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Traditionally, soil quality and contamination sources of hydrocarbon contaminated soils have been evaluated by the 16 un-substituted polycyclic aromatic hydrocarbons (PAHs) pointed out by the U.S. Environmental Protection Agency ($EPAPAH_{16}$) as well as total petroleum hydrocarbon (TPH) concentrations. Un-substituted PAHs constitute more than half of the total concentration of PAHs in pyrogenic sources; in petrogenic sources alkyl-substituted PAHs constitute more than 90 % of the total concentration. An evaluation of soil quality and contamination sources based on $EPAPAH_{16}$ is not representative of petrogenic sources.

This study contributes with a contaminant fingerprinting strategy representative of both petrogenic and pyrogenic sources of hydrocarbon contaminated soil. Furthermore, the presence of selected oxygenated PAHs in hydrocarbon contaminated soils is investigated and evaluated.

Chemical fingerprinting of hydrocarbon-contamination in soil

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Abstract

Chemical fingerprinting analyses of 29 hydrocarbon-contaminated soils were performed to assess the soil quality and determine the main contaminant sources. The results were compared to an assessment based on concentrations of the 16 priority polycyclic aromatic hydrocarbons pointed out by the U.S. Environmental Protection Agency ($EPAPAH_{16}$) and total petroleum hydrocarbon (TPH).

The chemical fingerprinting strategy proposed in this study included four tiers: (i) Qualitative analysis of GC-FID chromatograms, (ii) comparison of the chemical composition of both un-substituted and alkyl-substituted polycyclic aromatic compounds (PACs), (iii) diagnostic ratios of selected PACs, and (iv) multivariate data analysis of sum-normalized PAC concentrations. The assessment criteria included quantitative analysis of 19 PACs and C1-C4 alkyl-substituted homologues of naphthalene, fluorene, dibenzothiophene, phenanthrene, pyrene, and chrysene; and 13 oxygenated polycyclic aromatic compounds (O-PACs).

The chemical composition of un-substituted and alkyl-substituted PACs and visual interpretation of GC-FID chromatograms were in combination successful in differentiating pyrogenic and petrogenic hydrocarbon sources and in assessing weathering trends of hydrocarbon contamination in the soils. Multivariate data analysis of sum-normalized concentrations could as a stand-alone tool distinguish between hydrocarbon sources of petrogenic and pyrogenic origin, differentiate within petrogenic sources, and detect weathering trends. Diagnostic ratios of PACs were not successful for source identification of the heavily weathered hydrocarbon sources in the soils.

The fingerprinting of contaminated soils revealed an underestimation of PACs in petrogenic contaminated soils when the assessment was based solely on $EPAPAH_{16.}$ As alkyl-substituted PACs are dominant in petrogenic sources, the evaluation of the total load of PACs based on $EPAPAH_{16}$ was not representative. Likewise, the O-PACs are not represented in soil quality assessments based on $EPAPAH_{16}$ and TPH. The ∑O-PACs ranged between < limit of detection (LOD) (0.03 mg kg^{-1} (dw)) and 150.61 mg kg^{-1}(dw). The pyrogenic contaminated soils contained considerable amount of O-PACs corresponding to between 6 and 18 % of the $\sum EPAPAH_{16}$.

Keywords

Chemical fingerprinting; polycyclic aromatic compounds; oxygenated PACs; soil; source identification; PCA

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants included in the U.S. Environmental Protection Agency list of priority pollutants due to toxic, mutagenic, and carcinogenic properties [1,2]. They are formed primarily during incomplete combustion of biomass and fossil fuels (pyrogenesis) or through petrogenic processes over millions of years at lower temperature [3].

Elevated concentrations of PAHs are found at industrialized or urban areas and concentrations of PAHs generally decrease exponentially from point sources [4] but even in the most remote areas of the world, PAHs are present in the soil environment due to diffuse atmospheric deposition [5,6]. PAHs in soil are often found in mixtures with other groups of compounds which are released together with PAHs from the source, e.g. alkyl-substituted PAHs, heterocyclic polycyclic aromatic compounds (PACs) containing sulfur and nitrogen (hereafter all PAHs and PACs are jointly denoted as PACs), alkanes, and oxygenated PACs (O-PACs). Moreover, a variety of degradation products including O-PACs, hydroxylated PACs, and carboxylic acid-substituted PACs are formed through chemical oxidation [7], photooxidation [8], and biological transformation processes [5]. The O-PACs have attracted attention as they are more persistent than other degradation products [7,9], are toxic [10], and may be found in significant concentrations at organic contaminated sites [9,11,12].

Many countries have put up soil quality criteria. In the screening of contaminated soils, a number of un-substituted PACs, often the $EPAPAH_{16}$ and TPH or subsets of these, are used to categorize the soils (e.g. [13-16]). The limited number of parameters used to characterize a highly complex mixture of compounds might be an oversimplification.

First of all, the information obtained by quantifying a selected number of un-substituted PACs is inadequate for source apportionment of hydrocarbon sources [17]. The relative abundance of individual hydrocarbons forms a chemical pattern characteristic of a specific source which can be used to differentiate between them [17-19]. Source identification is important for use in liability cases and for understanding how and where hydrocarbons enter the environment. To enable source identification and source apportionment it is necessary to include sets of hydrocarbons that work as indicators for different types of contaminations; both the major sources, i.e. pyrogenic versus petrogenic sources, and the contribution of specific sources (e.g., creosote, heating oil). Secondly, the alkyl-substituted PACs make up a significant part of the petrogenic PACs [20] but are not represented in the soil criteria. In pyrogenic sources, i.e. PACs derived from combustion of organic materials, the un-substituted PACs make up approximately one-third to two-thirds of the total PAC concentration while up to 99 % of the PACs in petrogenic sources such as crude oil and diesel fuel are alkyl-substituted PACs [20]. When petrogenic sources are assessed by the un-substituted $EPAPAH_{16}$ an underestimation of the PAC contamination is likely [20]. Finally, degradation products of hydrocarbons are not included in the traditional assessments of hydrocarbon-contaminated soil. In contrast, during remediation of organic polluted soils the $EPAPAH_{16}$ and TPH are measured regularly to fulfill regulations. When the concentration of $EPAPAH_{16}$ and TPH is below the threshold limit, the soil is considered uncontaminated. However, O-PACs are released together with

PACs [10], some are formed during biotransformation of PACs in the soil [5], and are persistent in soil [10]. O-PACs may constitute a substantial portion in complex organic contaminations [9] and O-PACs may contribute significantly to the total toxic hazards [10,21]. The O-PACs are not included in monitoring programs today [10].

Oil hydrocarbon fingerprinting is traditionally used for identification of sources of oil spills, to assess weathering and biodegradation effects and for apportionment of multiple spill sources [19,22,23]. Multivariate pattern recognition and regression techniques have proved valuable tools for analysis of the complex data often obtained from oil hydrocarbon fingerprinting studies [24-27].

The objective of this study was therefore to suggest and apply a contaminant fingerprinting strategy for hydrocarbon-contaminated soil and to compare the assessments of soil quality and contamination sources with those obtained using the $EPAPAH_{16}$ and TPH concentrations as the sole criteria. The chemical fingerprinting approach was applied to 29 soils from the Copenhagen area. A tiered strategy was applied including (i) qualitative examination of GC-FID chromatograms of TPH; (ii) a comparison of the concentrations of un-substituted and alkyl-substituted PACs, (iii) calculation of diagnostic ratios of selected PACs, and (iv) multivariate pattern recognition using principal component analysis (PCA). Finally, the concentrations of 13 O-PACs were examined. The data set contains quantitative data of 19 un-substituted PACs (including $EPAPAH_{16}$); C_1-C_4 alkyl-homologues of naphthalene, fluorene, dibenzothiophene, phenanthrene, pyrene, and chrysene; and 13 O-PACs. Qualitative data was obtained for TPH. All analyses were performed in the same laboratory. In addition, the soil samples were analyzed for seven PACs and TPH according to the Danish soil quality criteria [14,28,29] at a commercial laboratory.

