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Pressurised liquid extraction–comprehensive two-dimensional gas chromatography for fast-screening of polycyclic aromatic hydrocarbons in soil

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Abstract

Pressurised liquid extraction (PLE) was applied to the extraction of polycyclic aromatic hydrocarbons (PAHs) from contaminated soils from Husarviken in Stockholm, Sweden. The extraction step was followed by conventional gas chromatography (GC), comprehensive two-dimensional gas chromatography (GC × GC) (both with flame ionisation detection) and gas chromatography–quadrupole mass spectrometry (GC–MS) analysis. Qualitative and quantitative aspects of the results are considered. Qualitatively, results from all chromatographic analyses are in good agreement, and PLE provides a reliable extraction technique with all PAHs extracted in one extraction step; no carry over was observed. With respect to PAH quantification, some variability in results was noted, with better agreement in PAH concentrations for GC and GC × GC measurement, as compared to GC–MS. GC analysis compares favourably with GC × GC apart from the few exceptions where peaks are not fully resolved from other co-extracted analytes, which compromises GC-FID measurement. For example, acenaphthene shows a much higher concentration when measured by GC-FID, demonstrating the superior separating powers of GC × GC; the latter is the preferred technique if precise and accurate quantification of analytes are required. GC–MS results compare reasonably with GC × GC for low-molecular mass PAHs but not for high-molecular mass PAHs; results for GC–MS are consistently higher than those for GC × GC for high-molecular mass PAHs. Since PLE–GC × GC is proposed as a broad screening tool, the demand for precise quantification may be relaxed in the present situation. GC × GC has the added advantage of providing chemical structural information within the two-dimensional contour presentation. Reproducibilities for GC × GC results (peak area) and ^2t_R were acceptable with relative standard deviations (R.S.D.) of 8 and 1%, respectively (at the mg/kg level), and good repeatability within samples was achieved.

Keywords: Soil; Gas chromatography, comprehensive two-dimensional; Pressurized liquid extraction; Polynuclear aromatic hydrocarbons

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) consist of several hundred individual compounds, containing at least two condensed rings, which are produced most importantly via anthropogenic combustion as a major

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source of PAH inputs to the environment [1]. PAHs are dispersed in the atmosphere and deposited onto terrestrial, lacustrine and marine surfaces. The amounts of PAH in soils are of importance because of both their possible toxicity to humans, and their effects on soil organisms and plants [2]. PAHs in soils are usually present as complex mixtures that may vary vastly in the relative abundance of individual components. High concentrations are often found in areas where coal, coal tar, or heavy petroleum distillates have been produced or used, e.g. at gas works sites, metal or bitumen production sites, and wood impregnation sites where creosote has been used. Many of these sites are situated in populated areas and future use of the land for housing and offices may require site remediation. Such remediation projects may require fast-screening tools to estimate PAH levels in soil with some accuracy, which may be complicated by low concentration levels of some PAHs, especially those that are toxic. Co-extracted compounds (e.g. petroleum hydrocarbons, asphaltenes, polar PAH degradation products etc.) may interfere during subsequent gas chromatographic (GC) analysis, especially since they may be present at much higher concentrations than the target PAHs, and are difficult to remove from the PAH fraction, unless sophisticated clean-up procedures are employed.

It is essential to carefully balance sampling, extraction and clean-up, with subsequent instrumental analysis for any PAH screening procedure. As Jennings stated [3], 'no degree of sophistication in the final analysis can compensate for or correct compositional changes caused by sampling errors . . . '. Initial stages of sampling, clean-up, pre-concentration, extraction etc. must therefore be undertaken with utmost care. Pressurised liquid extraction (PLE) has been gaining popularity as an extraction technique compared to conventional techniques such as liquid–liquid extraction, soxhlet extraction, ultrasonic extraction etc., which use large amounts of solvent, and are tedious, time-consuming and labour intensive. The more recent techniques of supercritical fluid (SFE) and microwave-assisted extraction (MAE) have been compared with PLE, detailing their advantages, disadvantages and listing selected applications [4,5]. Applications of PLE have been steadily increasing since its introduction in 1995, when it was commercially available as the accelerated solvent extraction (ASE) method. PLE utilises organic solvents to (sequentially) extract analytes from a range of sample matrix with control of temperature and pressure as the main factors. Other variables affecting extraction efficiency are extraction time, solvent choice, solvent volume, and sample load. PLE has been used to extract persistent organic pollutants (PAHs, PCBs, and pesticides) from soil, marine sediment and urban dust [6–8]. A clean-up step prior to instrumental analysis is often necessary, adding complexity and cost, possibly compromising solute recovery, whilst reducing throughput of a screening technique. PLE offers the possibility of in-cell clean-up, and so reliable and exhaustive extraction, with removal of matrix interferences or even fractionation of analytes, may be achieved [9,10].

