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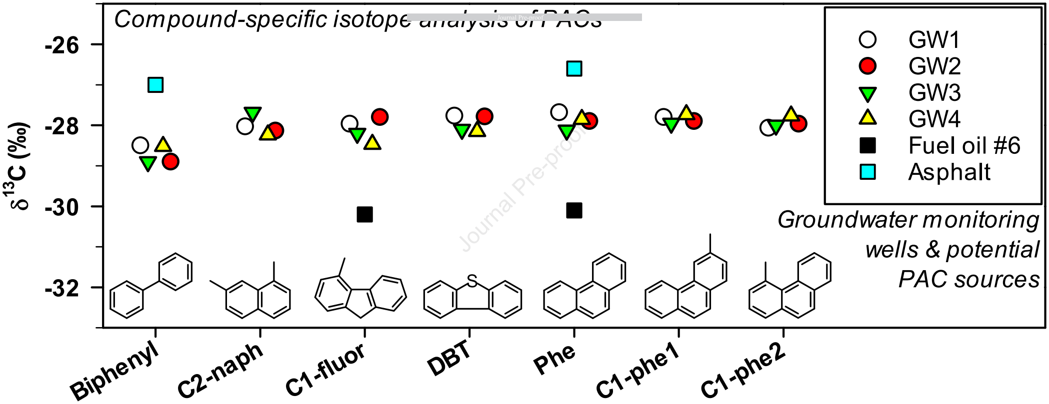
Compound-specific isotope analysis of PACs
$\delta^{13}C$ (‰)
-26
-28
-30
-32
GW1
GW2
GW3
GW4
Fuel oil #6
Asphalt
Groundwater monitoring wells & potential PAC sources
S
Biphenyl
C2-naph
C1-fluor
DBT
Phe
C1-phe1
C1-phe2

Isotope forensics of polycyclic aromatic compounds (PACs) in a contaminated shallow aquifer

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ABSTRACT

Diesel was accidentally released into the shallow subsurface at an industrial site in the province of Québec, Canada, in the late 1980s. Subsequent remediation efforts removed much of the contamination; however, traces of petroleum hydrocarbons continue to impact the local aquifer. In addition to the historical diesel spill, more recent yet unconfirmed accidental releases from ongoing on-site and neighbouring industrial activities may have potentially contributed to elevated levels of polycyclic aromatic compounds (PACs) in groundwater. To identify the main source(s) of contamination, compound-specific stable carbon isotope ratios ($\delta^{13}C$) of PACs in groundwater monitoring wells were compared to those in asphalt produced from a nearby plant and in fuel oil #6 oil being used by local industry. The $\delta^{13}C$ values of five individual compounds (biphenyl, C2-naphthalene, C1-fluorene, dibenzothiophene and phenanthrene) and two groups of combined C1-phenanthrenes/anthracenes in all groundwater samples were within analytical uncertainty (± 0.5‰). Moreover, the $\delta^{13}C_{PAC}$ values in groundwater samples were distinct from those in asphalt and fuel oil #6, indicating negligible contributions from these sources. The similarity in $\delta^{13}C_{PAC}$ values across monitoring wells, including one situated in the former source zone containing a floating hydrocarbon phase, pointed to a common source of subsurface contamination that was attributed to the historical diesel spill. These results thus demonstrate that $\delta^{13}C_{PAC}$ values can be used for source apportionment in shallow aquifers decades after the original spill event.

Keywords: compound-specific; carbon isotopes; PAHs; groundwater; diesel

1. Introduction

Polycyclic aromatic compounds (PACs), in particular the relatively more water soluble two- or three-ring PACs, pose a major risk to groundwater resources at petroleum-contaminated sites (Han et al., 2013; Logeshwaran et al., 2018; Ololade et al., 2021). While establishing the principal source of subsurface contamination is often straightforward, in many cases multiple sources, either historical or current, can contribute to elevated concentrations of PACs in groundwater (Shao et al., 2014; Li et al., 2017; Raza et al., 2017). As understanding the source(s) of contamination is crucial for cost-effective groundwater remediation (Gzyl et al., 2014), techniques that can successfully delineate PAC sources are of great value to hydrogeological investigations.

One method capable of accurate PAC source discrimination in environmental samples is compound-specific carbon isotope analysis (carbon-CSIA). Using this approach, very small variations in natural abundances of ^{12}C and ^{13}C in PACs are expressed as per mil (‰) differences relative to the international standard (Vienna Peedee belemnite):

$$\delta^{13}\mathrm{C} = \left[\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{sample} - (^{13}\mathrm{C}/^{12}\mathrm{C})_{standard}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{standard}}\right] \times 1000 \qquad (1)$$

The δ^{13}C values of PACs will reflect that of the source organic matter as well as any subsequent isotopic fractionation caused by biogeochemical, diagenetic, or thermal alteration (Galimov, 2006). As carbon isotope fractionation effects associated with biodegradation of PACs are generally negligible (O'Malley et al., 1994; Mazeas et al., 2002), variations in $\delta^{13}\mathrm{C}_{\mathrm{PAC}}$ values at a study site can thus be used to differentiate isotopically distinct sources (Philp, 2007; Buczyńska et al., 2013).

