

On-Site Profiling and Speciation of Polycyclic Aromatic Hydrocarbons at Manufactured Gas Plant Sites by a High Temperature Transfer Line, Membrane Inlet Probe Coupled to a Photoionization Detector and Gas Chromatograph/Mass Spectrometer

THOMAS CONSIDINE AND
ALBERT ROBBAT, JR.*

Tufts University, Chemistry Department, Center for Field Analytical Studies and Technology, 62 Talbot Avenue, Medford, Massachusetts 02155

Received September 7, 2007. Revised manuscript received November 13, 2007. Accepted November 18, 2007.

A new high temperature transfer line, membrane inlet probe (HTTL-MIP) coupled to a photoionization detector (PID) and gas chromatograph/mass spectrometer (GC/MS) was used to rapidly profile and speciate polycyclic aromatic hydrocarbons (PAH) in the subsurface. PID signals were in agreement with GC/MS results. Correlation coefficients of 0.92 and 0.99 were obtained for discrete and composite samples collected from the same exact location. Continuous probe advancement with PID detection found coal tar, a dense nonaqueous phase liquid, in soil channels and saturated media. When samples were collected conventionally, split, solvent extracted, and analyzed in the field and confirmation laboratory, GC/MS measurement precision and accuracy were indistinguishable; despite the fact the field laboratory produced data five times faster than the laboratory using standard EPA methods. No false positive/negatives were found. Based on these findings, increased confidence in site conceptual models should be obtained, since PID response indicated total PAH presence/absence in "real-time," while GC/MS provided information as to which PAH was present and at what concentration. Incorporation of this tool into a dynamic workplan will provide more data at less cost enabling environmental scientists, engineers, and regulators to better understand coal tar migration and its impact on human health and the environment.

Introduction

The U.S. Environmental Protection Agency (EPA) estimates 45,000 former manufactured gas plants (MGP) need cleanup (1). With remediation costs approaching \$86 million for some MGP sites, site owners must delineate the nature, extent, concentration, direction, and rate of contaminant movement to protect the environment and better manage costs. Coal tar, a dense nonaqueous phase liquid, contains thousands of components that migrate at different rates from source material into aqueous environments making location and

movement difficult to determine. Polycyclic aromatic hydrocarbons (PAH) and their alkylated homologues serve as useful indicators.

Direct push (DP) equipment is a ubiquitous tool for rapidly collecting subsurface samples. Steel rods are pushed or driven into the ground to collect unconsolidated soil, soil gas, sediment, or water. A large variety of attachments are used to collect samples; analyze contaminants in situ; or collect geophysical data that are continuously logged as rods are advanced (2). Obtaining continuous and discrete information about the subsurface is critical to the development of three-dimensional conceptual site models, which are used to illustrate the presence and downward movement of pollutants (3, 4).

Two types of trucks have been employed. The most popular is the Geoprobe, which sits on the back of a pickup truck and hammers rods into the subsurface. In contrast, the cone penetrometer (CP) sits inside a 20–40 ton truck and uses downward hydraulic pressure to push rods into the earth. Although the cone penetrometer costs more to operate than the Geoprobe, it is also used to measure hydraulic conductivity, friction sleeve resistance, and dynamic pore pressure as well as organics and metals in situ (5). More recent developments include laser induced fluorescence (LIF) (6, 7), Raman and infrared (8, 9), and thermal extraction (TE) mass spectrometry (10–12) for organics, and laser induced breakdown (13), gamma (14) and X-ray fluorescence (15) spectroscopy for metals. Electron capture (ECD), flame ionization (FID), and photoionization (PID) detectors have been used with Geoprobe's membrane inlet probe (MIP) and an unheated transfer line to detect volatile organics (16, 17). However, rapid quantitative delineation of VOCs and SVOCs remains a significant challenge (18).

Toward this end, a thermal extraction cone penetrometry (TECP) probe was developed. The TECP was based on a flexible, 280 °C, high temperature transfer line (HTTL) and 400 °C sampling probe. The TECP efficiently extracted analytes, 50–90%, when soil temperatures reached 300 °C and at 45 mL/min carrier gas flow rate (19–21). The transfer line lifetime decreased, however, when the wall coating deactivated as moisture content exceeded 15%. In this study, we combine the HTTL with Geoprobe's membrane in a new sample cell design to speciate PAH in both vadose and saturated conditions.

Our goal was to rapidly profile the subsurface and quantify contaminants in the field. The HTTL-MIP was connected, on the one hand, to a PID and, on the other, to a freeze-trap that condensed vapors for on-site analysis by GC/MS. The PID response and GC/MS results for total PAH produced correlation coefficients of 0.92 and 0.99 for discrete and composite samples, respectively. Field and laboratory GC/MS data were statistically the same when samples were solvent extracted.

Experimental Section

Cone Penetrometry System. The HTTL-MIP was pushed through the earth by Precision Sampling (Lone Tree, CO). Two vertical hydraulic rams advanced the rods at a velocity of 0.75 ft/s. GPS and sensors were used to determine the probe subsurface location. Refusal was sensed by measuring the probe's tip and friction sleeve resistance and dynamic pore pressure. A 1-ft pipe section contained the sampling probe, which was cut to house the heater block into which the MIP was threaded. The membrane was made by infusing stainless steel mesh with a thin film of Teflon polymer, which facilitated the transport of organics while excluding water

* Corresponding author phone: 617-627-3474; fax 617-627-3443; e-mail: arobbat@tufts.edu.

