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## Optimised accelerated solvent extraction of PCBs and PAHs from compost

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This study is the first thorough method optimisation for accelerated solvent extraction (ASE) of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) from chemically dried compost. For PCBs, optimised solvent composition, temperature, pressure, number of static cycles, duration, and flush volume were as follows: toluene/acetone 1:3 (v/v), 120°C, 2000 psi, 3 × 5 min, and 50%, respectively. Limits of quantification and method precision were between 0.16 and 2.46 µg kg<sup>-1</sup> dw and 6–17% respectively for individual PCBs. Absolute recoveries of isotope-labelled extraction standards used for each of the analytes ranged from 65 to 105% and relative recoveries were between 85 and 99%. The method proved to be robust and was successfully applied to different compost samples.

The optimisation of PAHs extraction was performed and resulted in the following conditions: solvent: hexane/acetone 1/3 (v/v), temperature: 140°C, pressure: 1500 psi, extraction time: 3 × 5 min, and 50% flush volume. Limits of detection and method precision for individual PAHs were between 1.1 and 37.2 µg kg<sup>-1</sup> dw and 12–34% respectively. Absolute and relative recoveries ranged from 24 to 68% and from 85 to 99%, respectively. Optimal extraction conditions for PAHs were more difficult to determine due to the inhomogeneous distribution of PAHs in samples. However, the method appeared to be feasible and suggestions for further improvements are presented.

**Keywords:** ASE; Polychlorinated biphenyls; Polycyclic aromatic hydrocarbons; Sample preparation

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## 1. Introduction

Persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are nowadays ubiquitously present in a variety of solid samples, such as sediment, soil, sewage sludge and compost (i.e., solid residues from the aerobic decomposition process of crude kitchen waste from private households and green waste from garden and public green areas). Among these, the latter is neglected from an analytical point of view. Although there is an increasing awareness among environmental analytical chemists that each matrix requires individual analytical treatment (see, e.g., the EU project Horizontal [1]), compost and digestate (i.e., the product of the anaerobic digestion process of the above mentioned feedstock materials with subsequent aerobic treatment), are, in practice, often implicitly or intentionally regarded as equal to other solids and treated accordingly [2–4]. This equalisation bears the risk of inaccurate quantification of important organic pollutants such as PCBs and PAHs due to varying extraction efficiency of a given analytical technique for different solid matter composition.

One of the most important characteristics of solid samples is organic matter (OM), into which organic pollutants are predominately partitioned. OM content and composition vary widely between different matrices. Typical mass fractions are 0.1 to 5% (median value around 0.5%) in global coastal sediments [5] and <12% in Western European topsoils [6] (assuming 50% organic carbon). In contrast, OM content in compost usually is around 40% (median value,  $n = 170$ , compost database of [7]) and can sometimes be as high as 70% [8]. This high OM content makes it a very challenging matrix for organic pollutant analysis, since a high number of interfering substances and matrix constituents are co-extracted.

Besides the sheer amount of OM, the affinity of analytes to such solid matrices and consequently their extractability are highly dependent on the OM composition [9], which varies in different solid materials and probably also within different compost samples themselves. Moreover, a recent review on organic pollutants in compost and its feedstock illustrated that the analytical protocols used for compost analysis differed widely at all steps of the analytical chain from sampling, sample preparation, extraction and clean-up to analysis [7].

Taking into account the ubiquitous distribution of PCBs and PAHs and their semivolatility, special care is required during sample and extract manipulations to avoid analyte losses and/or (cross-)contamination. In the light of the ongoing discussion about the quality of recycling fertilisers and soil improvers with regard to soil protection, accurate and robust quantification of organic pollutants in compost and digestate is mandated for a proper risk assessment of these products. Here, we report a method that has been specifically adapted and optimised for these analytically challenging matrices.

Accelerated solvent extraction (ASE<sup>TM</sup>, Dionex Corporation, Sunnyvale, CA, USA), also termed pressurised fluid extraction (PFE, see EPA 3545a method), pressurised liquid extraction (PLE, Elsevier Science), enhanced solvent extraction (ESE) or high pressure solvent extraction (HSPE) [10], is a low solvent consuming, fast, effective, and automated extraction technique. It employs high temperature and pressure to increase the contact of the solvent with the matrix and the analyte. Consequently, extraction time and solvent consumption are reduced compared to other extraction techniques such as Soxhlet. (For details on the ASE principles,

see [10–14].) ASE has been chosen for the extraction of a wide range of compounds from various matrices [10, 12, 13, 15, 16]. In particular, it has been used for extraction of PCBs and PAHs from soil [11, 17–22], sediment [23–28] and sewage sludge samples [14, 17, 24, 29]. In comparison with other extraction techniques, such as Soxhlet, supercritical fluid, ultrasonic and microwave-assisted extraction, ASE proved to perform generally equally well or better [17, 18, 20–22, 26, 29].

PCBs and PAHs were previously extracted from compost samples using ASE [30, 31]. However, in these studies samples were lyophilised and extracted with the solvents required by local ordinances and guidelines for lyophilised sludge extraction, i.e., toluene or acetone/hexane 1:1 (v/v) and acetone/dichloromethane 1:1 (v/v). The remaining extraction conditions were set as suggested by Dionex (Application notes 313 and 316). This study presents the first-time optimisation of ASE conditions for the extraction of PCBs from compost including method validation and quality assurance. An optimised and validated method is also presented for PAHs, although it was more difficult to establish due to enhanced sample inhomogeneity compared to PCBs.

## 2. Experimental section

### 2.1 Chemicals and materials

Mixtures containing each of the seven Institute of Reference Materials and Measurements (IRMM) PCBs (i.e., PCB #28, #52, #101, #118, #138, #153, #180) at  $10\ \mu\text{g mL}^{-1}$  in isooctane and each of the respective  $^{13}\text{C}_{12}$ -labeled congeners at  $40 \pm 2\ \mu\text{g mL}^{-1}$  in nonane were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The recovery standard 1,2,3,4-tetrachloronaphthalene (TCN) in nonane was obtained from the same supplier at a concentration of  $100\ \mu\text{g mL}^{-1}$ .

The 16 EPA PAHs (i.e., naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BPE)), their deuterated analogues (i.e., D<sub>8</sub>-NAP, D<sub>8</sub>-ANY, D<sub>10</sub>-ANA, D<sub>10</sub>-FLU, D<sub>10</sub>-PHE, D<sub>10</sub>-ANT, D<sub>10</sub>-FLT, D<sub>10</sub>-PYR, D<sub>12</sub>-BaA, D<sub>12</sub>-CHR, D<sub>12</sub>-BbF, D<sub>12</sub>-BkF, D<sub>12</sub>-BaP, D<sub>12</sub>-IPY, D<sub>14</sub>-DBA, and D<sub>12</sub>-BPE) and the recovery standard indeno[1,2,3-*cd*]fluoranthene were purchased from LGC Promochem (Wesel, Germany). Concentrations are specified in [32].

Acetone, toluene, isooctane, methanol, N-N-dimethylformamide (DMF) and cyclohexane (all suprasolv, for gas chromatography), potassium hydroxide pellets, sodium sulphate, and sulphuric acid (all for analysis) were purchased from Merck (Darmstadt, Germany). Hexane (96%, for pesticide residue analysis) was obtained from Scharlau (Barcelona, Spain). Deionised water was further treated with a Milli-Q Gradient A10 water purification system (Millipore, Billerica, MS, USA). Silanised glass wool was purchased from Macherey & Nagel (Düren, Germany). Hydromatrix (diatomaceous earth) was procured from Varian, Inc. (Walnut Creek, CA, USA). Silica gel 60 (0.063–0.200 mm) for column chromatography was obtained from Merck. Helium and nitrogen gas (both 5.0) were purchased from Pangas (Dagmarsellen, Switzerland).

## 2.2 *Precleaning and conditioning*

Nitrogen was cleaned by a Big Moisture Trap and a Big Supelcarb<sup>TM</sup> HC (Model 23991 and 24564, both Supelco, Bellefonte, PA) in series. Silica gel, sodium sulphate and hydromatrix were baked at 500°C overnight. The activated silica gel was washed with dichloromethane in a separatory funnel and dried applying nitrogen. This silica gel was conditioned acid (60 g silica gel and 40 g sulphuric acid were mixed over night in a TURBULA shaker-mixer (Willy A. Bachofen AG, Maschinenfabrik, Basel, Switzerland)) and neutral (90 g silica gel and 10 g Milli-Q water, same mixing procedure as above). For basic conditioning 168 g potassium hydroxide were dissolved in 700 mL methanol. Activated silica gel (300 g, not washed with dichloromethane) were added and mixed for 90 min at 55°C by the Rotavap without applying vacuum. The silica gel was transferred to a separatory funnel, washed with dichloromethane and dried by applying nitrogen. All glassware was washed in a laboratory washing machine (WA Combi, CE 0044) using the reagents Labopur Assa and Des 1000 (all from Renggli, Rotkreuz, Switzerland) and further cleaned by heat exposure (at least 4 h at 500°C).

## 2.3 *Sample collection and preparation*

It is important that environmental and non-spiked samples are used in optimisation studies, since real samples represent the aging process better [33]. Additionally, spiked samples cannot account for the strongly bound residues and thus might exhibit different extraction efficiencies with varying extraction conditions than real world samples. Compost and digestate were collected from commercial composting and digestion plants in Switzerland. Sample preparation took place within 24 h. For each sample, three to six full profiles of a windrow were collected with a stainless steel rake and shovel. Samples (60 L) were filled in alumina containers (pre-cleaned with acetone and hexane), hermetically closed and transported to the laboratory. The compost and digestate samples were homogenised in a commercial concrete mixer, which was rinsed thoroughly with tap water before use. Subsamples were taken for subsequent analysis, and stones and other discernable debris were removed manually by tweezers.

