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Validation of one-step cleanup and separation method of polychlorinated biphenyls, organochlorine pesticides, and polycyclic aromatic hydrocarbons from atmospheric gas- and particle-phase samples

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ABSTRACT

A one-step cleanup method is described for the determination of PAHs, PCBs and OCPs in air (gas and particulate phase) samples. Analytes were extracted from ambient air samples using soxhlet extraction with a solvent mixture of dichloromethane and petroleum ether (1:4) for 24 h. They were concentrated, separated and fractionated on a florisil and alumina column. The amounts of florisil (1 g or 2 g) with/without alumina were tested in the cleanup column. The study systematically investigated the effects of solvent types, and the amounts of florisil and alumina, on the performance of the cleanup process. The first fraction was eluted with 25 mL hexane, and analyzed for PCBs. The second fraction was collected via 40 mL hexane–ethyl acetate (1:1) solvent mixture, and analyzed for OCPs and PAHs. The optimized method yielded average recoveries between 88% and 99% for PCBs; 56% and 118% for PAHs; and 51% and 128% for OCPs. Other validation parameters were also investigated, such as MDL, LOQ, linear range, sensitivity (r^2). An oven-program optimization and adjustment of GC–MS were performed. For internal quality control, surrogate recoveries and field blanks values were calculated. External calibration curves were prepared for PAHs, and internal calibration curves were preferred for OCP and PCBs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), chlorinated hydrocarbons (organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are classified as priority micropollutants by most environmental authorities around the world, and are the subject of increasing scientific attention [1].

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous atmospheric pollutants that are known to exhibit carcinogenic and mutagenic properties [2]. They are formed and released into the atmosphere from both natural and man-made sources. Natural sources include volcanoes and forest fires, while man-made sources include automobile emissions, cooking stoves, power plants, refineries and industrial activities where high-temperature combustion of fossil fuels occurs. The extensive use of pesticides to improve agricultural productivity is an important source of environmental organic pollutants. Although many countries have banned most OCPs, they and their metabolites are still present in the environment [3,4]. Similarly, the production and industrial uses of PCBs have been restricted; PCBs can still be introduced into the environment as byproducts of a wide variety of chemical processes, e.g., the non-controlled incineration of different materials such as waste oils, electrical equipment and any other samples contaminated with different mixtures [5,6].

In general, sample preparation prior to chromatographic analysis starts with solvent extraction using a mixture of non-polar and polar solvents; a cleanup procedure then eliminates lipids and sulfur from the environmental samples, and the various compounds are fractionated using adsorptive column chromatography [7]. Various studies in the literature have reported the determination of chlorinated and non-chlorinated hydrocarbons in various samples [8–15].

There are numerous sample matrices in environmental studies such as sediment, particulate matter, soil, mussel, fly ash, sludge, water, etc., in which several types of pollutants should be determined. In atmospheric studies, there is a need to determine various classes of compounds, such as PAH, PCBs, OCPs, PCNs (polychlorinated naphthalenes) within one sample. These compounds are of global concern for many reasons, including their

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toxicity, carcinogenicity and their ability to travel long distances from their sources to places where they have never been used. It is therefore essential to produce a data set with certain QA/QC parameters, so that researchers are able to compare their own results with others all around the world, thereby allowing concentrations, sources and control techniques to be correctly determined. Ambient concentrations of PCBs and some of the OCPs should be monitored, and their source need to be identified for signatories to the Stockholm convention [16].

Determination of all of these compounds in any matrix involves the use of large quantities of solvents and time-consuming procedures if performing separate extraction and cleanup procedures. An optimal method would therefore minimize operator times, solvent use and contamination risk [7]. However, we are not aware of any previous study dealing with extraction and a single-step cleanup procedure with full validation. Many of the performance parameters associated with method validation are usually evaluated. However, without results of adequate quality or reliability, it is not possible to verify whether a proposed method provides accurate results for use in critical decisions involving real samples [17].

In this paper we report an optimized procedure that involves a single-step cleanup and separation procedure by adsorption chromatography which allows simultaneous determination of PAHs, OCPs and PCBs in atmospheric samples. Alumina and florisil were used as sorbents to separate compounds of interest in two fractions, and samples were analyzed after cleanup by GC-ECD (for OCPs) and GC–MS (for PCBs and PAHs). The literature includes different cleanup procedures for fractionation of different types of semivolatile organic compounds [7,10,18,19]. The present study uses alumina and florisil together in a cleanup column to separate OCPs, PAHs and PCBs in one step. Validation parameters are discussed, such as recovery, precision, linearity, range, sensitivity, LOD, LOQ and internal quality control.

2. Experimental

2.1. Air sampling

A high-volume polyurethane foam (PUF) sampler (Andersen PUF sampler, USA) was used, which is designed to simultaneously collect suspended airborne particulates and airborne organic vapors. The flow rate was adjusted to 0.225 m^3 min^{-1} for 24 h sampling duration. Particle phase organics were collected by a 90-mm diameter glass fiber filter (GFF), while gaseous phase organics were captured by a two-piece polyurethane foam (PUF) cartridge. The samples were collected in two phases, during two summer months (June 25 to August 23, 2007) and two winter months (December 13, 2007 to February 12, 2008). A total of 120 samples were collected and analyzed in both seasons.

2.2. Target PAH, PCB and OCP compounds

The PCB (with IUPAC nomenclature), OCP and PAH compounds were as follows: PCB-18, PCB-20, PCB-28, PCB-31, PCB-44, PCB-52, PCB-101, PCB-105, PCB-108, PCB-149, PCB-153, PCB-170, PCB-180, and PCB-194; Alpha-Hexachlorocyclohexane (α-BHC), Beta-Hexachlorocyclohexane (β-BHC), Gamma-Hexachlorocyclohexane (γ-BHC) (Lindane), Delta-Hexachlorocyclohexane (δ-BHC), Heptachlor, Aldrin, Dieldrin, Heptachlor epoxide, Endosulfan I, 4,4′-DDE, Endrin, Endosulfan II, 4,4′-DDD, Endrin aldehyde, Endosulfan sulfate, Endrin ketone, and Methoxychlor; Acenaphtylene (ACY), Acenapthene (ACE), Fluorene (FLU), Anthracene (ANT), Phenanthrene (PHE), Fluoranthene (FLT), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b) fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenz(a,h)anthracene (DahA), Indeno(1,2,3-cd)pyrene (IND), Benzo(g,h,i)perylene (BghiP).

