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# Quantification and Interpretation of Total Petroleum Hydrocarbons in Sediment Samples by a GC/MS Method and Comparison with EPA 418.1 and a Rapid Field Method

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**Total petroleum hydrocarbons (TPH) as a lumped parameter can be easily and rapidly measured or monitored. Despite interpretational problems, it has become an accepted regulatory benchmark used widely to evaluate the extent of petroleum product contamination. Three currently used methods (GC/MS, conventional EPA 418.1, and a rapid field method PetroFLAG) were performed to quantify the TPH content in samples collected from a site contaminated by transformer oil. To standardize the method and improve the comparability of TPH data, crucial GC-based quantification issues were examined, e.g., quantification based on internal standards (ISTD) vs external standards (ESTD), single vs multiple ISTD, and various area integration approaches. The interpretation of hydrocarbon chromatographic results was examined in the context of field samples. The performance of the GC/MS method was compared with those of EPA 418.1 and PetroFLAG. As a result, it was observed that the ISTD quantification method was preferred to the ESTD method, multiple ISTD might be better than single ISTD, and three different area integration approaches did not have a significant effect on TPH results. Evaluation of the chromatograms between a reference sample and three unknown samples showed that the extent of contamination varied appreciably with sample depth. It was also found that there existed a good positive correlation between GC/MS and both EPA 418.1 and PetroFLAG, and that EPA 418.1 produced the higher overall estimate while GC/MS and PetroFLAG resulted in lower, more statistically comparable TPH values.**

Crude and refined petroleum products constitute a major class of contaminants that environmental professionals are likely to encounter in conventional or environmental forensic site investigations and remediations. Compared to time-consuming, complex separation methods identifying individual compounds in weathered petroleum products, total petroleum hydrocarbons (TPH) as a collective parameter can be relatively easily and rapidly measured and monitored. TPH is, thus, an accepted regulatory benchmark widely used to evaluate petroleum contamination by

environmental professionals. The Association for the Environmental Health of Soils (AEHS)'s eighth annual survey of states' cleanup standards for hydrocarbon-contaminated soil and groundwater has been published recently.<sup>1</sup> By 1998, all 50 states had set site cleanup standards or guidelines based on TPH measurements by various methods. These methods may include specific determination of known toxic fractions (e.g., benzene, toluene, ethylbenzene, xylene (BTEX), methyl *tert*-butyl ether (MTBE), and/or polyaromatic hydrocarbons (PAHs)).

Methods of measuring TPH and its components have been explored extensively. Currently a variety of analytical methods are used to measure TPH due to the complicated composition of petroleum mixtures. No single method, however, can be used as a representative, nonspecific procedure for TPH measurement. TPH measurements generally include several crucial steps: retention of volatile  $<C_8$  compounds and selection of an appropriate solvent or mixture of solvents to extract the petroleum hydrocarbons from environmental samples; preparation of calibration standards by mixing petroleum products or specific hydrocarbons in a proper ratio; and instrumental analysis of the calibration standards and sample extractions. All of these steps may result in selective capture of individual components of hydrocarbon mixtures. Major problems can arise in risk-driven site cleanup decisions. This is because environmental or human health risk may arise from various subfractions or specific components of petroleum hydrocarbon mixtures, which are not selectively determined by some TPH methods.<sup>2</sup>

Various approaches to instrumental analysis allow us to classify the TPH methods into (a) gravimetric, EPA 413.1,<sup>3</sup> method 9070;<sup>4</sup> (b) spectroscopic, EPA 418.1,<sup>5</sup> PetroFLAG;<sup>6</sup> (c) gas chromatography, methods 8015B,<sup>7</sup> NWTPH;<sup>8</sup> (d) others, <sup>1</sup>H and <sup>14</sup>C nuclear