While carbon-CSIA has been successfully used to characterize and identify PAC sources in other environmental media (e.g., Jautzy et al., 2013; Ahad et al., 2015; Bosch et al., 2015; Jautzy et al., 2015; Ahad et al., 2021), few hydrogeological investigations have exploited this technique for the purpose of source apportionment. In one of the earliest environmental applications of carbon-CSIA, (Trust Hammer et al., 1998) determined $\delta^{13}C_{PAC}$ values in groundwater samples collected at two creosote-contaminated sites in Florida, USA. The similarity in $\delta^{13}C$ values (within 1‰) for 12 of 16 compounds at both sites suggested a potential creosote-specific pattern in $\delta^{13}C_{PAC}$ values for use in source apportionment. Unfortunately, no follow-up investigation validating the usefulness of this 'isotopic fingerprint' to delineate subsurface creosote contamination was carried out. Nonetheless, the twenty-five-year-old publication by (Trust Hammer et al., 1998) remains one of the only examples in the scientific literature demonstrating the potential of carbon-CSIA to discriminate sources of PACs in contaminated aquifers.

Here, we exploit carbon-CSIA to identify the main source or sources of PAC contamination in a shallow aquifer near an industrial site in the province of Québec, Canada. A decades-old diesel spill is suspected as the principal reason for elevated concentrations of PACs in several groundwater monitoring wells. However, inputs from a nearby asphalt plant and the more recent utilization of fuel oil #6 at the site may have also potentially contributed. The $\delta^{13}C$ values of PACs in groundwater monitoring wells from across the plume were compared to those in the locally produced asphalt and in the fuel oil #6 currently being used by the local industry. This study presents one of the few instances in which $\delta^{13}C_{PAC}$ values have been successfully applied for the purpose of source identification in a hydrogeological investigation.

2. Materials and methods

2.1. Site description

Groundwater underlying an industrial site in Québec, Canada, was contaminated in 1988 by accidental release of diesel. A program to remediate the aquifer and contain the spill was implemented in 1989 by the installation of hydrocarbon recovery wells and groundwater monitoring wells. The floating phase recovery system began operating in 1990 and resulted in the removal of more than 11,000 L of hydrocarbons from the aquifer over a period of 131 months. During this period, the number of wells with floating phases decreased from 34 to 6. The rehabilitation system was stopped in 2001 since at the time it was believed that the residual hydrocarbon saturation would not detrimentally impact the water quality of nearby municipal extraction wells (Figure 1).

An ongoing environmental monitoring program has examined groundwater quality, piezometry and thickness of floating phases in several wells twice a year (May and November). A sampling campaign carried out in October 2016 detected concentrations of several PACs (acenaphthene, fluorene and phenanthrene) above provincial guidelines in groundwater monitoring wells outside the zone of remediation (Table 1). The concentrations of PACs were determined by AGAT Laboratories in Québec City, Québec (Accreditation #405). For reference (Figure 1), well GW2 is situated within the former source zone and wells GW3 and GW4 within an area identified as a potential former source zone of the original diesel spill. Wells GW1, GW3 and GW4 are situated 50-100 m southwest of GW2.

Fuel oil #6 has been the main energy source at the industrial site since the 1990s (the specific location of the site and further details of the historical contamination and asphalt plant are withheld to preserve client confidentiality). The fuel is stored on-site in two aboveground tanks that are fed by an underground pipeline that runs close to and upgradient of the former source zone

(Figure 1). The assumption is that contamination in groundwater in 2016 may have originated from an undetected spill from the tanks or pipeline. The asphalt plant is situated on the neighbouring property very close to the former source zone (Figure 1). Thus, another assumption was that asphalt production was the source of subsurface petroleum hydrocarbon contamination detected in 2016, particularly in well GW4 (Figure 1).

