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Journal of Chromatography A, 852 (1999) 545–558

JOURNAL OF
CHROMATOGRAPHY A

Quantitative determination of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides in sewage sludges using supercritical fluid extraction and mass spectrometric detection

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Received 23 February 1999; received in revised form 18 May 1999; accepted 18 May 1999

Abstract

Supercritical CO₂ extraction (SFE) proved to be a valuable, fast, quantitative and partly selective extraction technique for determining polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and chlorinated pesticides (OCPs) in sewage sludges of different catchment areas based on a comparison study with certified reference materials (CRMs) and on recovery data. Most PCB extracts could be measured directly after SFE whereas for PAHs a short clean-up improved the final separation by high-resolution capillary gas chromatography. Due to the amount of coextracted compounds and the low levels of OCPs, extracts obtained by SFE had to be submitted to a multistep clean-up for final measurement. Average concentrations of 6.9 mg/kg dry mass (dm) for the sum of the 16 Environmental Protection Agency PAHs, 0.1 mg/kg dm for the sum of the seven PCB congeners and 0.002–0.072 mg/kg dm for the OCPs were found in the sewage sludges. Compared to studies performed earlier in our laboratory PAHs are still present in similar concentrations whereas PCB levels have decreased significantly. OCPs could be detected in only low amounts. A correlation between sludge type and degree of contamination could only be found for PAHs. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Environmental analysis; Sewage sludge; Polynuclear aromatic hydrocarbons; Polychlorinated biphenyls; Organochlorine compounds; Pesticides; Supercritical fluid extraction

1. Introduction

Agriculture plays an important role in Switzerland in waste recycling thereby reintroducing substances as plant nutrition elements (N, P, K, Ca, Mg) into natural cycles. The application of sewage sludge as fertiliser to agricultural lands represents an econ-

omical way to use the high amounts of sludge produced by the waste water treatment plants. Currently approximately $2.1 \cdot 10^8$ kg dry mass (dm) of sewage sludge are produced annually of which $1.07 \cdot 10^8$ kg (51%) are applied in agriculture [1]. In the last couple of years agriculture has moved towards environmental friendly techniques with the goal of producing high quality food products. This also requires the use of fertilisers of high quality. For sewage sludge and compost, limit values for heavy

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metals have been established as a quality criterium [2]. These inorganic compounds are analysed on a routine basis. However, the characterisation and long term observation of organic contaminants in sludge has received little attention so far. A possible explanation might be the fact that no limit values have been legally implemented except for AOX, a summary parameter for adsorbable, organically bound halogens [2]. It is well known that sewage sludge contains a wide array of xenobiotic (anthropogenic) organic compounds which might have a negative impact on soil organisms [3–7]. Among these organic contaminants non polar, persistent compounds exhibiting a high accumulation potential, are important. Typical representatives are the polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and chlorinated pesticides (OCPs), three groups which are ubiquitous in the environment. PCBs were widely used in the electrical industry in transformers and capacitors as well as in consumer products like ink, paper and paints. PAHs originate from industrial waste as well as from domestic sludge, atmospheric rainfall, airborne pollutants, runoff of road surfaces etc. They are also produced in smaller amounts naturally by forest fires and possibly microbiological synthesis. OCPs have partly been extensively used in agriculture in former times [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), hexachlorocyclohexanes (HCHs) etc.]. The chemical–physical properties of most of the compounds mentioned are similar. They show high octanol–water distribution coefficients, are highly lipophilic and therefore tend to adsorb to solid particles of the sewage sludge.

Analytical methods for analysing these compounds include extraction, one or several clean-up steps and finally separation and quantification of the analytes using liquid chromatography (LC) or high-resolution gas chromatography (HRGC). These traditional methods involve the use of large amounts of organic solvents and several reconcentration and clean-up steps before final quantification.

The aim of this study was to evaluate the use of supercritical CO₂ extraction (SFE) as a fast extraction method for PCBs, PAHs and OCPs and to try to use the final extract for quantification without any clean-up step. Certified reference materials (CRMs) for PCBs and PAHs were used to validate

the extraction step. Finally sludges of different catchment areas were analysed for PCBs, PAHs and OCPs applying SFE.

2. Experimental

2.1. Sample characterisation and pretreatment

Sewage sludges from different catchment areas were sampled: four samples containing predominantly domestic sewage were obtained from separate sewer systems (A-type); six samples containing a mixture of domestic sewage, storm water runoff, and *small* amounts of industrial waste water were obtained from combined sewer systems (B-type); two samples containing a mixture of domestic sewage, storm water runoff and *higher* amounts of industrial waste water were obtained from combined sewer systems (C-type). Sewage sludges were sampled in glass bottles precleaned with hexane and acetone and freeze-dried the day after collection. Dried samples were homogenized by grinding with a hammer mill to a particle size of ≤ 1 mm. Samples were stored in glass bottles with aluminium foil protected covers in the dark at room temperature until analysis.

2.2. Certified samples for testing extraction efficiency

BCR reference materials (sludges) certified for PAHs (CRM 088) and PCBs (CRM 392) were prepared by the Community Bureau of Reference from Brussels (BCR) and obtained from the Institute for Reference Materials and Measurements (IRMM) Geel, Belgium. Certified contents are shown in Tables 1 and 2. For OCPs no CRM was available.

2.3. Solvents, chemicals and standards

Dichloromethane (DCM), toluene, hexane, heptane, acetone, acetonitrile and methanol for organic trace analysis (SupraSolv) were from Merck (Darmstadt, Germany). Deionized water was produced from a Milli-Q Plus 185 water system (Millipore, Volketswil, Switzerland). Anhydrous sodium sulfate (Na₂SO₄) was from Merck of analytical grade. It was activated before use at 600°C for 12 h. Stan-

Table 1

Certified contents of different PAHs of a sewage sludge (CRM 088) and comparison with results obtained after SFE

PAH	Certified value (mg/kg dm)±95% CI	SFE ^a (n=2)	Recovery (%)
PYR	2.16±0.09	2.52, 2.65	119
BaA	0.93±0.09	1.12, 1.21	125
BaP	0.91±0.09	0.91, 0.99	104
Benzo[e]pyrene	1.02±0.07	1.06, 1.11	106
BbF	1.17±0.08	1.93, 2.04 ^b	n.c.
BkF	0.57±0.05	0.65, 0.75	122
IND	0.81±0.06	0.82, 0.86	104
Benzo[b]naphtho[2,1-d]thiophene	0.42±0.05	0.45, 0.42	104
Mean recovery (%)			112

95% CI=95% confidence interval of the mean of means.