2. Experimental

2.1 Chemicals and reagents

Dichloromethane, *n*-pentane, *n*-hexane, and acetone of HPLC grade (Rathburn) were used in the extraction and cleanup. Anhydrous sodium sulfate (pro analysis, Merck) was rinsed three times with dichloromethane and left to dry in a fume hood over night before drying in an oven at 85°C for 20 h. Silica gel 60 (0.063-0.200 mm, Merck) was rinsed sequentially with acetone (Baker), *n*-pentane, and dichloromethane. When dry, the silica gel was activated at 180°C for 20 h. Ottawa sand (20-30 mm mesh) from AppliChem (Darmstads, Germany) was pre-cleaned by heating at 450°C overnight.

For PAC quantifications, mixtures of 19 individual PACs, naphthalene, acenaphthylene, acenaphthene, dibenzothiophene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*c,d*]pyrene, dibenz[*a,h*]anthracene, and benzo[*g,h,i*]perylene (including the EPAPAH_{16}), were used as quantification standards. An internal standard solution (IS) containing 20 µg mL^{-1} of each of naphthalene-d8, acenaphthene-d10, fluorene-d10, dibenzothiophene-d8, phenanthrene-d10, pyrene-d10, chrysene-d12, benzo[*k*]fluoranthene-d12, benzo[*g,h,i*]perylene-d12, and a recovery standard solution contained 20 µg mL^{-1} of acenaphthylene-d8, anthracene-d10, fluoranthene-d10, benz[*a*]anthracene-d12, and benzo[*a*]pyrene-d12 were prepared; both in isooctane.

For O-PAC quantification, a mixture of 13 individual O-PACs was used: 1-idanone, 1-napthol, 1-napthaldehyd, 2-phenylphenol, 9-fluoranone, 1,2-acenaphthenequinone, anthracene-9,10-dione, 4H-cyclopental[*def*]phenanthrenone, benzo[*a*]fluorenone, 7H-benz[*de*] anthracene-7-one, benz[*a*]anthracene-7,12-dione, naphthacene-5,12-dione, and 6H-benzo[*cd*] pyrene-6-one. All quantification standards were purchased at Sigma-Aldrich. An internal standard solution of 20 µg mL^{-1} anthraquinone-d8 was prepared. Anthraquinone-d8 was purchased at Chiron. The recovery standard solution was the same as for PAC analysis.

2.2 Soil sampling

A total of 29 contaminated soils were sampled from Copenhagen Recycling Centre from April 2010 to October 2012 and stored at -18^{o}C until analysis. The specific origin of the soils was confidential but they all originated from the island of Zealand (Denmark) which has a cold-temperate, coastal climate. The prerequisite for sampling a soil was an exceeding of the PAC or the TPH threshold limits specified in the Danish soil quality criteria [14]. For soil characteristics, the soil samples were thoroughly mixed, air-dried, and filtrated through a two mm sieve. Soil characteristics were determined according to the procedure described by Boll *el al.* (2015) [30](Supplementary Data, Table S1).

2.3 Extraction and quantification of PACs and alkyl-homologues PACs

Integrated extraction and cleanup was performed by pressurized liquid extraction (PLE) with a Dionex ASE 200 accelerated solvent extractor as described previously[31]. The extracts were used for quantification of the 19 PACs and of C_1-C_4 alkyl-homologues of naphthalene, fluorene, dibenzothiophene, phenanthrene, pyrene, and chrysene, and for qualitative analysis of TPH.

Qualitative analysis of TPH was accomplished using an Agilent 6890 GC equipped with a FID. The column was a 30 m ZB-5 capillary column (0.25 mm id- 0.25 μm film thickness) with hydrogen as carrier gas at a flow rate of 2.0 mL min^{-1}. Aliquots of 1 μL were injected in split mode (1:2) mode at 300^{o}C and the oven temperature program as follows: 60^{o}C (held for 2 min.) and then increased to 310^{o}C with 20^{o}C min^{-1} (held for 5.5 min) giving a total analysis time of 20 min.

Quantitative analysis of the 19 un-substituted PACs was conducted as described previously [31]. We used a GC (Agilent 6890N) interfaced to a quadrupole mass spectrometer (MS) operating in electron ionization mode (Agilent 5975B) for the analysis. The GC was equipped with a 60 m ZB-5 (0.25 mm I.D. × 0.25 μm film thickness) capillary column. Helium was used as carrier gas with a flow rate of 1.1 mL min^{-1}. Aliquots of 1μL were injected in splitless mode. Injector, ion source, and quadrupole temperatures were 325^{o}C, 230^{o}C, and 150^{o}C, respectively. The oven program was: 35^{o}C (held for 3 min), increased to 100^{o}C (25^{o}C min^{-1}), then to 247^{o}C (5^{o}C min^{-1}), and to 320^{o}C with a rate of 3^{o}C min^{-1} (held for 10.67 min) leading to a total analysis time of 70 min. Selected ion monitoring (SIM) was used to analyze 21 mass-to-charge (m/z) values in the range of m/z 128-288, divided into eight groups with 2-4 ions in each. Two six-point internal calibration curves (high and low concentrations) were used for quantification of the 19 PACs; concentrations were corrected for recovery. For specification of recovery and internal standards used to quantify the 19 PACs, please see Supplementary Data, Table S5.

Quantitative analysis of homologue series of PACs was performed using the same GC-MS system as described by Gallotta *et al.* (2012) [32]. Briefly, aliquots of 1μL were injected in pulsed splitless mode with injection temperature of 315^{o}C. The column temperature program had an initial temperature of 40^{o}C which was held for 2 min, 25^{o}C min^{-1} to 100^{o}C then followed by an increase of 5^{o}C min^{-1} to 315^{o}C (held for 13.4 min). The transfer line, ion source and quadrupole temperatures were 315^{o}C, 230^{o}C, and 150^{o}C, respectively. A total of 55 m/z's divided into 12 groups were acquired in SIM mode (for specification, see [32]). The dwell time for each m/z was 25 ms with 2.81 scans s^{-1}. In absence of appropriate alkyl-substituted PAC calibration standards, the relative response factors (RRFs) of alkyl-substituted PACs described by Hawthorne *et al.* (2006) [20] and calibration curves from the respective un-substituted PACs were used for estimating the concentration of alkyl homologues series of PACs. For dibenzothiophene and benzothiophene no alkyl RRFs were available and the RRF of their respective un-substituted PACs assumed to be 1.0 were used [20].

The quantitative analysis of Danish EPAPAH$_7$s (fluoranthene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, and dibenz[*a,h*]anthracene), and TPH at a commercial laboratory was done accordingly to the REFLAB4 and REFLAB1, respectively [33,34].

2.4 Extraction and quantification of O-PACs

Extraction was performed by PLE with a Dionex ASE 200 accelerated solvent extractor. Briefly, a 5 mL stainless steel extraction cell was packed with two cellulose filters followed by 1.0 gram of Ottawa sand. 2 g of soil was mixed thoroughly with 2 gram of Ottawa sand in a mortar and quantitatively added to the extraction cell. 200 µL of the internal standard solution was added directly on top of the sample and left for 20 min. Extraction was performed using *n*-hexane/acetone (1:1, v/v) at 150°C and two static cycles of 5 minutes each. The extracts were fractionated as follows: An open glass column (15 mm) was packed with 5 g deactivated silica gel (10% water) and eluted with 5 mL *n*-hexane, 15 mL *n*-hexane:dichloromethane (3:1,v/v), and 30 mL dichloromethane in succeeding order to recover PACs and O-PACs in fractions 2 and 3, respectively. Recovery standards were spiked to each fraction. The analysis of the O-PACs was performed using the same GC-MS as for the PAC analysis. The temperature program was 90°C for 1 minute, increase by 8°C min^{-1} up to 300°C and hold for 10 minutes. The 13 PACs were detected by SIM as described earlier [35]. The monitored m/z's for the measured compounds are shown in Supplementary Data, Table S4. Two six-point internal calibration curves (low concentrations (0.008 to 0.3 µg mL^{-1}) and high concentrations (0.3 to 5µg mL^{-1}) were used for quantification of the O-PACs; concentrations were corrected for recovery.

