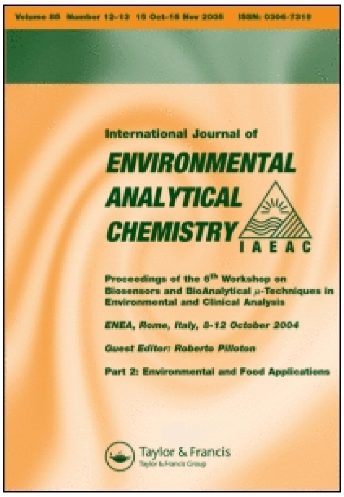

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COMPARISON OF SOXHLET AND SHAKE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM COAL TAR POLLUTED SOILS SAMPLED IN THE FIELD

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This study compares three extraction methods for PAHs in coal tar polluted soil: 3-times repeated shaking of the soil with dichloromethane—methanol (1:1), Soxhlet extraction with dichloromethane, and Soxhlet extraction with dichloromethane followed by Soxhlet extraction with methanol. The extraction efficiencies were determined for ten selected PAHs in triplicate samples of six soils sampled at former gasworks sites. The samples covered a wide range of PAH concentrations, from 0.6 to 397 mg/kg soil. Soxhlet extraction with dichloromethane followed by Soxhlet extraction with methanol, in general, was the most efficient method yielding 30 to 50 % higher concentrations than the other methods.

KEY WORDS: Polycyclic aromatic hydrocarbons, coal tar, soil, extraction, gaschromatography.

INTRODUCTION

Assessment of the risks associated with soils contaminated by coal tar in terms of polycyclic aromatic hydrocarbons (PAHs) is usually based on concentrations of the compounds measured in collected soil samples. No generally accepted standard procedures currently exist for extraction and quantification of PAHs in soil samples. Quantification of the compounds in the extract can be done by common GC and HPLC techniques, but a major uncertainty is associated with the efficiency of the selected extraction method.

Several extraction methods for soils have been reported in the literature involving different combinations of physical procedure and extractant: Soxhlet extraction with dichloromethane (DCM)[1,2,3], DCM in combination with shaking[4] and with ultrasonic treatment[5,6]. Also toluene[7] as well as a mixture of methanol and benzene[8] have been used as solvents. Supercritical Fluid Extractions (SFE) with carbon dioxide[9] and carbon dioxide/methanol[10] has also been used in some cases.

The extraction efficiencies of the different methods have been reported in a few cases. Cover *et al.* (1987)[11] showed that Soxhlet extraction with DCM gave slightly higher efficiency than a short vigorous shaking of the soil with DCM. Brilis and Marden (1990)[12] compared Soxhlet extraction with acetone/hexane to ultrasonic treatment involving DCM/acetone, and Aprill and Sims (1990)[13] compared Soxhlet extraction with acetone/DCM to shake extraction by DCM using a Tissumizer™. In both cases the highest efficiency was found for the methods involving Soxhlet extraction. However, extraction of PAHs by Soxhlet extraction with methanol/benzene gave less efficiency than by ultrasonic treatment with water/DCM as the extractant[8]. The extraction efficiencies of SFE with carbon dioxide were comparable to those of Soxhlet extraction with DCM; SFE gave extraction efficiencies between 80% and 100%, with a tendency to discriminate against high-molecular-weight PAH[9]. The efficiencies reported in the literature vary among methods from 10% up to a factor of 2. Due to the fact that most studies, except two[9,10], involved spiked soils instead of real polluted soils, and that in most cases the choice of physical procedure and extractant was confounded, no conclusions can be made as to best physical procedure and best extractant for measuring PAHs in polluted soils.

The Soxhlet procedure is usually rather time and man-power consuming and for many purposes a shake extraction procedure would be preferred. However, the literature indicates that the shake extraction should be more than a simple short-term shaking of the soil with the extractant in order to meet the efficiency of the Soxhlet procedure. The previously published studies also indicate that DCM together with a more hydrophilic extractant has a higher efficiency and would be a good choice for extraction of PAHs from soils.