^a After clean-up as described in Section 2.5.^b Interference, probably BjF.

n.c.=Not calculated.

dards: PAHs: A standard mixture containing the 16 priority PAHs (NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benz[a]anthracene, CHR: chrysene, BbF: benzo[b]fluoranthene, BkF: benzo[k]-fluoranthene, BaP: benzo[a]pyrene, IND: indeno[1,2,3-cd]pyrene, DBA: dibenz[a,h]anthracene, BGP: benzo[ghi]perylene at a concentration of 10 µg/ml in toluene and deuterated internal standards [²H₁₀]acenaphthene (ACE-d₁₀), [²H₁₂]chrysene (CHR-d₁₂), [²H₈]naphthalene (NAP-d₈), [²H₁₂]perylene (PER-d₁₂) and [²H₁₀]phenanthrene (PHE-d₁₀)

at a concentration of 4000 ng/µl dissolved in the same solvent, were purchased from Dr. Ehrendorfer, Augsburg, Germany. Calibration solutions (0.040–4.98 µg/ml) were prepared by dilution of the stock solution with toluene. The final concentration of the deuterated internal standards in the calibration solutions was 5 µg/ml. PCBs: A standard mixture containing seven PCB congeners (IUPAC Nos. 28, 52, 101, 118, 153, 138 and 180) at a certified concentration of 10 µg/ml in isoctane was obtained from Dr. Ehrendorfer. ¹³C₁₂-Labelled standards (IUPAC Nos. 52 and 153; isotopic enrichment 99% ¹³C) were obtained as solutions in nonane at a

Table 2

Certified contents of different PCBs of a sewage sludge (CRM 392) and comparison with results obtained after SFE

PCB congener No.	Certified value (µg/kg dm)±95% CI	SFE (n=3)	Recovery (%)
28	100±10	98, 94, 96	96
52	79±9	85, 78, 76	101
101	134±11	112, 110, 112	83
118	97±12	73, 73, 74	75
153	288±18	286, 280, 283	98
138	268±19 ^a	183, 181, 184 ^b	n.c.
180	313±24	334, 329, 332	106
Mean recovery (%)			93

95% CI: See Table 1.

^a Not certified (indicative value for ΣPCB 138+163).^b In our study PCB 138 was separated from PCB 163.

n.c.=Not calculated.

concentration of 40 $\mu\text{g}/\text{ml}$ from Cambridge Isotope Labs. (CIL, supplier: I. Schneider, Innerberg, Switzerland). Calibration solutions (0.006–0.500 $\mu\text{g}/\text{ml}$) were prepared by appropriate dilution of the stock solution with isooctane. The final concentration of the ^{13}C -labelled internal standards in the calibration solutions was 0.5 $\mu\text{g}/\text{ml}$. OCPs: A standard mixture of chlorinated pesticides [aldrin, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, dieldrin, α -endosulfan, endrin, β -HCH, γ -HCH, heptachlor, heptachlor-epoxide, hexachlorobenzene (HCB)] at a concentration of 10 $\mu\text{g}/\text{ml}$ in isooctane was obtained from Dr. Ehrensdoerfer. As internal standard α -endosulfan- d_4 in crystalline form in a purity of 97% was obtained from CIL (I. Schneider). Calibration solutions were prepared in the same way as for PCBs.

2.4. Extraction by supercritical CO_2

Sea sand (purified by acid and calcined) and copper (fine powder, particle size $<63 \mu\text{m}$) was from Merck and used without further pretreatment. Round filters (diameter 1.1 cm) for SFE were from Macherey-Nagel, Oensingen, Switzerland (article MN 85/220 BF).

SFE was performed on a Hewlett-Packard 7680T extractor with an eight-position thimble-holder for automated sequential extraction. A Hewlett-Packard 1050 quaternary LC pump was used for the delivery of the modifiers to be mixed with the supercritical CO_2 . CO_2 SFC/SFE grade was from Air Liquide, Paris, France. Both instruments were controlled by a Vectra VL2 4/66 personal computer and dedicated SFE software. Before filling the extraction thimble two layers of MN 85 filters were placed just above the cap at the bottom of the thimble. Then 1 to 3 g of dried sludge (1 g for PCBs and PAHs, 3 g for OCPs) was mixed with 1 g of copper powder. For PAHs only, 20% (0.5 g) of deionized water was added to increase the extraction efficiency. The remaining thimble volume was filled with sea sand. Before closing the thimble again two MN 85 filters were placed just below the cap in order to prevent it from being clogged by small sewage particles.

2.4.1. SFE extraction conditions for PAHs

Samples ($n=2$) were extracted in a three-step procedure according to a US Environmental Protection Agency (EPA) method with minor modifications

[8]. Extraction step 1: pure CO_2 at a flow-rate of 2 ml/min, chamber temperature 80°C, pressure 121 bar (density 0.3 g/ml), static extraction time: 10 min, dynamic extraction time: 10 min, extract trapping conditions: nozzle temperature 60°C, trap temperature 5°C, trap packing material octadecylsilane (ODS), elution from the trap with 0.5 ml of toluene (for direct injection into the gas chromatograph) or isooctane (for subsequent clean-up). Extraction step 2: CO_2 with 1% methanol and 4% DCM at a flow-rate of 4 ml/min, chamber temperature 120°C, pressure 335 bar (density 0.63 g/ml), static extraction time: 10 min, dynamic extraction time: 30 min, extract trapping conditions: nozzle and trap temperatures 80°C, no elution from the trap. Extraction step 3: pure CO_2 at a flow-rate of 4 ml/min, chamber temperature 120°C, pressure 335 bar (density 0.63 g/ml), static time 5 min, dynamic time 10 min, extract trapping conditions: nozzle and trap temperatures 80°C, elution from the trap with 0.7 ml of toluene (isooctane for subsequent clean-up) into the same vial (total volume of extract 1.2 ml). Finally the trap was prepared for the next extraction by rinsing with 3 ml DCM–acetone (1:1) and reconditioning with 3.5 ml of toluene or isooctane, respectively. Extracts were either directly submitted to analysis by gas chromatography–mass spectrometry (GC–MS) or to a clean-up step (see Section 2.5) prior to GC–MS analysis.

