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Determination of organic priority pollutants and emerging compounds in wastewater and snow samples using multiresidue protocols on the basis of microextraction by packed sorbents coupled to large volume injection gas chromatography–mass spectrometry analysis

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ABSTRACT

This paper describes the development and validation of a new procedure for the simultaneous determination of 41 multi-class priority and emerging organic pollutants in water samples using microextraction by packed sorbent (MEPS) followed by large volume injection–gas chromatography–mass spectrometry (LVI–GC–MS). Apart from method parameter optimization the influence of humic acids as matrix components on the extraction efficiency of MEPS procedure was also evaluated. The list of target compounds includes polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalate esters (PEs), nonylphenols (NPs), bisphenol A (BPA) and selected steroid hormones. The performance of the new at-line microextraction-LVI–GC–MS protocol was compared to standard solid-phase extraction (SPE) and LVI–GC–MS analysis. LODs for 100 mL samples (SPE) ranged from 0.2 to 736 ng L^{-1} were obtained. LODs for 800 μL of sample (MEPS) were between 0.2 and 266 ng L^{-1}. In the case of MEPS methodology even a sample volume of only 800 μL allowed to detect the target compounds. These results demonstrate the high sensitivity of both procedures which permitted to obtain good recoveries (>75%) for all cases. The precision of the methods, calculated as relative standard deviation (RSD) was below 21% for all compounds and both methodologies. Finally, the developed methods were applied to the determination of target analytes in various samples, including snow and wastewater.

1. Introduction

Generally, simultaneous multi-residue analysis of organic pollutants is a helpful tool to get a fast survey of the contamination levels of samples. Priority hazardous substances are recognized on the basis of their wide spread occurrence in environment and their toxic properties. In compliance with national and international directives e.g. by Environmental Protection Agency (EPA) and European Community (EC) [1,2] regular comprehensive environmental monitoring is demanded which requires appropriate analytical methods for fast and sensitive detection of relevant compounds. Within the last decades several studies have revealed that organic trace substances suspected for ecological and health risks are increasingly detected in natural or treated water bodies. Concerning to the compounds, analytes such as polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs) and so on have been so far included in the lists of priority pollutants. However, many other compounds such as steroid hormones, pharmaceuticals or personal care products among others have now also become prominent agents of concern to environmental scientists. For screening and monitoring programs with high sample throughput, automated, cost-effective and user-friendly strategies for water analysis are needed. Usually, the determination of traces of organic compounds in water needs combinations of analyte enrichment and GC-(FID, ECD, MS) or HPLC analysis [3,4]. Solid phase extraction SPE [5], solid phase microextraction [6,7] and stir bar sorptive extraction (SBSE) [8,9] have been reported as sensitive and reliable techniques for analyte extraction. Whereas SPME is suited for an automated online combination with several instrumental methods, its capability to detect low concentrated substances in little sample volumes (1–2 mL) is limited. SPE and SBSE are known as more difficult to automate but semi-automated protocols have been described already [10,11]. Microextraction by packed sorbent (MEPS) is a recently developed technique that was introduced by Abdel-Rehim [12–14] in the field of sample preparation. MEPS can combine sample processing, extraction and injection steps fully automated as an at-line sampling/injecting device to GC or LC [15–19]. In MEPS approximately 2 mg of the sorbent is thermo packed inside a syringe (100–250 μL) as a plug or

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between the barrel and the needle as a cartridge. Sample extraction and enrichment takes place on the sorbent bed.

MEPS is not only a miniaturized format of solid-phase extraction (SPE) which is able to handle sample volumes as small as 10 μL, this technique integrates the sorbent directly into the syringe not in a separate column as in commercial SPE. Thus, a fully automated method using MEPS is a promising approach to reduce time and labor effort in sample preparation and analysis [20–30].

In the present work, MEPS coupled to large-volume injection gas chromatograph mass spectrometer (LVI–GC–MS) has been optimized to the simultaneous determination of a large variety of analytes including PAHs, PCBs, phthalate esters (PEs), nonylphenols (NPs), bisphenol A (BPA), mestranol (MeEE2) and 17α-ethynylestradiol (EE2) in water samples. Comparison of a MEPS protocol with a common SPE method optimized in terms of different phases and elution solvents was also carried out. The presence of dissolved humic substances (HS) generally influences the determination of organic compounds in water [31,32]. The extent of this matrix effect depends both on the concentration and the origin of HS. Thus, apart from optimization and evaluation of the MEPS and SPE methodologies, an aim of this study was to investigate the influence of humic acids on the extraction efficiency of the target compounds and sensitivity of their determination in real samples such as snow and wastewater.

2. Experimental

2.1. Reagents and materials

The abbreviations and analytically relevant data of the target analytes are present in Table 1. PAHs (kit 610-N) were obtained from Supelco (Bellefonte, PA, USA). CEN PCB Congener Mix 20 (10 ng μL^{-1} in iso-octane), dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, n-butyl benzyl phthalate, bis(2-ethylhexyl) phthalate and di-n-octyl phthalate (10 ng μL^{-1} each in cyclohexane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

The technical mixture of nonylphenols (94%), 17α-ethynylestradiol (99.4%) and mestranol (99.4%) (Pestanal®) were obtained from Riedel-de Haën (Seelze, Germany) and Igepal® (4-n-nonyphenol) and bisphenol A (>99%) from Sigma-Aldrich (Milwaukee, WI, USA).

PCBs labelled ^{13}C mix, 99% (5 ng μL^{-1} in nonane), fluorene-d_{10} (98%), fluoranthene-d_{10} (98%), 6-methyl chrysene (10 ng μL^{-1} in acetonitrile), benzo [a] pyrene-d_{12} (10 ng μL^{-1} in cyclohexane) and bisphenol A-d_{16} (98%) were supplied by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA).

Methanol, acetone, ethyl acetate and *n*-hexane (chromatographic analysis grade) were purchased from Merck (Darmstadt, Germany).

Individual stock solutions were prepared at a concentration of 1000 mg L^{-1} in methanol. Mix standard solutions at different concentrations were prepared in acetone and used to spike bi-distilled water (Modulab® Analytical purification system, Christ, Stuttgart, Germany).

The humic acid mixture was obtained from Carl Roth GmbH (Karlsruhe, Germany, technical grade). Two modified artificial wastewaters were prepared in accordance to DIN 38412 T24 [33]. German standard methods for the analysis of water, wastewater and sludge; bio-assays (Group L): determination of biodegradability by use of special methods of analysis (L 24, Beuth Verlag GmbH, Hennef) by dissolving 14.72 g of NH_4Cl, 0.825 g of $MgCl_2{\cdot}6H_2O$, 2 g of $CaCl_2{\cdot}2H_2O$ and 22.2 g of Na_2SO_4 (water A) and 53.56 g of $C_7H_5NaO_2$, 102.45 g of $C_2H_3NaO_2$, 14.07 g of $KHSO_4$ and 3.5 g of NaCl (water B) in 1 L of water in both cases.