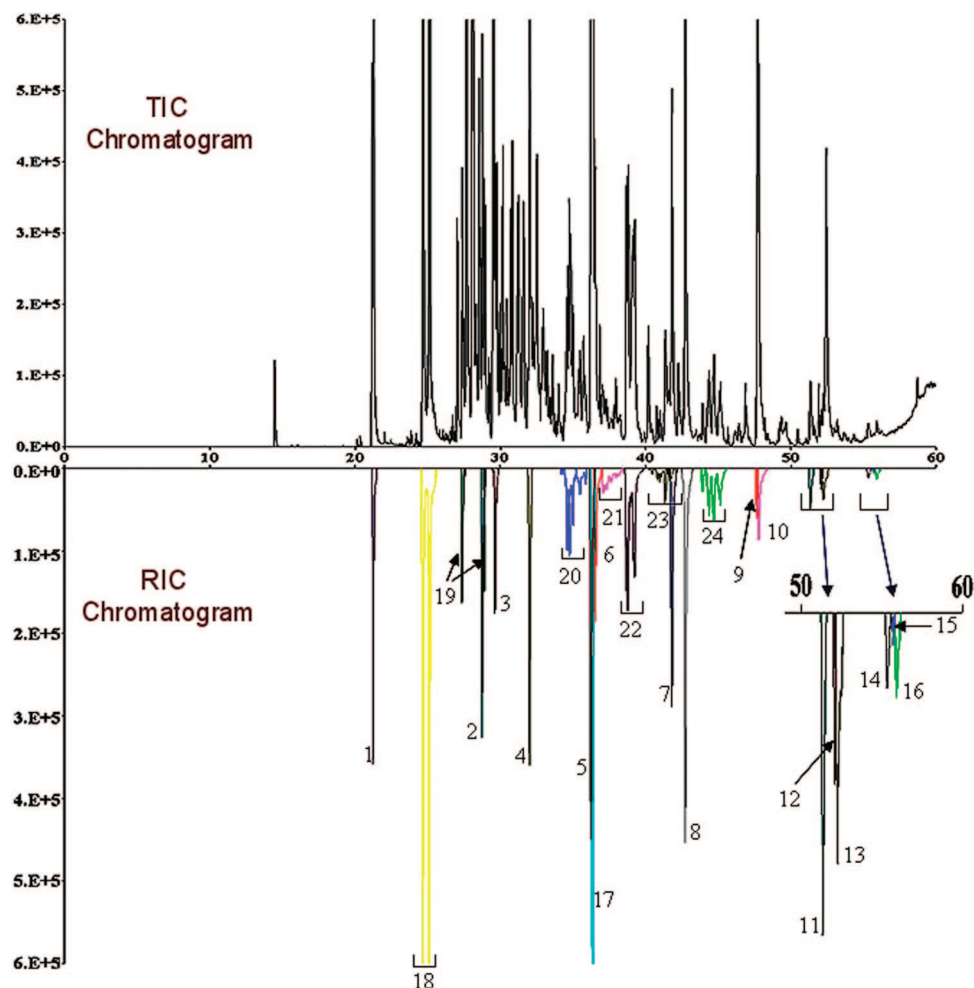


FIGURE 1. Total and reconstructed ion chromatograms for soil sample 2 (10% coal tar) produced by the slower, EPA SW-846 GC/MS 8270C method modified for forensic analysis. Sample extracted with methylene chloride prior to analysis. See Table 1 for compound identity.

from entering the probe. The heated transfer line was woven through a series of 4-ft pipes threaded on each end. It was connected on one end to the MIP and on the other to a 4-port valve housed inside an Agilent GC oven (Santa Clara, CA). The materials used to make the heated transfer line and the thermodynamics that explain heat transfer from the sampling probe to soil have been described previously (20, 21). The electronics used to control temperature and carrier gas flow rate for the HTTL and freeze-trap were designed and built at Tufts University.

Soil-bound organics were desorbed, vaporized, collected, and swept from the MIP through the HTTL to the PID by nitrogen. The PID provided continuous organics detection as the probe was advanced. When PID signals spiked, probe advancement was stopped and the valve switched from the PID to the freeze-trap, see the Supporting Information for schematic. Samples were collected for 5 min in a 78-mm long glass sleeve.

Gas Chromatography/Mass Spectrometry. Once the sample was collected, it was analyzed by thermal desorption (TD, Tufts University) GC/MS by ballistically heating the tube from ambient to 280 °C in seconds. See the Supporting Information for field and laboratory instrument operating conditions, target compound ions, and abundances. Ion Signature Technology (North Smithfield, RI) quantitative deconvolution data analysis software was used to analyze the field and bench data (22–24).

Field Samples. Confirmation samples were collected by Precision Sampling in 4-ft plastic sleeves, homogenized,

cataloged, and sent to Jupiter Laboratory (Jupiter, FL) for analysis. Samples ranged from loose, clean sand to stiff, clayey silt to peat-like bog sediment, with some samples containing visible amounts of an oily tar-like material.

Bench Samples. Three samples from two different MGP sites in North Carolina were used. Soils 1 and 2 came from the same site, whereas soil 3 was obtained from a different site. The first two samples were prepared by manually removing organic debris and adding known amounts of clean, dry sand to make 5 and 10% coal tar mixtures. The third sample contained 100% coal tar. Each sample was homogenized using an electric drill with a metal paint mixer attachment. Silar Services (Blue Bell, PA) prepared the samples and made splits for Tufts and Jupiter to analyze. Tufts prepared samples by weighing 2 g of soil into a 7-mL vial and adding 2 mL of methylene chloride. After shaking for 5 min, the extract was removed and transferred to a 1-mL vial for analysis.

Reagents and Standards. Methylene chloride, HPLC grade (Fisher Scientific, Pittsburgh, PA), was used as received to extract samples. Standard solutions of PAH and phenanthrene-*d*₁₀ (internal standard) were purchased from Supelco (Bellefonte, PA) and used to generate calibration curves for each target compound. PAH response factors were calculated as the ratio of $A_x C_{is} / A_{is} C_x$, where C_x was the amount of target analyte injected and A_x was the observed signal. C_{is} and A_{is} were the corresponding internal standard concentration and signal response. A known amount of internal standard was injected into the glass sleeve prior to analysis.