2.3. Materials

All the glassware was washed with commercial detergent in hot water, and then rinsed sequentially with tap water, deionized water, acetone, and several times with hexane. PUFs were soxhlet-extracted with acetone for 24 h prior to first use. The PUF plugs were removed from the extractor, loosely wrapped with solvent rinsed aluminum foil, and air-dried under a fume hood. The GFFs were baked in a muffle furnace at 450 °C for 5 h before sampling in order to remove organic substances, and then conditioned in a desiccator and weighed. Pre-baked GFF and pre-cleaned PUF cartridges were brought to the sampling location, and were placed into the sampler. The GF filters were kept in the desiccator after sampling, and post-weighed again to calculate total suspended particles (TSP). Careful precautions were taken to prevent contamination of the samples and glassware.

All solvents and reagents used in the study were of chromatographic grade. PCB congener standard (100 μg mL^{-1}), internal standard (PCB30 and PCB204, 100 μg mL^{-1}), and surrogate standard (PCB14, PCB65, PCB166, 100 μg mL^{-1}) were purchased from Absolute Standards (USA). OCP standard solution (2000 μg mL^{-1}) was obtained from Dr. Ehrenstorfer (Germany). OCP internal standard (Pentachloronitrobenzene, 100 μg mL^{-1}) and OCP surrogate solution (2,4,5,6-Tetrachloro-*m*-xylene and Dibutyl chlorendate, 2000 μg mL^{-1}) were obtained from Absolute Standards (USA) and Fisher Scientific (UK), respectively. PAH standards (PM 610, 100 μg mL^{-1}) were purchased from AccuStandards (USA). PAH surrogate solution (Acenaphthene-d10, Crysene-d12, Perylene-d12, Phenanthrene-d10, 1000 μg mL^{-1}) was from Ultra Scientific (USA).

Sodium sulfate, florisil (0.150–0.250 mm) and neutral aluminum oxide (0.063–0.2 mm) were purchased from Merck Company (USA). The granulated sodium sulfate was anhydrous and of 99% purity for drying of solvents and gases. Glass microfiber filters (90 mm dia., pore size: 2.7 μm) were from Whatman Company (USA). All the samples were spiked with surrogate standards prior to their extraction. Prior to extraction, 20 μL of 32 μg mL^{-1} deuterated PAH mixture, 40 μg mL^{-1} OCP surrogates, and 50 μg mL^{-1} PCB surrogate were added to the samples in order to determine the recovery efficiencies for checking the internal quality control.

2.4. Preparation of chemicals for cleanup column

Extraction and analysis of atmospheric samples containing trace amounts of semi-volatile organic compounds (SVOCs) exist is very time-consuming [20]. In order to analyze a large number of samples collected over a long period of time, strict quality control procedures need to be followed. The one of the most critical step for determining very low amounts of analyte in the samples is cleanup, since if something is wrong at this step, the sample is lost and is not recoverable provided that the sample integrity at each analytical step from the sampling step to the final instrumental analysis step is kept.

2.4.1. Preparation of sodium sulfate and glass wool

Sodium sulfate (Na_2SO_4) was used to dry the extracts, and was pre-cleaned using hexane, oven-dried at 50 °C and conditioned at 225 °C prior to use. The dry Na_2SO_4 was then transferred to an amber glass bottle with a Teflon-lined cap and stored in a desiccator.

Glass wool used in the experiments was also cleaned using hexane and dichloromethane, oven dried and stored in a desiccator.

2.4.2. Preparation of alumina and florisil

Alumina is a highly porous granular aluminum oxide (Al_2O_3). The alumina solid is packed into a column topped with a water-absorbing substance, over which the sample is eluted with a suitable solvent, which leaves interferences in the column. Florisil is an activated form of magnesium silicate with basic properties and is a white substance with a ratio (15:85) of magnesium oxide–silicon dioxide. Florisil has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons, for the separation of nitrogen compounds from hydrocarbons, and for the separation of aromatic compounds from aliphatic/aromatic mixtures. Alumina is a white oxide of aluminum. It is used to contain the co-extracted lipid material and many unwanted contaminants [21].

Both neutral aluminum oxide (0.063–0.2 mm) and florisil (149–250 μm) were activated at 400 °C for 20 h. Aluminum oxide was deactivated with 1.5% Milli-*Q* water [7]. During the cleanup procedure, conditioning of the alumina is critical. The deactivation procedure should be carried out on the same day as the cleanup procedure. The deactivated alumina should be used without delay, because it is very hygroscopic.

2.5. Extraction and preconcentration of samples

GFF and PUF samples were soxhlet-extracted with a mixture of dichloromethane (DCM) and petroleum ether (PE) (1:4) with volumes of 150 mL and 650 mL, respectively, for 24 h, at four cycles per hour. The volume of the extracts reduced to 10 mL by rotary evaporator at 500 mbar and 40 °C. They were transferred to 15 mL vials by washing the walls of the balloons with solvent mixture (DCM:PE, 1:4) several times for further volume reduction to 1 mL under a gentle stream of nitrogen. Extracts were transferred to aluminum oxide–florisil columns for cleanup and fractionation of the analytes.

2.6. Preparation of adsorption column

The adsorption column was 10 cm long and 0.5 cm width (diameter), and prepared by placing glass wool in the tip of the column to support sorbent material. Aluminum oxide, florisil, and sodium sulfate (1 g each) were put to the column. The sodium sulfate was used to reduce water and moisture content in the samples on the top of the column.

2.7. Instrumentation and applied methods

A HP (Hewlett Packard) 6890N series gas chromatograph equipped with an electron-capture detector (GC-ECD, Agilent, USA) was utilized for the determination of OCPs. A 60-m capillary column (Agient Tech. 0.25 mm id., 0.25 μm film thickness, cross linked 5% phenyl methyl siloxane, HP1 MS) and 15 mCi of nickel-63-type ECD detector was used for the separation and detection of OCPs. A HP 6890N series gas chromatograph (Agilent, USA), coupled with a HP 5973 mass spectrometer (Agilent, USA) was used for the determination of PCBs and PAHs. A 30-m (0.25 mm id., 0.25 μm film thickness, cross linked 5% phenyl methyl siloxane, HP 5MS) capillary column (Agilent Tech.) was used for the separation of PCBs and PAHs throughout the study. GC–MS parameters were optimized before analysis of samples. A splitless glass liner was chosen and the injection port temperature was set at 280 °C. Several temperature programs were tested to determine the best resolution parameters of the compounds. The optimized GC-ECD program for OCPs is as follows: The injector port temperature was 250 °C. The initial oven temperature was set to 50 °C for 1 min, and raised to 170 °C at 25 °C min^{-1} (held 5.8 min) and from 170 °C to 300 °C at 5 °C min^{-1} was held for 2 min. The optimized GC–MS program for PCBs is as follows: The initial oven temperature was set to 70 °C for 2 min; raised to 150 °C at 25 °C min^{-1} (held 1 min); from 150 °C to 200 °C at 3 °C min^{-1} (held for 1 min); then from 200 °C to 280 °C at 8 °C min^{-1} (held for 5 min). The optimized GC–MS program for PAHs is as follows: The initial oven temperature was set to 70 °C for 4 min, and raised to 250 °C at 7 °C min^{-1} (held 5 min); from 250 °C to 300 °C at 5 °C min^{-1} (held for 8 min). The MS was operated in electron impact mode (70 eV) and PCBs were identified on the basis of their retention time, and target and qualifier ions. The quadrupole temperature was set to 150 °C. The source of mass instrument was operated at 230 °C. The carrier gas for both instruments was helium with 99.999% purity, given at a rate of 1 mL min^{-1}. Nitrogen gas was used as a make-up gas in the GC-ECD instrument with 99.999% purity at a rate of 30 mL min^{-1}.

