Bull Environ Contam Toxicol (2016) 96:678–684
DOI 10.1007/s00128-016-1770-2

Validation of an Adapted QuEChERS Method for the Simultaneous Analysis of Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls and Organochlorine Pesticides in Sediment by Gas Chromatography–Mass Spectrometry

Fida Ben Salem[1,2,3] · **Olfa Ben Said**[1,2] · **Robert Duran**[2] · **Mathilde Monperrus**[3,4]

Received: 17 July 2015 / Accepted: 4 March 2016

Abstract A Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method has been adapted and validated for the simultaneous analysis of 16 PAHs, 12 PCBs and 9 OCPs in sediment. The sample preparation was adapted by modifying the nature of the extraction solvent, the extraction technique and the amount of sediment. The analytical performances were evaluated in terms of accuracy, linearity and quantification limits. The method was validated by the analysis of a reference marine sediment material (SRM 1941b). The obtained concentrations are in good agreement with the certified values with recoveries ranging 60 %–103 % for most of PAHs. Acceptable recoveries are obtained for PCBs, ranging 76 %–131 %, and for OCPs ranging 81 %–137 %. The method was applied to the analysis of sediments from the hydro-system Bizerte Lagoon/Ichkeul Lake (Tunisia). The Bizerte lagoon is mainly contaminated by PAHs whereas the Ichkeul lake is mainly by OCPs.

Keywords Extraction · Purification · Certified reference material SRM 1941b · Coastal sediment · Bizerte Lagoon · Ichkeul Lake

Sediments are a known repository for many persistent organic contaminants such as poly-aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). The determination of organic contaminants in sediment samples is very complex including an extraction and a purification steps before analysis. Proper sample preparation procedures are required to achieve optimum analytical results and to provide rapid, robust and sensitive analytical procedures. The main critical step in the analytical procedure for sediment analysis is the extraction which needs suitable solvent and extraction technique to obtain acceptable recoveries for the compounds of interest. Many extraction techniques used for the analysis of organic compounds have been developed. Traditionally, the standard technique was the Soxhlet extraction with non-polar solvents (de Boer and Law 2003). Soxhlet extraction present several drawbacks such as long extraction time and large volume of solvent, so alternative extraction techniques were developed like microwave-assisted extraction (Bartolomé et al. 2005; Moreno et al. 2006; Carvalho et al. 2008; Cueva-Mestanza et al. 2008; Itoh et al. 2008) and ultrasonic-assisted extraction (Vagi et al. 2007; Errekatxo et al. 2008). Moreover, the extraction step is generally followed by a clean-up step to remove any interfering substances, which involves a time consuming step commonly performed by solid phase extraction (SPE). All these methods have been used extensively for the analysis of several environmental matrices such as soils, sediments, biological tissues but they are not always easy to use and suitable for routine applications. Recently, novel approaches, combining the extraction and the purification steps, were developed called

Electronic supplementary material The online version of this article (doi:10.1007/s00128-016-1770-2) contains supplementary material, which is available to authorized users.

✉ Mathilde Monperrus
mathilde.monperrus@univ-pau.fr

[1] Laboratoire de Biosurveillance de l'Environnement, Faculté des Sciences de Bizerte, Université de Carthage, 7021 Zarzouna, Bizerte, Tunisia

[2] Equipe Environnement et Microbiologie – IPREM UMR 5254 CNRS, Université de Pau et des Pays de l'Adour, Pau, France

[3] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, IPREM UMR 5254 CNRS, Université de Pau et des Pays de l'Adour, Pau, France

[4] UFR Sciences et Techniques de la Côte Basque Allée du Parc Montaury, 64600 Anglet, France

selective pressurized liquid extraction (Subedi et al. 2015) and QuEChERS methods (Anastassiades et al. 2003; Pinto et al. 2011). QuEChERS methods involve an extraction step with acetonitrile partitioned from the aqueous matrix using anhydrous $MgSO_4$ and NaCl followed by a dispersive-SPE cleanup step with $MgSO_4$ and primary secondary amine (PSA). The sample handling requirements of such methods are friendlier and the time required to accomplish an extraction/clean up is significantly shorter. It provides effective recoveries with simple analytical steps, low solvent consumption and could be applied to any kind of solid matrices (mineral or organic) and appropriate to very volatile compounds (Rouvière et al. 2012). Mainly applied for pesticides in food matrices (Lehotay et al. 2010; Cieslik et al. 2011; Lee et al. 2011; Wilkowska and Biziuk 2011; Wang et al. 2012), the application of QuEChERS methods to other organic pollutants is still limited. A QuEChERS method was successfully applied for determining PAHs (Ramalhosa et al. 2009) and PCBs (Norli et al. 2011) in fish, pharmaceuticals and hormones in sewage sludge (Peysson and Vulliet 2013) and soil (Bragança et al. 2012). A QuEChERS method was also validated for trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) and BTEX (benzene, toluene, ethylbenzene and xylenes) in soil samples (Anastassiades et al. 2003). Recently, a QuEChERS method was applied to the determination of 136 pharmaceutical compounds and hormones in sewage sludge (Peysson and Vulliet 2013).

