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Polynuclear Aromatic Hydrocarbons– Characterization and Forensic Analysis

By Shan Tan Lu, PhD

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) ARE UBIQUITOUS CONTAMINANTS OF THE ENVIRONMENT

Polynuclear aromatic hydrocarbons are composed of hydrogen and carbon, and contain multiple ring structures, which are aromatic in nature. In addition to the ring structures, many PAHs contain varying numbers of side-chain carbons in different positions. The PAHs without any side-chains are considered parents or C_0-PAH. While PAHs with one single carbon side chain (methyl group) are said to be C_1-PAHs, two additional carbons attached are C_2-PAH, and so on. Side chains ranging from zero to four are the most common in the natural environment. PAHs with 2-5 rings are common in crude oil or petroleum products, whereas there can be up to six for coal tar oil (creosote).

Indeed, the alkylated PAH, such as C_1-C_4 PAH are more commonly found in natural environments than their parent PAH as they are more resistant to degradation e.g. weathering or biodegradation. Furthermore, the relative abundance of alkylated-PAHs along with their parents are typically able to differentiate their sources, e.g. petrogenics versus pyrogenics. Petrogenics sources are derived directly from crude oil or refined petroleum products. Pyrogenic sources include those derived from combustion of petroleum products, fossil fuel conversion (coal, oil shale, tar sand), and some high temperature distilled residuals such as Bunker C oil (No. 6 fuel oil) and coal tar oil.

CHARACTERIZATION OF PAHs IN VARIOUS SOURCES

The concentration of PAHs in crude oil and their characterization are a function of the initial organic matter and the maturity. As crude oil is produced from oil fields, it is then refined and separated into various petroleum products (such as gasoline, jet fuel, diesel, and various fuel oils) by distillation under mild conditions (<550°C). During mid-distillation of feedstock (crude oil), there is no significant formation of new PAHs, because distillation is relatively mild. Some pyrogenic PAHs can be formed during high temperature distillation. A series of 5-ring pyrogenic PAHs, such as benzo(e)pyrene, benzo (a)pyrene, benzo(b)fluoranthene, benzo(k) fluoranthene, and benzo(a)fluoranthene can be found in Bunker C oil (No.6 fuel oil) in significant concentration.

The most PAH enriched product is coal tar oil (creosote), which is a by-product of coal

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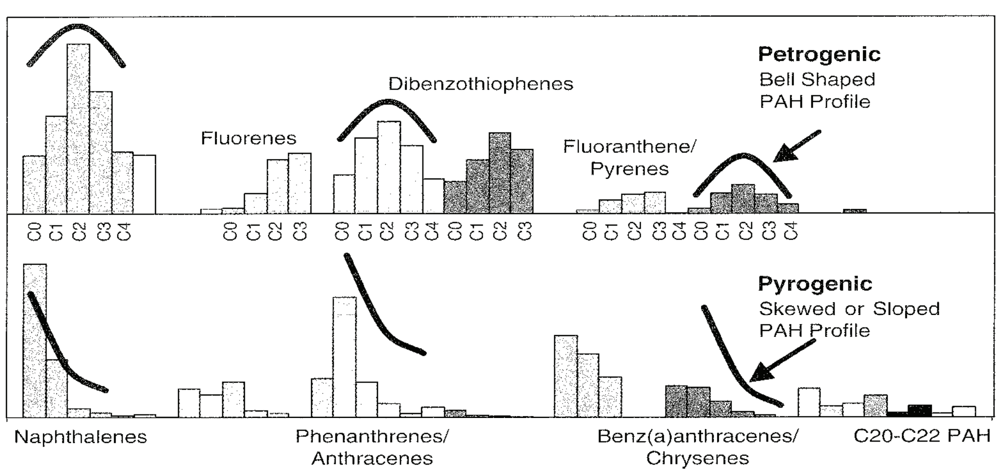

Stout et al. (2002)

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gasification (manufactured gas plants). The PAH present in coal tar oil is derived from (1) the PAH native to coal and (2) the pyrogenic PAH, which are formed when coal is retorted (i.e., treated at high temperature in a closed vessel). Coal tar oil contains various PAHs, and is especially enriched in parent naphthalene, phenanthrene, fluoranthene, pyrene, benzo(a) anthracene, and chrysene.

ANALYSIS OF PAHs

There are several EPA methods for determining the concentration of PAHs in soil and ground water, such as EPA method 8270 and 625. These methods determine 16 to 18 parent PAHs, which the EPA has designated as priority pollutants, along with one alkylated PAH, methyl-napthalene. ZymaX offers analysis of all EPA regulated PAH compounds, either full scan or selected ion monitor (SIM) mode.

