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Advances in 2-dimensional Separation Technologies for Estimating Coal Tar Weathering in Sediments

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Technical Update, December 2009

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PRODUCT DESCRIPTION

Coal tar is an extremely complex mixture, containing thousands of cyclic, straight, and branched aliphatics as well as polycyclic aromatic hydrocarbons (PAH), condensed ring sulfur and nitrogen compounds (PASH and PANH), and their functionalized analogs. The volatility, solubility, and adsorption characteristics of these compounds as well as their resistance to environmental degradation vary dramatically. This phase I report summarizes the benefits of multidimensional—in this case two-dimensional—gas chromatography/mass spectrometry (GC/MS) for identifying alkylated PAHs as well as sulfur aromatics and their C_1 to C_4 alkylated homologs in coal tar sediments. Also explored in this report is the addition of a second GC in order to assess whether GC-GC/MS and/or GCxGC/MS can provide sufficient increases in chromatographic separation space to unambiguously detect these important diagnostic compounds. Finally, the report addresses the question of whether two-dimensional GC/MS fingerprints can differentiate evaporation and dissolution from biodegradation. Crucial to such assessments is the ability to deconvolve mass spectral signals to produce quantitative data.

Results and Findings

Preliminary data showed the addition of a second GC to standard GC/MS operation resulted in a dramatic increase in separation, when the first GC used a much more polar stationary phase column than the second. By automating the GC-GC/MS process (also known as automated sequential gas chromatography/mass spectrometry), compound-specific retention times and mass spectral information for the C1 to C4 naphthalenes, fluorenes, phenanthrenes, and dibenzothiophenes were obtained. Additional work is needed to acquire the same alkylated homolog data for the larger molecular weight PAH and PASH compounds.

Research on crude oil showed that GCxGC/MS (also known as comprehensive gas chromatography/mass spectrometry) can be used to produce two-dimensional (2-D) and three-dimensional (3-D) maps of n-alkanes and alkylated PAH. The maps illustrated which homologs were lost due to evaporation, dissolution, and biodegradation. By incorporating the library information obtained from GC-GC/MS into a standardized GCxGC/MS method, compound-specific information on all homologs in coal-tar-contaminated sediment samples can be determined. This information will provide valuable insight into how coal tar weathers and which compounds may or may not become bioavailable / accessible over time. The information will also be crucial for conceptual site models, which rely on accurate estimates of the extent and rate of pollutant movement in the subsurface.

Challenges and Objective(s)

The primary objective of this report is to determine whether 2-D GC/MS, including automated sequential GC-GC/MS and comprehensive GCxGC/MS, provide the information needed to understand how coal tar weathers in fresh and saltwater environments. This report focuses on sediment but is applicable to investigation and remediation of vadose and groundwater contamination as well. The data produced can be used to assess whether cleanup is needed and whether dredging harbor sediments makes environmental and/or financial sense. For example, if it could be demonstrated that coal tar components no longer leach into aqueous environments or pose ecological risk, alternative remediation strategies could be justified.

Applications, Values, and Use

This report is intended for environmental scientists and engineers involved in investigating, cleaning, and monitoring coal-tar-contaminated sites. Success of the proposed GC-GC/MS and GCxGC/MS work will lead to better forensic environmental analyses. Complete libraries of alkylated PAH and PASH will facilitate more accurate assessments of weathering by GC/MS with spectral deconvolution. The combination of quantitative GC/MS data, with 2-D contour and 3-D component maps produced by GCxGC/MS, should significantly increase the information content of site conceptual models, which should lead to a better understanding of site-specific problems. Such information should result in decreased site investigation times and remedial activities concomitant with reductions in cost. Although GCxGC/MS will require additional research, work is already underway to produce complete libraries of alkylated PAH and PASH by GC-GC/MS.

EPRI Perspective

Current environmental GC/MS analyses produce imprecise and inaccurate data. This research showed that PAH and their alkylated analogs can be correctly quantified by GC/MS when spectral deconvolution software is used. Although the software is powerful, it is difficult to visualize separation maps compared to GCxGC/MS. Phase II is slated to focus on the following steps: 1) complete the GC-GC/MS library building effort; 2) conduct GCxGC/MS analysis of coal-tar-contaminated sediment samples and construct 2-D and 3-D partition and component distribution maps; 3) study component partitioning in sediment waters as a function of evaporation, dissolution, and biodegradation; and 4) test the deconvolution algorithms to determine if they can be used to quantify target analytes by GCxGC/MS, which would confirm GC/MS findings.

Approach

The goal of this report was to conduct a literature search to determine if multidimensional GC offers advantages over conventional forensic environmental methods. Both literature and preliminary data point to the fact that the proposed techniques are the only way to differentiate how coal tar evaporates, dissolves, and biologically degrades with time.

Keywords

Coal Tar
Automated Sequential Gas Chromatography/Mass Spectrometry (GC-GC/MS)
Comprehensive Gas Chromatography/Mass Spectrometry (GCxGC/MS)
Coal Tar Weathering
Evaporation
Dissolution
Biodegradation

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INTRODUCTION

Coal Tar in Fresh and Saltwater Sediments

A byproduct of gas production from coal is coal tar, which is a dense nonaqueous phase liquid (DNAPL). Coal tar contains thousands of organic compounds that migrate at different rates from the source material into aqueous environments. This makes their subsurface location and rate of movement difficult to determine. Many manufactured gas plant (MGP) sites are no longer in operation, yet pollution persists for decades. MGP sites are often located along waterbodies. Once coal tar reaches surface waters, how its components partition among the nonaqueous liquid, water, and sediment is not well understood. Because coal tar compounds partition onto sediment minerals and into sediment organic media as well as pore and bulk waters, understanding how coal tar weathers is complicated. This is also true of how coal tar partitions between vadose and saturated media. Typically, benzene, polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic sulfur hydrocarbons (PASH), and their alkylated analogs serve as useful indicators of environmental attenuation.

Also, understanding the compositional change in coal tar over time is important for directing remedial activities. For example, understanding the rates at which components evaporate, dissolve, degrade, and adsorb in the subsurface is critical to establishing an accurate site-specific conceptual model. Recent advancements in two-dimensional (2D) gas chromatography/mass spectrometry (GC/MS) and data analysis software offer new opportunities to address how coal tar weathers in fresh and saltwater sediments.

Objectives

The primary objective of this report is to determine whether 2D GC/MS, including automated sequential GC-GC/MS and comprehensive GCxGC/MS, provide the information needed to understand how coal tar weathers in fresh and saltwater environments. This report summarizes how these two techniques differ from conventional GC/MS and how the data produced address the following objectives.

1. Define the analytical technology, experimental procedures, data processing requirements, and samples needed to differentiate evaporation and dissolution from biodegradation.
    a. Outline the experimental detail needed to analyze coal tar by GC-GC/MS. Although time-intensive, this technique offers the best opportunity to separate target compounds from matrix interferences and to produce a database of retention time and mass spectrometry information to detect alkylated PAH and sulfur heterocycle homologs in coal tar.

   b. Outline the experimental detail needed to analyze coal tar by GCxGC with MS and flame ionization detection (FID). These techniques should provide the best visible chromatographic image of how coal tar weathers. The library produced from objective 1 will be used in the 2D experiments.

2. Define the data processing requirements for GC/MS and/or GCxGC/MS to quantify alkylated homologs of PAH and PASH from coal tar in pore water and sediment.
   a. Outline how mass spectral deconvolution software increases measurement confidence as a function of precision, accuracy, selectivity, and sensitivity.

3. Define the chemical information needed to answer the question of whether natural attenuation and/or active treatment are effective means of reducing coal tar pollution in the environment.
   a. Outline chromatographic profiles and diagnostic ratios helpful in distinguishing biodegradation from dissolution and evaporation.

2

GAS CHROMATOGRAPHY

The U.S. Environmental Protection Agency's (EPA) standardized GC/MS method for the analysis of PAH is SW 846, method 8270. The method employs a high resolution fused silica capillary column, 30m×0.25mm i.d., with a 0.25μm film containing 5%-phenyl-methylpolysiloxane stationary phase (HP-5MS or equivalent). The purpose of the stationary phase and rise in column temperature, for example, from 60 ^{0}C to 300 ^{0}C at 10 ^{0}C per minute is to slowly volatize and separate sample components from one another. Because coal tar contains thousands of compounds, total separation is not possible using a single column hence the innovation of 2D GC, which employs two columns whose stationary phases differ greatly in chemical composition.

