ELSEVIER

Journal of Chromatography A, 971 (2002) 173–184

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Characterization and source identification of hydrocarbons in water samples using multiple analytical techniques

Zhendi Wang[a,*], K. Li[a], M. Fingas[a], L. Sigouin[a], L. Ménard[b]

[a]*Emergencies Science and Technology Division, ETC, Environment Canada, 3439 River Road, Ottawa, Ontario, Canada K1A 0H3*
[b]*Golder Associés Ltée, 9200 boulevard de l'Acadie, Montréal, Québec, Canada H4N 2T2*

Received 4 March 2002; received in revised form 25 June 2002; accepted 3 July 2002

Abstract

This paper describes a case study in which multiple analytical techniques were used to identify and characterize trace petroleum-related hydrocarbons and other volatile organic compounds in groundwater samples collected in a bedrock aquifer exploited for drinking water purposes. The objective of the study was to confirm the presence of gasoline and other petroleum products or other volatile organic pollutants in those samples in order to assess the respective implication of each of the potentially responsible parties to the contamination of the aquifer. In addition, the degree of contamination at different depths in the aquifer was also of interest. The analytical techniques used for analyses of water samples included gas chromatography–mass spectrometry (GC–MS) and capillary GC with flame-ionization detection, solid-phase microextraction and headspace GC–MS techniques. Chemical characterization results revealed the following: (1) The hydrocarbons in sample A (near-surface groundwater, 0–5 m) were clearly of two types, one being gasoline and the other a heavy petroleum product. The significant distribution of five target petroleum-characteristic alkylkated polycyclic aromatic hydrocarbon homologues and biomarkers confirmed the presence of another heavy petroleum product. The concentrations of the TPHs (total petroleum hydrocarbons) and BTEX (collective name of benzene, toluene, ethylbenzene, and *p*-, *m*-, and *o*-xylenes) were determined to be 1070 and 155 μg/kg of water for sample A, respectively. (2) The deepest groundwater (sample B, collected at a depth ranging between 15 and 60 m) was also contaminated, but to a much lesser degree. The concentrations of the TPH and BTEX were determined to be only 130 and 2.6 μg/kg of water for sample B, respectively. (3) The presence of a variety of volatile chlorinated compounds to the groundwater was also clearly identified.

Keywords: Water analysis; Oils; Hydrocarbons; Polynuclear aromatic hydrocarbons; Benzene; Toluene; Ethylbenzene; Xylenes

1. Introduction

In November 1998, the Oil Research Laboratory of the Emergencies Science and Technology Division (ESTD), Environment Canada was requested by Golder Associé Ltée to undertake a case study in which a site and groundwater may be contaminated with gasoline and various chemicals.

The general background of the site is as follows: (1) the bedrock aquifer in the area is used by residents for domestic water purposes (individual wells); (2) a petroleum service-station was operated

*Corresponding author. Tel.: +1-613-990-1597; fax: +1-613-991-9485.
E-mail address: wang.zhendi@etc.ec.gc.ca (Z. Wang).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01003-8

on this site for about 10 years, and this service-station was a source of petroleum products only; (3) the adjacent property was owned by a chemicals handling company, which dealt with all kinds of pure or mixed organic and chlorinated compounds, including trichloroethane, tetrachloroethane, chloroform, toluene, ethylbenzene, and xylenes. The chemicals company allegedly had not handled petroleum products. Both operations were considered to be potentially responsible parties (PRPs).

In response to needs of this specific site investigation and spill identification, tiered analytical approaches which facilitated the detailed chemical composition analyses were used to determine individual petroleum hydrocarbons, their relative distribution patterns, and other non-oil related contaminants or source tracing marker compounds in spill samples. Multiple analytical techniques used for analyses of representative groundwater samples included GC–MS and GC–flameionization detection (FID), headspace GC–MS, and solid-phase microextraction (SPME–GC–MS). The SPME and headspace GC–MS techniques were used not only to verify the presence of volatile oil hydrocarbons detected by GC–MS and GC–FID, but also to identify a suite of volatile chlorinated compounds and other non-oil related chemicals for assessing the contribution of each potentially responsible party to the contamination of the aquifer.

When crude oil or refined product enters the surface or subsurface environment, it is immediately subject to a number of processes that are collectively known as weathering [1]. Some hydrocarbon compounds evaporate, some dissolve, some are dispersed, some are photooxidized, some adsorb onto suspended particulate materials, and the majority may eventually be biodegraded. Sometimes there is more than one spill or background hydrocarbons are present. The changes in chemical composition of spilled oils due to these factors complicate the identification of the residual spilled oil in the impacted environment. Under such circumstances, characterization of the whole spectrum of compounds from very volatile compounds to high-molecular-mass and degradation-resistant polycyclic aromatic hydrocarbons (PAHs) and biological marker hydrocarbons by multiple analytical techniques would be mandatory in order to obtain a comprehensive picture of the spill.

2. Experimental

2.1. Materials

Distilled chromatographic grade solvents were used without further purification. Calibration standards used for determination of individual and total petroleum hydrocarbons include *n*-alkane standards from C_8 to C_{30} including pristane and phytane, PIANO calibration standard for BTEX (collective name of benzene, toluene, ethylbenzene, and *p*-, *m*-, and *o*-xylenes) determination from Supelco, PAH standards (SRM 1491) from the National Institute of Standards and Technology (NIST), and biomarker (hopanes and steranes) standards from Chiron Laboratory of Norway.

A 21-component volatile organic standard mixture for headspace and SPME analysis was created by weighing known amounts of solid–liquid neat compounds and dissolved in an alkane mixture (D3710 Quantitative Calibration Mixture, Supelco Catalogue No. 48879). This stock solution was diluted ten times to give an intermediate standard. Addition of 1 μl of this mixture to 10 ml of water gave a final concentration of 0.2–1.1 μg/ml which included BTEX and alkanes from C_5 to C_{15}. An internal standard of [$^2H_8$]toluene (toluene-d_8) was also added to give a final concentration of 0.1 μg/ml.

