2015

Pyrolysis-GC-MS for the Rapid Environmental Forensic Screening of Contaminated Brownfield Soil

Azucena Lara-Gonzalo
University of Oviedo

Michael A. Kruge
krugem@mail.montclair.edu

I Lores
University of Oviedo

B Gutiérrez
University of Oviedo

José Luis Gallego
University of Oviedo, jgallego@uniovi.es

MSU Digital Commons Citation

Lara-Gonzalo, Azucena; Kruge, Michael A.; Lores, I; Gutiérrez, B; and Gallego, José Luis, "Pyrolysis-GC-MS for the Rapid Environmental Forensic Screening of Contaminated Brownfield Soil" (2015). *Department of Earth and Environmental Studies Faculty Scholarship and Creative Works*. 69.
https://digitalcommons.montclair.edu/earth-environ-studies-facpubs/69

Preprint: Lara-Gonzalo A., Kruge M.A., Lores I., Gutiérrez B., Gallego J.L.R. (2015) Pyrolysis-GC-MS for the rapid environmental forensic screening of contaminated brownfield soil. *Organic Geochemistry* **87**:9-20. http://dx.doi.org/10.1016/j.orggeochem.2015.06.012

Pyrolysis-GC-MS for the Rapid Environmental Forensic Screening of Contaminated Brownfield Soil

A. Lara-Gonzalo[a], M. A. Kruge[b], I. Lores[a], B. Gutiérrez[a], J. R. Gallego[a*]

[a] *Environmental Technology, Biotechnology and Geochemistry Group, Campus de Mieres, University of Oviedo, C/Gonzalo Gut. S/N, 33600 – Mieres (Asturias), Spain*
[b] *Department of Earth & Environmental Studies, Montclair State University, Montclair, NJ 07043 USA*

* Corresponding author. Tel.: + 34 985458064
E-mail address: jgallego@uniovi.es (J.R. Gallego)

ABSTRACT

An abandoned chemical plant in Asturias (Spain) was studied using a multi-faceted molecular fingerprinting approach, demonstrating that it is possible to: (1) carefully unravel tangled evidence resulting from multiple pollution sources, and (2) recognize major contaminants largely ignored by conventional analyses. This methodology employed a battery of GC-MS analyses of liquid chromatographic fractions of soil extracts, plus the pyrolysis products of the soil extract's asphaltene fraction and the whole soil itself. In this example, coal tar distillation and the subsequent production of naphthalene, phenols and polymer resins are responsible for most of the soil contamination. Styrene, naphthalene, indene, and their methylated derivatives and dimers (most notably, naphthyl-methylnaphthalene) are particularly abundant and/or distinctive. It is remarkable that most of the contaminants were detected simply by pyrolysis-GC-MS, demonstrating its effectiveness for rapid environmental forensic screening of organic contamination. Commonly used environmental analytical approaches would likely have overlooked the predominant pollutants at this site. This could lead to serious shortcomings in remediation planning and implementation. The novel methodology presented herein appears practical and applicable to complexly-contaminated brownfield sites around the world.

Keywords: Pyrolysis-GC-MS; environmental forensics; chemical fingerprinting; coal tar; soil pollution; polymer resins

1. Introduction

Industrial chemicals and by-products such as petroleum hydrocarbons, creosote, coal tar, POPs (Persistent Organic Pollutants as defined by the Stockholm convention) and their derivatives are contaminants of concern affecting many former industrial sites (brownfields). Their complex chemical composition makes determination of their origin difficult, especially when different mixtures of products are affecting the soil and subsoil, therefore generating a challenging problem for site remediation (Thavamani et al., 2011). In this sense, the need for comprehensive assessment has led to the development of the environmental forensics approach: the systematic investigation of a contaminated site or an event that has impacted the environment (Morrison, 2000).

One of the main tools of environmental forensics is chemical fingerprinting (Wait, 2000; Stout et al., 2002; Stout et al., 2006), which permits the identification of the nature of the contamination, the differences among sources of similar contamination, and the weathering degree of the main pollutants. In this way, the analysis of complex mixtures of organic contaminants by standardized methods (mainly GC-MS techniques) is essential. However, forensic fingerprinting may also require modified methods or customized approaches in order to identify distinctive features of site- or source-specific contamination (Uhler et al., 2010). In addition, complementary historical information related to former industrial activities, geology, geomorphology, and hydrology/hydrogeology of the site is required to determine the origin and sources of contamination.

Balancing the attributes of different analytical methods is therefore advantageous for comprehensive chemical fingerprinting of very complex mixtures of contaminants. In this context, a separation of fractions according to their polarity, and the differentiation between volatile, semivolatile, and high molecular weight compounds can be beneficial. In addition, if the presence of mixtures of high molecular weight contaminants is suspected, pyrolysis techniques can be a suitable supplementary option. In practice, pyrolysis-GC-MS (Py-GC-MS) may confirm or even improve upon the usual information obtained with the more common GC-MS fingerprinting methods. Pyrolysis-GC-MS has been successfully applied in environmental studies related to sediment contamination (de Leeuw et al., 1986; Richnow et al., 1995; Faure and Landais, 2001; Mansuy et al., 2001; Kruge and Permanyer, 2004; Kruge et al., 2010; Micić et al., 2010; 2011, Kruge, in press), wastewater effluents (Greenwood et al., 2012) and industrial waste (Ishikawa et al., 2005

In this work, to test the efficacy of Py-GC-MS in soil pollution assessment, we chose at a former chemical plant with highly contaminated soil, previously studied for remediation purposes (Peláez et al., 2013) and for microbial screening (Guazzaroni et al., 2013). In this study, multiple soil samples were collected in a grid pattern across the site and subjected to the initial characterization. However for the experiment reported herein, we employed a single, composited sample of contaminated soil. One key objective was to assess the ability of Py-GC-MS to identify a complex mixture of contaminants in a sample previously characterized by a battery of standard GC-MS approaches utilizing extraction and fractionation. In addition, Py-GC-MS was chosen to screen for contaminants of potential concern overlooked by standard analytical methods and/or ignored by current environmental regulations. Finally, all the information reported both by Py-GC-MS analysis and by the standard chromatographic characterization of volatile, semivolatile and heavy organic components was used to establish an environmental forensic hypothesis linking the former industrial activities with the main families of contaminants found.

2. Materials and methods

2.1. Study area and initial assessment

The samples used for this study were collected from a former chemical plant in Asturias, northern Spain (Fig. 1). The area affected comprises about 2.5 ha and it was entirely cleared of buildings then abandoned before this study started. There are irregularly-disposed wastes, lenses of tarry materials, broken pipes, and other debris dispersed in the surface soil throughout the site. The industrial activity in this area commenced at the end of the 1960s with naphthalene and phenol production by means of coal tar distillation. However, physical evidence indicated that other activities (especially waste disposal) have affected soil quality. Therefore, as a main part of the characterisation study, extensive historical data collection (personal interviews, legal registers, etc.) was carried out to obtain a list of processes at the plant likely to have produced contamination. A previous characterization of the site by remediation consultants had only highlighted PAHs (Polycyclic Aromatic Hydrocarbons) as contaminants of concern (unpublished data). In contrast, we hypothesized a heterogeneous distribution of contaminants based on the different industrial activities that took place in the site. Therefore thirty-three soil pits distributed within the studied brownfield were excavated and 1-kg soil samples were collected. As a first step we undertook apreliminary assessment of the usual parameters applied for quantification of soil pollution in this type of site; i.e. TPH (total petroleum hydrocarbons), BTEX (benzene, toluene, ethylbenzenes and xylenes), and PAH concentrations.

Additionally, the common physicochemical properties of the soils were measured using standard procedures. The natural background was obtained by means of three 5-kg representative samples from an area not affected by the contamination. Soil pH was measured in a suspension of soil and water (1:2.5) with a glass electrode, and the electrical conductivity was measured in the same extract (diluted 1:5). The following techniques were also applied: dichromate oxidation for organic matter content; Kjeldahl method for nitrogen content; Olsen method for phosphorus content; and the Bernard calcimeter for carbonate content. Organic matter was determined by the ignition method and Bouyoucos Densimetry method was used to establish textural data.

