Direct Determination of Soil Surface-Bound Polycyclic Aromatic Hydrocarbons in Petroleum-Contaminated Soils by Real-Time Aerosol Mass Spectrometry

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Direct Determination of Soil Surface-Bound Polycyclic Aromatic Hydrocarbons in Petroleum-Contaminated Soils by Real-Time Aerosol Mass Spectrometry

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Soil surface-bound polycyclic aromatic hydrocarbons (PAHs) were identified by use of Real-Time Aerosol Mass Spectrometry (RTAMS) in two NIST standard research material (SRM) soils (Montana SRM 2710 and Peruvian SRM 4355) each contaminated separately with three common petroleum hydrocarbons (diesel fuel, gasoline, and kerosene). The described contaminated soil analysis required no sample preparation. Direct laser desorption/ ionization mass spectrometric analysis of individual soil particles contaminated with each of the petroleum hydrocarbons at three different contamination levels (0.8, 8, and 80 ppth (wt/wt)) yielded detectable PAH cation distributions that ranged from *m/z* 128 to 234, depending on the fuel contaminant. The same analysis performed on uncontaminated SRM soils revealed very little (Peruvian) to no (Montana) detectable PAH species. Size analysis showed that most of the individual soil particles analyzed were between 1 and 5 μm in diameter. Tandem mass spectrometry (MS/MS) experiments identified alkyl-substituted two- and three-ringed PAHs in all three petroleum hydrocarbon contaminated soils. However, due to similarities in fragmentation patterns, MS/MS analysis of higher MW species (*m/z* > 200) was unable to distinguish between the possibility of highly alkyl-substituted three-ringed PAHs and hydrogenated four-ringed PAHs. The described technique offers the direct, rapid determination and characterization of surface-bound PAHs in petroleum-contaminated soils at part-per-million levels without prior extraction, separation, or other sample preparation methods.

Polycyclic aromatic hydrocarbons (PAHs) represent a class of compounds of great environmental concern due to their suspected mutagenic and carcinogenic properties.[1−6] Unease over the potential adverse health effects of PAH species is evident in the recent inclusion of 16 PAH compounds in the Environmental Protection Agency's priority contaminants list. PAH contaminants pose several potential health risks due to the persistence of these compounds in the environment,[7,8] their tendency to strongly bind to soil surfaces,[9−11] and their presence in a wide variety of common media (air, dust, soil, and food).[12] Possible risks are associated with skin contact; inhalation or ingestion of contaminated dust, soil, or air; and ingestion of contaminated food.

The origin of environmental PAH contamination is many different sources. Petroleum-based fuels and oils are known PAH sources, with total PAH content as high as 4 wt % for diesel fuel and 5 wt % for gasoline.[13] Pipeline ruptures, tanker failures, underground and aboveground storage tank leaks, and various other production and transportation accidents frequently produce hydrocarbon-contaminated soil and groundwater on enormous scales. Therefore, hydrocarbon spills represent a large and widespread cause of soil and groundwater PAH contamination. In addition, fossil fuel combustion produces PAH-containing airborne particulate matter. Petroleum hydrocarbon contamination may also occur naturally through seepage from underground oil and natural gas reserves. However, the transportation and storage needs for petroleum-based fuels in highly industrialized nations are the main source of bulk fuel-contamination problems.

In the case of a large terrestrial hydrocarbon spill, the spread of the contaminant is commonly tracked through the use of

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monitoring wells. Initial monitoring wells are used to determine the speed and direction of the underlying groundwater, with subsequent wells placed in, around, and "downstream" from the suspected contaminant plume. Detailed analysis of soil and groundwater samples from within the contaminant plume provides source identification, location, and total petroleum contamination levels. However, plotting the overall progression of the plume may prove costly and time-consuming due to the associated expense and time requirements for traditional analytical techniques (as much as 25−30% of the total cleanup cost).[14] Most commonly, each soil and water sample is collected, sealed, and then sent to an off-site laboratory for extraction and subsequent gas chromatography/mass spectrometric analysis. Other samples, including contaminated road and house dust, urban particulate, and combustion particulate emissions, are also commonly monitored in a similar manner.[13,15−17] Headspace solid-phase microextraction (SPME) gas chromatographs with pattern recognition software have been proposed as a simple, cost-effective, on-site analytical technique to lower the associated cost for petroleum contaminant characterization and identification.[14] However, the low resolution of the SPME-GC technique is inherently limited to petroleum contaminant detection and source identification and provides little information on specific contaminant classes of interest (PAHs in the present example).