2.2. Sample collection and preparation

To collect groundwater samples, five nets of three wells were installed, with top portion of well being grouted for intermediate and deep wells (level A=0–5 m; level B=7–12 m; level C=15–60 m). A Quebec laboratory had analyzed all water samples and reported the presence of a few of chlorinated compounds in some water samples. Two representative samples were sent to the ESTD for characterization and verification for the presence of gasoline and/or any other petroleum products. They were sample A (sampling depth: 0–5 m) and sample B (sampling depth: 15–60 m). Sample A was turbid (grey colour). Sample B was clear and colourless. The samples were extracted in whole and no filtration was performed to remove any possible particulate associated with the water turbidity.

Prior to the water sample extraction, a method blank was analysed using GC–FID and GC–MS.

The glassware was proofed to be clean and no contaminants of interest were detected.

The water samples were weighed (932 g for sample A, and 999 and 996 g for two bottles of sample B), quantitatively transferred to a 2-l separatory funnel, and spiked with appropriate surrogate mixtures. A 100-μl aliquot of *o*-terphenyl (200 μg/ml) and a 100-μl aliquot of a mixture of four deuterated PAHs {[$^2H_{10}$]acenaphthene (acenaphthene-d_{10}), [$^2H_{10}$]phenanthrene (phenanthrene-d_{10}), [$^2H_{12}$]benz[*a*]anthracene (benz[*a*]anthracene-d_{12}), and [$^2H_{12}$]perylene (perylene-d_{12}), 10 μg/ml each} dissolved in 1.0 ml of acetone were added to the separatory funnel. The water sample was allowed to sit for 15 min, and then successively extracted four times using 50 ml of dichloromethane (DCM) each time. Seal and shake the separatory funnel vigorously for ~3 min with periodic venting to release excess pressure. DCM creates excessive pressure rapidly, therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Upon completion of extractions, the extracts of samples A and B were combined, filtered and dried by passing through anhydrous sodium sulphate, and concentrated to approximately 0.5 ml using rotary evaporation and nitrogen blow-down techniques. The concentrated extract was then spiked with internal standards {5-α-androstane for determination of total petroleum hydrocarbons (TPHs) and *n*-alkane distribution, [$^2H_{10}$]ethylbenzene for BTEX and other alkylbenzene analysis, [$^2H_{14}$]terphenyl (terphenyl-d_{14}) for PAH analysis, and C_{30}-ββ-hopane for biomarker analysis}, and then adjusted to 1.00 ml prior to GC analyses.

2.3. Capillary GC and GC–MS

Analyses for alkane distribution and TPHs were performed on an Hewlett-Packard (HP) 5890 gas chromatograph equipped with a flame-ionization detector and an HP 7673 autosampler. Analyses of PAHs and biomarker compounds were performed on an HP 5890 GC/HP 5972 mass-selective detector. System control and data acquisition were achieved with an HP G1034C MS ChemStation (DOS series). GC–FID analysis provides a baseline resolution of *n*-alkanes from *n*-C_8 to *n*-C_{41} and *n*-C_{17}–pristane and *n*-C_{18}–phytane. Quantitation of the analytes was based on the internal standard compound 5-α-androstane. GC–MS analysis was performed utilizing a selected ion monitoring mode to improve detection limits. The concentrations of the target US Environmental Protection Agency (EPA) priority PAHs and oil-characteristic alkylated PAH homologous series, and biomarker compounds were determined based on the internal standards terphenyl-d_{14} and C_{30}-ββ-hopane. Detection limits by GC–MS in the selected ion monitoring (SIM) mode were 0.004–0.01 μg/ml for BTEX and other alkylbenzene compounds and 0.002–0.006 μg/ml for PAH compounds.

In order to achieve improved analytical precision and accuracy, a number of measures were added to the processing of samples to monitor quality control (QC) and to aid in assessment of the data quality with respect to the project objectives. An important part of this is the evaluation of specific QC samples for accuracy, precision, and potential contamination. The quality control measures include initial and continuing standard calibration; run of solvent blank, procedural blank, and check standard with samples; using the average relative response factors generated from the linear initial calibration to quantify the target PAH and BTEX compounds; performing method detection limit studies; and surrogate recoveries must fall in the range of 60–120%. For detailed chromatographic conditions, analysis quality control and quantification methodology, refer to Refs. [2,3].

2.4. Analysis of volatile organics compounds (VOCs) in water by headspace (HS) and SPME–GC–MS

2.4.1. Headspace analysis

A 10-ml aliquot of the water sample was pipetted into a capped 22-ml headspace vial. An internal standard of toluene-d_8 was added to all samples and standards alike (1.0 μg/ml final concentration). Samples were loaded onto the constant heating time magazine with each sample equilibrated at 85 °C for a nominal time of 40 min in the sample carousel heated by a silicone oil bath. An aliquot of headspace (1.0 ml) developed over the water phase was then injected into a bench top GC–MS system via a heated transfer line for analysis of water soluble organic compounds.

2.4.2. SPME analysis

Volatile organic compounds in water was also analysed by suspending a solid-phase microextractor fiber (75 μm Carboxen–polydimethylsiloxane) in the headspace above the water sample. A 10-ml aliquot of the water sample was transferred from the original 40-ml sample vial (shipped without headspace to minimize loss of volatile components) into a capped 22-ml HS vial. An internal standard of toluene-d_8 was added to all samples and standards alike. A small magnetic bar was added and the vial sealed with a PTFE-faced septum and aluminum cap. The SPME fiber, which has higher affinity for VOCs, was used to adsorb the VOCs from the headspace at room temperature with rapid stirring for 30 min to promote faster equilibrium. The SPME fiber was then inserted into the heated inlet of a bench top GC–MS system for analysis of VOC compounds.

After each GC–MS run, a peak table was constructed using the characteristic ions of each compound together with the retention time. Quantitation was by the internal standard method in which the response of the internal standard was used to correct for variation in instrumental conditions. Confirmation of compound was achieved by comparison of the ion ratio of target ion to qualifying ion to the theoretical value of the authentic compound. Detection limits were 0.001 μg/ml by SPME GC–MS and 0.1 μg/ml by headspace GC–MS for most compounds. For detailed instrumental operation conditions and VOC characterization methodology, refer to Refs. [4,5].

