

SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS WITHIN THE COALITE PLANT IN BOLSOVER, NORTH DERBYSHIRE USING ISOTOPE COMPOSITION

Wisdom Iwwurie, Emelife S.C., Snape C., & Sun C.

Department of Chemistry,
Federal University of Petroleum Resources, Effurun
Email: wivwurie@yahoo.co.uk

ABSTRACT

Five soil samples from varying distances from a coalite plant in Bolsover, North Derbyshire were analyzed for their isotopic compositions using gas chromatography – isotope ratio mass spectrometry (GC-IRMS). The isotopic composition (free and asphaltene – derived aromatics respectively) for the study areas are; for Bolsv.1, it ranged from -22.5 to -26.6 ‰ and -19.7 to -23.4 ‰, Bolsv 2 ranged from -20.7 to -26.6 ‰ and -19.7 to -22.6 ‰, Bolsv. 3 ranged from -21.6 to -26.6 ‰ and -19.0 to -23.3 ‰, Bolsv. 4 ranged from -23.7 to -27.3 ‰ and -23.4 to -25.1 ‰ and Bolsv.5 ranged from -23.2 to -24.6 ‰ and -23.6 to -27.3 ‰. These ranges showed that the PAHs in the soils were derived basically from coal related sources with predominant input from low and high temperature carbonization.

Keywords: Coalite Plant, Isotope Composition, GC-IRMS and PAHs.

INTRODUCTION

GC-IRMS has been widely employed to assess the biogenicity and biochemical transformation of molecular constituents in sedimentary organic matter [3, 6, 14] and it has been used successfully to estimate the contributions of terrestrial organic matter to the atmospheric particulate carbon in the marine troposphere [1] as well as sediments in marine environments [4]. O'Malley *et al.*, (1994, 1996); McRae *et al.*, 1996; Sun, 2001 have applied the technique of GC-IRMS in the environmental sciences to trace the sources and pathways of a large variety of anthropogenic organic emissions, thereby attracting the attention of many environmental scholars. Ballentine *et al* (1996) examined the $^{13}\text{C}/^{12}\text{C}$ isotope ratios of the fatty acids and PAHs derived from biomass burning under different conditions, and it was found that the isotopic signatures of the individual fatty acids surviving the smoldering laboratory burn were very close to those for the fatty acids present in unburned sugar cane plant (-19.9 to 23.6‰). Rooney *et al* (1998) used compound-specific isotope analysis as a tool to characterize mixed oils. In the study, mixtures of biodegraded and non-biodegraded oils were characterized by comparing the carbon isotope ratios of the gasoline – range fraction (GRF) of the oil to the GRF released from the pyrolysis of the asphaltene in the oil. Information obtained was found to be useful in assessing the source potential of the basin. Murray (2001) reported that isotopic signatures for n – alkanes derived from low and high temperature hydrolysis of a Chamot Hill shale all lie within a range of 2.5‰ (-28.5‰ to -31‰), being indicative of a single biological source for the components. In concluding, he noted that the narrow isotopic variation for the samples studied (-26.5 to -31‰) seemingly suggested a contribution from C_3 higher plants to the sediments. However, closer examination shows subtle differences and trends in isotopic signatures, which suggests possible contributions from other organic

Source Apportionment of Polycyclic Aromatic Hydrocarbons in Soils within the Coalite Plant in Bolsover, North Derbyshire using Isotope Composition

Wisdom Ivwurie; et al.

sources (marine derived organic material). The discussion so far highlights the fundamental issues in biodegradation and source apportionment studies. However a major constraint to obtaining reliable information during source apportionment is when PAHs and aliphatic hydrocarbons have been heavily biodegraded. This makes it difficult to obtain compositional and isotopic information to carry out reliable source apportionment studies. Love *et al* (1997) reported that the molecular integrity of biomarkers is well preserved in asphaltene when they are released through hydrothermal pyrolysis. If PAHs and asphaltenes are co-emitted in the environment and biodegradation of the latter constitute a constraint to reliable source apportionment studies, information obtained from the former, which is well preserved, can significantly aid source apportionment. It is therefore the objective of this work to try to apportion sources to the PAHs present in soils within the coalite plant in Bolsover, North Derbyshire using their isotope compositions by comparing them with the isotope compositions of primary sources.