The objective of the present study was the adaptation and the validation of a QuEChERS method for the simultaneous analysis of PAHs, PCBs and OCPs in sediment samples by GC–MS, in order to provide a routine method for the evaluation of the environmental quality of aquatic ecosystems. Two different techniques for the agitation during extraction were tested, different solvents or solvent mixtures were tested and the influence of the initial weight was investigated.

Materials and Methods

PCB standard solutions, either as compound mix solution, containing PCB 18, 28, 31, 44, 52, 101, 138, 118, 153, 149, 180, 194 and single compound solution of PCB 209 used as surrogate spiking standard were purchased from Sigma Aldrich (Saint Quentin Fallavier, France). The 16 priority PAHs classified as priority pollutants by the United States Environmental Protection Agency (USEPA) due to their toxic, mutagenic and carcinogenic characteristics (Kayal and Connell 1995) (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene), as well as 2 deuterated surrogate spiking standards phenanthrene-d10 and perylene-d12 were supplied as pure reference materials (purity: 99.5 %) also from Sigma Aldrich. OCPs standard solutions of HCB, o,p′-DDE, p,p′-DDE, p,p′-DDD, p,p′-DDT, α and β chlordane, *cis* and *trans* nonachlor and an surrogate spiking standard atrazine-d5 were purchased from Sigma Aldrich. All standard stock solutions were prepared in acetonitrile and stored at −20°C.

Organic solvents (hexane, acetone, acetonitrile and dichloromethane) were of analytical grade and were supplied by Sigma Aldrich. The QuEChERS extraction tubes were obtained from Agilent Technologies (Massy, France) and contained the citrate buffer salt mixture (4 g of $MgSO_4$, 1 g of NaCl, 0.5 g disodium citrate sesquihydrate and 1 g of trisodium citrate dehydrate). Dispersive SPE tubes (containing 900 mg of $MgSO_4$ and 150 mg of primary secondary amine (PSA) exchange were obtained from Agilent Technologies (Massy, France).

SRM 1941b was obtained from the National Institute of Standards & Technology (Gaithersburg, MD, USA). Real sediment samples used for the application were collected from the lagoon of Bizerte and the Ichkeul Lake (Tunisia). The surface sediments were sampled using a Van Veen grab sampler, placed in glass bottles and kept frozen at −20°C. Samples were then freeze dried in a ZirBus Vaco2 lyophiliser, homogenized using an agathe mortar and stored at 4°C before analysis.

The QuEChERS method previously validated by Yang et al. (2010) for the analysis of pesticides in soil was adapted and validated for the simultaneous analysis of PAHs, PCBs and OCPs. An aliquot of 5 g of sediment was weighed into a polypropylene tube (50 mL capacity). Then, 4 mL of ultrapure water was added, the tube was manually shaken and surrogate spiking standards (phenanthrene d10, perylene d12, PCB 209, Atrazine d5) were introduced at a concentration of 50 ppb each. Twenty (20) mL of extraction solvent (hexane/acetone, dichloromethane/acetone) were then added and the tube was shaken vigorously by hand for 1 min. Afterwards, the citrate buffer salt mixture was added and the tube was shaken vigorously either manually (5 min) or by ultrasonic agitation (15 min). Finally, the tube was centrifuged for 3 min at 2500 rpm and 10 mL of the supernatant were transferred into another polypropylene tube (15 mL capacity) already containing 900 mg of $MgSO_4$ and 150 mg PSA. The tube was shaken vigorously by hand for 30 s and centrifuged for 3 min at 2500 rpm. The extracts were then dried under a gentle argon stream using a Turbovap LV Evaporator system (Zymark, Hopkinton, MA, USA). The dried residue was re-dissolved with 1 mL acetonitrile and kept at −20°C until analysis. The basic QuEChERS extraction conditions using acetonitrile was compared with modified procedures using two mixtures of solvents: hexane/acetone (HA) (50:50 v:v) and dichloromethane/acetone (DA) (50:50 v:v) for the determination of the most efficient extraction solvent. Extraction techniques were adapted with comparison of manual or ultrasonic agitation and two amount of sediment used for extraction were tested (Table 1). Three replicates were considered for each experiment with two injections and procedural blanks were performed each day of analysis. An internal standard correction was used for the quantification of the analytes.

