

**Project ID Number:** 55396

**Project Title :** Evaluation of Isotopic Diagnostics for Subsurface Characterization and Monitoring: Field Experiments at the TAN And RWMC (SDA) Sites, INEEL

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**Principle Investigator:** Donald J. DePaolo, E.O. Lawrence Berkeley National Laboratory, Mailstop 70A-4418, Berkeley, CA 94720, (510) 643-5064, depaolo@socrates.berkeley.edu

**Co-Investigators :** Mark E. Conrad, E.O. Lawrence Berkeley National Laboratory, Mailstop 70A-4418, Berkeley, CA 94720, (510) 486-6141, MSConrad@lbl.gov

Eric C. Miller, Thomas R. Wood and Erick R. Neher, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID

**Graduate Students:** Donald L. Song

**Research Objectives:** The purpose of this project was to explore and refine applications of isotope ratio measurements for guiding environmental remediation strategies. The isotopic compositions of samples collected from field sites were analyzed to address both basic scientific issues and site-specific problems.

**Research Progress and Implications :** This report summarizes the primary results of a 3-year project. Initial efforts were concentrated on two sites at the Idaho National Engineering and Environmental Laboratory (INEEL). During the final year of the project, the focus of work was shifted to the Hanford site in Washington.

The Test Area North (TAN) site at INEEL consists of a 2 km-long plume of mixed wastes containing low-level radionuclides, sewage and chlorinated solvents that were injected into the groundwater between 1955 and 1972. Measurements were made of the hydrogen, carbon, oxygen and strontium isotopic ratios of groundwater samples to address questions about the source of the groundwater and the regional hydrology of the area. These data indicate that there is a significant input to the groundwater from playa lakes that were located to the west of the TAN site (these playas have been dry since the 1950s when the water that fed the playas was diverted for agricultural uses). This playa water strongly influences the direction of groundwater flow in the TAN plume.

Another goal of the work at the TAN site was to evaluate the level of intrinsic biodegradation of the contaminants in the plume. Mixing of the playa water with regional groundwater has produced a range of strontium isotopic compositions in the plume that can be used to estimate the degree of dilution of the injected wastewater. Relative to the changes in strontium isotope ratios, the concentrations of TCE in the plume decrease more rapidly, indicating that natural biodegradation of the TCE is occurring at the site. This finding is supported by a decrease in the carbon isotope ratio of dissolved inorganic carbon compounds (DIC) in the plume. Organic compounds, such as TCE, have low carbon isotope ratios that will be reflected in the carbon isotope ratios ( $\delta^{13}\text{C}$ ) of DIC produced as a byproduct of biodegradation. During FY99, the work on the TAN plume was expanded to help monitor an experiment designed to enhance biodegradation of the TCE in the plume. In addition to tracking changes in the  $\delta^{13}\text{C}$  values of the groundwater DIC, the  $\delta^{13}\text{C}$  values of the contaminants and biodegradation byproducts were also analyzed. These data confirmed that complete biologic dechlorination of the TCE was being stimulated by the nutrients injected into the disposal well.

Samples from the Radioactive Waste Management Complex (RWMC) at the INEEL were also analyzed for this project. Waste buried in drums in shallow pits at the RWMC contained significant amounts of chlorinated solvents and lubricating oils. Leaks in the drums have resulted in a plume of vapor-phase contaminants in the unsaturated zone. The primary goal of our work was to determine the extent of natural degradation of contaminants in the unsaturated zone. Over a two-year period, the concentrations and isotopic ratios of  $\text{CO}_2$  in gas samples taken from monitoring wells at the site were measured. The concentrations of  $\text{CO}_2$  in shallow gas samples (10-25 m) from the vicinity of the disposal

pits were significantly elevated relative to the concentrations of CO<sub>2</sub> in background wells. Further, the δ<sup>13</sup>C values of the CO<sub>2</sub> from the contaminated area were lower than the CO<sub>2</sub> from the background wells, suggesting that the CO<sub>2</sub> was derived from the organic contaminants. In addition, the <sup>14</sup>C content of several of the high-CO<sub>2</sub> samples was very low; indicating that they were produced from chemicals derived from fossil fuels.

In the final year of the project, work was focussed on obtaining isotopic data for groundwater samples from the Hanford site. As a result of production of fuel for nuclear weapons during the cold war period, significant amounts of radionuclides were released to the environment at Hanford. The goal of our work was to identify pathways and mechanisms of infiltration of the wastewater through the unsaturated zone to the groundwater. Preliminary results indicate that the strontium isotope ratio of the groundwater is a very effective indicator of the proportion of wastewater dumped at the surface that has mixed with the groundwater. In addition, other isotopic measurements are indicative of other processes such as evaporation, degradation of organic matter and interaction with carbonate minerals in the subsurface. All of these isotopic signals hold great promise for identifying specific waste streams and tracking their infiltration to groundwater.

The results of these studies clearly demonstrate how isotopic measurements can be used to help answer questions of critical importance for environmental management. Our primary findings are:

- 1. Natural (or intrinsic) biodegradation of chlorinated hydrocarbons can be documented by measurements of natural isotopic tracers.***
- 2. Engineered biodegradation can be verified by measurements of natural isotopic tracers.***
- 3. Natural isotopic tracers can be used for basic characterization of groundwater systems in lieu of injection experiments.***

Further, these studies have produced important field data about basic scientific processes such as the infiltration of water through the unsaturated zone and the potential for subsurface biologic activity in arid environments. At both the INEEL and Hanford, the scientific collaborations that have been developed between the researchers from the Berkeley Lab and the investigators from the sites have led to proposals of additional studies using the principles developed through this project.

### **Information Access**

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Conrad, M.E., D.J. DePaolo, B.M. Kennedy, and E.C. Miller, 1997, Carbon isotope evidence for degradation of mixed contaminants in the vadose zone: *Geol. Soc. Am., Abst. with Prog.* 26, no. 6, A186.