Cutting and milling of fresh and thus wet compost samples is difficult. Additionally, ASE extraction requires free flowing samples (Dionex application note 313 and 316). Hence, compost containing up to 65% of water had to be dried prior to milling/cutting and extraction. During sample drying, losses and (cross-)contamination need to be prevented. Such artefacts were reported for the ubiquitous and semivolatile PCBs and PAHs when applying common drying techniques such as air drying at ambient [34–36] or elevated temperatures [20, 37], and lyophilisation [20, 38]. Additionally, it was found that the extractability of heavier PAHs and PCBs was lower in dried compared to fresh soil samples [39]. For these reasons, chemical drying was chosen in this study. Since some samples dried with hydromatrix (2:1, w/w) could not be extracted by ASE due to a blocked system possibly caused by insufficient drying capacity, sodium sulphate (1:2, w/w) was selected as drying agent in this study. To compensate for hydration and friction energy, samples were kept on ice before and after mixing by the TURBULA shaker-mixer (7 min). Complying with [4] and [40], samples were milled by a cutting mill (Model SM 2000 Retsch GmbH & Co. KG, Haan, Germany) to <2 mm, and stored in amber glass jars at 4°C until analysis.

For method optimisation and validation, compost samples of three individual compost plants were blended to a representative 'average' compost.

## 2.4 ASE method optimisation

Extraction was carried out using an ASE 200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA). A cellulose filter (Dionex) was placed at the bottom of a 33 mL extraction cell, which had been completely disassembled and rinsed with acetone and hexane prior to use. Frits were cleaned in acetone (10 min) and hexane (10 min) in an ultrasonicator. The cell was filled half way with chemically dried compost or digestate and extraction standard (50 ng of each of the seven  $^{13}\text{C}_{12}$ -labelled IRMM PCBs in nonane ( $5\ \mu\text{g mL}^{-1}$ ) or 200 ng of each of the 16 deuterated EPA-PAHs in isooctane ( $10\ \mu\text{g mL}^{-1}$ )) was added. Thereafter, the cell was filled with the remaining sample and another filter was placed on top. The cell was closed to finger tightness. Typically, a 33 mL extraction cell contained some 4–7 g (dw) of net compost/digestate.

There is a vast literature dealing with the optimisation of ASE parameters (e.g., reviewed in [12, 16]), including some experimental design approaches [18]. Since parameters are interdependent and thought to act differently on different matrices a systematic evaluation of the literature is impossible. However, the solvent type seems to influence the extraction more selectively [13] than pressure and temperature. Consequently, in this study the solvent composition was optimised first. Extractions were conducted using hexane, toluene and dichloromethane with 0%, 25%, 50%, 75% (v/v) of acetone and 100% acetone using the remaining ASE conditions as suggested by Dionex (Application notes 313 and 316 for solid samples: 100°C, 2000 psi (13.79 MPa), prefill mode and purge time 60 s). Several authors found extraction efficiencies increasing with longer extraction time (from 5 to 10 or 15 min [17, 41] or more cycles (two instead of one [17, 24, 42]) Because extraction time was not a limiting factor in this study, three static cycles of 5 min were chosen to assure maximal possible extraction yield. Flush volume was set to 50% because collection vials could not receive a higher volume of extracts especially if toluene was used as a solvent.

After the ideal solvent mixture had been selected, the effect of different extraction temperatures was evaluated in new batches of compost material. The temperatures evaluated were: 80, 100, 120, and 140°C for PCBs and 80, 100, 120, 140, 160, and 180°C for PAHs. The time required to heat up the cell filled with solvent to the extraction temperature depends on the temperature chosen and is set by the system. It varied between five (80°C) and nine (180°C) minutes. The remaining parameters (pressure, number of cycles, extraction and purge time) were kept as mentioned above. The last parameter optimised was pressure. It was varied from 1000 to 2500 psi in steps of 500 psi applying optimised solvent mixtures and temperatures as explained above. The remaining parameters were kept as described above.

## 2.5 Clean-up

ASE extracts usually had an intense dark green to brown color and consisted of two or even three different phases, depending on the extraction solvent. Moreover, precipitates and coagulants were frequently present. Extracts were passed through a funnel filled with sodium sulfate to remove the water phase, which was probably re-extracted from the drying agent under the strong ASE conditions, as well as the solid fractions.

Then they were concentrated in a twelve position Syncore Analyst (Büchi Labortechnik AG, Flawil, Switzerland) using isooctane as a keeper (1 mL) unless toluene was used for extraction. Although there are sophisticated treatments that would allow for fractionation and concomitant clean-up of PCBs and PAH [43], we preferred to stay with traditional, but very robust clean-up techniques. Unfortunately, neither of the two clean-up techniques can handle the respective other compound class: PAHs are destroyed on acid silica gel and PCB recoveries were reduced in the liquid–liquid clean-up [44 and own preliminary experiments].

**PCB:** The clean-up procedure for PCBs was adapted from [45]. The concentrated extracts were applied to open glass columns (0.45 m, 1 cm i.d.) filled with (from bottom to top) glass wool, water free sodium sulphate (2 cm), deactivated silica gel (10% Milli-Q water, 10 cm), potassium hydroxide impregnated silica gel (10 cm), sulphuric acid impregnated silica gel (10 cm), water free sodium sulphate (2 cm), and prewashed with 50 mL hexane. The extracts were eluted with 150 mL hexane at a flow rate of 2–3 drops s<sup>-1</sup> applying nitrogen pressure. Concentration of the eluates to a volume of 4–5 mL was performed with a six position Syncore Analyst (Büchi Labortechnik AG) apparatus. The extracts were transferred into a 10 mL conical reaction vessel (Supelco, Bellefonte, PA, USA), and further concentrated to a final volume of approximately 200  $\mu$ L under a gentle nitrogen stream. The concentrated extracts were spiked with 10  $\mu$ L of the recovery standard (50 ng of TCN in isooctane) and transferred to 200  $\mu$ L GC-vials.

**PAH:** Filtration of the ASE extracts over sodium sulphate was not sufficient to remove the co-extracted water for certain combinations (e.g., hexane/acetone 1:3 (v/v)) of extraction solvents. In such cases, after evaporating solvents at 50°C and 40000 Pa in a twelve position Syncore Analyst, the aqueous phases were liquid–liquid extracted three times with 3 mL cyclohexane each. The extracts were combined and reduced to 1.5 mL in the Syncore Analyst. If no water was present, the extract was reduced directly to 1.5 mL. Clean-up steps by DMF:MilliQ water 9:1 (v/v) liquid–liquid partitioning and over water-deactivated silica gel were performed as described in [32].

## 2.6 GC-MS

PCBs were separated on an Agilent GC 6890 by on-column injection of 1  $\mu$ L of extract on a SGE HT-8 capillary column (50 m, 0.22 mm i.d., 0.25  $\mu$ m film thickness). As a retention gap, a 2 m fused silica capillary column (Agilent, 0.53 mm i.d.) was mounted prior to the separation column. Helium was used as a carrier gas at a constant flow of 1 mL min<sup>-1</sup>. The injector temperature was set to oven track mode (3°C above oven temperature at all times) and the oven temperature was programmed as follows: 1 min at 90°C, to 200°C at 20°C min<sup>-1</sup>, 10 min at 200°C, to 285°C at 3°C min<sup>-1</sup>, to 310°C at 10°C min<sup>-1</sup> and 20 min at 310°C. Detection was performed with an Agilent mass spectrometer 5973 in the electron impact mode with a 70 eV ionisation energy and single ion monitoring. Identification of a given analyte was assured by using two compound-specific ions with a mass ratio similar to the one determined by internal calibration. For all (labelled and unlabelled) PCBs, except for PCB #52, <sup>13</sup>C<sub>12</sub>-PCB #52, and TCN, the quantifier ion was [M]<sup>+</sup>. The qualifier ion was [M + 2]<sup>++</sup> for all corresponding PCBs. For PCB #52, <sup>13</sup>C<sub>12</sub>-PCB #52 and TCN, the quantifier ion corresponded to [M + 2]<sup>+</sup>, and the qualifying ion to [M]<sup>+</sup>, respectively.

Quantification was carried out using the internal standard method. Isooctane mixtures containing different amounts of analytes (5–250  $\text{pg}\mu\text{L}^{-1}$ ) and constant amounts of extraction (and recovery) standards (50  $\text{pg}\mu\text{L}^{-1}$ ) were used for calibration. Occasionally, PCB #118 had to be quantified via the qualifier ion  $[\text{M} + 2]^{+\bullet}$  of the internal standard due to disturbances at the mass of the quantifier ion. In some compost samples, both qualifier and quantifier ion of  $^{13}\text{C}_{12}$ -PCB #138 were interfered and consequently quantification was carried out in reference to  $^{13}\text{C}_{12}$ -PCB #153. These deviations from the normal quantification procedure did not cause any significantly altered results as evidenced for instance with standard addition experiments and inter-laboratory comparison (section 3.1.2). PAH quantification was performed as described in [32], using the internal standard method and deuterated extraction standards for each of the 16 EPA PAHs.