The analyses were performed by using a gas chromatograph (Agilent 7890A) coupled to a mass spectrometer with an electron impact ionization source (EI) Agilent 5975C. The GC–MS system was equipped with an Agilent DB5-MS UI column. The carrier gas was helium of high purity (99.9995 % from Air Liquide), it was used as carrier gas at 1 mL min^{-1} flow rate. The ion source temperature and the quadrupole temperature were kept at 230 and 150°C, respectively. A sample volume of 1 µL of the concentrated extract was injected in pulsed splitless mode at an inlet temperature of 280°C. The column temperature was programmed as follows: the initial oven temperature was set at 80°C for 1 min, increased to 160°C at 10°C/min (hold 5 min), then ramped at 3°C/min to 300° (hold 2 min). The MS interface temperature was maintained at 300°C. Quantification was carried out in the selected ion monitoring mode (SIM) selecting two characteristics fragments ions for each compounds For qualitative analysis during the method development, the full scan mode was used by monitoring the mass range from 39 to 498. Retention time and target monitoring m/z of the different compounds analyzed by GCMS are summarized in Table 1 Supplementary material.

Results and Discussion

The results obtained with the different tested extraction methods for the certified SRM 1941b are presented in Fig. 1. For all results recoveries were the criterion for the testing of the method efficiency. The results show that acetonitrile was the best solvent for PAHs extraction and the mixture DA was better than the HA mixture (Fig. 1a, Table 2). The best extraction efficiencies for most of PCBs were obtained with the DA and HA solvent mixtures (Fig. 1b, Table 2) whereas lower recoveries were obtained using acetonitrile. Thus, the DA mixture was found to be the best solvent for the simultaneous extraction of PAHs and PCBs. Pesticides were not analyzed during these experiments but previous studies showed that dichloromethane was the best solvent for the simultaneous extraction of PAHs, PCBs and pesticides (Thompson et al. 2002) as well as for OCPs in soil (Norli et al. 2011). The mixture DA was thus chosen for the simultaneous extraction of PAHs, PCBs and OCPs.

The comparison of the techniques used for extraction showed that the ultrasonic agitation improved extraction efficiencies compared to manual agitation for PAHs and PCBs (Fig. 1a, b, Table 2). These results are consistent with previous works that showed highest recoveries when sediment samples were extracted by ultrasonication (Pinto et al. 2011). It was also shown that the time of ultrasonication had no effect on the extraction efficiency (Anastassiades et al. 2003), thus 15 min of ultrasonication was applied in this study.

Regarding the mass of sample used for the analysis, when increasing the amount of sediment from 2 to 5 g for the extraction (experiments 4 and 5) no significant difference was observed for both PAHs and PCBs (Fig. 1a, b, Table 2). Therefore, a mass of 5 g of sediment was used to avoid problems with the limits of detection when working with real samples.

Analytical performances of the adapted method were evaluated in terms of linearity (R^2), detection and quantification limits (LOD, LOQ), recovery (R %) and repeatability (RSD %). Results are presented in Table 2 of the supplementary material. The linearity was evaluated using standard solutions in the range of 0–1000 ng g^{-1}. Good correlation coefficients ($R^2 > 0.95$) were obtained for all compounds, demonstrating that the method is linear over the range assayed. The limits of detection (LOD) and quantification (LOQ) were determined by considering 3 and 10 times respectively the standard deviation determined by analyzing 10 blank samples. The LOQ values range between 0.02 and 9.64 ng g^{-1}, 0.02 and 1.15 ng g^{-1}

Table 1 Overview of the different tested conditions performed for the adaptation of the QuEChERS procedure (solvent mixtures, extraction technique, amount of sediment), Exp = Experiment

Experiment name	Extraction solvent (V/V)	Volume of extraction solvent (mL)	Extraction technique	Amount of sediment (g)
Exp1	Acetonitrile	20	Manual agitation	2
Exp2	1:1 hexane:acetone	20	Manual agitation	2
Exp3	1:1 dichloromethane:acetone	20	Manual agitation	2
Exp4	1:1 dichloromethane:acetone	20	Ultrasonic agitation	2
Exp5	1:1 dichloromethane:acetone	20	Ultrasonic agitation	5

