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Determination of polycyclic aromatic hydrocarbons, phthalate esters, alkylphenols and alkyphenol ethoxylates in sediment using simultaneous focused ultrasound solid–liquid extraction and dispersive solid-phase extraction clean-up followed by liquid chromatography

Marcel Brenkus [a,b], Peter Tölgyessy [a,*], Veronika Koperová Návojová [a,b], Michal Kirchner [a], Svetlana Hrouzková [b,*]

[a] Water Research Institute, Slovak National Water Reference Laboratory, Nábrežie arm. gen. L. Svobodu 5, 812 49 Bratislava, Slovakia
[b] Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia

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ABSTRACT

The study presents a simple and non-laborious method for the determination of 16 polycyclic aromatic hydrocarbons (PAHs), 2 phthalate esters (PEs), 2 alkylphenols (APs) and 4 alkylphenol ethoxylates (APEOs) in sediment. The method employs sample preparation combining focused ultrasound solid–liquid extraction (FUSLE) and *in situ* clean-up followed by liquid chromatography with fluorescence and ultraviolet detection. Extraction of 0.5 g sediment samples with 7 mL acetone in the presence of activated silica (0.5 g) and powdered copper (0.2 g) using an ultrasonic probe for 1 min resulted in recoveries of target analytes $\geq$ 78 %. The analytical method was classified as "acceptable green analysis" by the analytical Eco-Scale assessment (AESA) and scored 0.54 in the AGREEprep greenness assessment for sample preparation. Matrix-matched calibration was used to quantify analytes with a linear range for PAHs 2–1000 ng g^{-1}, for PEs 100–5000 ng g^{-1} and for APs and APEOs 40–2000 ng g^{-1} dry weight. The reached limits of quantification (LOQ) for PAHs ranged from 1.1 to 3.1 ng g^{-1}, for PEs from 122 to 124 ng g^{-1}, for APs from 40 to 51 ng g^{-1} and for APEOs from 36 to 53 ng g^{-1}. The applicability of the method was demonstrated by the analysis of real sediment samples and natural matrix certified reference material.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PEs), alkylphenols (APs) and alkylphenol ethoxylates (APEOs) belong to ubiquitous environmental contaminants entering the hydrosphere as a result of anthropogenic activities from industry, agriculture and households [1–3]. Representatives of these three classes of compounds have been classified as priority substances/pollutants according to the EU Water Framework Directive (WFD) [4] and the US Environmental Protection Agency (EPA) [5] due to their risk to humans and the environment (toxic and genotoxic compounds with endocrine disruptive effects) [1–3]. In natural aquatic systems, these hydrophobic substances with very low water solubility tend to accumulate in bottom sediment [6]. Therefore, according to the WFD Guidance Document No. 25 [7], sediment was chosen as the preferred or optional monitoring matrix for these contaminant classes and is essential for investigating the long-term pollution status of water bodies.

For the purposes of environment protection and monitoring, researchers from the Dutch National Institute for Public Health and the Environment (RIVM) derived environmental risk limits (ERLs) for multiclass compounds in sediment based on ecotoxicity data and applying equilibrium partitioning [8,9]. Ecotoxicological serious risk concentrations (SRC_{eco}) for PAHs were determined in the range of 1.6–260 μg g^{-1}, for PEs in the range of 10–580 μg g^{-1} and for APEOs in the range of 40–360 μg g^{-1}, while the maximum permissible concentrations (MPCs) for PAHs were set between 0.031 and 8.1 μg g^{-1}, for APEOs between 0.15 and 8.7 μg g^{-1}, for dibutyl phthalate (DBP) at 2.1 μg g^{-1} and for nonylphenol (NP) at 0.105 μg g^{-1} dry weight (dw).

In the analysis of organic contaminants in solid matrices such as sediment, solid–liquid extraction (SLE) techniques are most commonly

* Corresponding authors.
E-mail addresses: peter.tolgyessy@vuvh.sk (P. Tölgyessy), svetlana.hrouzkova@stuba.sk (S. Hrouzková).

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used for sample preparation. Classical SLE – maceration – was characterized by low quantitative efficiency, and therefore various measures were introduced to increase its performance, such as the application of high temperature with high pressure and assistance with auxiliary energies, especially microwaves and ultrasound [10]. The latter technique, known as ultrasound-assisted extraction (UAE), was also used in many studies for the analysis of our target analytes in sediment.

To summarize the advances in UAE methods in use, we present Table 1 with characteristics of the methods representatively selected from the studies published in the last two decades. As Table 1 shows, the two employed alternatives of UAE include the less commonly used focused ultrasound solid–liquid extraction (FUSLE) performed with an ultrasonic (US) probe and more widespread sonication with US bath. The main difference between the two is that the probe device delivers ultrasound directly into the extraction media (direct sonication) with minimal energy loss, while the US bath transmits the energy through the water to a container or multiple sample tubes (indirect sonication) [31]. Therefore, the efficiency and intensity of the sonication process are much higher for the US probe than for the US bath, allowing for the use of much shorter sonication times. These factors contribute to achieving better reproducibility of results with US probe. However, the US bath is cheaper and more available and allows the extraction of multiple samples at the same time. It can be seen from Table 1 that the amounts of sample analysed were in the range of 0.125 to 0.5 g for the FUSLE methods and 0.025 to 20 g for the US bath methods. The analysis of small sample amounts, such as 0.025 g [23] and 0.125 g [27], did not require additional clean-up of the sample extract, but is associated with higher method detection (LOD) and quantification (LOQ) limits [23]. In general, large differences were shown between the FUSLE and US bath methods in terms of solvent volumes used for sample extraction and sample extract clean-up and in the duration of the sonication process. While in FUSLE methods the solvent volumes per sample were up to 33.5 mL [28], in US bath methods the solvent consumption per sample was up to 210.25 mL [13]. The sonication times varied from 2 min to 6 min for probe sonication and 10 min to 240 min for bath sonication. Due to the complexity of the sediment matrix (consisting of humic substances, sulphur, minerals, etc.), extraction procedures were in most cases followed by sample extract clean-up. The purification of the crude extract was carried out in a separate step by solid phase extraction (SPE) methods using different adsorbents (silica, alumina, magnesia silica gel, graphitised carbon, primary secondary amine). Reaction with activated copper was employed to remove elemental sulphur [15,28,29]. In some cases of determination of APs, APEOs and PEs, derivatization (silylation) of analytes was used [15,17,20]. Instrumental analysis of target analytes was performed using gas chromatography (GC) combined with mass spectrometry (MS) [11,13,15,17,18,20,22,23,28,29] and tandem mass spectrometry (MS/MS) [16,26] detection and liquid chromatography (LC) combined with MS [14], MS/MS [21,30], fluorescence (FLD) [12,19,24,25,27], photodiode array (PDA) [24] and ultraviolet (UVD) [25] detection. The LODs for the greater part of the methods met the requirements for determining MPCs for target analytes set by the Dutch RIVM. Only two of the presented methods included the determination of all three classes of target compounds: the FUSLE method combined with GC–MS [28] and the US bath method combined with GC–MS/MS [16]. The first one did not meet the MPC requirements for APs and APEOs, both were associated with higher solvent consumption (33.5 mL and 100.5 mL), and both employed SPE clean-up of the crude extract with magnesia silica gel performed in a separate step.

