# PS Combining Hydropyrolysis and Compound Specific Stable Isotope Measurements to Identify Sources of Biodegraded PAHs in Sediments\*

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### Abstract

Compound-specific 13C/12C isotope ratio measurements have successfully been demonstrated as a useful technique for polycyclic aromatic hydrocarbons (PAHs) source apportionment in a number of studies. However, where the PAHs matrix have been subjected to heavy biodegradation, and the isotopic signatures for PAHs are overlapping for some sources, further constraints are needed for unambiguous source apportionment.

Given that stable carbon isotopic ratios ( $\delta$ 13C) of PAHs are not significantly affected by biodegradation and that hydropyrolysis of asphaltenes can generate representative molecular profiles expected for non-biodegraded oils, this methodology has been used for source apportioning hydrocarbons in biodegraded environmental samples.

This protocol has been applied to river sediments, to reveal the variations in isotopic ratio (13C/12C) (-24 to -28 ‰) in Clyde River sediments, suggesting that the sources of PAHs are numerous, with (petroleum and combustion sources- biomass burning, coal derived, and vehicle particulate) are providing major inputs of the parent PAHs.

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qh''y g''RCJ u'kp'I ncui qy ''ctgc0''

<sup>\*</sup>Adapted from poster presentation at AAPG Annual Convention and Exhibition, Houston, Texas, USA, April 10-13, 2011

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It appeared that the core samples derived their PAHs from coal, petroleum, and combustion of coal, biomass and petroleum. The historical shift in energy use, with time, from coal and coal utilization (-23 to -26‰), coal combustion (-25 to -26‰) and for values (-27 to -30‰), abundant petroleum (-27 to -29‰) and (-30‰) biomass combustion has been revealed.

The localized high level of concentrations of Benzo(a)Pyrene (BaP) and Benzo(k)fluoranthene- (32 - 4225 µg/g) generally, has been ascribed to dumping, and therefore, needs attention. Also, the exceptionally high concentrations of Benzo(k)fluoranthene and BaP with 758.4 µg/g and 846.2 µg/g respectively, in sample 608, has specifically allowed for suggesting petrol and diesel exhausts as major sources of PAHs in Glasgow area.

Finally, this combined technique has proved successful in an unambiguous source apportionment of PAHs in river and estuarine sediments in which hydrocarbons have been biodegraded.

### COMBINING HYDROPYROLYSIS AND COMPOUND SPECIFIC STABLE ISOTOPE MEASUREMENTS TO IDENTIFY SOURCES OF BIODEGRADED PAHS IN RIVER SEDIMENTS

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#### Combining Hydropyrolysis and Compound Specific Stable Isotope

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#### Introduction: Polycyclic Aromatic Hydrocarbons (PAHs) in the

- roinogenicity and mutagenicity of PAHs, and the multiplicity of their sources in the environment, the

### Free versus Asphalthene- Bound Aromatic hydrocarbons for some different

#### A comparison of 81°C isotope ratios between free and bound aromatics for differen

PAHS	δ <sup>13</sup> C Instope Ratios (%s, PDE)							
	Law Young. Cont Tar		High Temp. Coal Tar		North Sea Oil			
	Free	Bound	Free	Brund	Free	Bound		
Fluorene	-24.9	-22.5	-23.5	-24.2				
Phenanthrone	-25.6	-22.6	-24.1	-21.0	-29.1	-27.9		
Anthrocene	-25.6	-23.6	-24.1	-31.0	-28.1	-27.9		
Fluoranthene	-25.6	-22.8	-24.9	-22.5	-28.5	-28.6		
Pyrene	-28.7	-21.4	-24.8	-31.5	-28.6	-39.4		
Benz (a) authrorene	-25.2	-23.9	-25.0	-33.7	-28.1	-28.8		
Chrysene	-25.8	-23.9	-25.6	-23.7	-28.1	-28.8		
Reum(h)fluorant hene	-25.9	-23.2	-26.1	-24.5	-29.1	-30.3		
Reum(k)fluorant bene	-25.9	-23.2	-26.1	-24.5	-29.1	-30.3		
Renzo(a)pyrenz	-26.1	-23.5	-26.0	-25.3		-29.1		
Indeao(1,2,3,- cd)pyrene			-25.6	-25.3		-30.2		
Dibenz(a,b)anthr ocene			-25.6	-25.4		-30.2		
Benzo(ghi)psryte			-26.6	25.4		-30.2		

