurrence in the environment.

The fate and distribution of BPA, NP and related short chain ethoxylates (NP1EO and NP2EO) in different environmental compartments depend largely on their physicochemical properties. From estimates based on $\log K_{ow}$ (NP = 4.48; NP1-2EO = 4.17–4.20) it is reasonable to expect the association of NP, NP1EO and NP2EO with solid matrices, as sediments and suspended particulate matter. Several studies indicate that the removal of NPs during sewage treatment process is mainly due to adsorption by sludge particles and that it accumulates in sediments under anaerobic or oxygen-deficient conditions and in biota [1–3].

BPA is the least hydrophobic compound among the target compounds ($\log K_{ow} = 3.4$), but on the basis of a simple equilibrium model it has been predicted that about 50% of BPA in the environment has the potential to bind to sediments or soils [4]. Thus, EDC sorption on solid particles (i.e. sludges, sediments, particulate matter, biota) implicates a potential hazard in terms of ecotoxicological impact, and a correct risk assessment needs the evaluation of their concentration levels in those environmental compartments.

Analytical methods for the determination of alkylphenols and alkylphenol ethoxylates in sediment have been recently reviewed [5]; extraction has been carried out by conventional system such as Soxhlet extraction with polar [6,7] or non-polar solvents [8], ultrasonication in static [9,10] or flow-through-mode [11], pressurized liquid extraction (PLE) [3,12–14], supercritical fluid extraction (SFE) [15] and microwave assisted solvent extraction [16]. In the last years,

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doi:10.1016/j.chroma.2003.09.050

a lot of work has been devoted to the determination of NP and NPEOs in freshwater or marine organisms [17–19]. The simultaneous extraction and determination of EDCs having different chemical characteristics, such as BPA, NP and parent compounds have been also reported in literature [10,20–22].

Recently, some studies have been carried out to establish the usefulness of surfactants for the recovery of solid environmental matrices polluted by hydrophobic organic contaminants [23–25]. Owing to their chemical properties, surfactants are known to improve the pollutant transfer into the water phase by decreasing the interfacial tension between water and hydrophobic compounds, driving the desorption by accumulating them in micelles [26]. However, little is known about the mechanisms of surfactant influences on sorbed compounds: only the solubilization of phenantrene on spiked sand using six different ionic and non-ionic surfactants [25] and the influence of the addition of an anionic surfactant (SDS) on the desorption of atrazine from soil have been recently studied [27]. At the best of our knowledge, none of the published paper reports the utilization of surfactant solutions in EDCs extraction from solids.

The aim of this work was to develop and validate a new extraction procedure, followed by RP-HLPC analysis with direct fluorescence detection, that permits the routinary and simultaneous determination of BPA, NP, NP1EO and NP2EO in solid environmental samples. We used an aqueous non-ionic surfactant solution (Tween 80) for extraction, followed by a clean up step by SPE. The optimized analytical protocol was applied to the analysis of target compounds in river sediments, river suspended matter, and aquatic macroinvertebrate organisms (oligochaetes *Lumbriculus variegatus*).

2. Experimental

2.1. Materials and chemicals

Technical grade 4-nonylphenol (NP), 4-nonylphenol monoethoxylate (NP1EO) and 4-nonylphenol diethoxylate (NP2EO), BPA (purity 99.9%) and analytical grade non-ionic surfactant Tween 80 (polyoxyethylene–sorbitan–monooleate) were purchased from Aldrich (Steinheim, Germany).

All solvent used (acetonitrile, methanol, acetone) were HPLC grade and were purchased from Merck (Darmstadt, Germany). Water for chromatography was purified (18 $M\Omega\,cm^{-1}$ quality) by a Milli-Q system (Millipore, Bedford, MA, USA).

Supelclean LC-18 SPE cartridges (1 g in 6 ml), and the SPE vacuum manifold were purchased from Supelco (Bellefonte, PA, USA).