The aim of the presented study was to develop a methodology for simple, non-laborious and environment friendly determination of PAHs, PEs, APs and APEOs in sediment at concentration levels below the MPC limits set by the Dutch RIVM. The methodology uses a novel concept of combining FUSLE and *in situ* clean-up with dispersive SPE (dSPE) performed in a single step, which was introduced in our previous works [32,33]. The final extract is reconstituted in acetonitrile (MeCN) and further analyzed by LC–FLD and LC–UVD instrumental methods.

2. Materials and methods

2.1. Standards and reagents

16-component (10 μg mL^{-1} each) standard PAH solution containing naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Ph), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP), indeno (1,2,3-c,d)pyrene (IcdP) in MeCN was manufactured by CPAchem (Bogomilovo, Bulgaria). Phenols-MIX 4 containing 4-*tert*-octylphenol (4-t-OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO), 4-nonylphenol (4-NP), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO), 100 μg mL^{-1} each in MeCN, was also from CPAchem. EPA method 606 phthalate esters mix containing, among others, di-n-butyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) at 2000 μg mL^{-1} each in methanol (MeOH) was obtained from Absolute Standards (Hamden, CT, USA).

The following isotopically labelled compounds were used as internal standards (IS): PAHs – phenanthrene-d10 (Ph-d10), anthracene-d10 (Ant-d10), fluoranthene-d10 (Fla-d10), benz(a)anthracene-d12 (BaA-d12), dibenz(a,h)anthracene-d14 (DahA-d14) from Neochema (Bodenheim, Germany) and benzo(a)pyrene-d12 (BaP-d12) from LGC Standards (Teddington, UK) prepared separately at 10 μg mL^{-1} in MeCN; and 4-n-butylphenol-2,3,5,6-d4-OD (4-BP-d4) obtained from Chiron (Trondheim, Norway) at 1000 μg mL^{-1} in isopropanol. All standards were > 99.0 % purity.

LiChrosolv grade MeCN, dichloromethane (DCM) and n-hexane (Hex), SupraSolv grade cyclohexane and Emsure grade hydrochloric acid (37 %) were purchased from Merck (Darmstadt, Germany). Chromasolv grade acetone (Acet) was from Honeywell (Hanover, Germany) and super gradient grade MeOH was from VWR (Amsterdam, Netherlands). Milli-Q water was produced by a Direct-Q 3 water purification system from Millipore (Molsheim, France).

Silica gel for column chromatography (ultrapure, 60–200 μm, 60A) from Acros Organics (Geel, Belgium), magnesia silica gel (Florisil, 100–200 mesh) from Alfa Aesar (Karlsruhe, Germany), and MP Eco-Chrom Alumina A (63–200 μm) from MP Biomedicals (Eschwege, Germany) adsorbents were activated at 140 °C overnight before use.

Copper powder (40–100 mesh, 99.5 %) from Centralchem (Bratislava, Slovakia) was activated with a solution of HCl in water (1:1, v/v) using sonication for 15 min. Then the copper powder was rinsed with MeOH (3 ×) and stored under cyclohexane.

Mixed solutions of analytes were prepared in concentrations of 0.025 μg mL^{-1} PAHs + 1.25 μg mL^{-1} PEs + 0.5 μg mL^{-1} APs and APEOs, 0.25 μg mL^{-1} PAHs + 12.5 μg mL^{-1} PEs + 5 μg mL^{-1} APs and APEOs and 2.5 μg mL^{-1} PAHs + 125 μg mL^{-1} PEs + 50 μg mL^{-1} APs and APEOs, respectively, in MeCN. An IS mixture solution of isotopically labeled PAHs (at 0.05 μg mL^{-1} each) and 4-BP-d4 (at 5 μg mL^{-1}) was also prepared in MeCN.

2.2. Sediments

River sediment collected from the Karloveské rameno branch of the Danube in Bratislava was employed for development of the sample preparation method. The < 63 μm particle size fraction of this sediment was purified by repeated extraction with a mixture of solvents (Acet/DCM/Hex, 1:1:1, v/v/v) under sonication using 30-min cycles (each with a new portion of extractant) until a matrix free of target analytes was obtained. Total organic carbon (TOC) content in the dried purified sediment was determined to be 14 mg g^{-1}. Matrix effects and further method performance were studied using < 63 μm fractions of air-dried sediments from the river Ipeľ collected in Salka (SED-1, TOC = 35 mg g^{-1}), from the Málinec water reservoir (SED-2, TOC = 59 mg g^{-1}), from the Turček water reservoir (SED-3, TOC = 73 mg g^{-1}) and with purified

Table 1
Characteristics of published analytical methods for the determination of studied analyte classes in sediment including details about particular analytes, extraction techniques, instrumental set-up and their comparison with the developed method.