3. Results and discussion

3.1. Optimization of instrumental parameters

3.1.1. GC–MS and GC-ECD

The complex organic matrix analysis requires sensitive and comprehensive instrumental studies. Therefore, we had to utilize two kinds of instruments in order to analyze all of the compounds. GC-ECD was utilized for analysis of the OCPs, and GC–MS was used to detect PAHs and PCBs. Instrumental parameters were optimized before analysis of samples, and given in the methodology.

3.1.2. GC–MS adjustment

The standard mixtures were initially analyzed using a scan mode in order to see the fragmentation pattern of each PAH and PCB compound. All the ions between 35 and 550 amu were scanned. In this way, standard purity can be also checked before starting the analyses. If the standard contains impurities and decomposition products, both can be seen in scan mode. After scanning the standard, target and qualifier ions were determined for each PAH and PCB compounds. One target and one or more qualifier ions were selected, and were usually monitored for quantitative analysis [22].

The entire chromatogram was divided in seven time-intervals for PAHs, and two time-intervals for PCBs in which specific ions were monitored. The sensitivity of the measurements was increased by decreasing background levels across the entire chromatogram. The monitored ions and SIM windows are given separately for PCBs and PAHs in Table 1. Supplementary document represents the SIM chromatograms of PAHs and PCBs, respectively.

3.2. Validation of the method

3.2.1. Calibration and validation parameters for PCBs

Internal standard calibration was used for quantification of PCBs. PCB-30 and PCB-204 were used as internal standards. The lowest amount of calibration standard, 5 μg L^{-1}, was analyzed ten times and the results of each component were divided by the average volume of air in order to calculate the limits of detection and quantification for the method. The method detection limit (MDL) is expressed as the concentration of analytes that gives a signal 3σ above the mean signal (where σ is the standard deviation of the lowest level standard). The quantification limit (LOQ) is expressed as the concentration of analyte that gives a signal 10σ above that lowest level standard. The method detection limits ranged from 0.0022 (PCB-180) to 0.030 (PCB-31) pg m^{-3} for PCBs. At least six calibration standards (each was injected 9 times) were prepared from the linear range 5.0 to 500 pg mL^{-1} for PCBs. The scatter plots of the calibration graphs were prepared. They were investigated visually for the outliers and linear range.

Table 1
SIM windows for PCBs and PAHs.

SIM window	Time period (min)	Monitored ions (mz^{-1})	Compounds
SIM windows for PCBs			
1	6–22	150, 151, 152, 186, 220, 222, 224, 256, 258, 260, 290, 292, 294	PCB-14, PCB-30, PCB-18, PCB-28, PCB-31, PCB-20, PCB-52, PCB-65, PCB-44,
2	22–40	158, 254, 256, 288, 290, 293, 324, 326, 328, 358, 360, 362, 394, 396, 398, 428, 430, 432	PCB-101, PCB-149, PCB-108, PCB-153, PCB-105, PCB-138, PCB-166, PCB-204, PCB-180, PCB-170, PCB-194.
SIM windows for PAHs			
SIM window	Time period (min)	Monitored ions (mz^{-1})	Compounds
1	8–12	127, 128, 129, 136, 137, 134	NAP, NAP-d8
2	12–15	151, 152, 153, 154, 160, 162, 164, 165, 166, 167	ACY, ACE d-10, ACE, FLU
3	15–21	176, 178, 179, 184, 187, 188, 189	PHE d-10, PHE, ANT
4	21–25	101, 200, 202	FLT, PYR
5	25–30	120, 226, 228, 229, 236, 240, 241	BaA, CHR-d12, CHR
6	30–35	126, 132, 252, 253, 260, 264, 265	BbF, BkF, BaP, PER-d12
7	35–47	138, 139, 250, 274, 276, 277, 278, 279	IND, DahA, BghiP

Table 2
Average % recovery values for PAHs and OCPs in the second fraction with different solvent mixtures ($N=3$).

PAHs	Hexane–toluene (4:1) 40 mL	Cyclohexane–ethylacetate (1:1) 40 mL	Hexane–ethylacetate (1:1) 40 mL	OCPs	Hexane–toluene (4:1) 40 mL	Cyclohexane–ethylacetate (1:1) 40 mL	Hexane–ethylacetate (1:1) 40 mL
NAP	105 ± 7.0	5 ± 3.0	65 ± 28	2,4,5,6-Tetrachloro-m-xylene (surrogate)	85 ± 8.0	BDL	BDL
ACY	93 ± 16	70 ± 19	66 ± 14	Alpha BHC	86 ± 7.0	5 ± 0.1	49 ± 6.0
ACE	86 ± 14	66 ± 16	60 ± 9.0	Beta BHC	90 ± 5.0	BDL	82 ± 8.0
ACE-d10 (surrogate)	86 ± 13	65 ± 15	56 ± 9.0	Gamma BHC	87 ± 6.0	2 ± 4	73 ± 13
FLU	100 ± 11	94 ± 11	81 ± 9.0	Delta BHC	91 ± 5.0	11 ± 1.0	80 ± 3.0
PHE-d10 (surrogate)	102 ± 9.0	105 ± 6.0	86 ± 6.0	Heptachlor	90 ± 6.0	7 ± 2.0	38 ± 8.0
PHE	105 ± 8.0	108 ± 5.0	86 ± 6.0	Aldrin	85 ± 5.0	4 ± 0.1	BDL
ANT	110 ± 10	106 ± 6.0	90 ± 5.0	Heptachloro epoxide	90 ± 5.0	20 ± 1.0	74 ± 11
FLT	108 ± 7.0	111 ± 5.0	107 ± 4.0	Endosulfan I	14 ± 9.0	80 ± 3.0	82 ± 10
PYR	105 ± 6.0	109 ± 5.0	99 ± 6.0	Dieldrin	94 ± 4.0	BDL	96 ± 13
BaA	111 ± 5.0	122 ± 12	108 ± 4.0	4,4′-DDE	11 ± 5.0	77 ± 4.0	101 ± 11
CHR	106 ± 7.0	99 ± 7.0	112 ± 8.0	Endrin	11 ± 4.0	75 ± 7.0	91 ± 3.0
CHR-d12 (surrogate)	117 ± 7.0	104 ± 7.0	107 ± 4.0	Endosulfan II	107 ± 5.0	95 ± 3.0	95 ± 9.0
BbF	94 ± 4.0	175 ± 1.0	118 ± 8.0	Endrin aldehyde	94 ± 4.0	2 ± 0.1	79 ± 16
BkF	101 ± 7.0	127 ± 14	115 ± 6.0	4,4′-DDD	BDL	70 ± 1.0	90 ± 4.0
BaP	97 ± 4.0	165 ± 10	102 ± 4.0	Endosulfan sulfate	318 ± 16	25 ± 0.1	101 ± 13
PER-d12 (surrogate)	57 ± 1.0	119 ± 14	105 ± 6.0	4,4′-DDT	92 ± 6.0	72 ± 1.0	94 ± 6.0
IND	80 ± 9.0	124 ± 11	109 ± 5.0	Endrin ketone	114 ± 6.0	80 ± 1.0	98 ± 6.0
DahA	86 ± 29	93 ± 12	114 ± 7.0	Methoxychlor	174 ± 1.0	83 ± 2.0	92 ± 13
BghiP	81 ± 7.0	109 ± 9.0	113 ± 6.0	Dibutyl chlorendate (surrogate)	107 ± 4.0	76 ± 2.0	103 ± 6.0