2.5 PCA

The 29 soil samples were analyzed by PCA. 54 variables were included in the analysis. These variables consisted of concentrations of individual compounds or groups of compounds in the soils: TPH; 19 un-substituted PACs (see Chemicals and reagents for specification); alkyl-homologues of naphthalene, fluorene, dibenzothiophene, benzothiophene, phenanthrene, pyrene, and chrysene (31 variables); and ∑EPAPAH$_{16}$, ∑19 PACs, and ∑Danish EPA PAH$_7$, respectively. The O-PACs were not included in the PC model as they were detected in < 70 % of the soils leading to a large number of missing values in the data set (see Supplementary Data, Table S3). If variables with too many missing values in the same soils are included in PC models it introduces some spurious correlations in data. Thus, the variation in the data matrix **X** of size *I* (29 soils) × *J* (54 compounds) is described by the outer product of the score matrix **T** (*I x K*), the loading matrix **P** (*J x K*) and the residual, *E* (*I x J*). The score matrix T is column-wise orthogonal while P is columns-wise orthonormal (Eq. 2).

$$\boldsymbol{X} = \boldsymbol{T}\boldsymbol{P}^{\boldsymbol{T}} + \boldsymbol{E} \qquad (2)$$

The principal components (PCs) are linear combinations of the original variables and are ordered accordingly to their explained variances, thus the first PC describing the highest variation in the data, and the following PCs account for less. The variables were normalized to the sum of the 54 variables included in the data set to remove concentration effects and focus the analysis on patterns. Data were then autoscaled prior to analysis to provide each compound with the same likelihood to influence the PC model independent on the absolute concentrations. A full cross validation (leave-one-out) was applied to the PC model. The explained variance of the PCs suggested flattened out after PC3, which indicates inclusion of PC1, PC2, and PC3 (combined explaining 72 % of the variation) and three PCs were therefore included in the final PC model. The PCA was performed in LatentiX version 2.1.

3. Results and discussion

3.1 Source identification

The PAC composition constitutes the backbone of source identification of hydrocarbons [18,25,26,36-38]. In addition, a wide range of source identification techniques exists. In this study, we use qualitative analysis of GC-FID chromatograms, the chemical composition of PACs, diagnostic ratios, and multivariate pattern recognition.

3.1.1 Qualitative analysis of GC-FID chromatograms

GC-FID chromatograms are often used as a powerful visual screening tool in fingerprinting of contamination of petrogenic origin [22,24,25,39]. The saturates, containing among others straight- and branched chained alkanes, are the dominating compound group in crude oil and petroleum products. In non-weathered petrogenic sources the distribution of the straight alkanes (*n*-alkanes) and the retention time region for the unresolved complex mixture (UCM) hump in the GC-FID chromatogram reflect the type of oil product by which the soil was contaminated [22]. Soil 9 (Figure 1) shows a well-characterized *n*-alkane profile ranging from C_6- to C_{28}-*n*-alkanes indicating a newly spilled heating oil/light fuel oil. The *n*-alkanes are generally the most susceptible for biodegradation of the hydrocarbons in soil [40] and this changes the hydrocarbon fingerprint over time. Soil 29 shows no *n*-alkane pattern, nearly no low-molecular-weight (LMW) hydrocarbons, and very few resolved peaks. A large UCM in the C_{20}- to the C_{50}-region dominates the chromatogram. The UCM of petroleum products is believed to originate from among others the presence of naphthenic acids either inherent in the oil or originating from microbial degradation of branched chain alkanes (paraffins) [41,42] and recognized by low abundance or complete absence of straight- and branched chain alkanes [41]. The GC-FID chromatogram of Soil 29 indicates presence of a heavily weathered heavy fuel oil or lubricating oil [43]. Soil 1 (Figure 1) reveals no *n*-alkane pattern; clear, resolved peaks of primarily un-substituted PACs dominate the GC-FID chromatogram which suggests pyrogenic hydrocarbon sources (Supplementary Data, Figure S2 shows the TPH chromatograms of the 29 studied soils). The qualitative analysis of GC-FID chromatograms reveals chemical composition features of hydrocarbons which are highly useful in source identification.

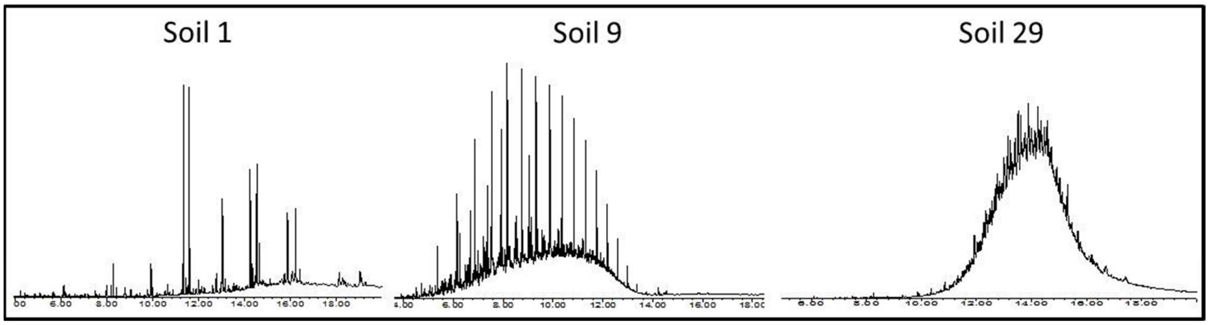

Figure 1 TPH chromatograms of Soil 1, Soil 9, and Soil 29.

3.1.2 Chemical composition of un-substituted and alkyl-substituted PACs

A more detailed analysis of the composition of un-substituted PACs and alkyl-substituted homologues series of PACs (naphthalene, dibenzothiophene, flourene, phenanthrene, pyrene, and chrysene) was applied to determine the overall petrogenic and pyrogenic source origin (Figure 2). The PAC fingerprints of Soil 1 (Figure 2a) reveal a soil contaminated with mainly pyrogenic PACs: The un-substituted PACs are dominant with a decreasing profile of alkyl-substituted PACs (see profiles of alkyl-substituted homologues of pyrene and chrysene in Figure 2a, left). A pronounced pattern of $EPAPAH_{16}$ (Figure 2a, right) is present in the soil: The high-molecular-weight (HMW) PACs being dominant over LMW PACs [23,44,45]. Both trends are characteristic of a pyrogenic chemical fingerprint. In contrast, Soil 9 exhibits the characteristic bell-shaped petrogenic distribution profiles of phenanthrene and pyrene homologues series (Figure 2b). The bell-shape is readily modified to a distribution profile of $C_0<C_1<C_2<C_3<C_4$ of the alkyl-substituted homologues (see alkyl homologue series of naphthalene and fluorene, Figure 2b, left) most likely due to weathering or degradation [45-47]. Soil 15 is a mixed petrogenic and pyrogenic source contaminated soil; it shows higher concentrations of un-substituted PACs resulting in lower relative concentrations of the alkyl-substituted PACs (see profiles of alkyl-substituted homologues of pyrene and chrysene Figure 2c, left) and a dominance of 4-6 ring PACs over 2-3 ring PACs. The clear changes in PAC fingerprints from pyrogenic (Figure 2a) to petrogenic (Figure 2b) sources demonstrate the power of the PAC composition as a tool to determine the sources of hydrocarbons in soil. Exclusively examining the $EPAPAH_{16}$ provides only weak diagnostic tools for differentiation between pyrogenic and petrogenic hydrocarbon sources. This is clear from the $EPAPAH_{16}$ analysis of soil 1, 9, and 15 leaving only the impression of a heavily PAC contaminated soil (Soil 1, Figure 2a), a lightly contaminated soil (Soil 9, Figure 2b) and a moderately contaminated soil (Soil 15, Figure 2c).