3. Results and discussion

3.1. Determination of hydrocarbon groups and petroleum product type identification

Assessment of chemical composition of petroleum product types in the water samples can be illustrated by qualitative and quantitative examination of their GC traces [6]. Crude oil compositions vary widely, depending on the sources of carbon from which the oils are generated and the geologic environment in which they migrated and from which reservoir. Refined petroleum products are obtained from crude oil through a variety of distillation, blending, and catalytic processes. Light distillates are typically products in the C_3–C_{12} carbon range. They include aviation gas, naphtha, and automotive gasoline. The GC trace of fresh light distillates are featured with dominance of light-end, resolved hydrocarbons and a minimal unresolved complex mixture of hydrocarbons (UCM). Mid-range distillates are typically products in a relative broad carbon range (C_6–C_{26}) and include kerosene, jet fuel, and diesel products. The GC chromatograms of diesel fuels, for example, are dominated by resolved peaks in the C_{10}–C_{17} range and show the characteristic and predominant central UCM. Classic heavy refined products include fuel no. 6 and lube type oil. Heavy fuels are typified with a broad resolved alkanes in the C_{14}–C_{36} range and a large UCM that can make up more than 50% of the total GC area.

Fig. 1 shows the GC–FID chromatographic traces of samples A and B for GC-detectable total petroleum hydrocarbons (TPHs) and *n*-alkane analysis. Fig. 2 shows the GC–MS chromatogram of the *m*/*z* 85 fragment of the saturated hydrocarbons for sample A. Because of the increased selectivity and

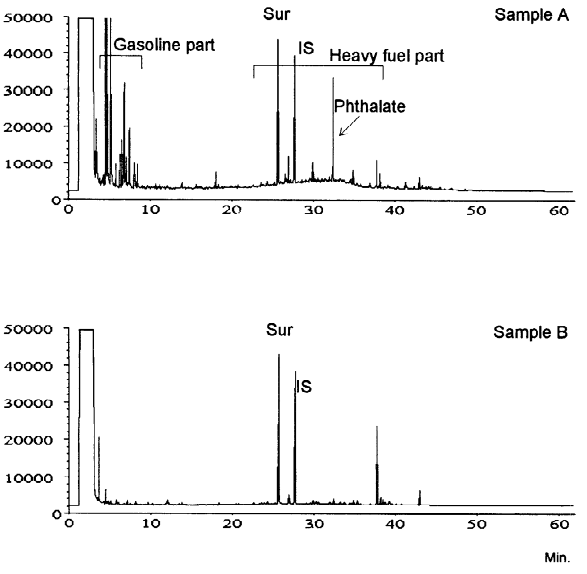

Fig. 1. GC–FID chromatograms of samples A and B for TPH and *n*-alkane analysis. Sur and IS stand for surrogate *o*-terphenyl and internal standard 5-α-androstane. The GC traces of the two samples are distinctly different from each other. The hydrocarbons in sample A are clearly demonstrated to be composed of two petroleum products.

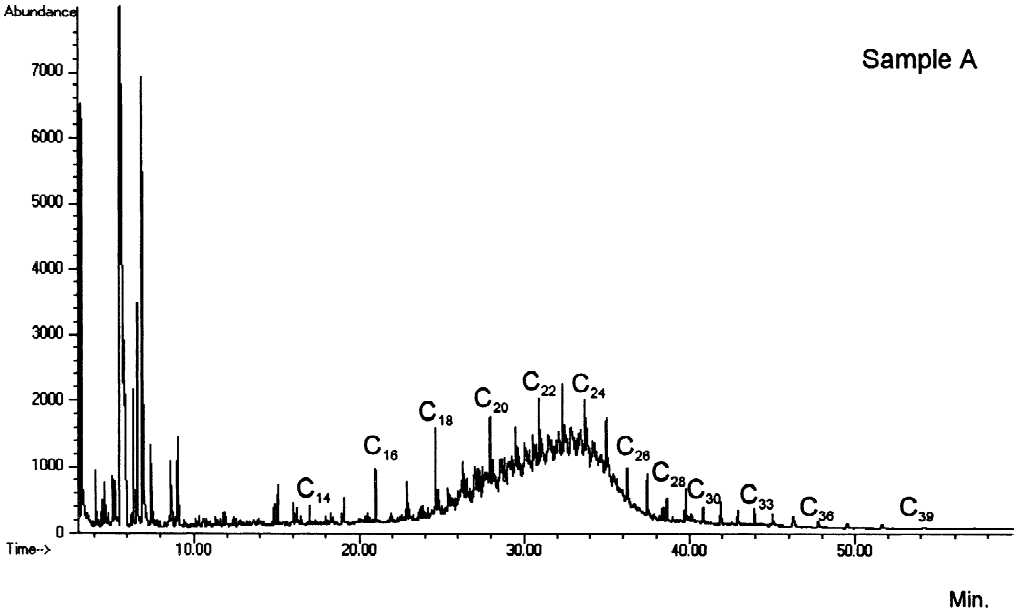

Fig. 2. GC–MS chromatograms of the m/z 85 fragment of the saturated hydrocarbons for sample A, more clearly showing the distribution of the low-abundant *n*-alkane and isoprenoid compounds in the heavy fuel portion of sample A.

higher sensitivity provided by the MS detector, the less-abundant *n*-alkane peaks in the heavier petroleum product, which were not distinguishable in the GC–FID chromatograms, can be more clearly identified. The identified *n*-alkanes including pristane and phytane were distributed in a range of *n*-C_{13} to *n*-C_{40}.

