Environmental Trends & Technologies

Co-Published by DPRA Inc. and ZymaX Forensics Laboratories

Summer 2009

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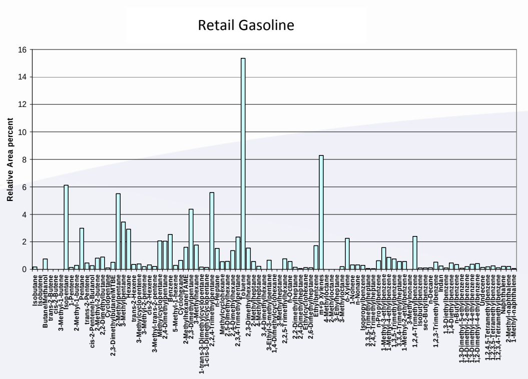
Fuel Fingerprinting: Gasoline

By Alan Jeffrey, PhD

Chemical analysis of a spilled petroleum product is an established way of identifying potential sources of the spill. Fuel fingerprints can provide a visual display that neatly illustrates the similarity of the spilled product and the source using gasoline range bar diagrams. An example of these diagrams can be seen in this comparison of retail gasoline from a nearby dispenser and a monitoring well free product in 2006. Analysis of 92 compounds commonly found in gasoline provides the resolution necessary to achieve a unique fingerprint.



Gasoline range bar diagrams are used to display the chemical analysis of various petroleum products, resulting in a unique chemical fingerprint.

Analysis of the free product from the same monitoring well in 2008, however, showed a very different fingerprint. Many of the

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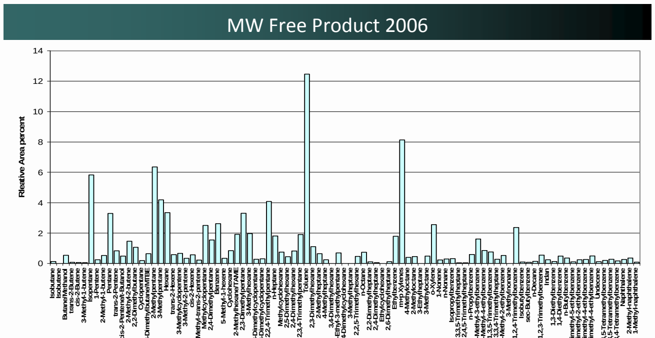
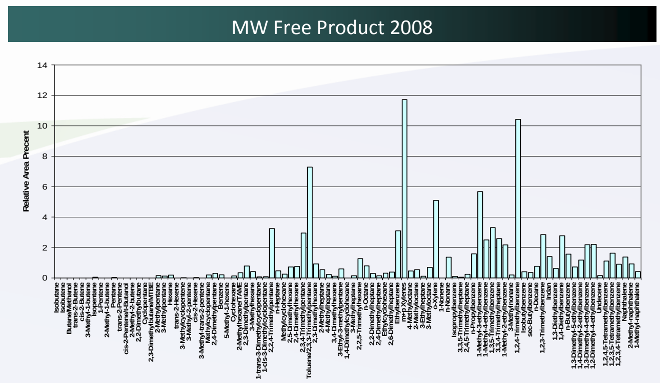


differences have been caused by weathering, resulting in the loss by evaporation of lighter hydrocarbons. Certain fingerprinting ratios, such as the iso-octane ratio (2,2,4-trimethylpentane/methylcyclohexane) are relatively unaffected by weathering: these two hydrocarbons have similar boiling points, water solubility, and biodegradability. A further advantage of the iso-octane ratio is that it is controlled by the formulation of the gasoline, in which different refinery streams are blended to produce the finished gasoline. Thus, the ratio is normally different in gasoline from different sources and even in different grades of gasoline. In the example illustrated above, the iso-octane ratio was 5.5 in 2006, but 12.8 in 2008. This showed that weathering alone could not account for the difference in the gasoline fingerprint in 2008, and indicated that there had been an influx to the well of gasoline from another source.