A treated wastewater sample from a wastewater treatment plant at Leipzig (input from about 10,000 inhabitant equivalents) was taken in March 2010. Snow samples were collected near a busy street at Leipzig (Germany) and from the institute's area of the Helmholtz Centre for Environmental Research- UFZ in February 2010.

2.2. SPE procedure

SPE of samples was carried out with Visiprep SPE manifold (Supelco, Bellefonte, PA, USA). In order to select the most efficient elution solvent for the MEPS procedure and finally to compare the MEPS performance with a common SPE protocol, a series of SPE experiments with spiked water were carried out. Under optimized conditions, 200 mg of C-18 sorbent (polar plus® C-18 bonded phase from J.T. Baker, Phillipsburg, NJ, USA) in 2 mL cartridges and 30 mL hexane:ethyl acetate mixture (50:50, v/v) for elution, 100 mL of spiked water at 250 ng L^{-1} of each analyte which contained 10% methanol (MeOH) were extracted and subsequently analyzed by LVI–GC–MS. MeOH was added according to A. Prieto et al. [9] in order to reduce the adsorption of the lipophilic substances on glassware surfaces. After conditioning using 5 mL of both hexane:ethyl acetate (50:50, v/v) mixture and bi-distilled water and loading of the sample, the cartridges were washed with 5 mL Milli-Q water and dried with nitrogen during 30 min. This wash step is useful particularly for the removal of polar matrix compounds as humic matter. Elution of analytes was performed using three portions of 10 mL of hexane:ethyl acetate mixture (50:50, v/v) and the extract concentrated using a TurboVap® II evaporator (Zymark, Idstein, Germany) at 50 °C to 0.25 mL to be 75 μL finally injected.

2.3. MEPS extraction

The microextraction was carried out with a MEPS device delivered by SGE Analytical Science (Griesheim, Germany). The 100 μL gas-tight syringe is equipped with a small container incorporated into the needle. This assembly called "barrel insert and needle" (BIN) is filled with 2 mg of sorbent commonly used for reverse phase chromatography or SPE. Silica gel sorbents (mean particle size 45 μm, pore size 60 Å) modified with C-18 were examined for the enrichment of the target analytes from water samples. The MEPS syringe was used in connection with a large volume injector type KAS 4 (Gerstel, Mühlheim an der Ruhr, Germany) and the samples were processed by a Multi Purpose Sampler MPS 2 (Gerstel) and controlled by the Maestro software of Gerstel. The extraction can be performed using two configurations which differ in sample volumes. Sample vials with volumes of 2 mL and 10 mL allow the extraction of different sample amounts despite the insertion depth of the MEPS syringe into the vial is limited. Thus, 800 μL of sample can be extracted from a 2 mL standard vial (tray "VT 98 cooler"). On the other hand, the use of 10 mL vials (tray "VT 32-10") enables to extract up to 2 mL of the sample.

The extraction process was fully automated using the MPS 2 device. Prior to each sample extraction, the MEPS-BIN was conditioned using ten 100 μL portions of hexane:ethyl acetate (50:50, v/v) mixture and three 100 μL portions of both MeOH and bi-distilled water. All portions were discarded into the waste vials. The extraction was realized in 100 μL aspiring steps at a speed of 10 μL s^{-1} (according to the experimental design). The sample was also discarded into the waste automatically. After sample extraction the BIN was dried by 5 cycles of drawing and pressing air through the sorbent at a rate of 10 μL s^{-1}. Subsequently, two portions, first of them of 50 μL and the second one of 25 μL of ethyl acetate:hexane mixture (50:50, v/v) were drawn through the BIN and each portion injected at 2.5 μL s^{-1} of injection speed (according to the experimental design)directly into the large volume injector

Table 1
Abbreviations, analytical relevant data and the ions monitored for each analyte studied. The first ion was used as quantifier and the second one as qualifier. Corresponding internal standards are also included.

Name (abbreviation)	Target ions for SIM mode *m/z*	CAS No.	Log K_{ow}[a,b]
Polycyclic aromatic hydrocarbons (PAHs)			
Acenaphthylene (Acy)	152, 153	208-96-8	3.94
Acenaphthene (Ace)	153, 154	83-32-9	3.92
Fluorene (Flu)	165, 166	86-73-7	4.18
Fluorene-d_{10} (Flu-d_{10})	176, 174	81103-79-9	–
Phenanthrene (Phe)	178, 179	85-01-8	4.46
Anthracene (Ant)	178, 179	120-12-7	4.45
Fluoranthene (Flr)	202, 203	206-44-0	5.16
Pyrene (Pyr)	202, 203	129-00-0	4.88
Benzo[a]anthracene (B[a]A)	228, 229	56-55-3	5.76
Fluoranthene-d_{10} (Flr-d_{10})	212, 106	93951-69-0	–
Chrysene (Chr)	228, 229	218-01-9	5.81
6-Methyl chrysene (6-mChr)	242, 207	1705-85-7	6.07
Benzo[b]fluoranthene (B[b]F)	252, 253	205-99-2	5.78
Benzo[k]fluoranthene (B[k]F)	252, 253	207-08-9	6.11
Benzo[a]pyrene (B[a]P)	252, 253	50-32-8	6.13
Dibenzo[a,h]anthracene (D[ah]A)	276, 277	53-70-3	6.75
Benzo[g,h,i]perylene (B[ghi]P)	276, 277	191-24-2	6.63
Indeno[1,2,3-cd]pyrene (Ind)	276, 277	193-39-5	6.70
Benzo [a] pyrene-d_{12} (B[a]P-d_{12})	252, 253	63466-71-7	–
Nonylphenols (NP)			
4-Nonylphenol (4-NP)	107, 220	104-40-5	5.76
n-Nonylphenol (n-NP technical mixture)	135, 149	25154-52-3	5.71
Compound	***m/z***	**CAS No.**	**Log K_{ow}[a,b]**
Polychlorinated biphenyls (PCBs)			
2,4,4′-Trichlorobiphenyl (PCB-28)	256, 186	7012-37-5	5.62
2,4′,5-Trichlorobiphenyl (PCB-31)	256, 186	16606-02-3	5.69
$^{13}C_{12}$ 2,4,4′-Trichlorobiphenyl ($^{13}C_{12}$ PCB-28)	270, 198	–	–
2,2ĭ,5,5′-Tetrachlorobiphenyl (PCB-52)	292, 220	35693-99-3	6.09
$^{13}C_{12}$ 2,2ĭ,5,5′-Tetrachlorobiphenyl ($^{13}C_{12}$ PCB-52)	304, 232	–	–
2,2ĭ,4,5,5′-Pentachlorobiphenyl (PCB-101)	326, 256	37680-73-2	6.80
3,4,3′,4′-Tetrachlorobiphenyl (PCB-77)	292, 220	32598-13-3	6.63
2,3,3′,4,4′-Pentachlorobiphenyl (PCB-105)	326, 256	32598-14-4	6.79
2,3ĭ,4,4ĭ,5-Pentachlorobiphenyl (PCB-118)	326, 256	31508-00-6	7.12
$^{13}C_{12}$ 2,2ĭ,4,5,5′-Pentachlorobiphenyl ($^{13}C_{12}$ PCB-101)	338, 268	–	–
2,2′,4,4′,5,5′-Hexachlorobiphenyl (PCB-153)	360, 290	35065-27-1	6.80
$^{13}C_{12}$ 2,2′,4,4′,5,5′-Hexachlorobiphenyl ($^{13}C_{12}$ PCB-153)	372, 302	–	–
2,2′,3,4,4′,5′-Hexachlorobiphenyl (PCB-138)	360, 290	35065-28-2	7.44
3,3′,4,4′,5-Pentachlorobiphenyl (PCB-126)	326, 256	57465-28-8	7.36
2,2′,3,3′,4,4′-Hexachlorobiphenyl (PCB-128)	360, 290	38380-07-3	7.31
2,3,3′,4, 4′,5-Hexachlorobiphenyl (PCB-156)	360, 290	38380-08-4	7.60
$^{13}C_{12}$ 2,2′,3,4,4′,5′-Hexachlorobiphenyl ($^{13}C_{12}$ PCB-138)	372, 302	–	–
2,2′,3,4,4′,5,5′-Heptachlorobiphenyl (PCB-180)	394, 324	35065-29-3	8.27
3,3′,4,4′,5,5′-Hexachlorobiphenyl (PCB-169)	360, 290	32774-16-6	7.41
2,2′,3,3′,4,4′,5-Heptachlorobiphenyl (PCB-170)	394, 324	35065-30-6	8.27
$^{13}C_{12}$ 2,2′,3,4,4′,5,5′-Heptachlorobiphenyl ($^{13}C_{12}$ PCB-180)	406, 336	–	–
Phthalate esters (PEs)			
Dimethyl phthalate (DMP)	163, 77	131-11-3	1.60
Diethyl phthalate (DEP)	149, 177	84-66-2	2.42
Di-n-butyl phthalate (DBP)	104, 149	84-74-2	4.50
n-Butyl benzyl phthalate (BBP)	91, 149	85-68-7	4.73
Bis(2-ethylhexyl) phthalate (DEHP)	149, 167	117-81-7	7.60
Di-n-octyl phthalate (DOP)	149, 279	117-84-0	8.10
Bisphenol A (BPA)	213, 228	80-05-7	3.32
Mestranol (MeEE2)	227, 310	72-33-3	4.68
17α-Ethynilestradiol (EE2)	213, 296	57-63-6	3.67
Bisphenol A-d_{16} (BPA-d_{16})	224, 242	96210-87-6	–