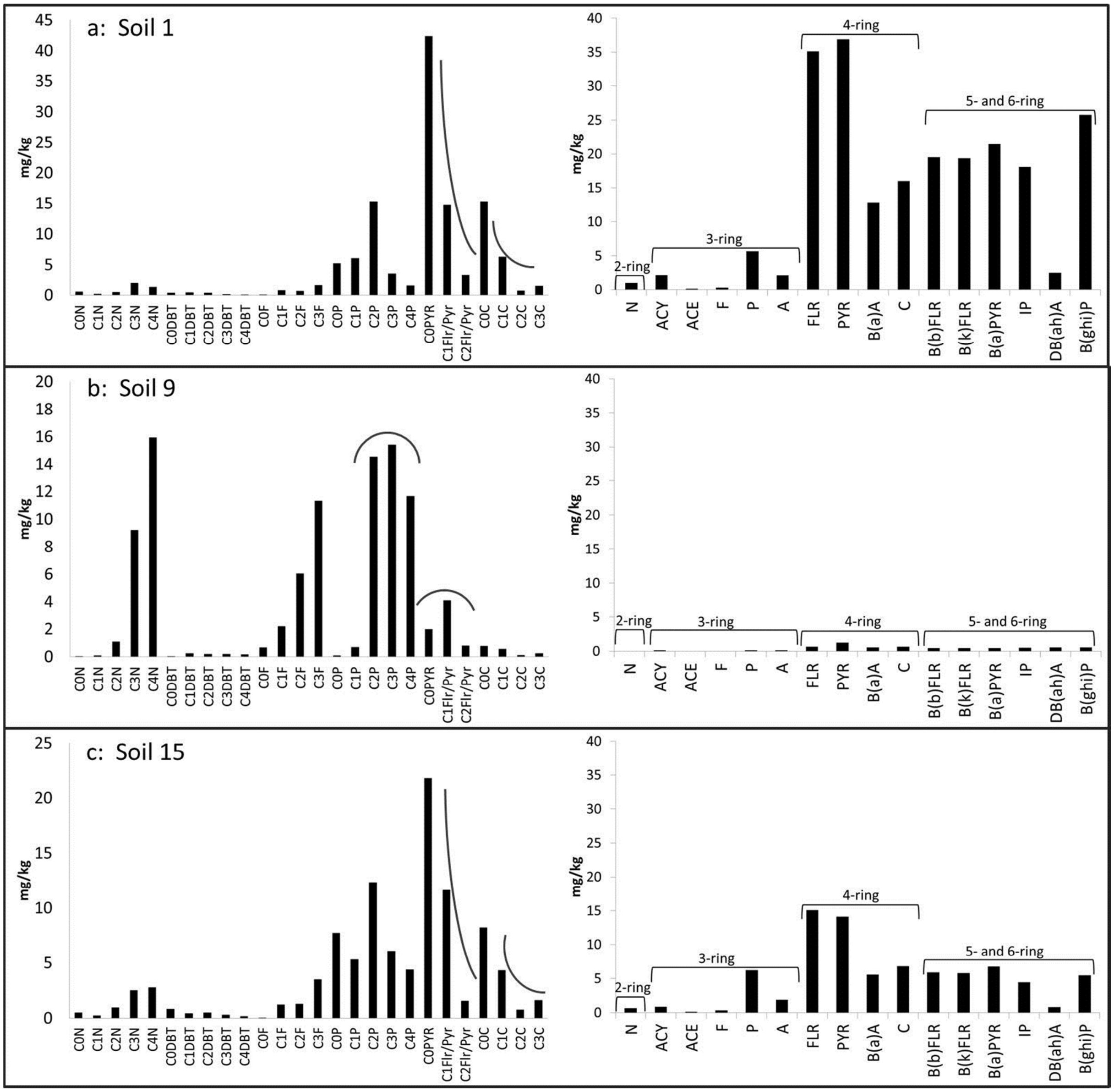

Figure 2. PAC fingerprints of Soil 1(a), Soil 9 (b), and Soil 15 (c) showing concentrations of alkyl-substituted PAC homologues series of naphthalene (N), dibenzothiophene (DBT), fluorene (F), phenanthrene (P), pyrene (PYR), fluoranthene (FLR), and chrysene (C) (left), and EPAPAH$_{16}$ (N, acenaphthylene (ACY), acenaphthene (ACE), DBT, F, P, anthracene (A), FLR, PYR, benz[*a*]anthracene (B(a)A), chrysene(C), benzo[*b*]fluoranthene (B(b)FLR), benzo[*k*]fluoranthene (B(k)FLR), benzo[*a*]pyrene (B(a)PYR), indeno[1,2,3-*c,d*]pyrene (IP), dibenz[*a,h*]anthracene (DB(ah)A), and benzo[*g,h,i*]perylene (B(ghi)P) (right). For clarity, varying Y-axes of the alkyl-substituted PAC homologues are applied.

3.1.3 Diagnostic ratios

Four diagnostic ratios of un-substituted PACs were applied: LMW/HMW PACs (i.e. 3-4 ring PACs /5-6 ring PACs) [48]; anthracene/(anthracene + phenanthrene) (Ant/(Ant+Phe)) [38]; benz[*a*]anthracene/(benz[*a*]anthracene + chrysene) (BaA/(BaA+Chr)) [3,48]; and fluoranthene/(fluoranthene + pyrene) (Flr/(Flr+Pyr)) [38,49] (see Supplementary Data, Figure S1). Four of the petrogenic contaminated soils (Soil 6, 10, 19, and 29) were not included in the analysis as they displayed concentrations of un-substituted PACs (including anthracene, phenanthrene, benz[*a*]anthracene, chrysene, fluoranthene, and pyrene) below LOD.

The ratios of LMW/HMW PACs have previously been used to differentiate between petrogenic and pyrogenic sources in sediment [48] and in urban run-off, dust, rain, and canopy throughfall [50]. For high temperature processes, such as combustion of fossil fuels in engines, organic molecules are cracked to free reactive radicals forming stable HMW PACs (pyrolysis) while LMW PACs and alkyl-substituted PACs are usually formed during low temperature processes (petrogenesis) [17]. Pyrogenic sources are thus dominated by HMW PACs and petrogenic sources by LMW PACs. Two soils, Soil 24 and Soil 28, were highlighted as petrogenic contaminated soils by ratios above 1. Soil 9, 20, and 22, which are classified as highly petrogenic contaminated soils according to fingerprinting of the sources (e.g. Figure 2) and multivariate data analysis (Figure 3), are not grouped together with the petrogenic contaminated soils. The misclassification may reflect the soil matrix and the degree of weathering/degradation of the contamination source; the LMW are susceptible to evaporation [50-52] and are more readily degraded than HMW PACs in the soil [5]. The alkyl-substituted homologues series of naphthalene and fluorene of Soil 9 and Soil 15 (Figure 2b and 2c) indicates weathered PAC fingerprints. Most of the contamination sources in the soils of our study are old and heavily affected by weathering and thus the concentrations of LMW PACs may be low resulting in lower ratios of LMW/HMW. Based on this, the ratio of LMW/HMW PACs is not suitable for source differentiation of weathered hydrocarbon sources in soil.