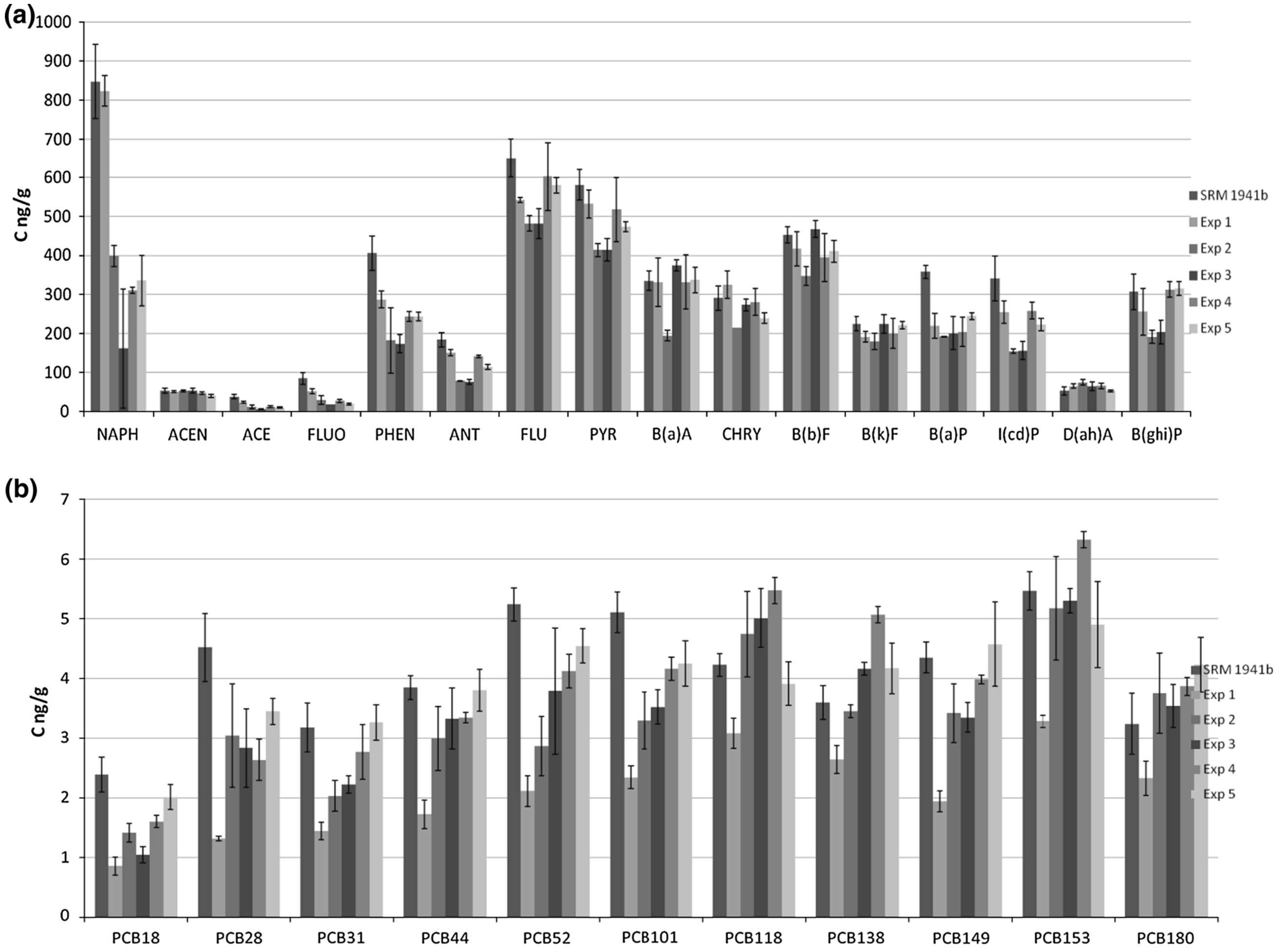

Fig. 1 Comparison of concentrations obtained with the different tested experiments for the SRM 1941b for PAHs (**a**) and PCBs (**b**) *NAPH* Naphthalene, *ACEN* Acenaphthylene, *ACE* Acenaphthene, *FLUO* Fluorene, *PHEN* Phenanthrene, *ANT* Anthracene, *FLU* Fluoranthene, *PYR* Pyrene, *B(a)A* Benzo[a]anthracene, *CHRY* Chrysene, *B(b)F* Benzo[b]fluoranthene, *B(k)F* Benzo[k]fluoranthene, *B(a)P* Benzo[a]pyrene, *I(cd)P* Indeno[1,2,3-cd]pyrene, *D(ah)A* Dibenzo[a,h]anthracene, *B(ghi)P* Benzo[ghi]perylene

and 0.01 and 1.27 ng g^{-1} for PAHs, PCBs and OCPs, respectively. These low LOQs allow application of the QuEChERS method followed by GC–MS to monitor simultaneously these compounds in environmental studies.