The purpose of this study is to compare Soxhlet procedures and shake extraction procedures, by employing a DCM/methanol extractant, in terms of relative extraction efficiencies of ten PAHs commonly found in coal tar polluted soils. The shake procedure has been defined as 3 times extraction with a mixture of DCM and methanol (1:1), and the Soxhlet procedure has been defined as extraction with DCM followed by extraction with methanol.

The approach of this investigation has been to compare methods that would be easily applicable on a routine basis for actual investigations. Since tar polluted soils may be very inhomogeneous, some including aggregated fragments of old pitch, it was considered mandatory to use real field soil samples. Six soil samples from three former gasworks sites have been used for the comparison of the methods. Homogenization of the field samples has been introduced to minimize the uncertainty, but homogenization has not been enhanced to a level not applicable in a routine investigation.

MATERIALS AND METHODS

Soil samples

Six soil samples form former gasworks sites were collected. Three of the samples (A1, A2 and A3) were collected at a site in Holte (Copenhagen suburb), where Søllerød Gasworks previously was located. The samples were taken 3 m below surface, just above the water table, and represent three levels of coal tar pollution. At Frederiksberg Gasworks site (Central Copenhagen), two samples (B1 and B2) with different levels of coal tar pollution were collected form a soil pile, created by the recent excavation of the soil around a coal tar tank. The last soil sample (C1) was collected in connection with the excavation of the coal tar tank at Korsør Gasworks (eastern Zealand), 1 m from the tank and 1.5 m below the soil surface. All samples were stored in closed metal containers at 10°C until they were analysed. From the metal container approx. 0.5 kg soil was transfered to a glass bottle with PTFE-lined screw-cap and homogenized by mechanically shaking and rotating the glass bottle. Because of the risk of volatilizing naphthalene, we chose not to dry the samples as a step in the homogenization procedure. For each soil, six subsamples, each of 25 g, were taken, three for shake extraction and three for Soxhlet extraction.

Shake extraction

A 25 g wet soil sample was combined with 25 g anhydrous Na_2SO_4 and 50 ml solvent (DCM/methanol 1:1). The sample was shaken for 30 min, followed by centrifugation in order to promote phase separation. The supernatant was transferred to another flask, and the procedure was repeated twice. During the last extraction, the soil and solvent remained unseparated for 24 h, before the sample was centrifuged. The supernatants were combined and reduced by means of a rotary evaporator to 2 to 3 ml. The extract was stored in glass vials with PTFE-lined screw-caps, until it was analyzed on the GC. This extraction procedure is named Method I.

Soxhlet extraction

A 25 g wet soil sample and 25 g anhydrous Na_2SO_4 were placed in a soxhlet thimble and mixed with a spoon. The sample was sequentially Soxhlet extracted, first with 300 ml DCM for 24 h, whereafter a second flask containing 300 ml methanol substituted the DCM flask and the extraction continued for another 24 h. The extracts were both separately reduced to 2 to 3 ml and each analysed on the GC. The concentration in the DCM extract is named Method IIa, while the sum of the concentration of the individual compounds in both extracts from the Soxhlet extraction is named Method IIb.

GC procedure

PAH analysis was performed by GC-FID using a J&W Scientific DB-5 capillary column ((5% phenyl)methylpolysiloxane), with dimensions 30 m × 0.53 mm i.d. × 1.5 μm film thickness. Carrier gas (N_2) linear velocity was 25 cm s^{-1}. Temperature programming used to achieve separation was 40°C for 2 min, then temperature increase at 15°C min^{-1} to 225°C holding for 8 min, then, followed by temperature increase at 15°C min^{-1} to 300°C and holding for 23 min. The chromatograms were collected on a data system and processed by chromatography software "820 Maxima" (Millipore). Each extract was analysed twice.

Reagents

Dichloromethane (Merck 6044) and methanol (Merck 6009), both 99.8% pure, were used without further purification. The PAHs used as standards were from SUPELCO (Polynuclear Aromatic Hydrocarbons Kit 610-N) and 1-methylnaphthalene from Merck (no. 820809). Anhydrous Na_2SO_4 was from Merck (no. 6649).