- PAH derived from different sources in the UK. vary in their "ICX"G
  For oil samples, the molecular and lactopic profiles for their
  corresponding suphishers-ederwided PAHs are similar to those
  corresponding suphishers-ederwided PAHs are similar to those
  the samples. The molecular and isotopic profiles for their
  corresponding suphishers-ederwided PAHs are similar to those
  the form of the samples of the samples of the samples of the samples
  that the samples of the samples of the samples of the samples
  form -22 and -25%.
- to the profiles were observed for the free and

#### **PAHs Source Apportionment Techniques**

### Molecular versus Compound-specific isotope analysis (CSIA)

Nolecular Approach
Solely rely on PAH molecular profiles and/or selected diagnostic ratios believed to be source-indicative!

### Remains largely ambiguous or to some extent arbitrary¹

- SIA
  Seen as new technology revolutionising the traditional way of studying the origins, fate and transport of PAHs in the environment' Highly responsive to different PAHs formation chemistries' Source unique d'°C isotopic profiles for different sources' Still (naisgificantly) affected by biodegradation'

- (1) Sun 2001 (Unpublished PhD Thesis) (2) Snape et al., 2001

#### PAHs in the environment

- Ambiguous source apportionments of PAHs caused by the effect of biodegradation on these cor with the resultant isotopic signature and molecular fractionation in the in-situ single source conta were worked on 1.23 set 4.
- some aurrors has commoned the use of stotope measurements with other geochemical techniques 5.5. However, none of the previous authors emphasized and addressed the problem of biodegradation of hydrocarbons in river and estuarine sediments. The present protocol had been used to source-apportion PAHs in a number of in-situ single source contamination of belsover soils, Archive soils and Nigerian biodegraded oils.
- But none on river and estuarine sediments that have been transported from their point sources and re deposited elsewhere except for this study.

- Readily affected by flushing with drilling fluids' Hence, less favoured for geochemical analysis

#### Aims, Scope and Hypothesis

- Aims and Scope:

  To develop a protocol based on hydropyrolysis to release bound hydrosprobens from asphaltenes in conjunction with the use of d<sup>12</sup>C compound-specific stable isotope measurements on hydrocarbons
- source-apportion environmental hydrocarbons where severe degradation is operative; and apply this protocol to river and estuaring sediments.

  To apply the protocol to discount contaminants inherent in drill-cutting samples resulting from flushing with drilling fluids
- resulting from flushing with drilling fluids

  Applications create useful research and isotopic information of biogeochemical
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  expected for the primary sources like bituminous cost<sup>2</sup> and non-biodegraded out
  pathways that di<sup>2</sup>C isotopic reasurements are sensitive tor<sup>2</sup> lower sources and the company of the primary sources are sources and the company of the primary sources are sources and the company of the primary sources are sources.

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#### Samples Investigated and Experimental Protocol

#### Clyde River loose sediments which are coarse-grained with little/no biodegradation

- Clyde River/Estuarine core sediments which are very fine grained, wet and muddy with significant biodegradation
- Unocal Drill-cutting samples which are wet.





Case study 1: The PAHs in Bolsover soil samples closed to a former carbonisation plant

4	4. Fluc
Proc aromatics	5. Phe
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, , , , , , , , , , , , , , , , , , , ,	7. Fluo
	8. Руге
After.	9. Ben
Boundarorration	10. CH
The second of	11. Be
	12. Be
Register Time, mine the date that the	13. Be
Free and bound aromatic distribution	14. Inc

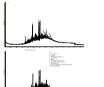
	Name and No of PAHs	Free aromatics	Bond aromatics
	4. Fluorene	-22.5	-20.5
muties	5. Phenanthrene	-22.7	-19.7
	6. Anthracene	-22.7	-19.7
	7. Fluoranthene	-24.8	-19.9
	8. Pyrene	-24.7	23.3
	9. Benz(a)anthracene	-25.4	-22.8
ornation	10. Chrysene	-25.4	-22.8
	11. Benzo(b)fluoranthene	-25.2	-22.0
NN No.	12. Benzo(k)fluoranthene	-25.2	-22.0
	13. Benzo(a)pyrene	-24.4	-22.2
,	14. Indeno(1,2,3-cd)pyrene	-26.6	-23.3
	15. Dibenz(a,h)anthracene	-26.6	-23.3

d<sup>13</sup>C Parent PAHs with isotopic ratios avily alkylated) rather than a high temperature coal tar was the major source of the free aromatic hydrocarbons in the soil samples, as indicated by both molecular and isotopic profiles obtained for the bound aromatics (asphaltene released via HyPy)