Automated Sequential Gas Chromatography

In this paper, we demonstrate the efficiency of using automated sequential 2D GC-GC/MS to make coal tar-specific libraries of target compounds. GC-GC/MS provides the best means of separating aliphatic from aromatic compounds. GC-GC/MS provides exact retention times and clean mass spectra of target compounds. This information is needed to correctly identify and quantify coal tar components and to determine how coal tar weathers in the environment.

Because the matrix interferes with target compound identification, EPA method 8270 results in loss of analyte when reporting limits are raised above method detection limits and incorrect estimates of target compound concentrations. Our aim is to show that once the GC/MS library is made, EPA method 8270 with the Ion Fingerprint deconvolution data analysis software will correctly identify target analytes and estimate their concentrations to find differences among weathered samples.

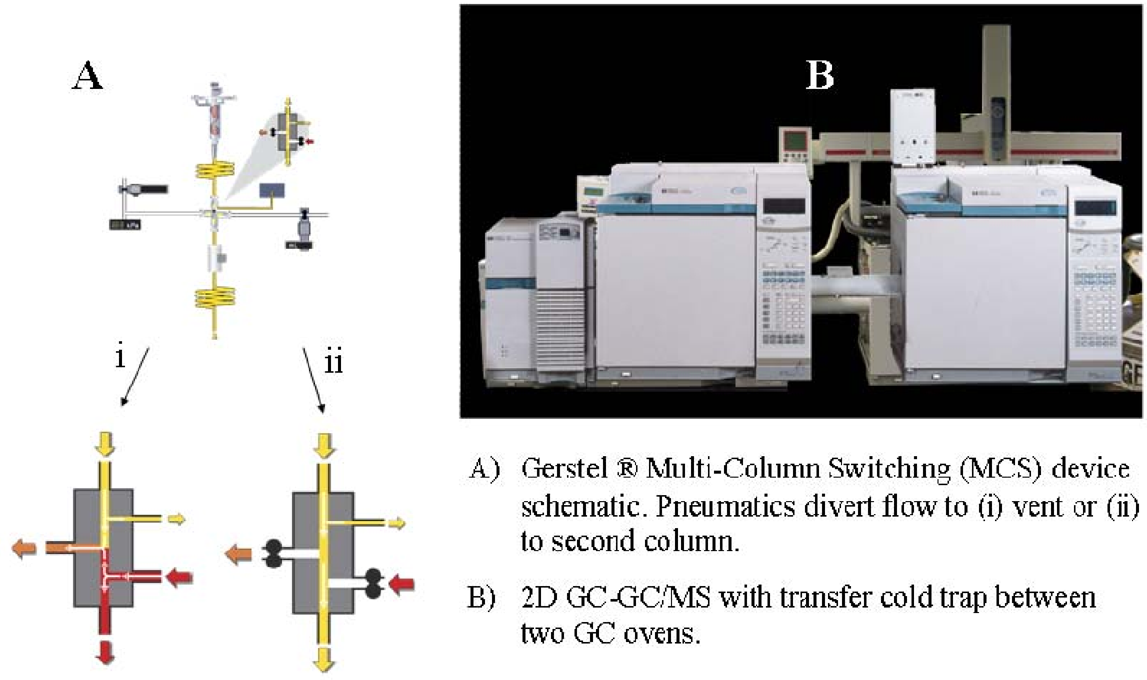
Multidimensional GC-GC extends the separation power over single column GC methods (MacNamara *et al.*, 2004). As sample components begin to separate on the first column a small, 1-min, fraction of the sample is transferred to the second column, whose stationary phase is chemically different from the first. Only the fraction cut to the second column is allowed to elute on the second column. The remainder of the sample, i.e., the portions before the cut and after the cut, is sent to waste. The greater the dissimilarity of the stationary phases the greater is the gain in separation space and, thus, column capacity (de Geus *et al.*, 1996). In this context, the goal is to obtain a clean mass spectrum for each sample peak. Reviews of multidimensional GC-GC for petroleum, environmental pollutants, and foods and flavors have been published (Bertoncini *et al.*, 2005; de Boer *et al.*, 2003; Komura, 1997; Marriott *et al.*, 2003).

Previously, we demonstrated that GC-GC/MS provides the separation space needed to build libraries of alkylated naphthalenes, fluorenes, phenanthrenes, and dibenzothiophenes in diesel fuel, see (Zeigler *et al.*, 2008). Figure 2-1 illustrates the instrumentation used in that study. Because diesel fuel is a medium boiling range petroleum distillate, not all of the higher molecular weight alkylated PAH were found, which are needed for coal tar forensic environmental investigations. We showed that GC/MS, with IFD spectral deconvolution, unambiguously identified all isomers of alkylated PAH from naphthalene through phenanthrene in the sample and proved that selected ion monitoring (SIM) of ions and selected ion extraction (SIE) of full scan data resulted in severe overestimation of analyte concentration. Finding also showed that using a single alkylated PAH homolog fragmentation pattern underestimated that homolog's concentration. This study indicates that once all of the isomeric alkylated PAH patterns are known, measurement selectivity, precision, accuracy, and sensitivity increases.

To date, no work has been published on the detection of PAH and PASH and their alkylated analogs in coal tar by GC-GC/MS. Although not part of this scoping study, we did analyze a coal tar sample supplied by an EPRI member to assess whether new alkylated PAH or PASH compounds could be found. Figure 2-2 shows the GC-GC/MS profile of a 1-min fraction of the coal tar sample at 38 min. The fraction was transferred from a HP-17MS column (a medium polarity stationary phase) to a HP-5MS column (a low polarity stationary phase). Evident from the figure are the well separated C_1 and C_2 dibenzothiophene peaks, which were identified by mass spectrometry deconvolution software and confirmed by the sulfur-specific detector. The latter detector only responds to those compounds in the sample that contain sulfur. The MS indicated the presence of dibenzothiophenes, which are three-ring PASH. Although the peaks for the C_3 and C_4 dibenzothiophenes overlap, the mass spectrometry data analysis software easily deconvolved the spectra and identified the compounds.

We plan to use the GC-GC/MS data to develop a library of fragmentation patterns for each PAH and PASH alkylated homolog. No C_3-dibenzothiophene MS patterns exist in the NIST or Wiley mass spectrometry databases, which are the standard MS libraries used by analysts to identify unknowns. Based on our previous work and the structure of dibenzothiophene, there may be as many as a half-dozen unique fragmentation patterns needed to identify all possible isomers. For example, Figure 2-3 depicts several possible MS patterns for C_4-naphthalene. Note that the MS pattern shown in the blue box captures the correct mass spectrum for five of the seven peaks found in the coal tar sample, while the other two patterns correctly capture the mass spectrum for the corresponding peak in the red and black boxes, respectively, see section on mass spectrometry data analysis software.

This initial data on coal tar is consistent with the earlier published findings on crude oil and confirms current environmental forensic GC/MS methods will produce erroneous data, since a single pattern cannot correctly identify all isomers. It also means the concentration estimations reported by these forensic methods will be wrong. Although the GC-GC/MS combinatorial library building process is time-consuming, it is essential because it provides the information needed to correctly estimate the concentration of all target compounds in coal tar. Once done, however, retention time and spectral information can be used to quantify target compounds by EPA method 8270 GC/MS and GCxGC/MS using the spectral deconvolution software in the same amount of time as current forensic environmental methods.



A) Gerstel ® Multi-Column Switching (MCS) device schematic. Pneumatics divert flow to (i) vent or (ii) to second column.

B) 2D GC-GC/MS with transfer cold trap between two GC ovens.

Figure 2-1
Multidimensional, Automated Sequential, Agilent GC-GC/MS Instrument and Diagram of Gerstel's Flow Switch Used to Transfer a Fraction of the Total Sample from Column 1 to Column 2. This Technology Was Used to Identify Alkylated PAH and PASH Fragmentation Patterns in Diesel Fuel and Coal Tar.