Gas chromatography/mass spectrometry (GC/MS) is a powerful analytical technique commonly used for the PAH analysis of petroleum-contaminated soils. However, due to insufficient chromatographic and mass spectrometric resolution,[18−21] sample preparation methods are often employed to isolate the PAH compound class prior to analysis.[8,13,22−24] Nonetheless, GC/MS analysis of contaminated soil and groundwater offers a wealth of information on the petroleum contaminant but at the expense of sample preparation and extended analysis time. Solid-phase microextraction (SPME) techniques have been used to speed sample extraction from soil and water[25−27] but eliminate the

possibility of subsequent sample preparation steps to simplify the analysis and target a specific class of compounds. Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) has recently been shown to identify hundreds of components in petroleum hydrocarbon contaminated soils.[28,29] FTICR MS overcomes the mass resolution limitation of traditional GC/MS methods and allows assignment of elemental compositions for every peak in the mass spectrum on the basis of accurate mass alone.[30,31] However, like traditional GC/MS methods, a sample preparation step is required to isolate the extractable organics from the bulk soil, and FTICR MS instruments designed for this type of analysis are currently neither widely available nor transportable. Enzyme-linked immunosorbent assay (ELISA) test kits designed for environmental analyses[12,32] offer a rapid, low-cost method for the detection of PAH contaminants in soil and dust samples, yet are limited in application. The ELISA tests provide information only on total PAH contamination and cannot be used to identify multiple PAH components in soil/dust samples because of the assays' cross reactivities with other PAH components.[12]

Laser ablation/ionization aerosol mass spectrometry has rapidly grown over the past decade to become an important analytical tool for the analysis of individual aerosol particles.[33−41] In addition, transportable instruments have recently been developed to allow on-site, real-time aerosol characterization.[42−44] Although past research has primarily concentrated on airborne particulates, recently it has been shown that the technique may also be expanded to bulk material, such as soil.[45] In this paper, real time aerosol mass spectrometry (RTAMS) is shown to offer the direct, rapid identification of soil-bound polycyclic aromatic hydrocarbons at part-per-million levels with little or no sample preparation. Laser desorption/ionization (248 nm) of the individual

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soil particles specifically targets aromatic species (PAHs) and effectively eliminates matrix contributions from other nonaromatic organic compounds present in either the fuel or soil. With sample analysis times typically less than 10 min, the sample capacity (samples analyzed/time) of the RTAMS instrument (based on a total of at least 1000 individual particles for each sample) far exceeds that of traditional GC or GC/MS by a factor of 4 or more. Furthermore, the compact nature of current laboratory-based ion trap instruments lends itself well to their being made transportable. A high sample throughput, limited sample preparation, and rapid analysis makes RTAMS an attractive alternative to traditional GC and GC/MS analyses for plotting the suspected boundaries and progression of a contaminant plume where large numbers of sample points are needed or as a qualitative means to determine PAH contamination in suspected soil/dust samples.

Here, we present the application of RTAMS in the identification of soil surface-bound PAHs in two standard NIST soils (SRM 2710 and SRM 4355) contaminated with three common petroleum hydrocarbons (diesel fuel, kerosene, and gasoline) at 0.8, 8, and 80 parts per thousand (wt/wt). Tandem mass spectrometry experiments aided in the identification of certain soil surface-bound PAH species as two- and three-ringed alkyl-substituted PAHs but could not discount the presence of three- or four-ringed hydrogenated PAHs with the same masses ($m/z > 200$) that might originate from hydrotreatment of the petroleum fuels. The described method provided direct, rapid identification of the soil surface-bound PAHs with no sample preparation, and the compositional information obtained correlated well with previous literature reports on the PAH content of diesel fuel, gasoline, and kerosene. In the future, the technique will be applied to contaminated real-world soil samples in an effort to establish RTAMS as a viable, rapid, high-throughput alternative to GC and GC/MS analyses for the determination of suspected PAH contamination in soil/dust samples.

EXPERIMENTAL SECTION

Both Montana (NIST SRM 2710) and Peruvian (NIST SRM 4355) soil samples and HPLC grade methylene chloride were used as received. Kerosene and gasoline samples were obtained from a local service station (Oak Ridge, TN) and the diesel fuel sample from Phillips Petroleum. Uncontaminated soil samples (200 mg) were weighed into glass vials and methylene chloride added until the soil was thoroughly saturated. The methylene chloride soil slurry was then spiked with one of the three fuels to the desired contamination level (0.8, 8, and 80 ppth (wt/wt)) through the addition of a 10% (v/v) mixture of the petroleum fuel in methylene chloride. The vial was sealed and vortexed for approximately 1 min before being blown to dryness under a gentle stream of air. This step most likely promoted the loss of more volatile, lower molecular weight PAHs such as naphthalene, which was evident in the lower than expected naphthalene cation signal at $m/z = 128$ for all three fuels analyzed. However, such losses are also expected in real-world samples that have undergone significant weathering. After the soil samples were dried, the vials were sealed until they were analyzed.

