## LAND STUDIES

#### Carbon Stable and Radio Isotope Analysis to Identify Methane Sources During a Remedial Action strategic Carbon. Provectus

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Stable carbon and radiocarbon isotope analysis is applied to  $CH_4$  source identification at a location near Detroit Michigan with cleaner solvent contamination that had undergone enhanced degradation treatment. Data showed:

- 1.  $\Delta^{14}C CH_4$  and  $CO_2$  data are modern; there is no contribution from petroleum gas or microbial degraded petroleum.
- 2.  $\delta^{13}$ C CH<sub>4</sub> shows the gas source at both sampling locations is biogenic, produced from organic carbon degradation.
- 3. Data suggested that each source is focused within its region, and there was little mixing of sources between the two wells, approximately 200 ft apart.
- 4. The most modern  $CH_4$  <sup>14</sup>C signature was observed at well MW16-1D and the gas was produced from microbial reduction of  $CO_2$ during the degradation of sewage (very young carbon) and/or subsequent leakage from the sewage lines.
- 5. The ISCR amendment was the primary source of carbon for  $CH_4$  production at MW15-1D.



 $\Delta^{14}$ C and  $\delta^{13}$ C Data Review





### **Carbon Isotope Analysis to Confirm Petroleum Natural Attenuation in the Vadose Zone Norfolk Naval Air Base**



CO<sub>2</sub> and CH<sub>4</sub> radiocarbon and stable carbon isotope ratios were used to assess natural attenuation at a fuel-contaminated soil site at the Norfolk Navy Base, Norfolk, VA (USA). Soil gas samples were collected spatially over a monitoring network. CO2 and CH<sub>4</sub> from regions with high petroleum concentrations were <sup>14</sup>C-depleted relative to uncontaminated areas. <sup>14</sup>C-depleted methane suggested methanogenic hydrocarbon degradation. The difference in  $CO_2$  age between background and plumeinfluenced areas indicated that approximately 90% of the  $CO_2$  at the latter was petroleum derived, making contaminant the primary source of carbon for the microbial assemblage. This study indicates that fuel hydrocarbons are a significant carbon source to in situ bacteria and that fuel hydrocarbon respiration resulted in the production of <sup>14</sup>C-depleted CO<sub>2</sub> (and ultimately CH<sub>4</sub>) with stable carbon isotope ratios indicative of microbial methanogenesis. However, the most weathered samples indicated there is considerable recycling of carbon because  $\delta^{13}$ C values for methane were uncharacteristically heavy(-45 to -26‰). The radiocarbon ages of CO2 and CH4 were definative in showing that petroleum carbon makes up approximately 90% of the carbon utilized by the in situ microbial assemblage. The radiocarbon measurement alone inconclusively demonstrates biodegradation is occurring on-site. Stable isotope ratios alone would likely fail to convey the importance of petroleum carbon to the CO<sub>2</sub> and  $CH_4$  pools as considerable recycling led to relatively heavier than expected values (20–40‰). Coupling of radiocarbon and stable carbon isotope measurements allows a better understanding of onsite biogeochemical conditions. These data provide strong support for the use of carbon isotope analyses to monitor natural attenuation and warrants more extensive seasonal and spatial sampling to better understand the dynamics of petroleum degradation under anoxic conditions.

#### **Concentrations and Stable Isotope Values of** BTEX in Gasoline-Contaminated Groundwater, strategic Carbon. **Port Hueneme Naval Air Station** Richard Coffin - Strategic Carbon LLC

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This work was undertaken to investigate the usefulness of stable carbon isotopic analysis as a monitoring tool for contaminant remediation. Concentrations and  $\delta$ 13C values of BTEX (benzene, toluene, ethylbenzene, and xylenes) were measured at a gasoline-contaminated site in southern California. The BTEX data were determined using a purgeand-trap connected to a gas chromatograph/ion trap mass spectrometer and to an isotope ratio mass spectrometer system. Concentrations ranged from below detection (<0.5 ppb  $\approx$  0.05  $\mu$ M C) to about 120 ppm ( $\approx$ 10 000 µM C) total BTEX, with toluene generally having the highest concentrations. For BTEX compounds at monitoring wells averaged across all sampling dates,  $\delta^{13}$ C values ranged from -23.8 to -26.6‰ (benzene), -22.9 to -25.2‰ (toluene), from -23.0 to -25.3‰ (p&m-xylenes), and from -22.4 to -25.0‰ (o-xylene). The data strongly suggest two sources of contamination: one with lighter ( $^{12}$ C-enriched)  $\delta^{13}$ C values emanating from the area near monitoring wells 1 and 2, and the other containing higher MTBE concentrations, an additive of unleaded gasoline, with heavier (<sup>13</sup>C-enriched)  $\delta^{13}$ C values coming from the vicinity of monitoring wells 8 and 9. The isotope data suggest that the leaded and unleaded gasoline at this site are isotopically distinct.