## 2.7 Method validation

The optimised methods were validated thoroughly, i.e., by determination of limits of quantification, linearity and absolute as well as relative recoveries, verification of precision, completeness of the extraction and sample stability. Robustness was tested by triplicate analysis of five different samples that covered the whole range of organic pollutant concentrations and OM content. Additionally, these five samples were also extracted under EPA conditions, to verify the higher extraction efficiencies of the optimised methods. Optimised PAH extraction conditions were tested against the optimised PCB method as well, to check whether PAHs could be extracted concomitantly with PCBs.

## 2.8 Statistics

Every analysis for method optimisation was carried out at least three times and mean and standard variations were determined. If relative standard deviation was unusually high compared to method precision, additional measurements were carried out and outliers were identified by the Grubbs outlier test [46]. To compare different extraction conditions the student's *t*-test or, if there were more than two treatments, the analysis of variance was applied.

# 3. Results and discussion

## 3.1 PCBs

### 3.1.1 ASE parameter optimisation

**3.1.1.1 Solvents** Extraction efficiency of PCBs from compost was affected by the solvent composition (figure 1). Standard deviations were small (max 13%,  $n=3$ ). However, an outlier (hexane 100%:  $\Sigma 7\text{PCBs} = 32.4\ \mu\text{g}\ \text{kg}^{-1}\ \text{dw}$ ) had to be removed from the dataset. Toluene/acetone 1 : 3 (v/v) extracted the significantly highest amounts of PCBs ( $\Sigma 7\text{PCBs} = 29.2\ \mu\text{g}\ \text{kg}^{-1}\ \text{dw}$ ,  $n=3$ ) and was consequently selected as solvent composition for extraction.

Theoretical principles on interactions between analytes and extraction solvents, such as the Hildebrand solubility parameters [47, 48], or octanol–water partitioning



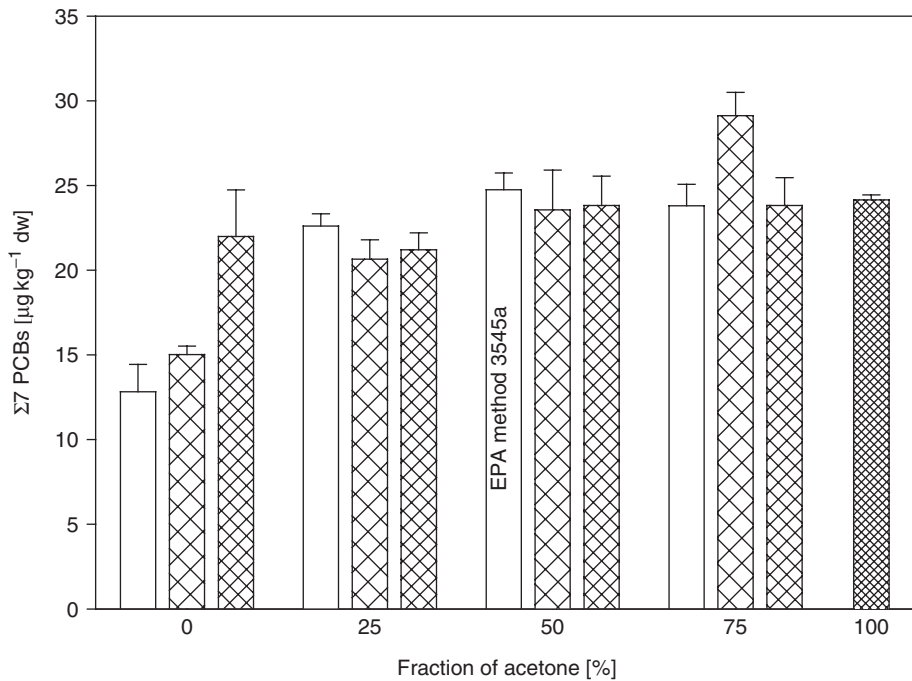


Figure 1. PCB concentrations ( $\Sigma 7$ PCBs,  $\mu\text{g kg}^{-1}$  dw) in compost obtained by ASE using hexane  $\square$ , toluene  $\square$ , dichloromethane  $\square$  with 0% ( $n=3$ ;  $n=3$ ;  $n=3$ ), 25% ( $n=3$ ;  $n=3$ ;  $n=3$ ), 50% ( $n=3$ ;  $n=3$ ;  $n=3$ ), 75% ( $n=3$ ;  $n=3$ ;  $n=3$ ) and 100% ( $n=3$ ) acetone  $\square$  at  $100^\circ\text{C}$ , 2000 psi and  $3 \times 5$  min.

coefficients ( $\log K_{ow}$ ) are of limited use in practice, because they do not consider the influence of the matrix constituents on analyte extractability. This is nicely illustrated here: among the pure solvents dichloromethane, toluene and hexane, the former exhibits the highest extraction efficiency for PCBs, which is in accordance with their close vicinity on the Teas plot [48]. Also, dichloromethane is the most polar of these three solvents and may have an advantageous extracting capacity regarding matrices with high organic matter content [49]. However, acetone seemed to play an overwhelming role as a solvent mediator and results in maximum extractability of PCBs from compost in combination with toluene.

**3.1.1.2 Temperature** Temperature did not show a significant effect on PCB extraction efficiencies (figure 2a). Apparently, already at the lowest temperature applied ( $80^\circ\text{C}$ ), the resulting diffusion rates and solubilities of the analytes, and activation energies of desorption, viscosities and surface tensions of the solvents allowed for efficient extraction. An outlier ( $80^\circ\text{C}$ ,  $\Sigma 7$ PCBs =  $49.3 \mu\text{g kg}^{-1}$  dw) had to be eliminated from the PCB dataset. Since  $120^\circ\text{C}$  extracted slightly higher PCB concentrations, this temperature was chosen for subsequent operations. In general, higher recoveries at higher temperatures have been reported [14, 21, 23, 27, 33, 50] levelling off or decreasing once a specific temperature (mostly over  $100^\circ\text{C}$ ) is exceeded.

**3.1.1.3 Pressure** The effect of pressure on the extraction efficiency was assessed with the optimal solvent combination and temperature (see above). It was found to

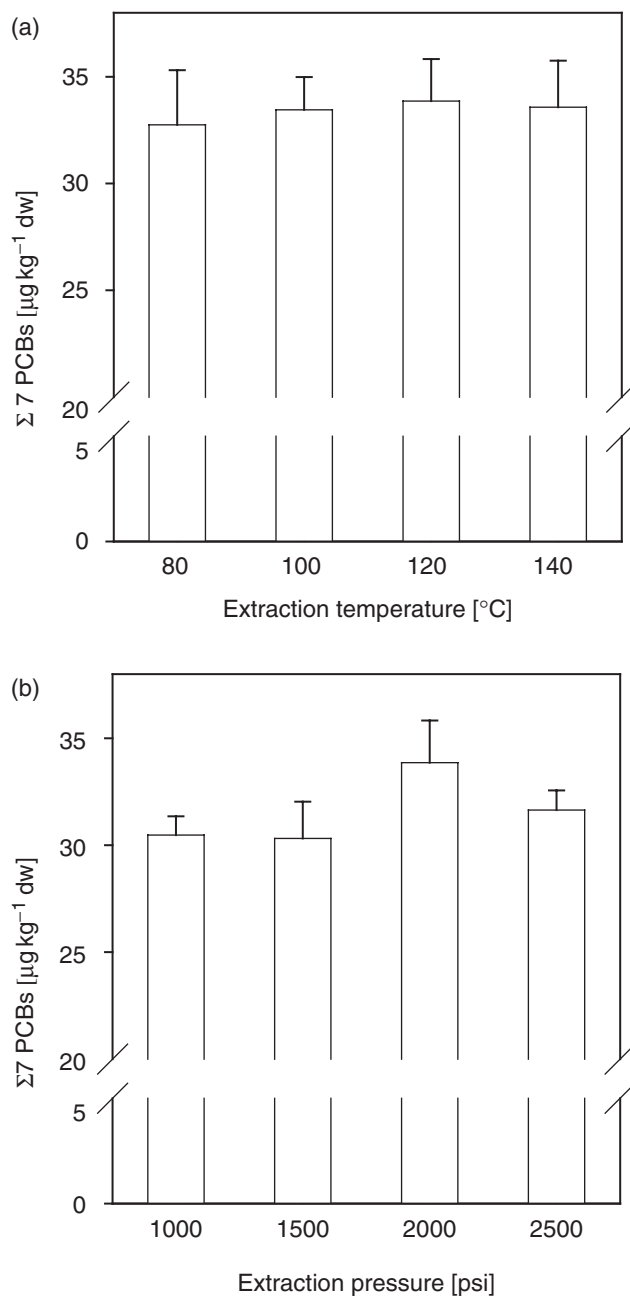


Figure 2. (a) PCB concentrations ( $\Sigma 7$ PCBs,  $\mu\text{g kg}^{-1}$  dw) in chemically dried compost obtained by ASE using toluene/acetone 1:3 (v/v) at 80 ( $n=4$ ), 100 ( $n=4$ ), 120 ( $n=6$ ), 140 °C ( $n=3$ ), 2000 psi and  $3 \times 5$  min; (b) PCB concentrations ( $\Sigma 7$ PCBs,  $\mu\text{g kg}^{-1}$  dw) in chemically dried compost obtained by ASE using toluene/acetone 1:3 (v/v) at 120 °C and at 1000 ( $n=3$ ), 1500 ( $n=3$ ), 2000 ( $n=6$ ) and 2500 psi ( $n=3$ ) and  $3 \times 5$  min.

be marginal (figure 2b) and 2000 psi was selected corresponding to Dionex Application note 316. In general, pressure is reported to influence extraction efficiency little [23, 41] but can be of importance, if wet samples are extracted [50].