2.4.2. SFE extraction conditions for PCBs

Sewage sludges ($n=2$) were extracted according to a US EPA method with some adaptations [9]: Extraction step: pure CO_2 at a flow-rate of 2.5 ml/min, chamber temperature 80°C, pressure 305 bar (density 0.75 g/ml), static extraction time: 10 min, dynamic extraction time: 40 min, extract trapping conditions: nozzle temperature 50°C, trap temperature 15°C, trap packing material Florisil, elution from the trap with 1.5 ml of heptane. The trap was prepared for the next extraction by rinsing first with 4.5 ml of acetone–DCM (1:1) and reconditioning with 4 ml of heptane. Final extracts were then directly submitted to GC–MS analysis.

2.4.3. SFE extraction conditions for OCPs

The method was slightly modified based on Ref. [9]. Extraction ($n=1$) was performed with pure CO_2 at a flow-rate of 1 ml/min, chamber temperature

50°C, pressure 299 bar (density 0.87 g/ml), static extraction time: 20 min, dynamic extraction time: 30 min, extract trapping conditions: nozzle temperature 50°C, trap temperature 20°C, trap packing material ODS, elution from the trap with 1.3 ml and 1.2 ml of heptane (two vials). The trap was prepared for the next extraction by rinsing first with 3 ml of acetone–DCM (1:1) and reconditioning with 2.5 ml of heptane. Extracts were then submitted to a multi-step clean-up as described in Section 2.6.

2.5. Clean-up for PAHs and PCBs

Silica gel 40 (particle size 0.063–0.2 mm) from Merck was activated at 300°C for 12 h. Deactivation with deionized water (5%, w/w) was performed 12 h before use. Aluminum oxide 90 (Al₂O₃, particle size 0.063–0.2 mm) from Merck was activated at 110°C for 12 h and deactivated in the same way as for silica gel.

This clean-up procedure has been described elsewhere [10]. Briefly, extracts were purified on a double layer column of silica gel (bottom layer) and aluminum oxide (top layer). The PCB fraction was eluted with a mixture of hexane–DCM (16:1) whereas PAHs were fractionated using hexane–DCM (4:1). After reconcentration, final extracts were redissolved in toluene for PAHs and heptane for PCBs for subsequent GC–MS analysis.

2.6. Clean-up for OCPs

Extrelut NT-3 (diatomaceous earth, 3 g) column was from Merck. C₁₈ solid-phase extraction (SPE) cartridge (500 mg) was from Baker (Supplier: Stehelin, Basel, Switzerland). Florisil (No. 46385) was from Fluka.

SFE extracts were submitted to a multi step clean-up as described in [11]. Briefly, extracts were adsorbed on diatomaceous earth in a Extrelut column and the OCPs eluted with acetonitrile. After evaporation to a small volume, extracts were subjected to SPE on a C₁₈ cartridge and eluted with acetonitrile. Finally, after reconcentration and redissolution in hexane, a Florisil clean-up was performed. Elution of OCPs from the Florisil occurred with a mixture of hexane–DCM (4:1). After reconcentration extracts were dissolved in heptane for GC–MS analysis.

2.7. HRGC and mass spectrometry analysis

2.7.1. PAHs

Extracts were measured using a Hewlett-Packard Model 5890 Series II plus gas chromatograph equipped with a Model 5972A mass-selective detector and a 30 m×0.25 mm I.D., 0.25 μm film thickness, HP5 MS fused-silica column. A deactivated retention gap (2 m×0.53 mm I.D.) was used to protect the analytical column. Samples (2 μl) were injected into an on-column injector system and chromatographed starting at 100°C (1 min hold), 5°C/min to 300°C (20 min hold) using helium as carrier gas at a linear gas velocity of 34.8 cm/s measured at a temperature of 100°C. Analysis was carried out using the injector system in the oven tracking mode to maximise chromatographic resolution. The oven tracking mode keeps the inlet temperature three degrees higher than the oven temperature to optimise repeatability. The MS system was operated under electron impact (EI) ionisation with a 70 eV ionisation voltage. Quantification using the internal standard method, was based on selected ion monitoring (SIM) as follows: naphthalene, naphthalene-d₈ *m/z* 128.0, 136.1, acenaphthylene, acenaphthene and acenaphthene-d₁₀ *m/z* 152.2, 154.2 and 164.3, fluorene *m/z* 166.2, phenanthrene/anthracene/phenanthrene-d₁₀ *m/z* 178.2, 188.3, fluoranthene/pyrene *m/z* 202.2, benz[*a*]anthracene/chrysene/chrysene-d₁₂ *m/z* 228.2, 240.3, benzo[*b/k*] fluoranthenes/benzo[*a*]pyrene/perylene-d₁₂ *m/z* 252.2, 264.4 and indeno[1, 2, 3-*cd*]pyrene/dibenz[*a,h*]anthracene/benzo[*ghi*] perylene *m/z* 276.2, 278.2. The electron multiplier voltage (EMV) was 2200 V absolute, dwell time for the different ion groups was 70 ms. MS temperature parameters: injector 103°C, transfer line 300°C. The MS system was set for highest sensitivity of the analytes using a manual tune (based on autotune) that optimised ions *m/z* 131, 219 and 264.