The calibration graphs were prepared on the different days and the equations were checked. After obtaining the calibration equation, some of the standards were read again and the concentrations of them were calculated. The percent relative error was always less than 5%. The r^2 values for the calibration plots were greater than 0.9903. Retention time, linear range, r^2, MDL, LOQ, target ion and selected ions for all detected PCB compounds are given in supplementary document.

3.2.2. Calibration and validation parameters for PAHs

Since internal standards were not available for PAHs at the time of analysis in our laboratory, analytes were quantified by the external calibration method. GC–MS was calibrated with standard mixtures of PAHs, ranging from 0.1 mg L^{-1} to 4 mg L^{-1} for PAHs with at least six levels, and r^2 values greater than 0.99892 were obtained for all PAHs and surrogates. The MDL and LOQ values were also determined using the same methodology. The detection limits were found to be within the range 0.06 (naphtylene and acenaphtylene) to 0.73 (benzo(a)perylene) pg m^{-3} for PAHs. Retention time, linear range, r^2, MDL, LOQ, target ion and selected ions for all detected PAH compounds are given in supplementary document.

3.2.3. Calibration and validation parameters for OCPs

GC coupled with an electron capture detector is a very sensitive technique, and is well suited to the analysis of semivolatile organic compounds such as polyhalogenated organic compounds. GC-ECD was used, which was previously calibrated by standard addition method using matrix. A chromatogram of 1 mg L^{-1} solution is given in supplementary document. The method detection limits ranged from 0.98 (aldrin) to 7.82 (methoxychlor) pg m^{-3} for OCPs. Pentachloronitrobenzene was used as an internal standard. Seven

level-calibration standards (5 pg mL^{-1} to 1000 pg mL^{-1}) were used to calibrate the GC-ECD system for OCPs. The r^2 values of calibration plots were greater than 0.9927. Retention time, linear range, r^2, MDL and LOQ values are given in supplementary document.

3.2.4. Internal quality control (surrogate recovery and blanks)

According to ISO/IEC 17025 (2005) [23], laboratories should include quality control procedures for monitoring the validity of the tests undertaken. The monitoring procedures should include the regular use of internal quality control. Internal quality control samples can be matrix CRM, standard solution or in-house material, blank sample and recovery of spiked or surrogate samples. Generally, internal quality samples are run regularly, between every 10 to 20 samples, during routine analysis of the samples. If there is an opportunity to analyze surrogate standards that are added before extraction of each sample, this will be a more dependable method than running internal quality samples every 10–20 samples, since surrogate standards provide an indication of what happens to each sample during all of the laboratory processes in order to detect contamination or sample loose problem.

All surrogate compounds were added to all samples ($N=120$) before the extraction step. Acenapthene-d10 and phenanthrene-d10 were used for the recovery calculations of 3-ring PAHs, chrysene-d12 for 4-ring PAHs and perylene-d12 for the 5- and 6-ring PAHs. The average percentage recovery and standard deviation values were $46 \pm 16\%$ (acenapthene-d10), $70 \pm 19\%$ (phenanthrene-d10), $82 \pm 29\%$ (chrysene-d12) and $72 \pm 26\%$ (perylene-d12) for particulate phase of the deuterated PAHs and $70 \pm 21\%$ (acenapthene-d10), $75 \pm 22\%$ (phenanthrene-d10), $70 \pm 18\%$ (chrysene-d12) and $61 \pm 18\%$ (perylene-d12) for gaseous phase of the deuterated PAHs. The average percentage recovery values for OCP surrogate standard (dibutyl chlorendate) were $74 \pm 24\%$ and $71 \pm 22\%$ for gas and particulate phases, respectively. The average percentage recovery values for PCB14, PCB65 and PCB166 for gaseous phase were $91 \pm 43\%$, $81 \pm 40\%$ and $94 \pm 34\%$, respectively; the values were $85 \pm 30\%$, $83 \pm 38\%$ and $99 \pm 40\%$, respectively for particulate phase.

Twelve field blank samples (6 for GFF, 6 for PUF) were collected to determine any contamination during sampling, sample handling, sample preparation, and analyses. Pre-baked GFF and pre-cleaned PUF cartridges were brought to the sampling location in sealed vessels and then placed into the sampler. They were kept in the sampler for several minutes prior to operation. They were then returned to the carrying vessels and then transferred to the laboratory for extraction and analysis in the same manner as the air samples. Filter blanks and PUF blanks were subjected to the same analytical procedure applied to the samples.

Field and laboratory blank samples were routinely analyzed in order to evaluate analytical bias and precision. Blank levels of individual compounds were normally very low and, in most cases, not detectable. The amounts in the field blank samples were less than 0.4% of the sample amounts for PCBs and for PAHs, and less than 0.03% of the sample amount for OCPs. Therefore, no blank correction was applied to the results.

3.3. Separation and elution of the analytes into the column

A 1 mg L^{-1} mixture of standard and surrogate solutions of PAH, OCP and PCB was prepared, and different elution solvents or solvent mixtures and also different amounts of florisil were used to collect the groups of compounds in either one or two fractions. Eluted compounds in fraction(s) were concentrated to 300–500 μL under nitrogen flow by washing the eluting solvent mixture several times. Then, the concentrated fractions were transferred to amber vials by gastight syringe. The concentration of samples was continued under nitrogen blow-down nearly to dryness. Finally, exactly 1 mL hexane was added to both fractions prior to analysis.