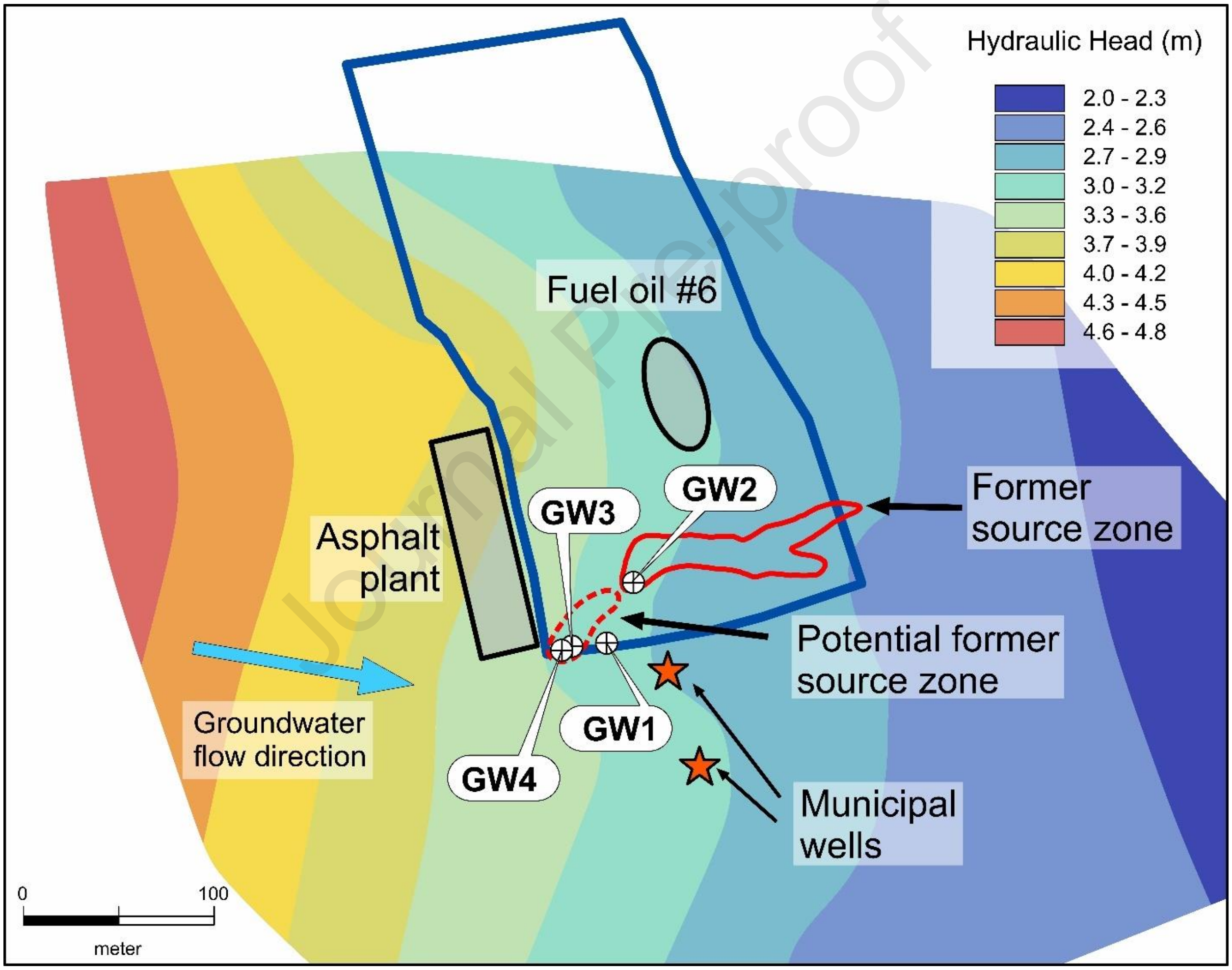

Figure 1. Simplified map of the study region showing locations of the asphalt plant and two aboveground tanks storing fuel oil #6, former source zone, potential former source zone, groundwater monitoring wells (GW1-GW4), municipal extraction wells, and direction of groundwater flow determined by the hydraulic gradient. The blue rectangular area represents the industrial site's property limits.

Table 1. Geochemical parameters and concentrations (μg L^{-1}) of 14 US EPA priority polycyclic aromatic hydrocarbons (PAHs) determined in four groundwater monitoring wells (GW1-GW4) at the study site in October 2016. Values followed by an asterisk (*) indicate concentrations above the provincial government (MDDELCC) tolerance limits. Values noted as < LOD were below the limit of detection.

	GW1	**GW2**	**GW3**	**GW4**
Geochemical parameters:				
Temperature (°C)	7.7	7.4	7.9	7.9
Conductivity (μS cm^{-1})	870	721	1616	2667
Dissolved oxygen (%)	10.4	22.5	8.6	7.0
pH	5.9	5.6	6.0	6.0
Oxidation-reduction potential (mV)	139.5	180.1	136.2	78.3
PAHs (μg L^{-1}):				
Acenaphthene	0.7*	2.7*	2.1*	0.7*
Anthracene	0.1	< LOD	< LOD	< LOD
Benzo[*a*]anthracene	< LOD	< LOD	< LOD	< LOD
Benzo[*a*]pyrene	< LOD	< LOD	< LOD	< LOD
Benzo[*b*]fluoranthene	< LOD	< LOD	< LOD	< LOD
Benzo[*k*]fluoranthene	< LOD	< LOD	< LOD	< LOD
Chrysene	< LOD	< LOD	< LOD	< LOD
Dibenz[*a,h*]anthracene	< LOD	< LOD	< LOD	< LOD
Fluoranthene	< LOD	< LOD	< LOD	< LOD
Fluorene	0.9	3.0*	3.0*	1.3*
Indeno[*1,2,3-cd*]pyrene	< LOD	< LOD	< LOD	< LOD
Naphthalene	0.2	17.0*	0.5	0.3
Phenanthrene	2.4*	3.1*	3.9*	3.0*
Pyrene	< LOD	< LOD	< LOD	< LOD

2.2 Compound-specific carbon isotope analysis (carbon-CSIA) of PACs

For groundwater samples, 3 L of water was extracted twice using 50 mL of dichloromethane per litre using 1 L glass separatory funnels. Two μg of an isotopically characterized surrogate standard (m-terphenyl; $\delta^{13}C = -27.5‰$) was added to each sample prior to extraction of PACs to assess potential isotope fractionation associated with the sample preparation procedure. The extract was evaporated down to a few millilitres, transferred into hexane, and then passed through a glass chromatography column containing ~ 5 g 100% activated alumina (top) and ~ 6 g 100% activated silica (bottom). Thin layers of activated copper and sodium disulphate were added to the top of the column to remove elemental sulphur and any remaining water, respectively. The extracts were passed through the column and separated into fractions using hexane (F1) and 70:30 hexane:dichloromethane (F2). PACs eluted in F2. For the fuel oil #6 sample, PACs were extracted by adding 1.6 g to 100 mL of ultrapure MilliQ water to a 500 mL glass separatory funnel and extracting twice with 20 mL dichloromethane. For the asphalt sample, approximately 35 g of material was extracted in a large Soxhlet for 8 hours using 500 mL of dichloromethane. The extracts for these two samples were subsequently separated into F1 and F2 fractions by column chromatography as described above. Field and laboratory method blanks analyzed by gas chromatography – mass spectrometry revealed no contamination by PACs.