The GC-TPH is defined as the sum of all resolved and unresolved distillable hydrocarbons detected by GC. The UCM appears as the ''envelope'' or hump between the solvent baseline and the curve defining the base of resolvable peaks. GC-TPH was quantified using the following equation:

$$\text{TPH}\ (\mu\text{g/g}) = \frac{A_{\text{TPH}} W_{\text{IS}} D}{A_{\text{IS}} RRF_{\text{TPH}} W_{\text{S}}}$$

where A_{TPH} = the corrected total area of the sample chromatogram, units are area counts; RRF_{TPH} = average of relative response factors (RRF) of target *n*-alkanes (*n*-C_8 to *n*-C_{34}) plus pristane and phytane over the entire analytical range, which was obtained from calibration standards by the internal standard method;. A_{IS} = response for the internal standard 5-α-androstane in the sample; W_{IS} = amount (μg) of internal standard added to the sample; D = dilution factor. If dilution was made on the sample prior to analysis. If no dilution was made, $D = 1$, dimensionless; W_{S} = mass of sample extracted (g).

The major chemical composition features of hydrocarbons in the samples are summarized as follows:

(1) The GC traces of the two samples are distinctly different from each other. The GC-TPH were determined to be 1070 and 130 μg/kg water for samples A and B, respectively.

(2) GC–FID chromatograms provide a fingerprint picture of major oil components and information about the extent of weathering of the oil. The hydrocarbons in sample A are clearly demonstrated to be composed of two products: low-molecular-mass hydrocarbons attributed to a light petroleum product eluting before 10 min; and higher-molecular-mass hydrocarbons attributed to a heavy petroleum product with a retention time range between 22 and 40 min. The characteristic profile of an unresolved complex mixture of hydrocarbons is very apparent. Sample B demonstrated a much smaller but similar characteristic UCM profile to sample A.

(3) The GC profile of the hydrocarbons eluting

before the retention time of 10 min (sample A) suggests the product to be gasoline, while the retention time window of the UCM (in the range of 22–40 min) indicates that the heavy petroleum product is likely to be a heavy fuel, but it is definitely not a mid-range petroleum product such as diesel or jet fuel [6].

(4) The heavy petroleum product has highly weathered, which is demonstrated by a low abundance of *n*-alkanes and large UCM hump.

3.2. Determination of light BTEX, alkylbenzene, and other VOC compounds

Fig. 3 presents the ion chromatograms at *m*/*z* 78, 91, and 120 for analysis of BTEX and C_3-benzene compounds in sample A. The prominent distribution pattern of highly abundant BTEX and eight C_3-benzenes is very characteristic of gasoline. Table 1 lists the quantitative results of BTEX and C_3-benzenes. The total concentrations of BTEX and C_3-benzenes were determined to be 155 and 33, and 2.6 and 1.4 μg/kg of water (ppb) for samples A and B, respectively. The concentration of BTEX in sample A is approximately 60 times higher than in the sample B. This fact implies that the gasoline contamination to the deeper groundwater (15–60 m) due to migration must be significantly less than to the subsurface water (0–5 m).

Automotive gasoline is a generic term used to describe volatile, inflammable petroleum fuels used primarily in internal combustion engines. It is a complex mixture of hydrocarbon compounds predominately in the C_3–C_{12} range, with a nominal boiling-point range of 40–230 °C. Gasolines are blended from several refinery process streams from

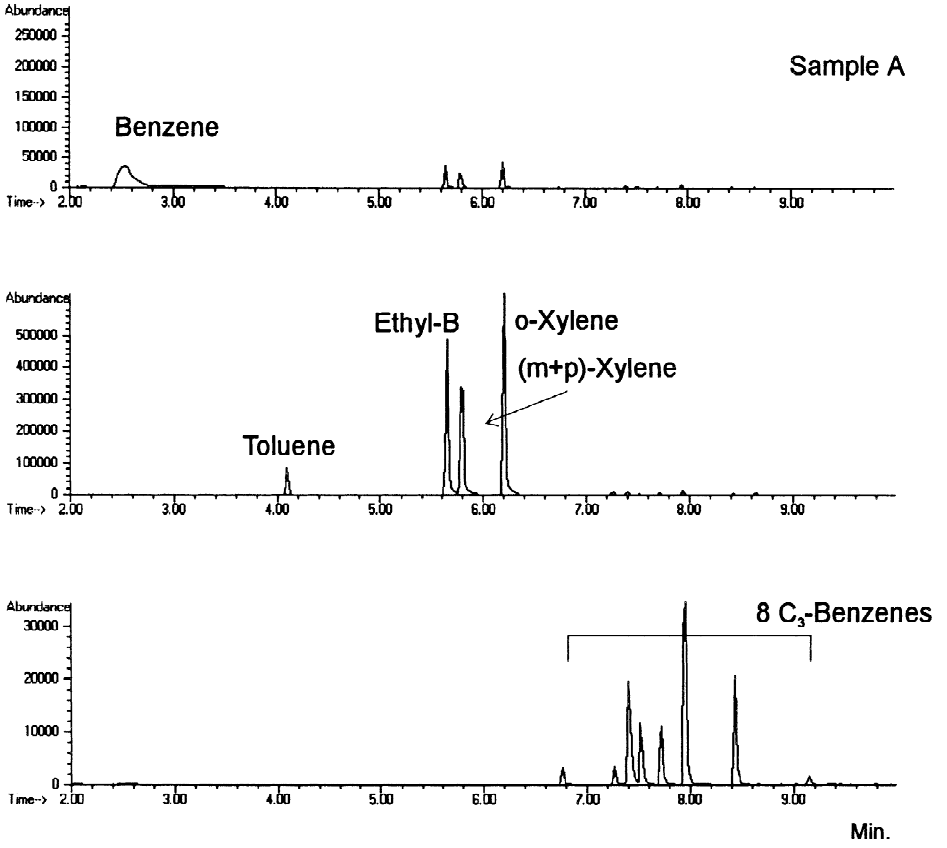

Fig. 3. Extracted ion chromatograms of BTEX and C_3-benzene compounds at *m*/*z* 78 (top), 91 (middle) and 120 (bottom) for sample A. The prominent distribution pattern of abundant BTEX and eight C_3-benzenes is very characteristic of gasoline.