[a] Experimental values, from Database of physico-chemical properties. Syracuse Research Corporation: http://www.syrres.com/esc/physdemo.htm.
[b] Software calculated value, from SciFinder Scholar Database 2008: http://www.cas.org/products/sfacad/.

of the GC–MS instrument. After the extraction/elution process, ten wash cycles, each with 100 μL of elution solvent mixture, were used to clean the sorbent in order to avoid carryover effect.

2.4. Large volume injection and GC-MS analysis

Analyses were performed at a GC-MSD instrument (Agilent Technologies, San José, CA, U.S.A.) that consists of an Agilent 6890 series gas chromatograph equipped with a programmed temperature vaporizer (PTV) injector (KAS 4, Gerstel) and an Agilent 5973 Mass Selective Detector.

The PTV was operated in solvent vent mode and used an empty baffled deactivated glass liner (7cm × 2 mm I.D.). During injection in split mode at a rate of 2.5 μL s^{-1} the PTV was set at 50 °C (inlet temperature) and at 87.6 kPa (vent pressure). The solvent mixture ethyl acetate:hexane (50:50, v/v) was purged out with a vent flow of 70 mL min^{-1} within 0.7 min (vent time), then, splitless mode was programmed for 1.5 min while the temperature increased at

720 °C min^{-1} to 300 °C and held to 300 °C during 5 min. Analytes were separated on a HP-5MS (30 m × 0.25 mm, 0.25 μm, Agilent Technologies) column. The oven temperature was programmed as follows: start at 50 °C for 2 min, increase at 15 °C min^{-1} to 100 °C, increase at 10 °C min^{-1} to 290 °C and held at 290 °C for 15 min to achieve a running time of 39 min. The transfer line, ion source and quadrupole analyser temperatures were maintained at 300, 230 and 150 °C, respectively. The LVI–GC–MS method was optimized by A. Prieto et al. [9].

Helium was used as carrier gas at constant flow conditions of 1.5 mL min^{-1}. The directly coupled mass spectrometer analyzed the substances after electron impact ionization in selected ion monitoring (SIM) mode. The target ions of the analytes are listed in Table 1.

2.5. Data processing

Most of the works that optimize the MEPS use the "one variable at a time" (OVAT) approach. This approach, as well as time consuming, can lead to erroneous conditions since interactions among parameters are not considered. On the contrary, experimental design approaches consider some related variables at the same time, take into account variable interactions. In this sense, and since two (fill and injection speed) instrumental variables were considered for the extraction/elution efficiency by the MEPS syringe a Central Composite Design (CCD) was built (see Table S.1: Design matrix and responses as chromatographic peak areas) using Statgraphics Plus program for Windows.

2.6. Methods validation

Calibration curves were constructed from duplicate analysis at each concentration level in both cases MEPS procedure (1–1000 ng L^{-1}) and SPE methodology (25–1000 ng L^{-1}). Repeatability, extraction efficiency and recoveries were determined at concentration level of 250 ng L^{-1}. Blank analysis (n = 4) was run after each batch of samples to check carryover. The repeatability was evaluated on relative chromatographic peak areas (with respect to internal standards) of 250 ng L^{-1} standard solution using five replicates that were analyzed in the same day by the same analyst. RSD values were calculated within a day for all analytes. The reproducibility was calculated using ten replicates which were analyzed in different days.

LODs and LOQs were calculated as the signal of the blank plus three and ten times the standard deviation, respectively, of five blank extractions following the IUPAC recommendations. In the case that no peak was found at the retention time of the analyte, the LODs and LOQs were estimated as three and ten times the signal-to-noise (S/N) ratio, respectively.

In a previous work of A. Prieto et al. [8] it was observed that methanol should be added before sampling in order to obtain good recoveries of PAHs and PCBs compounds. In this sense, assays were performed on 500 mL (SPE procedure) or 5 mL (MEPS protocol) of water in presence of methanol at 10%, spiked at 250 ng L^{-1} concentration levels for the analytes. Subsequently, 5 aliquots were extracted and analyzed by means of MEPS-LVI-GC-MS and SPE-LVI-GC-MS procedures under optimised experimental conditions in order to determine the recovery percentages of the target analytes.

3. Results and discussion

3.1. Optimisation of the SPE methodology

In preliminary experiments several sorbent materials (C-18, Oasis HLB, Lichrolut) were examined to select the most efficient material for the extraction and elution of the target analytes. In all cases 200 mg of each material and different elution solvents (hexane, hexane:ethyl acetate mixture (50:50, v/v) and ethyl acetate) were tested. Hexane and ethyl acetate are two solvents most commonly used in multiresidue methods (MRMs) for the determination of organic compounds. Moreover, they often serve as elution solvents in SPE of organic pollutants from water samples and during clean-up steps. They can also constitute the medium in which the final extract is dissolved. Ideally, no solvent exchange and/or concentration step is necessary and final extracts could be injected as they are, using LVI technique to compensate for a lower analyte concentration and GC analysis, without the employment of solvent exchange.

