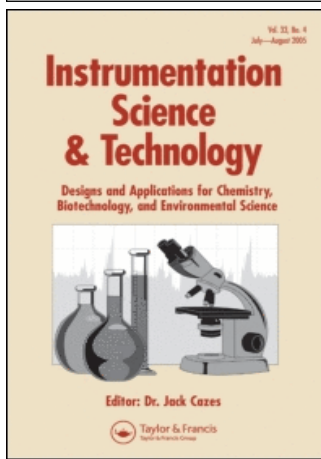


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SUBSURFACE DETECTION OF ENVIRONMENTAL POLLUTANTS

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ABSTRACT

The design of an in situ sampling device capable of thermally desorbing organics bound to subsurface soils at depths of up to 20 meters is described. The system consists of a heated transfer line and sampling probe that is hydraulically pushed to depth by a cone penetrometer. Results are presented illustrating the thermal extraction efficiency for polycyclic aromatic hydrocarbons (PAHs). Field tests were conducted under real-world conditions at a vehicle maintenance facility where 50 gal drums of petroleum by-products had been buried. PAH data were collected demonstrating the depth profiling features of the tool.

INTRODUCTION

Estimates made by the U. S. Environmental Protection Agency suggests that hazardous waste site cleanup costs will exceed \$300 billion over the next ten years,¹ while Russel and coworkers² have projected cleanup costs to be between \$480 billion and \$1 trillion through the year 2020. The following questions can be posed: Do inadequate site investigations contribute to these staggering costs? Can field-based analytical instrumentation and methods provide on-site project engineers with the data of sufficient quality to better delineate site contamination and thus, provide a better understanding of site conditions?

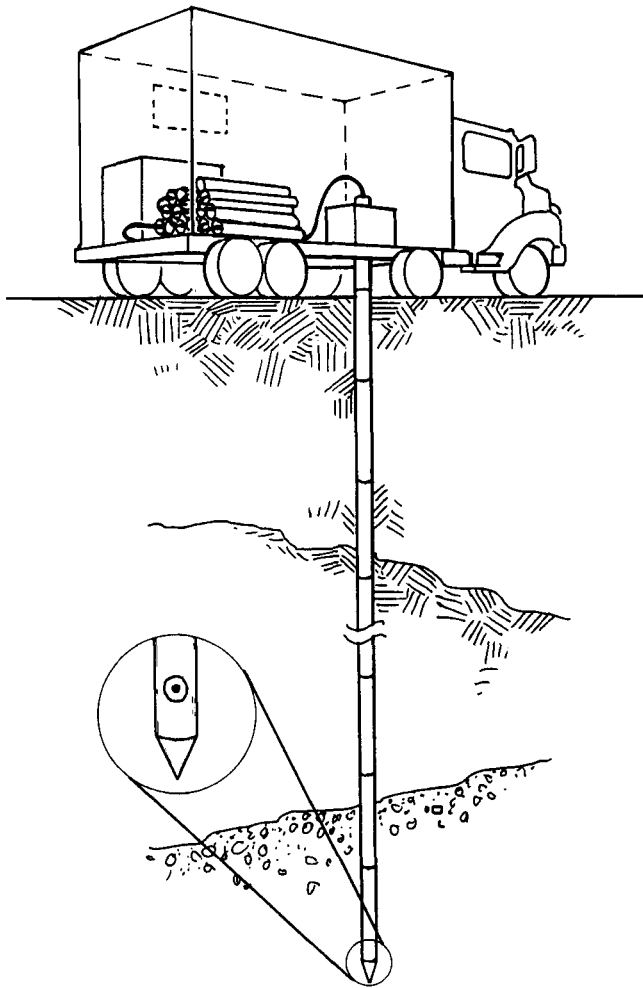


Figure 1. Thermal extraction cone penetrometer (TECP) sampling probe and truck.