**3.1.2 Method validation.** The above described optimised ASE method (solvent: acetone/toluene 3:1 (v/v), temperature: 120°C, pressure: 2000 psi, time: 3 × 5 min, flush volume: 50%) combined with the subsequent clean-up steps was validated with a series of analytical quality control experiments. Specifically, limits of quantification, linearity, precision, absolute and relative recoveries, completeness of extraction, sample stability and robustness, are presented.

*3.1.2.1 Limits of quantification and linearity* Limits of quantification (LOQ, table 1) as determined by a signal to noise ratio of 10 in compost extract chromatograms were between 0.16 and 2.46 µg kg<sup>-1</sup> dw for individual PCBs. Average blank levels were < LOQ. The method proved to be linear from LOQ up to 46 µg kg<sup>-1</sup> dw for individual PCBs.

Table 1. Analytical figures of merit for quantification of PCBs and PAHs in compost.

	Precision (%) <sup>a</sup>	Limit of quantification (µg kg <sup>-1</sup> dw) <sup>b</sup>	Blank levels (µg kg <sup>-1</sup> dw) <sup>c</sup>	Absolute recoveries (%) <sup>d</sup>	Relative recoveries (%) <sup>e</sup>
<b>PCBs</b>	<i>n</i> = 10		<i>n</i> = 5	<i>n</i> = 18	<i>n</i> = 4
PCB #28	nd	2.46 <sup>f</sup>	nd	105 (89–125)	96 (90–97)
PCB #52	8 (2.48)	0.44	0 (0.0–0.2)	65 (57–70)	97 (95–98)
PCB #101	6 (5.95)	0.27	0.18 (0.1–0.5)	93 (82–100)	98 (97–100)
PCB #118	8 (4.74)	0.16	0.13 (0.1–0.3)	97 (88–104)	97 (94–102)
PCB #138	8 (6.68)	0.38	0.15 (0.0–0.7)	na	98 (92–101)
PCB #153	11 (8.59)	0.21	0.18 (0.0–0.8)	90 (78–99)	98 (97–99)
PCB #180	17 (4.03)	0.48	0.05 (0.0–0.4)	87 (79–92)	100 (94–102)
<b>PAHs</b>	<i>n</i> = 8		<i>n</i> = 5	<i>n</i> = 18	<i>n</i> = 4
Naphthalene	22 (22.8)	0.14	3.72 (2.59–3.99)	27 (22–32)	99 (97–103)
Acenaphthylene	12 (3.9)	0.05	0.17 (0.13–1.31)	36 (29–42)	89 (89–90)
Acenaphthene	19 (18.4)	0.16	0.39 (0.26–1.90)	24 (20–29)	89 (89–91)
Fluorene	34 (23.0)	0.08	0.38 (0.22–1.35)	34 (28–39)	89 (88–91)
Phenanthrene	27 (252.5)	0.07	1.61 (0.84–2.13)	43 (36–52)	91 (88–109)
Anthracene	20 (36.3)	0.16	0.11 (0.08–0.42)	43 (35–53)	88 (88–95)
Fluoranthene	16 (576.0)	0.21	0.88 (0.43–1.31)	50 (41–60)	87 (85–104)
Pyrene	17 (426.5)	0.22	0.85 (0.31–1.38)	49 (40–59)	86 (84–103)
Benzo[ <i>a</i> ]anthracene	26 (250.0)	0.08	0.35 (0.10–0.38)	54 (44–65)	85 (83–98)
Chrysene	33 (444.9)	0.27	0.48 (0.05–0.53)	54 (42–76)	88 (83–99)
Benzo[ <i>b</i> ]fluoranthene	21 (369.1)	0.13	0.45 (0.05–1.02)	60 (37–72)	87 (83–92)
Benzo[ <i>k</i> ]fluoranthene	24 (168.9)	0.12	0.19 (0.09–0.67)	65 (51–78)	91 (84–98)
Benzo[ <i>a</i> ]pyrene	31 (209.0)	0.32	0.34 (0.06–0.84)	65 (53–75)	86 (81–96)
Indeno[1,2,3- <i>cd</i> ]pyrene	17 (184.3)	0.17	0.45 (0.00–1.22)	68 (55–76)	95 (90–99)
Benzo[ <i>ghi</i> ]perylene	11 (201.5)	0.36	0.44 (0.25–1.61)	63 (51–71)	95 (91–100)

<sup>a</sup>Relative standard deviation of repeated analysis of an 'average' compost and respective mean concentrations (µg kg<sup>-1</sup> dw) in brackets. <sup>b</sup>Derived from compost sample extract chromatograms (ten times noise). <sup>c</sup>Blank levels extrapolated to compost, median (min, max). <sup>d</sup>Recoveries of the isotope-labelled extraction standards added before extraction, determined by means of a recovery standard added before injection. Spike level was 7–10 µg kg<sup>-1</sup> dw for each PCB and 30–40 µg kg<sup>-1</sup> dw for each PAH, median (min, max). <sup>e</sup>Recoveries of spiked analytes. Fortification levels were as follows: individual PCB: 3.4, 6.7, 10.1 and 13.2 µg kg dw; individual PAH: 63, 127, 190 and 244 µg kg<sup>-1</sup> dw, median (min, max). <sup>f</sup>Derived from fortified (3.4 µg kg<sup>-1</sup> dw) sample, 0.39 µg kg<sup>-1</sup> dw if derived from the lowest calibration standard (5 ng mL<sup>-1</sup>). nd: Not detectable. na: Not available due to interferences.

**3.1.2.2 Precision** Precision (relative standard deviations of ten replicates) was between 6 and 17% for individual PCBs (table 1), which corresponds well with overall method uncertainties as calculated from error propagation at these concentration levels [51].

**3.1.2.3 Recoveries** Recoveries of isotope-labelled extraction standards (absolute recoveries) from compost samples increased with increasing molecular weight and ranged from 65 to 105% (table 1). Interfering substances may have caused relatively high recoveries of PCB #28. However this compound was never detected in real samples. Losses of analytes were compensated by the use of each of their respective  $^{13}\text{C}_{12}$ -analogues as extraction standards, as evident by the relative recoveries (96–100% for all analytes at four different spike levels, table 1).

**3.1.2.4 Extraction completeness** Three sample replicates were re-extracted with the optimised conditions to assess the completeness of the extraction. This secondary extraction accounted for 0% (PCB #52) to 4.5% (PCB #101, #153) of the first one, with a method blank holding between 0% (PCB #28, #52, #118) and 3% (PCB #101). These findings indicate that the extraction is complete under the conditions applied. However, it cannot be excluded that there are non-extractable fractions of PCBs. This could only be verified by adding isotope-labelled compounds to feedstock material and following their fate during a real world composting process.

**3.1.2.5 Sample stability** Samples were stored up to 17 months at 4°C in amber glass jars. Digestate and compost were mixed with sodium sulphate as described above. PCB contents were analysed at the beginning of the experiment ( $n=2$ ), after three ( $n=1$ ), eight ( $n=1$ ) and 17 months ( $n=2$ ). Extraction was performed according to the EPA Method 3545a. Overall, PCB contents were observed to be stable over a period of 17 months. All our samples were analysed within five months.

**3.1.2.6 Robustness** Unfortunately, accuracy of the applied method could not be verified since no certified compost material exists. Application to other types of reference materials such as soils or sediments is not feasible for reasons given above. However, in addition to the multiple extractions performed with compost samples for method optimisation, a selection of samples covering a wide range of properties (sample A–E, table 2) was analysed three times to assess the robustness of the method. The relative standard deviations observed in triplicate analysis were lower than method precision in three samples (sample A–C) and not considerably higher in the remaining two samples (sample D–E). Consequently, the method can be considered as sufficiently robust.

The optimal extraction condition (toluene/acetone 1:3 (v/v), 120°C) is not in accordance with the EPA Method 3545a and the Dionex application note 316 recommending hexane/acetone 1:1 (v/v) and 100°C for the extraction of PCBs from soils, clays, sediments, sludges, and solid wastes. Therefore, the optimised method was tested against the 'second best' (figure 1) EPA Method by parallel analysis of the same samples (sample A–E, table 2). It was found that the optimised conditions extracted PCBs more efficiently from all five samples (figure 3). For all compost samples with a low PCB content (sample A–C) the difference was significant on a 95% level. One outlier (EPA Method, sample C:  $\Sigma 7$  PCBs  $19.68 \mu\text{g kg}^{-1}$  dw) had to be removed from the dataset. This value was confirmed with three additional measurements.