Fig. 1. (Left) Location of the study site. (Right) Detailed scheme of the study site (groundwater flow direction is indicated). The old buildings, demolished in 2006, have been drawn in their approximate original positions as follows: Industrial Production (P1: Naphthalene, P2: Phenols, P3: Resins), Waste Storage (ST1: PCBs and coolants; ST2: "Tinol"), Auxiliary Installations (I1: Underground storage tanks and heating system; I2: Offices and laboratories; I3: Commodities stock; I4: Electric power station)

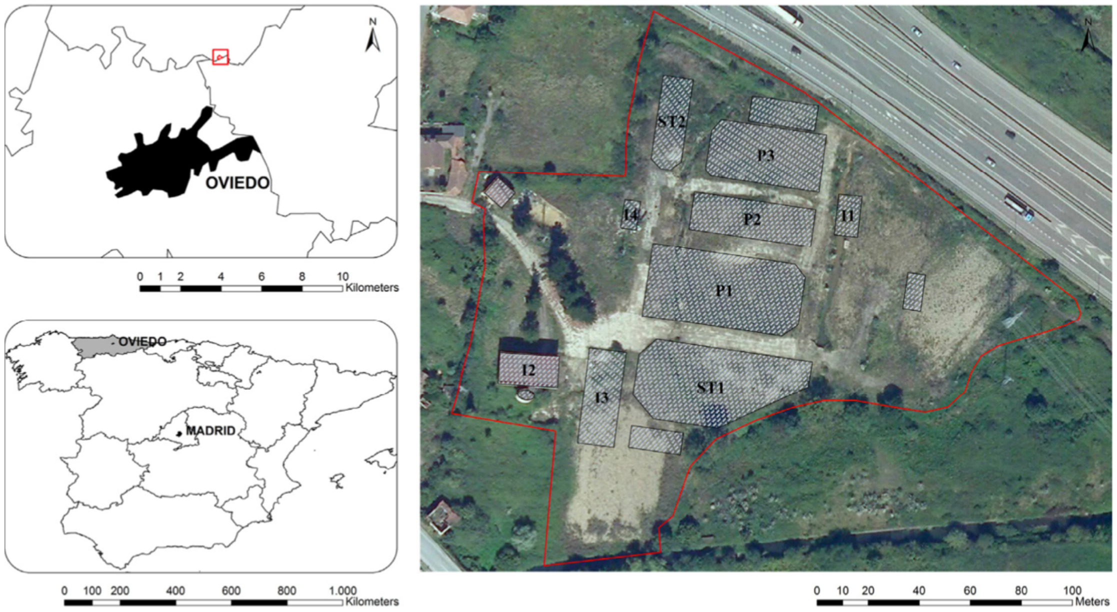
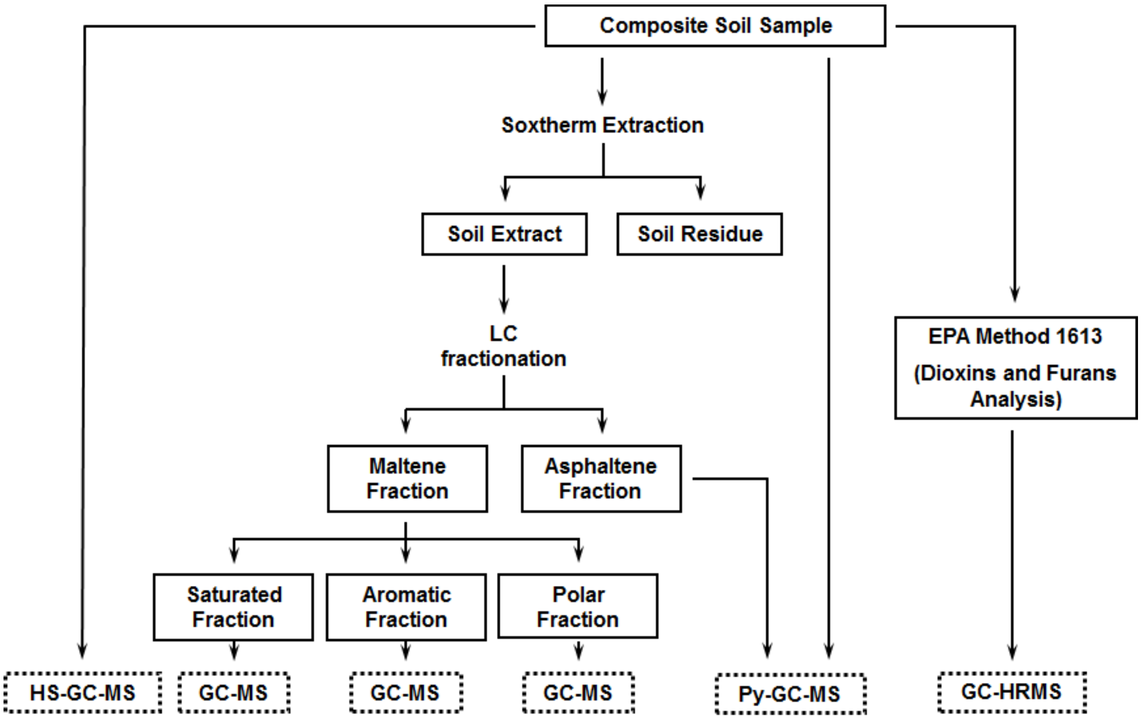


Fig. 2. Flow-chart representing the analytical procedures employed.



2.2. Chemical fingerprinting

2.2.1. Overview and samples

Ten samples of contaminated soil (0.5 kg each, from the top 50 cm of soil) were taken with a hand-auger at “hot spots” detected in the initial characterization process described above (we considered physical evidence, historical data and quantification of PAH, BTEX and TPH). All samples were transferred to dark bottles, sealed and stored at 4 ºC before being analyzed. Then, they were thoroughly mixed to obtain a composite blend of soil, homogenized and sieved (2 mm mesh size). Aliquots taken from this initial composite sample were used for all the different analyses performed in this study.

As mentioned above the strategy proposed in this work, applied to the study site, consists of different analytical techniques used to obtain as much information as possible to obtain a comparison with the performance of Py-GC-MS (Fig. 2). Particularly, for the general outline of semivolatile compounds a solvent extraction followed by liquid chromatographic (LC) fractionation and GC-MS analysis of saturates, aromatics and polars was carried out. Volatile compounds were separately studied by HS-GC-MS (Head-Space GC-MS). Dioxins and furans were determined and quantified by HRGC-HRMS (High Resolution GC-MS) after a specific extraction, given their toxicity at very low concentrations. Finally, pyrolysis GC-MS was also performed with aliquots of the initial composite sample and with the asphaltene fraction of the composite sample's extract.

2.2.2. Extraction, LC fractionation and GC-MS

Soil samples were extracted with hexane:dichloromethane (1:1, v/v) in a Soxtherm system (Gerhardt). The extract was concentrated by rotary evaporation. Aliquots of the Soxtherm extract were fractionated and gravimetrically quantified by LC into saturated (SAT) and aromatic (ARO) hydrocarbons, polar (POL), and asphaltene (ASP) fractions. In brief, LC was carried out in two steps: in the first one, maltenes and asphaltenes were separated by filtering through 0.45 µm filters using hexane and dichloromethane, respectively; then, in the second step, maltenes were fractionated into saturated, aromatic, and polar fractions by LC in columns filled with silica gel and alumina (dried overnight at 240ºC). The aliphatic hydrocarbons were eluted with hexane, the aromatics with a mix of dichloromethane:hexane (4:1, v/v) and finally, the polars with methanol.

Analysis of the LC fractions was carried out by GC-MS. The injection of the extracts was performed on a 7890A GC System (Agilent Technologies) coupled to a 5975C Inert XL MSD with Triple-Axis Detector (Agilent Technologies). A capillary column DB-5ms (5% phenyl 95% dimethylpolysiloxane; 30 m × 0.25 mm i.d. × 0.25 µm film) from Agilent Technologies was used with helium as carried gas at 1 mL/min. The initial oven temperature was 40 ºC (held for 5 min) and ramped at 5 ºC min^{-1} up to 300 ºC and held for 20 min. The mass spectrometer was operated in electron ionization mode (EI) at 70 eV. It was calibrated daily by autotuning with perfluorotributylamine (PFTBA) and the chromatograms were acquired in full-scan mode (mass range acquisition was performed from 45 to 500 m/z).

2.2.3. HS-GC-MS

The head space determinations (HS-GC-MS) were carried out in a GCMS-QP2010 Plus from Shimadzu. An Agilent Technologies DB-5ms (30 m × 0.25 mm i.d. × 0.25 µm film) column was used with helium as carried gas at 1 mL min^{-1}. The initial oven temperature was 35 ºC (held for 7 min), ramped at 3 ºC min^{-1} up to 45 ºC (held for 1.5 min) and then raised to 300 ºC at a rate of 10 ºC min^{-1} and held for 5 min. The mass spectrometer was operated in electron ionization mode (EI) at 70 eV. The HS step was performed in an AOC-5000 autosampler system (Shimadzu).

2.2.4. Dioxins and furans

To carry out the tetra- through octa-chlorinated dioxins and furans analysis the soil samples were extracted, cleaned up, fractionated and then analyzed by isotope dilution and HRGC-HRMS according to EPA Method 1613 requirements.

The dioxin and furan identifications were performed with a Trace GC Ultra coupled to a DFS high resolution magnetic sector mass spectrometer (GC-HRMS) from Thermo Scientific. In this case, the capillary column was a TR-DIOXIN-5ms 60 m × 0.25 mm i.d. × 0.25 µm film (Thermo Scientific). The initial oven temperature was 140 ºC (held for 1 min), ramped to 200 ºC at 20 ºC/min and held for 3 min, then raised to 310 ºC at 3 ºC/min and held for 8 min and finally raised to 325 ºC and held 5 min. The carrier gas was helium at a column flow of 1 mL min^{-1}. The HRMS detector was operated in MID (multiple ion detection) mode. The congener identification and quantification of the dioxins and furans as well as the toxicity equivalents calculation were carried out by isotope dilution analysis following the EPA Method 1613 suggestions and using the software TargetQuan by Thermo Scientific.