Carbon isotope values ($\delta^{13}C$) of PACs were determined using a TRACE 1310 gas chromatograph (GC) equipped with an Thermo Fisher Scientific (Mississauga, ON, Canada) TG-5MS column (60 m × 0.32 mm × 0.25 μm) interfaced with a Delta V (Thermo Fisher, Bremen, Germany) isotope ratio mass spectrometer (IRMS) via a GC IsoLink system. The $\delta^{13}C$ values were determined using CO_2 calibrated against international carbonate standards (CO_2 obtained from Oztech Trading Corp., Safford, AZ, USA). Samples were injected in triplicate at two different solvent levels to target compounds that were present at both high and low concentrations to keep peak sizes within the linear range of the standard mixture described below (m/z signal of ~ 0.2 to 5 V). The 1σ standard deviation for each compound shown on Figure 3 thus corresponds to at least n = 3, with the exception of the asphalt sample, where only one injection was possible due to insufficient mass. In this case, the highest 1σ standard deviations found for C1-fluorene (0.6‰)

and phenanthrene (0.5‰) were assigned to this sample. A mixture containing 5-α-androstane (-31.35‰), phenanthrene (-25.39‰) and dibenzothiophene (DBT; -27.68‰) obtained from the Biogeochemical Laboratories at Indiana University was injected after every 3-4 sample injections to assess accuracy. As the differences in δ^{13}C between the known values of the above standards and those determined in the standard mixture were < 0.3‰, there was no need for additional correction. No significant differences were found between the δ^{13}C values of the m-terphenyl surrogate determined in samples (-27.8 ± 0.5‰) and its pre-determined value of -27.5‰, indicating no significant isotopic fractionation associated with the sample preparation procedure.

3. Results and Discussion

To facilitate discrimination of sources, an effort was made to isotopically characterize the same suite of PACs across as many samples as possible. A representative m/z 44 chromatogram generated by GC-IRMS (sample GW4; Figure 2) illustrates the peaks that were identifiable and measurable in all four groundwater samples: three unsubstituted parent PACs (biphenyl, DBT and phenanthrene), two alkylated PACs (C2-naphthalene and C1-fluorene) and two groups of combined alkylated PACs containing unidentified C1-phenanthrenes/anthracenes (labelled as C1-phen gr. 1 and C1-phen gr. 2). Due to a greater number of interfering compounds in the chromatograms, only two of the above-mentioned PACs were determined in the asphalt (biphenyl, phenanthrene) and fuel oil #6 (C1-fluorene, phenanthrene).

