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Evaluation of Isotopic Diagnostics for Subsurface Characterization and Monitoring: Field Experiments at the TAN and RWMC (SDA) Sites, INEL

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Research Objective

This research is aimed at improving methods for characterizing underground contamination sites and for monitoring how they change with time. Particular emphasis is placed on identifying and quantifying the effects of intrinsic remediation, and verifying the efficacy of engineered remediation activities.

Isotopic measurements of elements like C, O, H, He, Cl, and Sr, which are present in groundwater and soil gas, provide a quantitative measure of material balance. They can be used to identify the sites of origin of contaminants in groundwater, and to determine if contaminants are being destroyed as a result of natural processes or engineered processes. Isotope ratios can also be used to trace the migration of fluids that are pumped down wells to destroy or confine underground contaminants, such as steam and grout, and they can be used to diagnose what chemical reactions are occuring underground and what materials are reacting. For example, destruction of TCE usually produces carbon dioxide, but carbon dioxide can also come from dissolution of calcite.

There are many isotopic ratios that can be measured in groundwater and vadose zone gas that could be valuable for characterizing remediation sites and monitoring remediation activities. We concentrate on a few that are particularly useful for the problems being addressed at the TAN (Test Area North) and RWMC (Radioactive Waste Management Complex) sites of the Idaho National Engineering Laboratory. The isotopes we are using are carbon-13, carbon-14, helium-3, strontium-87, chlorine-37, and oxygen-18.

Research Progress and Implications

This report summarizes work completed after 1.5 years of a 3-year project.

Sampling

Application of the isotopic techniques requires field sampling and the return of the samples to the laboratory for analysis. At RWMC, vadose zone gas samples are obtained routinely for monitoring of CCl_4 and other contaminants. The sampling is done via a series of monitoring wells that surround the site of the buried materials. Wells located relatively far from the burial trenches penetrate to the water table whereas those close to the burial trenches penetrate to about 200 feet depth.

The character of subsurface gas at RWMC varies seasonally and with the operation of the VVE system, so it is necessary to sample the system relatively often to characterize it. A subset of samples from the normal weekly monitoring of RWMC was sent to us at LBNL in November 1996, February 1997, March 1997, and June 1997. The sampling is continuing. A partial set of water samples from TAN groundwater was sent to us in July of 1997, and the remainder of sample set was sent in October 1997. The TAN groundwater plume evolves at a much slower timescale than the RWMC vadose zone plume, so sampling needs to be done only a few times during the course of the study.

Measurements

The RWMC gas samples have been measured for $^{13}C/^{12}C$ ratios, $^{14}C/^{12}C$ ratios, and the concentrations of CO_2, O_2, and N_2. Noble gas concentration and isotopic analyses are planned but have not yet been carried out. TAN water samples have so far been measured for $^{13}C/^{12}C$ ratios, $^{18}O/^{16}O$ ratios, D/H ratios, the concentration of dissolved inorganic carbon (DIC) and selected anions and cations, and $^{87}Sr/^{86}Sr$ and $^{14}C/^{12}C$ ratios.

Results

1) There is substantial production of CO_2 in the subsurface of the RWMC site. This production is far above the background values that can be observed outside from the Subsurface Disposal Area (SDA). The vadose zone CO_2 has a low $^{13}C/^{12}C$ ratio and therefore appears to be an oxidation product of organic material. It is not yet possible to determine with confidence which organic material is being oxidized and by what mechanism, but our preliminary assessment is that the source of the CO_2 is oxidation of the lubricating oil rather than oxidation of the chlorinated solvents.
2) Initial ^{14}C analyses of the CO_2 indicate the presence of an additional, radioactive source for the CO_2 in the vadose zone of RWMC. This source is tentatively identified as buried reflector blocks from nuclear reactors. Evidence of migration of the ^{14}C is found in the "background" monitoring well about 1 km southeast of the trenches.
3) A map of the $^{18}O/^{16}O$ and D/H values of groundwater at TAN indicate a region near and to the south of the injection well that has relatively high $^{18}O/^{16}O$. These waters also have D/H values that indicate they have been subject to evaporation. These isotopic data indicate a significant contribution of evaporated water, presumably from the TSF-07 disposal pond.
4) The $^{13}C/^{12}C$ values of TAN groundwater DIC are 2-3‰ lower in the vicinity of the plume, indicating a possible contribution from degradation of contaminants.
5) Analysis of $^{87}Sr/^{86}Sr$, $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in TAN groundwater from below the lower confining layer of the upper aquifer indicates that the waters below and above the layer have distinct isotopic signatures, which confirms that there is no exchange across the lower confining layer.
6) The contaminant plume water has a traceable signature for $^{87}Sr/^{86}Sr$; comparison of the plume as represented by the Sr isotopic data and the distribution of TCE may yield information on the amount of in-situ degradation in the plume.

Implications

The results to date confirm that isotopic analysis of groundwaters and vadose zone gases are useful for diagnosing chemical processes occurring in the subsurface, and tracing the migration of waters from different sources. At both the RWMC and TAN sites there is evidence of biodegradation of organic material in the subsurface, although the evidence to date suggests that the most problematic contaminants are not being degraded at a significant rate. This needs to be confirmed with more analytical work and modelling.

Planned Activities

Over the next year, sampling and analysis of vadose zone gases and groundwaters will continue. At RWMC the objective will be to discern any changes with time, and to better charaterize seasonal variations. There will also be an effort to measure samples of shallow soil gas. A set of measurements will also be made in conjunction with a tracer test in June 1998. AT TAN an additional set of samples will be measured for $^{87}Sr/^{86}Sr$, $^{13}C/^{12}C$, $^{14}C/^{12}C$, $^{18}O/^{16}O$, and D/H; partly to confirm the data from the first sampling and also to extend the coverage to wells outside the immediate area of TAN. AT both RWMC and TAN, samples of chlorinated hydrocarbons will be measured for $^{37}Cl/^{35}Cl$ and $^{13}C/^{12}C$ as a direct means of assessing the effects and extent of natural degradation.