All experiments were carried out on a modified Finnigan MAT ion trap mass spectrometer similar to that described by Ramsey and co-workers with only minor differences in sample introduc-

tion.[41,45,46] Sample particles were temporarily immobilized on a clean cotton swab and introduced by gently tapping the swab over the mass spectrometer inlet. Soil particles introduced to the 500-μm converging nozzle passed through 500-μm and 250-μm skimmers before entering the main vacuum chamber. The two regions (between the nozzle and first skimmer (~5 Torr), and first and second skimmers (5×10^{-2} Torr)) are pumped separately by two 500 L/min mechanical pumps. Soil particles that successfully travel through the nozzle and both skimmers comprise a collimated particle beam that next passes through a pair of focused CW Ar$^+$ laser beams. Scattered light from the soil particles is collected by fiber optics and detected by two separate photomultiplier tubes (PMTs). The signals from the two PMTs were converted to TTL pulses and used to record the particle time-of-flight (aerodynamic particle size) between the two CW Ar$^+$ laser beams and trigger an external KrF (nominally 1 J/cm^2/pulse at 248 nm) focused laser beam that strikes the soil particles as they reach the center of the ion trap. The resulting ions were then stored and mass analyzed using standard techniques[47] including tandem MS analysis.[48] All mass spectra, including the particle size distributions, result from the observation of at least 1000 individual soil particles. The mass spectra shown are the sum of those individual spectra that exhibited total relative ion counts (RIC values) of at least 3 times that of the background level. In an effort to reduce the number of spectra presented and determine the limit of detection for the three contaminants in this study, Peruvian soils were analyzed over the entire range of contamination (0.8, 8, and 80 ppth (wt/wt)), while Montana soils were limited to 8 and 80 ppth petroleum contamination. At similar contamination levels, both Peruvian and Montana soils show almost identical PAH distributions; therefore, only one (Peruvian soil analysis) will be presented.

RESULTS AND DISCUSSION

Uncontaminated Soil Analysis. Uncontaminated soil samples were first analyzed to obtain particle matrix mass spectra blanks and determine particle size distributions. Figure 1 shows the mass spectra of the two uncontaminated soil samples. Montana soil (Figure 1a) contains significant amounts of both Cs$^+$ and Pb$^+$, while Peruvian soil (Figure 1b) consists of both Cs$^+$ and Rb$^+$ with small amounts of Fe$_2$O$^+$. Both soils contain mass lines at m/z 72, characteristic of FeO$^+$, and have relatively low background ion signals at the laser fluence used in the analysis. Both the Montana and Peruvian soils analyzed by the mass spectrometer display similar size distributions centered at approximately 3 μm in diameter, with Peruvian soil showing a slightly larger tailing distribution toward larger particle diameters (~10 μm). Because of the relatively intense Pb$^+$ ion signal in Montana soil (Figure 1a), Peruvian soil was used for the MS/MS study in order to avoid complications that might arise from PAH species in the range 206 < m/z < 208.

Gasoline-Contaminated Soil Analysis. Dried contaminated (8 and 80 ppth) Montana and contaminated (0.8, 8, and 80 ppth)

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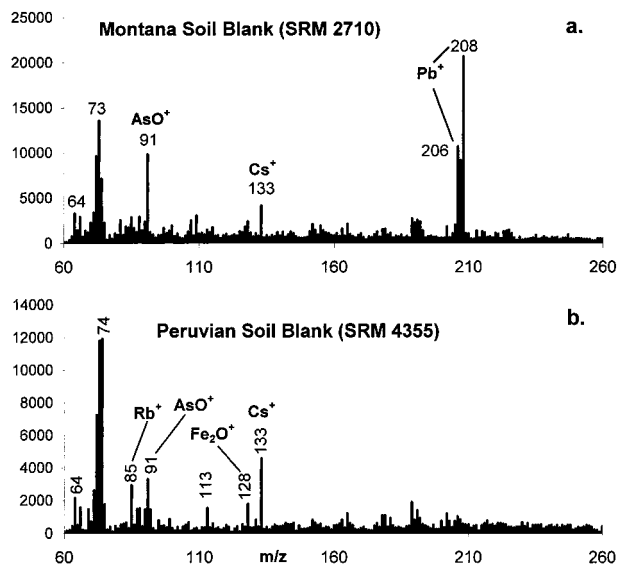
Figure 1. Averaged positive RTAMS spectra of uncontaminated (a) Montana (SRM 2710) and (b) Peruvian (SRM 4355) soils each resulting from the analysis of 1000 individual soil particles. Both soils display relatively low background ion signal at the laser power used in the analysis and consist primarily of metal and metal oxide cations.