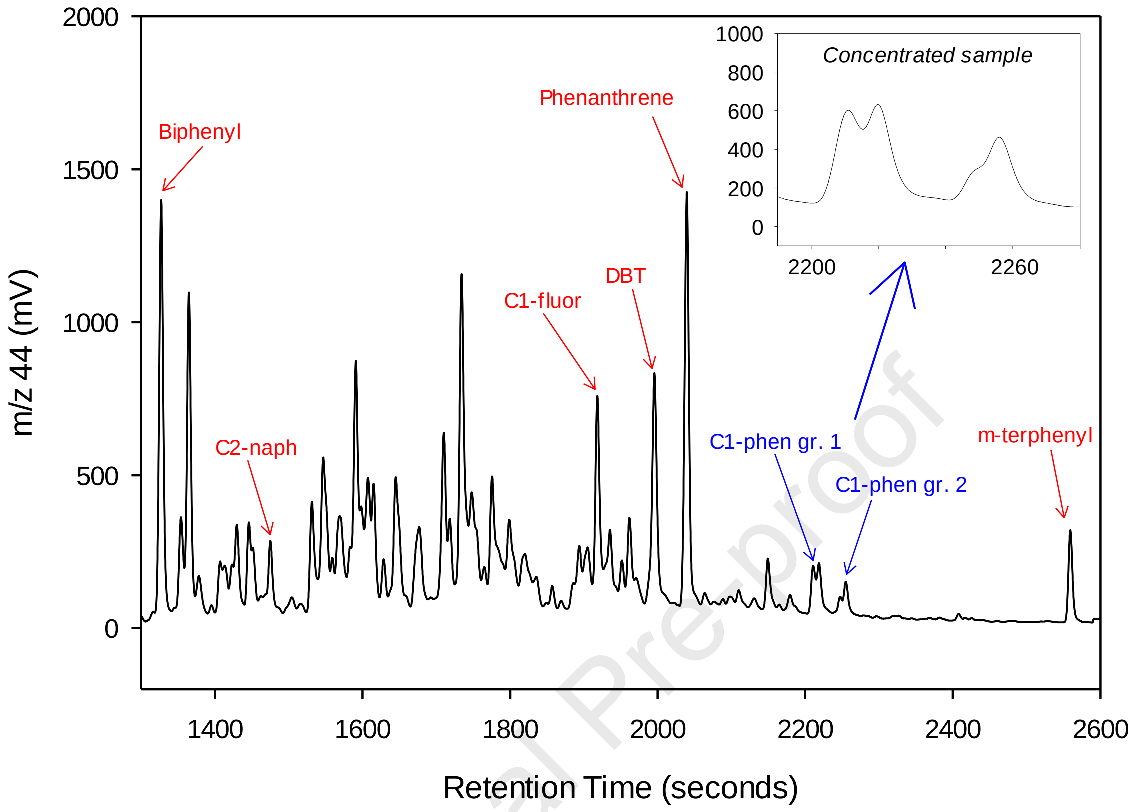

Figure 2. A representative m/z 44 chromatogram generated by GC-IRMS (sample GW4) illustrating the suite of peaks that were identifiable and measurable in all four groundwater samples. The m-terphenyl peak corresponds to the surrogate standard. As described in Section 2.2 and shown here in the inset, the $\delta^{13}C$ values for the smallest peaks (in this case the two groups of combined C1-phen compounds) were determined from injections of concentrated samples.

In groundwater samples (GW1-GW4), the average $\delta^{13}C$ values (± 1σ) for biphenyl (-28.7 ± 0.5‰), C2-naphthalene (-28.0 ± 0.4‰), C1-fluorene (-28.1 ± 0.4‰), DBT (-28.0 ± 0.3‰), phenanthrene (-27.9 ± 0.4‰), C1-phen gr. 1 (-27.8 ± 0.5‰) and C1-phen gr. 2 (-27.9 ± 0.5‰) all fell within a relatively narrow range (Figure 3). The 1σ standard deviation for each of the seven PACs measured in the four groundwater samples was generally less than or equal to the analytical uncertainty associated with δ^{13}C analyses (± 0.5‰). Slightly more negative δ^{13}C values were found for biphenyl compared to the other six PACs, although this trend appeared to be less pronounced in samples GW1 and GW4 (Figure 3). Apart from C1-fluorene ($P = 0.071$), paired two-tailed Student t-tests carried out using groundwater data indicated significant differences ($P = 0.001$-0.044) between the average δ^{13}C values for biphenyl (-28.7 ± 0.5‰) and the average δ^{13}C values for each of the other PACs or grouped PACs. Despite this small discrepancy, the average δ^{13}C value for PACs (-28.1 ±0.3‰) and PACs excluding biphenyl (-28.0 ±0.2‰) in samples GW1-GW4 were the same within error. The overall similarity in $\delta^{13}C_{PAC}$ values across all four groundwater samples thus provides compelling evidence for a common source of subsurface contamination.

In contrast, the δ^{13}C values for PACs determined in asphalt and fuel oil #6 samples were significantly different from those in groundwater samples (Figure 3). The δ^{13}C values for C1-fluorene (-30.2‰) and phenanthrene (-30.1‰) in fuel oil #6 were significantly more negative, whereas the δ^{13}C values for biphenyl (-27.0‰) and phenanthrene (-26.6‰) in asphalt were significantly more positive. These trends imply little to no contribution from these two sources to groundwater PACs.