Sequentially, 1 g of aluminum oxide, 1 or 2 g (determined as 1 g after optimization) of florisil and 1 g of sodium sulfate were poured into the column. The column was activated with the 10 mL hexane. The sample was loaded into the column, and solvent or solvent mixtures were eluted from the column. Many individual experiments were performed in order to determine the most suitable solvent and the most efficient amounts for the solid matrices.

3.3.1. Collection of the samples in one fraction

Different solvent mixtures were tested to recover the compounds from the cleanup column. At least three trials were performed throughout each optimization experiment, and 1 mg L^{-1} standard mixture of PAH, PCB and OCPs was used for all recovery tests.

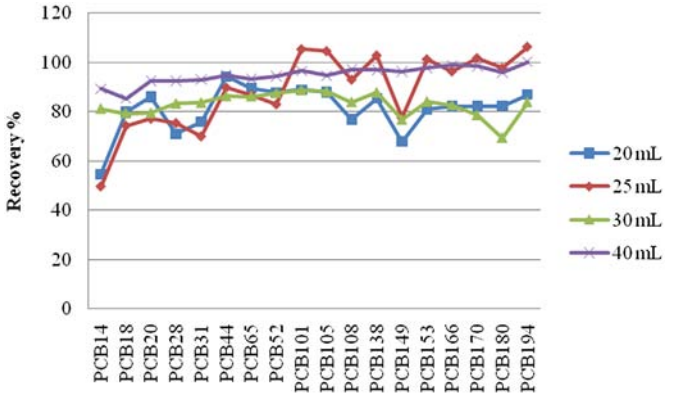

Fig. 1. Percent recovery values for PCB compounds using different volumes hexane.

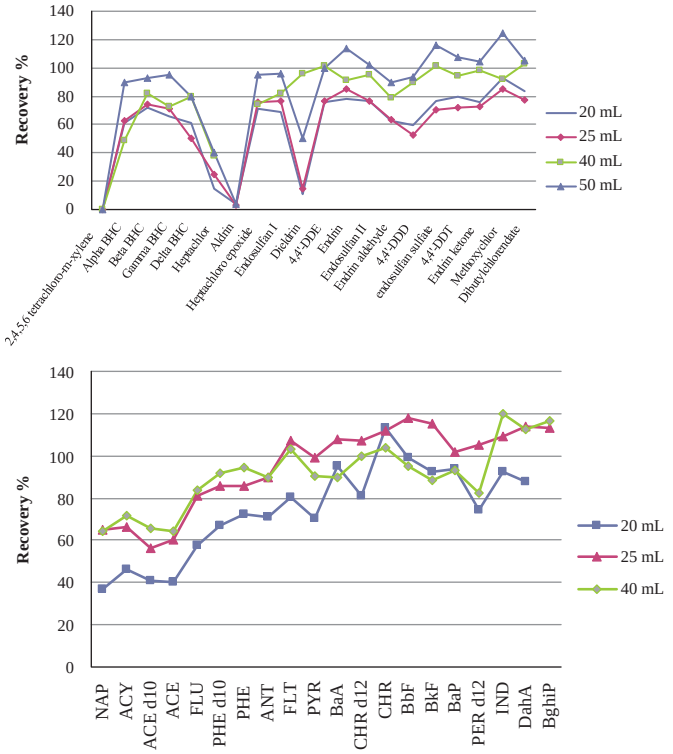

Fig. 2. Percent recovery values for PAH and OCP compounds using different hexane–ethyl acetate (1:1) volumes.

Initial attempts were made to recover all types of compounds in one fraction. In the first set of experiments, PCBs, PAHs and OCPs were eluted in one fraction by using different solvent combinations to adjust the polarity of the elution solvent. The following solvent mixtures (20 mL in total) were tested: (i) hexane–toluene (4:1), (ii) hexane–dichloromethane (4:1), and (iii) hexane–ethyl acetate (1:1). However, the recoveries of OCPs, PAHs, and PCBs in single fraction were not satisfactory. 4,4′-DDE, endrin and endrin aldehyde were recovered in very low amounts, and endosulfan I was not recovered. The recovery of endosulfan sulfate (300%) and