In addition, ZymaX Forensics analyzes a list of 50 PAHs (including parents and their alkylated PAHs) that can be used to distinguish sources in soils, sediments, sludge, oils, and other matrices. The analytical method is called "Extended PAHs", and is conducted by GC-MS (SIM). The detection limits are very low: 0.1 ug/L, 0.005 mg/kg, and 2.5 mg/kg for ground water, soil, and NAPL samples, respectively. ZymaX can also provide an interpretation of the data to determine the most probable sources in multi-impacted sites.

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Dr. Shan Tan Lu is the Laboratory Manager of ZymaX Forensics Laboratories. He has over 20 years of experience in forensic and petroleum geochemistry and has managed the Forensic Geochemistry Laboratory for ZymaX Forensics for over 10 years. He has developed environmental forensic analytical methods to determine fuel types from product samples and has also provided expert consulting services for petroleum geochemistry. Dr. Lu has also authored over 20 environmental journal articles related to forensic and petroleum geochemistry and analysis.

GIS-More Than Maps, Part II

By Justin Hone

In our last newsletter, I offered a typical scenario in which you were tasked with developing cost allocation evidence or remediation protocols for a petroleum hydrocarbon plume found beneath an oil refinery and tank farm. We saw how GIS, or a 'geographical information system', is the only timely and cost-effective approach to track the many geographic variables you will encounter. We also found that data input quality and queries are the foundation of your arguments and that the intuitive advantage of three-dimension analyses should not be overlooked. Have we forgotten another important dimension? And how do we share our GIS environment once it's up and running?

The Fourth Dimension

Time is one of the most important variables when assessing a site – time since the release of a contaminant, time until concentrations fall below actionable limits, pre- and post-remedial conditions, plume migration, etc. Time is almost always included in GIS models to allow querying within a desired range, but the tools available today allow for a much more fluid approach.

Like a virtual flip book, any data, which is linked to a date or time, can be animated using sequential snap-shots at any desired interval. You might reconsider your cost allocation percentages after seeing storage tank removals correspond with new contaminant detections, watch a hydrocarbon plume drift across your site over ten years of monitoring before deciding where to install your remedial sentry wells, or monitor ongoing impacted soil excavations and adapt your grading plans and soil transport needs on the fly. The importance of knowing a site's chronology is nothing new. We can now visualize this variable in a way that offers us an enhanced perspective on site history and a more tangible forecast of future objectives.

A Window to the World

GIS often serves as a central information hub for many forms of digital data including map features, environmental data, architectural and engineering plans, aerial photographs, text, graphics, spreadsheets, and video. While this centralizing of information makes sense internally for a corporation to better communicate and stay on target, the hub scheme can also be ideal for external contributors or audiences.

A GIS internet portal can allow authorized individuals or even the public to access the information through any web browser. Users can manipulate, upload, or download geo-spatial information based on permissions granted by the portal administrator. A web-enabled GIS portal might be used by your legal team to develop allocation strategies, by your engineers to upload and analyze the results of recent soil compaction test, or it might provide a simple map interface for public review required by the local city government before redevelopment begins at your site.

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Mr. Hone has been an Associate Geologist with DPRA since 2006 and received his BS in Geophysics from the University of California at Riverside. Since entering the environmental field in 2004, he has managed expert witness and litigation support projects, forensic site assessments, and remedial activities. Mr. Hone has utilized forensic techniques such as carbon isotope ratio analysis, interactive geo-spatial models, and aerial photography interpretation to investigate several chlorinated solvent, hydrocarbon, and nutrient releases. Mr. Hone's particular expertise is developing Geographical Information System (GIS) models and trial graphics to provide clients and juries with simplified concepts of otherwise complex geologic and hydrogeologic scenarios.

Creative People. Smart Solutions.

Planning for Compliance

By Brett Godsey, JD

Under environmental regulatory programs, facilities are required to develop and implement site-specific plans addressing potential sources of pollution. For instance, a facility may be required to have a Spill Prevention, Control, and Countermeasures (SPCC) Plan or a Storm Water Pollution Prevention Plan (SWPPP) The development of plans that meet the regulatory and permit requirements is only the first step towards achieving environmental compliance. A plan must be fully implemented and maintained. When a plan is developed by simply ensuring the plan meets the regulatory or permit conditions on paper without consideration of facility resources, organizational issues, personnel capabilities, and current operational procedures, then implementation and maintenance are less likely to be achieved. The following tips will help to focus plan development with an emphasis on sustainable compliance.

Tip #1: Ensure that appropriate facility personnel are included in the plan development process

The best resource available to an environmental professional when developing a plan is the facility personnel that will be impacted. A plan that is developed and handed to a facility without any prior involvement of appropriate personnel will be incompletely implemented or even ignored altogether.

Tip #2: Be wary of using standardized text from plan templates or former plans

Although the use of plan templates is a good practice for standardizing operations and reducing the cost of developing site-specific plans, care should be taken to avoid using language that does not accurately reflect facility operations or that includes plan commitments that are either inappropriate or unattainable.