#### Samples Location map around Glasgow City, UK for Case Study 2 and 3



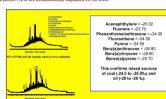
## Case study 2: The PAHs in River Sediments





#### Isotopic Values (%) of some major PAHs in Clyde Loose Sediments

The parent PAHs are conspicuously displayed on the UCM



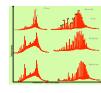
Case Study 3: Clyde core samples - Percentage yield of

Samples	Asph for	Hc	%	It has been revealed that			
	Hypy	Rec	Yield				
	(mg)	(mg)		asphaltene samples as small as 0.6			
616 Top	6.0	3.2	53	to 1.0 mg can yield appreciable and analysable hydrocarbon			
Middle	5.9	2.5	42	profiles using hydropyrolysis.			
Bottom	3.5	1.4	39	promes using nyaropyrorysis.			
567 Top	0.7	0.7	99				
Middle	0.8	0.7	86				
Bottom	0.9	0.9	99				
573 Top	1.1	1.0	99				
Middle	0.7	0.6	88				
Bottom	1.5	0.9	61				
577 Top	0.4	0.1	24				
Middle	0.8	0.8	98				
Bottom	0.9	0.9	99				
562 Top	0.5	0.1	20				
Middle	0.9	0.9	93				
Bottom	0.6	0.6	97				
608 Top	0.8	0.7	92				
Middle	0.6	0.6	94				
Bottom	0.5	0.1	20				
Case study 3: Yield of hydrocarbons in the							

se study 3: Yield of hydrocarbons in t bound and free phase in sample 616



-Hydrocarbon yields are generally higher in the bound phase compared to the free phase in Clyde sediments extracts
Case study 3: TIC of the Free and Bound aliphatic profile in Clyde River sediments compared (Core 616).



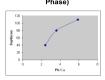
\*Loss of n-alkanes (due to biodegradation) in the free compared with (molecular) bound profile

#### Case study 3: Aliphatic Molecular Diagnostic Ratios in Sample 616

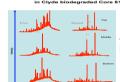


diesel engines' emissions 1.2 •CPI values range 0.6 to 1.6 support only petroleum- and coal- derived sources<sup>2</sup>

#### Case study 3: Evidence of biodegradation increases with depth in core sample 616 (Free

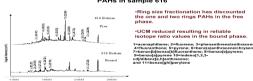


Case Study 3: The TIC of the Free and Bound aromatic profile in Clyde biodegraded Core 616 sediments compared.

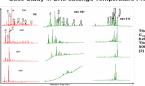


The big UCM in the free indicates petroleum input Note: Fl and Py are Fluoranthene and Pyrene respectively

Case 3: Clyde Core Sample: GC-IRMS profiles of free and bound



#### Case Study 4: Drill-cuttings Temperature Programme Experiment



The contaminants inherent in  $C_{\rm to}$  and  $C_{\rm to}$  have been evolved at temperature below 500 °C. The hydrocarbon profiles generated a 500 °C were from the oil at (2) 4940 – (2) 4955 feet depth.

Conclusions

Clyde Loose Sediments
The sources of PAHs in River Clyde loose sediments are petroleum- and coal-derived

Cype Estuarine Cure Samples (Blodegraded)

- Hydrogroylopis as capable for penaling geochemical vital information on asphaltenes of biodegraded hydrocarbons in

- Nordestuarine sediments

- Biodegic values from bound profiles are more reliable and really depict the original source information because the baselines

างหมองรายโทรเร. The findings imply that combining hydropyrolysis with อั<sup>12</sup>C isotope measurements of asphaltene from biodegraded hydrocarbons can be used to unambiguously source-apportion hydrocarbons in complex environment like river/estuarine

sediments.

-cutting Samples.

Biomarker profiles in the drill-cutting sample are from oil at the depth, not from turbophalt.

Hydropyrolysis, using temperature programming is capable of discounting contaminants inherent in drill-cuttings. Therefore rendering them as cheap samples for geochemical analysis in the oil industries, most especially where the drilling mud is not recorded.

#### Acknowledgements

Our special thanks to the British Geological Survey (BGS) and European Physical Science Research Council (EPSRC) for co-sponsoring the project. Many thanks to BGS for providing the Clyde River and Estuarine sediment and one samples