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- (4) Environmental Protection Agency, *Test Method for Evaluating Solid Waste, EPA SW-846*, 3rd ed.; the U. S. Government Printing Office (GPO), Washington, DC, 1996.
- (5) Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*; Government Printing Office: Washington, DC, 1983.
- (6) Dexcel Corp. *PetroFLAG® Hydrocarbon Analyzer User's Manual*; Hamden, CT, 1995; pp 4–16.
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magnetic resonance (NMR),<sup>9</sup> thin-layer chromatography (TLC).<sup>10</sup>

Gravimetric and spectroscopic methods were developed to rapidly identify the hydrocarbon contamination as TPH. Consequently, they tell us little about the individual components and fragments of petroleum products. In general, these methods exhibit low specificity, high detection limits ( $\geq 10$  ppm), and sensitivity to matrix effects, which require elective drying and separation steps. Briefly, EPA 418.1 may overestimate TPH as a result of (1) differences in infrared molar absorptivity for calibration standards and petroleum products, (2) detection of naturally occurring hydrocarbons, and (3) infrared dispersion by mineral particles. Negative bias may also be introduced by EPA 418.1 via (1) poor extraction efficiency of Freon-113 for high-molecular-weight hydrocarbons, (2) differences in molar absorptivity, and (3) removal of five- to six-ring alkylated aromatics during the silica gel cleanup procedure.<sup>10,11</sup> TPH measurements have been greatly improved by GC methods. The advantages of GC analysis and the analytical bias associated with EPA 418.1 have been examined previously.

Purge-and-trap or solvent extraction capillary GC methods may overcome many such biases with the use of high-resolution columns. Moreover, TPH, by solvent extraction GC methods (usually with the flame ionization detector), can be used as a "fingerprint" to identify the source of semivolatile hydrocarbon contamination, the content of some potentially high-risk compounds, and the rough "age" of petroleum mixtures when combined with other information (e.g.,  $^{13}\text{C}/^{12}\text{C}$  ratios, oxygenate or Pb content, etc.). These methods have become the most popular tool for identification and quantification of petroleum products in both forensic and environmental work. As a result, high-resolution capillary GC-flame ionization detection (GC-FID) or high-resolution capillary GC with mass spectrometry detection (GC/MS) are the most widely used techniques for petroleum hydrocarbon analyses. Recently, researchers have documented the potential advantages of GC/MS over GC-FID because valuable additional compound-specific information (e.g., PAHs) and unique TPH distribution patterns required for risk-based assessment may be derived from the mass spectra.<sup>12</sup>

TPH represents a lumped parameter rather than an ensemble of individual compounds. Applying GC methods (both GC/MS and GC-FID) to TPH characterization relies on the total area (detector response) of the resolved and unresolved components of petroleum mixtures. Therefore, quantification methods differ from those of the conventional GC procedures for a single compound. A number of relevant issues need to be addressed in more detail in order to standardize the method and improve the comparability of TPH data.

Utilizing subsurface sediment samples from a contaminated site, our study examined crucial GC-based quantification issues including internal standard (ISTD) and external standard (ESTD) methods, single and multiple ISTD, and manual and other area integration approaches employed to obtain the total chromatographic area. The performance of this solvent extraction GC/MS method was further compared with those of other laboratory and field methods (e.g., EPA 418.1 and PetroFLAG).

## MATERIALS AND METHODS

**Sample Collection.** Sampling was conducted at a power station in the Pacific northwest, where mineral oil had been in historical use as a dielectric cooling fluid. Cores were collected via a hollow-stem auger drilling technique in solvent-washed core liners. These sediment cores were sealed with Teflon tape and end caps, placed in double Ziplock bags, photographed, stored in a cooler with ice—sufficient to maintain at 4 °C, and then sent to our laboratory by overnight courier. Each core sample was homogenized prior to subsampling for individual analyses. Subsamples were transferred into dark brown glass containers with Teflon caps and stored in dark, cold room at 4 °C.

**Methods. (1) GC/MS. Theoretical Considerations.** Generally speaking, ISTD methods are broadly applied for GC to quantify the concentrations of specific compounds in environmental samples due to matrix interferences that affect individual sample recovery and detection uniquely. Given that TPH is a collective parameter concerning various compounds with a broad range of carbon number, solubility, volatility, and persistence, the performance of single-ISTD quantification methods vs multiple-ISTD methods is worthy of examination. On the other hand, ESTD methods have been used by most of the previous TPH studies. The actual performance of ESTD methods vs various ISTD methods should be reevaluated.