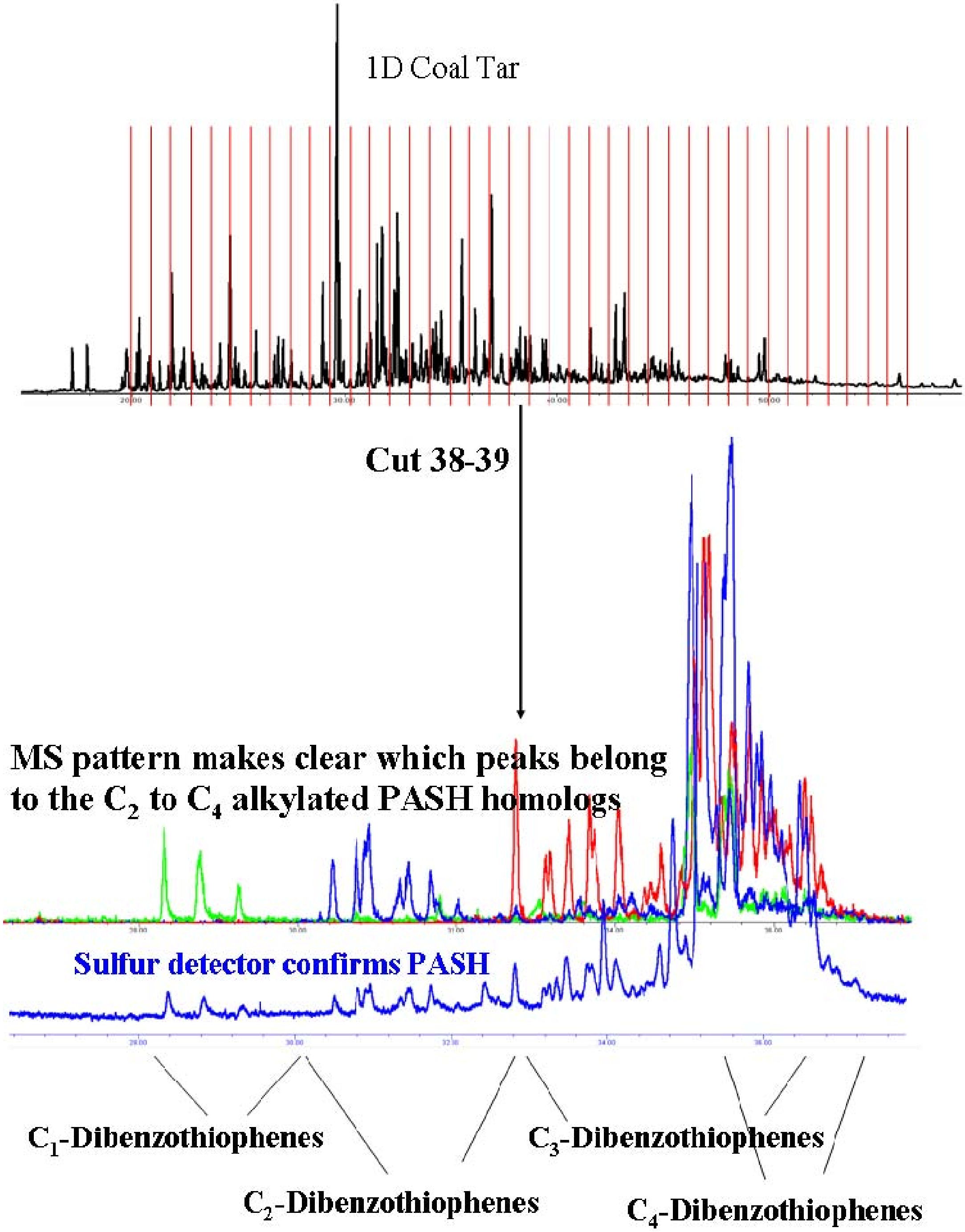


Figure 2-2
Library Building Using Automated Sequential GC-GC with MS and Sulfur Detectors and Retention Time Locking.

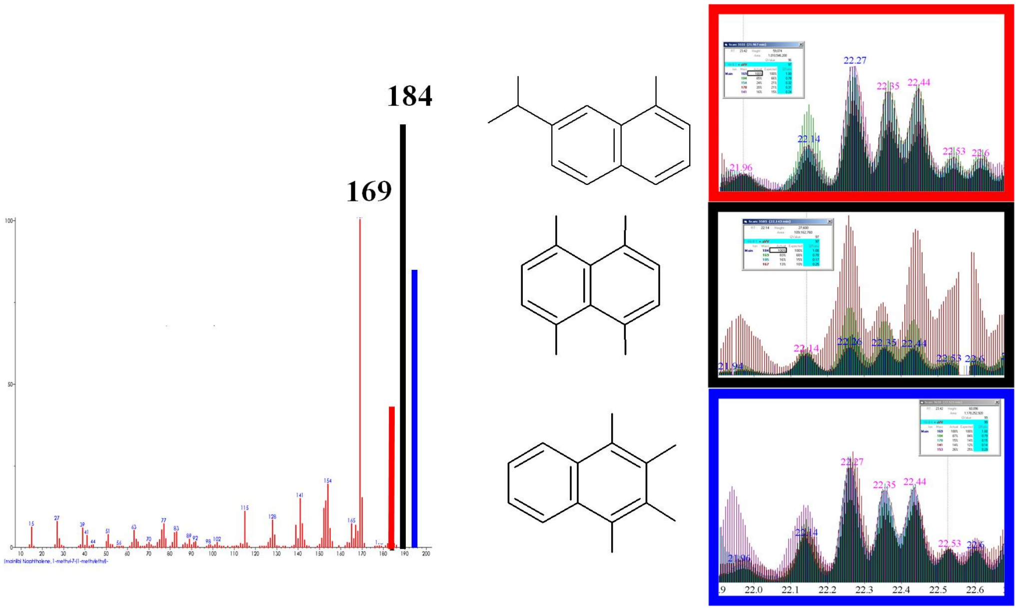


Figure 2-3
The Mass Spectra of Three C_4-naphthalene Isomers, Whose Molecular Ion Signal at m/z 184 Differs by a Factor of Three, see Red and Black lines.