Thermodynamically stable compounds are present in higher concentrations in sources originating from high temperature processes than less stable compounds [23,49]. Phenanthrene is the most stable 3-ring PAC [38] and pyrogenic sources contain relatively more of phenanthene than of anthracene. The ratio of Ant/(Ant+Phe) differentiates petrogenic sources (< 0.10) and pyrogenic sources (> 0.10) [38,49]. However, the ratio of 0.10 is not a clear-cut distinction as ratios > 0.10 have been reported for a variety of petrogenic sources [49]. The Ant/(Ant+Phe) ratio could not be used to differentiate between petrogenic and pyrogenic sources in this study (see Supplementary Data, Figure S1). The same principal of thermodynamically stable versus less stable compounds applies for benz[*a*]anthracene and chrysene and for fluoranthene and pyrene. The ratio of BaA/(BaA+Chr), however, showed no differentiation between petrogenic and pyrogenic sources. The ratio of Flr/(Flr+Pyr) did to some extent distinguish between petrogenic and pyrogenic sources. The four petrogenic contaminated soils (Soil 9, 20, 22, and 28) were classified with ratios below 0.4 indicating petrogenic sources; five sources were classified as petroleum combustion sources; and the remaining soils as combustion sources from grass, wood, and coal combustion. Yunker *et al.* (2002) evaluated the range of stability of PAC isomers and concluded that the isomers of fluoranthene and pyrene (ion 202) revealed the highest stability, followed by the isomer of anthracene and phenanthene (ion 178), and last benzo[*a*]anthrancene and chrysene (ion 228) (only isomeric pairs of PACs used in this study are listed here) [49]. According to this, the ratio of Flr/(Flr+Pyr) is the best indicator of thermodynamic (petrogenic) versus kinetic (pyrogenic) sources. Our study of urban soils affected by weathering processes confirms this.

3.1.4 Multivariate data analysis for source characterization

PCA was applied to the sum-normalized concentration data obtained from the 29 soil extracts. Multivariate pattern recognition studies provide a means to distinguish minor differences in the hydrocarbon fingerprints. As the main variance in the data set was explained by PC 1 and PC 2 the data analysis only focus on PC1 and PC2. Figure 3 shows the score (a) and loading (b) plots of PC1 versus PC2. First of all, the PCA revealed a clear differentiation between pyrogenic and petrogenic sources along PC1. The HMW un-substituted PACs representative of pyrogenic PACs have high negative loading coefficients (-0.2 to -0.15), the LMW un-substituted PACs, which may origin from both pyrogenic and petrogenic sources have slightly negative loading or positive coefficients (-0.15 to 0.05), and the C_2-C_3 alkylated PACs and TPH, characteristic of petrogenic sources, have positive loading coefficients (Figure 3b).

PC2 mainly describes the heaviness of the oil products for samples with large positive PC1 scores; thus samples with positive PC2 scores (marked cluster 'IV. Heavy petrogenic sources' in the score plot) contain a larger fraction of the more alkylated homologues, indicating a heavy oil product or a lighter but weathered oil. The group is also characterized by a higher sulfur content represented by larger relative concentrations of 3-4 ring alkyl-substituted PACs as well as sulfur containing heterocyclic polyaromatics such as C_1-C_3 alkyl-substituted benzothiophenes and dibenzothiophenes. In contrast, soils with negative PC2 and positive PC1 scores (samples marked cluster 'III. Lighter petrogenic sources' in the score plot) are lighter un-weathered oil represented by a large relative concentration of two-ring alkylated-PACs.

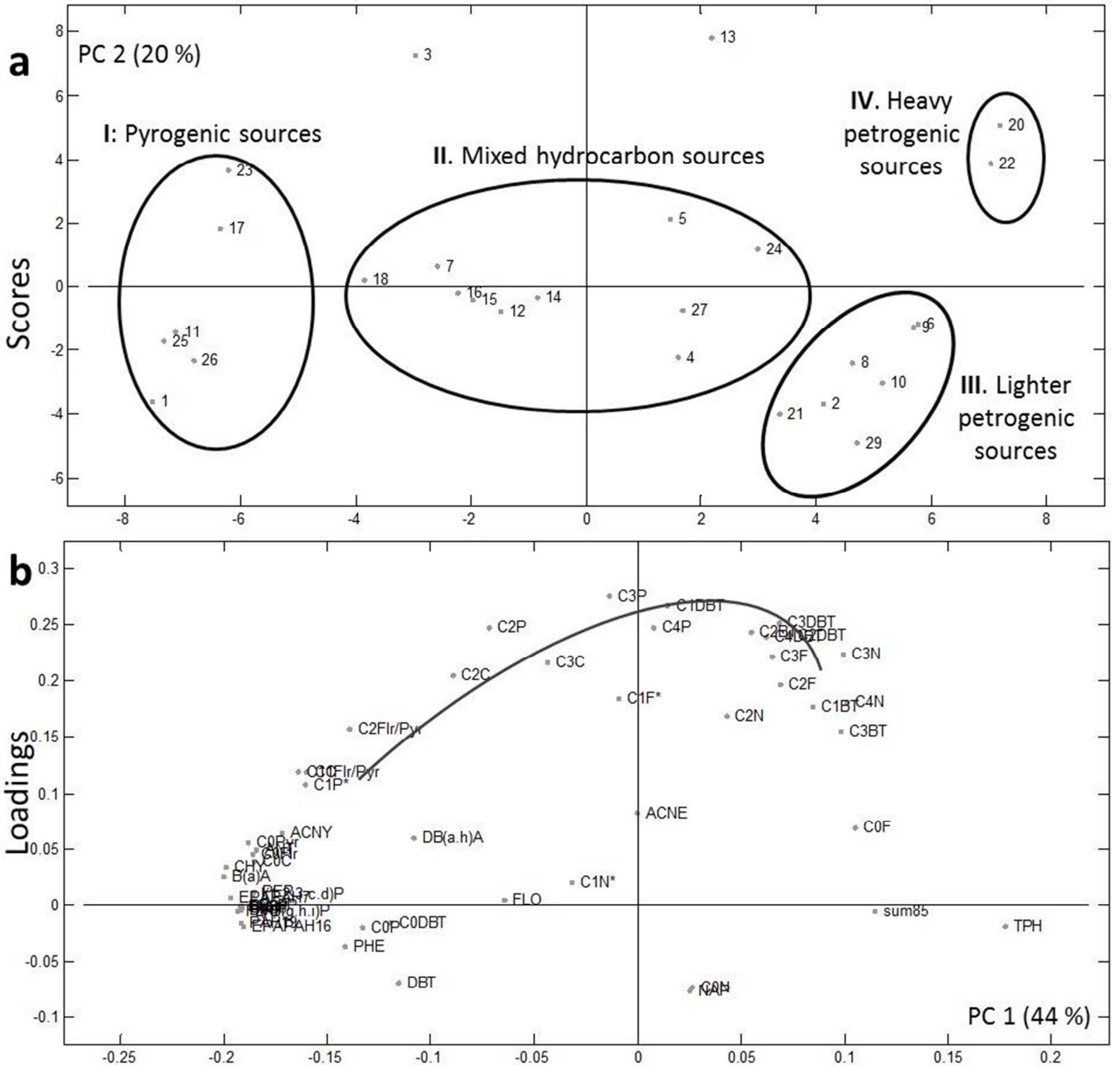

Figure 3. PCA of 29 soils showing PC1 vs. PC2 of scores (a) and loadings (b). Variations explained by the PCs are shown in brackets. Clusters I to IV are presented (circles) in the score plot while an alkylation trend (dark line) is shown in the loading plot.

In contrast, soil samples with negative PC1 scores are samples with mainly pyrogenic PAC input. These are represented by large positive loadings of the pyrogenic PACs, i.e. A, FLR, BaA, BbF, BkF, IP, and BghiP, and of the $\sum$EPAPAH$_{16}$. Soil samples with PC1 scores around zero (Cluster II) are soils with mixed hydrocarbons sources of both petrogenic and pyrogenic origin.