Petroleum mixtures such as tank bottoms, coal tars, and creosote may contain up to 90% PAHs, which are known carcinogens and concerned in risk-based correction action (RBCA).<sup>10</sup> PAHs consist of the fractions of petroleum products with high boiling points and low aqueous mobility.<sup>13</sup> These compounds may represent the bulk of the risk associated with coal tar/creosote-like petroleum contamination or significantly weathered heavy oil. To estimate semivolatile TPH toxicity reliably, it is necessary to carefully select calibration standards, ISTD and surrogate standards (e.g., at least including aromatics).

**Procedures.** Samples were freeze-dried in a Labconco freeze-dry system (Labconco Corp., Kansas City, MO). Ten grams of each of duplicate dried samples were further Soxhlet extracted with methylene chloride (Fisher, GC Resolv) for 12 h and concentrated to a graduated volume using a TurboVap II concentration workstation (Zymark Corp., Hopkinton, MA) with  $\text{N}_2$  as the auxiliary gas. Extracts were analyzed by GC/MS on a Hewlett-Packard 5890 series II gas chromatograph equipped with a HP 5972 mass-selective detector and a HP automatic liquid sampler. HP MS-ChemStation (DOS series) was used to program the data acquisition and analysis. External standards were prepared from Shell Diala oil (i.e., a transformer oil standard for the product used at the Pacific northwest site). The two internal standards were

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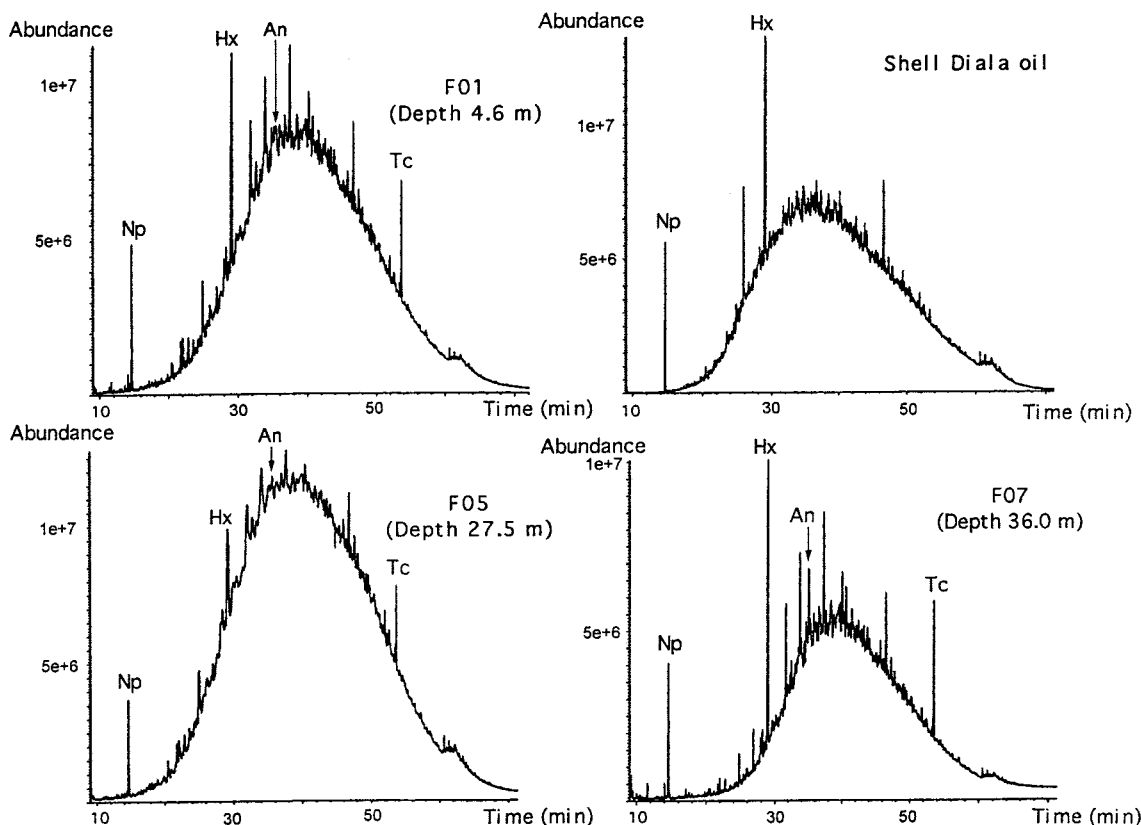