Peruvian soils were analyzed in an attempt to qualitatively identify soil surface-bound PAH species deposited by gasoline. Figure 2a−c shows the results of the gasoline-contaminated Peruvian soil analysis. At the lowest gasoline contamination level (0.8 ppth) (Figure 2a), Peruvian soil exhibits similar PAH distributions to those observed in more heavily gasoline-contaminated soils (Figure 2 b,c). Although the PAH distributions are clearly evident at the lowest level of gasoline contamination analyzed, the signal-to-noise ratio is relatively poor. Therefore, the limit of detection for the gasoline-contaminated soil is determined to be at or slightly below the 0.8 ppth bulk fuel contamination level. With published reports of gasoline PAH concentrations that range from 2600 mg/L for naphthalene to as low as 5 mg/L for pyrene,[13] the limit of detection for observed soil-bound PAH species in the current analysis is estimated to be in the low part-per-million range.[45] PAH distributions for the two gasoline-contaminated soils fall within the range $115 < m/z < 220$ and suggest the presence of both two- and three-ringed alkyl-substituted PAHs. The mass series at $m/z = 128, 142, 156, 170$, and 184 most likely arises from naphthalene and alkyl-substituted analogues. Similarly, a mass series at $m/z = 178, 192, 206$, and 220 suggests the presence of three-ringed PAHs and alkyl-substituted analogues. Evidence of four-ringed PAH species is limited to a single peak at mass 202. Speculation on the presence or absence of hydrogenated 4-ringed PAHs that might contribute to the intensity of the $m/z = 206$ peak will be addressed later in the discussion of the tandem MS results.

The observed gasoline-contaminated soil PAH distributions match literature reports for the PAH content of unleaded gasoline quite well. Previously, GC/MS analysis of neat gasoline noted the presence of both two- and three-ringed PAH species (along with their alkyl-substituted analogues) with a small amount of four-ringed PAHs.[13] In addition, FTICR MS analysis of unleaded gasoline also confirms (at the level of elemental composition for each resolved mass spectral peak) the presence of both two- and three-ringed alkyl-substituted PAHs, although without identifica-
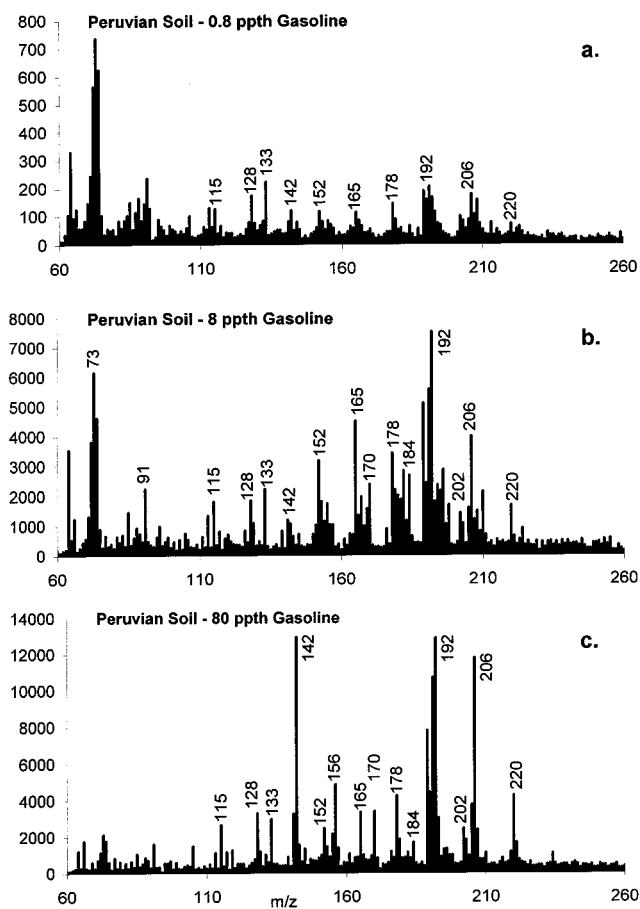

Figure 2. Averaged positive RTAMS spectra of gasoline-contaminated Peruvian soil (SRM 4355) at three different levels of contamination: (a) 0.8 ppth (b) 8 ppth, and (c) 80 ppth (wt/wt). Observed PAH distributions represent two- and three-ringed alkyl-substituted species with evidence of a four-ringed PAH species at m/z 202.

tion of the lower abundance high alkyl-substituted three or four-ringed PAHs,[49] due to instrumental limitations.