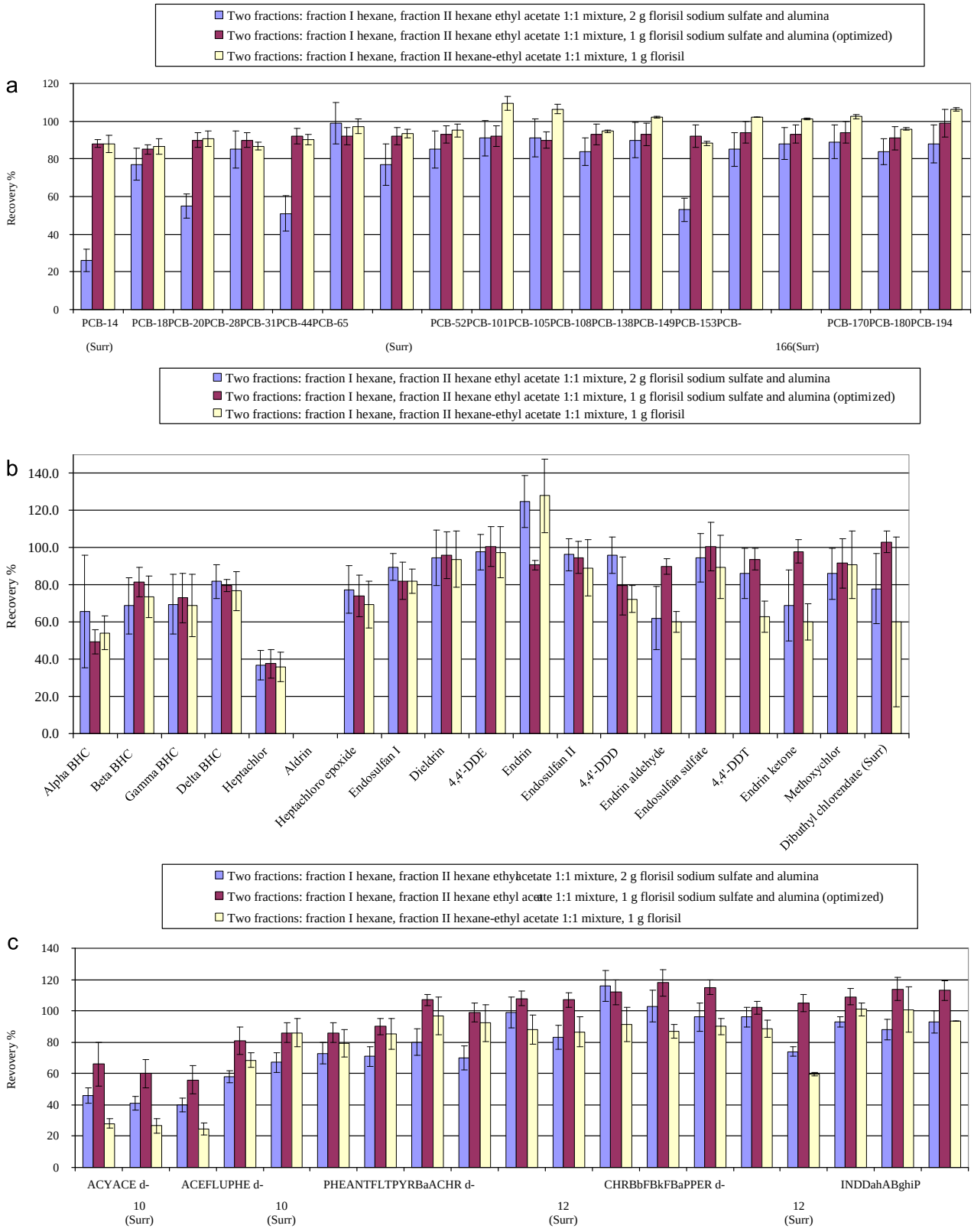

Fig. 3. (a) Recovery results of PCBs for three methods. (b) Recovery results of OCPs for three methods. (c) Recovery results of PAHs for three methods.

methoxychlor (175%) were overestimated using the first mixture. Since OCPs and PCBs may interfere with each other, higher recovery of some OCPs was observed by GC-ECD. The recoveries of PCB and PAH compounds were satisfactory, ranging from 70% to 110%. The solvent mixture of hexane–dichloromethane (4:1) and hexane–ethyl acetate (1:1) were more effective than hexane–toluene (4:1) to elute all of the compounds. However, again there was a problem of interference of PCBs in the determination of OCPs by GC-ECD. Thus, the method was deemed unsuitable for the collection of all the compounds in one fraction.

3.3.2. *Collection of the samples in two fractions*

It was observed that PCBs and some of the OCPs were collected in fraction I with hexane. It was obvious that all of the compounds cannot be eluted in a single fraction, so collection in two fractions was tried. Since all the PCBs were successfully recovered in the fraction I, hexane was retained as a solvent for the elution of PCBs in fraction I, and alternative solvent mixtures were tested for the fraction II. In the fraction I, all of the PCB compounds were successfully determined using 30 mL hexane for the elution. Thirty mL of hexane–toluene mixture (4:1) was loaded into the column to collect OCPs and PAHs in the fraction II. The recoveries of PAHs ranged from 57 to 117%. The recovery results for 4,4′-DDE, endrin, endrin aldehyde and endosulfan I were less than 40%. When more polar solvents like dichloromethane (30 mL) and cyclohexane–ethyl acetate mixture (1:1) (30 mL) were used after the elution with hexane–toluene (4:1), all of the unrecovered pesticides were found in the third fraction (dichloromethane or cyclohexane–ethyl acetate mixture).

PAHs and some of the OCPs were collected in fraction II with hexane–toluene (4:1), cyclohexane–ethyl acetate (1:1), and hexane–ethyl acetate (1:1) mixtures. The results are summarized in Table 2. As seen from the table, hexane–toluene (4:1) was not the best of the three mixtures for both PAHs and pesticides. The second mixture (cyclohexane–ethyl acetate (1:1)) was also not effective to recover some of the PAH compounds (NAP, ACE, ACE-d10, BbF, BaP) and OCP compounds (2,4,5,6-tetrachloro-*m*-xylene, all BHCs, heptachlor, heptachloroepoxide, aldrin, dieldrin, endrin aldehyde, endosulfan sulfate). The third mixture (hexane–ethyl acetate (1:1)) achieved sufficient recoveries for all of the PAHs. However, there are a few problematic compounds such as 2,4,5,6-tetrachloro-*m*-xylene, alpha BHC, heptachlor and aldrin. The most suitable mixture for the elution of the fraction II was identified as hexane–ethyl acetate (1:1).

The fraction I eluted with 20 mL hexane was analyzed in order to determine the presence of OCP compounds that were not in the fraction II. Some of OCPs were detected in the fraction I. The fraction I also contained almost all PAH compounds, at average recovery values of 15%. Similarly, the fraction II was also analyzed for the presence of PCB compounds. The recovery of PCB compounds in the fraction II was less than 19% (19, 15, 13, 13, and 4% for PCB18, PCB44, PCB65, PCB180 and PCB101, respectively).

The solvent amounts were also optimized for both fractions. Hexane volumes of 20, 25, 30, and 40 mL were used to elute PCBs (Fig. 1). The best recovery results were obtained by using 40 mL hexane; this volume was also sufficient to elute PAHs and some of the OCPs. A hexane volume of 20–25 mL was satisfactory to elute mainly PCBs and a few OCP compounds but not PAHs. If the volume of hexane was increased to 30 mL, NAP was eluted totally, and 25–30% of the three-ringed PAHs were co-eluted in the fraction I.

In order to reduce consumption of solvent mixture (hexane–ethyl acetate (1:1)), the volume of solvent should be minimum as much as possible. Solvent volumes ranging from 25 to 40 mL can be applied reasonably and satisfactorily for the elution of both PAHs and OCPs (Fig. 2). The optimized elution solvent and solvent mixtures were selected as 25 mL hexane for the elution of PCBs in the fraction I, and 40 mL hexane–ethyl acetate (1:1) mixture for the elution of PAH and OCPs in the fraction II.

In addition, different amounts (1 g or 2 g florisil) of the adsorbents were used to obtain higher efficiency in separation. Recoveries of the individual groups are given in Fig. 3. The recovery results for PCB compounds are given in Fig. 3a. The optimized method (1 g florisil+1 g alumina) resulted in more satisfactory recoveries than a combination of 2 g florisil+1 g alumina. The lower recoveries obtained with 2 g florisil+1 g alumina may be due to insufficient solvent (25 mL hexane).

OCP recoveries in the fraction II are shown in Fig. 3b. The higher recovery values were obtained for the optimized method. Other methods were also satisfactory for most of the compounds with the optimized 40 mL of solvent. The recovery values for the PAH compounds in the fraction II are presented in Fig. 3c. The most satisfactory results for all compounds were obtained for the optimized method. The other methods also performed sufficiently to achieve good recovery values except for ACY and ACE.

Hexane was the most convenient solvent for separation of the PCBs because of the nonpolar property of PCBs. Different types of solvent systems were used for the second fraction, as discussed above.

The optimized column (1 g florisil+1 g alumina+1 g Na_2SO_4 in a 0.5 cm i.d. column), determined as hexane (25 mL) for the fraction I and hexane–ethyl acetate (40 mL) (1:1) for the fraction II, was utilized for all collected samples. As discussed previously, the compounds were separated and collected in two fractions, and all PCBs were present in the fraction I. However it was not possible to separate and collect OCPs in one fraction. Some nonpolar compounds, such as heptachlor and aldrin, were eluted in the fraction I. The remaining OCP compounds were collected in the fraction II,

Table 3
Average recoveries (%) and standard deviations for the fractions and total recoveries (%) ($N=7$).