Soil characterization

The content of water in the soil samples was determined by heating the soil at 105°C for 24 h, and the loss upon ignition was determined on dried soil by heating the soil at 550°C for 2 h. In a slurry of distilled water and soil (1:1 by weight), pH was measured by a combination electrode. The texture of the soils was determined by the hydrometer method[14].

The results of the soil characterization are shown in Table 1. The soil types range from sand to sandy loam. The water contents range from 11% to 17% w/w (weight of water/weight of dry soil). The organic content, measured as weight loss upon ignition of dry soil, varied considerably, viz. from 0.3% w/w (dry weight) in soil A3 to 6% w/w (dry weight) in soil B1.

Statistical methods

In order to compare, on the basis of all ten PAHs, the methods two by two, a regression-based method is used. However, ordinary regression can only be used when one variable is measured without error. This assumption is obviously not fulfilled in this case and therefore one has to use functional relations. The assumptions required for the statistical method used is normally distributed data with homogeneous variance. In order to fulfil these requirements the results are transformed by the logarithm.

In order to state the model for comparison of two methods it is necessary to introduce some notations. Let *n* be the total number of samples analysed, let x_i, $i = 1, \ldots, n$ be the

Table 1 Texture, water content, loss upon ignition (IG) and pH of the six soil samples.

Parameter	*A1*	*A2*	*A3*	*B1*	*B2*	*C1*
Texture						
Clay, < 0.002 mm (%)	5	5	4	12	12	17
Silt, 0.002–0.02 mm (%)	3	3	3	6	10	10
Silt, 0.002–0.02 mm (%)	3	3	3	6	10	10
Fine sand, 0.02–0.2 mm (%)	15	18	11	23	20	26
Coarse sand, 0.2–2 mm (%)	49	59	63	36	40	31
Type[+]	Sand	Sand	Sand	Loamy sand	Sandy loam	Sandy loam
Water content (% w/dry w)	12	17	11	15	14	14
IG (% w loss of dry soil/w dry soil)	1.3	0.9	0.5	6.0	2.3	4.8
pH	7.4	8.2	7.6	7.9	8.5	7.5

[+]According to Hillel, 1980[15]

logarithm-transformed data corresponding to the first method and let y_i, $i = 1, \ldots, n$ be the logarithm-transformed data corresponding to the second method. Assume that the x's and the y's are all independent and that the measurements are normally distributed in the following way: $x_i \in N((\xi_i, \sigma^2_x)$ and $y_i \in N(\eta_i, \sigma^2_y)$. Because of the fact that both the x's and the y's are measured with error, the relation between them is stated as a relation between their mean values:

$$\eta_i = \alpha + \beta \cdot \xi_i \qquad (1)$$

The relation is linear in the logarithms, which does not correspond to linearity for the untransformed data. Let a prime on the x and y denote the untransformed data. Then a linear relation for the transformed data corresponds approximately to the following relation for the untransformed data:

$$y' = \mu \cdot \chi'^{\beta} \qquad (2)$$

Where $\mu = exp(\alpha)$ is a new parameter. To estimate the parameters in the model it is necessary to specify the relation between the variances σ^2_x and σ^2_y. In the case studied here we have assumed that the variances are equal. This assumption is expected to be reasonable because the major part of the variance refers to the heterogeneity of the PAHs in the soil, which is supposed to be equal for the different methods.

When the maximum likelihood estimates for the parameters are found, it is possible to compare the methods by means of tests of the parameters in the model. The first test is a test of the hypothesis of β being equal to one. This hypothesis corresponds to the hypothesis that the methods are proportional. This can be tested as a F-test. If the slope (β) is equal to 1, the transformed intercept, μ, expresses the ratio of the efficiency of the compared methods. When the hypothesis of β being equal to one has been accepted, one can test the hypothesis of μ being equal to zero corresponding to no differences between the methods. This test is performed as a paired t-test. For an in depth treatment of the theory consult[16,17]

It should be mentioned that the statistical analysis used does not take into account that Method IIa and Method IIb are linked (Method IIb is equal to Method IIa plus the Soxhlet extraction with methanol). This is assessed not to influence the conclusions when very distinct differences are found (confer later).