Analytes	Sample amount (g dw)	Extractant	Extraction	Clean-up	Analysis	Recovery (%)	LOD (ng g^{-1} dw)	Ref.
16 PAHs	15	+H_2O (40 %), 3 × 33.4 mL Hex:Acet (1:1, v/v)	US bath: 3 × 10 min	Miniaturized silica column	GC–MS	76–119	1	[11]
16 PAHs	1–2	20 mL Acet	US bath: 30 min, shaking for 30 min	10 mL extract + 25 mL H_2O => SPE with C18[a] (35 mL of solvents – Acet, MeOH)	LC–FLD	80–97	10–15	[12]
8 PAHs, 2 APs	1	3 × 30 mL Hex:DCM (1:1)	US bath: 3 × 10 min	SPE with alumina, conditioning, elution, reconstitution (120.25 mL of solvents – Hex, DCM)	GC–MS	>50 (PAHs), >61 (APs)	0.16–1.28 (PAHs), 1.86–8.04 (APs)	[13]
1 AP, 1 APEO	20	2 × 50 mL MeOH:Acet (8:2)	US bath: 2 × 120 min	No additional clean-up, reconstitution in 1 mL Milli-Q H_2O	LC–MS	61–86	0.2–5.0	[14]
3 APs, 4 APEOs	0.5	3 × 20 mL MeOH:Acet (1:1)	US bath: 3 × 20 min	Cu powder, extract solvent exchange to isooctane => SPE with Florisil, derivatization – silylation	GC–MS	74–128	5.97–13.3 (APs), 4.2–4.7 (APEOs)	[15]
16 PAHs, 5 PEs, 2 APs, 2 APEOs	1	1: 10 mL DCM:Hex (1:1) 2: 10 mL Hex:Acet (1:1) 3: 10 mL Hex:Acet (1:1)	US bath: 3 × 10 min	SPE with Florisil (70.5 mL of solvents – Hex, DCM, Acet, ethyl acetate)	GC–MS/MS	70–114	1–48 (PAHs), 4–11 (PEs), 38–48 (APs), 103–150 (APEOs)	[16]
2 PEs	5	3 × 15 mL 0.01 M HCL aqueous solution	US bath: 3 × 15 min	Acidification to pH 2 (HCl), 3 × reextraction with 3 mL DCM, derivatization – silylation	GC–MS	76–105	0.02–0.04	[17]
6 PEs	n.i.[b]	MeOH:DCM (1:1)	US bath: 30–60 min	No additional clean-up, evaporation, reconstitution in 1 mL DCM	GC–MS	44–108	232–572	[18]
2 APs	2	2 × 5 mL MeOH:H_2O (7:3)	US bath: 2 × 15 min	SPE with C18, 3 × elution with 1 mL MeOH and 1 mL MeCN, evaporation, reconstitution in 0.2 mL MeCN	LC–FLD	81–94	0.08 (LOQ)	[19]
3 APs, 2 APEOs	5	3 × 25 mL MeOH:DCM (1:1)	US bath: 3 × 20 min	SPE with C18 (20 mL of solvents – ethyl acetate, MeOH), derivatization – silylation	GC–MS	>72	0.02–0.24	[20]
2 APs	2	15 mL H_2O:MeOH:Acet (1:2:1)	US bath: 60 min	Extract diluted with 250 mL H_2O and acidified to pH 2 => SPE with graphitized carbon black (30.5 mL of solvents – DCM, MeOH)	LC–MS/MS	85–99	0.28–1.5	[21]
6 PEs	1	5 mL MeOH	US bath: 30 min	1 mL extract + 9 mL H_2O => HS SPME	GC–MS	90–111	1–79	[22]
17 PAHs	0.025	0.5 mL 18 % MeCN in DCM	US bath: 23 min	No additional clean-up	GC–MS	73–118	4.95–23.8	[23]
6 PEs, 3 APs	1	7 mL MeCN:DCM (3:1)	US bath: 10 min	SPE with Florisil, evaporation, reconstitution in 0.25 mL MeOH	UFLC–PDA-FLD	62–117	32.0–63.2 (PEs), 0.412–0.649 (APs)	[24]
16 PAHs	1	+ 1 mL H_2O + 4 mL Acet	US bath: 15 min	QuEChERS[c] dSPE: 1 mL extract + 25 mg PSA[d] + 90 mg $MgSO_4$	LC–FLD-UV	78–117	0.00108–0.314	[25]
20 PAHs	5 or 3	3 × 15 mL DCM:MeOH (9:1)	US bath: 3 × 30 min	SPE with alumina, eluent – 25 mL DCM:MeOH (9:1)	GC–MS/MS	40–120	0.001–0.013	[26]
15 PAHs	0.125	3 × 1.3 mL MeCN	μFUSLE: 3 × 2 min, without cooling	No additional clean-up	LC–FLD	77–101	n.i.	[27]
16 PAHs, 6 PEs, 1 AP, 2 APEOs	0.5	10 mL Acet	FUSLE: 2 min, at 0 °C	0.5 g Cu added to sediment, SPE with Florisil (23.5 mL of solvents – Hex, toluen, ethyl acetate, isooctane)	GC–MS (two methods)	n.i.	0.08–5.33 (PAHs), 45.9–187.4 (PEs), 580 (NP), 12,350 (NP1EO + NP2EO)	[28]
15 PAHs	0.25	15 mL DCM	FUSLE: 5 min, at 0 °C	Cleaning through Cu glass cartridge	GC–MS	47–109	5–32	[29]
3 APs	0.5	10 mL Acet:Hex (7:3)	FUSLE: 5 min, at 0 °C	Extract evaporated and reconstituted in 1.5 mL MeCN => dSPE with graphitised carbon	LC–MS/MS	87–113	0.9–31.3	[30]
16 PAHs, 2 PEs, 2 Aps, 4 APEOs	0.5	7 mL Acet	FUSLE: 1 min, without cooling	dSPE with 0.5 g silica + 0.2 g Cu powder (Simultaneous with extraction)	LC–FLD, LC–UVD	78–161	0.31–0.92 (PAHs), 37 (PEs), 12–15 (APs), 11–16 (APEOs)	This work

[a] Octadecyl silica.
[b] No information.
[c] Acronym for Quick, Easy, Cheap, Effective, Rugged and Safe method.
[d] Primary secondary amine.

(as in the case of the Danube sediment) water reservoir sediment with a TOC of 28 mg g^{-1}.

Natural matrix certified reference material (CRM) containing PAHs and PEs, BNAs in soil (CRM131-100), was obtained from RTC (Laramie, WY, USA). Due to the high certified concentrations of the analytes, 0.45 g of purified sea sand (Centralchem, Bratislava, Slovakia) was used to dilute 0.05 g of CRM.

2.3. Instrumental analysis

Sediment extracts were analysed by two LC methods employing an Agilent Technologies 1290 Infinity II LC system with 1260 FLD Spectra and 1290 DAD (diode array) detectors and an 1290 Multisampler (Santa Clara, CA, USA). The LC was equipped with two analytical columns and a column selection valve. In both LC methods, after injection of 15 μL of sample extract, the analytes were separated by gradient elution carried out with a mixture of water with 5 % MeCN (component A) and MeCN (component B) in the case of PAHs and PEs analysis and MeOH (component C) in the case of APs and APEOs analysis with a flow rate of 1 mL min^{-1}. The initial and post-run eluent composition for both methods was 40 % A and 60 % B or C, respectively, and the gradient changes were as shown in Table 2. A Zorbax Eclipse PAH column (4.6 × 150 mm × 3.5 μm, Agilent Technologies) thermostated at 32 °C was used for determination of PAHs and PEs, while an Arion Plus C18 column (4.6 × 100 mm × 3 μm, Chromservis, Prague, Czech Republic) maintained at 40 °C was used to determine APs and APEOs. For the first method (PAHs, PEs), Table 2a summarizes excitation and emission wavelength pairs for FLD detection of PAHs together with analyte retention times. Detection of Acy and PEs was performed by DAD at 225 nm. For the second method, the detection of APs and APEOs was carried out by FLD using fluorescence wavelengths listed in Table 2b, which also shows retention times of the analytes.

Table 2
Excitation (λ_{exc}) and emission (λ_{em}) wavelength pairs for FLD detection, retention times (t_R) of analytes and eluent composition changes for **a)** PAHs and PEs, **b)** APs and APEOs.

a)				
Analyte	λ_{exc} (nm)	λ_{em} (nm)	t_R (min)	Eluent composition A: B (%)
Nap	220	340	4.69	40: 60
Acy	–	–	5.36	
Ace	265	340	6.76	
Fle	265	320	6.98	
DBP	–	–	7.41	
Ph	250	368	8.06	35: 65
Ant	250	400	9.33	
Fla	240	455	10.72	
Py	240	395	11.69	
BaA	280	405	13.99	0: 100
Chr	260	385	14.49	
BbF	255	425	15.95	
DEHP	–	–	16.30	
BkF	255	420	16.62	
BaP	255	420	17.42	
DahA	300	405	18.56	
BghiP	300	425	19.77	
IcdP	245	495	20.48	0: 100
b)				
Analyte	λ_{exc} (nm)	λ_{em} (nm)	t_R (min)	Eluent composition A: C (%)
4-t-OP	232	310	19.18	40: 60
OP1EO	232	310	21.40	
OP2EO	232	310	22.67	29: 71
4-NP	232	310	25.64	
NP1EO	232	310	26.68	
NP2EO	232	310	27.14	0: 100

2.4. Focused ultrasound solid–liquid extraction (FUSLE)

The FUSLE was performed using a Branson Digital Sonifier SFX 550 cell disruptor and homogenizer (550 W, 20 kHz; Emerson Electric, St. Louis, MO, USA) equipped with a double step 1/8 in. microtip.