Gasoline non-hydrocarbon additives can also be useful in fingerprinting. These include the alkyl lead compounds in all leaded gasoline, and oxygenates such as MTBE and ethanol in newer unleaded gasoline. In this example, methylcyclopentadienyl manganese tricarbonyl (MMT), an octane-enhancing additive that is relatively rare in US gasoline, provided a unique way of fingerprinting the gasoline. MMT was present in both the retail gasoline and in the 2006 monitoring well free product, providing additional evidence of the retail gasoline in the monitoring well. MMT was not present in the 2008 monitoring well free product, indicating again a different source. Fingerprinting ratios coupled with the presence or absence of non-hydrocarbon additives



provides an established way of determining the potential source of a spilled petroleum product.

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Dr. Alan Jeffrey has a BS in Biochemistry, an MS in Organic Chemistry and a PhD in Oceanography. Dr. Jeffrey has over 20 years of US and international experience in environmental science and geochemistry. At ZymaX Forensics, Dr. Jeffrey has focused on the use of geochemical techniques to solve environmental problems, including sources of spilled hydrocarbon fuels, nitrates, and fugitive methane seeps. Dr. Jeffrey interacts with clients to determine the particular forensic issues at a site and sets up site specific forensic analytical schemes to clarify these issues. He has prepared over 100 proprietary reports for clients that interpret analytical data, place data in the context of other site information, and answer questions such as the identity of spilled petroleum products, the similarity or difference in the products in separate plumes, and the time of release of the products. Dr. Jeffrey has served as an expert witness, has been deposed and testified at trial in cases involving petroleum product spills, and is the author of fourteen publications on oceanography, petroleum geochemistry and environmental monitoring. He has conducted workshops in environmental forensics and has given numerous presentations at scientific meetings in the USA, Europe and Asia.

GIS - More Than Maps, Part I

By Justin R. Hone

Let's say your job is to develop cost allocation evidence or a remediation protocol for a petroleum hydrocarbon plume discovered beneath an oil refinery and tank farm. You must account for the proximity to above- and below-ground storage tanks, the groundwater gradient and depth of multiple aquifers, soil transmissivities, potential plume mixing from neighboring facilities, and have a database containing more than 300,000 records of soil and groundwater analytical results from various depths and times. Keeping track of all these variables in a cost-effective and timely manner is impossible without GIS.

GIS, or a 'geographical information system', consolidates all types of geographically referenced information into models which provide simple means for data analysis, management, and display in an intuitive and interactive environment. While GIS is a relatively new tool for the environmental professional, computerized GIS was first developed in the 1960's by the Canadian government to analyze rural land use data on a whopping 1:50,000 scale. With the explosion of inexpensive computing power and global positioning system (GPS) technologies in the early 1980's, GIS blossomed into a commercial product within reach of the environmental consulting sector's budget-minded grasp.

Input is Everything

The interactivity of GIS hinges on solid data queries telling the software what data you want to see at any given time. If your query is built like a bombproof bunker, a poorly constructed database can become the precarious foundation wobbling beneath.

For the scenario offered at the beginning of this article, your query might be "where is gasoline found in soil above remedial action levels and greater than 5 feet deep?" Each

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variable (i.e. “soil sample,” “> 5 feet deep,” “analyte: gasoline,” etc.) queries a database containing the relevant spatial data. If just one of these pieces of data is missing or incorrect, an entire theory can be rendered inert and your overall hypothesis can be called into question.

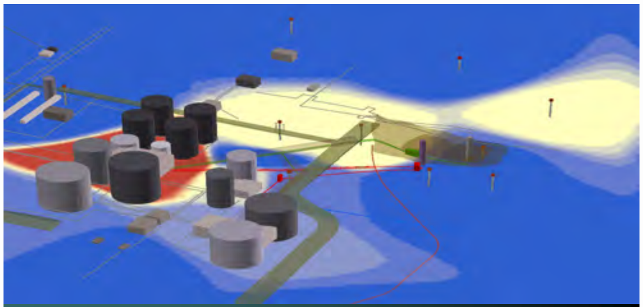
The Earth is Not Flat

GIS is commonly used to create two-dimensional maps for reports, slideshow presentations, or trial graphics. While useful for conveying most ideas, a flat page doesn’t always allow a true appreciation of the variables that may be the crux of your analysis.