For PAH analysis, the instrumental technique might be required to report all extracted components in the sample, or alternatively a subset of target or representative components might be chosen. A separate consideration is reduction in detection limits, analysis time and cost. Thus, the analysis goals will direct the types of information obtained by, and implementation strategy of, the method. Comprehensive two-dimensional gas chromatography (GC × GC) addresses all the above. GC × GC is now a proven, powerful, and reliable tool for the analysis of complex samples, such as the analysis of petroleum [11,12], essential oils [13], environmental pollutants such as PCBs and pesticides [14,15], volatile organic compounds [16], fatty acids [17], forensic [18] and drugs analysis [19]. Unlike multidimensional gas chromatography (MDGC), where only part of the sample undergoes a second dimension GC separation, GC × GC achieves a comprehensive, continuous separation of all components on two directly-coupled columns (^{1}D and ^{2}D) which are of a different selectivity. A modulation device between the two columns transfers analytes from ^{1}D to ^{2}D in a pulsing-type mechanism. Depending on the modulator, compression and focusing of solute may arise, normally through heating [20] or cooling processes [21,22]. Valves may also be used to sample components from ^{1}D to ^{2}D [23]. New modulators continue to be developed [24]. Whilst it has been stated that gas chromatography–quadrupole mass spectrometry (GC–MS) is today the most powerful tool in the identification of PAHs [25] the major drawback of GC–MS is the difficulty in separating positional isomers, and their often similar mass

spectra. Phillips recognised that for extremely complex mixtures, quantification by GC × GC may be more reliable than by GC–MS because interfering substances are better separated [20]. GC × GC can be used in separating essential oil enantiomers [26] and for separating PCB isomers [14], and so should be applicable for high-resolution PAH congener analysis.

GC × GC clearly has significant qualitative analysis advantages over single column analysis. Quantitative aspect of GC × GC data have been considered in several studies [11,15,16,24,27–29], and a general paper on data treatment of GC × GC has been published [30]. Synovec and co-workers have used chemometric approaches to resolve co-elutions of GC × GC peaks [31]. However, to the authors' knowledge, comparison of quantitative data across conventional GC, GC × GC and GC–MS techniques has not been reported. By combining PLE with GC, GC × GC and GC–MS analysis, this paper demonstrates the performance of in-cell PLE cleanup and GC × GC as a fast, multi-residue screening tool for environmental pollutants (PAHs) in soil samples.

2. Experimental

2.1. Samples and standards

PAH contaminated soil was collected at a former gasworks site at Husarviken in Stockholm, Sweden. Information on the treatment of the soil is described elsewhere [6,10]. The soil is reported to have a total organic content of 5.5%. All solvents used (acetone, *n*-hexane, dichloromethane and toluene) were of analytical grade. Silica gel 60 (0.063–0.20 mm) and anhydrous sodium sulphate ($NaSO_4$) were purchased from Merck (Darmstadt, Germany). The silica was deactivated with 10% water (w/w), and $NaSO_4$ was activated for 48 h at 550 °C before use.

The target analytes in the soil extracts were quantified using a reference standard mixture containing 24 PAHs (SRM 2260, National Institute of Standards and Technology, Gaithersburg, MD, USA). A mix of fully deuterated PAHs (naphthalene, acenaphthene, fluorene, anthracene, chrysene, pyrene and benzo[g]fluoranthene) was obtained from Cambridge Isotope Laboratories (sample ES-2003; Andover, MA, USA), and was used as internal standard for GC–MS analyses.

2.2. Extraction technique

Pressurized liquid extraction was performed using an ASE 200 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) equipped with 11 ml stainless steel extraction cells. Three soil extraction methods were used.

- *Method 1*: Extraction cells were lined with filter paper, packed with $NaSO_4$, followed by 1 g soil, mixed homogeneously with 5 g of $NaSO_4$, and topped with $NaSO_4$. ASE was performed using hexane/acetone (1:1 v/v) as the extracting solvent. All extractions were performed at 150 °C and 14 MPa, using one dynamic (7 min) and two static extractions (5 min each), a flush volume of 100%, and purge time of 60 s. The extracts were evaporated to 1 ml and underwent open column silica chromatography clean-up using 8 mm i.d. columns filled with 5 g silica. Samples were quantitatively transferred to the columns using 2 × 1 ml solvent and were eluted with 5 ml *n*-hexane (waste fraction) then 15 ml *n*-hexane:dichloromethane (3:1 v/v). Eluate was carefully evaporated to dryness using N_2 blow down and the residue was reconstituted in 1 ml of toluene. This method employs post-extraction clean-up.
- *Method 2*: In-cell cleanup was attempted by packing the extraction cells as above, but 4 g of silica was added before the soil/$NaSO_4$ (1:5) mixture. Hexane was used as the extracting solvent, and the extracts were then treated as described above but with the column chromatography step clean-up omitted.
- *Method 3*: This was performed as Method 2 but using hexane/dichloromethane (3:1, v/v) as a stronger extracting solvent.

Method 1 may be classified as an exhaustive non-selective PLE technique, and the other two methods as selective PLE techniques with simultaneous extraction and clean-up. All extractions were carried out in triplicate. Extraction cells were re-extracted to determine if analytes were totally removed in the first extraction.