Neutral aluminum oxide for chromatography was purchased by Fluka. Technical grade anhydrous sodium sulfate and acetic acid were supplied from Merck.

2.2. Standard solutions

A standard stock solution of 1000 $mg\,l^{-1}$ of each target compound was prepared by dissolving accurate amounts of pure standards in methanol. Working solutions of the individual standards and of mixture of all of them were achieved by serial dilution (0.1–5.0 $\mu g\,ml^{-1}$) of stock solutions with methanol. A 250 $g\,l^{-1}$ standard stock solution of Tween 80 was prepared in pure methanol. Stock and working standards were stored at 4 °C. The Tween 80 aqueous solutions for the extractions were freshly prepared by adding appropriate volumes of Tween 80 stock solution to 100 ml of Milli-Q water.

2.3. Sample collection

River sediment samples were collected from the Po river (Northern Italy), upstream (sample called "Po1") and downstream (sample "Po2") the confluence of its most polluted tributary, the Lambro river, and one from the Lambro river itself (sample "Lambro"). Sediments and suspended matters were also sampled in the Tiber river (Middle Italy) at four sampling sites, before (sample Tiber 1), along (sample Tiber 2) and after (samples Tiber 3–4) it receives important loads of urban wastewaters from the city of Rome. Bed sediments were collected using a grab sampler, transferred in precleaned glass bottles under refrigerated conditions to the laboratory, then frozen at −20 °C and finally freeze–dried. The liophilized samples were ground and homogenized using a mortar and stored in a tightly closed brown glass bottle in a desiccator at room temperature until extraction. River suspended matters were collected by filtering 10 l of water through precombusted (4 h at 480 °C) and preweighed Whatman GF/F glass fiber filters (0.7 μm nominal pore size). After filtration, filters were stored at −20 °C. Before extraction, filters were dried at 50 °C overnight and re-weighed to determine particle loading.

Oligochaetes (*L. variegatus*) of a laboratory rearing were exposed to river Po sediment, which contained 0.34, 0.69 and 0.27 $\mu g\,g^{-1}$ of NP, NP1EO and NP2EO, respectively measured by Soxhlet extraction and HPLC–FLD analysis. After 10 days of exposure, sediment was sieved and worms were kept in clean water for gut purging; afterward worms were frozen at −80 °C until the extraction.

2.4. Tween 80 extraction procedure

For extraction, 5 g of freeze–dried sediment were added into 100 ml Tween 80 aqueous solution. The suspension was then mixed thoroughly at room temperature by magnetic stir (about 300 rpm) and, at the end of extraction, was kept settling down for some minutes, transferred to 50 ml centrifugation tubes and centrifuged at 10,000 rpm for 15 min. Extraction time and Tween 80 surfactant concentrations were optimized testing different conditions.

Suspended matter extraction was performed with the Tween 80 aqueous solution under optimized conditions

(extraction time: 3 h and Tween 80 concentration: 10 g l^{-1}). The whole glass fiber filter was shaken at room temperature by a shaker table (120 rpm), followed by centrifugation of the extract solution.

About 1 g of frozen oligochaetes was mixed with anhydrous sodium sulfate, grinded in a mortar and put into 20 ml of 10 g l^{-1} Tween 80 aqueous solution. The extraction was carried out with the optimized extraction procedure.

2.5. SPE clean up of extracts

Centrifuged aqueous extracts (supernatant) were subjected to a preconcentration and clean-up step by SPE using LC-18 cartridges set up on a SPE vacuum manifold. Conditioning of the cartridges was performed with 5 ml of acetone, 5 ml of methanol and 5 ml of Milli-Q water at a flow rate of 3 ml min^{-1}. After sample loading (at 5 ml min^{-1}) and subsequent washing with 10 ml of Milli-Q water, the cartridges were dried with a vacuum system for 45 min.