As described above, the PC model was in accordance with the chemical interpretation of the contamination sources of the soils except for Soil 21. The PC model classified Soil 21 as a "lighter petrogenic source" while the TPH analysis and the chemical composition of un-substituted and alkyl-substituted PACs of Soil 21 clearly pointed at a pyrogenic pollution source. Soil 21 displays very high concentrations of naphthalene; as mentioned above, LMW un-substituted PACs may origin from both pyrogenic and petrogenic sources which might explain the discrepancy in source apportionment in the PC model. The inclusion of more soils in the model in the future will create a more robust model and the ability to extract even more detail source related information from the data set. In addition, source samples of e.g. creosote and soot samples to represent pyrogenic samples and different crude oils and refined petroleum products to characterize petrogenic sources, would improve the range of fingerprints represented by the model.

3.2 Including alkyl-substituted PACs in quantitative analysis of PACs

The $\sum$EPAPAH$_{16}$ concentrations in the soils varied from below LOD to 267 μg g^{-1} (dw) while the $\sum$alkyl-substituted PAC concentrations varied between 1.54 and 131 μg g^{-1} (dw) (all concentrations are specified in Table S2 in Supplementary Data).The chemical fingerprints of EPAPAH$_{16}$ and the alkyl-substituted PAC homologues series of selected PACs are presented for Soil 25 and Soil 22 in Figure 4. Soil 25 represents a typical pyrogenic contaminated soil while Soil 22 is an example of a petrogenic contaminated soils.

The EPAPAH$_{16}$ fingerprint of Soil 25 (Figure 4, left) shows a dominance of 4-6 ringed PACs ($\sum$EPAPAH$_{16}$ = 266 μg g^{-1} (dw)). In contrast, Soil 22 contains negligible concentrations of the un-substituted EPAPAH$_{16}$ ($\sum$EPAPAH$_{16}$ = 1.98 μg g^{-1} (dw)). The evaluation of the PAC contamination load based solely on the EPAPAH$_{16}$ fingerprints of Soil 25 and Soil 22 gives the impression of a heavily PAC contaminated soil (Soil 25) and an uncontaminated soil (Soil 22). Figure 4 (right) shows the chemical fingerprints of alkyl-substituted PAC homologues series of Soil 25 and Soil 22. The C$_1$-, C$_2$-, C$_3$-, and – when possible – C$_4$-alkyl-substituted PAC homologues were calculated as groups of alkyl-isomers [53], e.g. the C$_2$-naphthalenes are made up of 12 isomers and the concentrations of C$_2$-naphthalenes are the sum of the 12 C$_2$-naphthalene isomers. The chemical fingerprints of alkyl-substituted PAC homologues of Soil 25 and Soil 22 (Figure 4) reveal a different picture of the two soils than the evaluation based on EPAPAH$_{16}$; Soil 22 is not uncontaminated but contains substantial amounts of alkyl-substituted PACs. The high levels of alkyl-substituted PACs and negligible levels of un-substituted PACs is a characteristic chemical fingerprint for petrogenic contaminated soils in our dataset (Soil 9, 19, 20, 22 and 29).

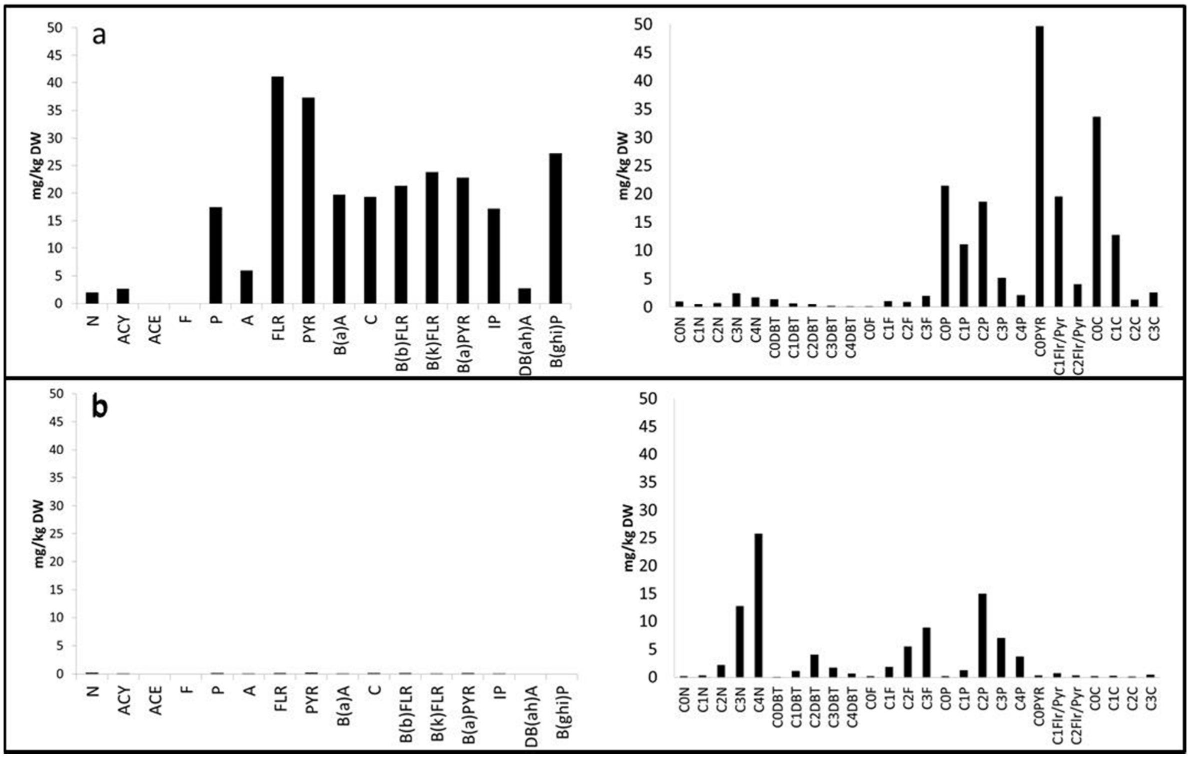

Figure 4. Contaminant fingerprints of Soil 25 (a) and Soil 22 (b), showing EPAPAH$_{16}$ (naphthalene (N), acenaphthylene (ACY), acenaphthene (ACE), dibenzothiophene (DBT), flourene (F), phenanthrene (P), anthracene (A), fluoranthene (FLR), pyrene(PYR), benz[*a*]anthracene (B(a)A), chrysene(C), benzo[*b*]fluoranthene (B(b)FLR), benzo[*k*]fluoranthene (B(k)FLR), benzo[*a*]pyrene (B(a)PYR), indeno[1,2,3-*c,d*]pyrene (IP), dibenz[*a,h*]anthracene (DB(ah)A), and benzo[*g,h,i*]perylene (B(ghi)P) (left), and alkyl-substituted PAC homologues series of N, dibenzothiophene (DBT), F, P, PYR, and C (right).

In Figure 5 the percentages of un-substituted PACs are compared with the percentages of alkyl-substituted PACs (see Table S2 for compound specification). Soil 25 contains 25 % alkyl-substituted PACs while Soil 22 holds 98 % alkyl-substituted PACs. If the alkyl-substituted PACs are included in the sum of PACs, the total concentration of PACs in Soil 22 increases from 1.98 μg g^{-1} (dw) ($\sum$EPAPAH$_{16}$) to 93.8 μg g^{-1} (dw) ($\sum$EPAPAH$_{16}$ + $\sum$alkyl-substituted PAC homologues). The $\sum$EPAPAH$_{16}$ is fairly representative for pyrogenic sources; the $\sum$EPAPAH$_{16}$ has been reported to make up one-third to two-thirds of the total PAC concentration [54]. In our study, $\sum$EPAPAH$_{16}$ made up three-fourth of the total PAC concentration in five soils with dominant pyrogenic sources, i.e. Soil 1, Soil 11, Soil 21, Soil 25, and Soil 26 (see Figure 5). The EPAPAH$_{16}$ is not representative for petrogenic sources; the ∑EPAPAH$_{16}$ make up < 10 % of ∑EPAPAH$_{16}$ + ∑alkyl-substituted PAC homologues in the petrogenic contaminated soils (see Figure 5) and this implies a risk of underestimating the concentration of PACs at petrogenic contaminated sites [17,20].