2.3. Chromatographic systems

An Agilent 6890 GC (Agilent Technologies, Burwood, Australia) fitted with a longitudinally

modulated cryogenic system (LMCS; Chromatography Concepts, Doncaster, Australia) was used for all GC and GC × GC analyses. The flame ionisation detector was operated at 330 °C, at a data collection frequency of 50 Hz. Agilent Chemstation software was used for data acquisition and instrument control. Auxiliary event controls were used to instruct the modulation control system to commence modulation at a precise time. Splitless injections (2 min) were used throughout. One microlitre aliquots were injected using an auto-sampler. GC–MS analyses were conducted in the laboratory of the Swedish authors [6]. A Fisons GC 8000 Top gas chromatograph coupled to an electron impact (EI) Fisons MD800 mass spectrometer was used for all GC–MS analysis, operated in the splitless injection mode.

2.4. Column sets and GC conditions

Two column sets were used for GC × GC experiments. Column set 1 comprised of a BPX5 (5% phenyl-dimethyl polysilphenylene-siloxane phase; low polarity) primary column; 30 m × 0.25 mm i.d. × 0.25 μm film thickness (d_f), directly-coupled to a BPX50 (50% phenyl-dimethyl polysilphenylene-siloxane phase; moderately polar) second column of 1.2 m × 0.1 mm i.d. × 0.2 μm d_f. The second set consisted of the same primary column as column set 1, with a LC-50 (liquid crystalline phase) second column of 0.8 m × 0.1 mm i.d. × 0.1 μm d_f. All columns were from SGE International (Ringwood, Australia) with the exception of LC-50 (J&K Environmental Ltd., Canada). Standards and extracts were analysed using a temperature program of 80 °C, hold for 2 min, then heated to 330 °C at a ramp rate of 8 °C/min with a carrier gas head pressure of 16 psi. For GC–MS, a 30 m × 25 mm i.d. × 0.25 μm d_f DB-5 capillary column (J&W Scientific, Folsom, CA, USA) was used. The MS was operated in full scan mode for identification and single ion monitoring (SIM) mode for quantification.

2.5. Quantification of chromatographic data

Quantification of GC and GC × GC results was performed based on peak areas using the external standard technique. Peak area and retention time information obtained with the Chemstation software were exported as a csv-file. An in-house program based on Matlab was then used to collate GC × GC peaks by modulation period, calculate the first and second dimension retention times (from which the analytes can then be accurately identified) and report total peak areas. Contour plots were prepared using the Transform software (Fortner Research, VA, USA). For GC–MS, the target compounds were identified by mass spectra and by comparison of GC-retention data with reference standards. Quantifications were performed using the internal standard technique, utilizing peak areas in samples and reference standards.

3. Results and discussion

3.1. Evaluation of PLE methods

The performance of the three different PLE methods was evaluated using GC–MS analysis of purified soil extracts. Method 1 has previously been validated by comparing it with traditional Soxhlet extraction using certified reference materials [6]. Thus, Method 1 may be regarded as a reference method against which the other two methods can be compared. In that study, the reference material used was “CRM 103-100 PAH contaminated soil” (US EPA, RTC Laramie, WY, USA). Results obtained using the PLE method were within the certified range, with recoveries by using PLE between 95 and 120% of the certified values. Fig. 1 compares results of the three methods, and it is apparent that there is no significant difference in PAH levels between the three extraction methods. Thus, the selective PLE methods with sorbent filled cells perform equally well as the non-selective PLE where a post extraction column chromatography clean-up step is employed. Previous work has shown that in-cell or a post-PLE clean-up steps are required for interferent removal for environmental PAH samples [6]. The selective methods are preferable as they combine extraction and clean-up in one step, and yield extracts ready for GC–MS analysis. However, for low level samples, concentration to a lower volume is recommended. Of the two selective PLE methods, Method 2 is preferable as it produces cleaner (less coloured) extracts. On the other hand, Method 3 would be expected to co-extract carbonyl-substituted PAH derivatives, a class of relatively persistent PAH transformation products that are

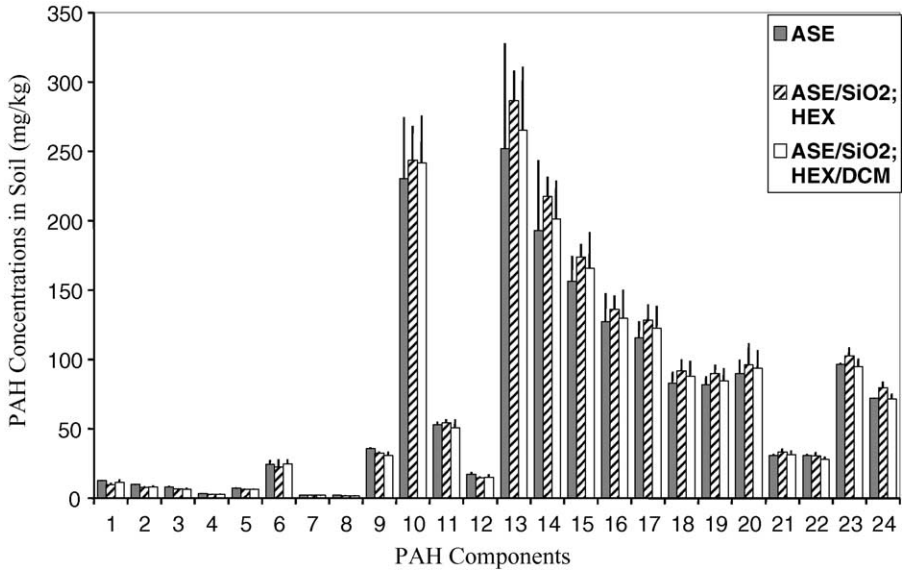

Fig. 1. Comparison of three PLE methods employed for the analysis of Husarviken soil sample extract. Method 1: PLE followed by open column chromatography clean-up; Method 2: PLE with in-cell clean-up using *n*-hexane; Method 3: PLE with in-cell clean-up using *n*-hexane/dichloromethane. Analysis of extracts was by using GC–MS. Error bars are included in the figure.