DESCRIPTION OF STUDY AREA

Description of Study Area and Soil Sampling

The studied areas are situated around the Coalite low temperature carbonization plant in Bolsover. Bolsover is a small town near Chesterfield, Derbyshire in England. It is 233 km from London and 42 km from Nottingham. The area is known for Coal mining. A schematic sketch showing the sample collection points is given in Figure 1. Five samples were collected according to their distances from the coalite plant. Bolsv.1 (20-30 metres from the plant), Bolsv.2 (50 metres from the plant), Bolsv.3 (500 metres from the plant), Bolsv.4 (M1 motorway roadside dust) and Bolsv. 5 (farm field soil). The different soils were dried at a temperature of 105°C for 3 to 4 hours and then ground to pass through a 60-mesh sieve.

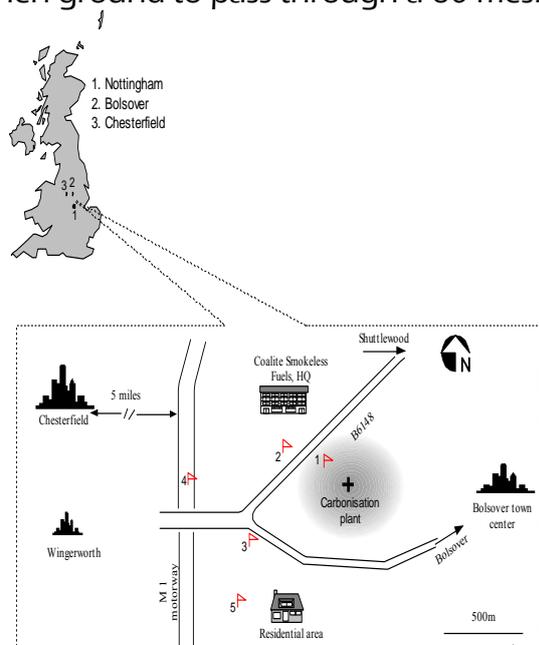


Figure 1: Schematic Diagram Showing Study Areas

Sample Extraction and Purification

The samples were extracted by soxhlet extraction and refluxing techniques using redistilled dichloromethane (DCM) and dichloromethane- methanol (93:7) mixture.

Wisdom Ivwurie; et al.

The weight of each sample extracted was altered to obtain sufficient amounts of PAHs analysis. 100 g of soil to 250 ml of solvent mixture was used for each extraction. When refluxing and soxhlet extraction were completed, the slurries were filtered to obtain the extract solution. The extract of each sample was concentrated using rotary evaporator at 30°C for DCM solutions and 45°C for DCM/methanol mixtures. The extract was concentrated and dried using a stream of N₂. Open column chromatographic separation was then carried out on each extract obtained and the neutral aromatics containing the PAHs together with the aliphatics were kept for analysis.

RESULTS AND DISCUSSION

GC-IRMS distribution is similar for Bolsv.1 and 2 for free and bound aromatics (table 1 and 2). The stable carbon isotope ratios observed for the free aromatics in Bolsv. 1 which vary from -22 ‰ to -25 ‰ (table 1) were consistent overall with low temperature coal tar being the major source [12, 13]. The heavier isotopic ratios for the bound aromatics bear close similarity to those for bound aromatics from low temperature coal tar, where isotopic ratios were close to the parent coal. Generally speaking, the higher boiling parent PAHs (3-6 rings) had lighter isotopic ratios, being close to those observed for high temperature coal tar, and begin to approach petrol/related emissions (values between -25.4 and 26.6‰). It is therefore suggested that the soil could have received some PAHs from either high temperature carbonization process or petrol, or both.

For Bolsv2, isotopic ratios vary from -20.7 to -26.6‰ for the free PAHs and -19.7 to -22.6‰ for the asphaltene derived (table 2). The asphaltene derived PAHs were heavier by 1.0 to 4.0‰ than the free counterpart. Isotopic ratios decreased with ring size. The asphaltene – derived aromatics having heavier isotopic ratios suggest that they were representative fragments of a parent coal. The isotopic ratio values were closely related to the values recorded for low temperature carbonization process (both free and asphaltene derived). It is worth mentioning that the isotopic value for the asphaltene derived PAHs was significantly heavier and more consistent than the free counterpart, suggesting that PAHs input in the former was from a single source. On the other hand, a wide isotopic range of -20.7 to -26.6‰ recorded for the free PAHs suggests the variable degree of biodegradation. Another possibility is inputs from other sources.