Recovery of analytes from SPE cartridges was achieved by eluting with acetone. The so-obtained extracts were then concentrated to an approximate volume of 0.5 ml under a gentle stream of nitrogen and reconstituted in methanol:H_2O 60:40 (v/v) to a final volume of 1 ml for further HPLC analysis.

The following SPE operating parameters were optimized: sample volume loading, eluent volume, and solid phase mass. Best recoveries were obtained with the following conditions: sample volume: 25–50 ml; eluent volume: 30 ml acetone; sorbent mass: 1 g.

2.6. Soxhlet extraction

About 5 g of freeze–dried river sediments were Soxhlet extracted with 400 ml of methanol for 10 h (9 cycles h^{-1}).

Methanol extracts were concentrated to 1–2 ml by rotary evaporation under vacuum and transferred onto a 15% water deactivated neutral alumina column (1.5 cm i.d., 4.5 cm h) which was previously washed with methanol. Alumina column was then eluted with 15 ml 10% acetic acid in methanol. The purified extracts were concentrated to 0.5 ml under a gentle stream of nitrogen using a TurboVap-II workstation (Zymark, Hopkinton, MA, USA) and filtered through a 0.45 μm PTFE filter before injection.

The frozen oligochaete samples (about 1 g f.w.) were mixed with anhydrous sodium sulfate and extracted with hexane/acetone (1:1, v/v) in the Soxhlet apparatus for 10 h (9 cycles h^{-1}). Hexane:acetone extracts were evaporated just to dryness, recovered with 1–2 ml of methanol, and purified onto an activated Florisil column (1.5 cm i.d., 4.5 cm h) which was previously washed with methanol.

2.7. HPLC analysis

The HPLC system consisted of a 9010 ternary pump (Varian, Walnut Creck, CA, USA) equipped with a 7125 Rheodyne injector valve with 50 μl loop and a Perkin-Elmer (Norwalk, CT, USA) LS 30 fluorescence detector. The selected wavelengths were 230 nm (excitation) and 302 nm (emission). Data collection and processing were provided by a Perkin-Elmer LCI-100 recorder. HPLC separation was performed at a flow rate of 1 ml min^{-1} using a 4 μm, 150 mm × 4.60 mm i.d. Synergi Polar-RP 80A (ether-linked phenyl) column (Phenomenex, St. Torrence, CA, USA), preceded by a guard column (4 mm × 3 mm i.d., 4 μm) of the same packing material.

Separation was performed under gradient elution conditions using methanol (solvent A) and water (solvent B) as mobile phase according to the following solvent programming: from initial conditions of a 60:40 (v/v) A–B ratio to a 80:20 (v/v) A–B ratio in 20 min; the final eluent composition was held constant for 15 min and then decreased linearly to the initial condition (A–B 60:40, v/v) in 5 min.

Five-level linear calibration curves, ranging from 0.1 to 2.0 μg ml^{-1}, were generated for BPA, NP, NP1EO, NP2EO and gave good fits ($r^2 > 0.997$). Regressions were performed using means of the peak areas acquired on different days. The relative standard deviation of the peak areas ranged from 3 to 12% ($n = 3$–14) for upper and lower standard levels, respectively.

2.8. Method validation

The recovery and overall method reproducibility were determined from five replicate analyses of spiked sediment samples from the Po river (sample Po1). Sediments have been previously characterized respect to the nonylphenol content [12,16] and analytical results for NP, NP1EO and NP2EO have been confirmed by a comparison with a conventional Soxhlet extraction procedure.

To make spiking of sediments, known amount of BPA, NP, NP1EO, NP2EO methanol solutions were homogeneously distributed on the surface of freeze–dried weighted sediments, in order to obtain a final concentration of 0.1–1.0 μg g^{-1} of each compound. Spiked samples were mixed for several minutes and kept in the dark at 40 °C for 24 h to allow analytes to interact with natural organic material. The next day the spiked samples were cooled and weighed before being extracted and analyzed.