of some environmental concern (data for this class are not shown here). Method 3 may be the method of choice if both classes of compound are of interest. Further studies are underway to validate the method for carbonyl-PAH analysis.

All PLE methods seem to provide exhaustive extraction of the soil samples, as neither GC, GC × GC nor GC–MS detected any significant amounts of PAHs in re-extracted sample cells. According to GC–MS data, less than 0.10 mg/kg of any individual PAH compounds was recovered during the re-extraction step.

3.2. GC × GC Analysis of soil extracts

The GC × GC colour plots for all the extracts were similar with no significant differences between the extracts that underwent column chromatography cleanup and in-cell clean-up and so interferences are equally well removed by all three methods. Fig. 2 shows the colour plot presentation of a soil extract (Method 2) analysed using the BPX5/BPX50 column set. The PAHs in the extracts were identified by comparing the first and second dimension retention times (^1t_R and ^2t_R) for the reference standards and the soil sample. Alternatively, superimposing the colour plot of the PAH standards onto the colour plot of the soil sample gave excellence coincidence of peak positions. The PAHs in the sample can be easily singled out and identified as illustrated in Fig. 2; the PAHs corresponding to the 24 standard components in the soil sample are numerically labelled. Table 1 lists the 24 PAHs that were present in the standard; all could be identified in the soil extracts. All PAHs were resolved chromatographically from co-extracted analytes and interferences, with the exception of two pairs of PAHs. Benzo(b)fluoranthene and benzo(k)fluoranthene (peaks 17 and 18) and indeno(c,d)pyrene and dibenz(a,c)anthracene (peaks 22 and 23) co-eluted at about 30 and 34 min, respectively (refer to the colour plot, Fig. 2). A second column set (BPX5/LC50) was used in an attempt to improve the resolution of the two pairs of PAHs. It successfully resolved indeno(c,d)pyrene from dibenz(a,c)anthracene, but not the benzofluoranthenes. However, the narrow temperature range and high bleed of the liquid crystal column is a severe drawback. As the lesser upper temperature limit of the BPX5/LC50 column set resulted in excessive retention times, the BPX5/BPX50 column set was still preferred.