For Bolsv3, the isotopic ratios had a range of -21.6 to -26.6 ‰ for the free PAHs and -19.0 to -23.3‰ for the asphaltene – derived PAHs (table 3). These values were similar to those obtained for both low and high temperature carbonization. The asphaltene – derived isotopic ratios were again heavier than their free counterparts by 1-3 ‰, but these values were close to those found for bound aromatics from low temperature coal tar [13]. Greater consistency was observed more for the isotopic values of the asphaltene – derived aromatics, indicating they were likely from a single source (coal utilization), and this differs from the wide isotopic ratio range observed for the free PAHs. Generally speaking, PAHs from the free Bolsv.3 samples received inputs from a combination of low, high temperature carbonization process and biomass conversion, whereas the asphaltene – derived was solely from coal utilization emission. Isotopic ratio analysis for Bolsv 4 gives a range of -23.7 to -27.3 ‰ for the free PAHs, while the range for the asphaltene – derived compounds was –

Wisdom Iwurie; et al.

23.4 to -25.1 ‰ (table 4). Isotopic values for the asphaltene – derived PAHs were similar to that recorded for low and high temperature carbonization coal tar, suggesting that they were derived from coal related sources, and were far heavier than the higher boiling PAHs of the free counterpart, which arise from coal conversion. Given that the molecular profile for the asphaltene derived PAHs was dominated by alkyl substituted PAHs, input from a low temperature process is more likely than from a high temperature process. Low boiling PAHs in the free neutral aromatic had isotopic ratios within the range for low and high temperature process, but the higher boiling ones progressively becomes lighter in isotopic ratios, suggesting that PAHs could be from other sources. Light values of the order of -27.7 ‰ recorded for the higher boiling PAHs in the free extract were quite similar to isotopic values for petrol and diesel engines [13]. The isotopic ratio range of -23.4 to -25.1 ‰ respectively, supports input from coal.

For Bolsv5 (table 5), the isotopic ratio range for the free extract (being -23.3 to -24.3 ‰) bears close similarity to low temperature coal tar. The asphaltene derived PAHs gave rather lighter ratios except fluorene, phenanthrene, anthracene and pyrene, which had isotopic value range of -23.6 ‰ to -25.6 ‰, being consistent with coal utilizations. The lighter isotopic values obtained for other higher boiling PAHs could imply biomass or even petrol input, suggesting that this sample (asphaltene – derived Bolsv. 5 sample) had mixed input sources. The light isotopic ratio of -27.3 ‰ benzo(b/k) fluoranthene and other PAHs with close isotopic values in the asphaltene – derived Bolsv. 5 samples indicates that petroleum and related sources were the likely contribution [13]. It can therefore be suggested that the free farm field sample had PAHs from multiple sources, namely high and low temperature carbonization process as well as biomass. Whereas the PAHs from the asphaltene derived is thought to be from a mixed sources of both petroleum and related sources.

CONCLUSION

The bulk isotopic data (both free and asphaltene-derived aromatics) for the study areas ranged from -19.0 to -27.3 ‰. This range show that the PAHs were derived from coal related sources with predominant input from low and high temperature carbonization and from other sources such as petrol and diesel engines. This is however as expected since the study areas are around a coalite plant.

TABLES

Table 1: Isotopic Data for Free and Bound Aromatics in the Soil Bolsv. Sample No.1

Name and No of PAHs	Free Aromatics	Asphaltene-Derived Aromatics
4. Fluorene	-22.5 *	-20.5
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
10. Chrysene	-25.4	-22.8 *
11. Benzo(b) Fluoranthene	-25.2	-22.0
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 *
Alkylated Derivatives		
16. Methylfluorene	-22.6	-20.7
17. Methylpyrene	-24.9	-23.4
18. Ethylchrysene	-25.6	-23.0 *
Standard Deviation	0.1-0.2	0.1-0.2

Key: * Represents Isotopic Ratios of PAH and/or Eluting Aromatics at the Listed Retention Time

Table 2: Isotopic Ratio Data for Free and Asphaltene Derived Aromatic Constituents in Bolsv. Soil sample No.2