2.2.5. Py-GC-MS

Pyrolysis-gas chromatography-mass spectrometry was performed using a CDS 2000 Pyroprobe, coupled to a Thermo Finnigan Focus DSQ GC-MS equipped with a J&W DB-1MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness). The GC oven temperature was programmed from 50 °C to 300 °C (at 5 °C min-1), with an initial hold of 5 minutes at 50 °C and a final hold of 5 minutes at 300 °C. Pyrolysis was performed for 20 seconds at 610 °C. The MS was operated in full scan mode (50-500 Da, 1.08 scans sec^{-1}). Triplicate measured aliquots of dry, homogenized soil (up to several mg) and soil extract asphaltenes (< 0.1 mg) were pyrolyzed directly, without derivatization. Decadeuteropyrene was added as an internal standard to the soil samples.

3. Results and discussion

3.1. Initial characterization

The background information obtained about the activities that took place in the plant (Fig. 1) for more than 30 years can be summarized as follows:

(a) As the principal activity at the site during the 1970's and 1980's, two separate units produced naphthalene, phenol, and other compounds from coal tar.
(b) Another unit of production was dedicated to the manufacture of polymer resins. A considerable amount of other chemical products (pesticides, solvents, etc.) was stored, although probably not manufactured, in the plant.
(c) In the 1990's the plant was closed and then used for years to store unspecified chemical waste, to finally be incompletely demolished in the early 2000's.

Regarding the geology and hydrogeology of the site, a typical soil column in the affected area presented a highly polluted sandy surface layer between 5 and 50 cm thick with interbedded pebble layers in which infiltrating water had accumulated. Immediately below, there was a non-permeable clay stratum up to 4 m thick, which confined most of the contamination to the top two meters. The water table was below 5 m, in a more permeable alluvial layer with groundwater flowing primarily towards the southeast (Fig. 1).

In an initial screening at the site, Peláez et al. (2013) identified PAHs and hydrocarbons in general as the main contaminants affecting the soil (Table 1). With the exception of lead, they found no significantly high concentrations of inorganic contaminants (average concentrations: As, 16 mg kg^{-1}; Cd, 0.5 mg kg^{-1}; Cr, 48 mg kg^{-1}; Cu, 54 mg kg^{-1}; Hg, 1 mg kg^{-1}; Pb, 450 mg kg^{-1}; Zn, 85 mg kg^{-1}). Following these considerations the remediation approach on-site implemented was focused on PAHs (Peláez et al., 2013).

Congruent with the above geological description, the soils at the site contain 43% sand content with the remainder being clay (19%) and silt (38%) (average of three samples). The pH was around 8.2. There were only minor amounts of organic matter, nitrogen and phosphorus as the excavated material contained only a small portion of the upper soil horizons, whereas notable amounts of Ca (3,180 mg/kg), Mg, K and Na were detected.

Table 1. Results from 33 samples analyzed for the initial hydrocarbon characterization.

Comp.	***PAHs***					***BTEX***	***TPH***				
	2-ring	3-ring	4-ring	5-6 ring	Total		C_{10}-C_{16}	C_{16}-C_{22}	C_{22}-C_{30}	C_{30}-C_{40}	Total
Average (mg/kg)	1506.5	200.7	87.3	18.3	1812.9	6.5	3600	1080	800	470	5950
Std. deviation	3795.7	385.8	241.1	40.5	4051.4	20.5	8025	3110	1505	885	12120

2-ring PAHs (naphthalene); 3-ring PAHs (fluorene + acenaphthylene + acenaphthene + phenanthrene + anthracene); 4-ring PAHs (fluoranthene + pyrene + benz[*a*]anthracene + chrysene); 5-6 ring PAHs (benzo[*b*]fluoranthene + benzo[*k*]fluoranthene + benzo[*a*]pyrene + dibenz[*a,h*]anthracene + benzo[*ghi*]perylene + Indeno[1,2,3-*cd*]pyrene); BTEX (benzene + toluene + ethylbenzene + xylenes); TPH (total petroleum hydrocarbons).

3.2. Molecular fingerprinting

3.2.1. Semi-volatiles

The average results (three samples, less than 5% error) obtained by gravimetric determinations indicated that the percentage of saturates in the extracts was 20%, aromatics another 20%, 13% for polars and 47% for asphaltenes. As is routinely done in petroleum studies (e.g., Fan and Buckly, 2002), the three maltene fractions (saturates, aromatics and polars) were each analyzed separately by GC-MS, reducing the problem of GC coelution when analyzing complex mixtures. The asphaltene fraction is not GC-amenable, but since it comprises nearly half of the extract, it was deemed to be of interest and the alternative approach of pyrolysis-GC-MS was employed for it (Sec. 3.2.4).

The total ion chromatogram (TIC) and the single ion monitoring (SIM) chromatograms of the saturate fraction reveal a partially weathered mixture with a clear predominance of linear and branched alkanes, hopanes, and an important UCM (unresolved complex mixture) hump (Fig. 3a, Table 2). The presence of linear alkanes from C_{12} - C_{30} (typical of commercial petroleum distillates) is evident. Pristane and phytane abundances are higher than those of *n*-heptadecane and *n*-octadecane, thereby providing supporting evidence of the weathering experienced by the mixture (Gallego et al., 2010). In addition, a clear petrogenic origin of the mixture is indicated by the presence of petroleum biomarkers such as tricyclic and pentacyclic terpanes (Fig. 3a). In conclusion, most of the compounds present in this fraction seem to be associated with old fuel oil spills (Barnier et al., 2014); this is further supported by the presence of alkenes in higher quantities (Fig. 3a) than usual in crude oils, indicative of refined products (Speight, 2002).

TIC and SIM chromatograms of the aromatic fraction is shown in Fig. 3b. Parent PAHs (such as phenanthrene, peak A10 and m/z 178) are dominant whereas alkyl-PAHs (e.g., methylphenanthrenes, A13 and m/z 192) are clearly in a lower relative concentrations, thereby suggesting that the pyrogenic component (from coal tar processing) is much more important than the petrogenic one (the fuel oil mentioned above). The predominance of the pyrogenic component was also verified by means of the calculation of commonly-employed PAH ratios, such as anthracene/anthracene + phenanthrene (0.20 in our samples) and fluoroanthene/fluoroanthene + pyrene (0.58). Both ratios clearly indicate a combustion (pyrogenic) origin (Yunker et al., 2002; Boehm, 2005). Unusual compounds identified as naphthyl-methylnaphthalene isomers (Fig. 4) are among the most abundant compounds in the aromatic fraction (peaks A21 in Fig. 3b) and are likely evidence of the naphthalene manufacturing process once active at the site. A compound identified as an isomer of tetramethylbiphenyl (peak A8) is also present in a relatively high concentration and is likely derived from resins used at the site in polymer manufacture, as discussed in detail in section 3.2.4. Peak A16, one of the most abundant compounds in the aromatic fraction, is tentatively identified as a C_9-alkylbiphenyl isomer and would thus likely provide further forensic evidence of polymer resin usage. Pentacyclic aromatic hydrocarbons (benzofluoranthenes, benzopyrenes) were detected but are relatively much less abundant than the 3- and 4-

Fig. 3. GC–MS chromatograms. (a) TIC saturate fraction-top- and SIM (m/z 57 and 191) -bottom-; (b) TIC aromatic fraction-top- and SIM (C_0–C_3 naphthalenes, m/z 128, 142, 156 and 170; C_0–C_3 phenanthrene/anthracenes, m/z 178, 192, 206 and 220; and fluoranthene/pyrene, benz[*a*]anthracene/chrysene, and benzofluoranthenes and benzopyrenes of m/z 202, 228 and 252), * indicates naphthyl–methylnaphthalene isomers (Fig. 4.); (c) TIC polar fraction. See Table 2 for peak identifications.