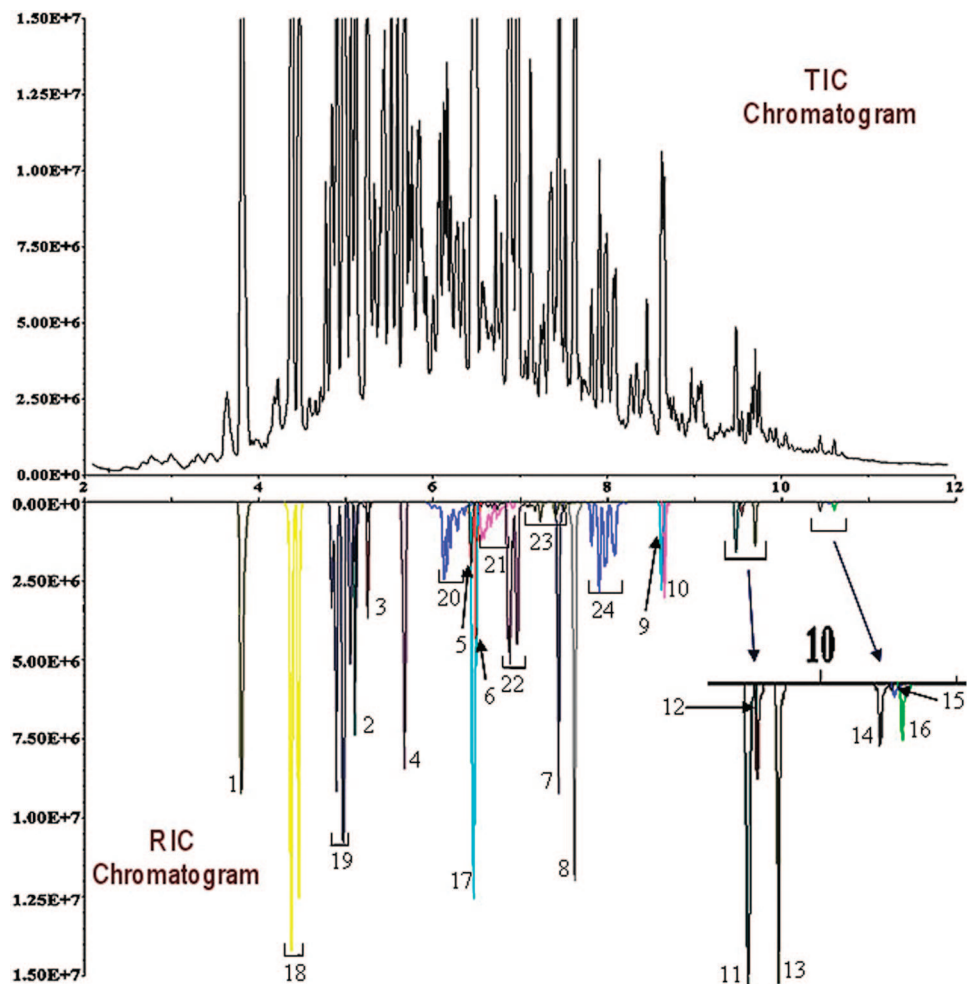


FIGURE 2. Total and reconstructed ion chromatograms for soil sample 2 (10% coal tar) produced by the faster, EPA SW-846 GC/MS 8270C method modified for field analysis. Sample extracted with methylene chloride prior to analysis. See Table 1 for compound identity.

Results and Discussion

Our work focused on answering three specific questions. First, can field GC/MS provide data of comparable quality to EPA method 8270 so as to minimize/eliminate the need for off-site confirmation analysis? Second, how close are GC/MS results when samples are collected by HTTL-MIP and by standard cone penetrometry methods? Third, how well do results compare when organics passing through the HTTL-MIP are analyzed by PID and GC/MS and does the HTTL-MIP *with* online detection provide data quick enough to support on-site decision making? These questions must be answered before regulators and environmental engineers can rely on new technology to assist in determining the nature, extent, direction, concentration, and rate of contaminant movement through the subsurface.

Can Quantitative Field Data of Known Quality Be Produced Fast Enough to Minimize the Number of Off-Site Analyses? Coal tar and two soils fortified with coal tar were extracted and analyzed by modifying the standard EPA SW-846, method 8270C in two ways. First, the GC run-time was slowed to meet the requirements of forensic environmental analyses and second, accelerated to produce much faster analyses. In addition to PAH, alkylated PAH and other biomarkers can be used to assess coal tar degradation over time. Our purpose for comparing these methods was to demonstrate data equivalency. Examples of total ion current (TIC) and reconstructed ion current (RIC) chromatograms are shown in Figures 1 and 2. The large unresolved chro-

matogram in Figure 2 is due to two factors: (1) the independent testing laboratory diluted their sample 100 times, Figure 1, compared to the sample in Figure 2, and (2) by increasing the temperature program rate of the fast method, compounds resolved in the slow run coelute in the fast run.

Table 1 shows the data for precision and accuracy. The average precision for the faster analysis is 19% for all target compounds across all samples, with the average %RSD for PAH at 18% and alkylated PAH at 20%. This is well within the 50% benchmark EPA set for soils. The measurement accuracy criterion is contingent on site-specific action levels outlined in the agency's Soil Screening Guidance Document. Action levels (AL) are based on establishing cleanup goals that meet one of two dilution attenuation factors (DAF). 20DAF is based on reductions in contaminant concentrations that occur due to natural processes in the subsurface as pollutants travel to clean waterbodies. 1DAF is used for sites characterized by shallow water tables, fractured media, karst topography, or source sizes greater than 30 acres.