Kerosene-Contaminated Soil Analysis. Kerosene-contaminated Montana and Peruvian soils, over the same range of contaminant levels previously presented in the gasoline-contaminated soils, were each analyzed to qualitatively identify soil surface-bound PAH species. Figure 3 shows the results of the analysis of kerosene-contaminated Peruvian soil. As previously mentioned in the gasoline-contaminated soils, Peruvian soil samples were analyzed at a lower contamination level than the Montana soil samples. Mass spectral analysis of the two soils revealed PAH species in the range $115 < m/z < 220$. As with the gasoline-contaminated soil analysis, two prominent PAH series dominated the mass spectrum. A mass series at $m/z = 128, 142, 156, 170$, and 184, characteristic of naphthalene and alkyl-substituted naphthalenes, is the most abundant series in the mass spectrum. Similarly, a mass series at $m/z = 178, 192, 206$, and 220 suggests the presence of three-ringed PAHs and their alkyl-substituted analogues. The observed distributions for kerosene are similar to those obtained for gasoline-contaminated soils with the primary differences being the relative abundance of the two prominent PAH series. Again, the soil analysis at the lowest level of kerosene

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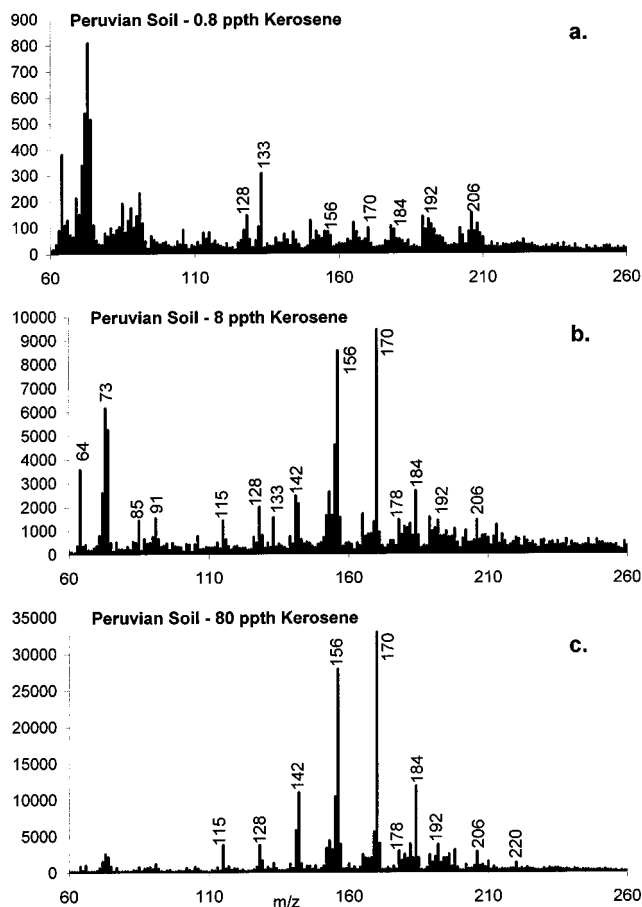
Figure 3. Averaged positive RTAMS spectra of kerosene-contaminated Peruvian soil (SRM 4355) at three different levels of contamination: (a) 0.8 ppth, (b) 8 ppth, and (c) 80 ppth (wt/wt). Although the observed PAH distributions represent both two- and three-ringed alkyl-substituted species, the relative abundance of the distributions are greater than those in the gasoline-contaminated soils.

Figure 4. Averaged positive RTAMS spectra of diesel fuel-contaminated Peruvian soil (SRM 4355) at three different contamination levels: (a) 0.8 ppth, (b) 8 ppth, and (c) 80 ppth (wt/wt). Note the considerable increase in the number and relative abundance of PAH species throughout the mass spectrum; however the 2-, 3-, and 4-ringed alkyl-substituted PAH distributions are clearly evident.

contamination revealed PAH distributions similar to those obtained at higher levels of contamination, albeit at lower signal-to-noise. On the basis of the observed mass spectral response at low kerosene contamination, the limit of detection is at or slightly below the 0.8 ppth level. Comparison of the soils at similar contamination levels revealed no differences in the detected PAH species and only small differences in the relative abundances of the PAH species observed. Previous reports on the composition of kerosene and other petroleum middle distillates[50,51] suggests the presence of 2-, 3-, and 4-ringed PAH species as well as their associated alkyl-substituted analogues. Furthermore, a separate, recently published FTICR MS analysis of standard kerosene confirmed their presence.[49]