The accuracy of the adapted method was evaluated by determining the recoveries obtained for the SRM 1941b. The obtained data with the adapted method showed acceptable recoveries for the heaviest PAHs ranging from 60 % to 103 % for respectively Phenanthrene and Benzo[ghi]perylene with values of relative standard deviation lower than 10 %. For the lighter PAHs, the recoveries ranged from 23 % to 75 % for respectively Fluorene and Acenaphthylene with higher RSD % (9 %–19 %). As expected, the values for PAHs were higher according to the molecular weight. Lower recoveries and lower repeatability for lighter molecular weight can be attributed to loss, mainly by evaporation during the sample preparation. For PCBs recoveries ranging from 76 % to 131 % for respectively PCB28 and PCB180 and from 81 % to 137 % for respectively Hexachlorobenzene and β chlordane for pesticides with RSD % lower than 15 % for both compounds families were obtained.

Our results are almost in the same range of recoveries than those obtained in previous studies for heavy PAHs (Concha-Grana et al. 2010; Thompson et al. 2002), but better and more reproducible than those obtained for PCBs (53 %–149 %) and pesticides (71 %–420 %) using a microwave extraction and dichloromethane as solvent extraction with the same SRM 1941b (Wang et al. 2012). Moreover, it is more efficient than the method used by Brondi et al. (2011) for pesticides (48 %–115 %) using a QuEChERS method with MeCN as extraction solvent and without ultrasonic agitation. The results provided show that there are certain limits concerning lower molecular weight PAHs.

Table 2 Concentrations of the target PAHs, PCBs and OCPs in the certified SRM 1941b obtained with the different experiments (see Table 1) and comparison with the certified values SRM 1941b [concentration ng g^{-1} ± SD standard deviation (n = 3)], – not determined

Compounds	SRM 1941b	Exp1	Exp2	Exp3	Exp4	Exp5
PAHs						
Naphthalene	848 ± 95	824.0 ± 38.9	398.5 ± 26.5	161.5 ± 152.0	310.8 ± 7.7	335.6 ± 64.5
Acenaphthylene	53.3 ± 6.4	50.9 ± 2.7	52.9 ± 2.9	53.7 ± 5.6	47.8 ± 3.4	40.1 ± 3.5
Acenaphthene	38.4 ± 5.2	24.0 ± 2.4	12.0 ± 4.3	5.8 ± 0.9	12.7 ± 2.8	11.2 ± 1.7
Fluorene	85 ± 15	52.1 ± 6.6	29.4 ± 11.3	18.4 ± 0.2	27.5 ± 3.4	19.5 ± 2.4
Phenanthrene	406 ± 44	287.1 ± 21.8	182.5 ± 84.1	174.0 ± 23.3	243.6 ± 13.1	243.7 ± 11.8
Anthracene	184 ± 18	151.3 ± 8.4	78.6 ± 1.3	75.9 ± 7.1	141.9 ± 3.3	114.2 ± 6.2
Fluoranthene	651 ± 50	541.8 ± 6.6	482.0 ± 20.3	482.0 ± 38.1	602.5 ± 88.0	580.0 ± 20.1
Pyrene	581 ± 39	532.4 ± 36.1	414.1 ± 17.2	414.4 ± 28.7	517.8 ± 81.7	473.3 ± 13.1
Benzo[a]anthracene	335 ± 25	332.1 ± 62.3	194.3 ± 13.7	374.7 ± 14.1	332.3 ± 68.7	337.2 ± 32.3
Chrysene	291 ± 31	325.2 ± 35.1	215.4 ± 0.2	273.5 ± 14.9	280.8 ± 34.1	239.3 ± 13.5
Benzo[b]fluoranthene	453 ± 21	417.0 ± 43.9	347.5 ± 24.2	467.6 ± 21.9	394.6 ± 61.2	410.6 ± 28.1
Benzo[k]fluoranthene	225 ± 18	191.4 ± 14.0	179.3 ± 20.6	224.2 ± 24.3	201.1 ± 38.2	221.6 ± 9.8
Benzo[a]pyrene	358 ± 17	219.9 ± 31.7	191.8 ± 0.6	201.2 ± 42.3	204.5 ± 38.0	244.6 ± 9.3
Indeno[1,2,3-cd]pyrene	341 ± 57	255.6 ± 28.7	154.9 ± 5.4	156.5 ± 22.8	258.4 ± 21.7	222.7 ± 15.5
Dibenzo[a,h]anthracene	53 ± 10	65.6 ± 5.4	75.1 ± 6.5	65.2 ± 10.8	66.3 ± 7.2	53.5 ± 2.5
Benzo[ghi]perylene	307 ± 45	256.0 ± 60.0	191.6 ± 17.0	203.1 ± 30.4	312.8 ± 20.2	315.6 ± 17.2
PCBs						
PCB 18	2.39 ± 0.29	0.86 ± 0.15	1.42 ± 0.16	1.04 ± 0.14	1.61 ± 0.10	2.01 ± 0.21
PCB 28	4.52 ± 0.57	1.32 ± 0.04	3.04 ± 0.86	2.83 ± 0.66	2.64 ± 0.35	3.45 ± 0.22
PCB 31	3.18 ± 0.41	1.44 ± 0.15	2.03 ± 0.26	2.22 ± 0.15	2.77 ± 0.46	3.27 ± 0.30
PCB 44	3.85 ± 0.2	1.73 ± 0.24	2.99 ± 0.54	3.33 ± 0.51	3.34 ± 0.09	3.80 ± 0.35
PCB 52	5.25 ± 0.28	2.11 ± 0.25	2.87 ± 0.49	3.79 ± 1.06	4.12 ± 0.28	4.54 ± 0.29
PCB 101	5.11 ± 0.34	2.34 ± 0.19	3.29 ± 0.48	3.52 ± 0.29	4.16 ± 0.20	4.25 ± 0.38
PCB 118	4.23 ± 0.19	3.08 ± 0.25	4.74 ± 0.72	5.01 ± 0.49	5.47 ± 0.22	3.91 ± 0.36
PCB 138	3.6 ± 0.28	2.64 ± 0.23	3.45 ± 0.10	4.16 ± 0.11	5.07 ± 0.14	4.17 ± 0.42
PCB 149	4.35 ± 0.26	1.94 ± 0.18	3.42 ± 0.49	3.35 ± 0.25	3.98 ± 0.07	4.57 ± 0.70
PCB 153	5.47 ± 0.32	3.28 ± 0.10	5.17 ± 0.87	5.3 ± 0.2	6.32 ± 0.14	4.90 ± 0.72
PCB 180	3.24 ± 0.51	2.33 ± 0.29	3.75 ± 0.66	3.54 ± 0.36	3.87 ± 0.15	4.23 ± 0.46
Pesticides						
Hexachlorobenzene	5.83 ± 0.38	–	–	–	–	4.72 ± 0.31
o,p′-DDE	0.38 ± 0.12	–	–	–	–	0.70 ± 0.13
p,p′-DDE	3.22 ± 0.28	–	–	–	–	3.18 ± 0.37
p,p′-DDD	4.66 ± 0.46	–	–	–	–	3.94 ± 0.43
p,p′-DDT	1.12 ± 0.42	–	–	–	–	1.44 ± 0.04
α chlordane	0.85 ± 0.11	–	–	–	–	0.73 ± 0.07
β chlordane	0.5 ± 0.09	–	–	–	–	0.69 ± 0.08
cis-Nonachlor	0.38 ± 0.05	–	–	–	–	0.41 ± 0.04
trans-Nonachlor	0.44 ± 0.07	–	–	–	–	0.45 ± 0.05