Imagine being able to dive under the ground surface of your site in three-dimensions. First, you sit within an underground storage tank excavation and view gasoline detected in the surrounding soil samples, noting precisely where the leak occurred and how far the plume has migrated. You then look down to see how far you are from an underlying bedrock aquifer and whether or not groundwater has been impacted. Using GIS in a way that mimics how you think about the everyday world – in 3D – opens up new levels of insight and efficiency.

More to Come…

Stay tuned for More Than Maps, Part II, discussing the important dimension of time and a relatively new tool being used by the GIS community for data dissemination and cooperation – the web portal.



3-D portrayal of data using GIS allows for better visualization and interpretation of data resulting in a more effective analysis.

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DPRA has provided GIS solutions in a wide variety of business applications including trial graphics and deposition aids, satellite imagery integration, web-mapping development, integration of spatial and mapping functions into database applications, data conversion, data review, and quality control review projects. Our clients include the U.S. EPA, DOE, DoD, and Ontario Canada's Ministries of the Environment and Natural Resources as well as many law firms and private industries.

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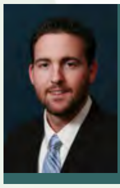

Mr. Hone has been an Associate Geologist with DPRA since 2006 and received his BS in Geophysics from the University of California at Riverside. Since entering the environmental field in 2004, he has managed expert witness and litigation support projects, forensic site assessments, and remedial activities. 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.

EPA Moves Ahead With Greenhouse Gas Regulation

By Trisha Van Stright

On June 27th the House narrowly passed a climate change bill which calls for a nationwide cap-and-trade program on greenhouse gas (GHG) emissions, among other measures. The bill represents a landmark step towards combating climate change and transitioning to a clean energy economy, however debate over a Senate version is not expected to begin until the fall, with passage uncertain.

Although both President Barack Obama and EPA Administrator Lisa Jackson have expressed their preference for new legislation to regulate GHGs, they are not waiting for action from the Hill. Two important EPA-led developments which have recently completed the public comment phase will, once finalized, pave the way for significant regulation of GHG emissions even in the absence of new climate legislation by Congress.

The first action, a mandatory GHG reporting rule, is actually required by the FY2008 Consolidated Appropriations Act. The proposed rule calls for annual emissions reporting from those entities which emit 25,000 metric tons (MT) or more of GHGs per year. The 25,000 MT threshold is expected to encompass about 85-90% of total national US GHG emissions, while leaving small businesses and most of the agricultural sector free from the burden of reporting requirements. The data collected from this reporting will provide an “accurate and comprehensive” assessment of national emissions to inform future GHG policy decisions, and is necessary for a cap and trade program. If implemented as proposed, reporting will be required beginning in 2011 (for the 2010 calendar year.) For more information, see http://www.epa.gov/climatechange/emissions/ghgrulemaking.html.

Secondly, on April 24th EPA published a Finding in response to the 2007 Supreme Court decision, where the Court held that GHGs are air pollutants covered by the Clean Air Act (CAA) and EPA must determine whether GHG emissions from new motor vehicles cause or contribute to harmful air pollution. The EPA’s positive findings that GHGs do “threaten the public health and welfare,” and that emissions from motor vehicles contribute to GHG pollution obligate the Agency to regulate

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GHG emissions from motor vehicles as well as from other sources. For more information, see http://www.epa.gov/climatechange/endangerment.html.

Although there is a consensus that the CAA is ill-suited to regulate GHGs, it appears that the EPA is gearing up to use its authority under the CAA to regulate GHGs until, Administrator Jackson says, "comprehensive legislation to address this issue and create the framework for a clean energy economy" can be passed by legislators.

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Ms. Trisha Van Stright received her BS in Physics in 2003 and has been an Environmental Scientist and GIS Analyst with DPRA's San Diego Office since June of 2005. She provides interdisciplinary technical support and project management for environmental forensics, land records analysis, and Institutional Control effectiveness review projects. Clients for these projects range from private parties to federal agencies including EPA Headquarters Office of Site Remediation Enforcement. Ms. Van Stright has a keen interest in sustainability and climate science. She strives to stay abreast of policy and regulatory developments, on alert for new opportunities and challenges that may affect the environmental industry.