Table 2. PCB and PAH contents of selected compost and digestate samples in Switzerland (all data in  $\mu\text{g kg}^{-1}\text{dw}$ ).<sup>a</sup>

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H	Sample I
<b>PCBs</b>									
Product	Compost	Compost	Compost	Compost	Compost	Compost	Compost	Compost	Digestate
Feedstock	Green waste	Green waste	Green waste	Green waste	Green waste	Green waste	Green waste	Green waste	Kitchen waste
Catchment area	Rural	Rural	Rural	Urban	Rural	Urban	Urban	Urban	Urban
Water content [% w/w]	57	42	34	53	65	47	41	43	51
OM content [% w/w]	25	53	79	40	27	62	43	52	45
No. of analyses/	3/0	3/0	3/0	3/0	3/0	1/0	1/0	1/0	1/0
No. of outliers									
PCB #28	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB #52	0.41 (4%)	1.96 (2%)	1.03 (4%)	5.41 (27%)	4.63 (1%)	0.49	0.73	2.16	1.93
PCB #101	0.83 (4%)	2.57 (1%)	1.92 (3%)	9.38 (10%)	14.38 (9%)	1.26	2.35	5.65	4.42
PCB #118	0.58 (3%)	3.13 (4%)	1.64 (5%)	6.80 (5%)	6.18 (8%)	0.91	1.83	3.87	3.56
PCB #138	1.26 (7%)	2.80 (3%)	2.54 (6%)	10.72 (19%)	25.99 (12%)	1.76	3.85	5.07	7.80
PCB #153	1.80 (6%)	3.46 (3%)	3.02 (4%)	14.32 (11%)	25.77 (14%)	2.26	4.32	8.99	5.25
PCB #180	1.24 (6%)	1.92 (3%)	2.76 (1%)	9.22 (37%)	20.30 (23%)	1.39	2.34	3.27	2.46
$\Sigma 7$ PCBs	6.12 (4%)	15.84 (2%)	12.91 (3%)	55.86 (18%)	97.24 (13%)	8.06	15.42	29.01	25.42
<b>PAHs</b>									
No. of analyses/	2/0	2/0	3/0	4/0	2/0	3/0	6/1	3/0	3/0
No. of outliers									
Naphthalene	14.3 <sup>c</sup> (10%)	90.5 (5%)	11.3 <sup>c</sup> (13%)	16.3 <sup>c</sup> (15%)	27.6 <sup>c</sup> (16%)	5.8 <sup>c</sup> (15%)	8.8 <sup>c</sup> (15%)	72.3 (54%)	148.2 (10%)
Acenaphthylene	1.3 <sup>c</sup> (3%)	2.1 (5%)	2.3 (2%)	2.4 (24%)	3.6 (2%)	0.8 <sup>c</sup> (11%)	1.0 <sup>c</sup> (12%)	18.3 (40%)	14.7 (10%)
Acenaphthene	2.2 <sup>c</sup> (11%)	1.1 <sup>c</sup> (2%)	1.3 <sup>c</sup> (5%)	2.4 (23%)	8.6 (12%)	1.0 <sup>c</sup> (9%)	1.6 <sup>c</sup> (12%)	6.8 (47%)	926.6 (5%)
Fluorene	2.7 <sup>c</sup> (12%)	4.2 (1%)	1.9 <sup>c</sup> (6%)	4.9 (20%)	14.6 (8%)	1.9 <sup>c</sup> (7%)	3.3 <sup>c</sup> (8%)	24.9 (38%)	1215.0 (7%)
Phenanthrene	38.4 (1%)	68.5 (3%)	103.1 (1%)	80.0 (16%)	159.0 (12%)	49.3 (5%)	42.3 (6%)	552.0 (15%)	5776.3 (15%)
Anthracene	5.3 (1%)	5.9 (22%)	3.9 (6%)	10.2 (20%)	24.4 (8%)	3.3 (16%)	3.0 (10%)	108.1 (38%)	984.1 (16%)
Fluoranthene	89.6 (3%)	165.3 (3%)	182.9 (3%)	349.9 (22%)	497.4 (12%)	102.2 (8%)	137.4 (6%)	1160.3 (6%)	3401.7 (19%)
Pyrene	53.0 (6%)	54.4 (9%)	130.8 (3%)	151.4 (45%)	249.2 (15%)	73.1 (11%)	54.6 (8%)	611.1 (13%)	2044.6 (18%)
Benzo[a]anthracene	52.2 (4%)	54.3 (2%)	57.8 (2%)	156.7 (56%)	265.2 (6%)	46.1 (14%)	31.1 (20%)	517.5 (7%)	516.4 (15%)
Chrysene	87.6 (5%)	115.0 (16%)	103.3 (3%)	317.8 (24%)	432.6 (9%)	67.4 (6%)	83.5 (10%)	593.0 (1%)	508.2 (8%)
Benzo[b]fluoranthene	75.5 (5%)	117.1 (18%)	98.2 (6%)	300.4 (19%)	499.8 (13%)	78.8 (14%)	80.9 (13%)	590.6 (10%)	304.7 (4%)
Benzo[k]fluoranthene	30.8 (5%)	64.2 (51%)	49.6 (5%)	123.0 (31%)	225.5 (2%)	35.8 (12%)	26.4 (18%)	337.6 (12%)	160.6 (2%)
Benzo[a]pyrene	51.2 (1%)	70.5 (20%)	57.0 (5%)	155.6 (39%)	263.1 (14%)	54.0 (15%)	31.4 (22%)	413.1 (11%)	252.2 (5%)
Indeno[1,2,3- <i>cd</i> ]pyrene	59.0 (5%)	106.0 (14%)	80.0 (5%)	217.3 (16%)	322.6 (14%)	61.4 (17%)	50.8 (13%)	455.3 (7%)	200.9 (12%)
Benzo[ghi]perylene	61.6 (3%)	99.7 (9%)	105.0 (5%)	223.0 (15%)	294.9 (15%)	73.9 (12%)	59.2 (10%)	461.6 (7%)	197.5 (8%)
$\Sigma 15$ PAHs	624.5 (0.3%)	1018.9 (12%)	988.3 (1%)	2111.2 (25%)	3288.1 (11%)	654.8 (10%)	615.3 (10%)	5922.4 (9%)	16651.7 (13%)

<sup>a</sup>In brackets relative standard deviations, bold if higher than method precision. <sup>b</sup>Including road clippings. <sup>c</sup>Less than 10 times blank level, nd: not detectable.

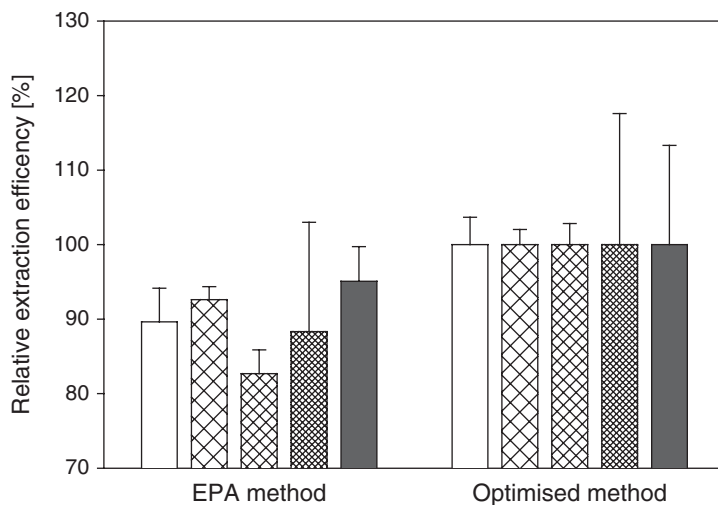


Figure 3. Relative extraction efficiencies and standard deviations of PCBs in different compost samples (□ low PCB concentration, low OM content; ▨ low PCB concentration, medium OM content; ▩ low PCB concentration, high OM content; ▤ medium PCB concentration, medium OM content; ▥ high PCB concentration, low OM content) determined with the EPA method ( $n=3$ ;  $n=3$ ;  $n=5$ ;  $n=3$ ;  $n=3$ ) and the optimised method of this study ( $n=3$ ;  $n=3$ ;  $n=3$ ;  $n=3$ ;  $n=3$ ).

No correlation was found between relative extraction efficiencies and OM content. However, in line with this study, it was reported before that the amount of PCBs might be underestimated using hexane/acetone 1:1 (v/v) [25] for sediments rich in organic carbon.

**3.1.2.7 Inter-laboratory comparison** To further test our method for PCB analysis, an inter-laboratory comparison was carried out in collaboration with the Laboratory of Organic Chemistry at the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in Dübendorf, Switzerland. For this purpose, six samples were analysed in both laboratories. Two sub-samples were taken of the initial compost or digestate sample (60 L), the first being air-dried for seven days and delivered to EMPA, the second being chemically dried and analysed in our laboratory (FAL) as described above. Results of this inter-laboratory study are compiled in table 3. Overall results are in good agreement and correlations highly significant. The 95% confidence intervals of slopes and intercepts included the value one and zero, respectively, indicating no significant difference between the laboratories for all compounds except PCB #52. At low concentrations (positive intercept), PCB #52 contents in EMPA samples were higher than in samples analysed at FAL. This may be due to deposition or (cross-) contamination during air-drying before sample deliverance to EMPA. In the chemically dried samples analysed in our laboratory, the risk for such artefacts was probably lower. However, slopes were  $<1$  for all PCBs except PCB #138, which might indicate that the optimised ASE conditions exhibit a somewhat higher extraction efficiency than Soxhlet extraction using toluene, which was used by the EMPA laboratory. In our laboratory, quantification of PCB #138 had to be carried out in relation to  $^{13}\text{C}_{12}$ -PCB #153 due to interferences in the  $^{13}\text{C}_{12}$ -PCB #138 mass

Table 3. Correspondence of PCB concentrations in compost samples ( $n = 6$ ) determined independently at EMPA<sup>a</sup> and our laboratory (FAL).