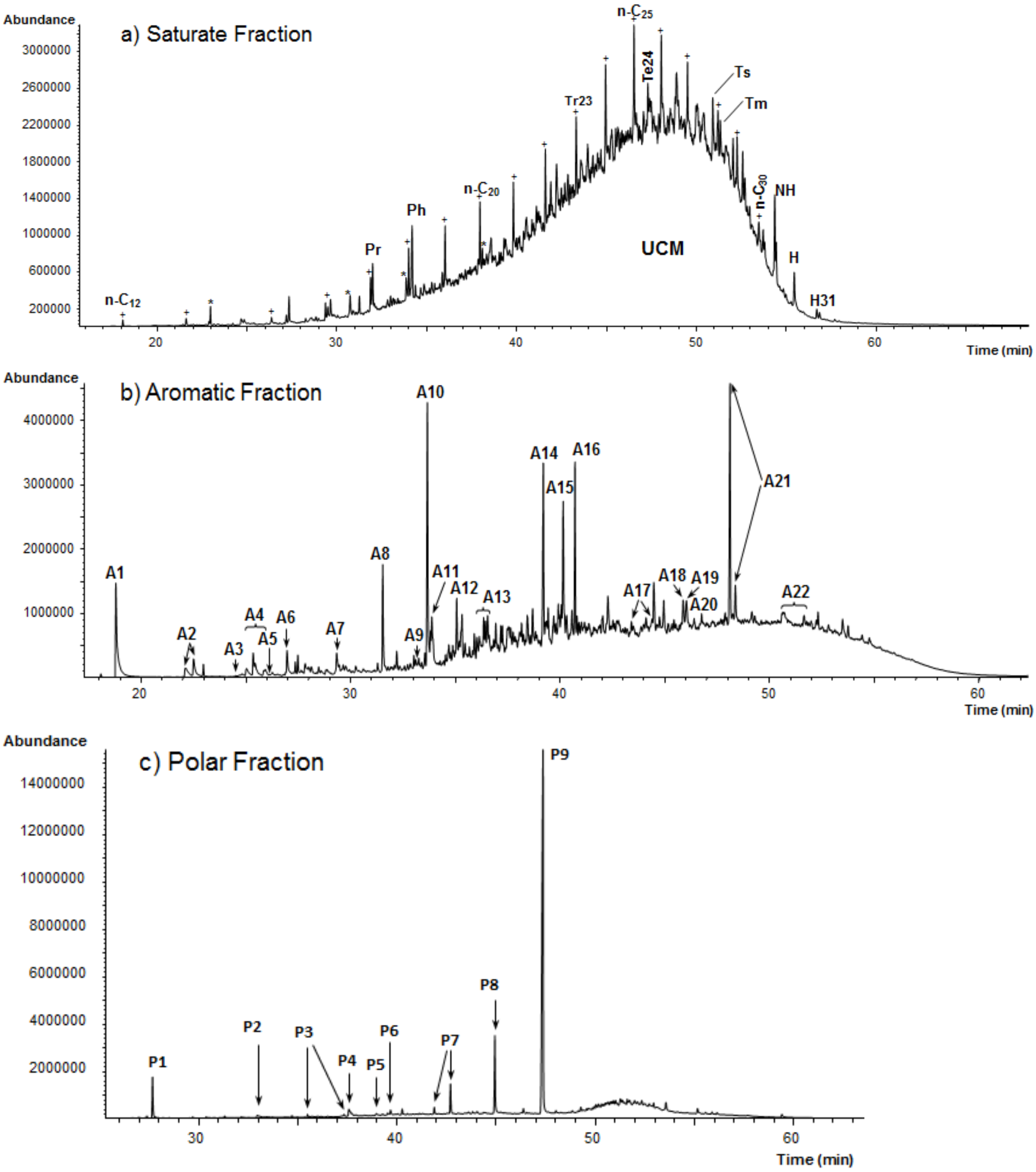


Table 2. Peak identifications for chromatograms in Figs. 3 and 5.

Peak	Compound	Peak	Compound
UCM	unresolved complex mixture	A21	1-(1-naphthylmethyl)naphthalene and 1-(2-naphthylmethyl)naphthalene
*	alkenes	A22	benzofluoranthenes benzopyrenes perylene
+	n-alkanes		
n-C_{12}	n-dodecane	P1	phenol, 2,4-bis(1,1-dimethylethyl)-
n-C_{20}	n-eicosane	P2	9h-fluoren-9-one
n-C_{25}	n-pentacosane	P3	alkyl phthalate
n-C_{30}	n-triacontane	P4	cyclopenta[def]phenanthrenone
Pr	pristane	P5	9,10-antraquinone
Ph	phytane	P6	phthalate
Tr23	tricyclic terpane	P7	phthalate
Te24	tricyclic terpane	P8	hexanedioic acid, bis(2-ethylhexyl) ester
Ts	18α(H)-22,29,30-trisnorneohopane	P9	DEHP (di-2-ethylhexylphthalate)
Tm	17α(H)-22,29,30-trisnorhopane	V1	benzene
NH	17α, 21β norhopane	V2	n-heptane
H	17α, 21β hopane	V3	pyridine
H31	R and S isomers of 17α(H), 21 β(H)-22-homohopane	V4	toluene
A1	naphthalene	V5	n-octane
A2	methyl naphthalenes	V6	ethylbenzene, m-xylene, p-xylene and/or o-xylene
A3	biphenyl	V7	styrene
A4	dimethyl naphthalenes	V8	n-nonane
A5	acenaphthylene	V9	propylbenzene
A6	acenaphthene	V10	cumene
A7	fluorene	V11	trimethylbenzenes
A8	1,2,3-trimethyl-4-propenyl-naphthalene	V12	n-decane
A9	dibenzothiophene	V13	indane
A10	phenanthrene	V14	indene
A11	anthracene	V15	acetophenone
A12	trimethylcarbazole	V16	n-undecane
A13	methylphenanthrenes methylanthracenes	V17	naphthalene
		V18	n-dodecane
A14	fluoranthene	V19	benzothiophene
A15	pyrene	V20	n-tridecane
A16	C_9-alkylbiphenyl isomer	V21	methylnaphthalenes
A17	hexachlorobiphenyl		
A18	benzo[a]anthracene		
A19	chrysene		
A20	heptachlorobiphenyl		

Fig. 4. Mass spectra corresponding to: (top) A21 peak in Figure 3b; (bottom left) 1-(1-naphthylmethyl)naphthalene reference spectrum; (bottom right) 1-(2-naphthylmethyl)naphthalene reference spectrum. Reference spectra obtained from NIST library (Agilent).

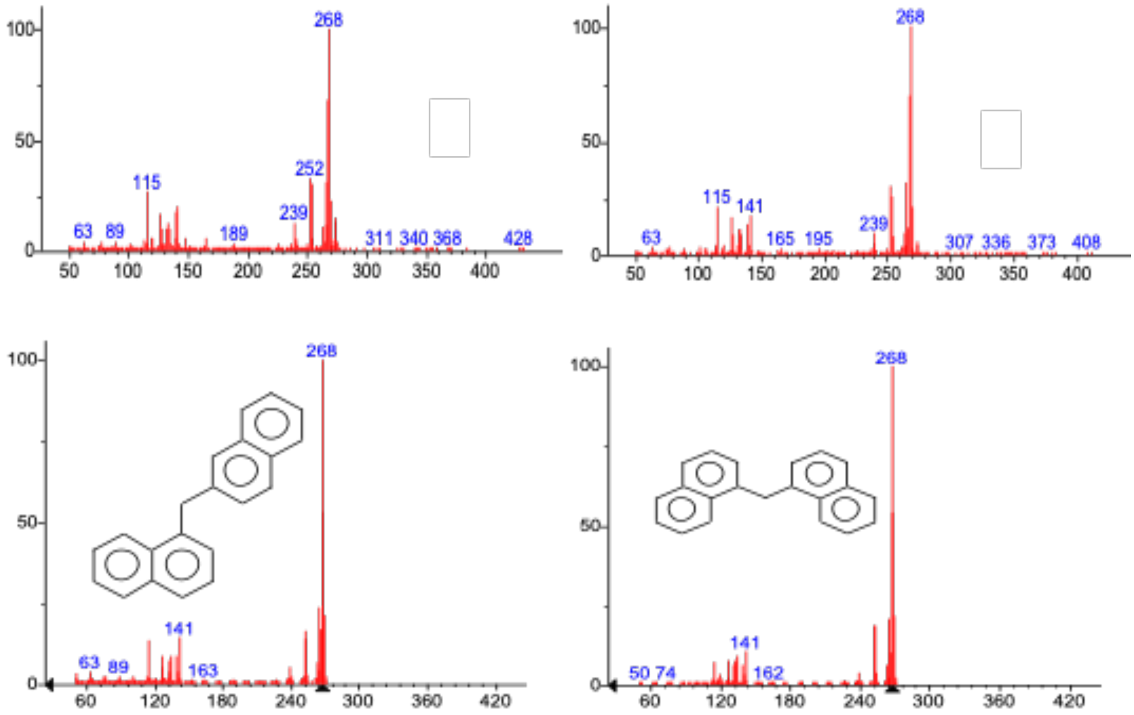
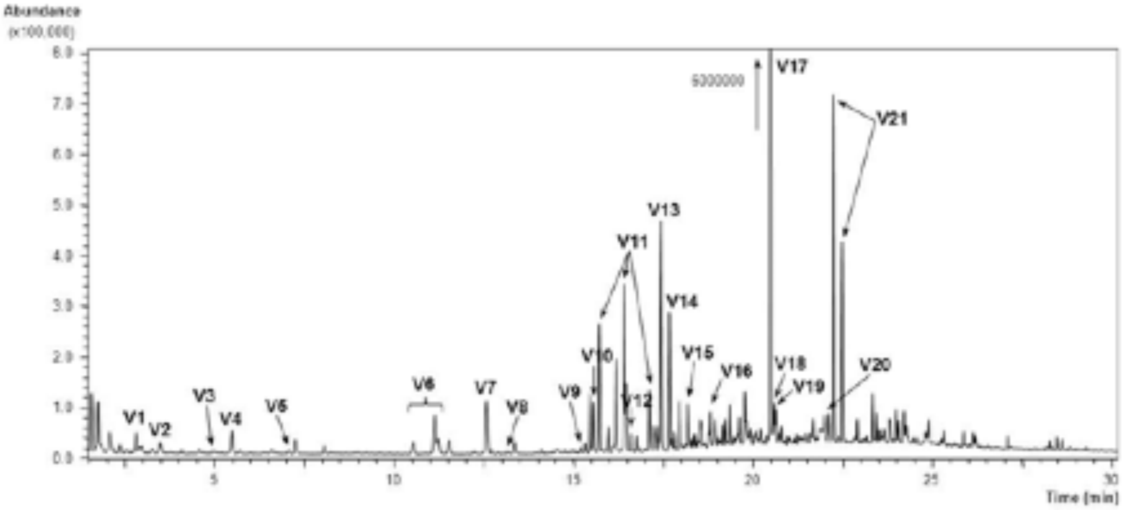


Fig. 5. TIC chromatogram of the volatile fraction obtained by HS-GC-MS. See Table 2 for peak identifications.



ring PAHs (Fig. 3a). S and N heterocycles (thiophenes and carbazole derivatives) are also detected in relatively low abundances, as are trace amounts of PCBs (polychlorinated biphenyls). Excepting polychlorinated dibenzofuran and dibenzo-*p*-dioxins (Sec. 3.2.3), no other chlorinated (such as pesticides) or brominated compounds were detected.