From the literature is known that the addition of methanol can reduce the adsorption of non-polar compounds on glassware surfaces [34,35]. Thus, in order to improve the recovery of the most lipophilic analytes such as PAHs and PCBs and based on previous results of A. Prieto et al. [9,8], the analysis of the target compounds was carried out with the addition of 10% of MeOH in all cases.

Under the defined conditions best recoveries were obtained with C-18 sorbent for the majority of the analytes (data not shown). Therefore, the C-18 sorbent was finally adopted for SPE analysis which allowed a direct comparison to MEPS in which a C-18 sorbent BIN was also applied.

The elution volume necessary for the quantitative recovery of the target analytes was also evaluated using different portions of elution solvents: 4 × 3 mL hexane (fractions from 1 to 4; F1-F4); 2 × 3 mL hexane:ethyl acetate (50:50, v/v) (fractions from 5 to 6; F5-F6); 3 × 4 mL ethyl acetate (fractions from 7 to 9; F7-F9) (see Fig. 1). The study was repeated in triplicate for each of the cartridges used (data not shown). Fig. 1a indicates that volumes higher than 6 mL of hexane (F1-F2) did not enhance the recovery of the PAHs and PCBs from the C-18 cartridges. Optimum elution of PEs, NP and steroid hormones (see Fig. 1b) requires between 3 and 6 mL of hexane:ethyl acetate mixture (50:50, v/v) (F5-F6). Although it is true that no volumes of the hexane:ethyl acetate mixture (50:50, v/v) enhance the recoveries of the PAHs and PCBs, 30 mL of this mixture was chosen as elution volume for all analytes according to the results obtained in the case of elution of PEs, NPs and hormones which can be observed in the Fig. 1b. In the case of these analytes recoveries between 85 and 100% were obtained after the elution with 18–22 mL of hexane:ethyl acetate mixture. Thus, 3 × 10 mL of hexane:ethyl acetate (50:50, v/v) mixture was chosen as elution solvent volume for the whole set of analytes.

3.2. Optimisation of MEPS procedure

The preliminary SPE experiments proved versatility and efficiency of the RP C-18 sorbent material in combination with the mixture of hexane:ethyl acetate (50:50, v/v) for extraction and elution of the target analytes. These principal parameters were transferred to the MEPS method. Thus, a C-18 BIN applied together with the hexane: ethyl acetate as elution mixture was the basis for optimizing the MEPS procedure.

First, fill and injection speed (1–25 μL s^{-1} range), optimum for the extraction/elution efficiency by the MEPS syringe, were evaluated using a Central Composite Design (CCD) (see Section 2.5). Fig. 2a–d show the response surfaces of some studied analytes PCB-31 (representative of PCBs), B[k]F (representative PAHs), DBP (representative PEs) and EE2 (representative of steroid hormones). Overall, best responses were observed when intermediate fill speed and low injection speed values were used. The responses of some analytes (PCB-105, PCB-118 and PCB-180) in the case of PCB compounds were not significantly influenced by variations of both parameters. Due to the high lipophilicity of PCBs and their low

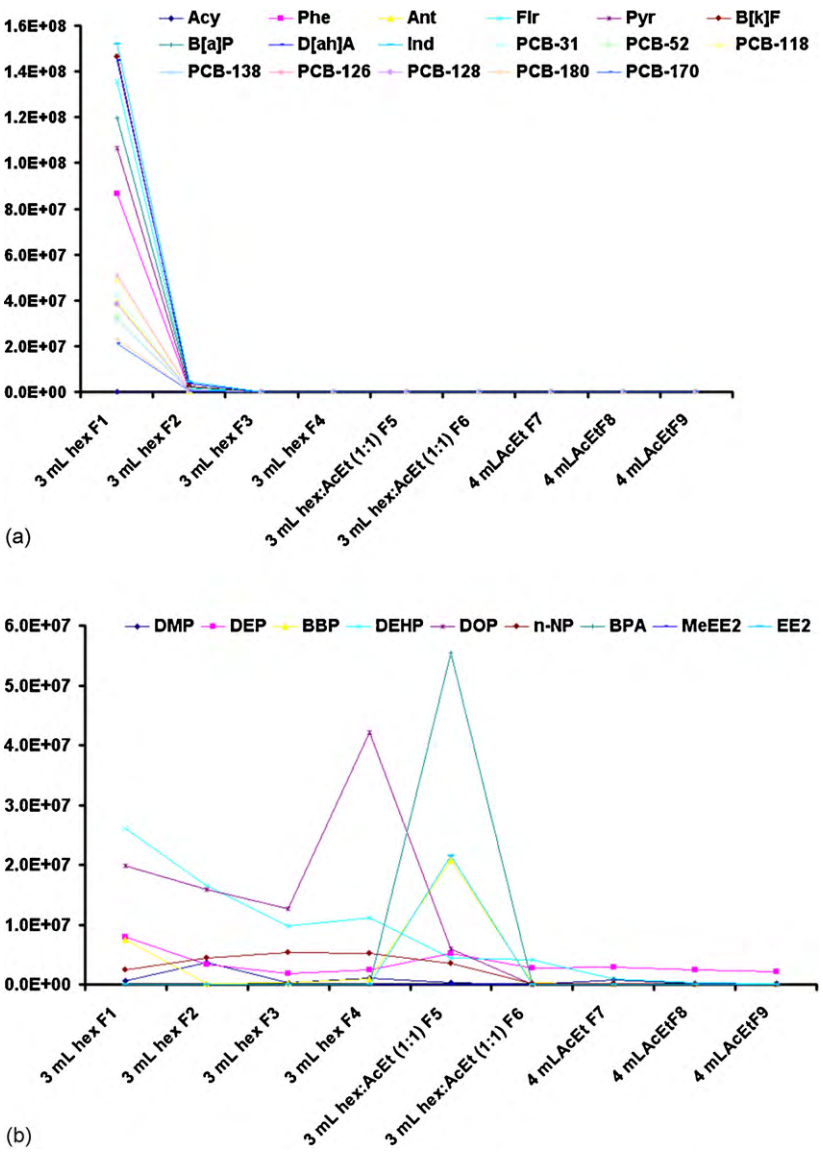

Fig. 1. Elution profiles of some target analytes during the elution with hexane (hex) and ethyl acetate (AcEt) from (a) PAHs and PCBs and (b) PEs, NPs and steroid hormones sequentially carried out on the same C-18 cartridges during the optimization of SPE procedure.

water solubility, fast and quantitative extraction and elution are guaranteed under all "fill/inject"- conditions examined. Therefore, 10 and 2.5 $\mu L\,s^{-1}$ were finally adopted as optimum fill and injection speed, respectively.

Besides sample load, elution/injection volume, drying step and carry over effects were also evaluated, as these have been found as critical steps for the MEPs analysis.