Diesel Fuel-Contaminated Soil Analysis. Again, dried diesel-contaminated Montana and Peruvian soils (at identical bulk fuel contamination levels as both gasoline- and kerosene-contaminated soils) were analyzed to qualitatively identify residual soil surface-bound PAH species arising from diesel fuel contamination. The mass spectra of diesel-contaminated Peruvian soil (Figure 4) reveal a higher complexity than those observed in both the gasoline-
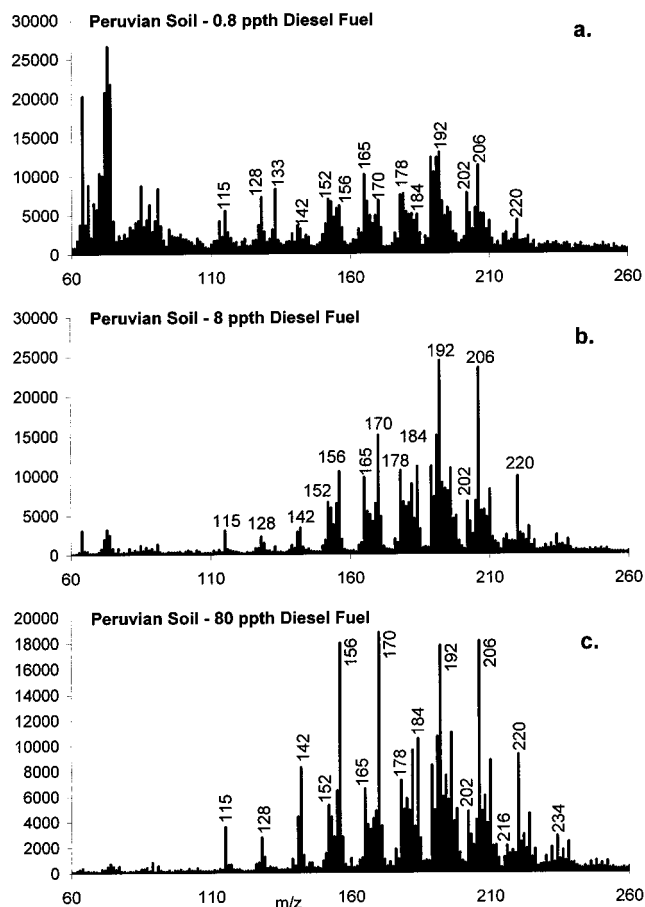
and kerosene-contaminated soils at identical contamination levels. The increase is most likely a result of the higher complexity of the fuel stocks and the processing methods used in diesel fuel production[52] (i.e., hydrotreatment). Despite the increase in complexity, similar distributions for alkyl-substituted two- and three-ringed PAH species previously observed in the gasoline- and kerosene-contaminated soils are clearly evident.

In contrast to gasoline- and kerosene-contaminated soils, diesel fuel-contaminated soils exhibit a more pronounced distribution at higher mass (m/z 202 and 216), characteristic of alkyl-substituted four-ringed PAHs, as well as an increase in the number and relative abundance of PAH species adjacent to the alkyl-substituted two- and three-ringed PAH distributions. Mass lines at m/z 202 and 216 suggest both four-ringed and methyl-substituted four-ringed PAH species. Furthermore, diesel-contaminated soils display an additional distribution (m/z 182, 196, 210, 224, and 238) at high relative abundance characteristic of both hydrogenated PAHs and hydrogenated alkyl-substituted PAHs not present in either the gasoline or kerosene mass spectra. Similar to both gasoline- and kerosene-contaminated soils, comparisons of the two different diesel-contaminated soil samples at

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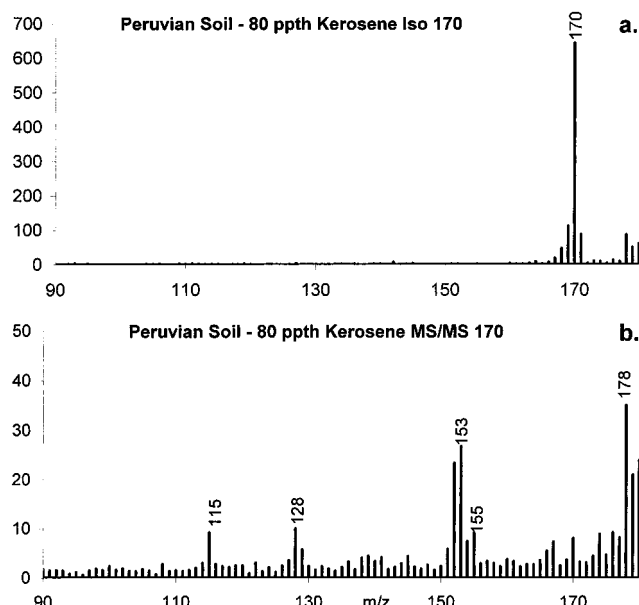
Figure 5. Averaged positive tandem mass spectra of m/z 170 from the 80 ppth kerosene-contaminated Peruvian soil sample. The tandem mass spectrum shows the loss of one (m/z 153 and 155) and more alkyl substituents from the isolated species shown in the upper panel (a), resulting in the characteristic naphthalene cation at m/z 128. Comparisons of the tandem MS spectrum to the NIST mass spectral database support the identification of the isolated species at m/z 170 as an alkyl-substituted naphthalene.