2.7.2. PCBs

Final extracts were quantitated using a Hewlett-Packard 6890 Model gas chromatograph equipped with a Model 5973 mass-selective detector and a 50 m×0.25 mm I.D., 0.25 μm film thickness, HT-8 fused-silica column (SGE, Infochroma, Zug, Switzerland). A deactivated retention gap (2 m×0.53 mm

I.D.) was used to protect the analytical column. Samples (1 μ l) were injected into an on-column injector system and chromatographed starting at 90°C (1 min hold), 20°C/min to 170°C (7.5 min hold), 3.5°C/min to 285°C and 10°C/min to 300°C (30 min hold) using helium as carrier gas at a linear gas velocity of 27 cm/s. Analysis was carried out using the injector system in the oven tracking mode. The MS system was operated under EI ionisation with a 70 eV ionisation voltage. Quantification using the internal standard method, was based on SIM as follows: IUPAC No. 28: m/z 256, 257.9; No. ^{13}C -52, 52: m/z 302, 304, 290, 291.9; No. 101,118: m/z 325.9, 327.8; No. ^{13}C -153, 153, 138: m/z 371.9, 373.8, 359.9, 361.9; No. 180: m/z 393.8, 395.8. EMV was 1941 V absolute, dwell time for the different ion groups was 150 ms. MS temperature parameters: injector 93°C, transfer line 290°C, quadrupole 106°C, ion source 230°C.

2.7.3. OCPs

For OCPs the same system and column was used as for PCBs. Extracts (1 μ l) were injected into an on-column injector system and chromatographed starting at 100°C then at 10°C/min to 200°C and 4°C/min to 300°C (30 min hold) using helium as carrier gas at a linear gas velocity of 27 cm/s. Analysis was carried out using the injector system in the oven tracking mode. The MS system was operated under EI ionisation with a 70 eV ionisation voltage. Quantification using the internal standard method, was based on SIM as follows: hexachlorobenzene: m/z 281.8, 283.8, 285.8, β -, γ -HCH: m/z 182.9, 218.9, heptachlor: m/z 271.7, 273.8, aldrin: m/z 262.8, 264.8, heptachlor-epoxide: m/z 182.9, 216.9, 236.8, α -endosulfan, α -endosulfan- d_4 , p,p' -DDE, dieldrin: m/z 242.9, 276.8, 338.9, 246.9, 280.8, 342.8, 318, 246, 262.7, endrin: m/z 262.8, 280.9, p,p' -DDD, p,p' -DDT: m/z 165, 235, 237. EMV was 1800 V absolute, dwell time for the different ion groups was 80 ms. MS temperature parameters: injector 103°C, transfer line 290°C, quadrupole 106°C, ion source 230°C. A limit of detection (LOD) of the different OCPs of 1 $\mu\text{g}/\text{kg}$ dm was calculated on the basis of a signal-to-noise ratio of 3 by spiking a sewage sludge at low concentration and subjecting it to the whole sample preparation.

3. Results and discussion

SFE has gained importance as a technique in sample preparation. In particular, the area of environmental analysis has been focused upon as the field where the majority of SFE research has been undertaken. It is generally accepted that SFE has many advantages over common liquid extraction: (i) extraction time is significantly reduced, (ii) the solvent mainly is CO_2 , a non toxic, low-cost medium available in high purity, (iii) its solvation characteristics can be adapted by changing either temperature or pressure of the fluid and, as a consequence, (iv) analytes can be extracted selectively from a matrix [12]. In the following two sections (3.1 and 3.2) extraction efficiency of the SFE for the different target analytes is discussed and concentrations in the sludges of different catchment areas using SFE are presented.

3.1. Extraction efficiency of SFE for PAHs, PCBs and OCPs in sludge samples

3.1.1. PAHs

Very little has been described about applications of the SFE for the extraction of PAHs from sludges [13]. Most of the studies have been focused on soil and sediments [14–18]. Generally polar or non polar modifiers are used during the SFE process, added either to the matrix prior to the extraction or on-line with the supercritical fluid. Moreover procedures, including silylation or acid and water addition [15,18] have been proposed to change the matrix properties such as to obtain a better removal of the PAHs. The SFE, as elaborated by the US EPA [8], is divided into three discrete steps: in step 1 the more volatile PAHs (NAP, ACY, ACE, FLU) are extracted using pure CO_2 at a rather low density and temperature. In step 2 the less volatile PAHs (FLT-BGP) are removed at a higher density and temperature and by adding modifiers (DCM and methanol). A short third step with pure CO_2 is used to purge the whole system of modifier and to prepare it for the next extraction. Before starting the extraction, 20% of water is added to the sludge to occupy polar sites in the matrix and some copper powder in order to eliminate elemental sulfur if present. Extracts are precipitated onto a solid trap (ODS) and then eluted

with toluene or isooctane for subsequent GC–MS analysis or clean-up, respectively. SFE conditions used were validated using a certified reference sludge (CRM 088). Results are presented in Table 1. As can be seen, SFE values are comparable with the certified ones except for PYR and BbF for which significantly higher amounts were measured. For BbF another, only partly resolved PAH isomer (BjF) with the same mass might be the reason whereas for PYR reasons for the higher amount are not obvious. Direct injection of the final extract into the GC system was only partially successful. Depending of the sludge origin quite broad peaks were observed and resolution between closely eluting isomers was not always satisfactory. After a clean-up, very clean extracts and easy to quantitate chromatograms were obtained as demonstrated in Fig. 1. In conclusion, SFE turned out to be a valuable alternative to liquid extraction. For direct GC–MS determination however the clean-up step on the solid trap after SFE has to be improved.