Several elution volumes (25–100 μL) injected in one or two portions of 25 or 50 μL (1×25 μL; 2×25 μL; 1×25 μL + 1×50 μL and 2×50 μL) were tested (see Fig. 3) and it was found that, in many cases, 50 μL or 75 μL of the elution mixture provides best analyte responses. On the contrary, in the case of Chr, B[b]F, Ind, DBP, and DOP 100 μL of elution solvent was required for most efficient elution. Finally, 75 μL (1×25 μL + 1×50 μL) was chosen not only as consensus elution volume but also in order to avoid peak splitting observed for the most volatile compounds when total volumes higher than 75 μL were injected consecutively (2×50 μL) into the PTV.

The number of extraction steps (2, 4, 6, 8 and 10×100 μL) was also evaluated (see Fig. 4). A reduction in the response of most of the compounds was obtained when ten 100 μL portions of sample were loaded on the MEPS BIN. Thus, eight 100 μL portions of sample were finally chosen as optimum.

In order to optimize the way of sample loading multiple draw-eject cycle mode was tested. Alternatively, an extract-discard mode described previously [36] was also studied. Here, each sample aliquot was pumped only once through the MEPS-BIN and the sample portion extracted was discarded into waste before the next aliquot from the sample was pumped. This procedure was applied to the extraction of 800 μL of sample with an analyte concentration of 2.5 $ng\,mL^{-1}$. Responses obtained with this mode were similar (B[a]P, B[ghi]P, Ind, DEHP, PCB-180, PCB-169, PCB-170) or even higher (for the rest of target analytes) than obtained by the multiple draw-eject procedure (Fig. 5). Additionally, at the extract-discard mode the mechanical stress to the MEPS syringe plunger is reduced which also extends the lifetime of the MEPS syringe. Therefore, this procedure was selected for further experiments.

The number of drying steps needed after the extraction process was examined next. 100 μL of air was pumped three, five and eight times through the MEPS BIN at a speed of 10 $\mu L\,s^{-1}$ to remove the residual water from the MEPS BIN. According to the results obtained in the analysis of variance (ANOVA), the number of drying steps of

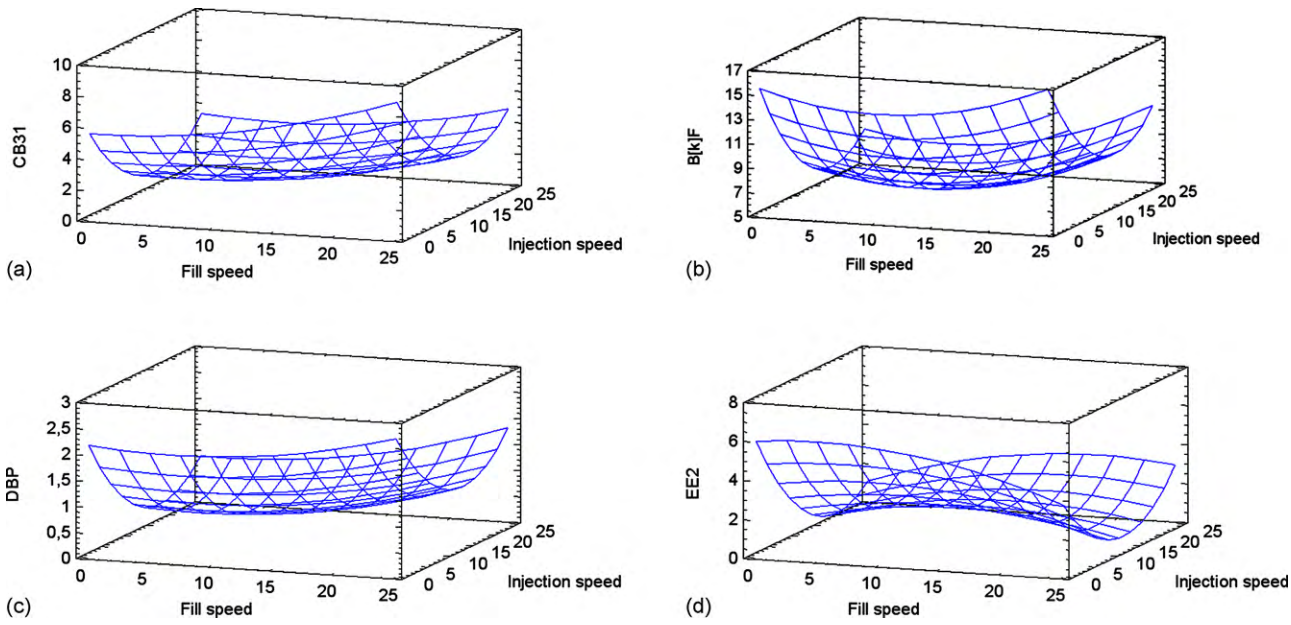

Fig. 2. Response surfaces of some studied analytes (a) PCB-31 (representative of PCBs), (b) B[k]F (representative PAHs), (c) DBP (representative PEs) and (d) EE2 (representative of steroid hormones) during the optimization of fill and injection speed of MEP syringe.

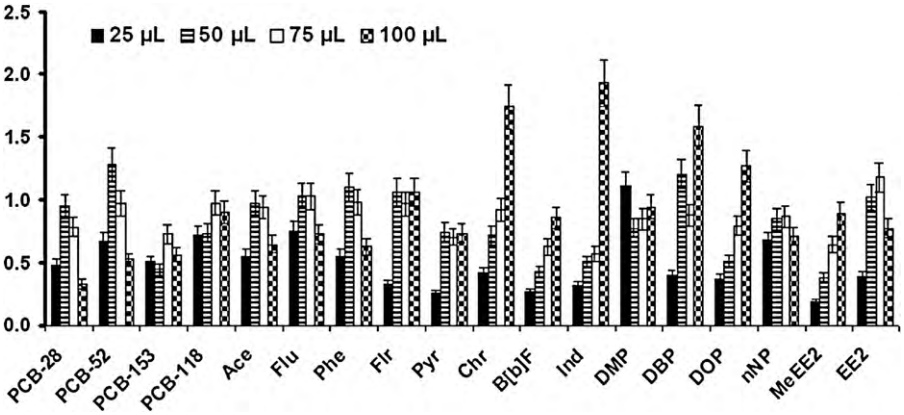

Fig. 3. Comparison of several elution/injection volumes (25–100 µL) for some selected analytes in the extraction with MEPS.