Figure 1. Comparison of the total ion chromatograms of one reference standard (Shell Diala oil) and three unknown samples over depth (F01, F05, F07): Np = naphthalene- $d_8$ ; Hx =  $n$ -hexadecane- $d_{34}$ ; An = anthracene- $d_{10}$ ; Tc = tetracosane- $d_{50}$ .

naphthalene- $d_8$  (99.2 atom % D, Protocol Analytical, Inc., Middlesex, NJ) and  $n$ -hexadecane- $d_{34}$  (99 atom % D, Protocol). The two surrogate standards were anthracene- $d_{10}$  (99.5% atom % D, Protocol) and  $n$ -tetracosane- $d_{50}$  (98.2% atom % D, Protocol). A HP-1 (60-m  $\times$  0.25-mm  $\times$  0.25- $\mu$ m film thickness) cross-linked methyl silicone gum column was used. The injector and detector temperatures were set at 280 and 300  $^{\circ}$ C, respectively. The initial temperature was kept at 50  $^{\circ}$ C for 1 min, ramped to 110  $^{\circ}$ C at 10  $^{\circ}$ C/min, to 270  $^{\circ}$ C at 3  $^{\circ}$ C/min, and to 300  $^{\circ}$ C at 15  $^{\circ}$ C/min and held at that temperature for 10 min. A 2- $\mu$ L aliquot was injected in the splitless mode with a 1-min purge-off. Helium was the carrier gas at 0.9 mL/min. The MS was scanned from 50 to 550 amu at 0.9 scan/s by selecting full-scan mode. The quantification of TPH in a sample from the same GC run was conducted via total chromatographic area counts based on both ISTD and ESTD, separately. Three integration approaches were used to obtain the total area of a total ion chromatogram: (a) manual integration along the lowest-point baseline; (b) sum of resolved individual compounds after integration with the lowest-point baseline held on; (c) sum of resolved individual compounds after integration with the baseline established by MS ChemStation integration.

**(2) EPA 418.1 Modified and PetroFLAG Methods.** Method details of EPA 418.1 as modified are provided in a reference.<sup>5</sup> Briefly, 20-g samples were extracted with Freon-113 (Aldrich, 99+-% spectrophotometric grade) by sonication for 15 min and then measured by infrared spectroscopy (Buck Scientific, model HC-404). Method details of PetroFLAG are documented in ref 6, which is basically a rapid field method. Samples were extracted by a mixture of methanol and other solvents, of which detailed

information was not provided by the company, and then measured by UV-visible spectroscopy (Dexsil, hydrocarbon analyzer).

## RESULT AND DISCUSSION

In this section we discuss the advantages of the GC-based TPH measurement (e.g., deriving valuable information on oil degradation from chromatograms) and GC quantification issues such as the ISTD and ESTD quantification methods in the context of TPH analysis, and we compare the GC/MS method with EPA 418.1 and PetroFLAG on the basis of measurement precision and statistical analysis.