A 0.5 g aliquot of air-dried sediment in a 15 mL Pyrex glass conical centrifuge tube (Corning, New York, NY, USA) was added with 100 μL of IS solution mixture and allowed to rest overnight in the refrigerator. Next day, 7 mL of Acet, 0.5 g of activated silica and 0.2 g of activated copper powder were added. The microtip of the US probe was placed in the centre of the tube and the FUSLE was conducted in a pulsed sonication mode (pulsed time on of 1 s and pulsed time off of 0.1 s at ultrasound amplitude of 50 %) at the room temperature. After 30 s, the microtip was positioned at the bottom of the tube and the FUSLE continued for the next 30 s. After sonication, the sample was centrifuged at 2000 rpm for 5 min (centrifuge Rotina 380, Hettich, Tuttlingen, Germany). The supernatant was transferred to a calibrated glass tube, the Acet extract was concentrated under a stream of nitrogen and replaced with MeCN in a final volume of 200 μL. The final extract was transferred into a dark 2 mL vial equipped with a glass insert and was then ready for LC analysis.

3. Results and discussion

3.1. LC methods

For PAH and PE determination, the Agilent Zorbax Eclipse PAH column recommended for PAH separation was selected. PAHs, with the exception of Acy, were detected by FLD allowing the use of one excitation wavelength and the monitoring of two emission wavelengths, which aided in the analysis of compounds with close retention times (e.g. Ace/Fle, Fla/Py, see Table 2a). The measurements were performed at maximum excitation and emission wavelengths. The UV DAD was convenient for the detection of Acy and PEs. Mobile phase flow rate, gradient elution and column thermostat temperature were optimized to obtain satisfactory analyte separation.

An Arion Plus C18 column, characterized by its high carbon load (18 %) and large surface area (420 m^2/g), was chosen for the determination of APs and APEOs. Three excitation and emission wavelength pairs of 232/310 nm, 275/300 nm and 225/310 nm were tested for FLD detection, the first of which gave the highest signal for all these substances with similar structure. Optimization of the gradient and flow of the mobile phase as well as the temperature of the column thermostat was performed in order to achieve a sufficient resolution of 4-NP and NP ethoxylates and at the same time to shorten the analysis time. The optimized conditions of both methods are presented in section 2.3.

3.2. Sample preparation

Sample preparation was based on previous studies focused on the determination of seven priority PAHs in biota samples (gammarids, mussels) [32,33]. Since the aim of the current study was to analyse a wider range of substances (including PEs, APs and APEOs) in a completely different matrix, it was necessary to develop and optimize a new sample preparation procedure. The amount of analysed sample was determined to be 0.5 g dw sediment, allowing to reach the appropriate limits of the method when employing instrumental analysis using LC with FLD and UV DAD detection. To remove elemental sulphur and enhance sample disintegration during FUSLE, 0.2 g of activated copper powder was further added to the sample [34]. Copper addition also showed a positive effect on the removal of slight turbidity of the extract. In the following experiments, aliquots of the purified river sediment were enriched with the studied analytes at concentrations of: PAHs at 10 ng g^{-1}, PEs at 500 ng g^{-1}, APs and APEOs at 200 ng g^{-1}. The spiked samples were left to rest overnight before analysis.

3.2.1. Extraction solvent

Solvents of different polarity and volatility used in previously reviewed studies were tested to select a suitable extraction solvent. The tested extraction media were DCM, Acet, Acet:Hex (1:1, v/v) and MeCN. In the initial experiment, copper powder, 0.5 g of activated silica and 5 mL of the tested solvent/solvent mixture were added to a spiked aliquot of the sediment, and the resulting slurry was sonicated with an US probe for 1 min. After subsequent centrifugation, the supernatant extract was evaporated, reconstituted in 200 μL of MeCN, and analysed by two LC methods. Fig. 1 shows the dependence of the normalized responses (average peak area normalized to the highest peak area of each compound) for selected analytes on the used extraction media. As can be seen, in general the highest responses were obtained for Acet, showing its suitability for the extraction of all tested compound classes. Acet is a naturally occurring compound with low toxicity whose volatility is advantageous for fast preconcentration of sample extracts. Therefore, Acet was chosen as the extraction solvent.

The second experiment was aimed at optimizing the volume of Acet for optimal performance of the FUSLE procedure. Test volumes of Acet were 3, 5, 7, and 9 mL, and average recoveries of the analytes were determined for triplicate analyses. To calculate the recoveries, the matrix-matched standards prepared by spiking the blank sediment extract with the analytes at the theoretical 100 % recovery concentration were analysed. The obtained results showed that the analytes recoveries generally increased with increasing volume of Acet from 3 to 7 mL, and at 9 mL, the recoveries remained at about the previous level or decreased. The recoveries of the studied analytes when using 7 mL of Acet ranged from 76 % to 109 %. Thus, 7 mL of Acet was chosen as the extraction media for the developed procedure.

3.2.2. Adsorbent for dSPE clean-up

The three most frequently used adsorbents – silica gel, Florisil and alumina oxide – were tested for dSPE clean-up performed simultaneously with the FUSLE. The recovery experiment was carried out with analytes-enriched sediment aliquots under previously optimized extraction conditions with the addition of 0.5 g of the tested adsorbent. The bar chart in Fig. 2 shows the average recoveries for all studied analytes calculated from four replicate analyses. It can be seen that the analytes recoveries for tested adsorbents were generally at a similar level, while the average values were in the order: silica (90 %), Florisil (89 %) and alumina (86 %). The relative standard deviations (RSD) of the analyte recoveries were in the ranges of 8–18 % for silica, 5–23 % for Florisil, and 7–34 % for alumina. Based on the obtained results, silica gel was chosen as the adsorbent for dSPE clean-up.

3.3. Matrix effect

After optimisation of the method, the effect of matrix interferences (matrix effect, *ME*) on the analysis results was evaluated for three sediment samples with different content of TOC. *ME* was calculated by comparing the peak areas of analytes (averages of triplicate analyses with blanks substracted) measured in spiked (concentrations as in 3.2.) blank matrix extracts and pure solvent solutions using the equation:

$$ME(\%) = \left(\frac{\textit{Peak area in matrix standard}}{\textit{Peak area in solvent standard}} - 1\right) \times 100$$

The *ME* can be classified as soft (0–20 %), medium (20–50 %), or strong (>50 %), while positive values represent matrix-induced signal enhancement and negative values represent a suppression effect. The results presented in Table 3 show that signal suppression was observed in the analysis of all target analytes (except for Acy in two matrices). The *ME*s were mostly medium or strong and dependent on the TOC content of the samples. While for the sediment SED-1 (TOC = 35 mg g^{-1}) a strong *ME* was evaluated for 29 % of the analytes, for SED-2 (TOC = 59 mg g^{-1}) it was for 54 % of the analytes and for SED-3 (TOC = 73 mg g^{-1}) it was for 88 % of the analytes. For PAHs, the *ME* values increased with increasing TOC content in the sediment, and for PEs, APs and APEOs they were mostly at about the same level. Therefore, for quantification, we decided to employ a matrix-matched calibration using a blank sediment matrix of the closest possible composition and TOC content to the analysed samples.

3.4. Method performance

The performance of the method was further studied in terms of linearity, method limits, recovery and accuracy (precision and trueness) by analysing spiked purified samples, real and CRM samples.