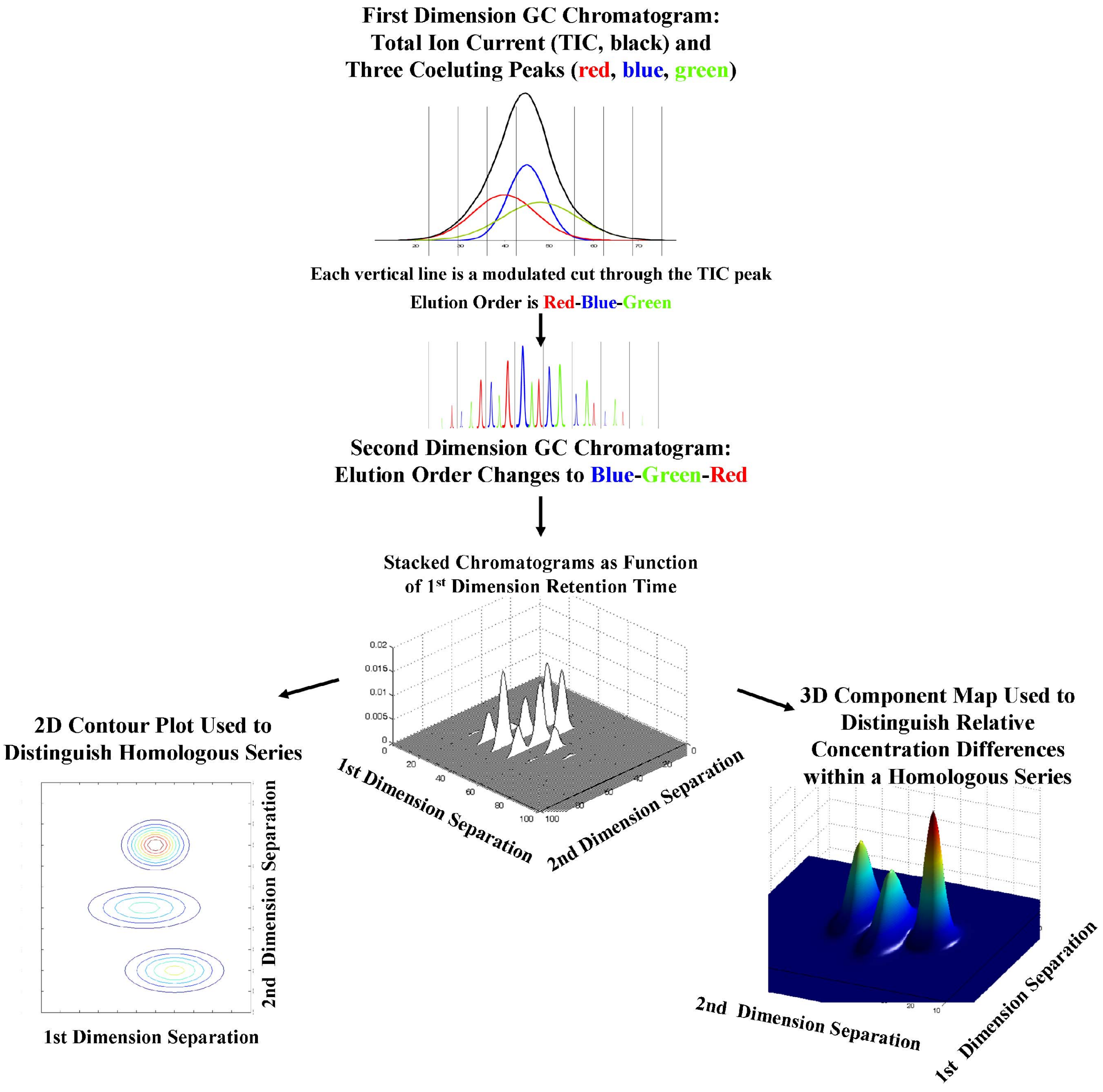
Comprehensive Gas Chromatography

Some consider GCxGC/MS to be the most powerful, information rich analytical tool for temperature stable, volatile and semivolatile organic compounds (Adahchour *et al.*, 2006; Marriott *et al.*, 2003; Mondello *et al.*, 2008). In contrast to GC-GC separations, where a 1-min fraction per injection is transferred from the first column to the second column, comprehensive GCxGC continually transfers the entire sample from a single injection from the first to the second column every few seconds. This means analysis times by GCxGC/MS equal GC/MS. To avoid overlap, much shorter second columns are used; see schematic of separation process and resulting 3D component map in Figure 2-4. The figure illustrates a three component separation, where they coelute on the first column and are separated on the second column. Evident is the change in elution order from red-blue-green to blue-green-red due to each compound's interactions with the different stationary phases. By stacking the second dimension chromatograms as a function of first column elution times, the resulting data can be transformed in 2D contour maps or 3D component maps. The former makes it easier to observe coal tar homolog changes as the sample weathers, while the latter makes it easier to observe relative concentration differences within the same homolog family.

Since peak capacity, n_C, is the maximum number of peaks that can be stacked next to one another without overlap in a single GC run, the peak capacity for GC-GC is the sum of the first column plus each second column fraction, y, (n_{C1} + (y *x* n_{C2})) (Bertoncini *et al.*, 2005). In contrast, GCxGC is the product of columns 1 and 2, (n_{C1} *x* n_{C2}) (Dalluge *et al.*, 2003). Although this technique does not provide quantitative data at the present time or clean mass spectra for every peak, GCxGC significantly increases the peak capacity compared to GC without sacrificing analysis time as does GC-GC.

A key limitation is the inability of commercially available software to quantitatively analyze GCxGC data due to slight shifts in retention times of densely populated and unresolved peaks from one chromatogram to the next (Reichenbach *et al.*, 2004; Reichenbach *et al.*, 2003; Wardlaw *et al.*, 2008). Rather than develop algorithms that match probabilistic peak retention times from one chromatogram to another as commercial companies try, we believe the spectral deconvolution algorithms we developed for GC-GC/MS and GC/MS will work for GCxGC/MS. Phase II will explore using the IFD deconvolution algorithms to quantitatively identify target compounds in the library.

Figure 2-5 depicts simulated coal tar data of a purported fresh and weathered sample based on what we would expect to see from GCxGC/MS data if spectral deconvolution were used to acquire the data. The 3D component map is based on crude oil results reported in the literature (Reddy *et al.*, 2002). The data depicts those compounds lost due to evaporation, dissolution, and biodegradation as well as recalcitrant compounds whose aged sample signals increase on a relative basis (Arey *et al.*, 2005; Arey *et al.*, 2007; Arey *et al.*, 2007; Arey *et al.*, 2007; DeMello *et al.*, 2007). This information should provide more accurate estimates of concentration and, thus, increased confidence that the diagnostic criteria typically used in forensic investigations of coal tar weathering are legally defensible. Regulators should not have a problem accepting the data since the same QC procedures used in EPA method 8270 can be applied to GCxGC/MS data. Moreover, GC/MS with spectral deconvolution has been used in many hazardous waste site investigations and cleanup, with data QC'd by state and federal regulatory agencies as well as Departments of Defense and Energy and the private sector.



First Dimension GC Chromatogram: Total Ion Current (TIC, black) and Three Coeluting Peaks (red, blue, green)

Each vertical line is a modulated cut through the TIC peak

Elution Order is Red-Blue-Green

Second Dimension GC Chromatogram: Elution Order Changes to Blue-Green-Red

Stacked Chromatograms as Function of 1st Dimension Retention Time

2D Contour Plot Used to Distinguish Homologous Series

3D Component Map Used to Distinguish Relative Concentration Differences within a Homologous Series

Figure 2-4
Illustration of the GCxGC Data Acquisition and Transformation Process.

What we would expect to find.

- loss of volatile benzenes, PAH, PASH
- loss of polar compounds
- increase in higher MW C_0 to C_4 PAH and PASH