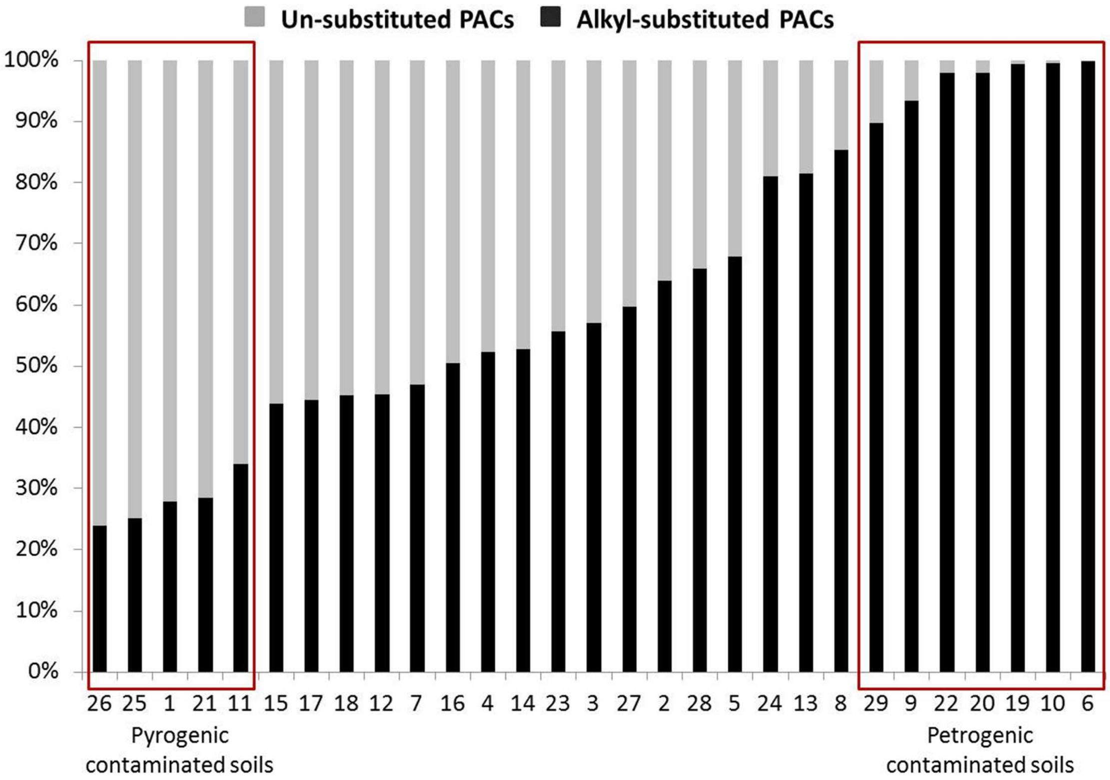

Figure 5. Percentages of alkyl-substituted PACs (Alkyl PACs, see Table S2) and un-substituted PACs (PACs, see Table S2) in the 29 soil samples. The primary pyrogenic and petrogenic contaminated soils are highlighted (red boxes).

3.3 O-PACs

The ∑O-PAC concentrations in soils ranged from < LOD (0.03 mg kg^{-1} (dw) for Soil 6 and 0.05 mg kg^{-1} (dw) for Soil 29) to 151 mg kg^{-1} (dw) (Soil 21) (Table S3 in Supplementary Data lists the O-PAC concentrations and LODs of all soils). Soil 21 had a very high concentration (140 mg kg^{-1} (dw)) of one specific carbonyl O-PAC, benz[*a*]anthracene-7,12-dione. A study on O-PACs in urban soils of Bratislava found benz[*a*]anthracene-7,12-dione to be dominant in highly contaminated soils and closely correlated to combustion derived PACs [55]. The concentrations of ∑O-PACs in the soils are comparable to concentrations in urban soils of Basel [56] and Bratislava [55] when the varying number and selection of O-PACs are taken into account, but lower than ∑O-PAC concentrations at former gasworks sites and wood preservation sites [10,57]. Generally, the hydroxyl-O-PACs (i.e. 1-Naphthol and 2-Phenylphenol) revealed lower concentrations than the carbonyl-O-PACs, which is in line with earlier studies [12,55]. Table 1 shows the O-PAC concentrations of three pyrogenic contaminated soils, Soil 1, Soil 16, and Soil 25, and two petrogenic contaminated soils, Soil 9 and Soil 22.

Table 1. Concentrations of O-PACs in selected soils with pyrogenic and petrogenic sources.

	Pyrogenic sources			Petrogenic sources	
	Soil 1	Soil 16	Soil 25	Soil 9	Soil 22
O-PAC	mg kg^{-1} (dw)				
1-idanone	0.08	*0.02*	n.d.	*0.02*	*0.01*
1-napthol	n.d.	n.d.	0.09	n.d.	n.d.
1-naphthaldehyde	0.06	n.d.	0.10	n.d.	*0.02*
2-phenylphenol	*0.01*	*0.01*	0.08	*0.00*	*0.01*
9-fluorenone	0.54	0.88	1.03	*0.02*	0.15
1,2-acenaphthenequinone	0.13	n.d.	2.45	n.d.	0.04
9,10-anthraquinone	1.59	4.01	1.70	*0.09*	0.15
4h-cyclopental[*def*]phenanthrenone	1.80	0.89	1.66	0.08	0.05
Benzo[*a*]fluorenone	1.90	1.01	1.30	*0.07*	0.20
7h-benz[*de*]anthracen-7-one	3.58	1.53	7.31	0.27	0.25
Benz[*a*]anthracene-7,12-dione	0.85	0.81	0.56	0.04	*0.04*
Naphthacene-5,12-dione	*1.02*	*0.51*	2.26	*0.05*	0.14
6H-benzo[*cd*]pyrenone	3.97	1.03	4.90	0.14	0.27
∑O-PACs	14.5	10.2	23.4	0.54	1.26
∑EPAPAH$_{16}$	218	60.6	267	6.80	1.98

n.d. = not detected. Values below LOD are in italics.

The soils with primarily pyrogenic sources of hydrocarbons (Soil 1, Soil 16, and Soil 25) did contain a considerable proportion of O-PACs corresponding to between 6 and 18 % of the ∑EPAPAH$_{16}$ levels. The soils with primarily petrogenic sources (Soil 9 and 22) were nearly depleted of the O-PACs included in this study. Figure 6 shows total summed selected ion chromatograms of O-PACs in Soil 1 (pyrogenic pollution sources) and Soil 22 (petrogenic pollution sources).