The TIC chromatogram of the polar fraction (Fig. 3c) notably indicated the presence of phthalates, especially DEHP (di-2-ethylhexyl phthalate, peak P9), a widely-used plasticizer typically manufactured in chemical industries. Also notable are a fatty acid derivative (peak P8, possibly from "tinol", a steel processing residue containing animal fats known to have been stored at the site), an alkyl-substituted phenol (peak P1, likely from coal tar) and several polycyclic aromatic ketones (P2, P4, P5, indicating weathering/biodegradation of hydrocarbons).

3.2.2. Volatile components

In order to more fully characterize the contaminated soil, the volatile components were characterized by headspace-GC-MS (Fig. 5, Table 2). Remarkably, naphthalene (peak V17) is an order of magnitude more abundant than the other constituents. Methylnaphthalenes (V21), indane (V13), trimethylbenzenes (V11), and indene (V14) are the next most abundant compounds. Lighter compounds (BTEX, i.e., benzene, toluene, ethylbenzene and xylenes (V1, V4, V6)) are present in relatively low concentrations, although this may be due to evaporation in situ or during sample handling. The predominance of naphthalene in the head space vapors likely reflects the intensive use of this compound in the above-mentioned manufacturing processes known to have occurred at the site.

3.2.3. Dioxins and furans

On the whole, the polychlorinated dibenzo-*p*-dioxins (PCDDs) were relatively more abundant than the polychlorinated dibenzofurans (PCDFs). In particular, the most abundant congener in these soils is octachlorodibenzodioxin (OCDF), representing 57.9% of the contribution to the sum of PCDDs and PCDFs (Table 3) while the second most abundant congener was 1,2,3,4,6,7,8-heptachlorodibenzodioxin (1234678-HpCDD) congener (10.7%) and octachlorodibenzofuran (OCDB) was the third (7.5%). Following the sink/source classification (Wagrowski & Hites, 2000; Dömtörövá et al., 2012), this profile is classified as ‘‘sink’’ for which PCDDs are predominant, rather than a ‘‘source’’ profile characterized by a PCDF predominance.

Regarding abundances, the studied soil presented 18.0 pg I-TEQ g^{-1} whereas regional studies (Bueno & Lavín, 2010) showed average values of 16.2 pg I-TEQ g^{-1}. Therefore there were no significant differences between this soil and the regional background, in terms of I-TEQ concentrations.

In light of the evidence (sink profile, levels close to background), it can be concluded that dioxins and/or furans were not generated at the site. This is also congruent with the absence of polychlorophenols (PCP, the most common dioxin precursors) in all aromatic fractions analyzed (Masunaga et al., 2003).

Table 3. PCDF/PCDD congener profile in the studied soil.

Family	*Compounds*	*Concentration (pg/g)*
PCDF (Furans, Fi)	*F4*	*18.52*
	F5	*23.95*
	F6	*48.66*
	F7	*41.78*
	F8	*45.0*
PCDD (Dioxins, Di)	*D4*	*0.3*
	D5	*1.4*
	D6	*9.6*
	D7	*64.8*
	D8	*349.2*

F4 = 2378-TCDF, F5 = 12378-PeCDF + 23478-PeCDF; F6 = 123478-HxCDF + 123678-HxCDF + 234678-HxCDF + 123789 HxCDF; F7 = 1234678-HpCDF + 1234789-HpCDF; F8 = OCDF; D4 = 2378-TCDD; D5 = 12378-PeCDD; D6 = 123478-HxCDD + 123678-HxCDD + 123789-HxCDD; D7 = 1234678-HpCDD; D8 = OCDD

3.2.4. Py-GC-MS

Pyrolysis-GC-MS of the contaminated soil (Fig. 6, Table 4) revealed a complex mixture of thermally desorbed "free" compounds, along with the products of the pyrolysis of macromolecular structures. There was a strong predominance of indene and methylindenes, as well as naphthalenes, including the parent compound and, in particular, 1-methylnaphthalene (Figs. 6a, 6d). Monoaromatic hydrocarbons are also abundant, particularly a methylstyrene isomer, as are phenols, notably 2,4-dimethylphenol (Figs. 6a, 6d, 6e). Three- and four-ring PAHs are also of major importance in the soil pyrolyzate, with the parent PAHs strongly predominant over their methylated analogs (Figs. 6a, 6d), as is the case with the PAH distribution seen in the aromatic fraction of the extract (Fig. 3b). These data are consistent with a coal tar molecular signature (Dominguez et al., 1996; D'Affonseca et al., 2008; Birak and Miller, 2009; Coulon et al., 2009; McGregor et al., 2011). Compounds identified as naphthyl-methylnaphthalene isomers in the soil pyrolyzate (also detected in the aromatic fraction, Figs. 3b and 4) and an additional methylated derivative, are likely evidence of the naphthalene manufacturing process once active at the site. *n*-Alkanes and alkenes are detected from C_8 to C_{29}, with C_{15} and C_{17} particularly prominent, suggesting a mixed petroleum and microbial derivation, with the latter inference supported by the presence of the C_{17} and C_{19} *n*-alk-2-ones as well as the C_{16} and C_{18} *n*-alkylnitriles (Figs 6a, 6b, 6f). *n*-Hexadecanoic acid and its methyl ester could indicate the presence of soil microbes. However, they may also derive from "tinol", as mentioned above (Sec. 3.2.1). The C_{27} - C_{32} hopanes (Figs. 6a, 6c) provide further evidence for the petrogenic component and were noted in the saturate fraction as well (Fig. 3a).

By weight the asphaltene fraction comprised nearly half of the solvent extract of the contaminated soil (Sec. 3.2.1). Although asphaltenes cannot be analyzed directly by GC, they are amenable to analytical pyrolysis (Fig. 7a). As with the whole soil

Fig. 6. Py-GC-MS chromatograms of whole soil: (a) TIC, (b) m/z = 83 + 85, (c) m/z = 191, (d) composite chromatogram created by sequentially plotting the molecular ions of the indicated aromatic hydrocarbons in the following order: m/z 104, 118, 116, 130, 128, 144, 142, 156 + 152, 154, 166, 180, 178, 192, 202, 216, 228, 268, 282, 252 , (e) composite chromatogram created by sequentially plotting the molecular ions of the indicated aromatic heterocompounds in the following order: m/z 94, 108, 122, 132, 117, 131, 144, 180, 208, (f) summed m/z 58 + 73 + 74 + 100 chromatogram showing the indicated aliphatic heterocompounds. See Table 4 for peak identifications.