**Evaluation of the Chromatograms.** Typically, chromatograms may demonstrate the effect of physicochemical and biochemical weathering on the chemical composition of hydrocarbons by comparing the retention time and elution profiles of unknown samples with reference samples.<sup>14,15</sup> For example, as petroleum products weather, more labile compounds are generally transferred or transformed. As a result, the gross chromatogram of a product becomes increasingly dominated by an unresolved complex mixture (UCM) of hydrocarbons and by hydrocarbons with high carbon numbers such as PAHs. UCM is represented by a large hump in the chromatogram. Such chromatographic features typically reflect that the product has been degraded or weathered significantly.<sup>7,16</sup> Heavier refined products, such as

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Table 1. Total Petroleum Hydrocarbons (TPH) Results Measured by the GC/MS Method for Power Substation Samples

		ISTD method								
		ESTD method			single ISTD, Hx <sup>a</sup>			multiple ISTD, Np + Hx <sup>b</sup>		
sample ID	depth (m)	TPH (10 <sup>3</sup> mg/kg)	recovery (%) <sup>c</sup>		TPH (10 <sup>3</sup> mg/kg)	recovery (%) <sup>d</sup>		TPH (10 <sup>3</sup> mg/kg)	recovery (%) <sup>e</sup>	
			An <sup>f</sup>	Tc <sup>f</sup>		An <sup>f</sup>	Tc <sup>f</sup>		An <sup>f</sup>	Tc <sup>f</sup>
a. Integration Approach 1: Manual Integration along the Lowest-Point Baseline										
F01	4.6	13.40	n/a <sup>g</sup>	65.8	10.13	n/a	67.1	16.06	n/a	79.0
F02	5.7	15.89	n/a	58.2	13.64	n/a	66.9	21.04	n/a	77.0
F03	6.1	15.27	n/a	60.9	12.30	n/a	66.1	19.57	n/a	78.0
F04	7.7	7.59	51.0	73.2	5.72	52.8	75.7	10.01	67.3	96.5
F05	8.4	19.84	n/a	48.0	19.59	n/a	61.2	25.37	n/a	61.4
F06	8.9	14.76	n/a	62.4	11.19	n/a	64.8	19.33	n/a	81.8
F07	11.0	7.15	59.0	73.4	5.36	60.4	75.3	9.24	76.2	94.9
F08	11.7	7.53	54.9	71.9	5.78	58.2	76.4	10.62	77.3	101.4
F09	12.9	15.70	n/a	55.8	13.38	n/a	65.0	22.88	n/a	81.3
F10	13.9	10.59	n/a	68.0	8.33	n/a	73.1	14.32	n/a	91.9
F11	14.5	0.13	58.1	65.0	0.13	73.9	82.7	0.24	98.1	109.7
F12	14.6	0.13	46.4	79.6	0.10	48.5	83.3	0.18	63.4	109.0
F13	15.3	0.06	49.6	80.5	0.04	51.7	84.0	0.08	67.9	110.1
mean			53.2	66.4		57.6	72.4		75.0	90.2
b. Integration Approach 2: Sum of Resolved Individual Compounds after Integrated with the Lowest-Point Baseline Held On										
F01	4.6	13.17	n/a	68.0	9.88	n/a	68.9	15.81	n/a	81.7
F02	5.7	15.78	n/a	60.1	13.42	n/a	68.6	20.88	n/a	79.6
F03	6.1	15.08	n/a	62.9	12.04	n/a	67.8	19.32	n/a	80.6
F04	7.7	7.15	52.7	75.6	5.34	54.1	77.6	9.43	69.6	99.7
F05	8.4	19.77	n/a	49.6	19.33	n/a	62.8	25.28	n/a	63.4
F06	8.9	14.83	n/a	64.5	11.15	n/a	66.4	19.44	n/a	84.5
F07	11.0	7.02	60.9	75.9	5.22	62.0	77.2	9.08	78.7	98.1
F08	11.7	7.22	56.7	74.3	5.50	59.7	78.3	10.19	79.9	104.8
F09	12.9	15.74	n/a	57.7	13.29	n/a	66.7	22.93	n/a	84.1
F10	13.9	10.52	n/a	70.2	8.20	n/a	74.9	14.23	n/a	95.0
F11	14.5	0.09	60.0	67.1	0.10	75.8	84.8	0.18	101.4	113.4
F12	14.6	0.03	47.9	82.3	0.02	49.7	85.4	0.04	65.5	112.6
F13	15.3	0.02	51.3	83.2	0.01	53.1	86.1	0.02	70.1	113.8
mean			54.9	68.6		59.1	74.3		77.5	93.2
c. Integration Approach 3: Sum of Resolved Individual Compounds after Integrated with the Baseline Established by MS ChemStation										
F01	4.6	13.72	n/a	77.6	10.39	n/a	79.2	16.47	n/a	93.2
F02	5.7	16.53	n/a	68.6	14.19	n/a	78.9	21.89	n/a	90.8
F03	6.1	15.55	n/a	71.8	12.53	n/a	78.0	19.93	n/a	92.0
F04	7.7	7.08	60.2	86.3	5.34	62.3	89.3	9.34	79.4	113.9
F05	8.4	19.90	n/a	56.6	19.63	n/a	72.2	25.45	n/a	72.4
F06	8.9	15.96	n/a	73.7	12.10	n/a	76.4	20.91	n/a	96.5
F07	11.0	7.41	69.6	86.6	5.55	71.3	88.8	9.57	89.9	112.0
F08	11.7	7.71	64.7	84.9	5.92	68.7	90.1	10.88	91.3	119.7
F09	12.9	17.16	n/a	65.9	14.62	n/a	76.7	25	n/a	96.0
F10	13.9	10.66	n/a	80.2	8.38	n/a	86.2	14.41	n/a	108.5
F11	14.5	0.01	68.5	76.6	0.01	87.3	97.6	0.03	115.8	129.5
F12	14.6	0.03	54.7	94.0	0.02	57.2	98.3	0.04	74.8	128.6
F13	15.3	0.02	58.5	95.0	0.02	61.0	99.1	0.03	80.1	129.9
mean			62.7	78.3		68.0	85.4		88.6	106.4