PCB <sub>EMPA</sub> = a * PCB <sub>FAL</sub> + b					
	Slope	Confidence interval (95%) of the slope	Intercept	Confidence interval (95%) of the intercept	R <sup>2</sup> of regression
PCB #28 <sup>b</sup>	–	–	–	–	–
PCB #52	0.74	0.52–0.97	0.62	0.05–1.18	0.9541
PCB #101	0.84	0.58–1.11	0.85	–0.76–2.47	0.9506
PCB #118 <sup>c</sup>	–	–	–	–	–
PCB #138	1.26	0.91–1.61	0.64	–3.37–2.10	0.9610
PCB #153	0.80	0.38–1.22	2.08	–0.92–5.01	0.8746
PCB #180 <sup>d</sup>	0.82	0.46–1.20	0.81	–0.66–2.25	0.9547

<sup>a</sup>PCB measurements (unpublished) carried out at Laboratory of Organic Chemistry at the Swiss Federal Laboratories for Material Testing and Research (EMPA). <sup>b</sup>nd at FAL. <sup>c</sup>na at EMPA. <sup>d</sup>One outlier removed.

traces, which may explain the exceptionally high slope of  $>1$ . PCB #28 was quantified by EMPA and ranged from 0.3–1.1  $\mu\text{g kg}^{-1}$  dw, whereas at FAL, it was below LOQ. The more sophisticated clean-up procedure (multiple adsorption chromatography) and detection devices (HRMS vs MS) at EMPA and perhaps some deposition during air drying may account for these differences. However, the PCB #28 contribution to the total sum of the six PCBs analysed at EMPA (#28, #52, #101, #138, #153, #180) was marginal (1–4%).

### 3.2 PAHs

For a given sample, results of repeated PAH analysis varied considerably more than those of PCBs. Even though several outliers were identified and removed from the dataset, relative standard deviations remained high. These observations correspond with reports in the literature: PAH concentrations analysed in ten samples taken from different profiles along a compost windrow were more heterogeneous than respective numbers for PCBs [52]. Measures to counteract this observed PAH inhomogeneity are reduction of particle size, larger sample volumes, or increased numbers of replicate analyses. However, the first is difficult to achieve with chemically dried materials and the second would require ASE hardware not available at our laboratory. Moreover, the particle size  $<2$  mm used in this study is in accordance with recommendations for soil, sludge and compost analysis [4, 40]. In the literature, particle size is apparently largely neglected or at least not reported upon (for compilation, see [7]). However, recent studies within the EU Project Horizontal addressed this problem systematically and suggested smaller particle size for compost and waste [1]. Despite these adversities, we decided to carry out a full method optimisation with increased numbers of replicate analyses where necessary, knowing that certain analytical figures of merit might suffer.

#### 3.2.1 ASE parameter optimisation

**3.2.1.1 Solvents** Repeated analysis of PAH contents using different solvent composition varied considerably and three outliers (hexane:  $\Sigma 15\text{PAHs} = 2048 \mu\text{g kg}^{-1}$  dw; hexane/acetone 3:1 (v/v):  $\Sigma 15\text{PAHs} = 4759 \mu\text{g kg}^{-1}$ , and toluene/acetone 3:1 (v/v):  $\Sigma 15\text{PAHs} = 5530 \mu\text{g kg}^{-1}$ ) were eliminated from the dataset by the Grubbs outlier test.

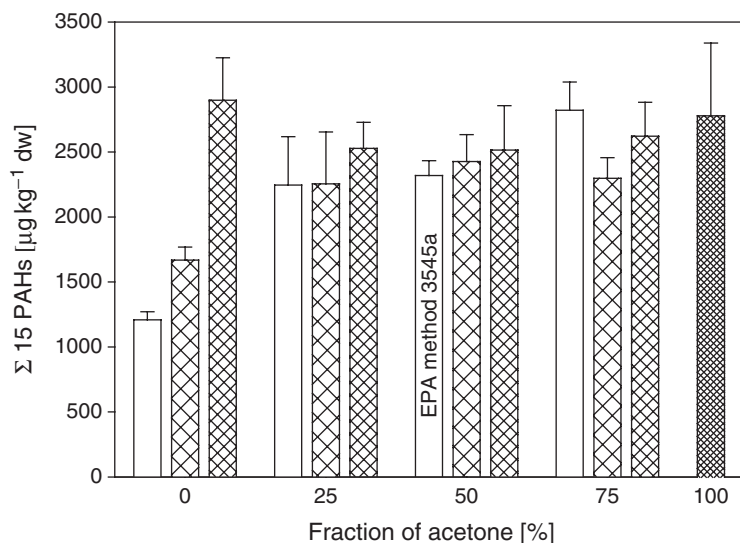


Figure 4. PAH concentrations ( $\Sigma 15\text{PAHs}$ ,  $\mu\text{g kg}^{-1}\text{ dw}$ ) in compost obtained by ASE using hexane  $\square$ , toluene  $\boxtimes$ , dichloromethane  $\boxplus$  with 0% ( $n=3$ ;  $n=3$ ;  $n=3$ ), 25% ( $n=4$ ;  $n=4$ ;  $n=3$ ), 50% ( $n=3$ ;  $n=3$ ;  $n=3$ ), 75% ( $n=3$ ;  $n=3$ ;  $n=3$ ) and 100% ( $n=3$ ) acetone  $\blacksquare$  at 100°C, 2000 psi and  $3 \times 5$  min.

The corresponding concentrations were confirmed by one (100% hexane) or two (hexane/acetone 3:1 (v/v) and toluene/acetone 3:1 (v/v)) additional analyses. Still, relative standard deviations remained high ( $n=3-4$ , max 20%). Highest PAH concentrations were obtained using 100% dichloromethane (figure 4). However, hexane/acetone 1:3 (v/v) was chosen as an alternative and equally powerful solvent combination, since it poses fewer hazards to the environment and might be more versatile towards different composts and digestates. Moreover, various authors found a combination of polar and non-polar solvents to be more effective for organic pollutant extraction, especially if wet samples were extracted [13, 22, 33, 42, 50].

If toluene was used for PAH extraction absolute recoveries were found to be very low (max 30%), which may be due to  $\pi$ -electron interactions of residual toluene with PAHs competing with DMF during the extract clean-up. To overcome this problem, the clean-up succession was changed: deactivated silica column followed by the DMF clean-up. In this case, the final extract was again dried over sodium sulphate in order to ensure removal of water prior to GC-injection.

**3.2.1.2 Temperature** Increasing amounts of PAHs were extracted with increasing temperature up to 140°C (figure 5a). One data point (100°C,  $\Sigma 15\text{PAHs} = 5143 \mu\text{g kg}^{-1}\text{ dw}$ ) was identified as an outlier and removed from the dataset. At 160°C the total concentration detected decreased, but at 180°C it was roughly at the 140°C level again. Similar results were observed in another study [21] for PAH concentrations in soil but interpretation of this phenomenon remains unclear. Standard deviations were much higher and selectivity lower at 180°C than at lower temperatures as observed by others [21, 42]. Therefore, 140°C was chosen as an optimal extraction temperature.



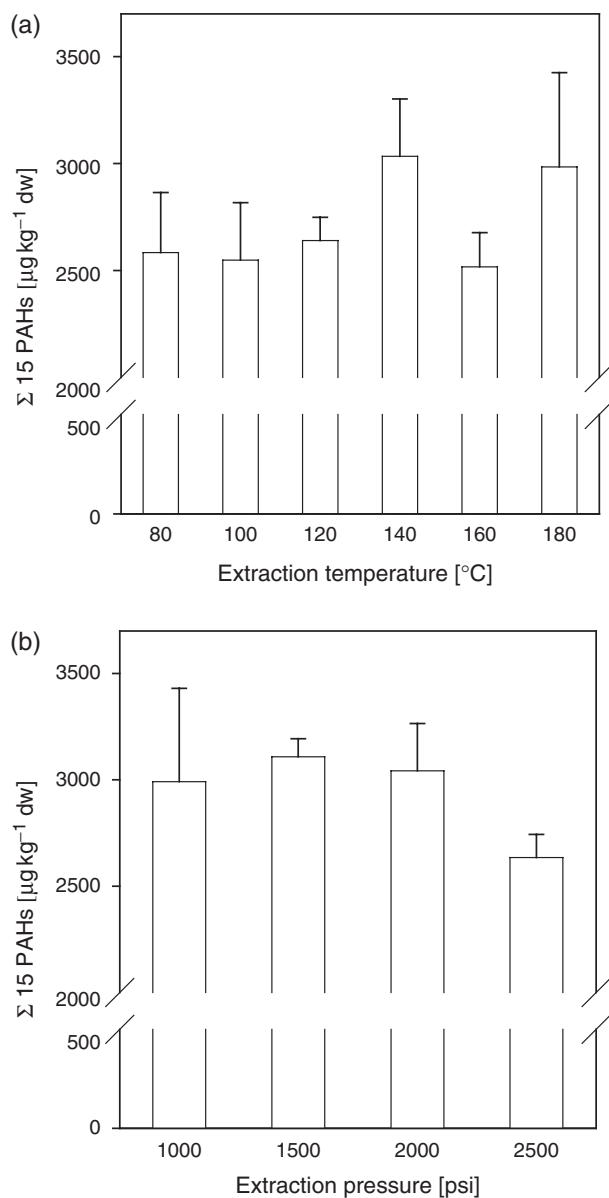


Figure 5. (a) PAH concentrations ( $\Sigma 15 \text{ PAHs}$ ,  $\mu\text{g kg}^{-1} \text{ dw}$ ) in chemically dried compost obtained by ASE using hexane/acetone 1 : 3 (v/v) at 80 ( $n=4$ ), 100 ( $n=4$ ), 120 ( $n=4$ ), 140 ( $n=4$ ), 160 ( $n=4$ ) and 180 °C ( $n=4$ ), 2000 psi and 3  $\times$  5 min; (b) PAH concentrations ( $\Sigma 15 \text{ PAHs}$ ,  $\mu\text{g kg}^{-1} \text{ dw}$ ) in chemically dried compost obtained by ASE using hexane/acetone 1 : 3 (v/v) at 140 °C at 1000 ( $n=4$ ), 1500 ( $n=5$ ), 2000 ( $n=6$ ) and 2500 psi ( $n=3$ ) and 3  $\times$  5 min.