SRM 1941b is a reference material with certified value of contaminants

The adapted method was applied to the analysis of real sediments samples from the hydro-system complex of the Bizerte Lagoon/Ichkeul Lake (Tunisia) constituting 2 different ecosystems. The recoveries of spiked surrogate spiking standards The results (Table 3) showed that Bizerte Lagoon sediments contained high PAHs levels with concentrations ranging from 121 to 3169 ng g^{-1} for respectively Acenaphthylene -Indeno[1,2,3-cd]pyrene whereas the Ichkeul Lake sediments exhibited a low PAHs concentration levels (from 3 to 202 ng g^{-1} for respectively

Table 3 Concentrations of PAHs, PCBs and OCPs in sediment samples collected from Bizerta Lagoon and Ichkeul Lake [concentrations ng g^{-1} ± SD (n = 3)]

Compounds	Bizerta lagoon	Ichkeul lake
PAHs		
Naphthalene	3169 ± 437	103 ± 8
Acenaphthylene	121 ± 30	2.41 ± 1.89
Acenaphthene	399 ± 131	5 ± 1
Fluorene	298 ± 5	5.1 ± 0.2
Phenanthrene	1882 ± 566	29.1 ± 7.4
Anthracene	323 ± 87	5.03 ± 0.56
Fluoranthene	1658 ± 262	13 ± 5
Pyrene	1790 ± 244	21 ± 6
Benz[a]anthracene	951 ± 662	6.1 ± 0.1
Chrysene	791 ± 478	7.3 ± 0.6
Benzo[b]fluoranthene	1827 ± 340	11.4 ± 3.5
Benzo[k]fluoranthene	674 ± 11	3.4 ± 0.1
Benzo[a]pyrene	1215 ± 189	8.6 ± 0.3
Indeno[1,2,3-cd]pyrene	2605 ± 836	202 ± 24
Dibenz[a,h]anthracene	607 ± 41	7 ± 5
Benzo[ghi]perylene	1290 ± 105	15 ± 11
PCBs		
PCB 18	0.244 ± 0.137	0.247 ± 0.139
PCB 28	0.195 ± 0.004	0.251 ± 0.001
PCB 31	0.215 ± 0.025	0.372 ± 0.018
PCB 44	0.175 ± 0.050	0.422 ± 0.055
PCB 52	0.948 ± 0.063	1.093 ± 0.021
PCB 101	0.206 ± 0.023	0.296 ± 0.014
PCB 138	0.223 ± 0.024	0.268 ± 0.032
PCB 118	<LOQ	<LOQ
PCB 153	0.387 ± 0.027	0.223 ± 0.058
PCB 149	0.234 ± 0.020	0.152 ± 0.026
PCB 180	0.314 ± 0.031	0.374 ± 0.079
PCB 194	1.396 ± 0.097	1.880 ± 0.115
Pesticides		
Hexachlorobenzene	<LOQ	0.10 ± 0.03
o,p′-DDE	<LOQ	<LOQ
p,p′-DDE	0.8 ± 0.2	1.5 ± 0.2
p,p′-DDD	0.56 ± 0.02	1.5 ± 0.7
p,p′-DDT	<LOQ	<LOQ
α chlordane	<LOQ	0.5 ± 0.2
β chlordane	<LOQ	0.4 ± 0.1
cis Nonachlor	<LOQ	0.4 ± 0.2
trans Nonachlor	<LOQ	0.3 ± 0.1