Toward this end, we have developed technology and methods that produce quantitative analysis of environmental contaminants in minutes by thermal desorption gas chromatography/mass spectrometry (TDGC/MS). The analysis is based on a ballistically heated thermal desorber to achieve large volume sample introduction and mass spectral data analysis algorithms that can “look through” complex matrix signals to identify and quantify target compounds.³ The TDGC/MS when used in a dynamic work plan framework provides data fast enough to influence the on-site decision making process.⁴ We have shown that on-site chemical analyses employing dynamic work plans can reduce the time and cost of hazardous waste site investigations.⁵

Cone Penetrometer (CP) systems can collect samples at much faster rates than can traditional drilling rigs. Figure 1 depicts the sampling probe used to collect subsurface soil and water samples. Typically, 5 cm o.d. pipes are threaded together and pushed

underground by truck weights of up to 40 tons. The challenge, therefore, is to design 1) a flexible heated, 300°C, transfer line that can be woven through the pipe and 2) a programmable thermal extraction sample collection probe that can heat the soil to at least 350°C. These target temperatures are based on past studies aimed at developing direct measuring thermal desorption gas chromatography sample introduction system.⁶⁻¹⁰ In this paper, we describe the design of a thermal extraction cone penetrometer (TECP) system for subsurface sampling of soil-bound organics from depths of up to 25 m.

EXPERIMENTAL

Heated Transfer Line

The materials used to fabricate the heated transfer line include: deactivated fused silica lined stainless steel tubing 30 m x 1 mm, i.d. 0.76 mm Silcosteel[®] (Restec Corp., Bellefonte, PA); Nextel 312 thermal insulation sleeving and Viton shrinkable tubing (Omega, Stamford, CT); heat shrinkable Teflon tubing (Patriot Plastics, Woburn, MA); aluminum foil with silicon adhesive backing ((Fisher Scientific, Pittsburgh, PA); polyimide moisture insulation tape (Newark Electronics, Chicago, IL); thermal insulated fiber glass cloth tape (Fisher Scientific). The heated transfer line is heated by connecting high temperature power lead wires (Newark Electronics) to both ends of the Silcosteel[®] tube. Temperature was measured using thermocouples C01-K and C02-K (Omega).

Heated Probe

The probe was made from a 1 m x 4.5 cm, 2.5 cm i.d., threaded steel pipe. A 20 mm i.d. hole was cut in the pipe at one-third the distance from the bottom. The heat was supplied by inserting an aluminum casing into the pipe, which contained a 10 cm x 1.5 cm heating cartridge L4A712, 240V/1000W. The same model thermocouples used to measure the transfer line temperature were used in the probe.

Equipment

The Silcosteel[®] was heated by passing current through the tube using an electrical isolation step-up transformer (Grainger, Haverhill, MA) with power and temperature controllers model DCIP-50245-F00 and model 988A-10FD-AARG, respectively (Watlow, St. Lois, MO).

A Hewlett Packard (Palo Alto, CA) model 5972 mass spectrometer was ruggedized for the field and used in combination with a Tufts University (Medford, MA) designed thermal desorption gas chromatograph.

Chemicals

A standard solution of polycyclic aromatic hydrocarbons was purchased from Ultra Scientific (North Kingston, RI). Methylene chloride and sodium sulfate were obtained from Fisher Scientific and used as received.