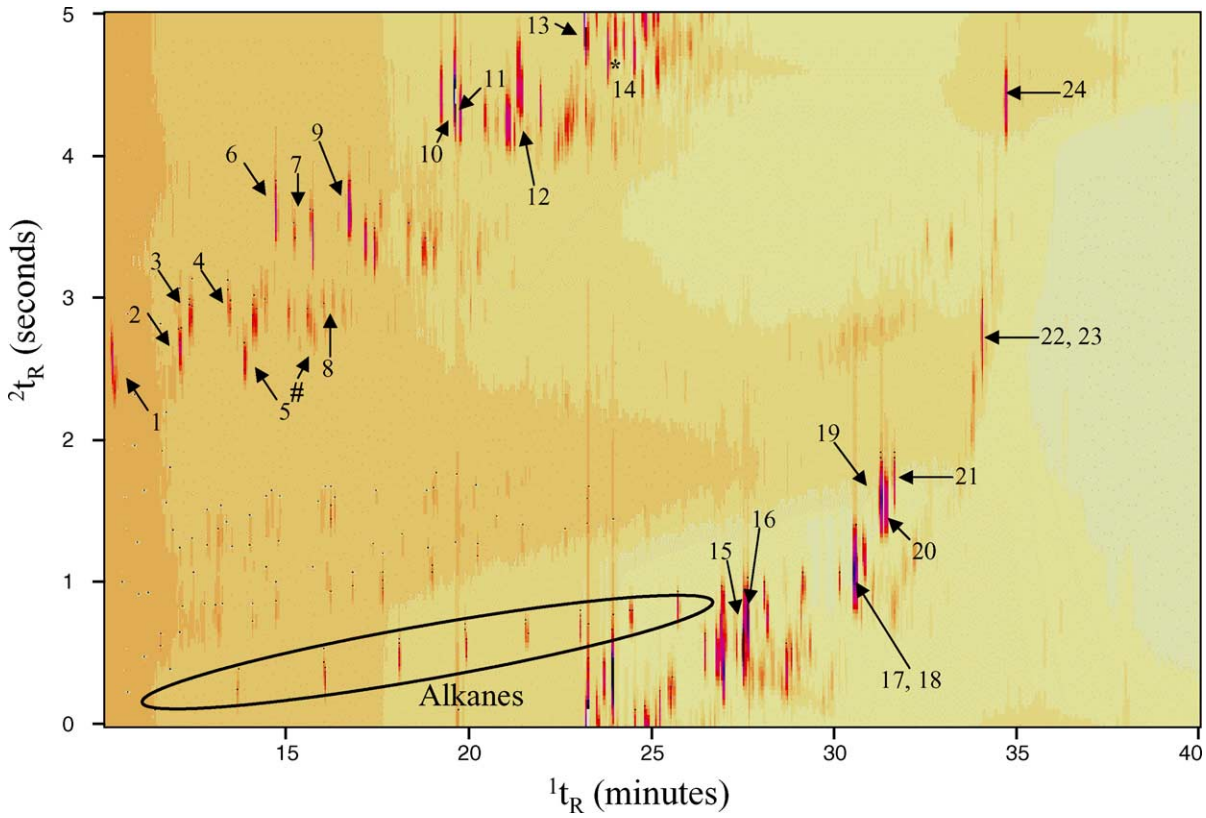

Fig. 2. Colour plot of GC × GC results for the analysis of the soil sample extracted using Method 2.

Compounds eluting beyond $^1t_R = 23$ min have relative ^2t_R times which exceed the modulation period (i.e. they exhibit wrap-around). Since acceptable resolution of the PAHs was obtained, no further modification to experimental conditions to lessen the extent of wrap-around was attempted. Different hydrocarbon classes will cluster or have structured retentions in the GC × GC plane [32], and in Fig. 2 alkanes (circled) are separated from other chemical classes. It is expected that the order of second column absolute retention time will be alkanes < alkenes < cycloalkanes < aromatics < polycyclic aromatics. Amongst the PAHs, different 'zones' can be distinguished; the bi-cyclic PAHs (peaks 1–5 and 8) form one identifiable zone, tricyclic PAHs with two "fully" aromatic rings form zone 2 (peaks 6, 7 and 9), tricyclic PAHs with three "fully" aromatic rings form zone 3 (peaks 10–12). Other structured regions can be proposed, with finally PAHs with six fused rings (peak 24; benzo(g,h,i,)perylene) forming the last zone (they are also the most strongly retained on column 2). The bands seen for the PAHs can be correlated with PAH 'topology' which can be described in various ways, such as correlation between angularity of PAHs and their molecular properties. The Clar's π-Sextet Model [25] is most commonly used to systematise molecular topology and PAH properties. The following structure-retention relationship seems to apply to GC × GC: the more Clar's Sextets, the higher the π-electron cloud polarisability, and the higher the second dimension retention. Thus, the compounds are distributed according to both volatility and polarity, and the colour plot illustrates the chemical relationships among sample components. In this way the two-dimensional colour plots provide much more information on the relative abundance of the different hydrocarbon classes and indeed the sub-classes of different ring-number PAHs, than either 1D-GC

Table 1
Concentrations of 24 PAHs (mg/kg) determined in the soil extract (analysed by the GC × GC technique) using the three extraction methods

Peak #: name	Method 1		Method 2		Method 3	
	Average concentration	R.S.D. (%)	Average concentration	R.S.D. (%)	Average concentration	R.S.D. (%)
1: naphthalene	13	11	11	17	10	9
2: 2-methylnaphthalene	7	6	3.3	13	4.8	7
3:1-methylnaphthalene	4.8	5	2.7	10	3.0	3
4: biphenyl	2.8	11	2.5	7	2.0	37
5: 2,6-dimethylnaphthalene	5	6	2.1	9	2.4	7
6: acenaphthylene	21	4	9.5	3	12	3
7: acenaphthene	2.3	21	0.9	10	1.0	12
8: 2,3,5-trimethylnaphthalene	1.7	15	0.5	34	0.6	29
9: fluorene	22	4	9.9	2	11	1
10: phenanthrene	167	3	72	1	87	1
11: anthracene	36	4	16	7	20	3
12: 1-methylphenanthrene	29	24	9.7	7	11	53
13: fluoranthene	274	1	108	1	133	1
14: pyrene	184	1	73	1	91	1
15: benzo(a)anthracene	23	4	8.8	2	11	1
16: chrysene	26	3	9.5	4	13	8
17+18: benzo(b)fluoranthene + benzo(k)fluoranthene	16	7	6.2	3	8	13
19: benzo(e)pyrene	65	7	25	14	32	8
20: benzo(a)pyrene	65	8	18	21	27	11
21: perylene	20	19	7.1	7	11	7
22+23: indeno(c,d)pyrene + dibenz(a,c)anthracene	16	6	6.6	5	8.6	2
24: benzo(g,h,i)perylene	29	6	11	5	11	10

Average values and R.S.D. (%) ($n = 3$) are presented at the level of each individual PAH in the extract.

or GC–MS. Of particular importance for a screening method is the ability of GC × GC to separate components coeluting in 1D-GC thereby reducing the need for expensive and tedious GC–MS analyses. Currently, the many overlapping peaks observed in 1D–GC for complex environmental samples may be often overlooked in routine analysis, simply because there are no better techniques available. In summary, GC × GC offers a cost effective and robust alternative to 1D-GC with potentially greater measurement accuracy. On the other hand, GC–MS may offer improved sensitivity (especially in selected ion monitoring mode) and the ability to provide component identification (scan mode) cannot be overlooked.