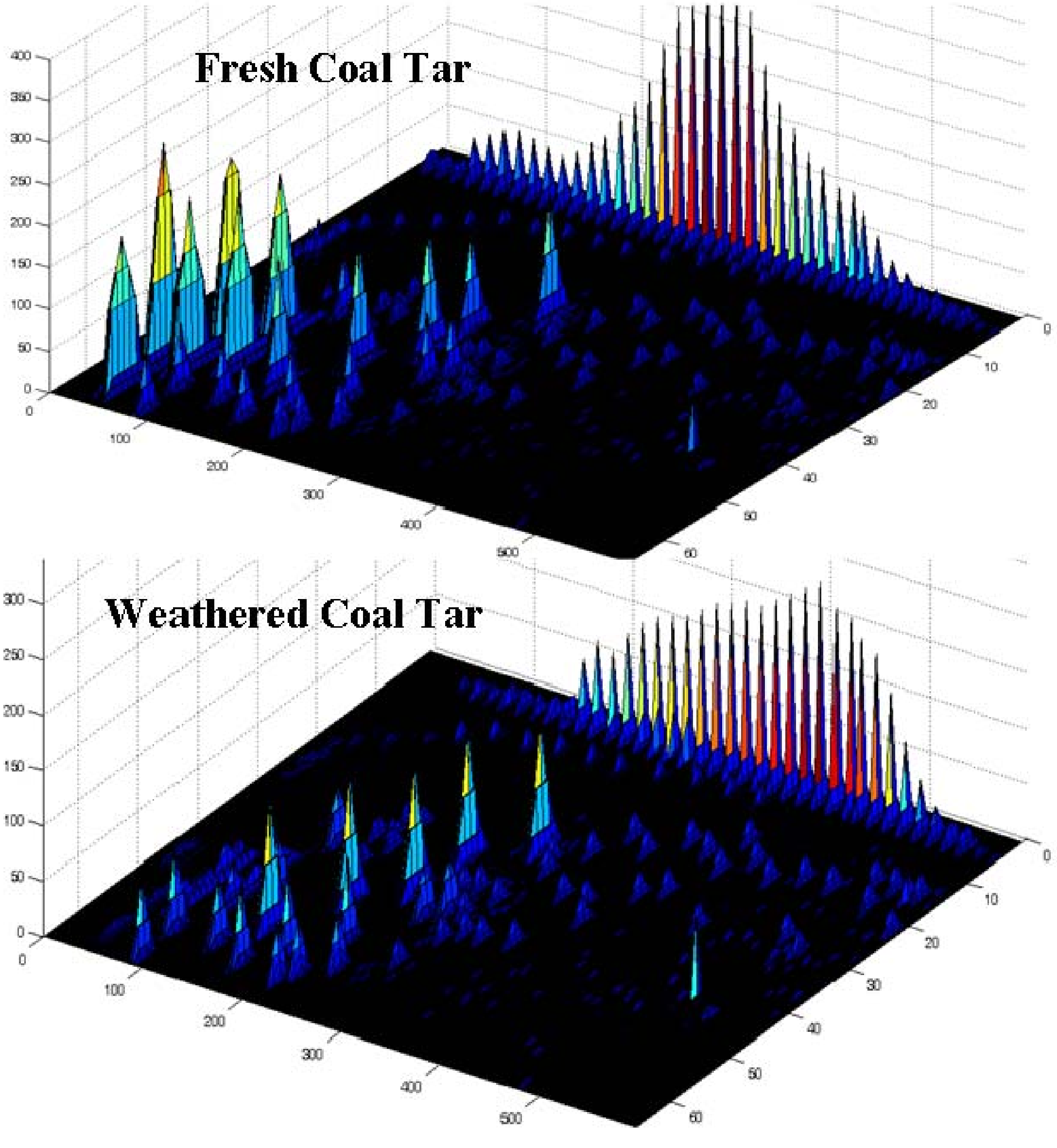
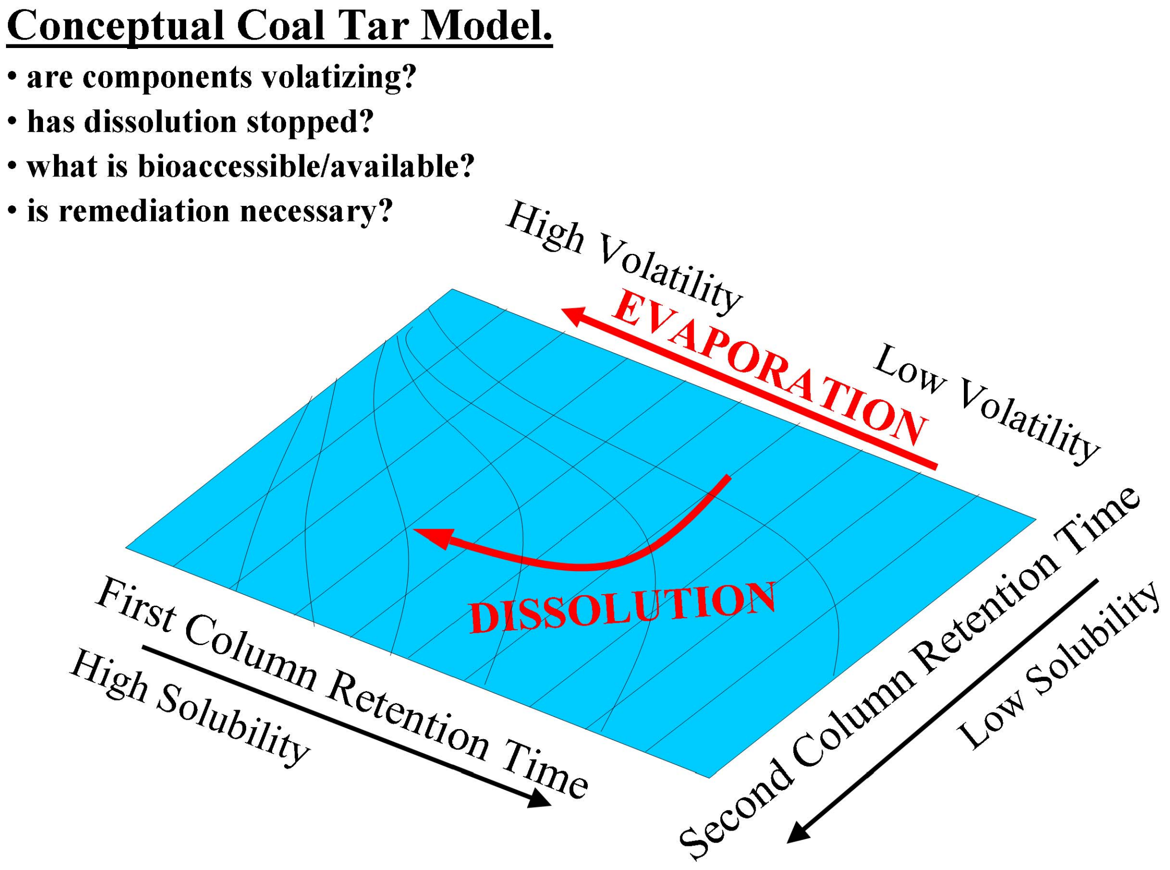


Figure 2-5
Simulated Fresh and Weathered Coal Tar GCxGC/MS 3D Component Maps.

The 2D map can be used to determine which compounds are more likely to evaporate or dissolve in aqueous environments, see Figure 2-6. The non polar column elution times correlate to vapor pressure (evaporation) while retention times on both columns are used to predict aqueous solubility.

The 2D and 3D visualization maps provide the forensic data needed to determine the effects of water washing and evaporation on coal tar weathering and whether analyte loss has reached steady state.



Conceptual Coal Tar Model.

- are components volatizing?
- has dissolution stopped?
- what is bioaccessible/available?
- is remediation necessary?

Figure 2-6
Partitioning Contour Map Illustrates the Correlation Between Retention Times on Evaporation and Dissolution.

3

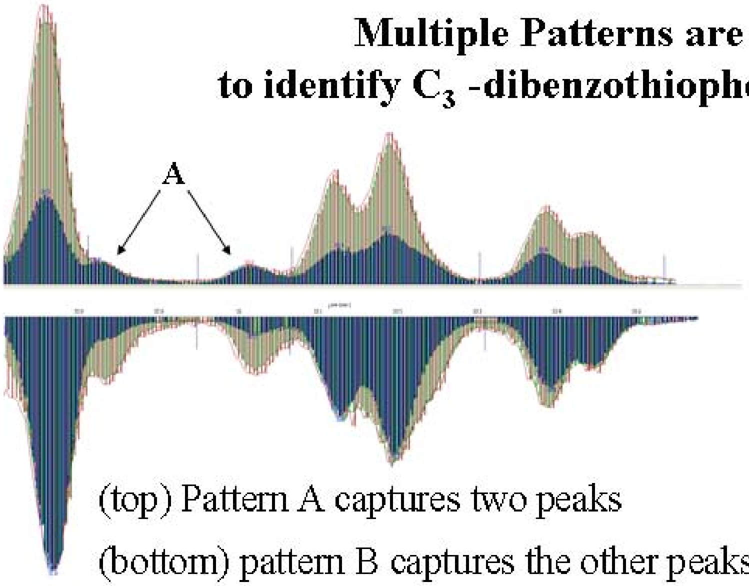
MASS SPECTRAL DECONVOLUTION

GC/MS is also a two dimensional technique. First, compounds are separated based on their retention in the column. As organics enter the MS, they are ionized by high energy electrons, which subsequently fragment into smaller masses. Second, each fragment ion is separated from all others by the instrument's mass filter, with each fragment ion detected according to its mass-to-charge (m/z) and abundance. The resulting MS pattern is typically compared to patterns in a library, for example, the NIST and Wiley libraries. Positive identification requires all of the m/z values and their relative abundances to match a library pattern within ± 20%, which happens rarely when two or more compounds enter the MS at the same time. Published studies have shown that a 2-component system can be identified using current library matching routines with 85% probability but the 3-component system above will yield < 50% probabilistic match. Because coal tar is so complicated, with at least 40 different target compounds eluting within 1-min (cut 38-39 in Figure 2-2), GC-GC/MS is needed to obtain clean mass spectra to make the libraries. Note: the 40 peaks correspond to alkylated dibenzothiophenes only, with other aliphatics and aromatics also eluting within that same 1-min retention window.

Standard MS instrument vendor data analysis software cannot account for additive ion signal when the sample interferes with the target compound. When this occurs, target ions are misidentified (false positive), ignored (false negative), and/or misestimated. Since the advent of modern analytical instrumentation, researchers have tried to retrieve lost data due to chemical noise through hardware improvements. In contrast, Robbat developed three independent mathematical algorithms, patented a deconvolution process that untangled characteristic, narrow band mass spectral signals, and published results documenting data quality in a wide range of applications (Breault *et al.*, 2005; Considine *et al.*, 2008; MacNamara *et al.*, 2007; Mauro *et al.*, 2000; Robbat, 2000; Robbat, 2001; Robbat *et al.*, 2008). Ion Signature licensed the deconvolution algorithms from Tufts University and incorporated them into a commercially available data analysis software package.

Figure 3-1 shows the deconvolved spectrum for C_3-dibenzothiophene compounds. Identification occurs when the deconvolved ion abundance ratios for the main (blue) and confirming ions (green, aqua blue and brown), after normalization to the main ion at each scan, meet the acceptance criterion set by the analyst and when the Q-value and/or Q-ratio exceed their acceptance criteria. The bar graphs in the figure depict the ion signals used to identify two different C_3-dibenzothiophene patterns, A and B, using the Ion Signature deconvolution software. If the sample and library ion ratios are the same, all three confirming ions, normalized to the main ion, will be the height of the main ion, with the pattern repeating itself at each peak scan. Ideally, if the scan-to-scan peak variance is zero, every scan will be like every other scan in the peak. Only those scans that fall within the acceptance criterion appear as bars and are integrated, which makes compound identification and quantification easy to inspect. The two patterns capture seven of the fifteen C_3-dibenzothiophene peaks that elute in the 1-min cut from column 1 to column 2 as denoted by the sulfur and MS detectors, see Figure 2-2.