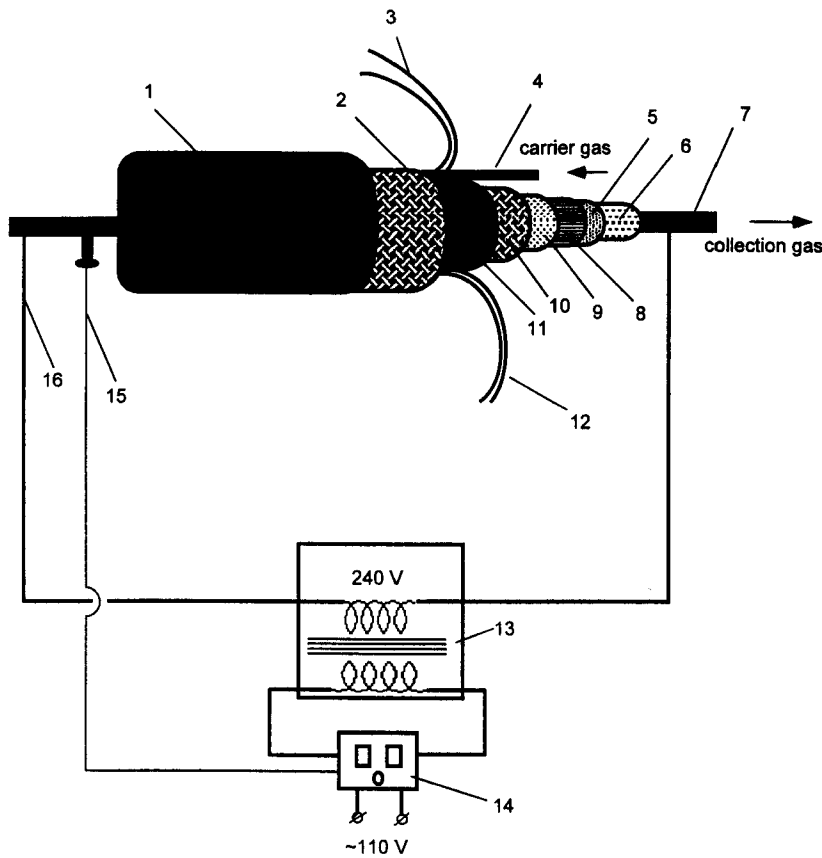


Figure 2. Materials and electrical circuitry for the heated transfer line: 1) heat shrink polyolefin sleeve, 2) fiber glass cloth tape, 3) high temperature power lead electrical wire, 4) Viton tube, 5) heat shrinkable Teflon tube, 6) Nextel 312 thermal insulation sleeving, 7) Silcosteel[®] tube, 8) aluminum foil silicon adhesive backing, 9) polyimide tape, 10) fiber glass cloth tape, 11) high temperature silicon tape, 12) probe thermocouple wire, 13) isolation transformer, 14) power and temperature controller, 15) thermocouple, 16) high temperature power lead electrical wires.

Thermal Extraction Cone Penetrometer Probe System

Figure 2 depicts the schematic of the heated transfer line and the electronic circuitry (13, 14) used to control the power and temperature. The figure shows the various layers within the transfer line including the moisture (1, 5, 9), electrical (5, 6, 9, 11), and thermal (2, 6, 8, 10) insulation sleeves, as well as the fused silica coated stainless steel tube known as Silcosteel[®].

The goal was to heat the transfer line to 300 °C and achieve a 15 cm bend radius so that the pipes in the truck can be stacked efficiently. This feature is important since cone penetrometer systems can reach subsurface depths of up to 60 m when the geology is amenable. The transfer line in this example would need to be woven through 60 pipe sections. Based on the design shown in the figure, a 10 cm bend radius was obtained,