3.3. Quantification of analytes

The soil extracts were quantified by 1D-GC, GC × GC as well as GC–MS. To the authors' knowledge, quantitative results for these three chromatographic techniques have not previously been compared. The PAH concentrations of the triplicate runs for each PLE method were averaged and the GC × GC results were compared with the concentrations from GC–MS (Fig. 3). The low-molecular weight PAHs do not vary much in their concentrations for all chromatographic techniques, whereas a significant difference in the concentrations from pyrene (peak 14) onwards is observed. The GC × GC results shows bias towards low values compared to GC–MS data. This might be due to the use of separate internal standards in GC–MS analysis that could compensate for analyte losses during post clean-up sample handling. Better GC × GC results would probably result if suitable internal standards were used.

To test this hypothesis, GC × GC and 1D-GC data were multiplied by the ratio of the GC–MS pyrene concentration and the GC × GC or 1D-GC pyrene concentration. These "pyrene corrected" data are compared in Fig. 4. Data for naphthalene and biphenyl

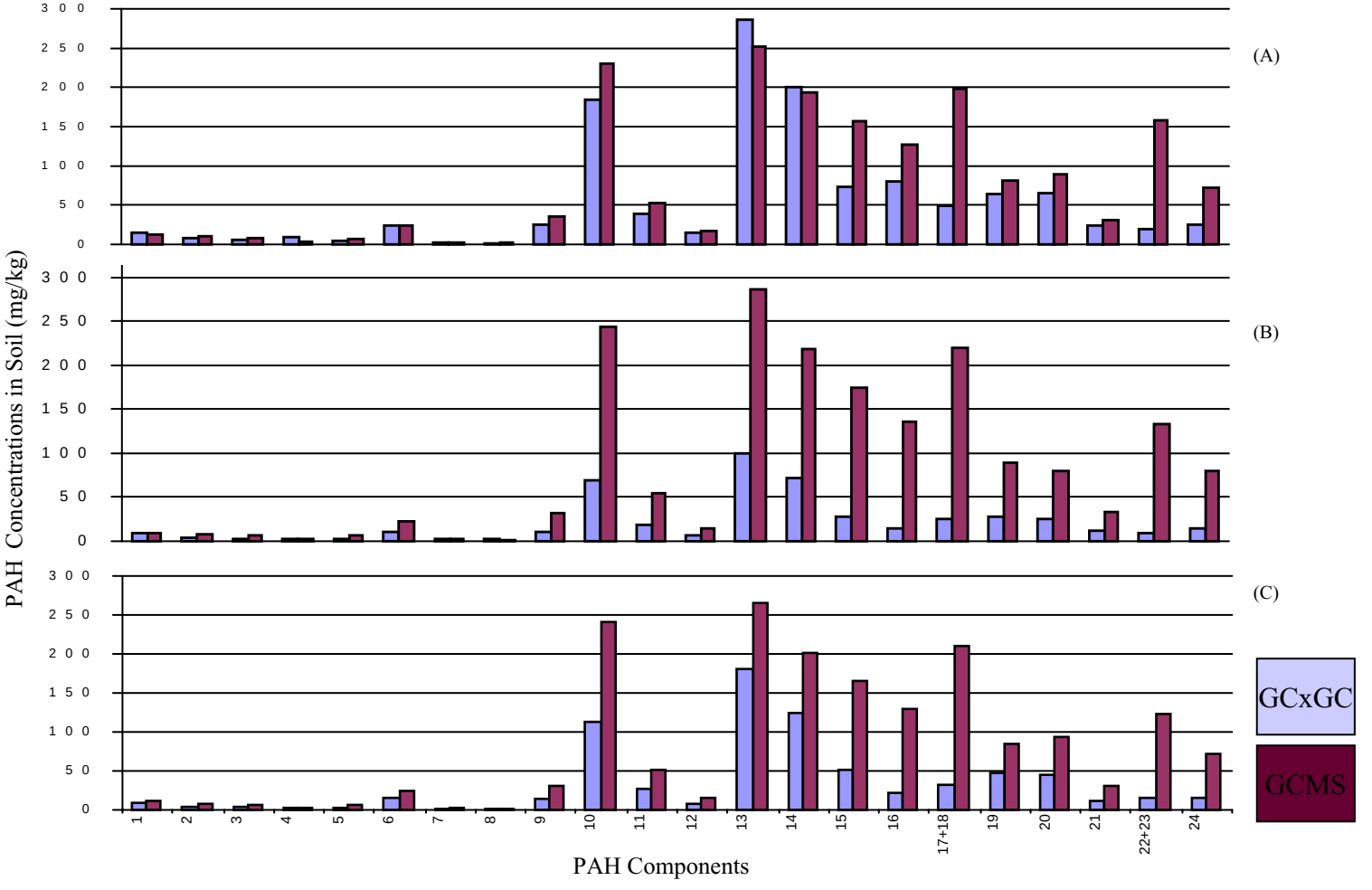

Fig. 3. Comparison of PAHs in the soil extracts analysed by GC × GC and GC–MS. Figures A–C corresponds to extraction Methods 1–3, respectively.