RESULTS AND DISCUSSION

PAH concentrations measured

The ten selected PAHs were determined in all six soils. The detection limit of the individual PAHs is estimated to 0.1 mg/kg. The results of the three methods are presented in Tables 2–4 for all soils and PAHs in terms of average concentration, AVG, of the three subsamples and the relative standard deviation, RSD (100·s/x, %). In the following general presentations of the results reference is primarily to the results of Method IIb.

Table 2 Concentrations of ten selected PAHs in six soil samples extracted by shaking with dichloromethane/methanol (1:1) (Method I). *

Soil:	*A1*		*A2*		*A3*		*B1*		*B2*		*C1*	
Analyte	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*
Napthalene	3.6	15	332	48	1.6	4	5.1	16	0.3	58	3.0	51
1-Methylnaphthalene	12.4	16	65.7	48	1.9	5	4.2	33	0.2	48	1.4	68
Acenaphthene	5.3	3	14.9	55	0.5	14	13.2	62	0.3	48	1.9	32
Fluorene	24.6	2	70.4	46	5.5	0	70.3	62	0.7	58	5.2	35
Phenanthrene	41.8	7	116	41	11.7	2	270	42	2.5	34	19.2	27
Fluoranthene	41.0	3	66.8	32	9.3	7	421	38	7.2	33	40.9	25
Pyrene	34.8	3	51.5	36	7.4	7	329	36	6.3	34	36.4	31
Benzo(a)anthracene	23.6	6	31.4	23	5.3	13	159	38	4.2	49	24.5	21
Benzo(a)pyrene	16.6	6	21.1	22	4.8	13	122	33	4.8	33	22.8	19
Dibenzo(a,h)anthracene	14.2	8	15.0	18	2.4	10	54.6	31	3.2	9	21.8	35

*AVG, average concentration of three subsamples

Table 3 Concentrations of ten selected PAHs in six soil samples extracted by Soxhlet with dichloromethane, (Method IIa).

Soil:	*A1*		*A2*		*A3*		*B1*		*B2*		*C1*	
Analyte	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*
Napthalene	7.8	3	353	21	2.6	2	6.1	61	0.7	17	6.3	32
1-Methylnaphthalene	12.6	6	61.8	20	2.8	2	3.1	54	0.4	40	1.6	43
Acenaphthene	6.3	3	10.4	11	1.2	0	3.7	17	0.7	11	2.7	43
Fluorene	25.4	3	58.1	14	6.1	5	42.2	91	1.8	39	11.2	98
Phenanthrene	42.9	2	106	20	13.5	11	88.4	25	2.9	55	23.1	60
Fluoranthene	41.0	4	59.2	21	10.3	9	125	12	5.2	35	53.1	69
Pyrene	35.2	3	43.6	20	8.9	7	101	18	4.5	37	48.2	71
Benzo(a)anthracene	26.1	4	31.1	12	5.1	4	91.3	22	3.9	42	34.9	60
Benzo(a)pyrene	18.6	5	24.0	13	3.9	1	75.2	10	5.9	10	31.3	48
Dibenzo(a,h)anthracene	15.5	20	22.5	16	5.8	4	63.6	23	4.8	11	32.3	57

Table 4 Concentrations of ten selected PAHs in six soil samples extracted by Soxhlet with dichloromethane and methanol (Method IIb).