Table 1
Analysis results of BTEX and other alkylbenzenes in the water samples A and B

Sample	Ion	Sample A ($\mu g/kg\ H_2O$)	Sample B ($\mu g/kg\ H_2O$)
Internal standard (IS)	116	2.00	2.00
BTEX			
Benzene	78	19.80	0.75
Toluene	91	7.30	0.59
Ethylbenzene	91	36.08	0.86
m-+*p*-Xylene	91	36.68	0.17
o-Xylene	91	54.79	0.20
C_3-Benzenes			
Isopropylbenzene	105	0.94	0.33
Propylbenzene	91	0.82	0.06
3-Ethyltoluene and 4-ethyltoluene	105	7.60	0.13
1,3,5-Trimethylbenzene	105	2.61	0.59
2-Ethyltoluene	105	5.82	0.03
1,2,4-Trimethylbenzene	105	10.15	0.16
1,2,3-Trimethylbenzene	105	4.61	0.08
Other target compounds			
Isobuthylbenzene	91	0.03	0.00
1-Methyl-2-isopropylbenzene	119	0.21	0.00
1,2-Dimethyl-4-ethylbenzene	119	0.18	0.02
Amylbenzene	91	0.02	0.01
n-Hexylbenzene	91	0.03	0.02
BTEX		154.6	2.6
C_3-Benzenes		32.6	1.4
BTEX + C_3-benzenes		187.2	4.0
Diagnostic ratios (B+T)/(E+X)		0.21	1.09

direct distillation of crude oil, catalytic and thermal cracking processes, catalytic reforming processes, and from alkylation and isomerization of the light distillate streams. There are more than 300 individual compounds recognized to date in gasoline. For practical purposes, however, it is sufficient to identify and characterize several dozens of major hydrocarbons in the C_3–C_{10} range by gas chromatography such as BTEX and eight C_3-benzene isomers. Other readily identifiable hydrocarbons include alkanes, alkyl cyclopentanes and cyclohexanes, and naphthalene.

The high abundance of BTEX and C_3-benzenes, and the distribution pattern of BTEX and C_3-benzenes, combined with the hydrocarbon group analysis results by GC–FID as described in Section 3.1, demonstrate that the groundwater at the investigated site has been contaminated by gasoline.

Kaplan et al. [7] studied numerous gasoline-contaminated sites and reported that the ratio of BTEX compounds, (B+T)/(E+X), can be used to evaluate the gasoline partitioning. They found that the average ratios for altered product, gasoline contaminated-water and soil are 0.65 (0.30–1.1), 0.97 (0.11–3.4), and 0.48 (0.07–2.6), respectively. As Table 1 shows, the parametric ratios of (B+T)/(E+X) were determined to be 0.21 and 1.09 for samples A and B, respectively. These ratio values clearly fall within the range of the average ratios for gasoline contaminated-water.

3.3. Headspace VOC assessment of water samples

Water samples from this site have been analyzed by a commercial lab which reported presence of chlorinated hydrocarbons. In order to validate the

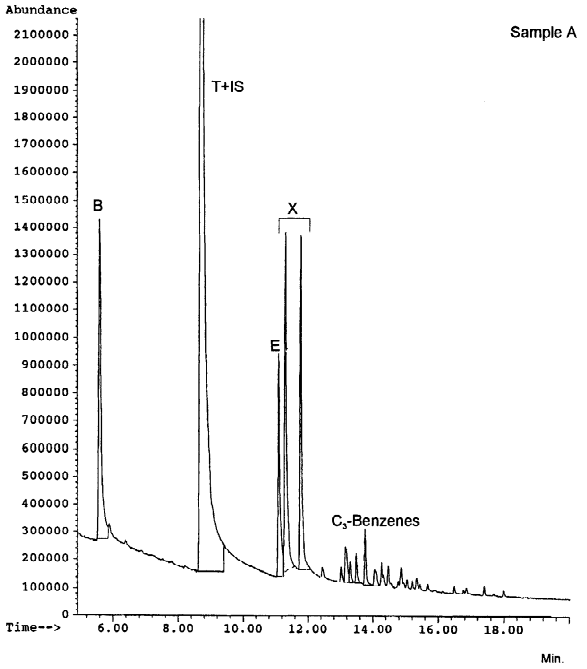

Fig. 4. GC–MS total ion chromatogram of sample A by the SPME sampling technique at ambient temperature. B, T, E, X, and IS stand for benzene, toluene, ethylbenzene, xylenes, and internal standard [$^2H_8$]toluene.

presence of the volatile components in the water samples, two headspace techniques were used. Fig. 4 presents a total ion chromatogram (TIC) of sample A by SPME at ambient temperature of 22 °C. SPME is a ''solventless'' sampling technique in which a fibre with a polymeric coating is either suspended in the headspace above the sample or immersed in it. Due to the high affinity of VOC for the coating, they are adsorbed and concentrated onto the fibre. Once the fibre is inserted into the heated injection part of a GC, the VOCs are immediately desorbed as a tight band onto the GC column. Thus, higher sensitivities for VOC compounds are obtained. Although having greater affinity of volatile BTEX and alkylbenzene compounds, the 100-μm polydimethylsiloxane fibre used in this work did not retain the more volatile chlorinated hydrocarbons well. For those VOC, conventional HS sampling gives a more uniform representation of the VOC present.

In contrast to the SPME technique, the automatic headspace technique is a universal ''clean'' sampling technique for all kind of volatile organic pollutants since only aliquot of HS (typically 1 ml) is injected into the GC. It does not offer any concentration of headspace VOCs of interest, but is well suited for samples containing various VOCs with favourable partition coefficient (low solubility and high volatility). Fig. 5 shows a TIC chromatogram obtained from an on-column injection of 1.00 ml of the headspace of sample B equilibrated at 85 °C. As seen in Fig. 5, the majority of peaks eluted in a time window of 2–14 min. Ten unknown compounds with remarkable abundances were positively identified in this time window (six of 10 are volatile chlorinated compounds). They are 2-methylbutane at 2.52 min, pentane at 2.77 min, 1,1-dichloroethene at 2.94 min, 1,1-dichloroethane at 3.78 min, 1,2-dichloroethene at 4.50 min, methylcyclopentane at 5.61 min, 1,1,1-trichloroethane (chloroform) at 5.87 min, benzene at 6.37 min, trichloroethylene at 7.55 min, and tetrachloroethylene at 10.60 min (Fig. 5). The concentrations of the 6 chlorinated compounds were de-