Name and No of PAHs	Free Aromatics	Asphaltene-Derived Aromatics
4. Fluorene	-22.1 *	-20.6
5. Phenanthrene	-23.0 *	-20.6
6. Anthracene	-23.1	-20.6 *
7. Fluoranthene	-22.8	-20.4
8. Pyrene	-22.8 *	-21.6 *
9. Benz(a) Anthracene	-24.7	-22.9
10. Chrysene	-25.3	-22.9
11. Benzo(b) Fluoranthene	-25.4 *	-21.1 *
12. Benzo(k) Fluoranthene	-24.7	-21.1
13. Benzo(a) Pyrene	-24.7	-21.1 *
14. Indeno(1,2,3-cd) Pyrene	-25.4 *	-22.6
15. Dibenz(a,h) Anthracene	-26.5	-22.6 *
16. Benzo(ghi) Perylene	-26.6	-22.6
Standard Deviation	0.1-0.2	0.1-0.3

Key: *Represents Isotopic Ratio of PAH and/or Eluting Aromatics at the Retention Time Listed

Table 3: Isotopic Data for Free and Bound Aromatics in the Soil Bolsv. Sample No.3

Name and No of PAHs	Free Aromatics	Asphaltene-Derived Aromatics
4. Fluorene	-22.5 *	-21.5 *
5. Phenanthrene	-22.7	-21.7
6. Anthracene	-22.6 *	-21.7 *

Source Apportionment of Polycyclic Aromatic Hydrocarbons in Soils within the Coalite Plant in Bolsover, North Derbyshire using Isotope Composition

Wisdom Ivwurie; et al.

7. Fluoranthene	-23.4	-21.8
8. Pyrene	-23.6 *	-21.8 *
9. Benz(a) Anthracene	-24.7	-23.4
10. Chrysene	-25.4 *	-23.4
11. Benzo(b) Fluoranthene	-25.3	-22.6 *
12. Benzo(k) Fluoranthene	-25.4	-22.6
13. Benzo(a) Pyrene	-24.7	-20.9
14. Indeno(1,2,3-cd) Pyrene	-26.5 *	-23.3
15. Dibenz(a,h) Anthracene	-26.6	-23.3
16. Benzo(ghi) Perylene	-26.6	-23.3
Standard Deviation	0.1-0.2	0.1-0.2

Key: *Represents Isotopic Ratio of PAH and/or Eluting Aromatics at the Retention Time Listed

Table 4: $\delta^{13}\text{C}$ isotopic Data for Free and Asphaltene Derived Aromatics Present in Bolsv. Sample No.4

Name and No of PAHs	Free Aromatics	Asphaltene-Derived Aromatics
4. Fluorine	-23.5 *	-23.3
5. Phenanthrene	-23.6 *	-23.4 *
6. Anthracene	-23.6	-23.4
7. Fluoranthene	-23.7	-25.0
8. Pyrene	-25.4 *	-25.3
9. Benz(a) Anthracene	-27.0	-25.1 *
10. Chrysene	-27.5	-25.1
11. Benzo(b) Fluoranthene	-27.5 *	-25.2
12. Benzo(k) Fluoranthene	-27.3	-25.2 *
13. Benzo(a) Pyrene	-27.3	-25.2
14. Indeno(1,2,3-cd) Pyrene	-27.3	-25.3
Alkylated Derivatives		
17. Methylfluorene		-23.4
18. Methylpyrene		-25.4 *
Standard Deviation	0.1-0.2	0.1-0.3

Key: * Represents Isotopic Ratios of PAH and/or Eluting Aromatics at the Listed Retention Time

Table 5: Isotopic Data for Free and Bound Aromatics in the Soil Bolsv. Sample No.5

Name and No of PAHs	Free Aromatics	Asphaltene-Derived Aromatics
4. Fluorene	-23.2*	-23.6
5. Phenanthrene	-23.3	-23.7
6. Anthracene	-23.3*	-23.7
7. Fluoranthene	-23.4	-26.3*
8. Pyrene	-23.8	-25.6
9. benz(a) Anthracene	-24.0*	-26.7*
10. Chrysene	-24.0	-26.7
11. Benzo(b) Fluoranthene	-24.6*	-27.3
12. Benzo(k) Fluoranthene	-24.6	-27.3*
13. Benzo(a) Pyrene	-24.3	-26.0
14. Indeno(1,2,3-cd) Pyrene	-24.3*	-26.1
15. Dibenz(a,h) Anthracene	-24.3	-26.1
16. Benzo(ghi) Perylene	-24.3*	-26.1
Standard Deviation	0.1-0.2	0.1-0.3

Key: *Represents Isotopic Ratio of PAH and/or Eluting Aromatics at the Retention Time Listed

