



# Resolving coal and petroleum-derived polycyclic aromatic hydrocarbons (PAHs) in some contaminated land samples using compound-specific stable carbon isotope ratio measurements in conjunction with molecular fingerprints<sup>☆</sup>

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## Abstract

It has been established previously [Anal. Commun. 33 (1996) 331; Analyst 123 (1998) 1519; Org. Geochem. 30 (1999) 881; Environ. Sci. Technol. 34 (2000) 4684] that, for thermal conversion regimes where volatiles survive to a significant degree (e.g. low and high temperature carbonisation, domestic combustion), the stable carbon isotopic signatures of polycyclic aromatic hydrocarbons (PAHs) are similar to those of the parent coals (ca.  $-25\%$ , cf.  $-23.5\%$  for the coals). This information has been used to unambiguously identify coal-derived PAHs in contaminated land sites. Aromatic hydrocarbons in a number of samples analysed from a former foundry site at Mansfield displayed variable compositions with those containing predominately alkylated benzenes and naphthalenes having carbon stable isotopic ratios in the range of  $-28$  to  $-30\%$ , typical of transport fuels. The aliphatic hydrocarbon distributions confirmed the petroleum origin and indicated that the oil had also been biodegraded. Less negative (enriched in  $^{13}\text{C}$ ,  $-25$  to  $-26\%$ ) isotopic profiles were obtained for the fractions rich in 3–6 ring parent PAHs, indicating a significant input from coal utilisation. Separating the aromatic by ring size enabled the coal-derived 3–6 ring PAHs to be identified in samples where petroleum-derived alkylated benzenes and naphthalenes dominated. A similar situation to this with only a small input from coal-derived PAHs was found for a soil heavily contaminated with diesel fuel from the Motherwell area. Carbon stable isotopic data taken in conjunction with PAH distributions indicate that the coal tar contaminating an area of Glasgow Green, which was believed to be dumped during the Second World War and was unearthed recently, probably originated from a high temperature coking plant as opposed to a gas works, as indicated by the isotopic signatures of the distributions of PAHs.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants that are of intensive public concern due to their toxicity, mutagenicity and/or carcinogenicity. Indeed, due to their low solubility, hydrophobic and lipophilic properties, PAHs, once emitted

into the environment, can be easily bio-accumulated to such an extent that can threaten the safety of food chains for both man and animals [5,6]. Therefore, the development of PAH source apportionment techniques has received considerable interest due to the need to better understand the fate and associative transformation pathways of environmental PAHs. Previous source elucidation studies of PAHs have involved both molecular approaches [7,8,9] and mathematical modelling [10,11]. However, PAH molecular fingerprints that are believed to be source-indicative have yielded largely ambiguous results because of the wide variety of emission sources, both natural and anthropogenic [12–15],

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complex environmental pathways and a number of physical and/or biogeochemical factors that may alter or even completely eliminate any such source-indicators [16–20].