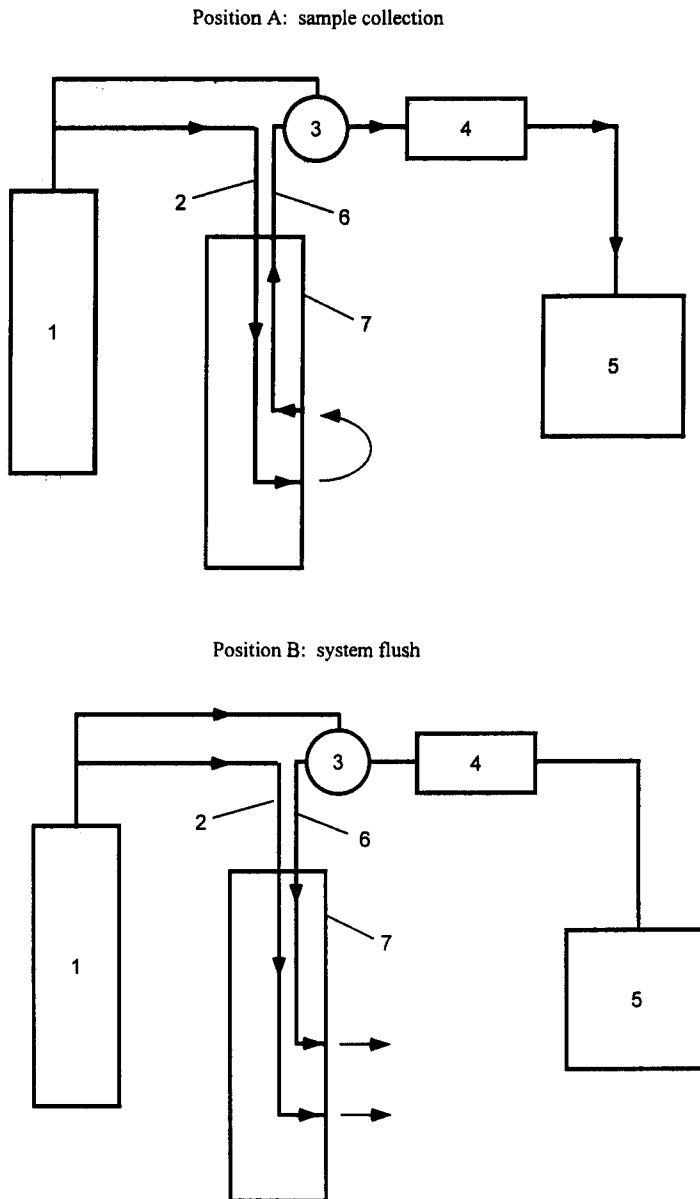


Figure 3. Sampling probe gas flow: 1) inert gas supply, 2) carrier gas, 3) valve, 4) collection chamber, 5) vacuum pump, 6) Silcosteel[®] tube, and 7) cone penetrometer pipe.

with the Silcosteel[®] temperature programmable from ambient soil temperatures up to 300 °C. The 30 m transfer line made for this study was woven through ten 1 m pipe sections to achieve subsurface depths of 10 m. The transfer line is heated by passing direct current through the stainless steel tube.