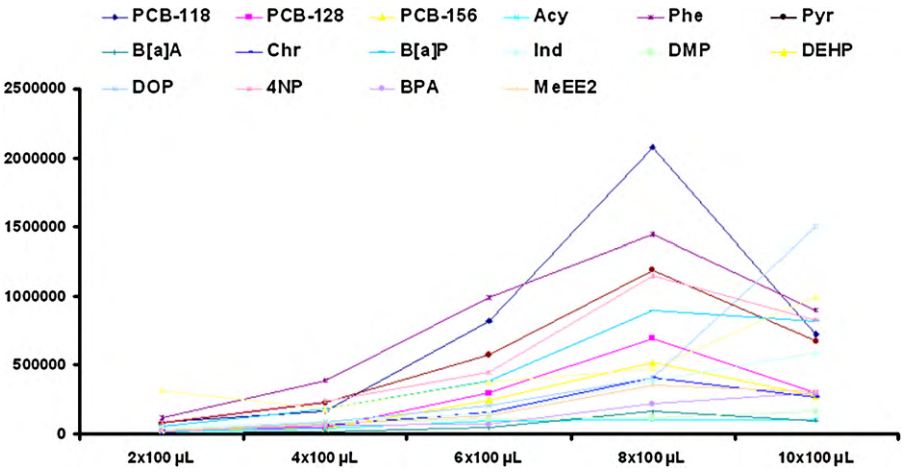

Fig. 4. Influence of the number of extraction steps on the responses of some analytes by means of MEPS.

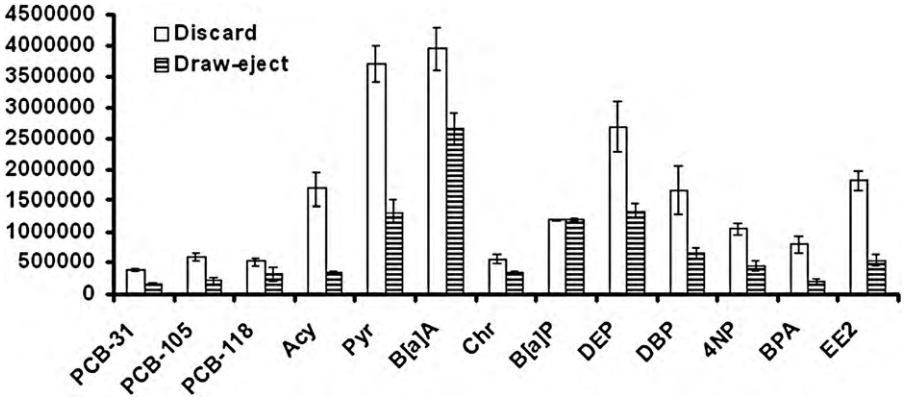

Fig. 5. Evaluation of the way of sample loading (multiple draw-eject cycle mode vs. extract-discard mode) in the case of some selected compounds as chromatographic responses.

the MEPS sorbent had no significant influence on the responses of all the compounds (F_{exp} = 1.0–1.9 < $F_{critical}$ = 3.3). Thus, air was pumped and discarded into an empty vial five times before elution of the analytes.

In order to evaluate possible carryover problems two, four, six, eight and ten wash-discard cycles each with 100 μL of the elution solvents mixture were passed through the MEP syringe after the extraction and elution steps of the target analytes. The results obtained using the different five protocols were compared. The carryover effect checked after the washing procedure using 10 portions of 100 μL of elution solvents mixture was reduced to 0.002–3.9% of the initial extracted analyte amounts and in the case of two, four, six and eight wash-discard cycles higher carryover values (>10%) were obtained for some analytes. Thus, ten wash-discard cycles each with 100 μL of elution solvents mixture was selected as optimum washing protocol.

3.3. Performance of the analytical methods

Table 2 summarizes the methods validation data. For quantification internal standard calibration was used, the isotopically labeled compounds selected as internal standards for the analytes are shown in Table 1.

The developed MEPS-LVI-GC-MS and SPE-LVI-GC-MS chromatographic procedures exhibits excellent linearity (R^2 > 0.99) for the majority of compounds in the 1–1000 ng L^{-1} and 25–1000 ng L^{-1} ranges in the case of MEPS and SPE, respectively. Precision (RSD < 21%) were obtained within a day (see Table 2) in all cases and similar RSD values were obtained among the days (data not shown) for most analytes in the case of reproducibility assays.

Calculated LODs for 100 mL samples (SPE procedure) were between 0.2 and 736 ng L^{-1}. LODs for 800 μL of sample (MEPS methodology) were between 0.2 and 266 ng L^{-1}. The LODs obtained by means of the MEPS procedure are similar to those obtained in the work of El-Beqqali et al. [37] for some PAHs (Ant, Chr, Flr, Flu and Pyr) using a MEPS method but it should be underlined that in the mentioned work a simultaneous determination was not performed.

These results demonstrate the high sensitivity of the MEPS procedure in comparison to the commonly applied SPE methodology which generally consumes more time and labor effort than the fully automated MEPS protocol. Furthermore, MEPS allows the extraction of only 800 μL of sample volume to detect the target compounds at ng L^{-1} concentration level.

In the case of some PAHs and PEs extraction efficiencies were lower (50–70%) but still acceptable for a multi-residue method [38].

Concerning recoveries, quite good recoveries were obtained for both methods (78–126%) in the case of all compounds. It should be emphasized the good recoveries obtained (81–113%) in the case of phthalates which cause often high noise in the chromatograms due to the cross contamination observed from many sample preparation products. On the other hand, MEPS avoids the contact with various materials and thus, the contamination with extra phthalates could be reduced. Similar recoveries were obtained (80–124%) for PAHs, PCBs, PEs and NP compounds when SBSE-GC-MS procedure was used [8].

3.4. The influence of the addition of humic acids in the MEPS extraction efficiency of the congeners studied

Interactions of non-polar organic pollutants with dissolved organic matter (DOM) are well known [31,32]. Humic matter can reduce the amount of extractable organic compounds and/or can interfere in their analysis. In this sense, the influence of humic acids on the extraction efficiency of the target analytes in the MEPS protocol was investigated. The recoveries of the analytes (at 250 ng L^{-1} concentration level) in two different artificial wastewaters, A and B waters (see the compositions in Section 2.1) spiked at different concentrations of humic acids (5, 10, 20, 30, 50, 70 and 100 mg L^{-1}) were determined with the MEPS-LVI-GC-MS procedure.

Fig. 6 shows the recoveries obtained at different concentration of humic acids for some of the analytes studied in the case of A wastewater. For the majority of analytes similar recoveries were obtained in presence of low and higher humic acids concentrations in the case of both A and B prepared waters. This means that the presence of organic matter has no or has a little influence on the detection of analytes. Thus, these kinds of matrix compounds were

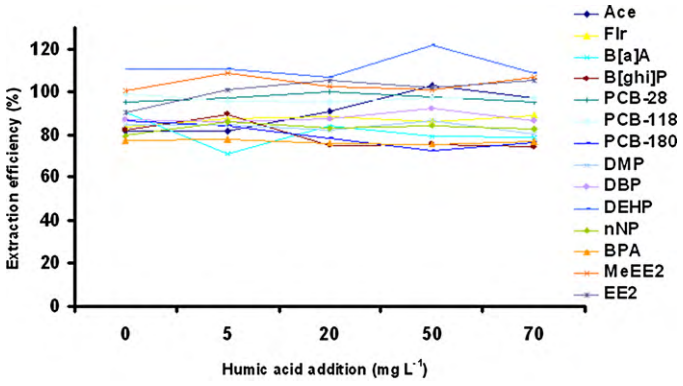

Fig. 6. Comparison of the recovery percentages (concentration 250 ng L^{-1}) obtained for some target compounds in artificial wastewater (named A) at different concentrations of humic acids (0–70 mg L^{-1}).