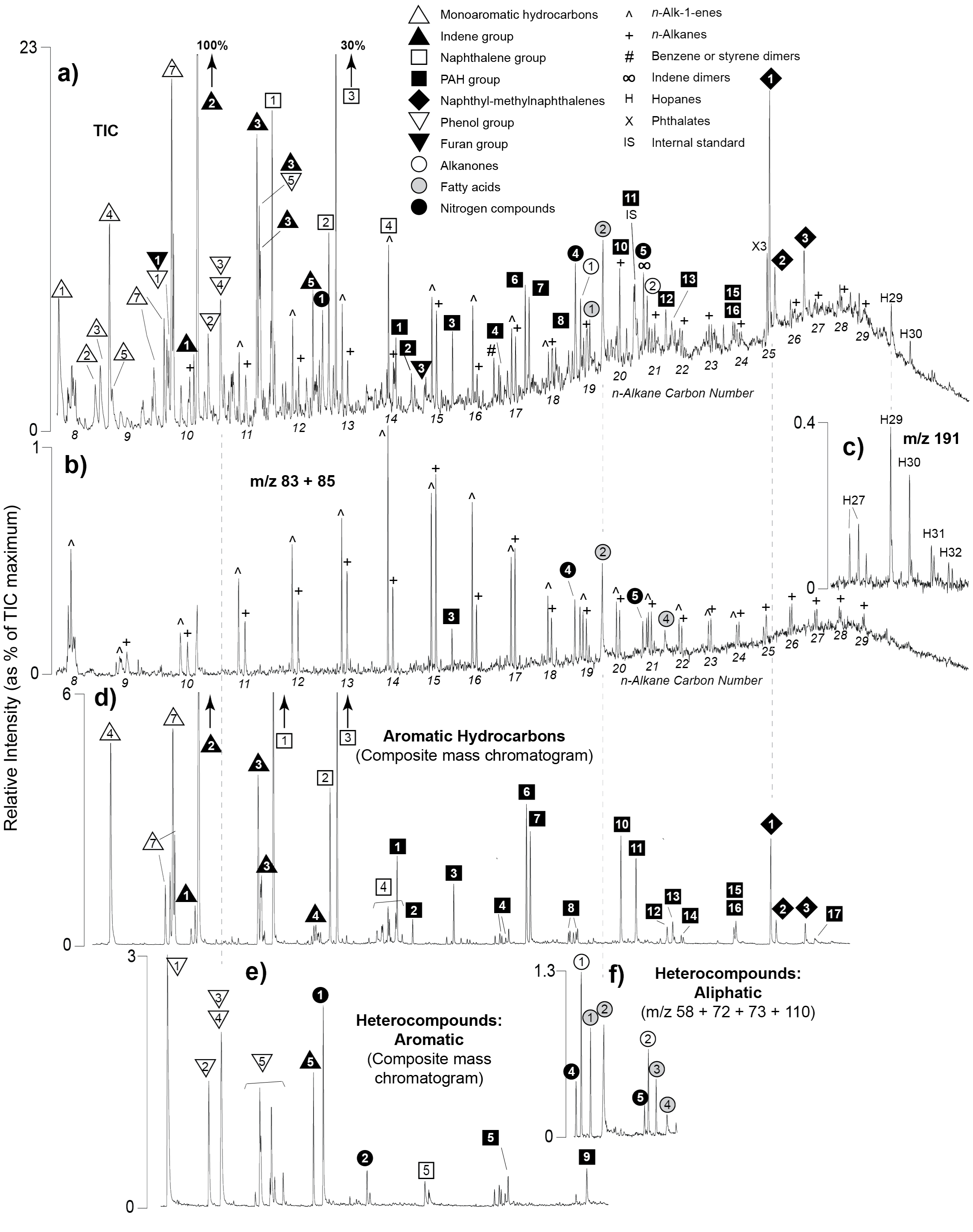
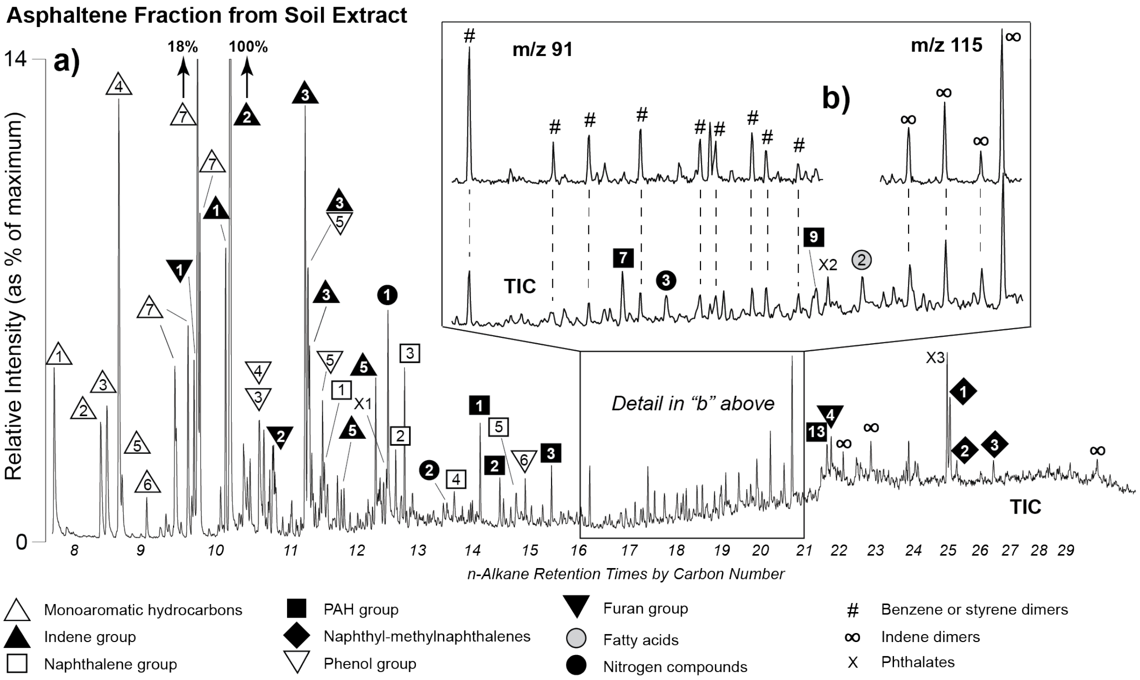


Table 4. Peak identification for pyrograms in Figures 6 and 7.

△	**Monoaromatic Hydrocarbons**	▽	**Phenol Group**
1	toluene	1	phenol
2	ethylbenzene	2	2-methylphenol
3	m- and p-xylene	3	3-methylphenol
4	styrene	4	4-methylphenol
5	o-xylene	5	dimethylphenol isomers
6	(1-methylethyl)benzene	6	2,4-bis(1,1-dimethylethyl)phenol
7	methylstyrene isomers	▼	**Furan Group**
▲	**Indene Group**	1	benzofuran
1	indane	2	methylbenzofuran
2	indene	3	dibenzofuran
3	methylindene isomers	4	dibenzochromene isomer
4	dimethylindene isomers	○	**Alkanones**
5	indenone isomers	1	n-heptadecan-2-one
☐	**Naphthalene Group**	2	n-nonadecan-2-one
1	naphthalene	◎	**Fatty Acids**
2	2-methylnaphthalene	1	n-hexadecanoic acid, methyl ester
3	1-methylnaphthalene	2	n-hecadecanoic acid
4	dimethylnaphthalenes	3	n-octadecanoic acid, methyl ester
5	naphthol isomers	4	n-octadecanoic acid
■	**PAH Group**	●	**Nitrogen Compounds**
1	acenaphthylene	1	indole
2	acenaphthene	2	methylindole
3	fluorene	3	carbazole
4	methylfluorenes	4	n-hexadecanitrile
5	9H-fluoren-9-one	5	n-octadecanitrile
6	phenanthrene		**Others**
7	anthracene	^	n-alk-1-enes
8	methylphenanthrene iosmers	+	n-alkanes
9	9,10-anthracenedione	#	benzene or styrene dimer
10	fluoranthene	∞	indene dimer
11	pyrene	H27	trisnorhopanes (Ts & Tm)
12	benzo[a]fluorene	H29	17α,21β norhopane
13	benzo [b] & [c] fluorenes	H30	17α,21β hopane
14	methylpyrenes	H31	17α,21β homohopanes
15	benzo[a]anthracene	H32	17α,21β bishomohopanes
16	chrysene	X1	phthalic anhydride
17	benzo [b] & [j] fluoranthenes	X2	dibutyl phthalate
◆	**Naphthyl-methylnaphthalenes**	X3	di(2-ethylhexyl) phthalate
1	naphthyl-methylnaphthalene isomer	IS	internal standard
2	naphthyl-methylnaphthalene isomer		
3	methylnaphthyl-methylnaphthalene		

Fig. 7. Py-GC-MS of asphaltene fraction of soil extract: (a) TIC, (b) detail of asphaltene pyrolyzate showing the distribution of benzene/styrene and indene dimers. See Table 4 for peak identifications.



pyrolyzate (Fig. 6a), there is a strong predominance of styrene, methylstyrene isomers, indene, methylindenes, and naphthyl-methylnaphthalenes. PAHs and aliphatics are relatively much less abundant in the asphaltene pyrolyzate than in that of the whole soil. A key detail present in the asphaltene results are the series of benzene (or styrene) and indene dimers (Fig. 7b). One such compound, a C_4-alkylbiphenyl isomer, was recognized as important component in both the aromatic fraction (peak A8, Fig. 3a) and the whole soil pyrolyzate (peak #, Fig. 6a), but the dimers are relatively more abundant and diverse in the asphaltene pyrolyzate (Figs. 7a, 7b). The styrenes and indenes are the primary constituents of "C9 aromatic resin oils" (so called because the compounds each contain 9 (±1) carbon atoms) used in the manufacture of adhesive polymers (Kim et al., 2000; Kumooka, 2006; Eastman Chemical Company, 2014). Benzofuran and methylbenzofuran are also detected in the pyrolyzates (Figs. 6a, 7a) and are used to make adhesive polymers as well (Kumooka, 2006). Styrenes, indenes, naphthalenes, and benzofurans are all common constituents of coal tar (D'Affonseca et al., 2008; Birak and Miller, 2009). This molecular forensic evidence is consistent with the oral history testimony, stating that coal tar was being refined at the site to produce aromatic resin oils and naphthalene for industrial use, and those polymers (which from our data we can infer may likely have been adhesives) were being manufactured at the site from these components. The presence of the styrene, indene, and naphthalene dimers further supports the latter inference.

On the whole, pyrolysis results although complex, are consistent with those obtained by GC-MS of the LC fractions. Only small differences in the abundance of predominant compounds and in absence/presence of some minor components were found, with the main exception of chlorinated compounds (PCBs, PCDDs, PCDFs) that were not found in the pyrolyzates. Nevertheless, other contaminants, such as the polymer derivatives indicated above, were only detected by the pyrolytic technique. Therefore, as illustrated by the complexly contaminated soil sample presented in this study, the strategy followed has been proven adequate to reveal the presence of unusual contaminants, most of them detectable by rapid pyrolysis-GC-MS screening.