3. Results and discussion

3.1. Optimization of extraction procedure

The influence of surfactant concentration on the extraction recovery (R (%)) was tested by extracting a low polluted river sediment (sample Po1) spiked at 1 μg g^{-1} level for each analyte with five different Tween 80 concentrations (0.1–10.0 g l^{-1}) (Fig. 1). R (%) curves increase with an increase in Tween 80 concentrations, reaching at 5.0 g l^{-1} a good recovery for the less hydrophobic compounds

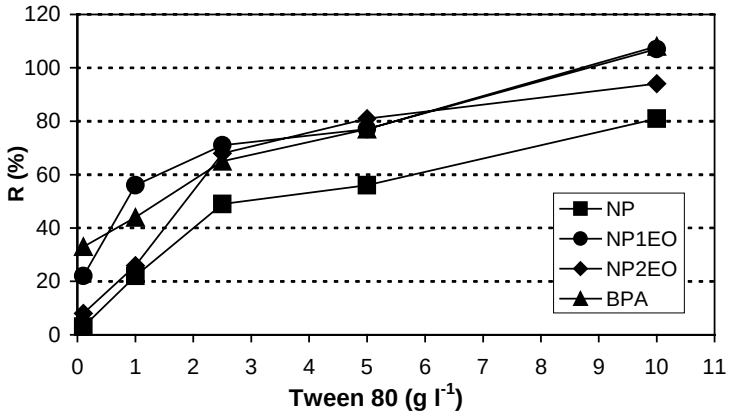

Fig. 1. Recovery percentage (R (%)) of NP, NP1EO, NP2EO and BPA from spiked sediments as a function of surfactant Tween 80 concentration (number of replicates = 3; extraction time = 3 h; extract volume processed by SPE = 25 ml).

NP1EO, NP2EO and BPA, which ranged from 77 to 81%, while the most hydrophobic one, NP, was recovered only for 56%. At 10.0 g l^{-1} Tween 80 concentration, the average recoveries were satisfactory, being 81 ± 9, 107 ± 10, 94 ± 3 and 108 ± 13% for NP, NP1EO, NP2EO and BPA, respectively.

Using a Tween 80 concentration of 10.0 g l^{-1}, extraction time (1–1.5–2–3–5 and 24 h) was optimized analyzing a non-spiked sediment from a high-polluted site of the Po river (sample Po2). Curves of R (%) versus time increased sharply during the first 2 h, reaching the steady state after 3 h. At this time, R (%) were 90±10, 89±11 and 95±5% for NP, NP1EO and NP2EO, respectively; R (%) for BPA could not be determined because this compound was not detected in the sediment. Longer times of extraction (5–24 h) did not enhance the extraction efficiencies, and 3 h was chosen as the optimum extraction time.

In order to achieve a further preconcentration and clean up of the solid matrix extracts, surfactant extraction solution was subjected to a SPE with C18 cartridges.

Recovery of analytes was evaluated as a function of initial sample volume, by processing different aliquots of the 100 ml Tween 80 sediment extracts (from sample Po2) on C18 cartridges with different sorbent masses (0.5–1–2 g). Increasing sample volume can increase concentration factor (Fc) but can also lead to the reaching of the breakthrough volume.

Plot of R (%) as a function of concentration factor showed that an increase in Fc did not correspond to an increase in recoveries of compounds (Fig. 2). The best SPE efficiency was achieved with Fc values between 25–50 and 1 g cartridge, being R (%) in the range of 82–95% for all analytes (n = 3). At higher Fcs, a decrease in R (%) was observed for all investigated compounds up to values ranging from 45 to 79%; a similar trend was observed for both the 0.5 and 2 g cartridges. This fact was probably due to the presence, in the complex matrix processed, of high concentrations of Tween 80 surfactant, which could compete with analytes in sorption mechanisms on Si-C18, saturating the sorbing capacity of the solid phase and causing a lower recovery.