Table 2
Figures of merit of developed methods.

Analyte	R^2 (%)		LOD (ng L^{-1})		LOQ (ng L^{-1})		Recovery (%)		Precision (RSD, %)		Extraction efficiency (%)	
	SPE (25–1000 ng L^{-1})	MEP (1–1000 ng L^{-1})	SPE (n = 5)	MEP	SPE (n = 5)	MEP	SPE 250 ng L^{-1}	MEP	SPE	MEP	SPE	MEP
Acy	0.9899	0.9931	39.7	4.0	50.1	7.4	110	104	11.9	12.6	74	53
Ace	0.9991	0.9941	101.1	23.6	127.3	40.4	112	82	7.9	19.0	70	60
Flu	0.9948	0.9918	66.1	10.7	107.3	18.4	90	114	16.4	7.7	57	66
Phe	0.9906	0.9865	4.4	32.2	4.4	54.5	88	92	9.4	14.2	63	52
Ant	0.9925	0.9812	2.9	4.0	3.4	7.2	98	85	13.6	11.8	69	30
Flr	0.9989	0.9970	5.8	9.4	6.8	12.7	117	99	11.5	6.4	97	61
Pyr	0.9980	0.9978	2.0	5.6	2.6	10.4	121	90	10.8	5.3	102	57
B[a]A	0.9945	0.9979	1.4	1.1	1.6	1.8	106	105	7.3	8.8	93	72
Chr	0.9930	0.9989	1.6	2.3	2.1	3.2	107	95	8.0	8.9	94	119
B[b]F	0.9960	0.9985	0.9	0.6	1.0	0.9	90	117	6.9	13.0	82	100
B[k]F	0.9954	0.9964	1.6	0.8	2.2	1.3	91	87	5.8	11.9	81	125
B[a]P	0.9990	0.9968	0.3	1.2	0.4	2.0	91	106	15.8	14.8	74	67
D[ah]A	0.9950	0.9897	1.2	0.7	2.0	1.2	93	87	13.0	10.2	75	84
B[ghi]P	0.9969	0.9940	0.2	0.5	0.2	0.8	88	90	14.1	12.2	70	90
Ind	0.9992	0.9945	0.2	0.7	0.5	1.4	85	105	16.6	7.8	67	99
PCB-31	0.9968	0.9892	14.3	26.1	27.3	26.3	117	78	8.6	5.0	105	96
PCB-28	0.9969	0.9937	12.5	14.7	22.1	15.3	110	92	17.3	12.3	90	58
PCB-52	0.9993	0.9946	29.7	11.7	68.8	12.3	113	85	20.9	3.6	84	77
PCB-101	0.9997	0.9977	42.1	7.9	99.0	8.3	103	91	20.9	3.4	93	62
PCB-77	0.9979	0.9987	29.7	1.8	70.7	2.3	95	91	17.7	8.2	106	93
PCB-105	0.9988	0.9950	27.9	7.5	62.9	8.0	96	89	15.0	6.1	98	83
PCB-153	0.9992	0.9960	40.0	10.2	97.4	10.7	126	87	20.2	1.9	90	77
PCB-118	0.9988	0.9989	27.2	0.2	63.1	0.7	120	91	21.3	4.2	90	85
PCB-138	0.9998	0.9969	36.8	7.3	83.9	8.3	113	93	11.3	2.4	88	87
PCB-126	0.9995	0.9987	4.2	5.1	8.4	5.6	120	91	10.5	3.1	91	99
PCB-128	0.9998	0.9974	42.9	9.5	97.7	10.5	117	90	5.8	3.5	111	114
PCB-156	0.9998	0.9954	19.4	10.7	43.8	11.2	115	89	13.0	3.4	97	94
PCB-180	0.9989	0.9972	20.7	8.1	43.4	9.2	104	91	8.5	2.6	90	84
PCB-169	0.9995	0.9977	9.8	9.9	18.9	10.4	104	88	8.5	2.5	88	88
PCB-170	0.9992	0.9969	18.2	11.4	36.4	12.2	110	87	14.0	2.8	87	80
DMP	0.9995	0.9958	735.7	58.5	2204.1	60.5	101	82	5.1	3.5	66	89
DEP	0.9983	0.9902	264.5	266.0	786.8	421.6	87	106	5.5	16.0	77	115
DBP	0.9993	0.9815	6.6	88.1	6.6	168.6	118	96	4.9	13.7	69	103
BBP	0.9906	0.9864	55.4	8.9	55.4	12.7	87	113	3.8	3.9	88	95
DEHP	0.9976	0.9875	25.4	2.1	25.4	8.1	95	87	11.0	11.7	81	81
DOP	0.9979	0.9911	52.9	58.8	52.9	58.9	89	81	6.9	4.6	59	111
n-NP	0.9852	0.9816	18.5	96.4	25.6	151.1	129	94	11	4	104	58
4-NP	0.9888	0.9900	8.9	37.5	9.0	40.1	111	99	17	6	94	51
BPA	0.9928	0.9868	32.3	176.5	33.0	292.6	86	97	2	19	68	102
MeEE2	0.9918	0.9843	6.0	48.5	6.8	48.8	129	113	13	6	109	68
EE2	0.9826	0.9890	9.3	124.6	9.3	135.7	99	98	9	4	80	31

efficiently removed while MEPS extraction was performed and its no tendency to interact with the analytes prior to the extraction process was demonstrated.

3.5. Application of the developed methods to real samples

The optimized and validated methodologies were applied to influent and effluent samples of a wastewater treatment plant at Leipzig (Germany) and snow samples taken at Leipzig in February 2010. The average analyte concentrations determined in snow by both MEPS and SPE protocols are shown in Table 3 as well as the results of the MEPS analyses of the wastewater samples with their corresponding uncertainties in Table 4.

In the snow samples taken near the busy street (bus station BS, BS5) and from the institutes parking place contained highest concentration of acenaphthylene (Acy) and acenaphthene (Ace) (>1000 ng L^{-1}) indicating the accumulation of diesel exhaust emissions [39]. The concentrations of the other PAHs determined at low ng L^{-1} were fairly similar at all sampling places. Concentrations of phthalate esters were detected at μg L^{-1} level for both snow and wastewater samples. In the case of DEP, DBP and DEHP concentrations between 985 and 9973 ng L^{-1} were observed which is in good agreement with other reports on wastewater pollutants [40,41]. BPA as component of numerous technical products was found up to 2000 ng L^{-1} level in snow sample at the UFZ parking place. Here the BPA is probably released by rub-off from polymeric car parts, varnish and wheels and was transported via particles into the sur-

Table 3
Average concentrations (ng L^{-1}) ($n = 4$) and standard deviations obtained in the analysis of snow samples by means of SPE-LVI-GC-MS and MEP-LVI-GC-MS.