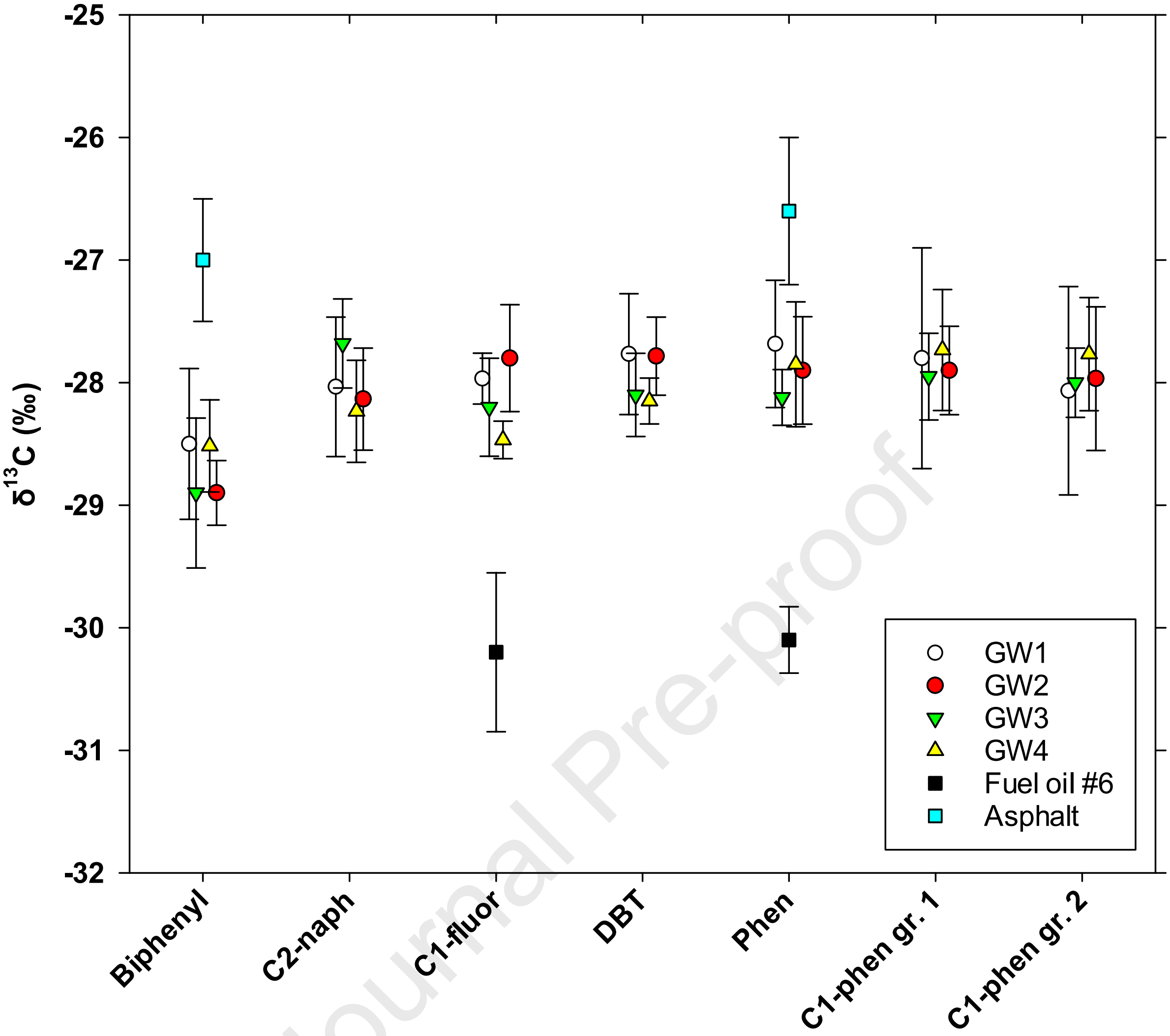

Figure 3. Carbon isotope values ($\delta^{13}C$) of the five individual compounds (biphenyl, C2-naphthalene, C1-fluorene, DBT and phenanthrene and two groups of combined alkylated C1-phenanthrenes/anthracenes (C1-phen gr. 1 and 2) determined in the four groundwater (GW1-GW4), fuel oil #6 and asphalt samples. The error bars represent the precision (1σ) of triplicate measurements, with the exception of the asphalt sample (see Section 2.2 for further details).

The groundwater monitoring campaign carried out in October 2016 detected a floating hydrocarbon phase in well GW2, which is situated within the former source zone (Figure 1). Accordingly, the isotopic similarity between GW2 and the other groundwater monitoring wells implies that diesel from the original spill is the common source of hydrocarbon contamination. The conservation of this original 'isotopic fingerprint' for more than 30 years implies that microbial degradation, to whatever extent it had occurred in the subsurface, had little impact on $\delta^{13}C_{PAC}$ values during this time, since this process would lead to progressive ^{13}C enrichment in residual substrate. Indeed, it is mainly because of this lack of any noticeable isotopic fractionation that these data could be used to identify the source of PACs at this site.

Further support for the negligible impact on $\delta^{13}C_{PAC}$ values caused by possible *in situ* biodegradation is provided by the isotopic pattern found for the two- and three-ring PACs in groundwater samples. The scant existing field-based evidence for small yet potentially observable carbon isotope fractionation in PACs due to subsurface biodegradation (i.e., around 1 to 2‰ increases in $\delta^{13}C_{PAC}$ values concomitant with substantial concentration decreases across contaminant plumes) has been mainly reported for naphthalene and its alkylated derivatives under anaerobic conditions (Richnow et al., 2003; Griebler et al., 2004; Steinbach et al., 2004; Blum et al., 2009; Prommer et al., 2009; D'Affonseca et al., 2011). As shown on Figure 3, the $\delta^{13}C_{PAC}$ values for C2-naphthalene in samples GW1-GW4 were identical to those determined in three-ring PACs (DBT, phenanthrene and its alkylated derivatives), for which no significant carbon isotope fractionation effects during aerobic biodegradation have been reported (Mazeas et al., 2002). Additionally, the $\delta^{13}C$ values for two-ring biphenyl were in fact more negative than the other PACs – the opposite direction one would expect to observe in the non-biodegraded residual substrate measured in groundwater samples.

While all compounds reported on Figure 3 are naturally present in diesel (Neff et al., 2000; Dobbins et al., 2006), biphenyl may also be generated by the microbial breakdown of organic sulfur compounds such as DBT under sulfate-reducing conditions (Kim et al., 1990; Armstrong et al., 1995). Since degradation products will be isotopically lighter than the reactant (Slater et al., 2001), the slightly more negative $\delta^{13}C$ values for biphenyl compared to DBT suggest a possible *in situ* origin. However, although groundwater at the study site was somewhat oxygen-depleted, redox conditions were not sufficiently anaerobic to allow for hydrogen sulfide formation (i.e., ORP values were positive; Table 1). The slight ^{13}C-depletion in biphenyl compared to DBT, if attributable to biodegradation of the latter, may thus have occurred at some point during the refining stage or in the reservoir itself.