The software can be used to produce a GC/MS library from coal tar for PAH and PASH where MS information is not available. Because of the stability of the aromatic backbone, the molecular ion is always present and differs only in its relative abundance, see Figure 2-3. Differences in functional groups and their location on PAH account for the majority of the ions, which limits the number of potential high intensity ions. Selected ion extraction, adding one of the high intensity ions at a time, can be analyzed to determine which ions co-maximize with the molecular ion in each coal tar fraction. From this, many patterns may emerge. Ion pattern co-maximization and invariance are obvious when using the deconvolution software. In contrast, standard instrument software cannot easily determine whether ions co-maximize and if the ion profiles are invariant from one peak scan to the next. As stated earlier, we published the results of this approach for most of the alkylated PAH but not the alkylated PASH (Zeigler *et al.*, 2008).



Multiple Patterns are needed to identify C_3 -dibenzothiophenes in coal tar

(top) Pattern A captures two peaks

(bottom) pattern B captures the other peaks in this region of the chromatogram

C_3-Dibenzothiophenes are important in diagnostic ratios for crude oil

Figure 3-1
Reconstructed Deconvolved Fragmentation Patterns for Two C_3-Dibenzothiophene Isomers Illustrating the Need for Multiple Patterns to Correctly Identify all Target PASH.

4

HOW WILL THE DATA PRODUCED BE USED TO ASSESS WEATHERING IN SEDIMENTS

The previous sections discussed how GC-GC/MS can be used to produce a library that contains retention time and mass spectrometry information for all alkylated PAH and PASH isomers. Based on this library, GCxGC/MS retention profile 2D and 3D surface plots can be used to determine which family of compounds and which compounds within that family are lost due to evaporation, dissolution, and degradation in sediment, bulk, and pore waters. For degradation differences between fresh and weathered samples, isomers not readily soluble in water or easily evaporated can be used to identify target compounds lost due to biodegradation. For quantitative analysis, GC/MS with spectral deconvolution will be used to quantify the target compounds, with GCxGC/MS visualization maps confirming GC/MS results.

Aliphatics

Former MGP sites are tens of decades old. Investigators have shown aliphatic hydrocarbons are among the first compounds biodegraded (Pirnik *et al.*, 1974). Coal tar samples nonetheless contain residual aliphatics but not the standard unresolved chromatogram peaks found in petroleum samples. Nonetheless, aliphatic compounds are among the most hydrophobic components in coal tar, so the loss of these compounds should be due to biodegradation and not water washing. Further, long chain alkanes have very low vapor pressures, e.g., log P^0 (atm) for hexadecane is -6 (Schwarzenbach *et al.*, 1993). Branched aliphatic molecules are more resistant to biodegradation and, typically, remain in coal tar until their corresponding straight chain hydrocarbons have degraded (Kennicutt II, 1988; Stompel *et al.*, 1982). Finally, aliphatics can be biodegraded *without* being “bioavailable,” i.e. dissolved in bulk water (Huesemann *et al.*, 2004).

Polycyclic Aromatic Hydrocarbons (PAH)

PAH tend to be less susceptible to biodegradation than their aliphatic counterparts (Wang *et al.*, 2001). Aromatics also comprise a much larger percentage of the bulk composition of coal tar than in crude oil.

As the number of PAH rings and degree of alkylation increases the amount of biodegradation decreases. For this reason, it is expected that large, highly alkylated PAH should become more concentrated in coal tar as weathering increases, with $C_0 > C_1 > C_2 > C_3 > C_4$ (Wang *et al.*, 1998; Wang *et al.*, 1995).

Further, as weathering increases the ratio of the sum of naphthalene, phenanthrene, fluorene, and dibenzothiophene and their alkylated homologs decreases relative to the sum of chrysene and its alkylated homologs. Unlike aliphatics, however, no studies have shown biodegradation of PAH without the PAH first being bioavailable. On the other hand, if biodegradation stops it does not necessarily imply that PAH are not bioavailable (Huesemann *et al.*, 2004). For example, PAH may be unavailable to site-specific microorganisms but might still be present in high enough concentration to become bioaccumulated up the food chain (Meador *et al.*, 1995).

Isomers of alkylated PAH have also been shown to biodegrade at different rates. For instance, bacteria degraded 1,3- and 1,6-dimethylnaphthalene (Wang *et al.*, 1998) *and* the 2- and 3-methyldibenzothiophene (Wang *et al.*, 1995) more quickly than other homolog isomers, while physical weathering did not significantly alter the ratio of these compounds relative to other isomers. It should be noted that some alkylated PAH isomers are strain dependent and that isomer specific diagnostic ratios can be misleading in some instances. Regardless, isomers of PAH are expected to have similar physicochemical properties so that changing isomer ratios can be taken as "qualitative proof" of biodegradation (Lamberts *et al.*, 2008).

Polycyclic Aromatic Sulfur Heterocycles (PASH)

Thiophenic sulfur compounds are abundant in coal tars (Burchill *et al.*, 1982; Kong *et al.*, 1982; Willey *et al.*, 1981). These PASHs are also resistant to evaporation and water washing (Hegazi *et al.*, 2004; Manowitz *et al.*, 1992) and are more resistant than their PAH counterparts to photooxidation (Andersson, 1993) and biodegradation (Meyer *et al.*, 2000). Some investigators showed that certain isomers of thiophene compounds are resistant to bacterial degradation, while others are degraded (Wang *et al.*, 1995). Moreover, some large ring PASH appear to be produced from microbial activity on smaller ring thiophenes (Gai *et al.*, 2008). Because of these factors, it is expected that sulfur heterocycles should be a powerful class of biomarkers for degradation, yet surprisingly, little work has been done to use these compounds in the context of coal tar site characterization.

Diagnostic Ratios

Much has been published concerning petroleum degradation in the environment. As stated earlier, petroleum is much richer in aliphatic compounds than coal tar, which means the latter has correspondingly less biomarkers. Biomarkers are compounds of plant origin which have not changed much during oil formation. However, marked similarities in composition exist between coal tar and crude oil for aromatic compounds and many of the same diagnostic ratios that are used for petroleum are amenable to coal tar weathering studies. Table 4-1 summarizes selected diagnostic ratios found in the literature search. Some diagnostics point to differences in source material, e.g., gasoline versus coal tar, while others indicate evaporation compared to biodegradation. In Phase II, the following diagnostic ratios as shown in the table below will be evaluated against the results obtained from 2D and 3D homolog and component maps. Inconsistencies will be flagged, with those diagnostics in agreement with the partitioning plots tabulated for future forensic investigations.

Table 4-1
Selected diagnostic ratios and usefulness in weathering studies.

Chemical Ratio	Diagnostic Indicators
Σ (C_8 to C_{14}) / Σ (C_{22} to C_{28})	Evaporation
Σ (C_{10} to C_{25}) / Σ (C_{17} to C_{25})	Evaporation
Σ (isoprenoid$_{13}$ to isoprenoid$_{16}$) / pristine	Evaporation
Σ (N + F + P + D) / Σ (P + D)	Evaporation and dissolution
Relative distribution of alkyl-PAH	Dissolution, biodegradation, photooxidation, general weathering
Σ (C_{12}-C_{18}) / Σ (equivalent MW isoprenoid)	Biodegradation
Σ (odd n-alkanes) / (Σ even n-alkanes)	Biodegradation
(1,3-dim-N + 1,6-dim-N) / Σ C_2-N	Biodegradation
Σ C / Σ D	Biodegradation
(2-me-D *or* 3-me-D) / 4-me-D	Biodegradation
Various ratios of C_1-D isomers	Biodegradation or Source
A / P and BaP / BeP	Photodegradation
Σ C / Σ P	General Weathering
C_2-D / C_2-P and C_3-D / C_3-P	General weathering
F/C_1-P and C_3-N/C_2-P and D /C_4-P	General weathering
(C_2-D *or* C_2-P) / C_2-C and (C_3-D *or* C_3-P) / C_3-C	General weathering
(Σ N *or* Σ P)/ Σ PAH	General weathering
(C_2-D / C_2-P) / (C_3-D / C_3-P) and (C_3-D / C_3-P) / (C_3-D / C_3-C)	Source
Σ 4-6 ring non alkylated PAH / Σ PAH	Source
Σ N / Σ PAH	Source
Σ P / Σ D	Source
Σ P / Σ (P + alkyl-P)	Source
C_0-C : C_1-C : C_2-C : C_3-C	Source

Symbols used: N = naphthalene, P = phenanthrene, F = fluorene, D = dibenzothiophene, C = chrysene, BaP = benzo[a]pyrene, BeP = benzo[e]pyrene, me = methyl, dim = dimethyl alkyl = alkylated

5

EQUIPMENT NEEDED TO ANALYZE COAL TAR BY MULTIDIMENSION GC/MS

Instrumentation for GC-GC/MS

GC-GC/MS analyses require two independent Agilent GC's, linked by a Gerstel MCS mass flow control switch or an Agilent Dean's switch and freeze trap/thermal desorption transfer line, see Figure 2-1. Alternatively, two low thermal mass Agilent GC ovens can be used with a standard GC/MS. Both instrument configurations require an autosampler and instrument control software for unattended multidimensional GC-GC/MS operation. Libraries containing retention time and corresponding MS information for the alkylated PAH and PASH need to be produced.