If the most stringent criteria is assumed, the quantitation limit (QL) will be one-half the site-specific AL (concentrations considered protective of human health and the environment), which is 1 DAF. The AL and QL for each PAH are listed in the Supporting Information. Therefore, measurement accuracy is based on each target compound's quantitation limit. For example, when measured concentrations are greater than

TABLE 1. Laboratory vs Field GC/MS, Concentration in mg/kg^a

number	compounds	soil 1 (5% coal tar)			soil 2 (10% coal tar)			soil 3 (100% coal tar)		
		laboratory	field (%RSD)	RPD	laboratory	field (%RSD)	RPD	laboratory	field (% RSD)	RPD
1	naphthalene	297	304 (10)	-2	274	266 (5)	3	22,974	16,347 (20)	34
2	acenaphthylene	57	89 (8)	-44	83	101 (5)	-20	4440	3626 (15)	20
3	acenaphthene	32	42 (11)	-27	38	45 (6)	-17	1264	1619 (29)	-25
4	fluorene	94	123 (11)	-27	118	141 (5)	-18	3942	5261 (22)	-29
5	phenanthrene	252	208 (9)	19	339	247 (1)	31	8236	6749 (20)	20
6	anthracene	75	61 (14)	21	80	73 (14)	9	2525	2985 (24)	-17
7	fluoranthene	62	40 (17)	43	103	143 (1)	-32	2361	3758 (26)	-46
8	pyrene	150	137 (12)	9	192	156 (3)	21	3484	4912 (28)	-34
9	benzo[a]anthracene	22	16 (16)	32	31	19 (18)	48	1253	759 (33)	49
10	chrysene	53	52 (16)	2	54	60 (11)	-10	2719	3109 (37)	-13
11	benzo[b]fluoranthene	46	56 (3)	-20	51	74 (17)	-37	1398	1979 (55)	-34
12	benzo[k]fluoranthene	12	11 (2)	8	15	13 (16)	14	638	621 (55)	3
13	benzo[a]pyrene	43	44 (4)	2	53	61 (15)	-14	1749	1719 (54)	2
14	indeno[1,2,3-d]pyrene	14	17 (8)	-19	27	29 (13)	-7	525	453 (52)	15
15	dibenz[a,h]anthracene	1	2 (6)	-50	3	4 (17)	-25	146	169 (47)	-15
16	benzo[g,h,i]perylene	16	22 (13)	-32	24	35 (18)	-37	386	514 (44)	-28
18	C ₁ -naphthalenes	375	363 (8)	3	715	403 (5)	56	24,122	12,151 (14)	66
19	C ₂ -naphthalenes	623	582 (12)	7	882	681 (11)	26	15,215	14,059 (28)	8
20	C ₁ -fluorenes	105	220 (15)	-71	152	266 (19)	-54	5687	11,313 (39)	-66
21	C ₂ -fluorenes	35	58 (15)	-50	62	72 (19)	-15	2202	3363 (38)	-42
22	C ₁ -phenanthrenes	301	284 (17)	6	409	364 (9)	12	15,692	15,218 (32)	3
23	C ₂ -phenanthrenes	65	134 (18)	-69	71	162 (16)	-78	6262	11,341 (35)	-58
24	C ₁ -fluoranthenes	168	256 (17)	-42	254	304 (16)	-18	11,865	18,131 (37)	-42

^a All samples extracted with methylene chloride. Methods made by modifying EPA method SW-846, 8270C. Lab, 60-min forensic analysis; Field, 12-min analysis. The % RSD for the 12-min method is based on three replicate analyses. RPD = 100 ((60-min - 12-min)/0.5 (60-min + 12-min)). Compound 17 is phenanthrene-d10.

five times the QL, the RPD should be <60% and when concentrations are less, the RPD should be <100%.

The average fast vs slow relative percent difference (RPD) for all PAH in all samples is 23%, with none above 50%, well within EPA's criteria for accuracy. Although no soil screening DAF information is available for alkylated PAH, all measurements produced RPDs < 80%, with the average RPD 38%. Quantitation of alkylated PAH is highly dependent on correctly identifying family members. Because isomers with different fragmentation patterns exist within homologous families of alkylated PAH, relying solely on a single ion from full scan or selected ion monitoring (SIM) data to quantify these compounds results in misestimating the concentration, especially in complex samples. This issue will be addressed in an upcoming paper. Results from Table 1 show that when soil samples are extracted and analyzed by GC/MS at speeds fast enough to confirm soil screening results, the data meet EPA's criteria for precision and accuracy and can be used in place of laboratory analyses.

How Similar are HTTL-MIP and Conventional Cone Penetrometry Collected Samples When Analyzed by GC/MS? Figure 3 shows TIC and RIC chromatograms for the 10% coal tar sample extracted by the HTTL-MIP. Solvent versus thermally extracted samples produced signals that differed by ~10³ TIC and 10² RIC. Also missing was the unresolved chromatogram, see Figure 2 for comparison. These differences are due to low thermal desorption temperatures and the Teflon membrane, which excluded highly polar and aliphatic compounds from entering the probe; making MS interpretation easier for those that did.

Overall, the average RSD was 46% for the 5, 10, and 100% coal tar samples, with PAH and alkylated PAH at 44% and 49%, respectively, see Table 2. Although the HTTL-MIP measurement precision was somewhat poorer compared to solvent extraction, the data were within EPA requirements. In contrast, the average RPD between the HTTL-MIP and solvent extracted samples was 133, 135, and 147%, respectively. As PAH concentration increased, measurement ac-

curacy decreased. Excluding the 100% coal tar sample, the average HTTL-MIP percent recovery for all analytes was 20 ± 13%.

Collection efficiency was limited by the probe's ability to rapidly and efficiently transfer heat to soil at the soil/membrane interface. When the probe was set to 130 °C, soil temperatures reached 110, 104, and 96 °C after 5 min at 1, 2, and 3 mm from the collection window. From this we estimated soil weight to be 0.285 g. Although these findings did not fall within EPA's accuracy benchmark, results can be attributed to limitations in the imposed heat transfer and collection time. For example, as sampling times increased so did accuracy. The 5-min collection period was a reasonable compromise between sample collection speed and data quality needed to confirm PID responses.