3.1.2. PCBs

A few papers have been published using SFE for the determination of PCBs in sewage sludges [19,20]. Recently a study has compared different extractions techniques for PCBs from sludges [21]. Unfortunately SFE has not been considered in this investigation. Due to the very non polar character of PCBs, SFE conditions are milder than for PAHs. They are extracted in one step, preferably without modifier and at lower temperature and pressure, although keeping density quite high. Moreover, extraction time is shorter compared to SFE for PAHs. Different trapping materials for PCBs were evaluated in detail by Bowadt et al. [20]. Florisil was the sorbent of choice taking into consideration cleanness of the extract and costs compared to ODS and was therefore used in our study. SFE conditions used were again verified using a CRM for PCBs in sludges (Table 2). With SFE, generally well comparable results were obtained except for PCB 118 which showed a recovery of 75% only. PCB 118 belongs to the mono-*ortho*-substituted PCBs, in which the rotation around the central single bond, combining the two biphenyl ring systems, is facilitated and therefore, a more planar configuration can be expected. Planar molecules (PAHs, dioxins for exam-

ple) tend to bind more strongly to the matrix and must be extracted under more rigorous conditions in SFE. This might be the reason why recovery of PCB 118 was somewhat lower compared to the other PCB congeners. Most of the SFE extracts could be analysed directly by GC–MS without a further clean-up (Fig. 2). For three sludges (one A-, B- and C-type sludge) a clean-up improved separation during GC. Summarising our observations, SFE can be recommended as a fast, efficient and selective extraction method for PCBs from sludges. Final extracts mostly do not need a further purification step before GC–MS analysis.

3.1.3. OCPs

Analytical methodologies covering the analysis of OCPs in sewage sludges have been described [22,23]. After liquid extraction, normally several clean-up steps are required to get a measurable extract. SFE extraction and trapping conditions were evaluated by spiking a synthetic matrix (sea sand) with a mixture of OCPs at the 50 ng/g level and calculating their recoveries (Table 3). Results for most of the pesticides were satisfactory with a mean of 91%. Applying the SFE conditions to real sludges it became evident that a direct analysis was not possible after inspection of the chromatograms. Matrix background and interferences made quantification of the target analytes difficult. As we observed that sewage sludge extracts contained high amounts of lipid-like compounds we decided to use a multi-

Table 3
Recovery data of the OCPs using SFE ($n=1$)

OCP	Recovery (%)
Aldrin	56
<i>p,p'</i> -DDD	87
<i>p,p'</i> -DDE	98
<i>p,p'</i> -DDT	121
Dieldrin	97
α -Endosulfan	93
Endrin	111
β -HCH	86
γ -HCH (lindane)	84
Heptachlor	81
Heptachlor epoxide	88
Hexachlorobenzene	95
Mean recovery (%)	91

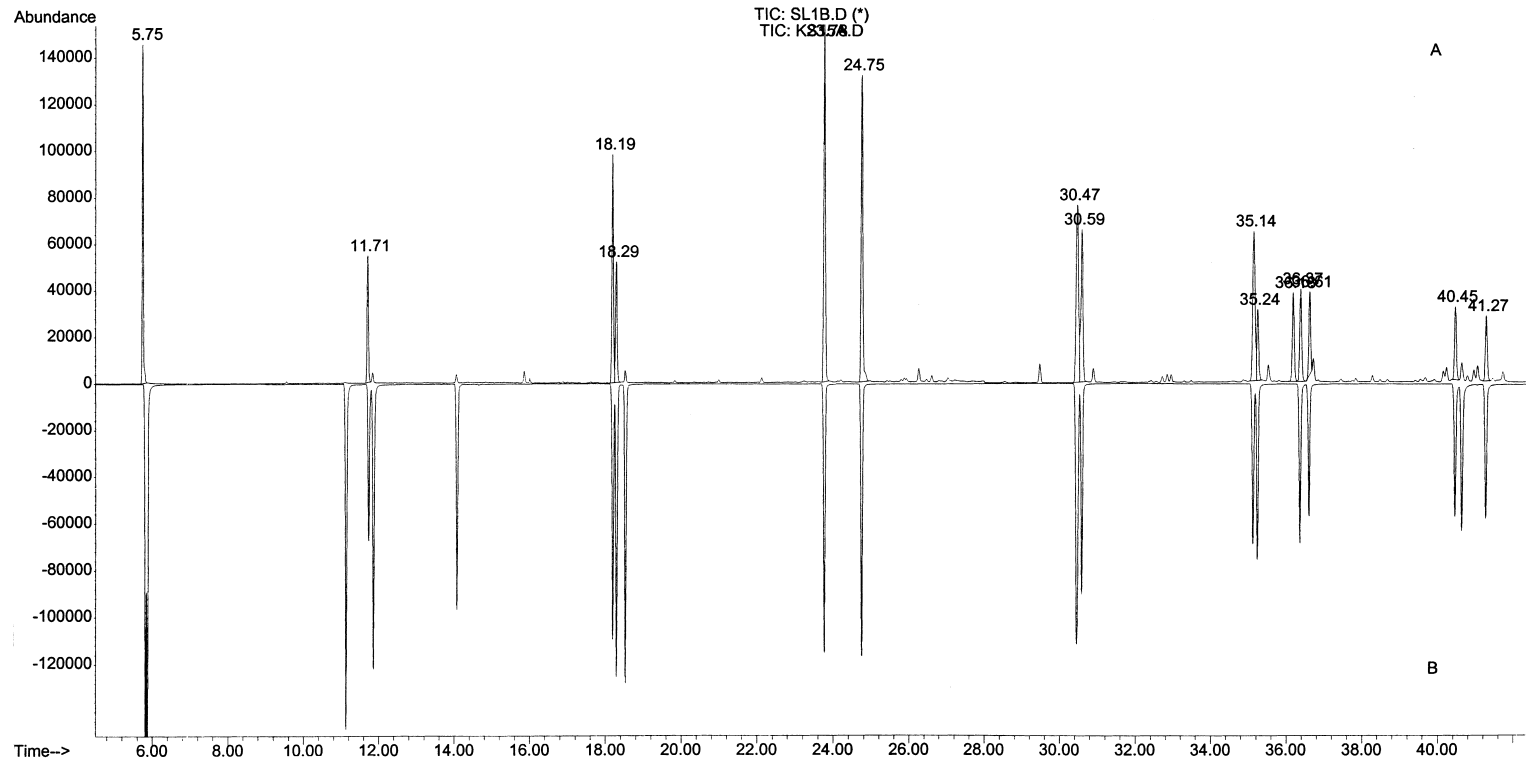


Fig. 1. Total ion chromatogram (TIC) of a PAH containing sewage sludge extract (A) after SFE and a PAH reference mixture solution (B). Time scale in min.