<sup>a</sup> Single internal standards (ISTD) method: Hx = *n*-hexadecane-*d*<sub>34</sub>. <sup>b</sup> Multiple-ISTD method (Np = naphthalene-*d*<sub>8</sub>): Np and Hx were mixed at 1:1. <sup>c</sup> Recoveries were based on the external standard (ESTD) (Shell Diala oil). <sup>d,e</sup> Recoveries were based on the relative response factors of the external standard to single ISTD (Hx) and multiple ISTD (Np + Hx), respectively. <sup>f</sup> Surrogate standards An = anthracene-*d*<sub>10</sub>; Tc = *n*-tetracosane-*d*<sub>50</sub>. <sup>g</sup> n/a, not available.

lubricating and heat transfer fluids, may also show the presence of UCM without weathering. Various ratios may also be calculated from chromatograms/spectra and used to identify the hydrocarbon source, characterize the degree of weathering, and evaluate the effect of a variety of environmental conditions.<sup>9,17,18</sup> We did not explore these ratios in this study.

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A simplified comparison of the GC profiles of the unknown samples with the reference sample Shell Diala oil (i.e., the primary petroleum compounds) in Figure 1 shows that the retention time windows of concern (e.g., 13–60 min covering the entire range of elution for TPH) and the GC trace patterns were very similar among the reference and unknown samples. It was also established that all the chromatograms showed the notable presence of unresolved mixtures (i.e., UCM) with similar shapes. It may also be noted in Figure 1 that the concentration or extent of contamination, on the other hand, changed with sample depth. The contaminant distribution patterns in this case may have been deter-

mined by hydrogeologic factors or biotransformation processes.