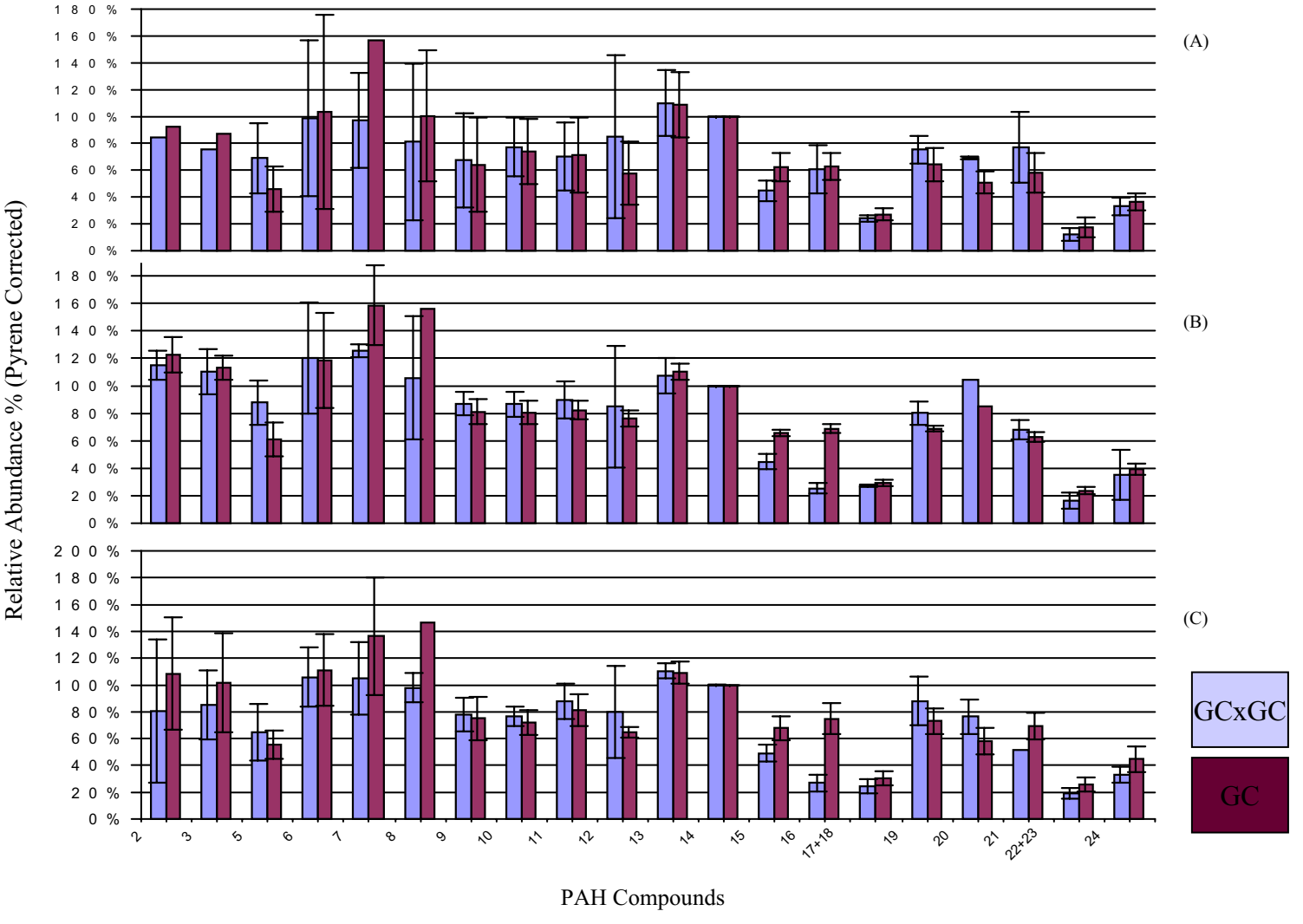

Fig. 4. Comparison of the pyrene-corrected data of quantified PAHs in the soil extracts analysed by conventional GC and GC × GC. Figures A–C correspond to extraction Methods 1–3, respectively. Error bars are included in the figure.

were not plotted in this figure as the uncertainties for the two analytes are too great. Most of the corrected GC × GC results are in good agreement with the results for 1D-GC with the exception of acenaphthene (peak 7) and 2,3,5-trimethylnaphthanlene (peak 8). In Fig. 2, it is observed that there is at least one peak (peak #), which co-elutes with acenaphthene in the first dimension but is resolved in the second dimension. This component will co-elute with acenaphthene in 1D-GC and thus acenaphthene will be inaccurately quantified, leading to a higher value compared with GC × GC. The advantage of GC × GC is clearly demonstrated; enhanced separation resulting in better quantification data and at the same time providing a wealth of information on chemical classes for compounds within the sample.