**3.2.1.3 Pressure** A lower pressure (1500 psi) than in the EPA Method 3545a was selected for PAH extraction (figure 5b) to reduce co-extraction of matrix constituents. An outlier had to be removed from the PAH dataset (1500 psi,  $\Sigma 15 \text{ PAH} = 3967 \mu\text{g kg}^{-1} \text{ dw}$ ).

### 3.2.2 Method validation

**3.2.2.1 Limits of quantification and linearity** LOQ for individual PAHs were between 0.05 and 0.60  $\mu\text{g kg}^{-1}$  dw. For all PAHs except ANT, average blank levels were > LOQ (table 1). These compounds exhibited average blank concentrations of 0.11 and 3.72  $\mu\text{g kg}^{-1}$  dw, respectively, which increases their LOQ to 1.1 and 37.2  $\mu\text{g kg}^{-1}$  dw (LOQ > 10 times average blank concentrations). These blank levels may seem high and are explained by the limited capacity of a 33 mL ASE cell only accommodating 4–7 g dw of chemically dried compost. Still, these ten fold blank concentrations were, with the exception of NAP, considerably lower than those usually observed in real samples (table 2). The method proved to be linear from LOQ up to 438  $\mu\text{g kg}^{-1}$  dw for individual PAHs.

**3.2.2.2 Precision** Precision for individual PAHs was between 12 and 34% ( $n=8$ ; table 1), which is slightly higher than acceptable (11% at the ppm level, 30% at the ppb level, [51]), and than for analysis for PCBs in compost/digestate. This higher variation is explained by the heterogeneity of the samples (see above).

**3.2.2.3 Recoveries** Recoveries of isotope-labelled extraction standards (absolute recoveries) increased with increasing molecular weight as found for PCBs (24–68%, table 1). These recoveries are comparable to those found in [32], especially if taking into account that in the optimised method of this study, samples had to be concentrated once more, i.e., after water removal by liquid–liquid extraction. Losses of analytes were compensated by the use of each of their respective deuterated analogues as extraction standards. Consequently relative recoveries of PAHs were good (85–99%, table 1). Quantification of DBA was difficult since absolute recoveries of the extraction standards were low (1–5%). DBA recoveries were also low in method blanks. During routine analysis DBA recoveries increased, which might be explained by shorter silica gel columns used. However, DBA usually accounts for 1–2% of the total sum of the 16 EPA PAHs [7, 32] only, and consequently, the sum of 15 PAHs is reported in this study.

**3.2.2.4 Extraction completeness** PAH re-extracts were 1% or 2% (for all PAHs heavier than FLT) to 25% for NAP of the first extract, whereas method blanks accounted for 0% (for all PAHs heavier than PHE) to 22% (NAP) of the first extraction. These findings indicate that the extraction is complete under the parameters applied. However, as explained above for PCBs, a non-extractable fraction of PAHs in compost cannot be excluded.

**3.2.2.5 Sample stability** PAH contents were analysed in compost and digestate dried with sodium sulphate at the beginning of the experiment ( $n=3$ ), after three ( $n=1-2$ ), eight ( $n=1-3$ ) and 17 months ( $n=2$ ). Extraction was performed according to the EPA Method 3545a. PAH concentration in all samples remained apparently constant up to eight months, but decreased by 26–51% ( $\Sigma 15\text{PAHs}$ ) over a period of 17 months. In this study, all samples were analysed within five months.

**3.2.2.6 Robustness** Due to the lack of certified reference material for compost, robustness was tested by triplicate analysis of five compost/digestate samples with varying PAH and OM contents (sample C, F–I, table 2). Relative standard deviations were higher than method precision for some single compounds (table 2) and an outlier

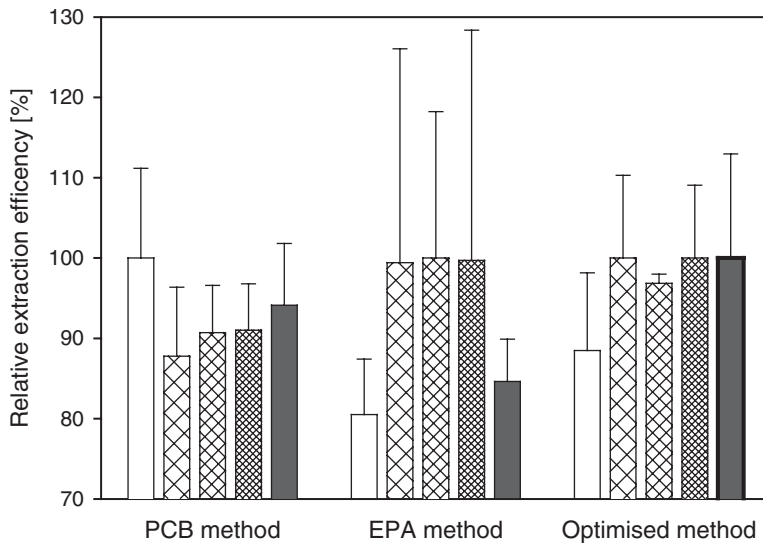


Figure 6. Relative extraction efficiencies and standard deviations of PAHs in different compost samples (□ low PAH concentration, low OM content; ▨ low PAH concentration, medium OM content; ▩ low PAH concentration, high OM content; ▤ medium PAH concentration, medium OM content; ■ high PAH concentration, medium OM content) determined with the optimised PCB ( $n=3$ ;  $n=3$ ;  $n=5$ ;  $n=3$ ;  $n=3$ ), the EPA ( $n=5$ ;  $n=6$ ;  $n=6$ ;  $n=6$ ;  $n=3$ ) and the optimised PAH method of this study ( $n=3$ ;  $n=5$ ;  $n=3$ ;  $n=3$ ;  $n=3$ ).

had to be removed from the dataset (sample G:  $\Sigma 15\text{PAH} = 1779.1 \mu\text{g kg}^{-1} \text{dw}$ ). Based on this observation, along with varying PAH results in repeated analysis as observed above (optimisation of ASE parameters, samples stability), PAH measurements were always confirmed by a second analysis. If results varied more than method precision for five or more individual PAHs, two additional analyses were carried out and outliers removed by the Grubbs outlier test.

The optimised PAH extraction method was tested against the EPA Method 3545a as well as compared with the optimised PCB method for the five samples used in the robustness test (see above). None of these extraction methods appeared to be consistently most efficient for all five compost samples (figure 6), which is in contrast to the results for PCBs (see above and figure 3). However, for three out of five samples, the method optimised in this study was found to extract most PAHs. The average relative extraction efficiency for the optimised method presented here ( $n=5$ ) was at 97%, for the other two methods it was at 93%. However, the differences between the extraction methods were not significant except for sample F. In general standard variations remained high even though outliers (EPA: sample F:  $\Sigma 15\text{PAH} = 1570.7 \mu\text{g kg}^{-1} \text{dw}$ , optimised PAH method: sample G: see above) were removed by the Grubbs outlier's test. Due to the slightly higher relative extraction efficiencies and the lower relative standard variations, it is suggested to prioritize the method optimised in this study over the EPA method and the method optimised for PCB extraction (see above). Even though the latter would allow for co-extraction of PCBs and PAHs, the overall time reduction would be minimal, since no joint clean-up could be found with acceptable recovery rates.

Besides inhomogeneity, differences in speciation of PAHs in various composts could be a reason of varying extraction efficiencies of the tested methods. PAHs originating from aerial deposition (both from particle bound aerosols or condensation from gas phase) probably ask for other extraction conditions than PAHs associated or incorporated into, e.g., charcoals, or ashes, which are occasional input materials of compost. However, molecular marker analysis [32] of the composts in question gave no indication of different PAH sources. Furthermore, PAHs might be differently sequestered during composting and/or digestion depending on the management of the process.

### 3.3 Initial results from a nation wide compost screening study

Sample selected specifically for the robustness test were also analysed for the other group of organic pollutants resulting in a comprehensive dataset covering a wide range of compost regarding input material, degradation process and catchment area (table 2). Almost all single PCB values (sample F–I) were slightly below the literature values [7] which may be explained by generally decreasing amounts of PCBs in the environment [53, 54]. PAH concentrations (sample A, B, D, F) were well within the literature values [7]. Different feedstocks (with or without kitchen waste), degradation processes (digestion versus composting), and catchment areas (rural vs urban) did not seem to have a systematic influence on PCB and PAH concentrations. However, further measurements are required and currently carried out in our laboratory in order to assess possible influences of these parameters more systematically.

## 4. Conclusions

This work illustrates that different types of solid samples need to be considered individually when establishing methods for the quantification of organic pollutants in such matrices. Although international harmonisation efforts for the establishment of standardised methods are needed (e.g., for sample preparation and storage, method reporting, etc.), uniform treatment of different types of solid samples is not adequate. Furthermore, sampling and drying have to be carried out very carefully if ubiquitous and semivolatile compounds such as PCBs and PAHs are to be analysed. Chemical drying is an alternative technique which does not expose the sample to high temperature nor to ambient air. ASE is an efficient, low solvent consuming and fast extraction technique well suited for the extraction of PCBs and PAHs from chemically dried compost/digestate. The method presented here proved to be a rugged and reliable routine screening tool for the analysis of PCBs. Method optimisation for the extraction of PAHs from compost was more difficult due to sample inhomogeneity and further larger efforts in sample preparation and extraction would be needed to reduce this problem. However, the performance of the method presented is still suitable to assess the sources and fate of PAHs in compost.