Soil:	*A1*		*A2*		*A3*		*B1*		*B2*		*C1*	
Analyte	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*	*AVG (mg/kg)*	*RSD (%)*
Napthalene	11.5	8	397	19	6.9	25	6.8	59	1.0	33	9.2	10
1-Methylnaphthalene	15.8	13	73.9	18	5.5	0	3.4	54	0.6	32	3.0	15
Acenaphthene	7.7	12	14.5	8	5.1	49	4.3	15	2.1	42	4.2	25
Fluorene	32.1	10	74.2	11	13.5	7	42.8	90	2.3	34	14.2	85
Phenanthrene	50.0	6	123	18	23.0	6	90.1	24	4.0	43	29.8	43
Fluoranthene	51.0	6	73.3	18	21.4	12	133	10	11.2	34	75.6	62
Pyrene	42.0	5	54.3	18	15.2	7	103	17	4.9	34	66.2	64
Benzo(a)anthracene	33.3	13	43.0	18	10.8	15	93.8	22	4.8	28	45.6	56
Benzo(a)pyrene	22.8	7	30.5	10	6.7	39	76.5	10	6.6	18	41.9	40
Dibenzo(a,h)anthracene	15.5	20	22.5	16	5.8	60	64.4	23	5.1	19	44.4	43

The results represent a large interval of PAH concentrations. The sum of the concentrations of the 10 PAHs varies between 40 mg/kg (soil B2) and 910 mg/kg (soil A3). The concentrations of the individual PAHs varies between 0.6 mg/kg and 134 mg/kg, except for soil A2, where the maximum concentration is 397 mg/kg. Within a soil, remarkable differences in concentrations of the PAHs were observed. For example, soil B1 contained 3.4 mg/kg of 1-methylnaphthalene and 134 mg/kg of flouranthrene. But also among soils, large differences were observed for the single PAHs: naphthalene amounts to 1.0 mg/kg in soil B2 and 397 mg/kg in soil A2.

The uncertainty of the methods in terms of precision, as estimated by the RSD computed on the basis of the three subsamples, varies considerably for different soils and also—but not as much—for different compounds. The RSD for the concentrations determined by Method IIb is between 5 and 20 % for soil A1 and between 10 and 90 % for soil B2.

The large range of concentrations covered in this study provides a good basis for evaluation of the efficiencies of the methods to be used on real, polluted soil samples. The inhomogeneity of the coefficients of variance may be a problem for the statistical analysis but should of course be viewed in light of the few observations they are based on.

Comparison of Method IIa and Method IIb

The first comparison examines the importance of supplementing the Soxhlet extraction using DCM with an additional Soxhlet extraction using methanol. Method IIa is the Soxhlet extraction using DCM while Method IIb is the combined Soxhlet extraction.

Figure 1 shows the correlation between the results of Method IIa and Method IIb for all PAHs and soils in terms of logarithm-transformed concentrations. The regression analysis (if presentation of statistical methods) for this combined data set, as well for the individual soils (with the exception of soil B1), revealed that the slope (β) is equal to 1 ($p > 0.05$). The regression analysis also showed that the intercept of the line (α) is different from zero in all cases ($p > 0.05$) indicating that the transformed intercept μ (= $exp(\alpha)$) is different from 1. This allows for calculating a ratio, $f_{IIa,IIb}$, between the two methods ($f_{IIa,IIb}$ = "Method IIa"/"Method IIb") expressing the relative efficiencies for measuring PAHs in soil. The results are shown in Table 5 for all soils and for the individual soils.

The estimated correlation coefficients, R^2, indicate that the chosen statistical approach is sound for the data set containing all the soils, but is dubious for soil A3 on its own. Soil A3 has low concentrations of PAHs. The overall ratio $f_{IIa,IIb}$ indicates that the Soxhlet extraction with DCM only gave an extraction efficiencies of 70% ($f = 0.70$–0.73) compared with the Soxhlet procedure with both DCM and methanol. However, large difference were observed among soils: For soil B1 the difference was only 5 %, while for soil A3 the difference was 50%. The Soxhlet extraction with methanol did not increase the extraction efficiencies of the more hydrophilic compounds, indicating that the effect of methanol is primarily related to physical aspects (statistical plots not shown).

This examination showed that Method IIa only provided a partial extraction of PAHs from polluted soil; hence it is excluded from the following data analysis.