**ISTD vs ESTD Methods.** Table 1 presents the TPH results and recoveries of surrogate standards corresponding to the samples measured by the GC/MS method. The results were grouped in columns corresponding to the following: the ESTD method, ISTD methods with single (*n*-hexadecane-*d*<sub>34</sub>) or multiple internal standards (naphthalene-*d*<sub>8</sub> and *n*-hexadecane-*d*<sub>34</sub>), and three total-area integration approaches (Table 1). The recovery is understood as a relative rather than an absolute parameter. The reason is that the relative response factors (based on molar concentrations) required to calculate the recoveries were basically lumped parameters corresponding to a mixture (i.e., Shell Diala oil) rather than the aforementioned individual internal standards.<sup>12</sup> This procedure was reversed by Wang and co-workers to calculate the relative response factor.<sup>9</sup> An average relative response factor for the TPH mixture was obtained by arithmetically averaging the relative response factors of all individual compounds that were mixed to make the calibration reference. Actually, the response factors of the calibration standard and the internal standards may not be necessarily the same. Careful selection of multiple ISTD mixtures may narrow this difference.

Examination of the recoveries of the two surrogate standards (anthracene-*d*<sub>10</sub> and *n*-tetracosane-*d*<sub>50</sub>) in Table 1 allows us to rank the ESTD and various ISTD methods in decreasing order of recovery. The multiple-ISTD method (ISTD, naphthalene-*d*<sub>8</sub> + *n*-hexadecane-*d*<sub>34</sub>) had the highest recoveries. The single-ISTD method (ISTD, *n*-hexadecane-*d*<sub>34</sub>) was lower, and the ESTD method was the lowest. In other words, depending on the composition of petroleum products, multiple-ISTD methods are the best choice for TPH measurements, especially when we do not know the composition of petroleum products. Single-ISTD methods can also be used if single representative (similar *C<sub>x</sub>* range and response, etc.) ISTD are available. ESTD methods are less desirable alternatives to ISTD methods for TPH measurement in this range although they have been applied by previous studies.<sup>8,16,17</sup>

Another issue closely associated with GC-based methods is the algorithm used to integrate chromatograms as a group. MS ChemStation supports several integration approaches. There exist various regulatory recommendations for integration from a baseline established through the lowest point in a chromatogram.<sup>17</sup> Other documents pose a general requirement such as "integration as a group".<sup>8</sup> Three approaches available in the MS ChemStation software were used to examine this issue. Clarification of this question is central to achieve more comparable TPH data. In our study, comparison of the three integration approaches (Table 1) indicated that there were no significant differences in the outcome. The results matched each other very well.

**Comparison with Two Other TPH Methods.** Table 2 presents the comparison of the TPH results measured by the three TPH methods (GC/MS, conventional EPA 418.1, and a rapid field method PetroFLAG). The comparison illustrated that reasonable positive correlations existed between GC/MS and both EPA 418.1 and PetroFLAG in this mass range. In other words, the three methods yielded similar trends in TPH concentration changes with depth. In addition, EPA 418.1 produced a higher overall estimate of TPH while the other two methods resulted in lower, more comparable values. It is worth emphasizing that, even though it

Table 2. Comparison between GC/MS and EPA 418.1 and PetroFLAG

sample ID	depth (m)	TPH (10 <sup>3</sup> mg/kg)		
		GC/MS	EPA 418.1	PetroFLAG
F01	4.6	16.47	30.82	11.64
F02	5.7	21.89	30.58	14.45
F03	6.1	19.93	27.78	14.69
F04	7.7	9.34	13.34	6.24
F05	8.4	25.45	60.04	22.05
F06	8.9	20.91	29.98	18.29
F07	11.0	9.57	20.19	14.02
F08	11.7	10.88	20.93	16.48
F09	12.9	25.00	59.92	27.13
F10	13.9	14.41	22.12	9.66
F11	14.5	0.03	0.04	0.02
F12	14.6	0.04	0.11	0.07
F13	15.3	0.03	0.04	0.02
mean RPD (%) <sup>a</sup>		4.5	12.3	7.5
(std dev (%), sample size)		(2.8, 5)	(5.5, 5)	(9.4, 9)
Statistic Analysis at Significance Level 0.05				
		df <sup>c</sup>	F or t <sup>d</sup>	P
ANOVA <sup>b</sup>		36	3.30	0.048
paired t-test (two-tailed)				
GC/MS–EPA 418.1		12	3.430	0.005
EPA 418.1–PetroFLAG		12	3.732	0.003
GC/MS–PetroFLAG		12	1.360	0.199

<sup>a</sup> Relative percent difference (RPD) between two duplicate samples. <sup>b</sup> Analysis of variance. <sup>c</sup> Degree of freedom. <sup>d</sup> F or t-values for ANOVA and t-test, respectively.

is basically a field method, PetroFLAG produced quite comparable results with GC/MS method.