However, there seems to be unaccountable losses (poorer recovery) of analytes for GC × GC, as compared to GC–MS, especially for the high-molecular weight PAHs (Fig. 3). These are not attributable to the extraction method, but are associated with the chromatographic and/or detection procedure. The quantitative transfer of analytes onto different columns might also be responsible for the discrepancies. Furthermore different instruments (i.e. GC × GC and GC–MS) were used and thus factors such as differences between injectors and liner size could have led to the differences between the two quantified data sets. Large differences for the quantified results can be observed for example in chyrsene (peak 16) and especially for the two co-eluting pairs, benzo(b)fluoranthene + benzo(k)fluoranthene and indeno(c,d)pyrene + dibenz(a,c)anthracene, where difference in concentrations up to 150 mg/kg can be observed. Quantification of chrysene by GC × GC yielded 15 mg/kg compared to 136 mg/kg by GC–MS (Fig. 3B). Additional internal standards should be used for the high-molecular weight PAHs, and will be required for further studies to check if the lower results for 1D-GC and GC × GC have any systematic source. The use of suitable internal standards for GC × GC analysis would compensate for analytes losses.

In the present study, a Matlab based program, designed for quantification of GC × GC data, was used to group the pulses for a given analyte according to its second dimension retention times (^2t_R), and sum their peak areas and heights to quantify each PAH in the extracts. With the separation powers of the GC × GC system, PAHs are isolated from other analytes, co-extracted interferences and impurities. Thus, quantification should be more accurate and reliable as compared to 1D-GC. Improved automated quantification software for GC × GC, and agreed quantification protocols, are desirable as it is tedious to quantify analytes by manual summation of their peak areas and peak heights, and semi-automated in-house programs, such as the program used in this study, still require

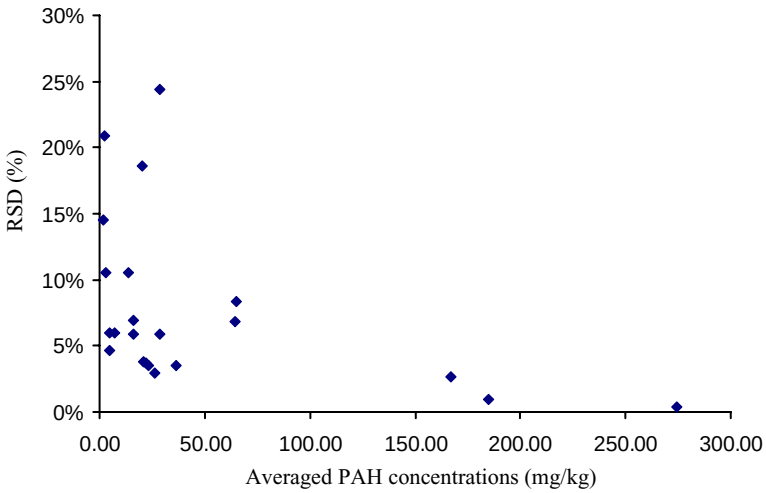

Fig. 5. Plot of R.S.D. (%) against the average PAH concentrations (analysed by the GC × GC technique) ($n = 3$) for extraction Method 2. Data are reported in Table 1 for all three extraction methods.

careful validation to ensure all peaks are correctly measured, just as validation of GC–MS data requires.

3.4. Reproducibility and repeatability of PLE off-line GC × GC

The analysis reproducibility of PAHs using PLE off-line GC × GC was calculated. It was found that the results are highly reproducible, with averaged R.S.D.s (all 24 PAHs) to be 0.4, 5 and 8% (±2 S.D.) for ^2t_R, peak areas and peak heights respectively. The GC × GC experiments were repeated using the same conditions, but with a different modulation period. There were no significant differences in peak areas and heights, or their reproducibility. Table 1 shows the repeatability of GC × GC results for the three extraction methods. Fig. 5 illustrates R.S.D. plotted against the average PAH concentrations for the triplicate results. R.S.D. values are higher at low concentrations, as expected. The results indicate that PLE off-line GC × GC should be a potential screening tool for environmental samples.

4. Conclusion

Although this study showed promising results, supporting ASE off-line GC × GC to be a fast, multi-residue screening tool, it is important to state that this is only a preliminary study which should support further experiments to more thoroughly validate the technique as a general procedure for routine pollutant screening. The results for GC × GC and GC–MS confirm that PLE is an exhaustive extraction technique, and in-cell clean-up for PLE gives the same or higher yields compared to column chromatography cleanup. Optimization of the GC × GC analytical parameters, through evaluation of different column sets or dimensions, together with automated software interpretation, will undoubtedly prove to be valuable. In future experiments, representative internal standards for both the low and high-molecular weight PAHs, should be used to compensate for losses. R.S.D. values for both reproducibility and repeatability studies are within the values recommended for techniques employed for screening purposes although there are no strict guidelines for such data. With optimization, PLE off-line GC × GC will offer faster extraction, enhanced resolution especially for isomers, improved analysis of complex mixtures, and chromatographic fingerprinting. The present study has demonstrated excellent separation of PAHs, however only the PAHs in the reference solution could be adequately identified (by position in the two-dimensional plot). Clearly the two-dimensional separation space suggests many PAH congeners and isomers are readily separated in the GC × GC experiment. The opportunity for use of fast mass spectral acquisition and identification offered by time-of-flight mass spectrometry (GC × GC-TOF MS) will be an important technical development for future environmental PAH screening studies.

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