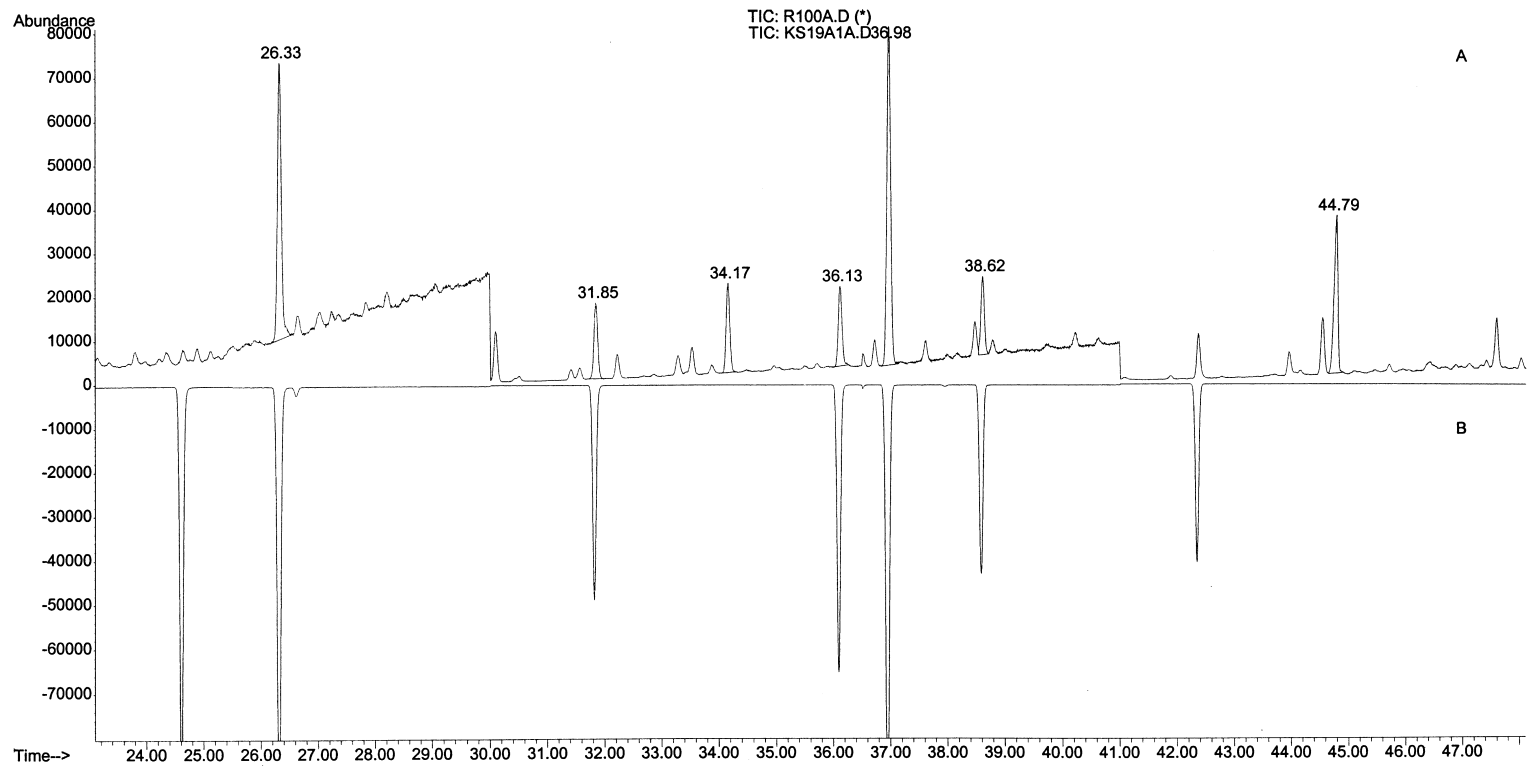


Fig. 2. TIC of a PCB containing sewage sludge extract after SFE (A) and a PCB reference mixture solution (B). Time scale in min.