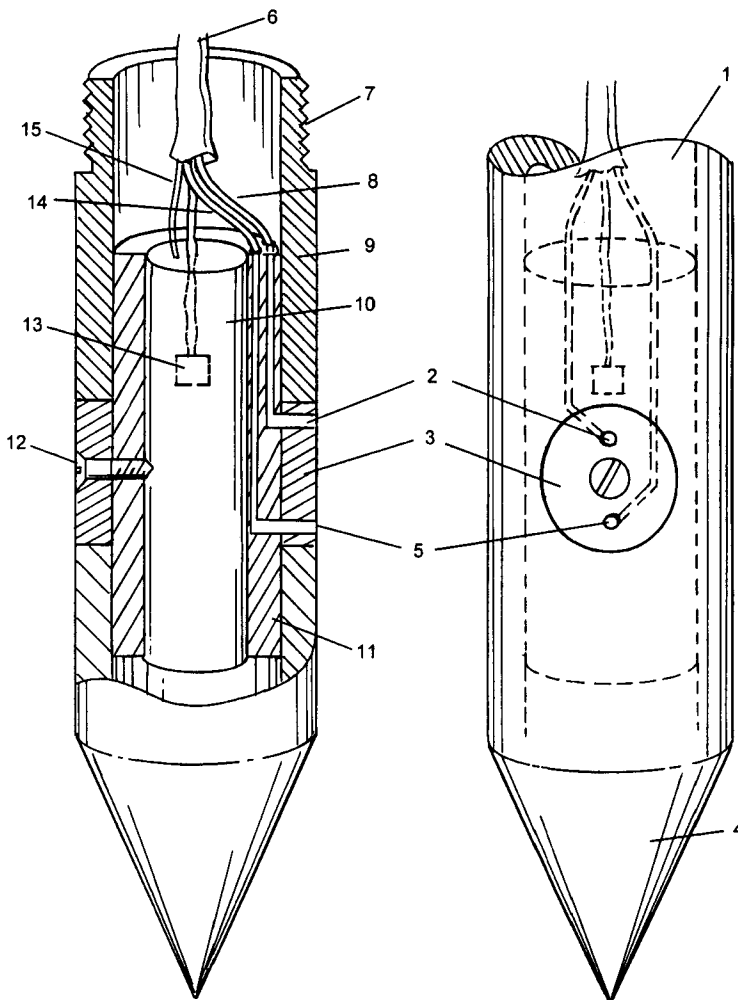


Figure 4. Thermal extraction cone penetrometer probe head construction: 1) TECP probe head, 2) collection inlet, 3) collection window, 4) cone tip, 5) carrier gas outlet, 6) heated transfer line, 7) pipe thread, 8) Silcosteel^R collection gas line, 9) pipe wall, 10) heater cartridge, 11) heater case, 12) collection arm, 13) thermocouple, 14) carrier gas line, and 15) electrical wires.

The following equations were used to calculate the power, P , needed to heat the Silcosteel[®] from 10°C (t_1) to 300°C (t_2), where

$$Q = m c_p (T_2 - T_1) \quad \text{and} \quad m = \gamma * S * L.$$

Q is the amount of heat to go from t_1 (283°K) to t_2 (573°K), m , γ , and c_p are the mass, density and specific heat capacity of the steel, S is the Silcosteel[®] cross section and L is the length of the Silcosteel^R transfer line.

$$P = 1.2 * V \{ \gamma * S^2 * c_p (T_2 - T_1) / \rho * \tau \}^{1/2}$$

Table 1

**Material Balance for the Thermal Desorption Closed Cell
and Transfer Line Experiments^a**

| | 250°C | | | 300°C | | | 350°C | | |
|------------------------|-------|--------|-------|-------|--------|-------|-------|--------|-------|
| | % Rec | % Soil | % Ads | % Rec | % Soil | % Ads | % Rec | % Soil | % Ads |
| Naphthalene | 60 | ND | ND | 65 | ND | ND | 75 | ND | ND |
| Acenaphthylene | 61 | ND | ND | 63 | ND | ND | 74 | ND | ND |
| Acenaphthene | 74 | 5 | 3 | 78 | ND | ND | 90 | ND | ND |
| Fluorene | 72 | 5 | 4 | 75 | 3 | 1 | 92 | ND | ND |
| Phenanthrene | 86 | 5 | 4 | 83 | 5 | 2 | 87 | 5 | 2 |
| Anthracene | 75 | 6 | 5 | 78 | 6 | 2 | 89 | 6 | 2 |
| Fluoranthene | 79 | 5 | 5 | 80 | 4 | 3 | 87 | 8 | 3 |
| Pyrene | 86 | 9 | 4 | 83 | 6 | 1 | 89 | 6 | 1 |
| Benzo(a)anthracene | 56 | 42 | 4 | 67 | 30 | 1 | 72 | 23 | 1 |
| Chrysene | 50 | 40 | 4 | 61 | 31 | 1 | 68 | 31 | 1 |
| Benzo(b)fluoranthene | 41 | 54 | 6 | 55 | 40 | 4 | 50 | 40 | 4 |
| Benzo(k)fluoranthene | 41 | 53 | 6 | 54 | 41 | 4 | 55 | 40 | 4 |
| Benzo(a)pyrene | 65 | 31 | 4 | 65 | 23 | 3 | 75 | 23 | 1 |
| Indeno(1,2,3-cd)pyrene | NA | NA | NA | 37 | 59 | 2 | 56 | 40 | 2 |
| Dibenz(a,h)anthracene | NA | NA | NA | 37 | 59 | 2 | 56 | 45 | 2 |
| Benzo(g,h,i)perylene | NA | NA | NA | 23 | 67 | 4 | 37 | 67 | 1 |