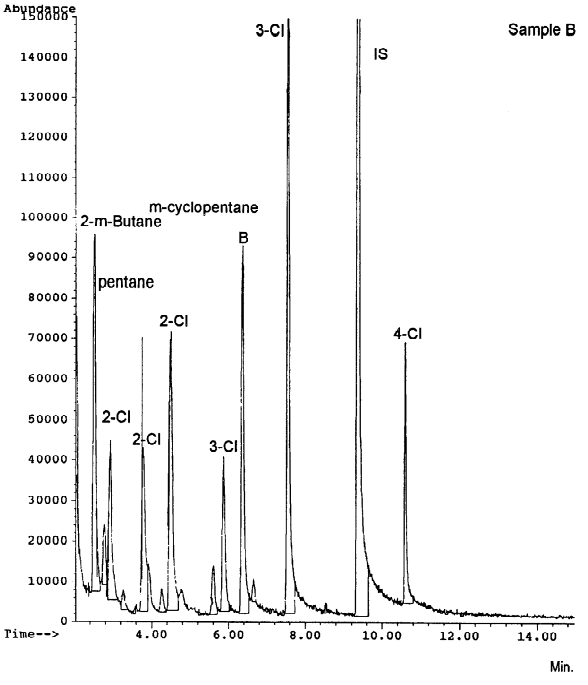

Fig. 5. GC–MS total ion chromatogram of sample B by the automatic sampling technique (equilibrated at 85 °C for a normal time of 40 min). Ten unknown compounds with remarkable abundances were positively identified in the time window of 2–14 min (seven volatile chlorinated compounds and three alkanes, see details in the text).

termined to be 0.1, 0.2, 0.2, 0.2, 0.3, and 0.1 μg/kg of water, essentially near the detection limit of HS analysis.

Fig. 6 shows the GC–MS scan chromatogram of sample A and B for identification of major unknown peaks. In addition to BTEX, C_3-benzenes and *n*-alkanes, two abundant ester compounds (hexadecanoic acid, butyl ester at 30.79 min and octadecanoic acid, butyl ester at 33.57 min), two phthalate compounds (benzyl butyl phthalate at 33.11 min and bis(2-ethylhexyl) phthalate at 35.66 min), and one chlorinated compound, tetra-chloroethane, at 5.60 min were positively identified. Compared to the headspace sampling technique (Fig. 5), it is apparent that GC–MS in scan mode was unable to detect most of the volatile chlorinated compounds due to lower sensitivity and strong interference from relatively abundant gasoline hydrocarbons such as BTEX and low-molecular-mass alkane compounds.

In many cases, particularly for complex hydrocarbon mixture or extensively weathered spill samples, there is no single technique which can unambiguously identify all components of interest in unknown spill samples and trace them to their respective sources. Multiple and integrated fingerprinting approaches are often necessary under such situations. Clearly, the use of the SPME and headspace GC–MS techniques complemented the GC–FID and GC–MS methods for this spill case study. The SPME and headspace GC–MS analyses not only verified the presence of BTEX and other alkylbenzene compounds, but also positively identified the presence of a variety of volatile chlorinated compounds. The detection of various chlorinated compounds in water samples indicates that the chemicals handling company also contributed to the contamination by spillage or leakage of various chemicals to the aquifer.

3.4. Distribution of target alkylated PAH homologues and biomarker compounds

In general, PAH compounds, especially the high-molecular-mass PAHs and their alkylated homologues are relatively stable. Therefore, the distribution patterns and the diagnostic ratios of these oil-characteristic PAHs can be used as fate indicators of oil and petroleum products in the environment and oil source markers [8–17].

Table 2 summarizes quantitative results of five target petroleum-characteristic alkylated PAH homologues and other EPA priority PAHs. Fig. 7 depicts

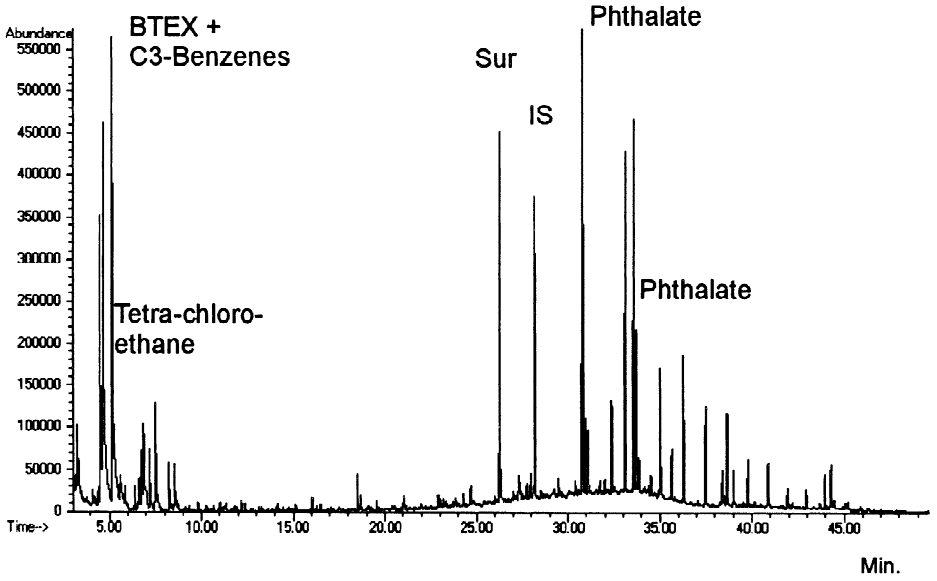

Fig. 6. GC–MS scan chromatogram of sample A for identification of major unknown peaks. Two abundant phthalate compounds (benzyl butyl phthalate at 33.11 min and bis(2-ethylhexyl)phthalate at 35.66 min) were positively identified.