Figure 6. Averaged positive tandem mass spectra of m/z 192 from the 80 ppth gasoline-contaminated Peruvian soil sample. The tandem mass spectrum shows significant dehydrogenation (to m/z 187) of the isolated parent ion (a) and an additional loss of 28 Dalton (C_2H_4) (shown in (b)). Comparisons of the tandem MS spectrum to the NIST mass spectral database and fragmentation similarities between the various alkyl-substituted three-ringed PAHs support the identification of the isolated species at m/z 192 as a methyl-substituted three-ringed PAH.

similar contamination levels revealed few differences in either the PAH species identified or their corresponding relative abundances. Moreover, GC/MS and FTICR MS analyses of diesel fuels have separately confirmed the presence of two-ringed and higher alkylated PAH compounds[49-51] as well as the hydrogenated PAH series (FTICR MS analysis).[49]

Tandem MS Analysis of Contaminated Soils. Tandem MS experiments performed on abundant PAH species from each of the three Peruvian soil contaminants analyzed were used to confirm previously proposed PAH assignments.[53-56] Because of compositional overlaps that are sure to exist between all three petroleum-based fuels, peaks thought to represent the two main observed distributions (alkyl-substituted two- and three-ringed PAH species) were selected for fragmentation. In the kerosene-contaminated soil sample, the peak at m/z 170 (thought to arise from a highly alkyl-substituted naphthalene) was selected for tandem MS analysis. Similarly, peaks at m/z 192 in gasoline and 206 in diesel-contaminated soils (thought to represent alkyl-substituted three-ringed PAH species) were isolated and subjected to tandem MS analysis.

Figure 5 shows the tandem MS analysis of m/z 170 in the kerosene-contaminated soil sample. Figure 5a (isolation) and b (fragmentation) reveal the loss of alkyl groups to produce a characteristic naphthalene (NAP) signal at m/z 128. Comparison of the proposed alkyl-substituted naphthalene to the NIST mass spectral database of trimethyl- and methylethyl-substituted naph-
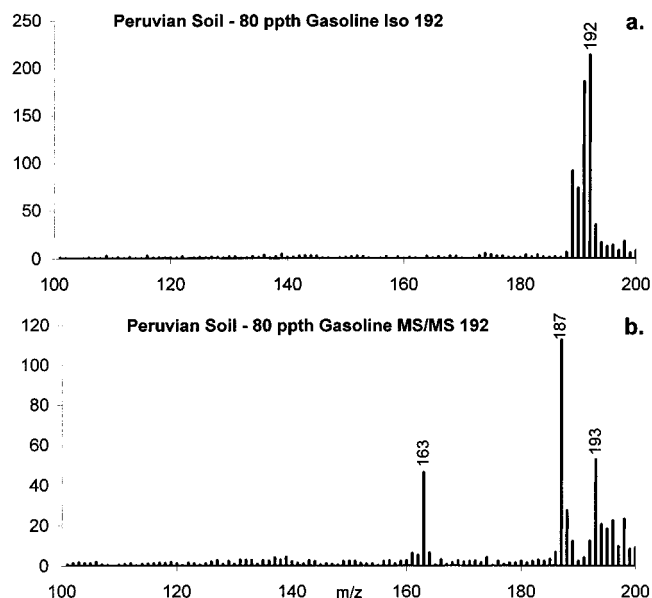
thalenes revealed that a small degree of dehydrogenation had occurred as a result of fragmentation in the ion trap. Dehydrogenation is evident in the mass shift of the characteristic (NAP-Me) peak from m/z 153 and 155 in the electron impact ionization (EI) NIST mass spectrum to m/z 151 and 153 in the ion trap tandem mass spectrum. Although a substantial amount of the m/z 155 remains, the distribution is shifted and slightly widened due to dehydrogenation. Such PAH dehydrogenation in ion trap tandem MS experiments has previously been documented in a PAH standard[45] and most likely arises from the differences in fragmentation methods [70 eV electron impact (NIST mass spectra) vs collisionally induced dissociation (ion trap mass spectra)]. Both the NIST mass spectrum and the RTAMS tandem mass spectrum reveal characteristic peaks at mass m/z 128 and 115 that support the assignment of the isolated species as an alkyl-substituted naphthalene.