After sample loading step, in order to improve analyte recoveries, it was crucial to completely dry the solid phase before elution, removing the residual water from previous washing by vacuum for at least 45 min. After testing different solvents (methanol and acetone) and different volumes of elution solvents (5–10–20–30 ml), cartridge elution was carried out with 30 ml acetone.

Recoveries, obtained with the optimized SPE procedure (25 ml of the sediment Po2 extract passed through 1 g cartridge, corresponding to a Fc of 25), were 89±21, 88±9 and 99 ± 9% for NP, NP1EO and NP2EO, respectively (n = 5). Fig. 3 shows typical chromatograms obtained injecting a standard solution of all target compounds and a sediment extract.

3.2. Method validation

The developed Tween 80 extraction–SPE–RP-HPLC procedure was validated by analyzing spiked sediment samples.

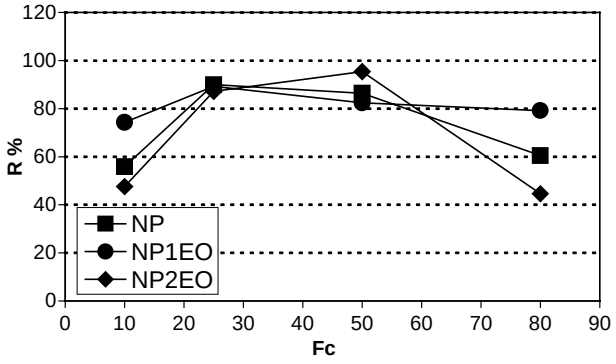

Fig. 2. Recovery percentage (R (%)) of NP, NP1EO, NP2EO from sediment extracts (sample Po2) processed by SPE (1 g C18 solid phase cartridge) as a function of concentration factor (Fc) (number of replicates = 3).

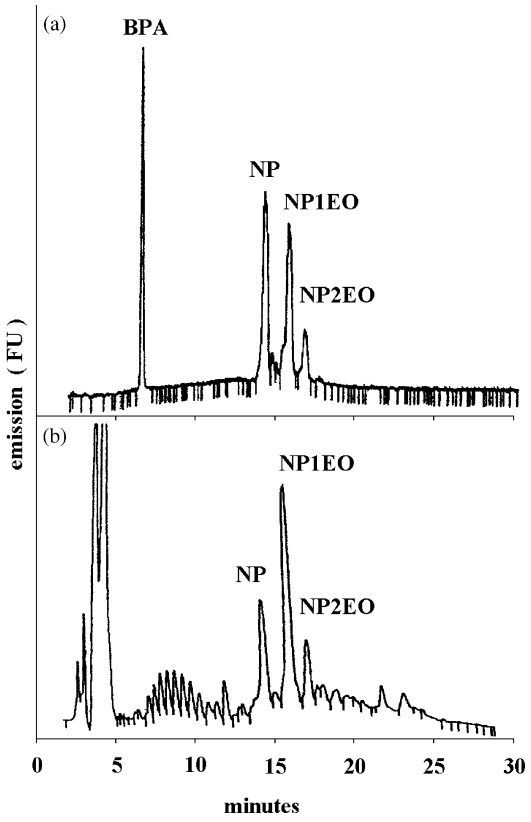

Fig. 3. Chromatograms of (a) a standard solution of target compounds (1 mg l^{-1}), (b) a river sediment extract (sample Tiber 2, NP 0.1 μg l^{-1}; NP1EO 1.8 μg l^{-1}; NP2EO 0.3 μg l^{-1}). Conditions as in Section 2.