Table 2
PAH analysis results

Sample	Sample A ($\mu g/kg\ H_2O$)	Sample B ($\mu g/kg\ H_2O$)
Alkylated PAHs		
Naphthalenes		
C0–N	0.75	0.61
C1–N	0.15	0.02
C2–N	0.30	0.01
C3–N	0.51	0.01
C4–N	0.18	0.01
Sum	1.90	0.67
Phenanthrenes		
C0–P	0.09	0.01
C1–P	0.15	0.01
C2–P	0.13	0.01
C3–P	0.05	0.01
C4–P	0.03	0.01
Sum	0.45	0.05
Dibenzothiophenes		
C0–D	0.02	0.00
C1–D	0.03	0.00
C2–D	0.03	0.00
C3–D	0.02	0.00
Sum	0.10	0.01
Fluorenes		
C0–F	0.03	0.00
C1–F	0.04	0.01
C2–F	0.08	0.01
C3–F	0.07	0.00
Sum	0.23	0.02
Chrysenes		
C0–C	0.01	0.00
C1–C	0.01	0.00
C2–C	0.01	0.00
C3–C	0.00	0.00
Sum	0.03	0.01
Total	2.72	0.76
Other PAHs		
Biphenyl	0.04	0.00
Acenaphthylene	0.00	0.00
Acenaphthene	0.02	0.00
Anthracene	0.00	0.00
Fluoranthene	0.03	0.01
Pyrene	0.02	0.00
Benz[*a*]anthracene	0.00	0.00
Benzo[*b*]fluoranthene	0.00	0.00
Benzo[*k*]fluoranthene	0.00	0.00
Benzo[*e*]pyrene	0.01	0.00
Benzo[*a*]pyrene	0.00	0.00
Perylene	0.08	0.00
Indeno[1,2,3-*cd*]pyrene	0.00	0.00
Dibenz[*a,h*]anthracene	0.00	0.00
Benzo[*ghi*]perylene	0.01	0.00
Total	0.21	0.01

Table 2. Continued

Sample	Sample A ($\mu g/kg\ H_2O$)	Sample B ($\mu g/kg\ H_2O$)
Recovery of surrogates (%)		
Acenaphthene-d_{10}	75	61
Phenanthrene-d_{10}	83	77
Benz[*a*]anthracene-d_{12}	81	106
Perylene-d_{12}	89	92

N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively. C_0, C_1, C_2, C_3, and C_4 represent carbon numbers of alkyl groups in alkylated PAH homologues.

The concentrations of target PAHs were not corrected for surrogate recovery.

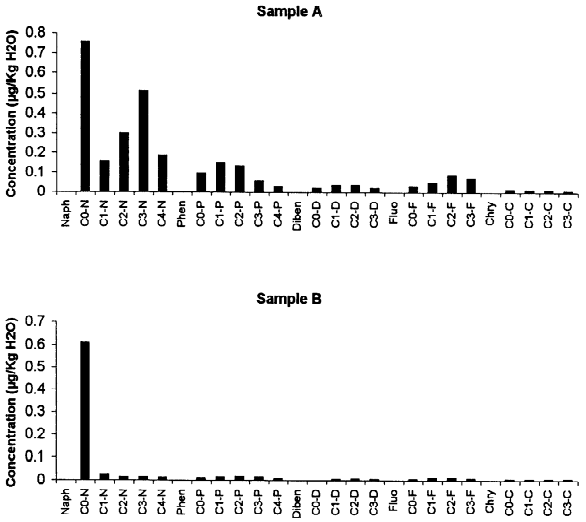

Fig. 7. Alkylated PAH fingerprints of the spill water samples, illustrating the PAH compositional features. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0, 1, 2, 3, and 4 represent carbon numbers of alkyl groups in alkylated PAH homologues. It is noticed that naphthalene shows unusually high abundance and an abnormal distribution pattern in its alkylated homologous family.

the distribution of the target PAHs in the samples. The total of five target petroleum-characteristic alkylated PAH homologues were determined to be 2.7 and 0.8 $\mu g/kg$ of water for samples A and B, respectively. Obviously, the concentrations of PAHs in the samples are extremely low, and most PAHs are under the detection limits in sample B.

It is well known that light distillate gasoline has considerable amounts of aromatic compounds, notably BTEX and C_3-benzenes, but it does not contain

any oil-characteristic high-molecular-mass alkylated PAH and biomarker compounds. The distribution patterns of the five target petrogenic alkylated homologous PAH series (naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes) clearly indicate the presence of another petroleum product, in addition of the presence of gasoline in the samples. Among the five PAH homologous series, the alkylated naphthalene series was the most abundant, followed by the alkylated phenanthrene and fluorene series.

It is interesting to note that naphthalene shows unusually high abundance and an abnormal distribution pattern in its alkylated homologous family. This is because a large portion of naphthalene was contributed from gasoline, in which naphthalene is a common constituent and has much higher water solubility relative to other PAHs [7]. The total naphthalene shown in Fig. 7 is the sum of naphthalene from both the gasoline and heavy fuel. Based on the distribution patterns of naphthalene and its alkyl homologues in oils and petroleum products, it is estimated that approximately 80 and 95% of naphthalene in water samples A and B were from gasoline and/or other sources, while 20 and 5% of naphthalene in samples A and B were contributed by the heavy petroleum product in water samples.

Trace of biomarker terpane compounds (at m/z 191) C_{23} and C_{24} tricyclic terpane, Ts [18α(*H*),21β(*H*)-22, 29,30-trisnorhopane], Tm [17α(*H*),21β(*H*)-22,29,30-trisnorhopane], C_{29}-αβ-hopane, C_{30}-αβ-hopane, and 22*S* and 22*R* epimers of C_{31} and C_{32} αβ-homohopanes were also detected (Fig. 8). The presence of these petrogenic biomarker compounds [18], in combination with TPH and PAH analysis results, unambiguously point toward to the conclusion that the water was not only contaminated by gasoline, but also by another heavy petroleum product.