3.3. Environmental forensic hypothesis: linking contaminants to industrial activities

The soil and asphaltene pyrolysis results in tandem with the extract data provide important insights into the origin and present state of the legacy contaminants. Due to the industrial and waste storage activities carried out in the area studied, the site was contaminated by a variety of organic compounds (Table 5), notably aromatic hydrocarbons, particularly naphthalene (Table 1; Figs. 3b, 4, 5, and 6). However, as reported above, classic approaches based on quantification of PAHs, TPH and BTEX clearly do not provide the full picture of the present soil contamination. This can lead to serious shortcomings in the application of investigation/remediation approaches (Blum et al., 2011). These standard approaches would have clearly overlooked the predominant pollutants at this site.

In the present example, most of the identified pollutants are clearly linked with coal tar distillation and the manufacture of naphthalene and phenols. Coal tar, which is

Table 5. Summary of main contaminants and their sources.

Compounds	**Probable sources**	**Comments**
PAHs	Coal tar processing Fuel oil spills	Predominance of parent PAHs (pyrogenic origin)
Aliphatics	Fuel oil spills Tar feedstock	Moderately weathered
Naphthyl-methylnaphthalenes	Coal tar processing Naphthalene manufacturing	Methylated derivative only found in Py-GC/MS
Indene, styrene and dimers	Coal tar processing and polymer resins manufacture	Mainly polymeric origin
Phenols	Coal tar processing Phenol manufacturing	Predominant in water (high solubility)
Phthalates	Resins manufacture	DEHP predominance
Chlorinated	Waste and solvent storage	Only PCBs in low concentrations
NSO Compounds	Coal tar processing	Carbazole, quinoleine, O-PAHs, etc.
Organic acids and esters, ketones	‘Tinol’ storage Soil microbes	Oleic acid and others

the main byproduct generated in the coal carbonization process, is a complex combination of PAHs, phenols and heterocyclic oxygen, sulfur and nitrogen compounds. In this work, the profile found (parent PAHs predominating) corresponds to a 500ºC process in a coke oven (Emsbo-Mattingly and Stout, 2011). Therefore, PAHs are the main component, typically up to 90% (Elliot, 1981; Schobert and Song, 2002), along with phenols and heterocyclic oxygen, sulfur and nitrogen compounds. In this work, the profile found (parent PAHs predominating) corresponds to a 500 °C process in a coke oven (Emsbo-Mattingly and Stout, 2011). While groundwater and throughflow water were not considered in this study, detailed GC-MS analysis (data not shown) revealed the predominance of naphthalene, phenols and cresols consistent with the high solubility of these compounds and with the industrial processes taking place in the plant (Benhabib et al., 2010). In addition, other NSO compounds (Blum et al., 2011), usually unmonitored in coal tar polluted soils, were also detected; some of them (e.g., quinoline) are very toxic (Eisentraeger et al., 2008).

In addition to the coal tar, molecular fingerprinting recognized a second source of pollution, namely fuel oil spills (i.e., of petrogenic origin) associated with a long-time continuous release of fuel oil used in the heating systems of the plant (for which physical evidence was observed and documented at the site some years before our sampling). However, cannot be ruled out that some alkanes derive from the original coal constituents given that not all of the coal feedstock is transformed into parent PAHs (Emsbo-Mattingly and Stout, 2011).

The phthalates detected in the polar fraction (Fig. 3c) and in the pyrolyzates (Figs. 6, 7) are likely related to naphthalene transformation, given that one of the main uses for naphthalene is as a raw material for the manufacture of phthalic anhydride, a common starting material for the production of phthalate plasticizers, resins and phthaleins (González Azpíroz et al., 2008). There was indeed a small plant for resins production at the site in the 1970s (Fig. 1).

Regarding PCBs, two possible origins could be hypothesized. A first possibility, insulating fluids in electrical transformers should be considered since the principal electrical installations were located within the study area (Fig. 1). A second possibility is the on-site storage of coolants, cutting fluids and other products possibly containing PCBs. We did also note the presence of petroleum products and NSO compounds, the molecular fingerprints of which could be compatible with mineral oil-based cutting fluids (Sánchez-Oneto et al., 2007). Given that cutting fluid waste storage was documented at the study site, this is a supplementary source of aliphatic hydrocarbons to be added to the fuel oil spill described above. Consequently, we also suggest this activity as a possible, partial source of the detected PCBs and the petrogenic hydrocarbons. On the other hand, no significant concentrations of dioxins and furans were found, thus ruling out the use of incineration and other thermal processes in the former chemical plant for the treatment of chlorinated waste. This is also congruent with the above-mentioned absence of PCP compounds.

Finally, evidence of animal fats was detected and this was linked to the former storage of 'tinol', a residue from steel manufacturing composed of a mixture of animal fats, mineral lubricants and chips (Fe oxides mainly). Soil microbiota active in the site

(Guazzaronni et al., 2013) must be noted as a second complementary source of organic acids and esters, also playing a main role in the moderate weathering observed in the hydrocarbon fingerprinting.

4. Conclusions

The site discussed in this paper exemplifies the complex legacy of contamination afflicting many brownfield zones in industrialized countries. The multi-faceted environmental forensic approach to molecular fingerprinting documented herein demonstrates that it is possible to carefully unravel tangled evidence resulting from multiple soil pollution sources, and recognize major contaminants ignored by conventional analytical procedures and overlooked by current environmental regulations. It seems self-evident that this approach would foster more effective site remediation procedures.

Specifically, LC fractionation was revealed to be a very useful tool for separation of complex mixtures of legacy contaminants in order to perform full-scan GC-MS identifications, much more powerful for forensic purposes than usual quantitative techniques. As a rapid alternative, Py-GC-MS, which require only minimal sample preparation, was sufficient to identify the majority of the contaminants present at the site, and therefore is very useful as a screening system to quickly obtain qualitative results in soil pollution studies.

In the illustrative example shown, the environmental forensic study identified as the main sources of pollution coal tar distillation and subsequent production of naphthalene, phenols and polymer resins. Therefore, PAHs and specifically naphthalene were the most abundant contaminants. Parent PAHs strongly predominate over alkylated PAHs, indicating a mostly pyrogenic origin congruent with coal tar processing. We identified a second, petrogenic source of hydrocarbons, likely the result of spilled fuel oil and/or mineral-oil based cutting fluids. Pyrolysis of the asphaltene fraction of the soil extract indicated the importance of the polymer resin contamination. In addition, a number of other volatile and semivolatile contaminants (including N and S heterocycles, phthalates, PCBs, organic acids, phenols and others) were also identified and linked to their most feasible industrial origin. Dioxins and furans were not found above background concentrations.

Regardless of the analytical techniques employed, the conclusions obtained should be very useful in the development of strategies for site remediation i.e., the site should be revisited for a new systematic sampling and analysis, now that a suite of target analytes has been established.

Acknowledgements

The authors would like to thank the Environmental Assay Unit of the Scientific and Technical Services (SCTs) of the University of Oviedo for its collaboration and technical support. We also acknowledge Carlos Fdez-Velarde (Consulnima S.L) and Rodrigo Rodríguez for the historical information supplied about the study site. I. Lores obtained a grant of the “Severo Ochoa” programme (Ficyt, Asturias, Spain). Suggestions made by the peer reviewers (Laurent Jeanneau and an anonymous reviewer), and Mark Yunker markedly improved the manuscript.

References

Barnier, C., Ouvrard, S., Robin, C., Morel, J.L., 2014. Desorption kinetics of PAHs form aged industrial soils for availability assessment. Science of the Total Environment 470-471, 639-645.

Benhabib, K., Faure, P., Sardin, M., Simonnot, M.D., 2010. Characteristics of a solid coal tar sampled from a contaminated soil and of the organics transferred into water. Fuel 89, 352-359.

Birak, P.S., Miller, C.T., 2009. Dense non-aqueous phase liquids at former manufactured gas plants: Challenges to modeling and remediation, Journal of Contaminant Hydrology 105, 81-98.

Blum, P., Sagner, A., Tiehm, A., Martin, P., Wendel, T., Grathwohl, P., 2011. Importance of heterocyclic aromatic compounds in monitored natural attenuation for coal tar contaminated aquifers: A review. Journal of Contaminant Hydrology 126, 81-194.

Boehm, P.D., 2005. Polycyclic Aromatic Hydrocarbons (PAHs). In: Environmental Forensics: Contaminant Specific Guide, Elsevier, pp. 313-337.

Bueno, J., Lavín, A., 2010. Bases para el diagnóstico del estado medioambiental de referencia del posible emplazamiento de una incineradora de residuos en el entorno del vertedero de Cogersa, ZoredaZero. Principado de Asturias (Spain). Public report. Available at http://www.cogersa.es/metaspace/file/42493.pdf (accessed: 21 Feb 2015).

Coulon, F., Orsi, R., Turner, C., Walton, C., Daly, P., Pollard, S.J.T., 2009. Understanding the fate and transport of petroleum hydrocarbons from coal tar within gasholders. Environment International 35, 248-252.