Can the Combination of PID and GC/MS with HTTL-MIP Sample Collection Provide Data Quick Enough and with Sufficient Quality to Investigate Pollutants in the Subsurface? The relationship between the direct measuring, real-time PID response was compared against GC/MS data for samples collected by the HTTL-MIP at the exact same location. Table 3 lists the below surface sample depths for each boring, their corresponding PID values, and total PAH as measured by the field and off-site laboratories. At each new boring the membrane was pushed ~0.2 in. below surface. The PID signal was recorded and subtracted from each subsequent PID reading as the probe was advanced into the subsurface. The adjusted negative PID response shown in Boring 1 signifies the absence of organics at that depth. In contrast, the magnitude of the adjusted positive values denotes relative amounts of organics at specific locations. All field results are based on discrete samples collected at known depths; see Boring 4, 8.45 ft, PID = 5,634,616, total PAH = 361 mg/kg. Also shown are the average calculated concentrations, e.g., 8.45-12.05 ft, PID 4,536,691, total PAH 266 mg/kg, based on the same approximate depth as the laboratory sample, e.g., 8.4-12 ft, 1,494 mg/kg. Note: all laboratory samples are composites and were collected <2 ft

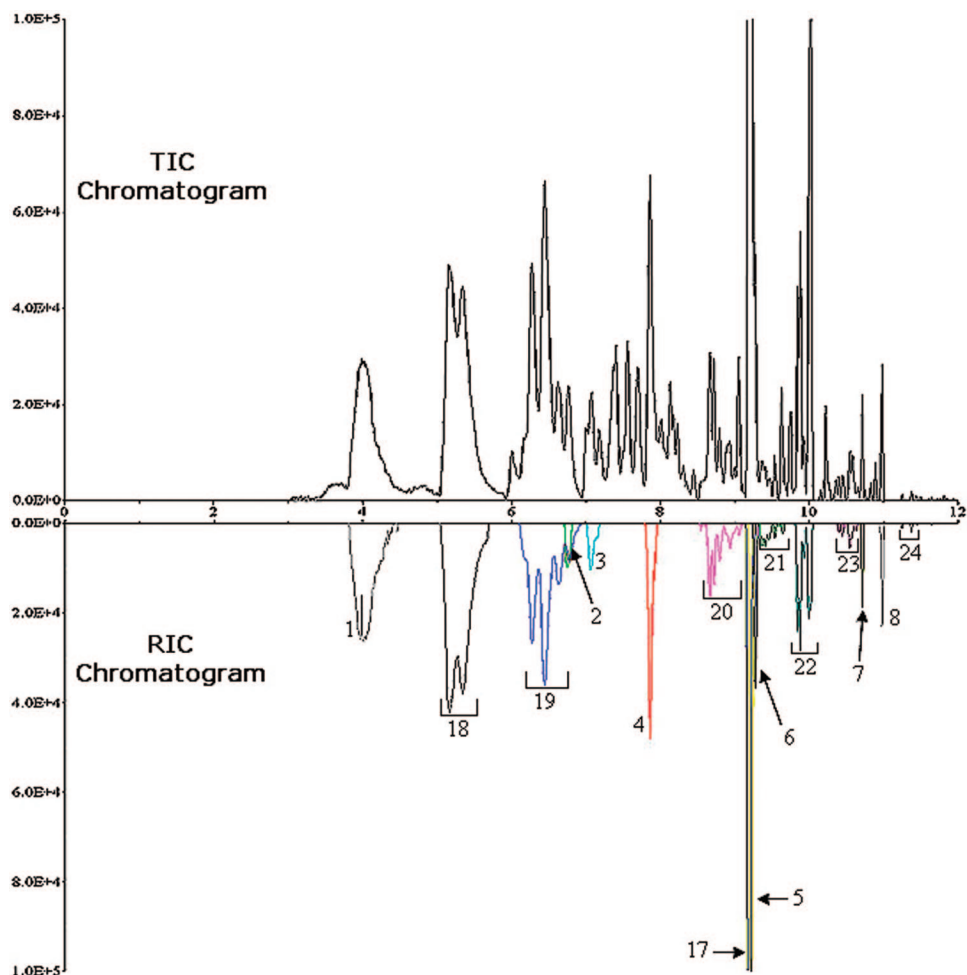


FIGURE 3. Total and reconstructed ion chromatograms for soil sample 2 (10% coal tar) produced by the faster, EPA SW-846 GC/MS 8270C method modified for field analysis. Sample extracted by probe prior to analysis. See Table 1 for compound identity.

TABLE 2. Solvent vs Thermal Extraction, Concentration in mg/kg^a

compounds	soil 1 (5% coal tar)				soil 2 (10% coal tar)				soil 3 (100% coal tar)			
	laboratory	field (n = 3) ave. (% RSD)	% rec.	RPD	Laboratory	field (n = 3) ave. (% RSD)	% rec.	RPD	laboratory	field (n = 3) ave. (% RSD)	% rec.	RPD
naphthalene	297	45 (6)	15	147	274	77 (57)	28	112	27055	7,661 (21)	28	112
acenaphthylene	57	20 (30)	35	97	83	11 (46)	13	153	4440	437 (22)	10	164
acenaphthene	32	13 (79)	41	86	38	8 (41)	21	130	1264	152 (18)	12	157
fluorene	94	42 (71)	45	76	118	26 (27)	22	128	3942	322 (15)	8	170
phenanthrene	252	70 (56)	28	113	339	67 (44)	20	134	8236	391 (43)	5	182
anthracene	75	13 (73)	17	141	80	13 (29)	16	146	2525	92 (56)	4	186
fluoranthene	62	3 (78)	5	184	103	7 (37)	7	174	2,361	53 (54)	2	191
pyrene	150	3 (61)	2	193	192	8 (38)	4	184	3484	62 (50)	2	193
total nonalkylated PAH	1019	209 (57)	20	132	1,227	217 (40)	18	140	53,307	9170 (35)	17	141
C ₁ -naphthalenes	375	113 (32)	30	107	715	236 (45)	33	101	24122	8384 (25)	35	97
C ₂ -naphthalenes	623	149 (54)	24	123	882	175 (45)	20	134	15215	2004 (28)	13	153
C ₁ -fluorenes	105	45 (80)	43	80	152	34 (35)	22	127	5687	255 (38)	4	183
C ₂ -fluorenes	35	4 (42)	11	159	62	12 (41)	19	135	2202	93 (58)	4	184
C ₁ -phenanthrenes	301	22 (37)	7	173	409	43 (34)	10	162	15692	359 (64)	2	191
C ₂ -phenanthrenes	65	0.4 (95)	1	198	71	8 (35)	11	159	6262	103 (76)	2	194
C ₁ -fluoranthenes	168	ND			254	2 (56)	1	197	11865	38 (59)	0.3	199
total alkylated PAH	1672	333 (57)	20	134	2545	510 (42)	20	133	81045	11236 (50)	14	151
total PAH	2691	542 (57)	20	133	3772	727 (41)	19	135	134352	20406 (42)	15	147