Instrumentation for GCxGC/MS

A single GC/MS is used for GCxGC/MS analyses, see Figure 5-1. Agilent manufactures a microfluidic modulator to carry out these experiments, but it is primarily used with FID detection, not MS. The pumping speed of the vacuum limits the flow rate on the second column that can be applied. Practically speaking this means the pressure differential between the first and second column may not be high enough to produce optimum cutting parameters from the first to the second column (Bueno *et al.*, 2004). In contrast, Zoex sells a thermal modulator that is not restricted by pressure differences and, in fact, is better suited to MS detection than Agilent's microfluidic switch. Figure 5-2 shows the thermal modulation loop and a GCxGC/MS instrument (courtesy of Zoex corporation). The Zoex modulator continuously freezes then desorbs portions of the first column as they are transferred to the second column. The Zoex system is advantageous compared to the microfluidic switch in that increased sensitivity is obtained by cryofocusing the analyte.

Data Analysis Software

Ion Signature Technology licensed the Ion Fingerprint Deconvolution (IFD) algorithms described in this report. For quantitative analysis, the IFD software automatically produces calibration and analysis reports. Future work will determine whether the IFD algorithms are amenable to analyze GCxGC/MS data. If able, a MATLAB program from MathWorks will need to be written to produce the 2D GC-GC/MS contour and 3D GCxGC/MS component maps. On the other hand, Zoex sells the GC Image 3D software with their GCxGC/MS modulator.

`Figure 5-1
Agilent 6890/5975 with Gerstel MPS2 Autosampler. Note: this instrument can also be used with Agilent's microfluidic Dean switch to analyze sample by GCxGC/FID. Research will determine if it can be used for GCxGC/MS.

Figure 5-2
Illustration of Thermal Modulation Loop used in GCxGC/MS Instrument. Note: continuous feed of sample from column 1 to column 2 is cryofocused then thermally desorbed onto the second column.

6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on an examination of the literature, our own previous experiments on crude oil, and those few performed on coal tar during this study, the following is concluded:

- 2-dimensional, automated sequential, GC-GC/MS provides the chromatographic separation, unattainable by standard GC/MS, needed to identify all of the fragmentation patterns to correctly identify and quantify alkylated PAH and PASH in coal tar contaminated sediment and water.
- Once obtained, retention time windows and corresponding MS patterns for the C_0 to C_4 alkylated PAH and PASH homologs can be inputted into a library and used with standard EPA GC/MS method 8270, with spectral deconvolution, to quantify all target analytes.
    - In this context, all of the standard EPA QC procedures can be followed to ensure data of known quality is produced and can be audited.
    - The quantitative data produced by this technique can be used with previously published forensic diagnostics to assess how coal tar weathers in sediment and water samples.
    - As stated by the EPA:
        - "[The Ion Signature deconvolution program is a] complete data analysis system for mass spectrometers, with complete report writing capability. The software uses mathematical algorithms to identify target compounds by deconvoluting their ion signals from non-uniform background interference signals contributed to the total ion current. IFD accurately identifies and quantifies target compounds in the presence of high levels of interferences and with minimal chromatographic separation.

          "By 'seeing through' the matrix interferences, the software reduces the need for sample re-analysis and dilution, and increases confidence in surrogate, internal standard, and target compound identification and quantification." (US EPA, 1998)
- 2-dimensional, compressive GCxGC/MS provides the chromatographic separation, at the same analytical speed of GC/MS, to produce 2D partition and 3D component maps.
    - The maps can be used to verify the spectral deconvolved GC/MS data and the diagnostic ratios typically used by forensic environmental scientists.

  - This data can be used to assess how, as a function of evaporation, dissolution, and degradation:
    - one alkylated isomer weathers compared to other isomers in the same homolog
    - an individual homolog weathers compared to other homologs in the same family, and
    - one PAH or PASH family behaves relative to all other families.
  - Unlike GC/MS data, where matrix mass makes it extremely difficult if not impossible to discern differences in composition as samples weather, these maps make visualization easy and provide the detail needed to develop site-specific, component-specific, partitioning maps.
- Because 2D GC/MS is an obvious extension of GC/MS, regulators should be willing to accept the 2D and 3D visualization data and maps as an expansion of site-specific conceptual model information. The information produced should enhance the understanding of how coal tar weathers, which PAH and PASH homologs are lost due to evaporation, dissolution, and degradation and which might/never be bioavailable/accessible.

Recommendations

Research is needed to produce two GC-GC/MS libraries, namely, 1) C_0 to C_4 naphthalene, fluorene, phenanthrene/anthracene, pyrene, chrysene, and 2) the corresponding alkylated 3-, 4-, and 5- aromatic ring sulfur compounds in coal tar. Once the libraries are made, research should be done to confirm that all target compounds can be quantified by EPA method 8270 in a coal tar contaminated sediment sample. Further studies are needed to confirm that the algorithms can be used to identify target analytes when analyzed by GCxGC/MS, with spectral deconvolution software. 2D distribution and 3D component maps should be produced and compared against information obtained from an EPRI member's site. The data should be entered into the member's site-specific conceptual model to determine if the additional information adds value to investigations/remediation activities in progress. Although the data is likely to be different, given the range of target compounds analyzed, comparability can be determined through the parent PAH data. Since the GC/MS and GC-GC/MS analytical instruments and IFD data analysis software are available to continue this study, Phase II of this project should focus on developing the methods and procedures to produce data of defensible and known quality so that environmental samples can be analyzed in routine fashion. In this context, the acquisition of the Zoex modulator and imaging software may be required.

7
REFERENCES

Adahchour, M., J. Beens, R. J. J. Vreuls and U. A. T. Brinkman. *Recent developments in comprehensive two-dimensional gas chromatography (GC × GC): IV. Further applications, conclusions and perspectives*. TrAC Trends in Analytical Chemistry, 25(8), pages. 821-840

Andersson, J. T. *Polycyclic aromatic sulfur heterocycles III. Photochemical stability of the potential oil pollution markers phenanthrenes and dibenzothiophenes*. Chemosphere, 27(11), pages. 2097-2102

Arey, J. S., R. K. Nelson, D. L. Plata and C. M. Reddy. *Disentangling Oil Weathering Using GCxGC. 2. Mass Transfer Calculations*. Environmental Science & Technology, 41(16), pages. 5747-5755

Arey, J. S., R. K. Nelson and C. M. Reddy. *Disentangling Oil Weathering Using GCXGC. 1. Chromatogram Analysis*. Environmental Science & Technology, 41(16), pages. 5738-5746

Arey, J. S., R. K. Nelson, L. Xu and C. M. Reddy. *Using Comprehensive Two-Dimensional Gas Chromatography Retention Indices To Estimate Environmental Partitioning Properties for a Complete Set of Diesel Fuel Hydrocarbons*. Analytical Chemistry, 77(22), pages. 7172-7182

Arey, J. S., R. K. Nelson, L. Xu and C. M. Reddy. *Using Comprehensive Two-Dimensional Gas Chromatography Retention Indices To Estimate Environmental Partitioning Properties for a Complete Set of Diesel Fuel Hydrocarbons, Correction*. Analytical Chemistry, 79(12), pages. 4736-4736

Bertoncini, F., C. Vendeuvre and D. Thiebaut. *Interest and applications of multidimensional gas chromatography for trace analysis in the petroleum industry*. Oil & Gas Science and Technology-Revue De L Institut Francais Du Petrole, 60(6), pages. 937-950