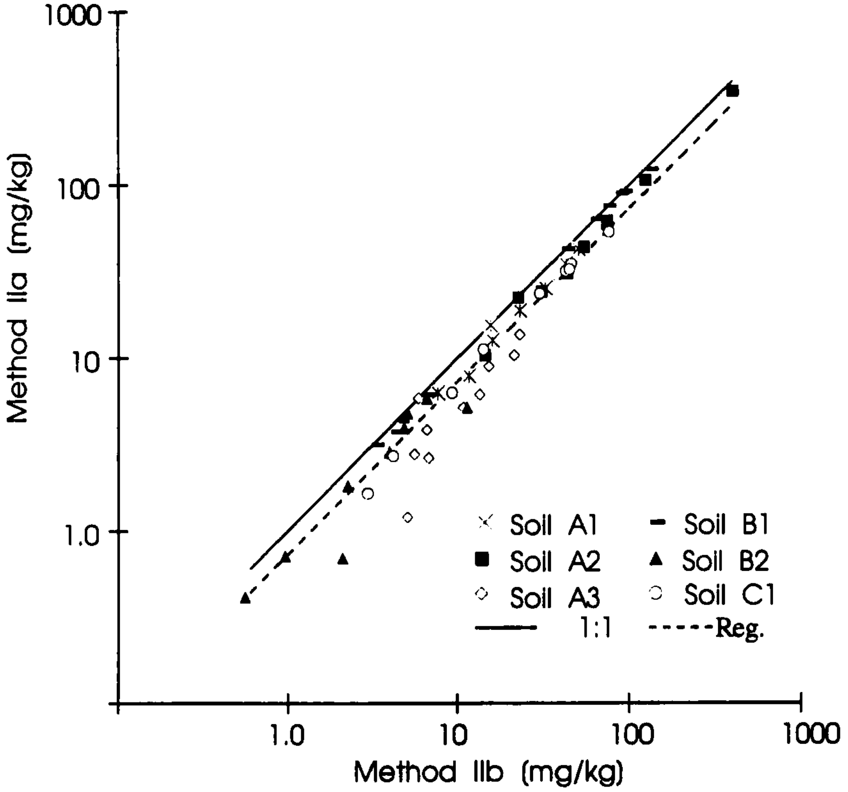

Figure 1 A log-log representation of the results for all PAHs and soils of Method IIa versus the corresponding results of Method IIb.

Table 5 Correlation coefficients for log-log model (R^2) for ten selected PAHs extracted from six soils by different methods and the estimated ratio (f) between their extraction efficiencies.

	IIa vs IIb		*I vs. IIB*	
Soils	$f_{IIa,IIb}$	R^2	$f_{I,IIb}$	R^2
All	0.73	0.96	0.68	0.87
All, excl. B1	0.70	0.95	0.56	0.84
A1	0.81	0.98	0.71	0.78
A2	0.82	0.99	0.85	0.97
A3	0.50	0.59	0.37	0.11
B1	0.95	1.00	1.78	0.86
B2	0.70	0.86	0.51	0.53
C1	0.71	0.99	0.48	0.97

Comparison of Method I and Method IIb

The second comparison should show whether the two-step Soxhlet extraction method (Method IIb) can be substituted by a simpler shake extraction method (Method I) involving the same extractants.

Figure 2 shows the correlation between the results of Method I and Method IIb for all PAHs and soils in terms of logarithm-transformed concentrations. Also in this case, regression analysis revealed that all slopes (β) are equal to 1 ($p > 0.05$), and that all intercepts of the lines (α) are different from zero ($p > 0.05$). As previous, this allows for calculating a ratio, $f_{I,IIb}$, between the two methods ($f_{I,IIb}$ = "Method I"/"Method IIb") expressing the relative efficiencies for measuring PAH in soil. The results are included in Table 5.