^a Field samples extracted by HTTL-MIP, operating conditions: flow rate = 36 mL/min, probe = 130 °C, collection time = 5 min, freeze-trap = -18 °C. Lab samples extracted by methylene chloride. All samples analyzed by GC/MS. % Rec, recovery = (field/lab × 100). RPD, accuracy = 100 ((Lab - Field)/0.5 (lab + field)). ND, non-detect.

TABLE 3. Total PAH for Borings 1–5, Concentration in mg/kg^a

location	depth, ft	PID	field (% RSD)	laboratory (% RPD)	depth, ft	field vs laboratory, % rec.
boring 1	2.00	-58,383				
	2.60	-38,847				
	3.10	-38,847				
	3.60	-38,847				
	4.20	-19,311				
	5.30	-19,311				
	5.35	136,977	3	190	4 to 5	2
	9.25	234,657	8	112	8 to 9	7
	15.10	1,250,530	70	1,010	15 to 16	7
	17.40	1,973,362	96			
boring 2	17.35	424,786	73			
	17.65	92,674	38			
	17.95	112,210	21			
	ave, n = 3	209,890	44 (60)	179 (41)	17 to 18	25
	19.05	1,850,916	18			
boring 3	12.05	1,524,579	84			
	12.65	821,282	37			
	13.65	821,282	12			
	14.25	547,778	9			
	14.65	352,418	8			
	15.25	450,098	14			
	ave, n = 4	542,894	11 (26)	454	13 to 16	3
boring 4	4.35	14,054,640	1,303			
	4.85	15,715,202	2,074			
	ave, n = 2	14,884,921	1,688	28,789	4 to 5	6
	5.35	7,588,217	224			
	6.00	3,974,054	448			
	8.45	5,634,616	361			
	9.05	4,462,454	427			
	10.05	5,712,760	246			
	11.05	2,626,068	117			
	12.05	4,247,558	178			
	ave, n = 5	4,536,691	266 (45)	1,494 (2)	8.4 to 12	18
	13.05	2,626,068	141			
	14.15	2,665,140	129			
	14.85	516,178	101			
ave, n = 3	1,935,795	124 (17)	268 (6)	13 to 14.9	46	
boring 5	22.00	255,714	5	NA	NA	
	23.00	3,518,230	151			
	28.35	3,283,797	380			

^a NA, samples not analyzed. % RSD, precision is based on the average concentration of discrete samples measured over the distance specified. % RPD, precision is based on the analysis of blind duplicates sent to lab, n = 2. % Rec, accuracy = (field/lab × 100). Negative PID signals indicate the absence of organics in the sample after background subtraction. Data are only shown for Boring 1, but were collected for all borings.

from corresponding HTTL-MIP samples. Soils between 4 and 16 ft and 23 and 28 ft contained <15% water. Saturated samples were 16 to 23 ft below grade.

A correlation coefficient of 0.92 was obtained between the PID and field GC/MS data; n = 29 discrete samples. When PID response was compared against samples where laboratory data was available, n = 8, the correlation coefficient was a remarkable 0.99 for field GC/MS and 0.97 for laboratory GC/MS. Five of the eight data points are based on the average PID and average field GC/MS responses, see borings 2–4. In no instance did the PID produce a positive signal, with no PAH detected by GC/MS (false positives). Similarly, no measurements were made where the adjusted PID was negative and PAH were detected (false negatives). Results indicate the PID can be relied upon to signal the presence/absence of PAH. When field and laboratory GC/MS results are compared the correlation coefficient was 0.993, which is

extraordinary given the significant differences in sample location, collection, preparation, and analysis.

PAH measurement precision by the laboratory was excellent, <10% RPD, for the two soil samples analyzed as blind duplicates (boring 4), while the high water content sample (boring 2) yielded an RPD of 41%. Individual PAH averaged 15% RPD for all samples. In contrast, the average total PAH precision was 29% for the field GC/MS, with 60% RSD for the saturated sample. Individual PAH precision averaged 49% for all samples. Both the laboratory and field GC/MS meet EPA's precision criteria. The latter is notable; especially when one considers that the field data are based on 3–5 distinctly different, discrete sample locations as compared to the single homogenized, composite sample analyzed by the laboratory.