Bueno, P. A. and J. V. Seeley. *Flow-switching device for comprehensive two-dimensional gas chromatography*. Journal of Chromatography A, 1027(1-2), pages. 3-10

Burchill, P., A. A. Herod and E. Pritchard. *Identification of sulphur heterocycles in coal tar and pitch*. Journal of Chromatography A, 242(1), pages. 51-64

Considine, T. and A. Robbat, Jr. . *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*. Environ. Sci. Technol., 42(4), pages. 1213-1220

Dalluge, J., J. Beens and U. A. T. Brinkman. *Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool*. Journal of Chromatography A, 1000(1-2), pages. 69-108

de Boer, J. and R. J. Law. *Developments in the use of chromatographic techniques in marine laboratories for the determination of halogenated contaminants and polycyclic aromatic hydrocarbons*. Journal of Chromatography A, 1000(1-2), pages. 223-251

de Geus, H.-J., J. de Boer and U. A. T. Brinkman. *Multidimensionality in gas chromatography*. TrAC Trends in Analytical Chemistry, 15(5), pages. 168-178

DeMello, J. A., C. A. Carmichael, E. E. Peacock, R. K. Nelson, J. Samuel Arey and C. M. Reddy. *Biodegradation and environmental behavior of biodiesel mixtures in the sea: An initial study*. Marine pollution bulletin, 54(7), pages. 894-904

Gai, Z., B. Yu, X. Wang, Z. Deng and P. Xu. *Microbial transformation of benzothiophenes, with carbazole as the auxiliary substrate, by Sphingomonas sp. strain XLDN2-5*. Microbiology, 154(12), pages. 3804-3812

Hegazi, A. H., J. T. Andersson, M. A. Abu-Elgheit and M. S. El-Gayar. *Source diagnostic and weathering indicators of tar balls utilizing acyclic, polycyclic and S-heterocyclic components*. Chemosphere, 55(7), pages. 1053-1065

Huesemann, M. H., T. S. Hausmann and T. J. Fortman. *Does Bioavailability Limit Biodegradation? A Comparison of Hydrocarbon Biodegradation and Desorption Rates in Aged Soils*. Biodegradation, 15(4), pages. 261-274

Kennicutt II, M. C. *The effect of biodegradation on crude oil bulk and molecular composition*. Oil and Chemical Pollution, 4(2), pages. 89-112

Komura, H. *Application of multidimensional gas chromatography (MDGC) to analyses of food flavors and fragrances*. Bunseki 7(pages. 568-574

Kong, R. C., M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao, R. N. Castle and S. A. Wise. *Capillary Column Gas Chromatographic Resolution of Isomeric Polycyclic Aromatic Sulfur Heterocycles in a Coal Liquid*. Journal of Chromatographic Science, 20(pages. 502-510

Lamberts, R. F., J. H. Christensen, P. Mayer, O. Andersen and A. R. Johnsen. *Isomer-Specific Biodegradation of Methylphenanthrenes by Soil Bacteria*. Environ. Sci. Technol., pages.

MacNamara, K., J. Howell, Y. Huang and A. Robbat, Jr. *Analysis of gin essential oil mixtures by multidimensional and one-dimensional gas chromatography*. Journal of Chromatography a, 1164(1-2), pages. 281-290

MacNamara, K., R. Leardi and A. Hoffmann. *Developments in 2-D gas chromatography with heartcutting*. Lc Gc North America, pages. 82-91

Manowitz, B. and Y. Jeon. *The effects of biodegradation and water washing on sulfur compound speciation in crude oils from the Bolivar Coastal Fields*. Preprints - American Chemical Society, Division of Petroleum Chemistry, 37(3), pages. 951-955

Marriott, P. J., P. Haglund and R. C. Y. Ong. *A review of environmental toxicant analysis by using multidimensional gas chromatography and comprehensive GC*. Clinica Chimica Acta, 328(1-2), pages. 1-19

Mauro, D., S. Smarason and A. Robbat Jr. Accelerated GC/MS Analyses of Samples from Former Manufactured Gas Plant Sites.

Meador, J. P., J. E. Stein, W. L. Reichert and U. Varanasi. *Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms*. Reviews of Environmental Contamination and Toxicology, 143(pages. 79-165

Meyer, S. and H. Steinhart. *Effects of heterocyclic PAHs (N, S, O) on the biodegradation of typical tar oil PAHs in a soil / compost mixture*. Chemosphere, 40(4), pages. 359-367

Mondello, L., P. Q. Tranchida, P. Dugo and G. Dugo. *Comprehensive two-dimensional gas chromatography-mass spectrometry: A review*. Mass spectrometry reviews, 27(2), pages. 101-124

Pirnik, M. P., R. M. Atlas and R. Bartha. *Hydrocarbon Metabolism by Brevibacterium erythrogenes: Normal and Branched Alkanes*. J. Bacteriol., 119(3), pages. 868-878

Reddy, C. M., T. I. Eglinton, A. Hounshell, H. K. White, L. Xu, R. B. Gaines and G. S. Frysinger. *The West Falmouth Oil Spill after Thirty Years : The Persistence of Petroleum Hydrocarbons in Marsh Sediments*. Environmental Science & Technology, 36(22), pages. 4754-4760

Robbat, A., Jr. *Productivity-Enhancing Mass Spectral Data Analysis Software for High Throughput Laboratories*. Environmental Testing and Analysis, 9(4), pages. 15-19, 33

Robbat, A., Jr. *Environmental applications of thermal extraction cone penetrometry and ultrafast gas chromatography/mass spectrometry*. Field Analytical Chemistry & Technology, 5(1-2), pages. 60-68

Robbat, A., Jr., A. Hoffmann, K. MacNamara and Y. Huang. *Quantitative identification of pesticides as target compounds and unknowns by spectral deconvolution of gas chromatographic/mass spectrometric data.* Journal of AOAC International, 91(6), pages. 1467-1477

Schwarzenbach, R. P., P. M. Gschwend and D. M. Imboden. *Environmental Organic Chemistry* John Wiley & Sons: New York, NY, 1993; 626

Stompel, Z. J., K. D. Bartle and B. Frere. *Structural analysis of tars from fluidized-bed pyrolysis of coal. 1. Gas-liquid chromatography of aliphatic and aromatic subfractions*. Fuel, 61(9), pages. 817-823

U.S. Geological Survey. "Scientific Investigations Report 2005-5191." Scientific Investigations Report 2005-5191. 2005

United States Environmental Protection Agency. "Innovations in Site Characterization -- Case Study: Hanscom Air Force Base, Operable Unit 1 (Sites 1, 2, and 3)." EPA-542-R-098-006. 1998

Wang, Z. and M. Fingas. *Use of Methyldibenzothiophenes as Markers for Differentiation and Source Identification of Crude and Weathered Oils*. Environmental science & technology, 29(11), pages. 2842-2849

Wang, Z., M. Fingas, S. Blenkinsopp, G. Sergy, M. Landriault, L. Sigouin, J. Foght, K. Semple and D. W. S. Westlake. *Comparison of oil composition changes due to biodegradation and physical weathering in different oils*. Journal of Chromatography A, 809(1-2), pages. 89-107

Wang, Z., M. Fingas, S. Blenkinsopp, G. Sergy, M. Landriault, L. Sigouin and P. Lambert. *Study of the 25-Year-Old Nipisi Oil Spill: Persistence of Oil Residues and Comparisons between Surface and Subsurface Sediments*. Environmental Science & Technology, 32(15), pages. 2222-2232

Wang, Z., M. Fingas and G. Sergy. *Chemical Characterization of Crude Oil Residues from an Arctic Beach by GC/MS and GC/FID*. Environmental Science & Technology, 29(10), pages. 2622-2631

Wang, Z., M. Fingas and L. Sigouin. *Characterization and identification of a "mystery" oil spill from Quebec (1999)*. Journal of Chromatography A, 909(2), pages. 155-169

Willey, C., M. Iwao, R. N. Castle and M. L. Lee. *Determination of sulfur heterocycles in coal liquids and shale oils*. Analytical Chemistry, 53(3), pages. 400-407

Zeigler, C., K. MacNamara, Z. Wang and A. Robbat Jr. *Total alkylated polycyclic aromatic hydrocarbon characterization and quantitative comparison of selected ion monitoring versus full scan gas chromatography/mass spectrometry based on spectral deconvolution*. Journal of Chromatography A, 1205(1-2), pages. 109-116

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