## **AQUATIC STUDIES**

### PAH Source Evaluation, Liepaja Harbor, Latvia

strategic Carbon.

The Liepaja harbor is a former Soviet military site. Remediation of the harbor basin, including dredging of the sediments heavily contaminated with petroleum hydrocarbons and heavy metals is necessary to convert the harbor for civilian use. Abandoned pollution sources on land still continue to leach contaminants into the harbor basin. Our long-term research objective therefore is to identify transport pathways into the harbor sediments and to assess the insitu degradation of pollutants in the system. The Liepaja harbor is treated as a complex system, where processes in the water column interact with the sediments and the nepheloid sediment boundary layer. For this research PAHs are used as the model organic contaminant. In this project the seasonal variation in biodegradation of PAHs is measured. This analysis is coupled with total bacterial production to establish the maximum degradation rate. With complex mixing of organic contaminants and need for

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understanding the ground water circulation it is difficult to determine the contaminant species. For this study a thorough assessment of PAH speciation has been used to determine the variation of sources. Stable carbon isotope analysis applied to understand the spatial variation in PAH sources showed 4 distinct sources. Changes in the source signatures coupled with estimates of microbial degradation and PAH concentrations indicated there was a continuous input form new PAH sources.

### Transport, Deposition and Biodegradation of Particle Bound Polycyclic Aromatic Hydrocarbons in a Tidal Basin of an Industrial Watershed



Polycylic aromatic hydrocarbons (PAHs) are common contaminants in industrial watersheds. Their origin, transport and fate are important to scientists, environmental managers and citizens. The Philadelphia Naval Reserve Basin (RB) is a small semi-enclosed embayment near the confluence of the Schuylkill and Delaware Rivers in Pennsylvania (USA). We conducted a study at this site to determine the tidal flux of particles and particle-bound contaminants associated with the RB. Particle traps were placed at the mouth and inside the RB and in the Schuylkill and Delaware Rivers. There was net particle deposition into the RB, which was determined for three seasons. Spring and fall depositions were highest (1740 and 1230 kg of particles, respectively) while winter deposition was insignificant. PAH concentrations on settling particles indicated a net deposition of 12.7 g PAH in fall and 2.1 g PAH in spring over one tidal cycle. There was no significant PAH deposition in the winter. Biodegradation rates, calculated from <sup>14</sup>C-labeled PAHsubstrate mineralization, could attenuate only about 0.25% of the PAH deposited during a tidal cycle in fall. However, in the spring, biodegradation could be responsible for degrading 50% of the settling PAHs. The RB appears to be a sink for PAHs in this watershed.

# Medically-Derived <sup>131</sup>I as a Tool for Investigating the Fate of Wastewater Nitrogen in Aquatic Environments



Medically derived <sup>131</sup>I( t1/2 = 8.04 d) is discharged from water pollution control plants (WPCPs) in sewage effluent. Iodine's nutrient-like behavior and the source-specificity of <sup>131</sup>I make this radionuclide a potentially valuable tracer in wastewater nitrogen studies. Iodine-131 was measured in Potomac River water and sediments in the vicinity of the Blue Plains WPCP, Washington, DC, USA. Dissolved <sup>131</sup>I showed a strong, positive correlation with  $\delta^{15}$ N values of nitrate ( $\delta^{15}$ NO3–) in the river, the latter being a traditional indicator of nutrient inputs and recycling. Surface water  $\delta^{15}$ NO3– values ranged from 8.7 to 33.4‰; NO<sub>3–</sub> + NO<sub>2–</sub> concentrations were 0.39–2.79 mg N L–1 (26–186 µM). Sediment profiles of particulate <sup>131</sup>I and  $\delta^{15}$ N indicate rapid mixing or sedimentation and in many cases remineralization of a heavy nitrogen source consistent with wastewater nitrogen. Values of  $\delta^{15}$ N in sediments ranged from 4.7 to 9.3‰. This work introduces <sup>131</sup>I as a tool to investigate the short term fate of wastewater nitrogen in the Potomac River and demonstrates the general utility of <sup>131</sup>I in aquatic research.