3.4.1. Linearity

Response linearity was evaluated by constructing calibration curves from the analyses of matrix-matched standards of the test analytes prepared by spiking the blank extract from the purified water reservoir sediment with a TOC of 28 mg g^{-1}. The studied range for PAHs was from 2 to 1000 ng g^{-1}, for PEs from 100 to 5000 ng g^{-1} and for APs and APEOs from 40 to 2000 ng g^{-1} dw. The response linearity was assessed using coefficients of determination (R^2) and RSDs of the relative response factors (RRF). The RRFs of the analytes were calculated relative to IS at each concentration level applying a blank correction. As can be seen in Table 4, the R^2 values for all target analytes and selected concentration ranges were greater than 0.99 and the RSD of RRF was in the range of 4.1–14 %, indicating good linearity.

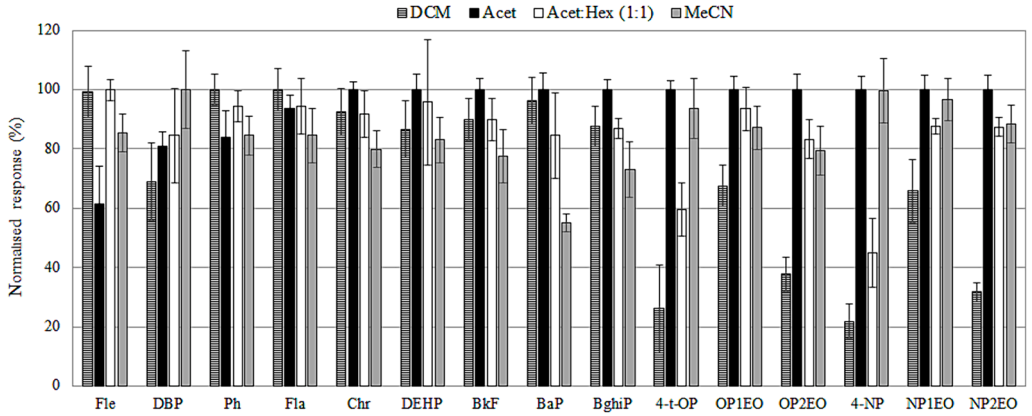

Fig. 1. Extraction efficiency of the tested extraction media expressed by the dependence of the normalized responses of selected studied analytes from sediment on the extraction media used. The *error bars* represent RSD of 3–4 replicate analyses.

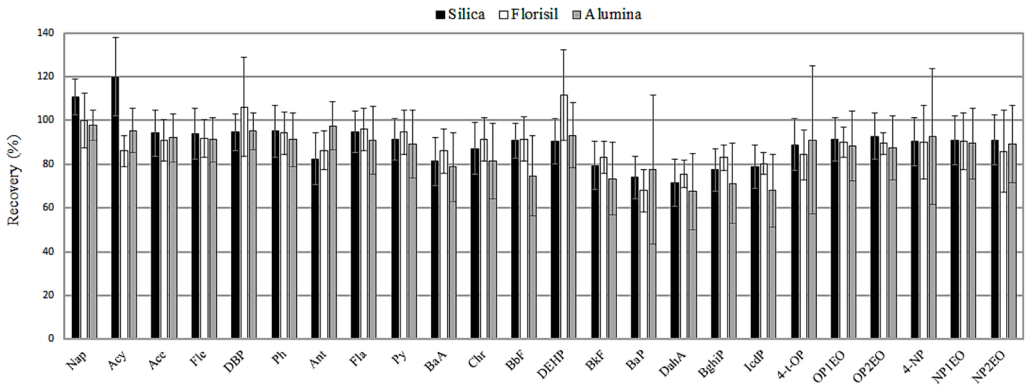

Fig. 2. Recovery of studied analytes from enriched river sediment using different dSPE clean-up adsorbents. The *error bars* represent RSD of 4 replicate analyses. (Abbreviations of analytes are listed in section 2.1.).

Table 3
Matrix effects (*ME*) expressed in % and RSD in % for the target analytes and selected sediments characterized by TOC values.

Analyte	*ME* (RSD) (%)[a]		
	SED-1	SED-2	SED-3
	(TOC = 35 μg g^{-1})	(TOC = 59 μg g^{-1})	(TOC = 73 μg g^{-1})
Nap	–39 (18)	–26 (20)	**–76** (9.6)
Acy	–4.7 (3.3)	12 (12)	15 (13)
Ace	**–62** (6.0)	**–93** (12)	**–102** (11)
Fle	–40 (5.1)	–48 (17)	**–61** (18)
DBP	**–70** (8.4)	**–56** (23)	**–69** (7.7)
Ph	–43 (13)	–44 (10)	**–67** (11)
Ant	–48 (10)	**–55** (13)	**–54** (11)
Fla	–36 (17)	–37 (9.2)	**–72** (13)
Py	–35 (18)	–47 (8.0)	**–93** (14)
BaA	–40 (7.8)	**–61** (16)	**–66** (14)
Chr	–44 (4.6)	–41 (10)	**–91** (17)
BbF	–23 (18)	–21 (9.0)	–40 (12)
DEHP	**–57** (11)	**–72** (12)	**–72** (18)
BkF	–46 (4.7)	–38 (8.6)	**–76** (17)
BaP	–25 (13)	–42 (8.2)	**–83** (17)
DahA	**–55** (7.1)	**–65** (8.2)	**–59** (14)
BghiP	**–52** (5.7)	**–62** (5.9)	**–82** (19)
IcdP	–46 (3.6)	**–51** (8.1)	**–106** (17)
4–t–OP	**–51** (9.0)	**–65** (3.6)	**–57** (8.3)
OP1EO	–50 (8.8)	**–62** (3.7)	**–55** (11)
OP2EO	–42 (8.9)	**–54** (4.0)	**–51** (12)
4–NP	–44 (11)	**–60** (7.2)	**–61** (20)
NP1EO	–4.9 (6.4)	–12 (7.7)	–32 (13)
NP2EO	**–80** (11)	**–77** (9.7)	**–82** (17)

[a] $n = 3$; spiked analyte concentrations: 10 ng g^{-1} for PAHs, 500 ng g^{-1} for PEs, 200 ng g^{-1} for APs and APEOs.
[b] Bold values are for strong *ME*.

3.4.2. Limits of the method

To determine the limits of the method, seven replicate analyses of the spiked water reservoir sediment (PAHs at 2 ng g^{-1}, PEs at 100 ng g^{-1}, APs and APEOs at 50 ng g^{-1} dw) were used. The LODs and LOQs were calculated as three and ten times the standard deviation (SD) of the results, respectively. The limit values presented in Table 4 show that the LOQ for PAHs ranged from 1.1 to 3.1 ng g^{-1}, for PEs from 122 to 124 ng g^{-1}, for APs from 40 to 51 ng g^{-1} and for APEOs from 36 to 53 ng g^{-1}. The values obtained were in all cases below the MPC limits set by the Dutch RIVM. When comparing the LODs with the values from the published methods listed in Table 1, it can be seen that the LOD of the developed method was better in many cases, which is also the case for both multiresidue methods [16,28] designed to analyse all three classes of compounds.

3.4.3. Recovery, analysis of real samples

The recovery of the method was evaluated using the same sediment samples as in the case of the *ME* study. The selected samples were analysed before and after addition of 10 ng g^{-1} (for PAHs), 500 ng g^{-1} (for PEs) and 200 ng g^{-1} (for APs and APEOs) levels of the studied analytes (see Table 5). For quantification, the same matrix-matched calibration curves were used as for the response linearity study. The recoveries achieved, except in three cases (161 %, 131 % and 143 %), were in the acceptable range of 78–120 % with RSDs from 0.44 to 21 % [35]. It can also be seen from Table 5 that the most contaminated sample was SED-3, in which the determined concentrations of 4-NP and nonylphenol ethoxylates exceeded the MPCs set by the Duch RIVM. This sample also had the highest TOC content.