Tip #3: Perform facility inspections before and after plan development

A site visit at the end of the process will ensure that the finalized plan is consistent with the facility operations and is a good opportunity to consult with facility personnel on any commitments made in the plan to ensure that they are reasonable and attainable.

Tip #4: Take into account organizational structure when developing a plan

Many facilities subject to plan requirements have complex organizational structures. The plan should be developed to take this into account to avoid unnecessary duplication of activities and ensure that responsibilities are clearly defined.

Tip #5: Ensure that plan commitments are reasonable and attainable

One of the biggest failures of plan development is the making of commitments that are unreasonable or even unattainable. Of course each plan must meet the minimum requirements prescribed by regulation or permit. However, many plan writers will incorporate standardized best management practices that will never be implemented at a given facility either because they require the commitment of extensive resources or are inconsistent with existing operations. The first step is to know the difference between what is required and what is not required when developing a plan.

Tip #6: Train appropriate personnel on the actual plan requirements and model the compliance activities

Any plan training should include all facility personnel that will hold any form of responsibility for plan implementation or maintenance. In addition, the training should address the site-specific conditions of the facility and the plan-specific measures. It is always helpful to demonstrate plan implementation activities (e.g., inspections, labeling, etc...).

A plan that is developed to ensure implementation of site-specific pollution prevention measures should never be treated as a commodity. One size does not fit all. Every facility is unique and an environmental professional that develops a plan must take time to ensure sustainable compliance. What is good for one facility may be entirely inappropriate for another, so ensure that you are addressing the facility's needs when developing a plan and not just merely meeting the minimum requirements for plan content.

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The Art of the Audit

By Brett Godsey, JD

The many benefits of a well-designed and fully-implemented environmental compliance audit program include:

- Identifying opportunities for performance improvement,
- Reducing risk/eliminating potential liabilities,
- Informing communication with stakeholders,
- Focusing expenditures, and Educating employees.

An audit program that puts substantial emphasis on knowledge of requirements without focusing similar attention on other factors impacting the audit process will not be as successful in taking full advantage of the many benefits described above and also will fail to minimize the inherent risks and limitations of auditing. The following tips represent important considerations in the development and implementation of a successful audit program.

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Tip #1: Maintain Objectivity and Independence

Auditors should be objective and free from bias and conflict of interest throughout the process. When internal auditors are directly accountable to facility personnel, act as advisors to facility personnel, or hire consultants to perform compliance tasks, they have a vested interest in the success of the facility. These pitfalls are not always eliminated by the use of external auditors. Many audit programs fail to recognize potential conflicts of interest by hiring consultants to audit programs and plans that they helped to create. In addition, using the same auditors over time may appear to help maintain consistency; but even the most skilled auditors may lose a sense of objectivity by developing a relationship with personnel or becoming unwilling to second guess their own findings or conclusions from previous audits.

Tip #2: Use Effective Evidence Collection Techniques

The audit must lead to evidence of sufficient quality and quantity that competent auditors working independently of each other will reach similar findings from evaluating the same evidence against the same criteria. An auditor is not only an expert on environmental requirements but is also a detective. They must be skilled at the identification of audit trails. The main evidence gathering techniques include interviews, physical inspection, and document review.

A strong interviewer will avoid the use of leading questions, ask obvious questions, repeat answers back to the interviewee, and allow personnel to clarify their responses. The interview is a time to build rapport by allowing the interviewee to shine and demonstrate his or her knowledge, and is not the time for the auditors to show off their knowledge, to admonish, or express any disrespect.

A physical inspection of a facility must be thorough. Too many times an auditor makes assumptions that lead to evidence being overlooked. Thoroughness includes the opening of covers on pits, tanks, and vaults. In addition, the auditor must never relinquish the leadership role to the facility guide.

During document review, auditors should ensure that the documents and records are consistent with evidence collected from interviews and physical inspection. In addition, consistency between documents should be evaluated to identify potential audit trails.

Tip #3: Maintain a Positive and Respectful Process

There is a great deal to a successful audit that has nothing to do with an auditor's training or knowledge of environmental laws and regulations. Auditing involves extensive communication between humans and all the potential pitfalls that are inherent when one person is reviewing the performance of another. Auditors that exhibit a positive and respectful demeanor will have more success in the collection of reliable evidence. In addition, facility personnel are more likely to learn from the audit and be responsive during the corrective action process. A good auditor remains positive, calm, matter-of-fact, and non-judgmental. The auditor must maintain a thick skin, be willing to admit to his or her own potential errors, and not become argumentative or defensive. When an audit becomes a power struggle or a test of wills, the entire process loses its objectivity and the audit outcomes will not lead to the desired benefits.

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Brett Godsey possesses twelve years experience working in the environmental consulting arena, where he has specialized in the areas of environmental compliance and regulatory analysis and development. Mr. Godsey's legal education combined with his environmental compliance work experience endows him with the ability to quickly identify environmental compliance issues and to develop innovative and sustainable solutions.