Acenaphthylene and Indeno[1,2,3-cd]pyrene). Concentrations of PAHs from Bizerte Lagoon were similar to those observed previously in sediment from the same ecosystem (Ben Said et al. 2010; Mzoughi et al. 2005). The sediments from Ichkeul Lake exhibited higher concentrations of pesticides than those from the Bizerte Lagoon. For both ecosystems no contamination by PCBs was observed with concentrations ranging from 0.15 to 1.88 ng g^{-1} for respectively PCB 149 and PCB 194. These results confirmed our assumption on the sources of contamination since the area of Bizerte Lagoon is subject to contamination by two industrial zones while the Ichkeul Lake is surrounded by a vast agricultural area. Further analysis of sediments using this rapid and efficient validated method would help to determine precisely the dispersion and the reactivity of these contaminants in the Bizerte area.

The simultaneous extraction of PAHs, PCBs and OCPs in sediment was successfully validated using a QuEChERS method combining a DA extraction with ultrasonic agitation. This method was found to be accurate and reproducible for the analytes of interest and sufficiently sensitive for the analysis of real sediment samples in the ng g^{-1} range. The simplicity, the rapidity and the low cost of the QuEChERS extraction are advantages for using this method in environmental studies as demonstrated by the analysis of PAHs, PCBs and OCPs contents in sediments in two distinct ecosystems.

References

Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. JAOAC Int 86:412–431

Bartolomé L, Cortazar E, Raposo JC, Usobiaga A, Zuloaga O, Etxebarria N, Fernandez LA (2005) Simultaneous microwave-assisted extraction of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalate esters and nonylphenols in sediments. J Chromatogr A 1068:229–236

Ben Said O, Goñi-Urriza M, El Bour M, Aissa P, Duran R (2010) Characterization of aerobic polycyclic aromatic hydrocarbon-degrading bacteria from Bizerte lagoon sediments, Tunisia. Microbiol Ecol 59:445–456

Bragança I, Plácido A, Paíga P, Domingues VF, Delerue Matos C (2012) QuEChERS: a new sample preparation approach for the determination of ibuprofen and its metabolites in soils. Sci Total Environ 433:281–289

Brondi SHG, de Macedo AN, Vicente GHL, Nogueira ARA (2011) Evaluation of the QuEChERS method and gas chromatography–mass spectrometry for the analysis pesticide residues in water and sediment. Bull Environ Contam Toxicol 86:18–22

Carvalho PN, Rodrigues PNR, Alves F, Evangelista R, Basto MCP, Vasconcelos MTSD (2008) An expeditious method for the determination of organochlorine pesticides residues in estuarine sediments using microwave assisted pre-extraction and automated headspace solid-phase microextraction coupled to gas chromatography–mass spectrometry. Talanta 76:1124–1129

Cieslik E, Sadowska-Rociek A, Molina Ruiz JM, Surma-Zadora M (2011) Evaluation of QuEChERS method for the determination of organochlorine pesticide residues in select groups of fruits. Food Chem 125:773–778

Concha-Graña E, Fernández-González V, Grueiro-Noche G, Muniategui-Lorenzo S, López-Mahía P, Fernández-Fernández E, Prada-Rodríguez D (2010) Development of an environmental friendly method for the analysis of organochlorine pesticide in sediments. Chemosphere 79:698–705

Cueva-Mestanza R, Sosa-Ferrera Z, Torres-Padrón ME, Santana-Rodríguez JJ (2008) Preconcentration of pharmaceuticals residues in sediment samples using microwave assisted micellar extraction coupled with solid phase extraction and their determination by HPLC–UV. J Chromatogr B 863: 150–157

de Boer J, Law RJ (2003) Developments in the use of chromatographic techniques in marine laboratories for the determination of halogenated contaminants and polycyclic aromatic hydrocarbons. J Chromatogr A 1000:223–251