Compounds	R (%) ± std first fraction	R (%) ± std second fraction	Total R (%)
Alpha-HCH	8 ± 12	49 ± 6.0	57
Beta-HCH	Below detection limit	82 ± 8.0	82
Gamma-HCH	9 ± 8	73 ± 13	82
Delta-HCH	19 ± 15	80 ± 3.0	99
Heptachlor	44 ± 17	38 ± 8.0	82
Aldrin	80 ± 5.0	Below detection limit	80
Heptachloroepoxide	Below detection limit	74 ± 11	74
Endosulfan I	Below detection limit	82 ± 10	82
Dieldrin	Below detection limit	96 ± 13	96
4,4′-DDE	Below detection limit	101 ± 11	101
Endrin	Below detection limit	91 ± 2.6	91
Endosulfan II	Below detection limit	95 ± 8.8	95
4,4′-DDD	Below detection limit	79 ± 16	79
Endrin aldehyde	Below detection limit	90 ± 4.2	90
Endosulfan sulfate	Below detection limit	101 ± 13	101
4,4′-DDT	Below detection limit	94 ± 5.8	94
Endrin ketone	Below detection limit	98 ± 6.2	98
Methoxychlor	Below detection limit	92 ± 13	92

were determined exactly. As shown in Table 3, the average recoveries of OCPs in the first fraction, in the second fraction and total recoveries were given. A previous study in the literature employed a cleanup procedure using silicic acid and alumina, and reported a similar situation, with PAHs being partly eluted in two fractions [24]. The important steps in the optimized method are summarized in Fig. 4.

3.3.3. *Comparison with other clean-up methods*

As we have mentioned in the introduction part, there is no comprehensive study dealing with extraction and a single-step cleanup procedure for the fractioning of PAHs, OCPs and PCBs in the same sample. However, there are some similar studies that use the same sorbents and solvents.

Raccanelli et al.[7] used an activated copper, florisil (1.5 g) and neutral aluminum oxide (8 g, deactivated with 1.5% milli-Q water) and silica (8 g) from top to bottom of clean-up column. In the three fractions they have collected PCBs, pesticides, aliphatic hydrocarbons (AHs) and PAHs in environmental samples. The first fraction was eluted with 30 mL hexane and AHs were collected. In the second fraction, PAHs and PCBs were collected with 70 mL hexane. In the third fraction, 75 mL (3:2) hexane/dichloromethane was used to elute pesticides and some of PAHs. The second and third fraction were combined and analyzed for PAHs on GC-FID. Consumption of solvent and sorbent amounts was more than our study and also PAHs were not collected in one fraction.

The study conducted by Berset et al. [10], the 2 g of deactivated aluminium oxide basic was used to elute only PAHs with 10 mL petroleum ether to be analyzed on HRGC-MS instrument in soil samples.

In the study of Parera et al.[18], recoveries achieved with florisil were slightly higher than those observed with silica gel and the volume of solvents required for the elution of the analytes were lower, fully activated florisil (15 g) was selected as the clean-up sorbent to fractionate short-chain chlorinated paraffins (SCCP) from PCBs in river sediments. The first fraction was eluted with 60 mL hexane for SCCPs and 200 mL hexane/dichloromethane (1:1, v/v) was used to elute the second fraction for PCBs. Higher volumes of solvent and higher amounts of sorbents were used compared with our study and the separation did not involve other species such as pesticides and PAHs.

To determine the concentrations of chlorinated paraffins in sediment samples, cleanup column were prepared with 5 g of silica gel (deactivated by addition of 3% (w/w) deionized water) [25]. For the first elution fraction, 40 mL of hexane was used. Only interferences like PCBs, hexachlorobenzene, heptachlor, chlordane (completely), toxaphene, hexachlorocyclohexanes (HCHs), endosulfan, *o,p′*- and *p,p′* -DDT, DDE, DDD (partially) were present in this hexane fraction. The second fraction of 25 mL DCM:hexane (1:1) contained chlorinated paraffins and possible contaminants from the first fraction that were not completely removed. In our study, some pesticides like alpha-HCH, beta-HCH, gamma-HCH, delta-HCH, heptachlor, aldrin were eluted with 25 mL hexane together with all PCBs.

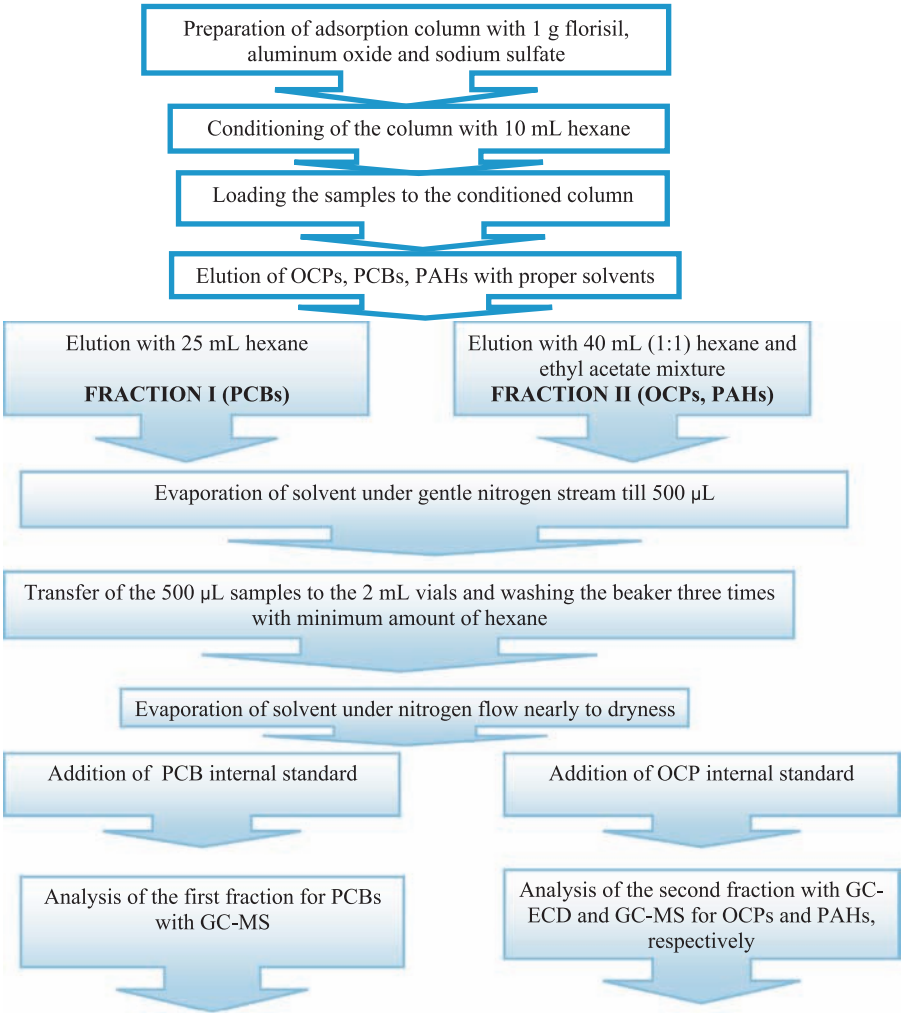

Fig. 4. Summary scheme of the application of the optimized method (pre-concentration and cleanup procedure after the soxhlet extraction).