ZymaX Forensics Becomes the First Commercial Laboratory Offering Nitrate Isotope Analysis Using "Denitrifier Method"

By Yi Wang, PhD, Director of ZymaX Forensics Isotope Laboratory

Nitrate contamination of groundwater supplies is an increasing health concern as urban areas continue to expand into rural areas. Farming, intensive livestock operations, septic sewage systems, and other practices in rural areas release organic and inorganic nitrogen into the environment, which ultimately show up in the groundwater as dissolved nitrate.

Fortunately, nitrate isotope analysis for ^{15}N and ^{18}O could help distinguish the sources of groundwater nitrate, such as synthetic nitrogen fertilizers, animal waste, human septic waste, etc.: for example, ammonia and nitrate derived from a fertilizer source has ^{15}N value around 0 permil (‰), the value of atmospheric nitrogen. Nitrate derived from sewage sources can have values greater than +20‰, significantly different from the fertilizer nitrogen isotopic value. Similar to using ^{15}N values, ^{18}O values can also be used to provide additional information to determine the source of nitrate in groundwater.

The traditional method to determine nitrate isotope ratios is the "silver nitrate method", which involves labor-intensive sample preparation prior to isotope analysis on an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS). Due to low nitrate concentrations in groundwater, this method requires liters or gallons of water to be sampled, shipped, and treated in the lab. Further, ion-exchange for nitrate becomes infeasible when there are relatively high sulfate or chloride concentrations in the same sample.

Since May 2009, ZymaX Forensics has started to offer ^{15}N and ^{18}O isotope analysis of dissolved nitrate using a cutting edge "denitrifier method". The classical denitrification pathway consists of the stepwise reduction of nitrate (NO_3^-) to nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and nitrogen (N_2) along the following pathway:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The "denitrifier method" applies microbial strains which lack N_2O reductive activity, thus the above reaction stops at N_2O. N_2O gas is produced from dissolved nitrate in water samples, whether the source is groundwater, surface water, or seawater. The N_2O gas from each sample is then introduced to a gas chromatograph-isotope ratio mass spectrometer (GC-IRMS) for simultaneous measurements of ^{15}N and ^{18}O isotopes.

Briefly, the "denitrifier method" has the following advantages over the traditional "silver nitrate method":

1. Sample required is no longer in liters or gallons; only 100mL or less!
2. The [NO_3^-] concentrations can be as low as ~0.1 mg/L!
3. Having sulfate and saline present in the sample water is OK; these constituents presented challenges using the silver nitrate method!
4. It has no interference with other N-bearing substances.
5. Precision is 0.2 and 0.5 permil (‰) for ^{15}N and ^{18}O isotopes, respectively.

The "denitrifier method" was developed by Dr. Yi Wang's advisor, Professor Daniel M. Sigman, at Princeton University in 2001, and has become popular worldwide in the academic field. Now ZymaX Forensics isotope lab has become the first commercial lab offering reliable, efficient and cost effective ^{15}N and ^{18}O isotope analysis using the "denitrifier method". Standard turnaround time is one month with rush service available upon request. For additional information, please contact Dr. Yi Wang (yi.wang@zymaxusa.com).

Dr. Yi Wang is the Director of ZymaX Forensics Isotope Laboratory. He has over 20 years of research experience in environmental forensics and is the author of over 40 publications. At Brown University he worked on compound-specific carbon and hydrogen isotope techniques and applications for use in the petroleum and environmental forensic fields. At Princeton University he focused on nitrogen and oxygen isotope techniques for use in groundwater nitrate source identification. He was a manager of three isotope laboratories in a span of ten years. Dr. Wang is a specialist in the analysis of isotope ratios for carbon, hydrogen, nitrogen, oxygen, and sulfur by Continuous Flow – Isotope Ratio mass Spectrometry.