4. Conclusions

Despite mostly successful remediation efforts, compound-specific isotope analysis of PACs revealed that diesel from a decades-old spill, rather than more recent suspected petroleum hydrocarbon inputs from asphalt and fuel oil #6, is the main source of groundwater contamination at an industrial site in the province of Québec, Canada. This deduction was facilitated by the similarity in $\delta^{13}C_{PAC}$ values across four groundwater monitoring wells, including one situated in the former source zone in which a floating hydrocarbon phase had been detected during sample collection. The lack of variation in $\delta^{13}C_{PAC}$ values indicated no discernible isotopic fractionation of two-ring or three-ring PACs after exposure to approximately 30 years of natural attenuation processes in the shallow aquifer. This finding confirms that carbon-CSIA of these compounds in hydrogeological investigations is better suited as a tool for source apportionment. While the application of dual isotope analysis (i.e., $\delta^{2}H$, $\delta^{13}C$) offers the potential for a more precise and quantitative source discrimination of PACs (Ahad et al., 2020), significant hydrogen isotope fractionation effects during biodegradation (Bergmann et al., 2011; Kümmel et al., 2016) could confound interpretations of field data. In any event, the results from this study demonstrate that in shallow groundwater systems, the sole use $\delta^{13}C_{PAC}$ values may be sufficient to ascertain the origin of subsurface hydrocarbon contamination.

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References

Ahad, J.M.E., Jautzy, J., Cumming, B.F., Das, B., Laird, K.R., Sanei, H., 2015. Sources of polycyclic aromatic hydrocarbons (PAHs) to northwestern Saskatchewan lakes east of the Athabasca oil sands. Org. Geochem. 80, 35-45.

Ahad, J.M.E., Macdonald, R.W., Parrott, J.L., Yang, Z., Zhang, Y., Siddique, T., Kuznetsova, A., Rauert, C., Galarneau, E., Studabaker, W.B., Evans, M., McMaster, M.E., Shang, D., 2020. Polycyclic aromatic compounds (PACs) in the Canadian environment: A review of sampling techniques, strategies and instrumentation. Environ. Pollut. 266, 114988.

Ahad, J.M.E., Pakdel, H., Labarre, T., Cooke, C.A., Gammon, P.R., Savard, M.M., 2021. Isotopic Analyses Fingerprint Sources of Polycyclic Aromatic Compound-Bearing Dust in Athabasca Oil Sands Region Snowpack. Environmental Science & Technology 55, 5887-5897.

Armstrong, S.M., Sankey, B.M., Voordouw, G., 1995. Conversion of dibenzothiophene to biphenyl by sulfate-reducing bacteria isolated from oil field production facilities. Biotechnology Letters 17, 1133-1136.

Bergmann, F.D., Abu Laban, N.M.F.H., Meyer, A.H., Elsner, M., Meckenstock, R.U., 2011. Dual (C, H) Isotope Fractionation in Anaerobic Low Molecular Weight (Poly)aromatic Hydrocarbon (PAH) Degradation: Potential for Field Studies and Mechanistic Implications. Environmental Science & Technology 45, 6947-6953.

Blum, P., Hunkeler, D., Weede, M., Beyer, C., Grathwohl, P., Morasch, B., 2009. Quantification of biodegradation for o-xylene and naphthalene using first order decay models, Michaelis–Menten kinetics and stable carbon isotopes. J. Contam. Hydrol. 105, 118-130.

Bosch, C., Andersson, A., Kruså, M., Bandh, C., Hovorková, I., Klánová, J., Knowles, T.D.J., Pancost, R.D., Evershed, R.P., Gustafsson, Ö., 2015. Source Apportionment of Polycyclic Aromatic Hydrocarbons in Central European Soils with Compound-Specific Triple Isotopes (δ^{13}C, Δ^{14}C, and δ^{2}H). Environmental Science & Technology 49, 7657-7665.

Buczyńska, A.J., Geypens, B., Van Grieken, R., De Wael, K., 2013. Stable carbon isotopic ratio measurement of polycyclic aromatic hydrocarbons as a tool for source identification and apportionment—A review of analytical methodologies. Talanta 105, 435-450.

D'Affonseca, F.M., Prommer, H., Finkel, M., Blum, P., Grathwohl, P., 2011. Modeling the long-term and transient evolution of biogeochemical and isotopic signatures in coal tar–contaminated aquifers. Water Resources Research 47.

Dobbins, R.A., Fletcher, R.A., Benner, B.A., Hoeft, S., 2006. Polycyclic aromatic hydrocarbons in flames, in diesel fuels, and in diesel emissions. Combustion and Flame 144, 773-781.

Galimov, E.M., 2006. Isotope organic geochemistry. Org. Geochem. 37, 1200-1262.

Griebler, C., Safinowski, M., Vieth, A., Richnow, H.H., Meckenstock, R.U., 2004. Combined application of stable carbon isotope analysis and specific metabolites determination for assessing in situ degradation of aromatic hydrocarbons in a tar oil-contaminated aquifer. Environ. Sci. Technol. 38, 617-631.

Gzyl, G., Zanini, A., Frączek, R., Kura, K., 2014. Contaminant source and release history identification in groundwater: A multi-step approach. J. Contam. Hydrol. 157, 59-72.

Han, D.M., Tong, X.X., Jin, M.G., Hepburn, E., Tong, C.S., Song, X.F., 2013. Evaluation of organic contamination in urban groundwater surrounding a municipal landfill, Zhoukou, China. Environ. Monit. Assess. 185, 3413-3444.