The sediment used as matrix was collected from the Po river (sample Po1). BPA was not present in this sediment, while small concentrations of nonylphenol and its low ethoxylates determined in a parallel assay were subtracted from those measured in spiked samples. Three different concentrations of each target compound were added to sediment, in order to achieve final concentration of 0.1–1.0 μg g^{-1}. Recoveries of spiked compounds were between 79 and 108%, most being between 85 and 94% for all analytes (Table 1). No trend in recovery was evident with regard to the degree of ethoxylation of nonylphenols, also if data were more scattered (higher R.S.D.) for the more lipophilic NP, especially at lower concentrations.

Table 1
Average recovery percentage (*R* (%)), repeatability (R.S.D.), limits of detection (LODs) for spiked sediments (sample Po1) by the combined Tween 80 extraction–SPE–RP-HPLC procedure ($n = 5$)

	Spiked sediment: 0.1 μg g^{-1}		Spiked sediment: 1 μg g^{-1}		LOD (μg g^{-1})
	R (%)	R.S.D. (%)	*R* (%)	R.S.D. (%)	
BPA	89	10	108	8	0.03
NP	79	20	89	12	0.06
NP1EO	91	14	107	5	0.04
NP2EO	83	11	94	9	0.03

The repeatability, expressed as R.S.D. of five replicate measurements, fell between 5 and 20% for all analytes, the worst values (14–20%) corresponding to the lowest spiked concentration (0.1 μg g^{-1}). We have to note that variance connected with the not complete homogeneity of the sediment sample cannot be separated by total variance in analytical method.

Limit of detection (LOD) was estimated as three fold the standard deviation of the sample at the lowest concentration (0.1 μg g^{-1}) [28], giving LODs from 0.03 to 0.06 μg g^{-1}.

An estimate of intra- and inter-days precision was obtained by analyzing the same sediment sample (spiked at the higher analyte concentration) three times during a working day and over three consecutive weeks, respectively, and the R.S.D.s for all compounds were below 10 and 15%, respectively.

Analytical results achieved by the optimized Tween 80 procedure applied to sediment samples were compared with those obtained by Soxhlet extraction, as shown in Table 2. Precision and accuracy of Soxhlet extraction procedure have been evaluated in a previous paper [12]. Concentrations of NP, NP1EO and NP2EO measured in the three sediments from Po and Lambro rivers using Tween 80 extraction method, were not statistically different (*t*-test at $P = 0.05$) with respect to those measured with Soxhlet extraction technique. This indicates that the Tween 80 extraction procedure proposed in this work is a suitable alternative extraction method for the determination of the target EDCs in river sediments, showing a better precision than Soxhlet procedure. Moreover, the overall achieved results show that the Tween 80 extraction procedure has a recovery efficiency in agreement with other extraction methods from solid matrices like Soxhlet, PLE or ultrasonic extraction. Petrovic et al. [13] reported recoveries of 89–94% with R.S.D. between 7 and 11% for the determination of NP, NP1EO and NP2EO in river sediments by pressurized liquid extraction. It is also reported that the elevated temperature used in PLE (100–120 °C) can led to significant thermal losses of APs during extraction, while lower temperature may in some cases lead to lower recoveries from the complex matrices like sediments [13]. Shang et al. [3] examined Soxhlet and sonication extraction techniques with single solvent or mixture of solvents, obtaining with both methods recoveries between 76 and 88% and R.S.D. of 3–8% for nonylphenol polyethoxylates.

A preliminary study for the application of this extraction method to the analysis of benthonic macroinvertebrates organisms (*L. variegatus*) exposed to river Po sediments have been carried out. Recoveries of NP, NPEO1 and NPEO2 from organisms were comparable with those obtained with Soxhlet extraction, with precision, estimated as R.S.D.s of three replicates, in the range of 9–30% (Table 2). No recovery experiment with spiked organisms were carried out because it is rather impossible to prepare a really representative spiked sample for biota since added

Table 2
Determination of NP, NP1EO and NP2EO in Po and Lambro river sediments and in oligochaetes extracted with both Tween 80 aqueous solution and Soxhlet procedures ($n = 3$–5)