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## References

- [1] CEN. Horizontal. Available online at: <http://www.ecn.nl/horizontal/> (accessed 01 September 2005).
- [2] Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten (VDLUFA). Bestimmung von polyzyklischen aromatischen Kohlenwasserstoffen in Böden, Klärschlämmen und Komposten, VDLUFA-Schriftenreihe 39/1995. VDLUFA-Verlag Darmstadt (1995).
- [3] US Environmental Protection Agency (US EPA). Method 3545A, Pressurized Fluid Extraction (PFE). Available online at: <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3545a.pdf> (accessed 01 September 2005).
- [4] Österreichisches Normungsinstitut. Bestimmung von polyzyklischen aromatischen Kohlenwasserstoffen (PAK) in Böden, Klärschlämmen und Komposten, ÖNORM L 1200. Wien: Österreichisches Normungsinstitut, Vienna (2002).
- [5] K. Seiter, C. Hensen, J. Schröter, M. Zabel. *Deep-Sea Res. Pt. I-Oceanog Res.*, **51**, 2001 (2004).
- [6] European Soil Bureau Network. Topsoil organic carbon content. Available online at: <http://eusoils.jrc.it/website/octop/viewer.htm> (accessed 01 September 2005).
- [7] R.C. Brändli, T.D. Bucheli, T. Kupper, R. Furrer, F.X. Stadelmann, J. Tarradellas. *J. Environ. Qual.*, **34**, 735 (2005).
- [8] T. Krauss. Untersuchung zu organischen Schadstoffgehalten in Komposten. PhD thesis, Fakultät für Chemie und Pharmazie der Eberhard-Karls-Universität Tübingen (1994).
- [9] W.L. Huang, P.A. Ping, Z.Q. Yu, H.M. Fu. *Appl. Geochem.*, **18**, 955 (2003).
- [10] E. Björklund, T. Nilsson, S. Bøwadt. *Trac.-Trends Anal. Chem.*, **19**, 434 (2000).
- [11] S. Lundstedt, B. Van Bavel, P. Haglund, M. Tysklind, L. Öberg. *J. Chromatogr. A*, **883**, 151 (2000).
- [12] L.J. Fitzpatrick, O. Zuloaga, N. Etxebarria, J.R. Dean. *Rev. Anal. Chem.*, **19**, 75 (2000).
- [13] H. Giergielewicz-Możajska, L. Dabrowski, J. Namiesnik. *Crit. Rev. Anal. Chem.*, **31**, 149 (2001).
- [14] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L. Porter, N. Avdalovic, C. Pohl. *Anal. Chem.*, **68**, 1033 (1996).
- [15] J.R. Dean, G.H. Xiong. *Trac.-Trends Anal. Chem.*, **19**, 553 (2000).
- [16] L. Ramos, E.M. Kristenson, U.A.T. Brinkman. *J. Chromatogr. A*, **975**, 3 (2002).
- [17] P. Popp, P. Keil, M. Moder, A. Paschke, U. Thuss. *J. Chromatogr. A*, **774**, 203 (1997).
- [18] O. Zuloaga, N. Etxebarria, L.A. Fernández, J.W. Madariaga. *Trac.-Trends Anal. Chem.*, **17**, 642 (1998).
- [19] N. Saim, J.R. Dean, M.P. Abdullah, Z. Zakaria. *Anal. Chem.*, **70**, 420 (1998).
- [20] J.D. Berset, M. Ejem, R. Holzer, P. Lischer. *Anal. Chim. Acta*, **383**, 263 (1999).
- [21] A. Hubert, K.D. Wenzel, M. Manz, L. Weissflog, W. Engewald, G. Schuurmann. *Anal. Chem.*, **72**, 1294 (2000).
- [22] J. Hollender, B. Koch, C. Lutermann, W. Dott. *Intern. J. Environ. Anal. Chem.*, **83**, 21 (2003).
- [23] M.M. Schantz, J.J. Nichols, S.A. Wise. *Anal. Chem.*, **69**, 4210 (1997).
- [24] E. Björklund, S. Bøwadt, T. Nilsson, L. Mathiasson. *J. Chromatogr. A*, **836**, 285 (1999).
- [25] C. Bandh, E. Björklund, L. Mathiasson, C. Näf, Y. Zebühr. *Environ. Sci. Technol.*, **34**, 4995 (2000).
- [26] D. Martens, M. Gfrerer, T. Wenzl, A. Zhang, B.M. Gawlik, K.W. Schramm, E. Lankmayr, A. Kettrup. *Anal. Bioanal. Chem.*, **372**, 562 (2002).
- [27] L. Dabrowski, H. Giergielewicz-Możajska, M. Biziuk, J. Gaca, J. Nameisnik. *J. Chromatogr. A*, **957**, 59 (2002).
- [28] E. Martinez, M. Gros, S. Lacorte, D. Barcelo. *J. Chromatogr. A*, **1047**, 181 (2004).
- [29] C. Miège, J. Dugay, M.C. Hennion. *J. Chromatogr. A*, **995**, 87 (2003).
- [30] C. Marb, C.M. Scheithauer, R. Köhler. Kompostierung von Bioabfällen mit anderen organischen Abfällen, Teil A: Untersuchung von Bio- und Grünabfallkomposten auf ihren Gehalt an Schwermetallen und organischen Schadstoffen. Bayerisches Landesamt für Umweltschutz, Augsburg (2001).
- [31] C. Vergé-Leviel. Les micropolluants organiques dans les composts d'origine urbaine: étude de leur devenir au cours du compostage et biodisponibilité des résidues après épandage des composts au sol. PhD thesis, Institut National Agronomique Paris-Grignon (2001).
- [32] T.D. Bucheli, F. Blum, A. Desaulès, Ö. Gustafsson. *Chemosphere*, **56**, 1061 (2004).
- [33] J. Gan, S.K. Papiernik, W.C. Koskinen, S.R. Yates. *Environ. Sci. Technol.*, **33**, 3249 (1999).
- [34] R.E. Alcock, C.J. Halsall, C.A. Harris, A.E. Johnston, W.A. Lead, G. Sanders, K.C. Jones. *Environ. Sci. Technol.*, **28**, 1838 (1994).

- [35] J. Chiarenzelli, R. Serudato, G. Arnold, M. Wunderlich, D. Rafferty. *Chemosphere*, **33**, 899 (1996).
- [36] I.T. Cousins, H. Kreibich, L.E. Hudson, W.A. Lead, K.C. Jones. *Sci. Total Environ.*, **203**, 141 (1997).
- [37] W. Auer, H. Malissa. *Anal. Chim. Acta*, **237**, 451 (1990).
- [38] M. Söderström, K. Nylund, U. Järnberg, T. Alsberg, L. Asplund. *Chemosphere*, **58**, 355 (2005).
- [39] W. Wilcke, M. Krauss, G. Barancikova. *J. Plant Nutr. Soil Sci.*, **166**, 93 (2003).
- [40] G. Zethner, B. Götz B, F. Amlinger. Qualität von Kompost aus der getrennten Sammlung. Monographien; Band 133. Federal Environment Agency Vienna (2000).
- [41] X.W. Lou, H.G. Janssen, C.A. Cramers. *Anal. Chem.*, **69**, 1598 (1997).
- [42] M. Jánková, M. Tomaniová, J. Hajšlová, V. Kocourek. *Anal. Chim. Acta*, **520**, 93 (2004).
- [43] C. Bandh, R. Ishaq, D. Broman, C. Näf, Y. Ronquistnii, Y. Zebühr. *Environ. Sci. Technol.*, **30**, 214 (1996).
- [44] M. Mandalakis, Y. Zebühr, Ö. Gustafsson. *J. Chromatogr. A*, **1041**, 111 (2004).
- [45] L.M. Smith, D.L. Stalling, J.L. Johnson. *Anal. Chem.*, **56**, 1830 (1984).
- [46] F.E. Grubbs. *Technometrics*, **11**, 1 (1969).
- [47] L.J. Fitzpatrick, J.R. Dean. *Anal. Chem.*, **74**, 74 (2002).
- [48] W.C. Scott, J.R. Dean. *J. Environ. Monit.*, **5**, 724 (2003).
- [49] M. Oehme. Quality Assurance Concept – Analysis of PAH, PCB and dioxins in soil. Swiss Agency for the Environment, Forest and Landscape (SAEFL), Bern (2000).
- [50] B.E. Richter. *J. Chromatogr. A*, **874**, 217 (2000).
- [51] S. Kromidas, Handbuch Validierung in der Analytik. Wiley, Weinheim (2000).
- [52] J. Breuer, G. Drescher, H. Schenkel, K. Schwadorf. Hohe Kompostqualität ist möglich. Räumliche und zeitliche Variabilität von Kompostinhaltsstoffen. Abschlussbericht, Universität Hohenheim, Landesanstalt für Landwirtschaftliche Chemie. Ministerium für Umwelt und Verkehr, Stuttgart (1997).
- [53] S. Painter, C. Marvin, F. Rosa, T.B. Reynoldson, M.N. Charlton, M. Fox, L. Thiessen, J.F. Estenik. *J. Great Lakes Res.*, **27**, 434 (2001).
- [54] S.N. Meijer, W.A. Ockenden, E. Steinnes, B.P. Corrigan, K.C. Jones. *Environ. Sci. Technol.*, **37**, 454 (2003).