REFERENCES

- [1] Abrajano, T.A. Jr., Murphy, D.E., Fang, J., Comet, P. and Brooks, J.M. (1994) $^{13}\text{C}/^{12}\text{C}$ Ratios in Individual Fatty Acids of Marine Mytilids with and without Bacterial Symbionts. *Organic Geochemistry*. 21, 611-617.
- [2] Ballentine, D.C., Macko, S.A., Turekian, V.C., Gilhooly, W.P. and Martincigh, B. (1996) Compound Specific Isotope Analysis of Fatty Acids and Polycyclic Aromatic Hydrocarbons in Aerosols: Implication for Biomass Burning. *Organic Geochemistry*. 25, 97-104.
- [3] Bjoeroy, M.; Hall, K. and Jumeau, J. (1990) Stable Carbon Isotope Ratio Analysis on Single Components in Crude Oils by Direct Gas-Chromatography-Isotope Analysis. *Analytical Chemistry*. 9, 331-337.
- [4] Fernandes, M.B. and Sicre, M.A. (2000) The Importance of Terrestrial Organic Carbon Inputs on Kara Sea Shelves as Revealed by *N*-Alkanes, OC and $\delta^{13}\text{C}$ Values. *Organic Geochemistry*. 31, 363-372.
- [5] Love, G.D., McAulay, A., Snape, C.E. and Bishop, A.N. (1997) Effects of Process Variables in Catalytic Hydropyrolysis on the Release of Covalently Bound Aliphatics Hydrocarbons from Sedimentary Organic Matter. *Energy and Fuels*. 11, 522-531.
- [6] Love, G.D., Snape, C.E. and Fallick, A.E. (1998). Differences in the Mode of Incorporation and Biogenicity of the Principle Aliphatic Constituents of a Type 1 Shale. *Organic Geochemistry*. 28, 797-911.
- [7] McRae, C., Snape, C.E.; Sun, C., Fabbri, D., Tartari, D., Trombini, C. and Fallick, A.E. (2000) Use of Compound Specific Stable Isotope Measurements to Source

Wisdom Ivwurie; et al.

Anthropogenic Natural Gas- Derived Polycyclic Aromatic Hydrocarbon in a Lagoon Sediment. *Environmental Science and Technology*. 22, 4684-4686.

- [8] Murray, I.P. (2001) Release of Covalently Bound Biological Marker Molecules from Sedimentary Organic Matter Via Catalytic Hydrolysis. Unpublished Ph.D Thesis, University of Strathclyde.
- [9] O' Malley, V.P., Abrajano, T.A. Jr. and Hellou, J. (1994) Determination of the $^{13}\text{C}/^{12}\text{C}$ Ratios of Individual PAH from Environmental Samples: can PAH Sources be Apportioned? *Organic Geochemistry*.21, 809- 822.
- [10] O'Malley, V.P., Abrajano, J.R. and Hellou, J. (1996) Stable Carbon Isotopic Apportionment of Individual Polycyclic Aromatic Hydrocarbons in St. John's Harbour, Newfoundland. *Environmental Science and Technology*. 30, 634-639.
- [11] Rooney, M.A., Matava, T., Nwankwo, B.C., Chung, H.M. and Lambert – Aikhionbare, D.O. (1998) Geochemical Characterization of the Hydrocarbons in the Petroleum System of the Southeastern Niger Delta (abs.). AAPG International Meeting Abstracts, Rio De Janeiro, Brazil.p 343.
- [12] Simcik, M.F., Eisenreich, S.J. and Liou, P.J. (1999) Source Apportionment and Source/Sink Relationships of Paths in the Coastal Atmosphere of Chicago and Lake Michigan. *Atmospheric Environment*.33, 5071- 5079.
- [13] Sun, Cheng-gong. (2001) Sourcing PAH in the Environment. Unpublished Ph.D Thesis. University of Strathclyde.
- [14] Wise, S.A., Sander, L.C. and May, W.E. (1993) Determination of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography. *Journal of Chromatography*, 642, 329-349.

Reference to this paper should be made as follows: Ivwurie W.; et al. (2016), Source Apportionment of Polycyclic Aromatic Hydrocarbons in Soils within the Coalite Plant in Bolsover, North Derbyshire using Isotope Composition. *J. of Environmental Sciences and Resource Management*, Vol. 8, No. 1, Pp. 32 – 39.