3.4.4. Accuracy, analysis of CRM

The accuracy of the method was evaluated in terms of intra-day precision (PRE_{intra}, repeatability) expressed as RSD from repeated analyses and trueness calculated as percent recovery [36]. The PRE_{intra} values shown in Table 4 from seven replicate analyses of spiked water reservoir sediment samples show good precision of the method with an RSD range of 5.2–15 %. The obtained relative recoveries presented in Table 5 indicate a satisfactory trueness of the method (see *3.4.3.*).

The method's accuracy was also verified by analysing natural matrix CRM with PAH and PE content. Due to the high certified concentrations of the analytes, the samples were diluted tenfold with purified sea sand prior to analysis. Table 6 shows reference and determined values, trueness and *Z* score evaluation for the selected analytes. Although the reported trueness values are higher than 120 % for 6 out of 15 analytes, the *Z* score values are in the satisfactory range from –0.74 to 1.6 for all analytes. Also, the results for all analytes lie in the 95 % prediction interval around the reference value stated in the certificate of analysis. To illustrate the chromatographic performance, the chromatograms from the CRM analysis are shown in Fig. 3.

3.5. Environmental impact of the method

Currently, in order to reduce negative impacts on the environment, the assessment of the greenness and environmental friendliness of analytical methods is increasingly being requested [37]. To show the environmental impact of the developed method two approaches were applied. The first one, aimed at assessing the impact of the entire analytical method proposed by Gałuszka et al. [38] is known as Analytical Eco-Scale Assessment (AESA). This concept is based on the allocation of penalty points (PP) to parameters of the analytical process (related to the use of hazardous chemicals, energy consumption, waste generation, etc.) that do not comply with the principles of green chemistry. The AESA results in a score calculated by subtracting the PPs from a base of 100, representing an ideal green analysis. The assessment

Table 4
Analytical characteristics of the developed method for the variety of analytes and IS used for the quantification purposes.

Analyte	IS[a]	Linear range (ng g^{-1} dw)	R^2	RRF[b]	RRF_RSD (%)	LOD (ng g^{-1} dw)	LOQ (ng g^{-1} dw)	PRE_{intra}[c] RSD (%)
Nap	Ph-d10	2–1000	0.9901	0.12	13	0.47	1.6	7.9
Acy	Ph-d10	2–1000	0.9990	0.58	8.4	0.84	2.8	14
Ace	Ph-d10	2–1000	0.9994	0.22	13	0.71	2.4	12
Fle	Ph-d10	2–1000	0.9993	1.6	13	0.47	1.6	7.8
DBP	Ph-d10	100–5000	0.9995	0.017	13	37	122	12
Ph	Ph-d10	2–1000	0.9958	0.84	12	0.53	1.8	8.9
Ant	Ant-d10	2–1000	0.9972	0.99	6.6	0.55	1.8	9.2
Fla	Fla-d10	2–1000	0.9996	1.1	4.1	0.56	1.9	9.3
Py	Fla-d10	2–1000	0.9998	7.5	8.0	0.34	1.1	5.7
BaA	BaA-d12	2–1000	0.9999	1.1	6.5	0.41	1.4	6.9
Chr	BaA-d12	2–1000	0.9999	1.1	4.4	0.35	1.2	5.9
BbF	BaP-d12	2–1000	0.9998	0.29	14	0.63	2.1	11
DEHP	BaP-d12	100–5000	0.9939	0.0014	12	37	124	12
BkF	BaP-d12	2–1000	0.9952	1.1	14	0.31	1.1	5.2
BaP	BaP-d12	2–1000	0.9968	0.77	7.6	0.42	1.4	6.9
DahA	DahA-d14	2–1000	0.9971	1.2	4.5	0.68	2.3	11
BghiP	DahA-d14	2–1000	0.9971	0.97	13	0.37	1.2	6.1
IcdP	DahA-d14	2–1000	0.9970	1.0	10	0.92	3.1	15
4-t-OP	4-BP-d4	40–2000	0.9988	0.055	8.6	15	51	10
OP1EO	4-BP-d4	40–2000	0.9936	0.063	9.1	14	46	9.2
OP2EO	4-BP-d4	40–2000	0.9981	0.012	12	16	53	11
4-NP	4-BP-d4	40–2000	0.9982	0.040	13	12	40	8.0
NP1EO	4-BP-d4	40–2000	0.9922	0.028	8.2	11	36	7.2
NP2EO	4-BP-d4	40–2000	0.9996	0.011	11	11	36	7.3

[a] Internal standard used for quantification; labeled PAHs were at 10 ng g^{-1} and 4-BP-d4 at 1000 ng g^{-1} dw.
[b] Relative response factor.
[c] Intra-day precision; $n = 7$; spiked analyte concentrations: 2 ng g^{-1} for PAHs, 100 ng g^{-1} for PEs, 50 ng g^{-1} for APs and APEOs.

Table 5
Recoveries of studied analytes from spiked dried sediment samples with different TOC values.