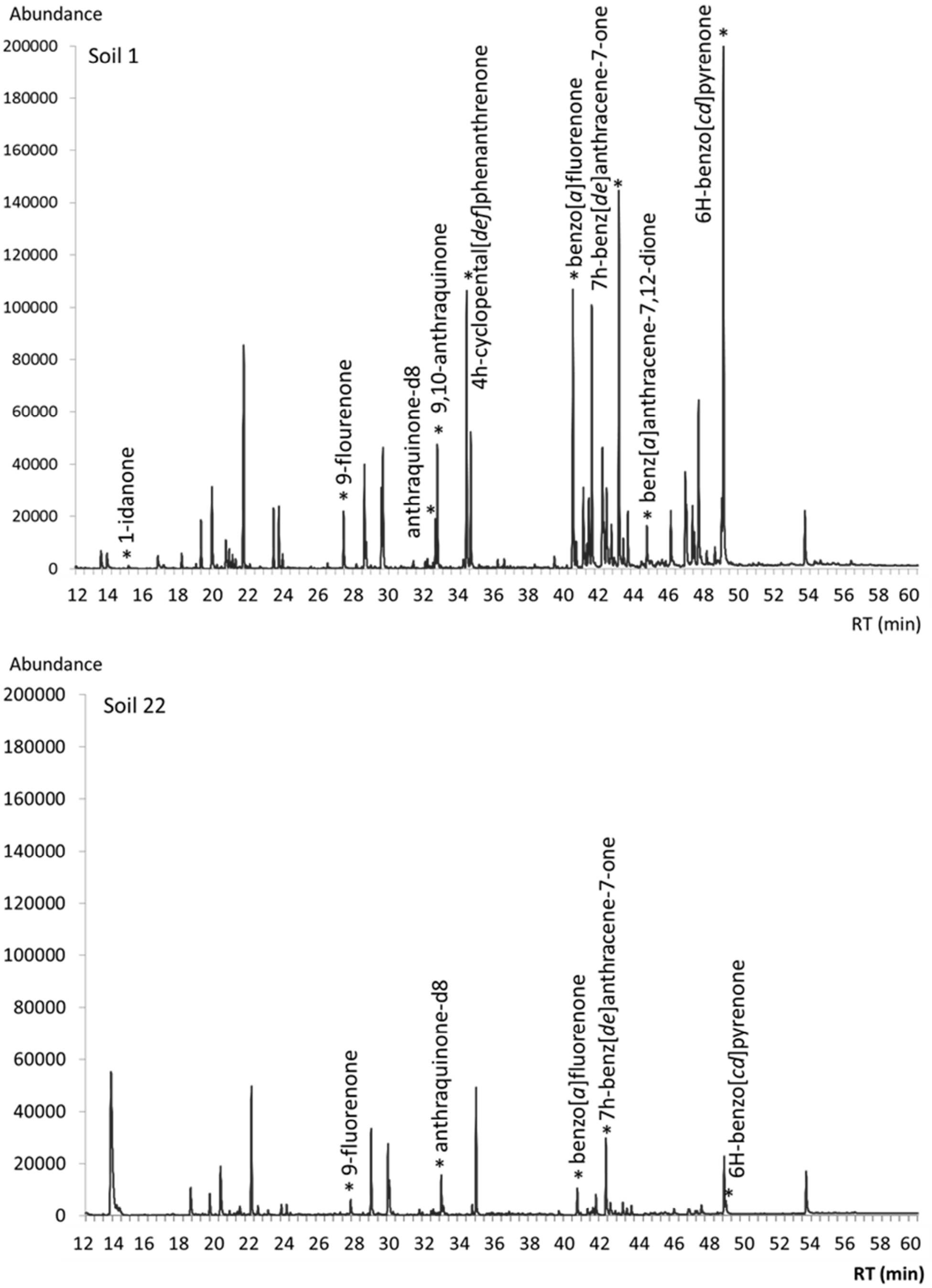

Figure 6. Total summed selected ion chromatogram of O-PACs in Soil 1 (top) and Soil 22 (bottom). 9 O-PACs are highlighted by an asterix: 1-idanone, 9-fluorenone, anthraquinone-d8 (internal standard), 9,10-

anthraquinone, 4h-cyclopental[*def*]phenanthrenone, benzo[*a*]fluorenone, 7h-benz[*de*]anthracene-7-one, benz[*a*]anthracene-7,12-dione, 6H-benzo[*cd*]pyrenone.

The ∑O-PAC concentrations have previously been shown to be highly correlated to ∑EPAPAH$_{16}$ [55]. In line with this, studies of O-PACs in heavily polluted soils with pyrogenic sources, e.g. old wood preservation, gasworks, and coke production sites, revealed much higher total amounts of O-PACs [10,58]. The proportion of ∑O-PACs to ∑EPAPAH$_{16}$ in the heavily polluted soils revealed proportions between 12 and 20 % ∑O-PACs (only the O-PACs quantified in our study were included in the comparison) [10,58]. This is comparable with our findings in pyrogenic contaminated soils with proportions of ∑O-PACs between 6 and 18 %. Combustion-related sources, i.e. coal and vesicular combustion, are known sources of O-PACs [59,60]. A plausible explanation for the low concentrations of O-PACs in soils with petrogenic sources is that the precursors of the determined O-PACs are primarily un-substituted PACs. The ratios between PACs and their likely derived O-PACs (e.g. naphthalene to 1-naphtol and anthracene to 9,10-anthraquinone) were examined by Bandowe *et al.* (2011); most carbonyl-O-PACs correlated significantly with their parent PAC [56]. O-PACs are present in petrogenic sources, for instance in crude oil where e.g. naphthenic acids and C_0-C_8 alkyl-substituted phenols are common, but these O-PACs are not included in this study.

4. Conclusion

The chemical fingerprinting in this study was a four point strategy of i) qualitative analysis of TPH chromatograms; ii) quantitative analysis of EPAPAH$_{16}$ as well as the alkyl-substituted homologues series of naphthalene, dibenzothiophene, fluorene, phenanthrene, pyrene, and chrysene; iii) source specific ratios of LMW/HMW PACs, Ant/(Ant+Phe), BaA/(BaA+Chr), and Flr/(Flr+Pyr); and iiii) multivariate pattern recognition of sum-normalized concentrations.

For source identification of hydrocarbon-contaminated soils, the composition of PACs as well as TPH chromatograms and multivariate data analysis were successfully applied to differentiate between and within petrogenic and pyrogenic sources. The selected source specific ratios of un-substituted PACs in this study were only to some extent applicable for distinguishing the sources; partly because the soils were affected by weathering and/or degradation resulting in loss of LMW PACs which blurred the differentiation of contamination sources and partly because the soils with highly petrogenic sources were excluded from the ratios as the concentrations of un-substituted

PACs in the soils were below LOD. To provide a robust identification of hydrocarbon sources in soils, the qualitative analysis of GC-FID chromatograms and the quantitative analysis of PACs cannot stand alone; a combination of the techniques is required. The multivariate pattern recognition, however, could distinguish between hydrocarbon sources of petrogenic and pyrogenic origin and differentiate within petrogenic and pyrogenic sources, respectively. This illustrates the power of multivariate data analysis for source characterization and identification.

The fingerprinting of 29 soils revealed that the $EPAPAH_{16}$ are not representative for petrogenic contaminated soils; the six petrogenic contaminated soils of this study (Soil 6, 9, 10, 20, 22, and 29) comprised between 94 and 99 % alkyl-substituted PACs of the total concentration of PACs. Exclusively quantifying the un-substituted PACs will result in an underestimation of the PAC input to petrogenic contaminated soils.

The quantification of O-PACs in the soils revealed concentrations of O-PACs between <LOD (0.03 mg kg^{-1} (dw)) and 150.61 mg kg^{-1} (dw). The proportion of O-PACs in pyrogenic contaminated soils corresponded to between 6 and 18 % of the $\sum EPAPAH_{16}$ while the petrogenic contaminated soils were nearly depleted of O-PACs. The O-PACs are not routinely included in the screening of contaminated soils. Thus, even when a remediated soil complies with the threshold limits in the soil criteria, the soil may contain considerable amounts of degradation products, including the O-PACs. The selected O-PACs of this study are likely degradation products of un-substituted PACs. In perspective, it would be interesting to examine potential oxidative degradation products of alkyl-substituted PACs in petrogenic contaminated soils.

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