Stable carbon isotope analysis of whole oils, source rocks and bulk hydrocarbon fractions is an established technique in the petroleum industry to aid source rock and oil correlations [21] and, with the availability of gas chromatography–stable carbon isotope ratio mass spectrometry ( $\delta^{13}\text{C}$  GC–IRMS) since the early 1990s, compound-specific applications have also proved to be a useful tool to investigate the carbon cycle at the molecular level [22–25]. More recently, the potential of using compound-specific isotope measurements for the source apportionment of environmental PAHs has been demonstrated by O'Malley et al. [25], Lichtfouse et al. [26] and the investigators [1,3,4]. Systematic examinations conducted by the authors [1–3] for coal conversion processes have revealed that the isotopic values of PAHs are controlled by the extent of ring growth required to form the PAHs during processing. For relatively mild conversion regimes (e.g. low and high temperature carbonisation, domestic combustion, etc.), the isotopic signatures of PAHs are simply similar to those of parent coals (ca.  $-25\%$ , cf.  $-23.5\%$  for the coals) whilst for highly efficient combustion and gasification processes, they are lighter (less negative) than the parent coals. Thus, it can be concluded that when PAHs are released as primary devolatilisation products with relatively minimal structural alteration, little in the way of isotopic fractionation occurs. However, when PAHs result from ring growth, the smaller hydrocarbons in the primary volatiles must undergo a series of complex transformations involving carbon–carbon bond formation, cyclisation and/or ring fusion. In one or all of these processes,  $^{12}\text{C}$  will be preferentially incorporated into the PAH where a kinetic isotope effect is operative. Although PAH distributions can be altered markedly by biodegradation, it has been demonstrated for low temperature coal tar that the isotopic values of the parent PAHs remain fairly constant [2,3]. Exceedingly isotopically light PAHs ( $\delta^{13}\text{C}$  values as low as  $-60\%$ ) were also reported for the first time by the authors [4] for natural gas (methane) utilisation. These characteristic isotopic variations provide an extremely promising basis for source apportionment in a number of environments, especially where coal-derived emissions are concerned.

We have previously applied the compound-specific measurements of PAHs to identify other sources than coal in soil samples from the Bolsover area from a low temperature carbonisation facility [3] and to identify PAHs with  $\delta^{13}\text{C}$  values close to  $-25\%$  that are consistent with PAHs emanating from coal burning for a Scottish rural location [27]. In this contribution, we use the information obtained on stable carbon isotope ratios of PAHs to unambiguously resolve coal and petroleum-derived PAHs in contaminated land from a former foundry site at Mansfield. Sub-division of aromatic fractions enables relatively small contributions from coal utilisation to be

identified. Information is summarised where a similar situation with a small coal-derived input of large-ring PAHs arises for a soil contaminated mainly with diesel fuel from the Motherwell area. Finally, for coal tar contaminating an urban parkland area (Glasgow Green), we demonstrate that high temperature carbonisation as opposed to gas works operations is the most likely source of the tar.

## 2. Experimental

### 2.1. Samples

A total of 12 samples from two depth series were collected from a location in the Mansfield area that was heavily contaminated by a former foundry suspected of using coal tar with other fuels. A soil sample was collected for the site near Motherwell area that was being remediated by removing the soil for treatment *ex situ* because of heavy contamination that was thought to arise mainly from petroleum (diesel fuel).

Two soil samples were provided by Glasgow City Council for the Glasgow Green Park site, one being from a few centimetres below the surface and another from a depth of approximately 2 m. This heavily contaminated site comprising a solitary residue was unearthed accidentally when future development of the site was being considered. The site received considerable attention from the Scottish media. It was possible that the contaminant (tar) was apparently dumped in this area around the time of the Second World War when plans to build a swimming pool were abandoned.

Additional samples examined for reference purposes include a high temperature carbonisation tar provided by Coal Products Ltd and three Town gas tars from individual sites by BG Technology Ltd.

### 2.2. Sample preparation and fractionation

All soil samples were dried in a vacuum oven overnight at  $40^\circ\text{C}$  and then ground to  $75\text{--}212\ \mu\text{m}$  for solvent extraction which was conducted by reflux in dichloromethane (DCM) for 16 h. Following solvent removal in a rotary evaporator, the DCM extracts were fractionated using open column alumina chromatography (fine grain activated neutral alumina; Brockmann Grade I) to generate neutral aromatic fractions. *n*-Hexane (HPLC grade) was used to elute the aliphatics with the subsequent elution of the neutral aromatics (containing PAHs) in toluene (analytical grade).

Further fractionation of neutral aromatics to generate their sub-fractions by different ring size was also conducted for some samples where reliable compound-specific isotope ratio measurements could not be achieved due to the complex constitution. A similar chromatographic procedure but a different solvent profile, namely blends of *n*-hexane with toluene (2, 4, 10 and 50%, v/v) and finally with neat

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