D'Affonseca, F.M., Blum, P., Finkel, M., Melzer, R., Grathwohl, P., 2008. Field scale characterization and modeling of contaminant release from a coal tar source zone. Journal of Contaminant Hydrology 102, 120-139.

de Leeuw, J.W., de Leer, E.W.B., Sinninghe Damsté, J.S., Schuyl, P.J. W., 1986. Screening of anthropogenic compounds in polluted sediments and soils by flash evaporation/pyrolysis gas chromatography-mass spectrometry. Analytical Chemistry 58, 1852-1857.

Domínguez, A., Alvarez, R., Blanco, C.G., Díez, M.A., 1996. Chromatographic evaluation of some selected polycyclic aromatic hydrocarbons of coal tars produced under different coking conditions and pitches derived from them. Journal of Chromatography A 719, 181-194.

Dömtörövá, M., Stachová, Z., Kočan, A., Čonka, K., Chovancová, J., Fabišiková, A., 2012. PCDDs, PCDFs, dioxin-like PCBs and indicator PCBs in soil from five selected areas in Slovakia. Chemosphere 89, 480-485.

Eastman Chemical Company, 2014. C9, Aromatic Resins. Available at http://www.eastman.com/Markets/Tackifier_Center/Tackifier_Families/Hydrocarbon_Resins/Pages/C9,_Aromatic_Resins.aspx (Accessed 22 May 2014).

Eisentraeger, A., Brinkmann, C., Hollert, H., Sagner, A., Tiehm, A., Neuwoehner, J., 2008. Heterocyclic compounds: toxic effects using algae, daphnids, and the Salmonella/microsome test taking methodical quantitative aspects into account. Environmental Toxicology Chemistry 27, 1590-1596.

Elliot M.A., 1981. Chemistry of coal utilization. Second supplementary volume. John Wiley & Sons, Hoboken, NJ.

Emsbo-Mattingly, S.D., Stout, S.A., 2011. Semivolatile residues of coal and coal tar. In: Stracher, G.B., Prakash, A., Sokol, E.V. (Eds), Coal and Peat Fires: A Global Perspective. Elsevier, pp. 173-208.

Fan, T., Buckley, J.S., 2002. Rapid and accurate SARA analysis of medium gravity crude oils. Energy & Fuels 16, 1571-1575.

Faure, P., Landais, P., 2001. Rapid contamination screening of river sediments by flash pyrolysis-gas chromatography–mass spectrometry (PyGC–MS) and thermodesorption GC–MS (TdGC–MS). Journal of Analytical and Applied Pyrolysis 57, 187-202.

Frysinger, G.S., Gaines, R.B., Reddy, C.M., 2002. GC x GC - A new analytical tool for environmental forensics. Environmental Forensics 3, 27-34.

Gallego, J. R., Sierra, C., Villa, R., Peláez, A. I., Sánchez, J., 2010. Weathering processes only partially limit the potential for bioremediation of hydrocarbon-contaminated soils. Organic Geochemistry, 41, 896-900.

González Azpíroz, M.D., Gutiérrez Blanco, C., Casal Banciella, M.D., 2008. The use of solvents for purifying industrial naphthalene from coal tar distilled oils. Fuel Processing Technology 89, 111-117.

Greenwood, P.F., Berwick, L.J., Croué, J.-P., 2012. Molecular characterisation of the dissolved organic matter of wastewater effluents by MSSV pyrolysis GC-MS and search for source markers. Chemosphere 87, 504-512.

Guazzaroni, M., Herbst, F., Lores, I., Tamames, J., Peláez, A.I., López-Cortés, N., Alcaide, M., Del Pozo, M.V., Vieites, J.M., Von Bergen, M., Gallego, J.R., Bargiela, R., López-López, A., Pieper, D.H., Rosselló-Móra, R., Sánchez, J. , Seifert, J., Ferrer, M., 2013. Metaproteogenomic insights beyond bacterial response to naphthalene exposure and bio-stimulation. ISME Journal 7, 122-136.

Ishikawa, S., Sakazaki, Y., Eguchi, Y., Suetomi, R., Nakamura, E., 2005. Identification of chemical substances in industrial wastes and their pyrolytic decomposition products. Chemosphere 59, 1343-1353.

Kim, J.K., Ryu, D.Y., Lee, K.H., 2000. The aromatic hydrocarbon resins with various hydrogenation degrees Part 1. The phase behavior and miscibility with polybutadiene and with polystyrene. Polymer 41, 5195-5205.

Kruge M.A., Permanyer, A., 2004. Application of pyrolysis-GC-MS for rapid assessment of organic contamination in sediments from Barcelona harbour. Organic Geochemistry 35, 1395-1408.

Kruge, M.A., Permanyer, A., Serra, J., Yu, D., 2010. Geochemical investigation of an offshore sewage sludge deposit, Barcelona, Catalonia, Spain. Journal of Analytical and Applied Pyrolysis 89, 204-217.

Kruge, M.A. (in press). Analytical pyrolysis principles and applications to environmental science. In: Barbooti, M. (Ed.), Environmental Applications of Instrumental Chemical Analysis. Apple Academic Press.

Kumooka, Y., 2006. Analysis of deteriorated rubber-based pressure sensitive adhesive by pyrolysis-gas chromatography/mass spectrometry and attenuated total reflectance Fourier transform infrared spectrometry. Forensic Science International 163, 132–137.

Mansuy, L., Bourezgui, Y., Garnier-Zarli, E., Jardé, E., Réveillé, V., 2001. Characterization of humic substances in highly polluted river sediments by pyrolysis methylation–gas chromatography–mass spectrometry. Organic Geochemistry 32, 223-231.

Masunaga, S.; Yao, Y.; Ogura, I.; Sakurai, T.; Nakanishi, J., 2003. Source and behaviour analyses of dioxins based on congener-specific information and their application to Tokyo Bay basin. Chemosphere 53, 315 -324.

McGregor, L.A., Gauchotte-Lindsay, C., Daéid, N.N., Thomas, R., Daly, P., Kalin, R.M., 2011. Ultra resolution chemical fingerprinting of dense non-aqueous phase liquids from manufactured gas plants by reversed phase comprehensive two-dimensional gas chromatography. Journal of Chromatography A 1218, 4755-4763.

Micić, V., Kruge, M.A., Koerner, P., Bujalski, N., Hofmann, T., 2010. Organic geochemistry of Danube River sediments from Pančevo (Serbia) to the Iron Gate dam (Serbia- Romania). Organic Geochemistry 41, 971-974.

Micić, V., Kruge, M.A., Köster, J., Hofmann, T., 2011. Natural, anthropogenic and fossil organic matter in river sediments and suspended particulate matter: a multi-molecular marker approach. Science of the Total Environment 409, 905-919.

Morrison, R.D., 2000. Environmental Forensics. CRC Press. London, pp. 351.

Peláez, A.I., Lores, I., Sotres, A., Mendez-García, C., Fernández-Velarde, C., Santos, J. A., Gallego, J.R., Sánchez, J., 2013. Design and field-scale implementation of an "on site" bioremediation treatment in PAH-polluted soil. Environmental Pollution, 181, 190-199.

Richnow, H. H., Seifert, R., Kästner, M., Mahro, B., Horsfield, B., Tiedgen, U., Böhm, S., Michaelis, W., 1995. Rapid screening of PAH-residues in bioremediated soils. Chemosphere 31, 3991-3999.

Sánchez-Oneto, J., Portela, J.R., Nebot, E., Martínez de la Ossa, E., 2007. Hydrothermal oxidation: Application to the treatment of different cutting fluid wastes. Journal of Hazardous Materials 144, 639-644.

Schobert, H.H., Song, C., 2002. Chemicals and materials from coal in the 21st century, Fuel 81, 15-32.

Speight, J.G., 2002. Handbook of Petroleum Product Analysis. Wiley-Interscience. Hoboken, NJ.

Stout, S. A., Uhler, A. D., McCarthy, K. J., Emsbo-Mattingly, S. D., 2002. Chemical fingerprinting of hydrocarbons. In: Murphy, B., Morrison, R. (Eds.), Introduction to Environmental Forensics. Academic Press, London, pp. 135-260.

Stout, S. A., Millner, G., Hamlin, D., Liu, B., 2006. The role of chemical fingerprinting in assessing the impact of a crude oil spill following Hurricane Katrina. Environmental Claims Journal 18, 169–184.

Thavamani, P., Mallaparu, M., Krishnamurti, G.S.R., McFarland, R., Naidu, R., 2011. Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: Implications to bioremediation. Environment International 37, 184-189.

Uhler, A.D., Stout, S.A., Emsbo-Mattingly, S.D., Rouhani S., 2010. Chemical Fingerprinting: Streamlining Site Assessment during the Sustainable Redevelopment Process. In: Brown K. et al. (Eds), Sustainable Land Development and Restoration: Decision Consequence Analysis. Butterworth-Heinemann, New York, pp. 325-343.

Wait, D.A., 2000. Evolution of organic analytical methods in environmental forensic chemistry. Environmental Forensics 1, 37-46.

Wagrowski, D.M., Hites, R.A., 2000. Insights into the Global Distribution of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans. Environmental Science Technology 34, 2952-2958.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33, 489-515.