Analyte	SED-1 (TOC = 35 μg g^{-1})				SED-2 (TOC = 59 μg g^{-1})				SED-3 (TOC = 73 μg g^{-1})			
	Determined (RSD) (ng g^{-1}, dw) (%)	Added (ng g^{-1})	Found (RSD) (ng g^{-1}, dw) (%)	Recovery (%)	Determined (RSD) (ng g^{-1}, dw) (%)	Added (ng g^{-1})	Found (RSD) (ng g^{-1}, dw) (%)	Recovery (%)	Determined (RSD) (ng g^{-1}, dw) (%)	Added (ng g^{-1})	Found (RSD) (ng g^{-1}, dw) (%)	Recovery (%)
Nap	41 (2.9)	10	51 (1.7)	103	14 (21)	10	25 (7.0)	110	34 (14)	10	42 (2.0)	78
Acy	39 (1.8)	10	50 (1.3)	108	32 (2.1)	10	41 (2.6)	95	152 (4.6)	10	163 (0.44)	114
Ace	nd	10	16 (5.3)	161	nd	10	11 (13)	110	1.4 (11)	10	12 (6.3)	108
Fle	3.7 (2.7)	10	17 (5.5)	131	2.8 (5.3)	10	13 (9.3)	102	3.8 (21)	10	14 (9.2)	104
DBP	nd	500	538 (3.4)	108	nd	500	418 (4.3)	84	nd	500	450 (4.1)	90
Ph	16 (3.6)	10	26 (3.3)	100	15 (8.9)	10	23 (5.3)	82	20 (14)	10	34 (6.2)	143
Ant	nd	10	11 (1.2)	108	nd	10	7.9 (1.2)	79	nd	10	9.5 (2.2)	95
Fla	21 (11)	10	32 (4.9)	104	40 (3.6)	10	50 (2.3)	100	66 (0.52)	10	78 (1.4)	120
Py	15 (13)	10	25 (4.8)	100	22 (6.2)	10	32 (0.55)	101	44 (4.5)	10	54 (1.9)	103
BaA	9.2 (7.5)	10	19 (5.9)	101	12 (9.5)	10	22 (2.1)	102	29 (8.2)	10	39 (1.6)	100
Chr	14 (5.0)	10	24 (1.7)	96	26 (2.1)	10	36 (0.73)	102	54 (4.6)	10	64 (2.4)	98
BbF	19 (3.4)	10	30 (3.0)	108	61 (0.82)	10	72 (1.1)	109	74 (3.0)	10	86 (1.5)	119
DEHP	nd	500	507 (3.1)	101	nd	500	488 (11)	98	nd	500	527 (5.4)	105
BkF	9.5 (1.8)	10	19 (1.6)	97	21 (1.7)	10	31 (3.4)	96	29 (2.8)	10	40 (1.8)	103
BaP	11 (4.0)	10	21 (3.4)	101	13 (7.3)	10	24 (2.3)	103	28 (3.1)	10	38 (1.0)	101
DahA	1.7 (16)	10	12 (4.7)	104	2.6 (3.6)	10	14 (1.0)	108	6.2 (8.7)	10	17 (3.3)	108
BghiP	10 (4.9)	10	20 (2.6)	96	18 (5.8)	10	28 (1.2)	100	47 (7.9)	10	57 (3.3)	101
IcdP	12 (3.6)	10	21 (3.3)	97	21 (3.1)	10	31 (1.7)	103	52 (7.6)	10	62 (1.7)	101
4-t-OP	99 (3.4)	200	274 (1.8)	87	101 (2.3)	200	329 (2.0)	114	106 (3.3)	200	310 (2.8)	102
OP1EO	82 (2.9)	200	281 (3.8)	99	126 (16)	200	349 (2.8)	111	195 (5.6)	200	386 (3.7)	96
OP2EO	101 (0.58)	200	258 (4.6)	79	106 (7.2)	200	307 (2.6)	101	101 (0.54)	200	320 (12)	109
4–NP	116 (3.8)	200	321 (9.7)	103	135 (11)	200	367 (2.0)	116	160 (14)	200	342 (0.91)	91
NP1EO	119 (4.4)	200	317 (6.7)	99	156 (3.2)	200	393 (4.7)	118	212 (7.4)	200	432 (2.7)	110
NP2EO	147 (2.7)	200	387 (5.0)	120	145 (2.3)	200	378 (16)	117	1217 (8.0)	200	1442 (1.9)	113

Note: Average values and RSDs are from four replicate analyses. nd – not determined.

Table 6
Results from the determination of selected PAHs and PEs in the natural matrix reference material CRM131-100 (BNAs in soil).

Analyte	Certified value[a]	Determined value[a,b]	Trueness (RSD)[b]	*Z* score[c]
	(μg g^{-1})	(μg g^{-1})	(%)	
Nap	3.51 ± 1.04	5.15 ± 1.31	147 (26)	1.6
Ace	2.35 ± 0.700	1.83 ± 0.166	78 (9.1)	–0.74
Fle	6.16 ± 1.97	6.47 ± 0.509	105 (7.9)	0.16
Ph	2.80 ± 0.638	3.85 ± 0.133	137 (3.5)	1.6
Ant	4.35 ± 0.844	4.32 ± 0.180	99 (4.2)	–0.039
Fla	2.17 ± 0.595	2.44 ± 0.0419	112 (1.7)	0.45
Py	2.30 ± 0.658	2.40 ± 0.0982	104 (4.1)	0.15
BaA	6.36 ± 1.64	7.63 ± 0.207	120 (2.7)	0.77
Chr	2.02 ± 0.481	2.22 ± 0.0725	110 (3.3)	0.42
BbF	2.10 ± 0.698	2.93 ± 0.161	139 (5.5)	1.2
BkF	1.39 ± 0.421	1.79 ± 0.0921	129 (5.2)	0.95
BaP	5.16 ± 1.68	6.60 ± 0.232	128 (3.5)	0.86
DahA	3.57 ± 1.28	3.52 ± 0.224	99 (6.4)	–0.037
DBP	7.51 ± 2.28	8.61 ± 1.14	115 (13)	0.48
DEHP	7.11 ± 2.35	9.04 ± 0.347	127 (3.8)	0.82

[a] Mean value ± SD.
[b] $n = 5$.
[c] *Z score* = (*determined value – certified value*) / *SD of certified value*.

of the method according to criteria established by Gałuszka et al. [38] is shown in Table 7. The calculated total AESA score of 65 classifies this method as an "acceptable green analysis". Upon closer examination of the AESA table, it can be seen that the highest number of PPs was attributed to the use of mobile phases in LC determination and not to the sample preparation itself.

The second evaluation approach used was focused on the sample preparation itself, known as AGREEprep – an analytical greenness metric for sample preparation [39]. For environmental impact assessment, AGREEprep uses criteria based on ten principles of green sample preparation (minimization of samples, minimization of chemicals, use of reusable and renewable materials, etc.) [40]. Using open access software (obtained from *mostwiedzy.pl/AGREEprep*), sub-scores on a scale of 0 to 1 are calculated for the ten impact categories, which are then used to calculate the final assessment score. The result of the assessment is obtained in the form of a pictogram with information on overall performance and structure of threats.

The characteristics significantly influencing the result of sample preparation method assessment were as follows. The procedure was carried out *ex situ* (score of 0) using 0.5 g of sample, 0.5 g of silica, 0.2 g of copper powder and 7 mL of Acet (score of 0.05) – a flammable and harmful/irritant solvent marked with two pictograms. For criterion 3

Table 7
Analytical Eco-Scale assessment of the developed method according to Gałuszka et al. [38].

	Penalty points
Reagents	
Acet (7 mL)	4
MeCN (mobile phase, 20 mL)	8
MeOH (mobile phase, 25 mL)	12
Activated silica (0.5 g)	0
Cu powder (0.2 g))	1
Instruments	
Ultrasonic probe (≤0.1 kWh per sample)	0
Centrifuge	0
Oven (silica activation) (≤1.5 kWh per sample)	1
LC	1
Occupational hazard (emission of vapours to the air)	3
Waste (>10 mL)	5
Total penalty points	Σ 35
Total AESA score	65