Errekatxo A, Prieto A, Zuloaga O, Usobiaga A, Etxebarria N, Fernández LA (2008) Simultaneous extraction of several persistent organic pollutants in sediment using focused ultrasonic solid–liquuid extraction. Anal Bioanal Chem 392:1471–1478

Itoh N, Numata M, Aoyagi Y, Yarita T (2008) Comparison of low-level polycyclic aromatic hydrocarbons in sediment revealed by Soxhlet extraction, microwave-assisted extraction, and pressurized liquid extraction. Anal Chim Acta 612:44–52

Kayal S, Connell DW (1995) Polycyclic Aromatic Hydrocarbons in Biota from the Brisbane River Estuary, Australia. Estuar Coast Shelf Sci 40:475–493

Lee SW, Choi JH, Cho SK, Yu HA, Abd El-Aty AM, Shim JH (2011) Development of a new QuEChERS method based on dry ice for the determination of 168 pesticides in paprika using tandem mass spectrometry. J Chromatogr A 1218:4366–4377

Lehotay SJ, Ae Son K, Kwon H, Koesukwiwat U, Fu W, Mastovska K, Hoh E, Leepipatpiboon N (2010) Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. J Chromatogr A 1217:2548–2560

Moreno DA, Ilic N, Poulev A, Raskin I (2006) Effects of *Arachis hypogaea* nutshell extract on lipid metabolic enzymes and obesity parameters. Life Sci 78:2797–2803

Mzoughi N, Dachraoui M, Villeneuve JP (2005) Evaluation of aromatic hydrocarbons by spectrofluorometry in marine sediments and biological matrix: what reference should be considered? C R Chim 8:97–102

Norli HR, Christiansen A, Deribe E (2011) Application of QuEChERS method for extraction of selected persistent organic pollutants in fish tissue and analysis by gas chromatography mass spectrometry. J Chromatogr A 1218:7234–7241

Peysson W, Vulliet E (2013) Determination of 136 pharmaceuticals and hormones in sewage sludge using quick, easy, cheap, effective, rugged and safe extraction followed by analysis with liquid chromatography-time-of-flight-mass spectrometry. J Chromatogr A 1290:46–61

Pinto CG, Herrero Martín S, Pérez Pavón JL, Moreno Cordero B (2011) A simplified quick, easy, cheap, effective, rugged and safe approach for the determination of trihalomethanes and benzene, toluene, ethylbenzene and xylenes in soil matrices by fast gas chromatography with mass spectrometry detection. Anal Chim Acta 689:129

Ramalhosa MJ, Paiga P, Morais S, Delerue-Matos C, Oliveira MB (2009) Analysis of polycyclic aromatic hydrocarbons in fish: evaluation of a quick, easy, cheap, effective, rugged, and safe extraction method. J Sep Sci 32:3529–3538

Rouvière F, Bulete A, Cren-Olive C, Arnaudguilhem C (2012) Multiresidue analysis of aromatic organochlorines in soil by gas chromatography-mass spectrometry and QuEChERS extraction based on water/dichloromethane partitioning. Comparison with accelerated solvent extraction. Talanta 93:336–344

Subedi B, Aguilar L, Robinson EM, Hageman KJ, Björklund E, Sheesley RJ, Usenko S (2015) Selective pressurized liquid extraction as a sample-preparation technique for persistent organic pollutants and contaminants of emerging concern. TRAC-Trend Anal Chem 68:119–132

Thompson S, Budzinski H, LeMenach K, Letellier M, Garrigues P (2002) Multi-residue analysis of polycyclic aromatic hydrocarbons, polychlorobiphenyls, and organochlorine pesticides in marine sediments. Anal Bioanal Chem 372:196–204

Vagi MC, Petsas AS, Kostopoulou MN, Karamanoli MK, Lekkas TD (2007) Determination of organochlorine pesticides in marine sediments samples using ultrasonic solvent extraction followed by GC/ECD. Desalination 210:146–156

Wang L, Zhao P, Zhang F, Li Y, Du F, Pan C (2012) Dissipation and residue behavior of emamectin benzoate on apple and cabbage field application. Ecotox Environ Safe 78:260–264

Wilkowska A, Biziuk M (2011) Determination of pesticide residues in food matrices using the QuEChERS methodology. Food Chem 125:803–812

Yang XB, Ying GG, Kookana RS (2010) Rapid multiresidue determination for currently used pesticides in agricultural drainage waters and soils using gas chromatography–mass spectrometry. J Environ Sci Health B 45:152–161