PAH recoveries as a function of sample collection are shown in Tables 3 and 4. The average percent recovery for

TABLE 4. PAH Results for Boring 4, Concentration in mg/kg^a

	laboratory		% rec.	RPD	laboratory (n = 2)		field (n = 5)		laboratory (n = 2)		field (n = 3)		% rec.	RPD
	laboratory (4–5 ft)	field 4.85 ft			8.4–12 ft (% RPD)	8.45–12.05 ft (% RSD)	13–14.9 ft (% RPD)	13.05–14.85 ft (% RSD)						
naphthalene	6,927	100	1	194	197 (9%)	0.1 (89%)	0.1	200	39 (14%)	0.02	0.1	200		
acenaphthylene	868	62	7	173	28 (1%)	5 (98%)	18	139	4 (4%)	1 (88%)	25	120		
acenaphthene	1,096	224	20	132	80 (0%)	18 (87%)	22	126	16 (4%)	3 (103%)	19	137		
fluorene	1,089	188	17	141	61 (1%)	35 (60%)	57	54	11 (3%)	8 (49%)	73	32		
phenanthrene	3,004	154	5	180	159 (0%)	79 (37%)	50	67	30 (4%)	52 (16%)	173	-54		
anthracene	781	32	4	184	43 (0%)	16 (53%)	37	92	8 (5%)	8 (19%)	100	0		
fluoranthene	1,049	6	1	198	51 (0%)	7 (45%)	14	152	8 (3%)	5 (16%)	62	46		
pyrene	1,626	6	0.4	198	79 (3%)	8 (45%)	10	163	11 (3%)	5 (12%)	24	75		
benzo(a)anthracene	477	0.3	0.1	200	22 (1%)	1 (41%)	4	183	3 (9%)	0.5 (11%)	12	143		
chrysene	421	0.2	0.05	200	19 (2%)	1 (50%)	5	180	2 (4%)	0.4 (10%)	13	133		
C ₁ -naphthalenes	4,878	1,169	24	123	312 (0%)	11 (79%)	4	186	65 (5%)	0.3	0.2	198		
C ₁ -fluorenes	1,123	105	9	166	101 (2%)	56 (51%)	55	57	16 (1%)	24 (9%)	133	-40		
C ₁ -phenanthrenes	3,221	24	1	197	217 (3%)	23 (52%)	11	162	39 (5%)	13 (10%)	20	100		
C ₁ -fluoranthenes	2,229	3	0.1	199	125 (0%)	6 (42%)	5	182	16 (8%)	4 (12%)	15	120		

^a Field samples collected by HTTL-MIP, operating conditions: flow rate = 65 ml/min, probe = 120 °C, collection time = 5 min. Freeze-trap = -5 °C. All field samples are discrete. Samples collected by conventional cone penetrometry. All lab samples are composites. % rec, accuracy = (field/lab × 100). RPD, accuracy = 100 ((Lab - Field)/0.5 (Lab + Field)). The absence of % RSD indicates analyte found in one of three sample measurements.

PAH and alkylated PAH by HTTL-MIP was 17 and 11%, respectively. These findings are somewhat poorer than bench study results, which were 20% for all analytes for the 5 and 10% coal tar samples. Lower than expected concentrations of naphthalene, acenaphthylene, and acenaphthalene were found. We attribute this loss to an inadvertent increase in carrier gas flow rate (from 36 to 65 mL/min) and warmer (-5 °C vs -18 °C) freeze-trap due to outdoor (37 °C) versus indoor (22 °C) temperatures. The confluence of these events resulted in volatile analyte breakthrough. On the other hand, higher recoveries were obtained in the field for fluorene, phenanthrene, anthracene, and C₁-fluorenes. Small amounts of benzo(a)anthracene and chrysene, not seen in the bench study, also passed through the membrane; presumably due to increased pressures at the soil/membrane interface.

Previous TECP work produced PAH recoveries between 16 and 74%, with an average recovery of 51 ± 21%. In that work, the probe was heated to 450 °C and soil temperatures reached 350 °C at 1 mm and 265 °C at 2 mm from the probe. Soil temperatures at the same distance from the HTTL-MIP were on average 2.8 times lower than the TECP. If the TECP percent recovery range is divided by 2.8, the HTTL-MIP recoveries fall within the adjusted range of 14–22% for bench and field data.

Comparison of field versus laboratory data as evidenced by the high RPDs in Table 4 do not fall within EPA's accuracy criteria based on each compound's action level. Nonetheless, our findings substantiate the HTTL-MIP, with PID and GC/MS detection, as valuable tools to rapidly characterize hazardous waste sites.

Based on the objectives outlined in this paper, the heated transfer line, sampling probe, and detectors proved to be rugged and field-ready. PAH and their alkylated analogs were extracted from soil at depths of up to 28 m despite limitations in the applied temperature. Work is in progress to find new membrane materials to obviate this problem. Although our overall goal is to develop a probe that can detect PAH in all media by changing the membrane temperature, it is unlikely higher probe temperatures will improve recoveries at soil/sediment water interfaces. Future research will address how mixed media might benefit from energized environments. Because the transfer line was maintained at 280 °C, little to no sample carryover was observed. Data from the PID and GC/MS were highly correlated substantiating the use of the probe as a profiling tool. Importantly, online PID detection

provides continuous evidence as to PAH presence/absence and helps to identify soil channels containing coal tar from source materials. In contrast, coal tar channels can only be found in traditional investigations by collecting continuous core samples to refusal and sending them off-site for analysis; a slow, inefficient, and costly proposition. The PID in combination with GC/MS can provide the detail needed in conceptual models to lead investigators into driving the probe into DNAPL plumes; an incredibly difficult proposition by any other means. For example, by following PAH it should be possible to find contaminant entry ways into groundwater. Finally, we showed field and laboratory data are statistically equivalent, with rates much faster than standard EPA methods can produce. Because the membrane probe produced lower PAH recoveries than the TECP, additional onsite confirmation analyses are needed to calibrate probe data. By combining data from direct sensing, in situ, and traditionally collected samples risk to human health and the environment is better gauged when assessing land usage proposals.

Acknowledgments

We greatly appreciate the encouragement and assistance of Andrew J. Coleman of the Electric Power Research Institute for funding; Brian Sladky of Silar Services for coordinating the bench and field activities and for obtaining permission to work at an MGP site; as well as Alex Nedolishny and Michael Claycomb of Precision Sampling for their cone penetrometry work. This project was made possible by the willingness of the utility and state regulator to test our technology on their property and to collect samples for confirmation analysis.

Supporting Information Available

HTTL-MIP schematic (Figure S1); gas chromatography/mass spectrometry conditions for field and laboratory analyses (Table S1); PAH main, qualifier ions and abundances (Table S2); and action levels and quantitation limits for each target compound (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- 1) *Cleaning up the Nation's Waste Sites: Markets and Technology Trends, September 2004*; United States Environmental Protection Agency: Washington, DC, 2004.