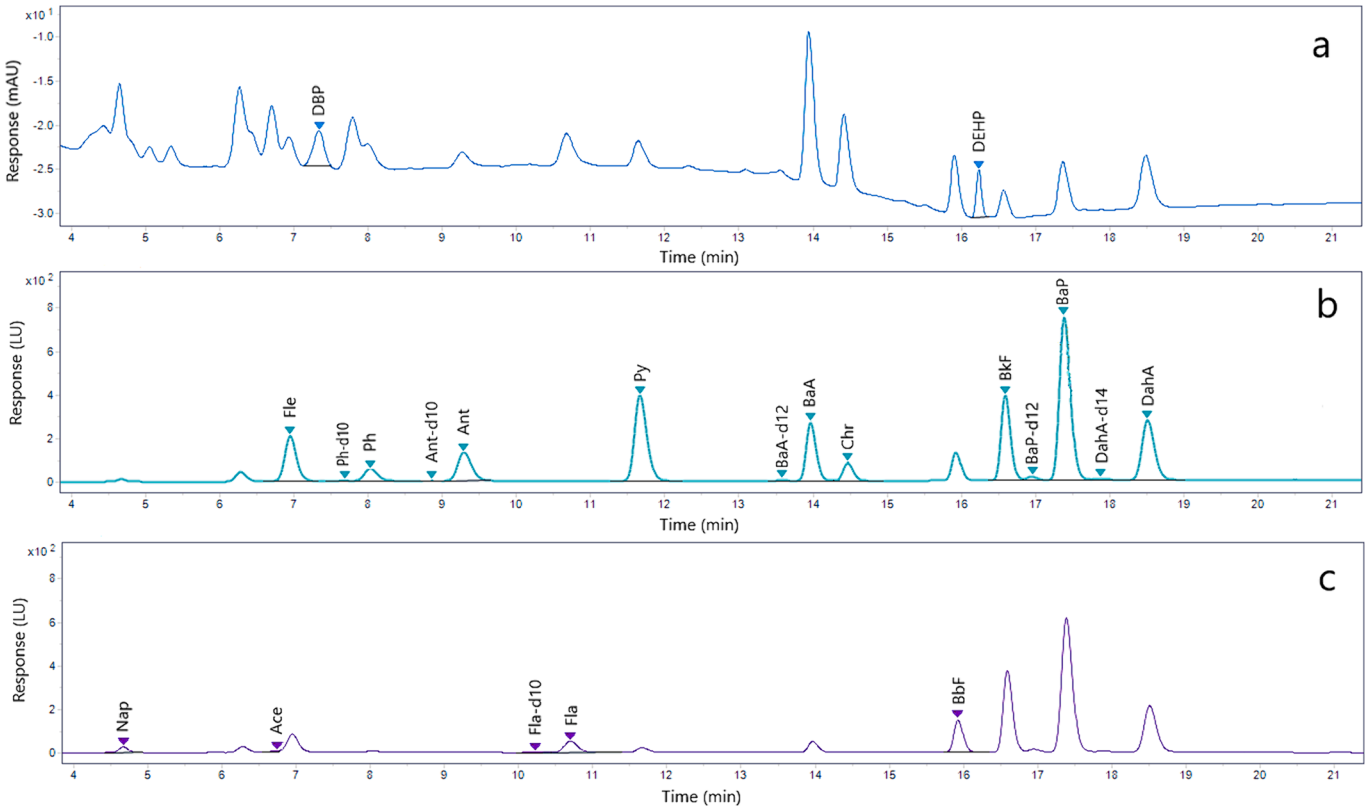

Fig. 3. Chromatograms of the separation of PEs and PAHs extracted from natural matrix CRM131-100 using LC combined with ultraviolet (a) and fluorescence (b, c) detection. Chromatograms from PAH detection were recorded at excitation and emission wavelength pairs programmed according to Table 2. (Abbreviations of analytes are listed in section 2.1.).

focusing on sustainable, reusable and renewable materials, a score of 0.75 was chosen due to the use of Acet, which can be produced from renewable sources. Criterion 4 (waste minimization) scored 0.6 and criterion 5 (sample minimization) scored 0.77 when calculated for a sample mass of 0.5 g. Maximize sample throughput criterion (6) received a score of 0.38 for an estimated sample throughput of 5 samples per h. Criterion 7 regarding integration steps and automation support split into two parts received a score of 0.75 for the 3 sample preparation steps performed and a score of 0.25 for the manual systems used. Criterion 8 on minimization of energy consumption was scored 1 due to the use of FUSLE for 1 min, which meant an energy consumption of < 10 Wh per sample. The greenest possible post-sample preparation configuration for analysis (criterion 9) was scored 0.25 for liquid chromatography use. Finally, a score of 1 was selected for criterion 10, regarding operator safety, because the operator is not exposed to chemicals when using appropriate dispensers. The total score of the sample preparation method calculated by the used computational program is 0.54 and the obtained pictogram is shown in Fig. 4.

In the pictogram in Fig. 4, the ten parts around the circle represent the performance criteria, with the length of each part reflecting the weight assigned to the respective criterion and the colour visualizing its performance. Regarding the performance of the assessed criteria, the worst result was obtained for criterion 2, which refers to the use of hazardous solvents and reagents, in our case the use of Acet. Although Acet is a non-chlorinated solvent with low toxicity, it is classified as hazardous and using 7 mL in sample preparation has the strongest effect on reducing the greenness score of the method.

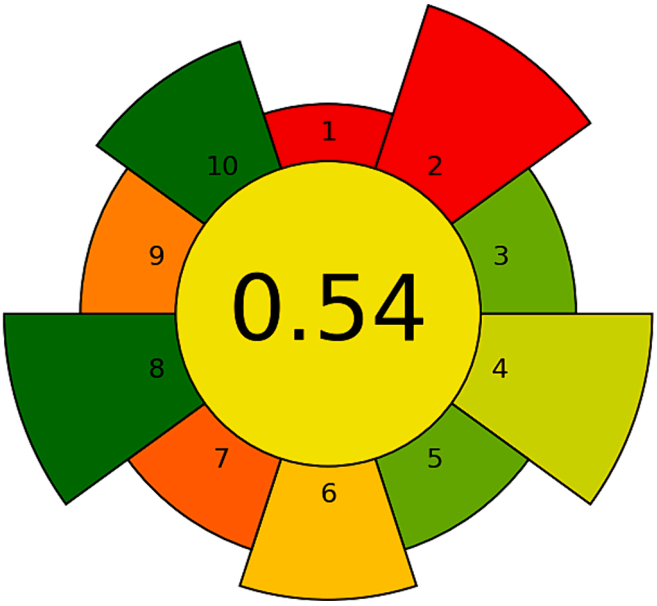

Fig. 4. Result of AGREEprep assessment of the developed method for the determination of studied analytes in sediment. 1 – sample preparation placement, 2 – hazardous solvents and reagents, 3 – sustainability, renewability, and reusability of materials, 4 – waste, 5 – sample size, 6 – sample throughput, 7 – integration and automation, 8 – energy consumption, 9 – post-sample preparation configuration for analysis, 10 – operator's safety.

4. Conclusion

A simple, non-laborious and environmentally friendly method was developed for the determination of selected PAHs, PEs, APs and APEOs in sediment. The method uses sample preparation combining FUSLE and *in situ* clean-up, which greatly simplifies the workflow compared to methods using crude extract purification in a separate step. Due to the complexity of the sediment matrix, the analysis requires employing a matrix-matched calibration using a sediment matrix as close as possible in composition and TOC content to the analysed samples. For determination of selected analytes from three compound classes, two LC methods coupled with FLD and UV DAD were used. The developed methodology and employed instrumentation allowed to achieve recoveries of target analytes $\geq$ 78 % and LOQs for PAHs ranging from 1.1 to 3.1 ng g^{-1}, for PEs from 122 to 124 ng g^{-1}, for APs from 40 to 51 ng g^{-1} and for APEOs from 36 to 53 ng g^{-1}. These figures of merit meet the requirements for MPC limits set by the Dutch RIVM. In the environmental impact assessment by the AESA, the method was classified as "acceptable green analysis" and scored 0.54 in the AGREEprep's greenness assessment for sample preparation. The applicability of the method was demonstrated by the analysis of real sediment samples and natural matrix CRM.

CRediT authorship contribution statement

Marcel Brenkus: Writing – original draft, Visualization, Validation, Investigation, Data curation. **Peter Tölgyessy:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Data curation, Conceptualization. **Veronika Koperová Návojová:** Visualization, Formal analysis, Data curation. **Michal Kirchner:** Writing – review & editing, Resources, Methodology. **Svetlana Hrouzková:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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