The performance of three adsorbents, i.e. silicagel, neutral and basic alumina, in the separation of short chain polychlorinated *n*-alkanes (sPCAs) from potential interfering substances such as PCBs and OCPs were evaluated [19]. Considering the recoveries of sPCAs and their separation efficiency from PCBs, OCPs and toxaphene, a two step cleanup method using silica gel column (with 5 g anhydrous Na_2SO_4, 2 g silica gel, 4.5 g acid silica gel and 6 g anhydrous Na_2SO_4 from bottom to top, 200 mL solvent was used for elution), and subsequent basic alumina (with 5 g anhydrous Na_2SO_4, 5 g alumina and 6 g anhydrous Na_2SO_4 from bottom to top, 150 mL solvent was used for elution) column following soxhlet extraction and GPC was developed. Four kinds of HCH (alpha-HCH, beta-HCH, gamma-HCH and delta-HCH) were eluted together with sPCAs on silica gel and basic alumina columns. However, they did not interfere with the monitoring of sPCAs in ECNI mode.

4. Conclusion

A one-step cleanup procedure was developed and validated for the determination of OCPs, PAHs and PCBs in atmospheric samples. PAHs, PCBs and OCPs were fractioned and recovered from an adsorption column using florisil and alumina. PCBs were eluted with hexane in first fraction, and OCPs together with PAHs were eluted with hexane–ethyl acetate (1:1) solvent in the second fraction. Aldrin and heptachlor were eluted in the first fraction.

This single-step cleanup method and fractionation give the opportunity to analyze three classes of compounds: PCBs, OCPs, and PAHs. This method resulted in satisfactorily high recovery values for most of the compounds, within the range 70% to 100%. Other validation parameters were also within acceptable ranges. In addition, due to the reduced number of steps employed in the cleanup step, the chance for sample and sorbent loss and contamination is reduced. The analyses performed by GC-ECD for OCPs, and by GC–MS for PAHs and PCBs, are generally acceptable on a routine basis.

The developed method was successfully applied to the cleanup of gas- and particle-phase atmospheric samples collected at high altitude from a suburban site in Turkey. Gas- and particle-phase ambient air samples (approximately 500 samples) were collected and analyzed. Concentrations, sources, and parameters affecting the measured concentrations of those SVOCs were discussed elsewhere [26].

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.04.049.

References

[1] V. Lang, J. Chromatogr. A 595 (1992) 1–43.
[2] Y. Kawanaka, E. Matsumoto, K. Sakamoto, N. Wang, S.J. Yun, Atmos. Environ. 38 (2004) 2125–2132.
[3] P. Gong, X. Wang, J. Sheng, T. Yao, Atmos. Environ. 44 (2010) 2518–2523.
[4] F Wong, H.A. Alegria, T.F. Bidleman, V. Alvarado, F. Angeles, A.A. Galarza, E. R. Bandala, I. Hinojosa, I.G. Estrada, G.G. Reyes, G Gold-Bouchot, J.V.M. Zamora, J. Murguía-González, E.R. Espinoza, Environ. Sci. Technol. 43 (2009) 704–710.
[5] M. Biterna, D. Voutsa, Environ. Int. 31 (2005) 671–677.
[6] A. Gambaro, L. Manodori, R. Zangrando, A. Cincinelli, G. Capodaglio, P. Cescon, Environ. Sci. Technol. 39 (2005) 9406–9411.
[7] S. Raccanelli, B. Pavoni, L. Maroli, A. Sfriso, Toxicol. Environ. Chem. 45 (1994) 121–137.
[8] E. Aries, D.R. Anderson, N. Ordsmith, K. Hall, R. Fisher, Chemosphere 54 (2004) 23–31.
[9] S. Ayris, G.M. Currado, D. Smith, S. Harrad, Chemosphere 35 (1997) 905–917.
[10] J.D. Berset, M. Ejem, R. Holzer, P. Lischer, Anal. Chim. Acta 383 (1999) 263–275.
[11] M.R. Criado, I.R. Pereiro, R.C. Torrijos, Talanta 63 (2004) 533–540.
[12] S. Karthikeyan, R. Balasubramanian, S.W. See, Talanta 69 (2006) 79–86.
[13] C. Miege, J. Dugay, M.C. Hennion, J. Chromatogr. A 995 (2003) 87–97.
[14] E.R. Noordkamp, J.T.C. Grotenhuis, W.H. Rulkens, Chemosphere 35 (1997) 1907–1917.
[15] A. Tor, M.E. Aydin, S. Ozcan, Anal. Chim. Acta 559 (2006) 173–180.
[16] A. Godduhn, L.K. Duffy, Environ. Sci. Policy 6 (2003) 341–353.
[17] M. Rambla-Alegre, J. Esteve-Romero, S. Carda-Broch, J. Chromatogr. A 1232 (2012) 101–109.
[18] J. Parera, F.J. Santos, M.T. Galceran, J. Chromatogr. A 1046 (2004) 19–26.
[19] Y. Gao, H. Zhang, J. Chen, Q. Zhang, Y. Tian, P. Qi, Z. Yu, Anal. Chim. Acta 703 (2011) 187–193.
[20] F.J. Santos, M.T. Galceran, Trends Anal. Chem. 21 (2002) 672–684.
[21] D.E. Wells, S.J. Johnstone, J. Chromatogr. 140 (1977) 17–28.
[22] E.O. Gaga, Ph.D. Thesis. Investigation of Polycyclic Aromatic Hydrocarbon (PAH) Deposition in Ankara, METU, Turkey, 2004.
[23] ISO/IEC 17025, General Requirements for the Competence of Testing and Calibration Laboratories, ISO, Geneva, Switzerland, 2005.
[24] A. Bozlaker, A. Muezzinoglu, M. Odabasi, J. Hazard. Mater. 153 (2008) 1093–1102.
[25] P. Stejnarova, M. Coelhan, R. Kostrhounova, H. Parlar, I. Holoubek, Chemosphere 58 (2005) 253–262.
[26] S. Yenisoy-Karakas, M. Oz, E.O. Gaga, J. Environ. Monit. 14 (2012) 1365–1374.