4. Conclusions

This paper describes a case study in which integrated multiple analytical techniques including GC–MS and GC–FID, SPME and HS (headspace) GC–MS techniques were used to identify and characterize trace petroleum-related hydrocarbons and other volatile organic compounds in water samples. The finger-

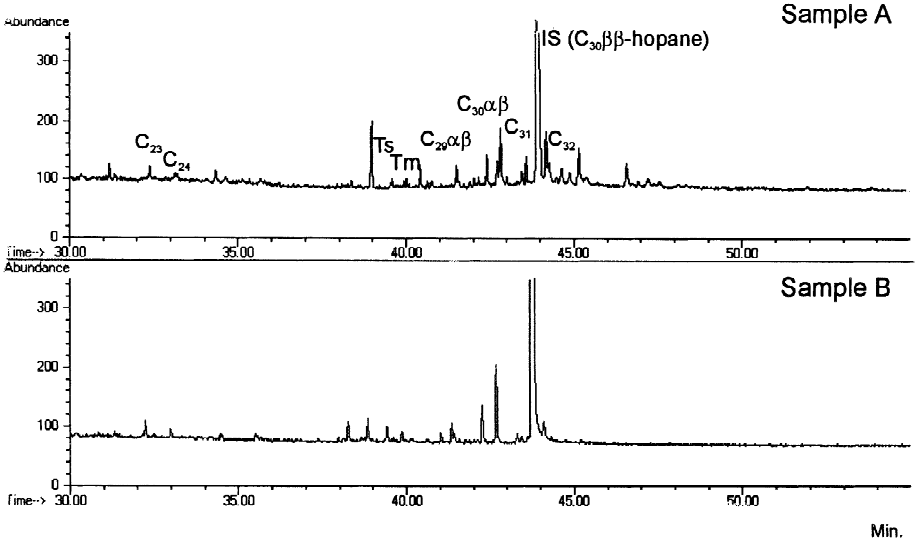

Fig. 8. GC–MS fragmentograms (m/z 191) of samples A and B. Detection of trace of biomarker terpane compounds (C_{23} and C_{24} tricyclic terpane, Ts: 18α(*H*),21β(*H*)-22,29,30-trisnorhopane, Tm: 17α(*H*),21β(*H*)-22,29,30-trisnorhopane, C_{29}-αβ-hopane, C_{30}-αβ-hopane, and 22*S* and 22*R* epimers of C_{31} and C_{32} αβ-homohopanes) clearly indicates the presence of another heavy petroleum product. IS = internal standard C_{30}-ββ-hopane.

printing results and data interpretation clearly indicates that:

(1) The contamination of gasoline to groundwater, especially to the near-surface groundwater, is evident. The detected hydrocarbons in sample A were shown to be composed of two sources of hydrocarbons: one from gasoline and the other from a heavy petroleum product. The significant distribution of five target petroleum-characteristic alkylkated PAH homologues and biomarkers unambiguously confirmed the presence of another heavy petroleum product.

(2) Sample B (15–60 m) was also contaminated, but to a much lesser degree in comparison with sample A. The concentrations of the TPH and BTEX compounds were determined to be 130 and 2.6 μg/kg of water for sample B, respectively.

(3) In addition, the contamination of a variety of volatile chlorinated compounds to the groundwater was also clearly demonstrated.

References

[1] R.E. Jordan, J.R. Payne, Fate and Weathering of Petroleum Spills in the Marine Environment: A Literature Review and Synopsis, Ann Arbor Science, Ann Arbor, MI, 1980.
[2] Z.D. Wang, M. Fingas, K. Li, J. Chromatogr. Sci. 32 (1994) 361.
[3] Z.D. Wang, M. Fingas, K. Li, J. Chromatogr. Sci. 32 (1994) 367.
[4] K. Li, M. Fingas, P. Boileau, S. Blenkinsopp, J.R.J. Pare, J. Belanger, M. Llompart, in: Proceedings of the 19th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Environment Canada, Ottawa, 1996, p. 89.
[5] M. Llompart, K. Li, M. Fingas, in: Proceedings of the 14th Technical Seminar on Chemical Spills, Environment Canada, Ottawa, 1997, p. 93.
[6] Z.D. Wang, M. Fingas, D. Page, J. Chromatogr. A 843 (1999) 369.
[7] I.R. Kaplan, Y. Galperin, H. Alimi, R. Lee, S. Lu, Ground Water Monit. Remediat. (Fall Issue) (1996) 113.
[8] A. Farran, J. Grimelt, J. Albaiges, A.V. Botello, S.A. Macko, Mar. Pollut. Bull. 18 (1987) 284.
[9] N.M. Fayad, E. Overton, Mar. Pollut. Bull. 30 (1995) 239.
[10] M.C. Kennicutt II, Oil Chem. Pollut. 4 (1988) 89.
[11] D.S. Page, P.D. Boehm, G.S. Douglas, A.E. Bence, in: P.G. Wells, J.N. Butler, J.S. Hughes (Eds.), Exxon Valdez Oil Spill: Fate and Effects in Alaska Waters, ASTM, Philadelphia, PA, 1995, p. 41.
[12] T.C. Sauer, P.D. Boehm, in: Proceedings of 1991 Oil Spill Conference, API, Washington, DC, 1991, p. 363.
[13] T.C. Sauer, J. Michel, M.O. Hayes, D.V. Aurand, Environ. Int. 24 (1998) 43.
[14] J.W. Short, T.J. Jackson, M.L. Larsen, T.L. Wade, in: S.D. Rice, R.B. Spies, D.A. Wolfe, B.A. Wright (Eds.), American Fisheries Society Symposium, Vol. 18, American Fisheries Society, Bethesda, MD, 1996, p. 140.
[15] S.A. Stout, A.D. Uhler, T.G. Naymik, K.J. McCarthy, Environ. Sci. Technol. 32 (1998) 260A.
[16] J.M. Teal, J.W. Farrington, K.A. Burns, J.J. Stegeman, B.W. Tripp, B. Woodin, C. Phinney, Mar. Pollut. Bull. 24 (1992) 607.
[17] Z.D. Wang, M. Fingas, M. Landriault, L. Sigouin, Y. Feng, J. Mullin, J. Chromatogr. A 775 (1997) 251.
[18] K.E. Peters, J.W. Moldowan, The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments, Prentice Hall, Englewood Cliffs, NJ, 1993.