The estimated correlation coefficients, R^2, are all fair, except for soil A3 (R^2=0.11) and soil B2 (R^2=0.53). No obvious explanation for these deviations exist since neither soil is extreme with respect to PAH concentrations or organic matter content (loss upon ignition; Table I) of the soil. The overall ratio, $f_{I,IIb}$, indicates that the shake extraction in average was 40% less efficient than the Soxhlet extraction (f=0.56–0.68). However, one exception exists: for soil B1 the shake extractions gave 80% higher results than the Soxhlet method (8 out of

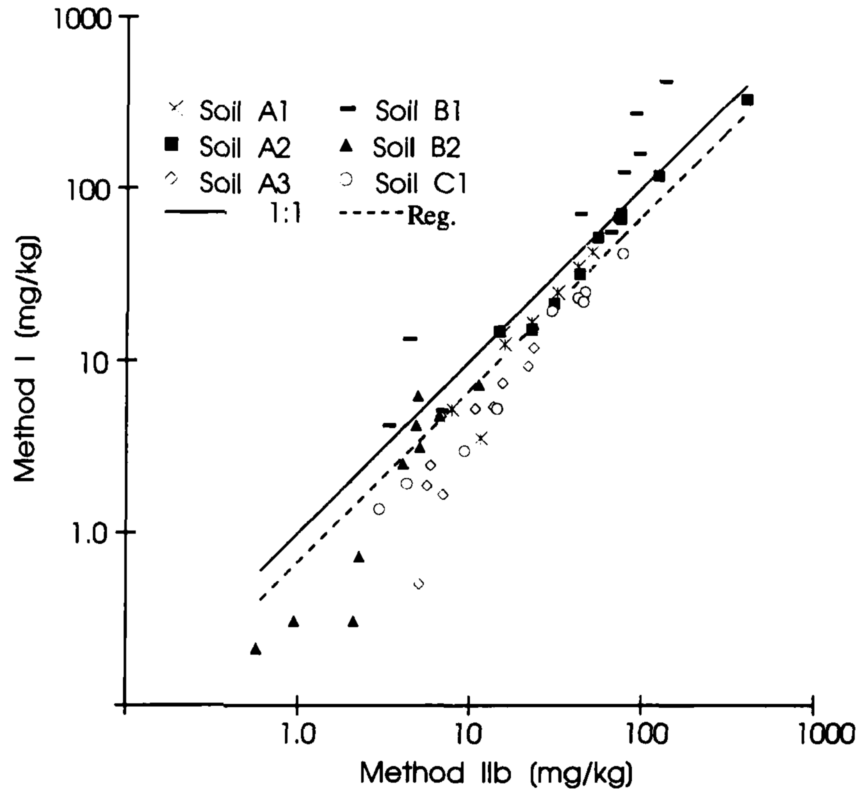

Figure 2 A log-log representation of the results for all PAHs and soils of Method I versus the corresponding results of Method IIb.

10 PAH concentrations were higher with Method I than in Method IIb). Large differences were also observed among the soils, where Method I gave lower concentrations than Method IIb (between f = 0.37 for soil A3 and f = 0.85 for soil A2). No explanations are available for these variations, but since no systematic differences were observed among the selected PAHs, the variations potentially could be related to the different physical handling of the samples in the two methods.

This examination showed that Method IIb (Soxhlet extraction with DCM followed by Soxhlet extraction with methanol) in general is more efficient for extracting PAHs from soil than a shake extraction (3 times with DCM/method, 1:1). However, the experiments also indicate that there may be exceptions (soil B1). This could hypothetically be related to the physical structure of the coal tar pollution present in the soil, since the shake extractions in some case may provide better dispersion of some coal tar coated particles in the soil or to unaccounted heterogeneities in the sampled soils.

CONCLUSION

The comparison of three methods for quantification of PAHs in coal tar polluted soils showed, on the basis of triplicate extraction of six soils from former gasworks sites, that the combination of Soxhlet extraction with dichlormethane and methanol is the most efficient method. A single Soxhlet extraction with dichlormethane or a repeated shake extraction with dichlormethane/methanol gave only 60 to 70 % of the sequential Soxhlet extraction. However, in one case the shake extraction yielded a better extraction.

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