^a 15 ppm each PAH ($T_{u, \text{line}} = 280^\circ\text{C}$; $Re_m = 5,700$; $V_o = 32$; $\omega_s = 0.6$ m/s; back yard soil).

ND - not detected; NA - not analyzed.

where ρ is the specific resistance of the steel and τ is the time needed to go from t_1 to t_2 . Based on the Silcosteel[®] dimensions, $V = 240$ volt, and stated temperature differential, a small 1 kW transformer should be capable of providing the necessary power to heat the transfer line to 300°C for field work.

Degradation of the silica lining is minimal as long as air is purged from the system using an inert gas (4). Imbedded in the transfer line are the electrical (3, 16) and thermal couple (12) wires needed to carry current to the probe head and to monitor both the transfer line (7) and probe (1, see Figure 3) temperatures. Thermocouples (15) were located at 10 m intervals to monitor the temperature to insure no condensation within the transfer line.

The TECP gas flow is shown in Figure 3. When the valve is in position B, the inert gas is directed to the Silcosteel[®] tube (6) for the purpose of purging the transfer line of air prior to heating. Once purged, the fused silica lined steel is conditioned at 150°C for 30 min before samples are collected. Soil gas and/or soil-bound organics are subsequently collected (4) by re-positioning the valve (3) and applying vacuum (5) ranging between 5-20 mm of water. Volatile organic compounds are trapped on Tenax adsorbent, with semi-volatile organics freeze trapped in an empty glass sleeve using dry ice. Should organics adsorb onto the Silcosteel[®] during collection, valve position B can be used again to cleanse the transfer line at elevated temperatures. Note that the TECP system is back-flushed to soil when large sample concentrations are collected. This step is intended to eliminate sample carry-over from one sample location to the next. The TECP system has been automated to control the probe and transfer line temperatures as well as the carrier, flush, and collection gas lines.

The probe head (1) construction is shown in Figure 4. The heated transfer line (6) is connected by electrical wire (15) to the heater cartridge (10) and the carrier gas (14) and collection (8) lines. Thermocouple (13) senses the temperature at the collection arm (3). A 2 cm hole is made in the pipe (9). The collection arm is fixed (12) to the heater cartridge case (11) so that it sits flush with the pipe. The subsurface push is facilitated by the cone (4). The TECP is lengthened by threading (7) additional pipe sections to the probe assembly.

RESULTS AND DISCUSSION

Experiments were performed to determine optimum TECP transfer line and sample probe conditions. To model the operation of the sample probe, the transfer line was attached to a closed cell thermal desorption (TD) unit originally designed for introducing solid samples into a gas chromatograph (GC).³ The TD can be ballistically heated up to 350 °C in under 6 sec. For this analysis a fortified soil was prepared to contain 15 ppm of each PAH. A known quantity of soil was placed into the TD and heated. The PAH were swept from the TD unit using nitrogen under positive pressure through the transfer line and into a glass sleeve where the vapor was freeze trapped.

Material balance studies were conducted varying the TD soil temperature (250 °C to 350 °C), the diameter (0.75 mm to 2.16 mm i.d.) and length (12 m to 30 m) of the Silcosteel[®] transfer line, and the carrier gas linear velocity (ω , 0.01 m/sec to 0.6 m/sec) and collection volume, V_0 . The results showed that transfer line efficiency was independent of tube diameter and length as long as V_0 and ω were ≥ 30 times the system's dead volume and 0.4 m/sec, respectively. Plots of PAH recovered versus Reynolds number approached constancy, namely, $\sim 5 \times 10^3$ at these values. Table 1 shows the percentages of PAH recovered from the soil as a function of temperature.