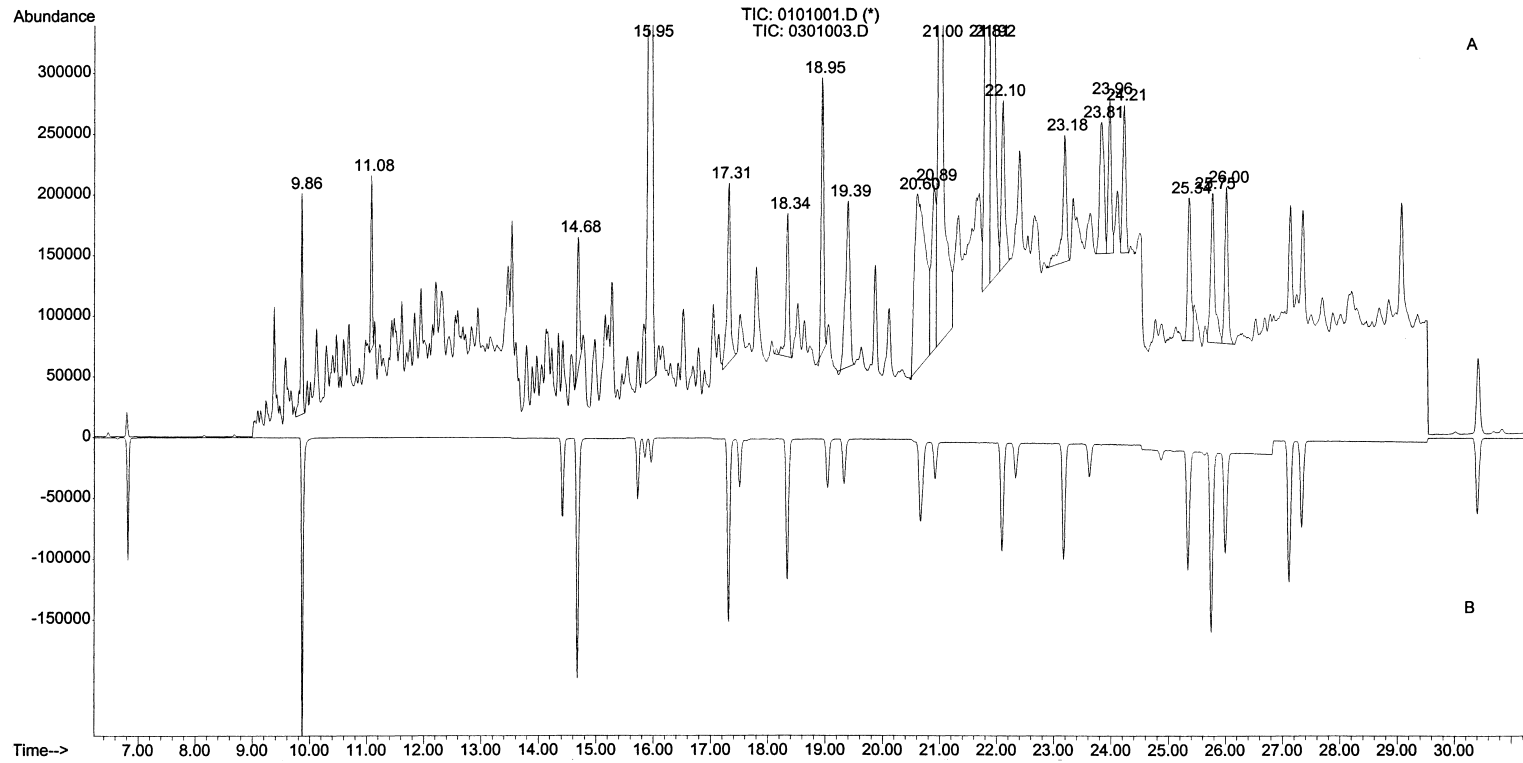


Fig. 3. TIC of an OCP containing sewage sludge extract (A) after SFE and multi-step clean-up and an OCP reference mixture solution (B). Time scale in min.

step clean-up procedure described for lipid rich material [11]. This involves liquid–solid partitioning using diatomaceous earth, clean-up on C₁₈ and final purification on a Florisil column. A final extract containing OCPs is shown in Fig. 3. Therefore, SFE may well be used to extract OCPs rapidly from sludges. However, under the conditions used, other matrix compounds are coextracted which must be removed by a clean-up procedure before GC–MS analysis.

3.2. Concentrations of PAHs, PCBs and OCPs in the sludges from different catchment areas

Three different sludge types, one containing primarily domestic sewage from separate sewer systems (type A) and two others containing lower (type B) and higher (type C) amounts of industrial waste water from combined sewer systems were analysed for the three organic pollutants group described. Contents found are presented in Table 4.

3.2.1. PAHs

Domestic sewage sludges exhibited lower PAH levels compared to the industrial ones. The highest amounts were found in the B-type sludges (maximum 22 mg/kg dm). Often, higher amounts of industrial waste water cause a significant dilution, and this might explain why the C-type sludges revealed somewhat lower PAH levels compared to the B-type ones. Finally, atmospheric inputs through storm water run off for example in the B- and C-type sludges are an important PAH source and contribute to higher PAH concentrations. A comparison with other studies turned out to be difficult as frequently only part of the 16 PAHs were measured. In an earlier study performed in our laboratory concentrations between 1.7 and 15 mg/kg dm Σ 16 PAHs were found with a mean of 6.3 mg/kg dm [10], in good agreement with a value of 6.9 mg/kg dm of the current study. Sometimes a typical representative of the PAHs, for example the highly carcinogenic compound BaP, is used to characterise the contamination degree of PAHs in a matrix. Indeed a strong correlation to the Σ 16 PAHs can be found. According to the regression line, BaP makes roughly 10% of the Σ 16 PAHs and may serve as an indicator for

the PAHs measured. Due to the ongoing emissions of PAHs, these compounds are still present in relevant concentrations in sewage sludges.

3.2.2. PCBs

As for PAHs, PCBs were detected in all sewage sludges. A mean value of 94 μ g/kg dm was calculated. Generally the higher chlorinated PCBs (Cl₅–Cl₇) were dominant while the PCBs containing three or four chlorine atoms were measured in only low amounts. These findings reflect the more pronounced persistence of the higher chlorinated PCBs. A correlation between PCB levels and sludge type was not observed meaning that besides industrial inputs diffuse sources play an important role for the PCB burden in sewage sludges. PCB congener 118, the most toxic of the measured PCBs, was found to be a good indicator of the Σ seven PCBs measured ($r^2=0.92$). As Switzerland does not have any limit values for organic pollutants in sludges, those of Germany were taken as a basis for comparison (200 μ g/kg dm/PCB congener) [24]. All measured PCB congeners were well below this limit value. Compared to an earlier study of us [10] PCB levels in sludges seem to have decreased significantly probably due to the complete ban of these compounds.

3.2.3. OCPs

There are virtually no data available on chlorinated pesticides in Swiss sewage sludges. One study has reported values of lindane (mean 39 μ g/kg dm), HCB (35 μ g/kg dm) and DDT and its metabolites (70 μ g/kg dm) [22]. A recent French study has published guide values for OCPs in sewage sludges (lindane: 100, heptachlor: 10, heptachlor-epoxide: 100, aldrin 50, dieldrin: 300 and DDT: 100 μ g/kg dm) [25]. In our study the most frequent compounds found were DDD/DDE/DDT (10/11; 10 out of 11 sludges), lindane and aldrin (9/11), heptachlor-epoxide (8/11) and α -endosulfan (7/11) (Table 4). Except for heptachlor-epoxide (max. 165 μ g/kg dm) levels of all other compounds were well below the guide values mentioned above. Lindane is still used in minute amounts as seed dressing agent. All other OCPs are not applied in agriculture and levels will therefore further decrease in future.