Figure 6 shows the tandem MS analysis of m/z 192 in the gasoline-contaminated soil sample. The suspected identity of the peak was that of a methyl-substituted three-ringed PAH. The assignment is confirmed by the characteristic peaks at m/z 163 and 187 in the tandem mass spectrum and peaks m/z 165 and 189 in the NIST EI spectrum. As in the previous example, comparison to the NIST mass spectral database revealed very similar patterns but they were shifted 2 Da lower in the ion trap tandem mass spectra due to dehydrogenation losses. The tandem MS analysis of m/z 206 in the diesel-contaminated soil (shown in Figure 7) continues this trend. A characteristic peak for dimethyl- or ethyl-substituted three-ringed PAHs is located at m/z 191 in the mass spectra of many possible species from the NIST database. All alkyl-substituted anthracene and phenanthrene possibilities share very similar fragmentation patterns that result

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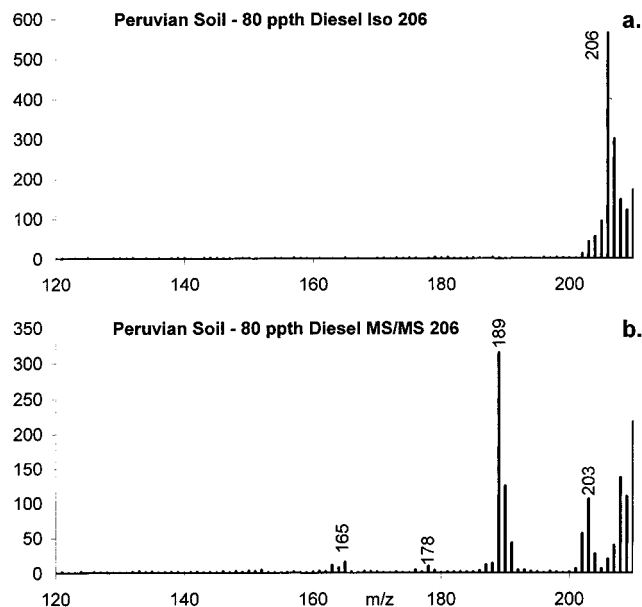
Figure 7. Averaged positive tandem mass spectra of m/z 206 from the 80 ppth diesel-contaminated Peruvian soil sample. Similar to Figure 6, the tandem mass spectrum shows significant dehydrogenation (to m/z 203) of the isolated parent ion (a), a loss of 14 Daltons (CH_2), and an additional loss of 28 Da (C_2H_4) (shown in (b)). Because of the similarities in fragmentation between alkyl-substituted three-ringed and hydrogenated four-ringed PAHs, comparisons of the tandem MS spectrum to the NIST mass spectral database were inconclusive for identification purposes.

in almost identical mass spectra under 70 eV electron impact ionization conditions. In addition, the presence of four-ringed hydrogenated PAHs cannot be discounted because they also share very similar fragmentation patterns as the other anthracene and phenanthrene (three-ringed) possibilities.[53−56] Hydrogenated PAHs exist in diesel fuels because heavier feedstocks (from which diesel fuels originate) typically undergo some form of hydrogenation to increase the economic potential of the fuel.[52] Unfortunately therefore, differentiation between three- and higher ringed alkylated PAH species and the isobaric four- and higher ringed hydrogenated PAHs is not currently possible solely by conventional or laser-ionization mass spectrometry. Therefore, their relative contributions to both the mass spectra and tandem mass spectra cannot be apportioned.

In conclusion, from direct analysis of petroleum-contaminated soils by RTAMS, soil surface-bound PAHs can be qualitatively determined to consist, primarily, of two- and three-ringed unsubstituted and alkyl-substituted PAHs. The soil surface-bound PAH compositions for each of the three fuels correspond well with previous reports of each fuel's PAH content. As seen in the RTAMS mass spectra, differences in the PAH composition of the three fuels (PAH fingerprint) could be used to confirm the type or class of the contaminant on-site. With analysis times typically less than 10 min and little or no sample preparation needed, the proposed method offers a rapid means of identifying PAH contaminants at low part-per-million levels in soil. Furthermore, a transportable RTAMS instrument could allow on-site real-time analysis of suspected contaminated materials and reduce the number of traditional GC/MS analyses required for overall site characterization. This, in turn, would substantially lower the analytical costs and speed the process of site characterization. Future experiments will concentrate on expanding the scope of application to real-world contaminated soils in an effort to provide a rapid method of screening suspected PAH-contaminated soil and dust samples.