Jautzy, J., Ahad, J.M.E., Gobeil, C., Savard, M.M., 2013. Century-long source apportionment of PAHs in Athabasca oil sands region lakes using diagnostic ratios and compound-specific carbon isotope signatures. Environmental Science & Technology 47, 6155-6163.

Jautzy, J.J., Ahad, J.M.E., Gobeil, C., Smirnoff, A., Barst, B.D., Savard, M.M., 2015. Isotopic evidence for oil sands petroleum coke in the Peace-Athabasca Delta. Environmental Science & Technology 49, 12062−12070.

Kim, H.Y., Kim, T.S., Kim, B.H., 1990. Degradation of organic sulfur compounds and the reduction of dibenzothiophene to biphenyl and hydrogen sulfide by *Desulfovibrio desulfuricans* M6. Biotechnology Letters 12, 761-764.

Kümmel, S., Starke, R., Chen, G., Musat, F., Richnow, H.H., Vogt, C., 2016. Hydrogen Isotope Fractionation As a Tool to Identify Aerobic and Anaerobic PAH Biodegradation. Environmental Science & Technology 50, 3091-3100.

Li, J., Li, F., Liu, Q., 2017. PAHs behavior in surface water and groundwater of the Yellow River estuary: Evidence from isotopes and hydrochemistry. Chemosphere 178, 143-153.

Logeshwaran, P., Megharaj, M., Chadalavada, S., Bowman, M., Naidu, R., 2018. Petroleum hydrocarbons (PH) in groundwater aquifers: An overview of environmental fate, toxicity, microbial degradation and risk-based remediation approaches. Environmental Technology & Innovation 10, 175-193.

Mazeas, L., Budzinski, H., Raymond, N., 2002. Absence of stable carbon isotope fractionation of saturated and polycyclic aromatic hydrocarbons during aerobic bacterial biodegradation. Org. Geochem. 33, 1259-1272.

Micic, V., Straub, K., Blum, P., Kappler, A., 2007. Natural attenuation of naphthalene and benzene at a former gasworks site. Water Science and Technology: Water Supply 7, 145-153.

Neff, J.M., Ostazeski, S., Gardiner, W., Stejskal, I., 2000. Effects of weathering on the toxicity of three offshore australian crude oils and a diesel fuel to marine animals. Environ. Toxicol. Chem. 19, 1809-1821.

O'Malley, V.P., Abrajano Jr, T.A., Hellou, J., 1994. Determination of the $^{13}C/^{12}C$ ratios of individual PAH from environmental samples: can PAH sources be apportioned? Org. Geochem. 21, 809-822.

Ololade, I.A., Arogunrerin, I.A., Oladoja, N.A., Ololade, O.O., Alabi, A.B., 2021. Concentrations and Toxic Equivalency of Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyl (PCB) Congeners in Groundwater Around Waste Dumpsites in South-West Nigeria. Archives of Environmental Contamination and Toxicology 80, 134-143.

Philp, R.P., 2007. The emergence of stable isotopes in environmental and forensic geochemistry studies: a review. Environmental Chemistry Letters 5, 57-66.

Prommer, H., Anneser, B., Rolle, M., Einsiedl, F., Griebler, C., 2009. Biogeochemical and Isotopic Gradients in a BTEX/PAH Contaminant Plume: Model-Based Interpretation of a High-Resolution Field Data Set. Environmental Science & Technology 43, 8206-8212.

Raza, M., Hussain, F., Lee, J.-Y., Shakoor, M.B., Kwon, K.D., 2017. Groundwater status in Pakistan: A review of contamination, health risks, and potential needs. Critical Reviews in Environmental Science and Technology 47, 1713-1762.

Richnow, H.H., Annweiler, E., Michaelis, W., Meckenstock, R.U., 2003. Microbial in situ degradation of aromatic hydrocarbons in a contaminated aquifer monitored by carbon isotope fractionation. J. Contam. Hydrol. 65, 101-120.

Shao, Y., Wang, Y., Xu, X., Wu, X., Jiang, Z., He, S., Qian, K., 2014. Occurrence and source apportionment of PAHs in highly vulnerable karst system. Sci. Total Environ. 490, 153-160.

Slater, G.F., Lollar, B.S., Sleep, B.E., Edwards, E.A., 2001. Variability in carbon isotopic fractionation during biodegradation of chlorinated ethenes: Implications for field applications. Environ. Sci. Technol. 35, 901-907.

Steinbach, A., Seifert, R., Annweiler, E., Michaelis, W., 2004. Hydrogen and Carbon Isotope Fractionation during Anaerobic Biodegradation of Aromatic Hydrocarbons - A Field Study. Environmental Science & Technology 38, 609-616.

Trust Hammer, B., Kelley, C.A., Coffin, R.B., Cifuentes, L.A., Mueller, J.G., 1998. $\delta^{13}C$ values of polycyclic aromatic hydrocarbons collected from two creosote-contaminated sites. Chem. Geol. 152, 43-58.

Highlights

- Compound-specific $\delta^{13}C$ values were used to identify sources of PACs in groundwater.
- Potential sources included a historical diesel spill, asphalt and fuel oil #6.
- $\delta^{13}C$ values were similar in all wells, including several in the former source zone.
- The historical diesel spill was thus revealed as the main source for PACs.
- No discernible isotopic fractionation effects after > 30 years in the subsurface.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.