	NP		NP1EO		NP2EO	
	Average concentration ($\mu g\,g^{-1}$)	R.S.D. (%)	Average concentration ($\mu g\,g^{-1}$)	R.S.D. (%)	Average concentration ($\mu g\,g^{-1}$)	R.S.D. (%)
Tween 80						
Po1	0.3	20	0.5	14	0.2	13
Po2	2.4	12	3.6	5	1.3	4
Lambro	2.2	9	1.2	16	0.6	27
Oligochaetes	1.2	9	4.3	3	0.2	30
Soxhlet						
Po1	0.3	55	0.7	48	0.2	60
Po2	2.5	9	3.6	12	1.4	9
Lambro	2.6	14	1.3	19	0.5	44
Oligochaetes	0.9	14	3.9	2	0.4	25

Table 3
Analyte and organic carbon (OC) concentrations measured in river sediments (from Tiber river), suspended matter (from Tiber river), by the combined Tween 80 extraction–SPE–RP-HPLC procedure ($n = 3$–5)

Sample	OC (%) ($n = 3$)	Average concentration ($\mu g\,g^{-1}$)				R.S.D. (%)			
		BPA	NP	NP1EO	NP2EO	BPA	NP	NP1EO	NP2EO
Sediment Tiber 1	2.6	nd	0.4	0.3	0.1		17	20	18
Sediment Tiber 2	2.9	nd	1.0	1.8	0.3		11	15	2
Sediment Tiber 3	2.6	nd	0.9	1.4	0.1		10	3	3
Sediment Tiber 4	2.8	nd	0.5	1.1	0.3		17	3	8
Suspended matter Tiber 1	4.5	nd	2.4	1.3	nd		10	6	12
Suspended matter Tiber 2	5.8	0.6	5.0	1.8	1.2	16	6	14	28
Suspended matter Tiber 3	6.2	nd	3.1	2.1	2.1		11	13	6
Suspended matter Tiber 4	9.0	0.5	7.3	2.4	2.4	13	25	9	5

molecules can not behave as those accumulated in the tissue.

3.3. Method application to river sediments, river suspended matter and biota

We tested the performance of the developed extraction method in routine analysis by analyzing four grab river sediments and suspended matter (SPM) samples collected in the same sites from the Tiber river (Table 3). BPA was detected only in two samples of particulate matter from Tiber river with concentrations in agreement with previous published data on suspended particles in Elbe river [29].

Significant concentrations of NP, NP1EO and NP2EO were determined in sediments and in SPM collected along the water course of Tiber river. In almost all sediment samples, NP1EO was present in higher concentrations than NP and NP2EO and the maximum values of all compounds were found in the Tiber 2 site, where the water course receives an highly industrially polluted tributary (river Aniene). Our values in sediments are similar to those reported for UK [9], German [29], Portuguese [13] and Swiss [30] rivers, despite the APEOs banning in Italy, as in other European countries, since 1995 in household cleaning products and restriction on industrial cleaning uses [31].

4. Conclusions

This study demonstrates that aqueous solutions of non-ionic surfactant Tween 80 allow the efficient extraction of phenolic EDCs with different hydrophobicity, like nonylphenols, nonylphenol mono- and diethoxylates and BPA, from environmental solid matrices.

The Tween 80–SPE–RP-HPLC method allows the simultaneous extraction of these compounds at the low $\mu g\,g^{-1}$ level, showing a precision (average R.S.D. ranging from 5 to 20%) and an accuracy (average recoveries of 79–108% for all analytes) in agreement with conventional extraction methods (Soxhlet, PLE). Application of the optimized analytical protocol to natural solid matrices of different complexity, confirms that Tween 80 surfactant extraction can be an alternative suitable extraction method for sediments, suspended matter or biota and offers some advantages respect to Soxhlet methods, like absence of solvents, reduced extraction time (3 h) and a real improvement in operator safety and costs, using a relatively simple procedure suitable even for routine analyses.

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