- (2) Kram, M. L.; Keller, A. A.; Rossabi, J.; Everett, L. G. DNAPL characterization methods and approaches, Part 1: performance comparisons. *Ground Water Monit. Rem.* **2001**, 109–123. Fall.
- (3) Robbat, A., Jr.; Smarason, S.; Gankin, Y. V. Dynamic work plans and field analytics, the keys to cost-effective hazardous waste site investigations. *Field Anal. Chem. Technol.* **1998**, 2, 253–265.
- (4) Simpson, R. L., III; Bock, C. L.; Robbat, A., Jr. Dynamic workplans and field analytics: Metals assessment by inductively coupled plasma/optical emission spectroscopy. *Remediation* **1999**, 9(4), 65–78.
- (5) Adstadt, J. H.; Martin, A. F. Analytical chemistry and the cone penetrometer: In situ chemical characterization of the subsurface. *Mikrochim. Acta* **1997**, 127, 1–18.
- (6) Robbat, A., Jr.; Kenny, J. E.; Smarason, S.; Pepper, J. W.; Wright, A. O. Laser-induced fluorescence and fast gas chromatography/mass spectrometry with subsurface thermal extraction of organics: Field analytical technologies for expediting site characterization and cleanup. *Remediation* **1998**, 9, 95–111.
- (7) Kram, M. L.; Keller, A. A.; Massick, S. M.; Laverman, L. E. Complex NAPL site characterization using fluorescence Part I: Selection of excitation wavelength based on NAPL composition. *Soil Sediment Contam.* **2004**, 13, 103–118.
- (8) Rossabi, J.; Riha, B. D.; Haas, J.; Eddy-Dilek, C. A.; Lustig, A.; Carrabba, M.; Hyde, K.; Belo, J. Cone penetrometer-based raman spectroscopy for NAPL characterization in the vadose zone. *Vadose Zone Sci. Technol. Solutions* **2000**, 1, 431–444.
- (9) Garcia-Gomez, R. S.; Pandiyan, T.; Aguilar-Iris, V. E.; Luna-Pabello, V.; Duran de Bazua, C. Spectroscopic determination of poly-aromatic compounds in petroleum contaminated soils. *Water, Air, Soil Pollut.* **2004**, 158, 137–151.
- (10) Myers, K. F.; Karn, R. A.; Eng, D. Y.; Hewitt, A. D.; Strong, A. B.; Brannon, J. M. In situ thermal desorption of VOCs in vadose zone soils. *Field Anal. Chem. Technol.* **1998**, 2, 117–125.
- (11) Robbat, A., Jr. Environmental applications of thermal extraction cone penetrometry and ultrafast gas chromatography/mass spectrometry. *Field Anal. Chem. Technol.* **2001**, 5, 60–68.
- (12) Davis, W. M.; Wise, M. B.; Furey, J. S.; Thompson, C. V. Rapid detection of volatile organic compounds in groundwater by in situ purge and direct-sampling ion-trap mass spectrometry. *Field Anal. Chem. Technol.* **1998**, 2, 89–96.
- (13) Miles, B.; Cortes, J. Subsurface heavy-metal detection with the use of a laser-induced breakdown spectroscopy (LIBS) penetrometer system. *Field Anal. Chem. Technol.* **1998**, 2, 75–87.
- (14) Palmer, R. L.; Tepper, G. C. Development of a high-pressure xenon ionization chamber gamma-ray spectrometer for field deployment in cone penetrometers. *J. Radioanal. Nucl. Chem.* **2001**, 248, 289–294.
- (15) Elam, W. T.; Adams, J. W.; Hudson, K. R.; McDonald, B. J.; Gilfrich, J. V.; Galambos, J. In situ environmental XRF. *Adv. X-ray Anal.* **2000**, 42, 137–145.
- (16) Griffin, T. W.; Watson, K. W. A comparison of field techniques for confirming dense nonaqueous phase liquids. *Ground Water Monit. Remediat.* **2002**, 48–59. Spring.
- (17) McAndrews, B.; Heinze, K.; DiGiuseppe, W. Defining TCE plume source areas using the membrane interface probe (MIP). *Soil Sediment Contam.* **2003**, 12 (6), 799–813.
- (18) *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, March 2001*; United States Environmental Protection Agency: Washington, DC, 2001.
- (19) Gorshteyn, A.; Robbat, A., Jr. Rapid in situ collection and analysis of semivolatile organics by thermal extraction cone penetrometry gas chromatography/mass spectrometry. *Field Anal. Chem. Technol.* **2000**, 4, 85–92.
- (20) Gorshteyn, A.; Smarason, S.; Robbat, A., Jr. Speciation of subsurface contaminants by cone penetrometry gas chromatography/mass spectrometry. *Environ. Sci. Technol.* **1999**, 33, 2474–2480.
- (21) Gorshteyn, A. Y.; Kataenko, Z.; Smarason, S.; Robbat, A., Jr. Subsurface detection of environmental pollutants. *Instrum. Sci. Technol.* **1999**, 27, 111–121.
- (22) Gankin, Y. V.; Gorshteyn, A.; Smarason, S.; Robbat, A., Jr. Time-condensed analyses by mass spectrometry. *Anal. Chem.* **1998**, 70, 1655–1663.
- (23) Robbat, A., Jr.; Smarason, S.; Gankin, Y. V. Fast gas chromatography/mass spectrometry analysis in support of risk-based decisions. *Field Anal. Chem. Technol.* **1999**, 3, 55–66.
- (24) Mac Namera, K.; Howell, J.; Huang, Y.; Robbat, A., Jr. Analysis of gin essential oil mixtures by multidimensional and one-dimensional gas chromatography/mass spectrometry with spectral deconvolution. *J. Chromatogr., A* **2007**, 1164, 281–290.

ES702252Q