Also shown are the amounts that remained in the soil after thermal desorption and the percent adsorbed onto the silica coated steel. Note that the PAH are listed according to their GC elution order in the table. No PAHs were detectable in either the soil or Silcosteel[®] at the higher temperatures for the more volatile PAH. On the other hand, the mass balance for these PAH do not equal 100%, suggesting that the cold trap was inefficient at collecting the hot vapor.

Recoveries for the less volatile PAHs also increased with temperature concomitant with a decrease in adsorption on the Silcosteel[®]. Back-flushing for 5-min at 350 °C reduced the percent adsorbed to non detectable levels. Note that the PAH collection efficiency improved as compound volatility decreased. Work is in progress to design and test a Peltier cooled sample collection system.

Although the TECP probe can be heated to 450°C, soil temperatures vary with distance and the heat capacity of the soil under investigation. For the soil used in the mass balance experiments, the temperature measured at the probe/soil interface reached 300°C after 10 min dropping to 280°C at 2 mm from the collection window. The TECP probe and closed cell data comparison study is shown in Table 2. TECP measurement accuracy approximates one-half that of the closed cell system. Recall that the closed cell thermal desorption process depicts the ideal case. The data represents the maximum amount of PAH that can be recovered at 350°C without losing the vapor to the soil

Table 2
Comparison of TECP vs. Closed System

| | TECP % Recovery ^a | | | | | Closed Cell % Recovery ^b | | |
|------------------------|------------------------------|--------|--------|-------|----------------|-------------------------------------|----------------------|----|
| | 50 ppm | 25 ppm | 15 ppm | 5 ppm | Avg. Rec % RSD | 15 ppm | % Diff. ^c | |
| Naphthalene | 20 | 37 | 26 | 37 | 30 | 23 | 65 | 54 |
| Acenaphthylene | 34 | 36 | 36 | 33 | 35 | 5 | 63 | 44 |
| Acenaphthene | 41 | 39 | 33 | 30 | 36 | 18 | 78 | 54 |
| Fluorene | 49 | 36 | 38 | 37 | 40 | 17 | 75 | 47 |
| Phenanthrene | 37 | 32 | 35 | 34 | 35 | 7 | 83 | 56 |
| Anthracene | 37 | 32 | 34 | 34 | 34 | 7 | 78 | 56 |
| Fluoranthene | 65 | 53 | 48 | 36 | 50 | 34 | 80 | 38 |
| Pyrene | 64 | 53 | 45 | 68 | 57 | 15 | 83 | 31 |
| Benzo(a)anthracene | 49 | 37 | 36 | 41 | 40 | 12 | 67 | 40 |
| Chrysene | 27 | 37 | 31 | 41 | 34 | 16 | 61 | 44 |
| Benzo(b)fluoranthene | 29 | 27 | 29 | 23 | 27 | 12 | 55 | 51 |
| Benzo(k)fluoranthene | 29 | 28 | 27 | 22 | 26 | 12 | 54 | 52 |
| Benzo(a)pyrene | 25 | 23 | 36 | 24 | 27 | 26 | 65 | 59 |
| Indeno(1,2,3-ed)pyrene | 26 | 19 | 20 | 23 | 22 | 14 | 37 | 41 |
| Dibenz(a,b)anthracene | 26 | 19 | 19 | 23 | 22 | 14 | 37 | 41 |
| Benzo(g,h,i)perylene | 17 | 16 | 16 | 16 | 17 | 4 | 23 | 26 |

^a $T_{\text{pipe}} = 450^{\circ}\text{C}$; $t_{\text{soil}} = 280^{\circ}\text{C}$; $T_{\text{tr, line}} = 280^{\circ}\text{C}$; $Re_m = 6,000$; $\omega = 1.2$.