Table 4
Contents of PAHs, PCBs and OCPs in the different sewage sludges ($\mu\text{g}/\text{kg dm}$)

Compound	Group	Sludge type											
		A1	A2	A3	A4	B1	B2	B3	B4	B5	B6	C1	C2
NAP	PAH	215	73.0	478	37.9	99.5	74.1	155	90.7	83.7	98.3	144	117
ACY	PAH	3.60	4.30	23.8	3.7	17.1	21.2	17.6	16.3	14.1	19.6	22.2	17.7
ACE	PAH	282	34.1	506	21.1	80.9	115	198	60.7	98.8	113	214	92.8
FLU	PAH	72.7	45.6	633	19.4	131	130	195	122	128	153	406	154
PHE	PAH	152	198	1482	115	736	1183	802	858	604	711	1720	943
ANT	PAH	13.6	12.2	64.8	8.8	104	135	68.1	87.4	76.7	79.7	220	69.2
FLT	PAH	171	429	572	141	1611	3767	701	1533	1198	1038	1779	1135
PYR	PAH	153	305	331	139	1336	3260	604	1184	955	901	1404	952
BaA	PAH	76.3	81.9	81.2	54.1	574	1701	209	432	428	410	523	376
CHR	PAH	119	104	85.6	77.6	823	2186	354	587	713	490	868	675
BbF ^a	PAH	226	119	124	108	965	2918	489	733	901	587	1071	841
BkF	PAH	99.2	56.3	69.2	48.8	417	1267	215	315	385	263	440	339
BaP	PAH	150	92.5	103	78.2	705	2093	270	512	598	470	622	428
IND	PAH	156	75.5	82.1	68.3	665	1827	283	472	602	402	560	442
DBA	PAH	34.2	20.0	33.5	19.8	161	422	75	115	142	107	116	108
BGP	PAH	138	75.9	77.1	65.8	620	1542	275	461	517	412	558	434
Sum 16 PAHs	PAH	2060	1726	4745	1006	9046	22 641	4910	7578	7445	6254	10 669	7122
Congener No. 28	PCB	7.8	9.08	1.43	1.88	3.9	2.18	5.7	3.98	9.3	3.94	3.75	2.4
Congener No. 52	PCB	11.6	7.73	4.2	3.83	7.73	5.4	27.2	7.65	7.58	16.6	11.7	8.55
Congener No. 101	PCB	20.2	15.8	8.93	6.83	14.8	10.7	23.8	14.9	9.15	30.7	23	20.1
Congener No. 118	PCB	16.2	12.7	7.05	5.78	14.6	8.25	20.3	12	7.73	28.1	20.9	15.8
Congener No.153	PCB	22.5	18.9	9.45	8.85	19.3	15.1	29.7	26.4	13.3	30.8	30.6	24.9
Congener No. 138	PCB	17.7	14.4	7.35	6.3	15.3	11.2	26	19.1	9.64	28.6	25.4	21.2
Congener No. 180	PCB	11	9.38	4.8	4.28	8.8	9.7	14.9	15.9	6.38	13.7	14.6	13.6
Sum seven PCB congeners	PCB	107.0	88.0	43.2	37.8	84.4	62.5	147.6	99.9	63.1	152.4	130.0	106.6

Hexachlorobenzene	OCP	n.d.	13.1	n.d.	n.d.	2.2	n.d.	n.d.	2.7	1.3	n.a.	n.d.	n.d.
β -HCH	OCP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.9	n.d.	n.a.	n.d.	n.d.
γ -HCH	OCP	34.4	32.9	5.2	6.4	27.6	7.1	n.d.	57	16.1	n.a.	n.d.	2.8
Heptachlor	OCP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.7	n.d.	n.a.	n.d.	n.d.
Aldrin	OCP	4.5	n.d.	6	6.3	11.4	6.4	n.d.	28.9	8.6	n.a.	14.6	7.4
Heptachlor epoxide	OCP	124	165	97.2	142	n.d.	n.d.	7.5	50.8	120	n.a.	n.d.	85.6
α -Endosulfan	OCP	13.8	23.7	1.4	15.7	n.d.	n.d.	n.d.	20.9	19.7	n.a.	n.d.	8.3
Dieldrin	OCP	105	n.d.	n.d.	n.d.	n.d.	n.d.	23.4	41.3	37.4	n.a.	n.d.	n.d.
Endrin	OCP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22.3	n.d.	n.d.	n.a.	n.d.	n.d.
<i>p,p'</i> -DDE	OCP	47.6	62.4	38.5	36.6	n.d.	63.3	76.7	80.1	55.9	n.a.	97.2	35.7
<i>p,p'</i> -DDD	OCP	15.4	35	20.3	17.7	n.d.	36.4	47.9	10.4	42.1	n.a.	27	24
<i>p,p'</i> -DDT	OCP	9.3	16.7	7.5	10.9	n.d.	8.8	10.9	15.3	14.5	n.a.	15.5	11.6

^a Coeluting isomer BjF.

n.d.=Not detected.

n.a.=Not analysed.

4. Conclusions

SFE has proven to be a fast and efficient extraction method for PAHs, PCBs and OCPs. PAH extracts could be measured by GC–MS after a short clean-up step whereas PCBs could be determined directly after SFE. For OCPs direct analysis was not possible. Matrix compounds had to be removed by a multi-step clean-up. Sludge concentrations of PAHs typically reached levels in the low mg/kg dm whereas PCBs and OCPs were found in low µg/kg dm. BaP for the PAHs and congener No. 118 for the PCBs showed to be useful indicators of the Σ of the substances measured. Future studies will concentrate on the improvement of the SFE on-line clean-up for PAHs and OCPs. The use of negative chemical ionisation MS for measuring OCPs in the sludges might be a promising detection technique for this complex matrix.

Acknowledgements

T. Candinas, G. Chassot, T. Kupper, W. Stauffer (IUL) and D. Herren (Interlabor Belp, Switzerland) are greatly acknowledged for their cooperation in this project.

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