Previous research has argued that a modified EPA method 9071 (similar to EPA 418.1) detected compounds other than petroleum hydrocarbons and, therefore, gave erroneously high TPH values while GC-FID yielded more reliable results.<sup>20,22</sup> Douglas and co-workers further summarized the reasons why EPA 418.1 might result in either negative or positive method bias.<sup>11</sup>

The PetroFLAG user's manual suggests that TPH values measured by PetroFLAG are very likely to be overestimated, even higher than those by EPA 418.1, because the PetroFLAG system responds to the full range of hydrocarbons, and therefore, it also detects some naturally occurring hydrocarbon-like compounds.<sup>6</sup> The reason the PetroFLAG method gave significantly lower TPH values than EPA 418.1 in our experiment was not obvious. Part of the reason may be due to the proprietary absorptometry instrument's response setting. It is possible that it was not matched to the actual response factor for the samples. Another contributing factor may be that the generally higher molecular weight compounds in the samples absorb less UV–visible intensity than

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the lower molecular weight, particularly aromatic, compounds in diesel oil or fuel oil.

The precision values for these three methods are presented in Table 2 in terms of mean relative percentage difference (RPD) on duplicate sediment samples. The GC/MS method yielded good method precision (RPD 4.5%) while EPA 418.1 was less precise (RPD 12.3%). The performance of PetroFLAG (RPD 7.5%) fell into the range between those of GC/MS and EPA 418.1. From our experience, PetroFLAG performance is empirical (i.e., dependent on both sample attributes and instrument settings). Duplicate results can be obtained only by strict adherence to the same procedure for similar samples. To use the PetroFLAG method, the optimum TPH concentration in a sediment sample is above 100 mg/kg of dry weight. Nonetheless, it is still an inexpensive and rapid field test method.

Statistical analysis (SPSS 8.0 for Windows, SPSS Inc., Chicago, IL) was executed to estimate the significance of observed differences between the methods (Table 2). The ANOVA resulted in a critical *F*-value of 0.048 (*P*-value for *F*-test). It was quite close to the significance level of the test (i.e.,  $\alpha = 0.05$ ). This means that the null hypothesis may be rejected, but the difference was not remarkable. Further paired *t*-tests were applied to specifically identify the level of significance. The *P*-values were 0.005, 0.003, and 0.199 for the GC/MS-EPA 418.1, EPA 418.1-PetroFLAG, and GC/MS-PetroFLAG paired *t*-tests, respectively. Compared at the same significance level of test ( $\alpha = 0.05$ ), it can be seen that there was a significant difference between the GC/MS method and EPA 418.1, and between EPA 418.1 and PetroFLAG. No significant differences were observed between the GC/MS and PetroFLAG methods. Moreover, on the basis of the *P*-values of the paired *t*-tests, we conclude that there was a slightly greater difference

between EPA 418.1 and PetroFLAG than between EPA 418.1 and GC/MS methods. In summary, even though the three currently used TPH methods presented good positive correlations between them, the EPA 418.1 gave higher TPH values and showed significant differences from both the GC/MS and PetroFLAG methods. PetroFLAG gave the lowest TPH values and showed no significant differences from the GC/MS method.

We conclude that multiple internal standard GC/MS methods have the most promise for quantitative, reproducible evaluations of petroleum product contamination of sediments. Preliminary sampling of sediments and GC/MS analyses will permit the selection of appropriate PetroFLAG calibration and the instrument settings. Then mass sampling, followed by rapid, inexpensive PetroFLAG measurements with a subset of GC/MS confirmations, should result in more efficient site characterization or treatment monitoring programs.

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