^b $t_{\text{soil}} = 300^{\circ}\text{C}$; $T_{\text{tr, line}} = 280^{\circ}\text{C}$; $Re_m = 5,700$; $\omega_g = 0.6$ m/s; $V_0 = 32$.

^c % Difference is between average TECP recovery and closed chamber recovery.

Table 3
TECP Field Study, Berlin Vermont^a

| | TECP Measured PAH/Soil Concentration | | | | |
|------------------------|--------------------------------------|--------|--------|--------|--------|
| | Push 1 | | Push 2 | | |
| | 97 cm | 142 cm | 130 cm | 155 cm | 190 cm |
| Naphthalene | 2 | 2 | 4 | ND | ND |
| Acenaphthylene | 9 | 6 | 14 | ND | 5 |
| Acenaphthene | 2 | 2 | 3 | 2 | 3 |
| Fluorene | 7 | 3 | 10 | 4 | 3 |
| Phenanthrene | 11 | 5 | 7 | 2 | 4 |
| Anthracene | 11 | 5 | 7 | 2 | 4 |
| Fluoranthene | 44 | 3 | 6 | 2 | 3 |
| Pyrene | 29 | 4 | 6 | 5 | 4 |
| Benzo(a)anthracene | 45 | 11 | 6 | 3 | 2 |
| Chrysene | 45 | 11 | 6 | 3 | 2 |
| Benzo(b)fluoranthene | 5 | 0.4 | 0.5 | ND | ND |
| Benzo(k)fluoranthene | 6 | 0.3 | 0.5 | ND | ND |
| Benzo(a)pyrene | 12 | 0.6 | ND | ND | ND |
| Dibenz(a,h)anthracene | 2 | ND | ND | ND | ND |
| Indeno(1,2,3-cd)pyrene | 3 | ND | ND | ND | ND |
| Benzo(g,h,i)perylene | 6 | ND | ND | ND | ND |

^a $T_{\text{pipe}} = 450^{\circ}\text{C}$; $T_{\text{soil}} = 280^{\circ}\text{C}$; $T_{\text{tr, line}} = 280^{\circ}\text{C}$; $Re_m = 6,000$; $\omega_g = 1.6$ m/s; $V_0 = 30$.

environment during sample collection. In contrast, the TECP can lose PAH during the collection process, see Figure 3. Nonetheless, measurement precision was excellent. The results obtained over an order of magnitude are as good as what is achievable through soil/solvent extraction.

The TECP transfer line and sample probe system was tested in the field by Applied Research Associates (South Royalton, VT) at a vehicle maintenance facility in Vermont. Located on the property was an underground storage tank and several pits where 50 gal drums of petroleum had been buried. Ground water monitoring wells had previously been installed around site. Prior to collecting subsurface soil samples, the TECP was tested for mechanical ruggedness and its ability to collect subsurface-bound organics.

The TECP exhibited minimal heat loss to the surroundings and met the electrical and thermal safety standards for field operation. After passing several mechanical push tests, the TECP system was used to develop a subsurface profile near one of the ground water monitoring wells. The TECP probe sampled the soil from the surface to depths just above the water table at approximately 30 cm intervals.

Table 3 illustrates the results obtained during two depth profiling pushes. PAHs were found at depths of 97 cm and 142 cm during the first push and at 130 cm, 155 cm, and 190 cm for the second push. The total time needed to collect and analyze the sample and to back-flush the transfer line prior to collecting the next depth sample was approximately 15 min. Unfortunately, data comparison studies between the TECP collected samples and actual soils collected at depth from the same location were not possible since Applied Research Associates was unable to re-enter the hole without breaking the cone penetrometer pipe. Nevertheless, these results appear promising suggesting that direct on-line chemical measurements of subsurface contaminants, stack gas emissions, or process control gases may be possible within a couple years.

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