Analyte	CA		BS		BS 5m		PR	
	SPE	MEP	SPE	MEP	SPE	MEP	SPE	MEP
Acy	191 ± 45	174 ± 33	186 ± 24	177 ± 3	1343 ± 116	1259 ± 36	3428 ± 176	3263 ± 148
Ace	<LOD	<LOD	2153 ± 104	2098 ± 79	<LOD	<LOD	<LOD	<LOD
Flu	<LOD	<LOD	<LOD	57 ± 2	<LOD	36 ± 1	<LOD	28 ± 2
Phe	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	53 ± 16	39 ± 1
Ant	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	38 ± 11	23 ± 2
Flr	6.01 ± 0.1	5.59 ± 0.04	7.3 ± 1.2	8.3 ± 0.4	<LOD	5 ± 0.1	8.1 ± 0.5	8.3 ± 0.2
Pyr	9.4 ± 0.4	8.9 ± 0.1	10.1 ± 0.7	9.2 ± 0.2	6.0 ± 0.2	7 ± 0.1	19 ± 2	17.8 ± 0.5
B[a]A	25.1 ± 0.2	24.02 ± 0.03	23.2 ± 0.5	23.8 ± 0.1	25.1 ± 2	23 ± 0.03	32 ± 5	30 ± 1
Chr	52.2 ± 4	46.21 ± 0.08	46 ± 2	43.5 ± 0.1	46.2 ± 0.3	43 ± 0.03	45 ± 3	48 ± 0.5
B[b]F	28 ± 3	26.21 ± 0.04	29 ± 4	27.1 ± 0.1	29 ± 5	26 ± 0.04	35.5 ± 6.4	32.9 ± 0.2
B[k]F	58 ± 4	55.02 ± 0.02	61 ± 6	55.9 ± 0.3	53 ± 4	55 ± 0.1	59 ± 3	56.9 ± 0.1
B[a]P	46 ± 3	44 ± 0.03	51 ± 2	43.7 ± 0.1	46 ± 4	43 ± 0.02	45 ± 5	44.6 ± 0.1
D[ah]A	68 ± 5	63.08 ± 0.05	62 ± 4	63.1 ± 0.2	59 ± 6	62.0 ± 0.1	59 ± 7	63.1 ± 0.2
PCB-31	<LOD	<LOD	31.6 ± 2.3	35.8 ± 0.8	<LOD	<LOD	<LOD	<LOD
PCB-52	<LOD	<LOD	<LOD	<LOD	<LOD	15.9 ± 0.3	<LOD	50 ± 8
PCB-101	<LOD	<LOD	<LOD	9.3 ± 0.4	<LOD	9.7 ± 0.1	<LOD	24 ± 4
PCB-77	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	11 ± 1
PCB-105	<LOD	<LOD	<LOD	11.2 ± 0.4	<LOD	10.2 ± 0.4	<LOD	18 ± 3
PCB-153	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	14 ± 2
PCB-138	<LOD	<LOD	<LOD	9.1 ± 0.1	<LOD	<LOD	<LOD	<LOD
PCB-128	<LOD	<LOD	<LOD	11.7 ± 0.6	<LOD	<LOD	<LOD	<LOD
PCB-156	<LOD	<LOD	<LOD	13.0 ± 0.1	<LOD	<LOD	<LOD	15.5 ± 1.5
PCB-169	<LOD	<LOD	55 ± 3	52.2 ± 1.4	<LOD	<LOD	<LOD	<LOD
DMP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DEP	2431 ± 74	2523 ± 60	3322 ± 285	3461 ± 276	5541 ± 211	5623 ± 284	6498 ± 281	6533 ± 262
DBP	1496 ± 59	1527 ± 71	1558 ± 79	1464 ± 99	1832 ± 74	1896 ± 82	2795 ± 79	2828 ± 56
BBP	79 ± 9	84 ± 8	121 ± 7	125 ± 6	141 ± 6	150 ± 5	269 ± 11	281 ± 4
DEHP	258 ± 30	264 ± 38	436 ± 29	451 ± 20	323 ± 19	314 ± 27	343 ± 48	356 ± 40
DOP	899 ± 128	966 ± 113	115 ± 8	104 ± 1	158 ± 16	151 ± 4	<LOD	<LOD
n-NP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4-NP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BPA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2945 ± 163	2643 ± 147
MeEE2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	60 ± 7	53 ± 1
EE2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	182 ± 23	151 ± 9

CA = Control Area UFZ; BS = bus station UFZ; PR = Parking UFZ.

rounding snow. PCBs concentrations were below the LODs in the majority of samples.

It is also noticeable that in the case of wastewater, the concentrations of two of the considered pollutants (Ace and DMP) were higher in the treated water (effluent samples) than in influent wastewater which points to a contamination probably caused by plastic parts used for microfiltration by porous (0.4 μm) polymer-membranes included in this small-size domestic wastewater treatment system "BUSSE MF" (Busse, Leipzig, Germany).

Table 4
Average concentrations (ng L^{-1}) (n = 4) and standard deviations obtained in the analysis of wastewater samples by means of MEP-LVI–GC–MS.

Analyte	Inffluent	Effluent 1	Effluent 2
Acy	947 ± 160	n.d	23 ± 1
Ace	688 ± 37	396 ± 19	1898 ± 179
Flu	25 ± 1	<LOQ	31 ± 2
Ant	n.d	n.d	n.d
B[a]A	27.2 ± 0.3	23.1 ± 0.4	n.d
Chr	45 ± 1	43 ± 1	n.d
B[b]F	58 ± 2	26.0 ± 0.4	n.d
B[k]F	57.4 ± 0.2	55.2 ± 2	n.d
B[a]P	44.3 ± 0.4	44 ± 1	n.d
Ind	78 ± 3	63 ± 2	n.d
DMP	1433 ± 145	315 ± 8	5435 ± 221
DEP	9973 ± 303	1773 ± 48	3505 ± 236
BBP	154 ± 11	132 ± 6	158 ± 11
DEHP	4752 ± 360	985 ± 48	1172 ± 30
DOP	166 ± 20	153 ± 12	131 ± 22
n-NP	330 ± 12	194 ± 11	167 ± 10
4-NP	40 ± 3	49 ± 2	52 ± 3
MeEE2	57 ± 4	52 ± 5	56 ± 4
EE2	751 ± 16	<LOQ	151 ± 12

n.d = not detected.

4. Conclusions

Two sample preparation methods based on MEPS and SPE combined by LVI–GC–MS run have been developed. Both methods permit the accurate multi-residue determination of 41 organic pollutants in water at low levels (ng L^{-1}) for a 100 mL and 800 μL (SPE and MEPS sample volumes) without the need for standard addition procedure.

The use of only 11 isotopically labelled standards which compensate for losses during sample preparation demonstrate the effectiveness of the extraction procedure.

The applicability of both methodologies has been demonstrated by the analysis of various samples of wastewater and snow, where many of the target analytes have been detected. Indeed, the developed multi-residue approaches will permit saving much time and costs as compared to chemical directed analysis. However, the time needed for a MEPS extraction (~15 min) is clearly reduced when compared with the SPE procedure. Besides, the possibility to extract small sample volumes (800 μL) is also of special value for analysis of complex samples such as wastewater. Furthermore, the miniaturized scale of MEPS allows developing sample preparation techniques on the basis of reduced solvent consumption.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.07.070.

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