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

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Executive Summary

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. Initial efforts were concentrated on two sites at the Idaho National Engineering and Environmental Laboratory (INEEL); the Radioactive Waste Management Complex (RWMC) and the Test Area North (TAN) site. During the final year of the project, additional work was begun on groundwater at the Hanford site in Washington.

Gas samples from the RWMC were analyzed. The waste drums buried at the RWMC contained significant amounts of organic contaminants including chlorinated solvents and lubricating oils. Leaks in the drums have resulted in a plume of vapor-phase contaminants in the unsaturated zone. The primary goals of our work were to determine the extent of natural degradation of contaminants in the unsaturated zone and to identify the area of influence of a vapor extraction system currently operating at the site. Over a 2-year period, the concentrations and isotopic ratios of CO_2 in gas samples taken from monitoring wells at the site were measured. The concentrations of 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_2 in background wells. Further, the carbon isotope ratios of CO_2 from the contaminated area were lower than those from the background wells, suggesting that the CO_2 was derived from the organic contaminants. In addition, the ^{14}C content of the high-CO_2 samples was very low; indicating that they were produced from chemicals derived from fossil fuels.

The TAN site consists of a 2 km-long plume of mixed wastes containing low-level radionuclides, sewage and chlorinated solvents. 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 clearly show that there is a significant input to the groundwater from a playa lake that was located to the west of the TAN site prior to the 1950s (since then, the water that fed the playas has been diverted for agricultural uses). The playa water is the main factor determining the direction of groundwater flow in the TAN plume. In addition, radiocarbon dating of groundwater samples dominated by playa water indicate that average infiltration rates for the playa water are very low (~3 cm/yr).

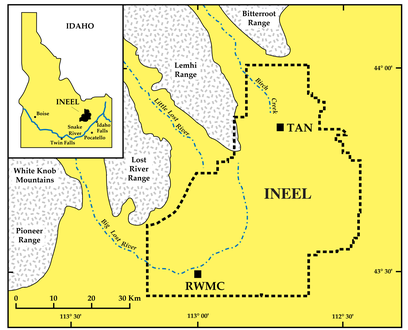
Another goal of the work at the TAN site was to monitor levels of subsurface biologic activity in order to evaluate the extent of biodegradation of the contaminants in the plume. Mixing of the playa water with regional groundwater produced a range of strontium isotopic compositions in the plume that can be used to estimate the degree of dilution of the injected waste waters. Relative to the changes in strontium isotope ratios, the concentrations of trichloroethene (TCE), the primary contaminant of concern in the plume, dropped off more rapidly, indicating that significant natural degradation of 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 and sewage, have low carbon isotope ratios that will be reflected in the carbon isotope ratios of DIC produced as a byproduct of biodegradation. During FY99, the work on the TAN plume was expanded to monitor an experiment designed to enhance *in situ* biodegradation of the TCE in the vicinity of the injection well. By tracking changes in the carbon isotope ratios of TCE and its byproducts during the experiment, we were able to confirm that complete biologic dechlorination of the TCE was being stimulated by the nutrients injected into the disposal well.

During the final year of the project, a survey of the isotopic compositions of groundwater at the Hanford site was conducted to evaluate the potential of natural isotopic tracers for identifying pathways and mechanisms of infiltration of wastewaters through the unsaturated zone to the groundwater. Preliminary results (not discussed here) indicate that the strontium isotope ratio of the groundwater is a very effective indicator of the proportion of water 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 isotope measurements can be used to help answer questions of critical importance for environmental management. Our primary findings demonstrate that:

- *Natural (or intrinsic) biodegradation of chlorinated hydrocarbons can be documented by measurements of natural isotopic tracers.*
- *Engineered biodegradation can be verified by measurements of natural isotopic tracers.*
- *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.



Map of the Idaho National Engineering and Environmental Laboratory (INEEL) with the locations of the Radioactive Waste Management Complex (RWMC) and the Test Area North (TAN) site.

Acknowledgments

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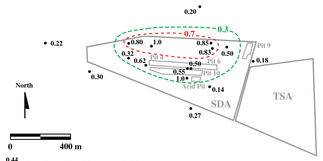
The Radioactive Waste Management Complex (RWMC)

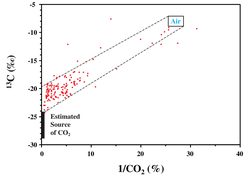
The he RWMC contains radioactive wastes from DOE activities. The wastes were packaged in drums and buried in shallow pits (~1.5 m deep). In addition to the radionuclides, the waste drums also contain significant amounts of chlorinated solvents mixed with lubricating oils. Leakage from the drums has resulted in a plume of vapor phase contaminants in the vadose zone. A vapor extraction system is currently being used to remediate the solvent plume at the RWMC. This system consists of three treatment units that pump vapor from extraction wells. The vapor is then treated and released to the atmosphere. The effectiveness of this system is not well understood. The contaminant levels in the extracted vapors drop to very low levels when the extraction units are in operation, but rebound quickly when the units are shut down. At the current rates of contaminant removal, estimates of the time necessary to meet the regulatory goals range from 100 to 200 years of operation.

In situ bioremediation of the wastes to represents an attractive alternative to vapor extraction. There is some evidence that natural biodegradation of the contaminants is already occurring at the RWMC. In addition to the chlorinated solvents that were buried at the site (primarily carbon tetrachloride, perchloroethene, trichloroethene and trichloroethane), the vapor plume also contains several other chlorinated compounds (e.g., chloroform, dichloroethene) that are byproducts of bacterial degradation of the primary contaminants. The main objective of our work at the RWMC was to use isotopic measurements to assess the potential for bioremediation of the organic contaminants at the site.



Average CO_2 concentrations in gas samples collected from 10 to 25 m depth at the RWMC between October, 1996 and November, 1998. CO_2 concentrations are lower at greater depths, but are still higher in the vicinity of the disposal pits.

Isotope Data - The ^{13}C values of the CO_2 were significantly lower in the area of elevated CO_2 concentrations. Allowing for isotopic shifts caused by diffusive fractionation of the CO_2, this data indicates that the ^{13}C value of the source is between -24 and -29‰ (see the figure to the right). This is typical of organic compounds, including chlorinated solvents and lubricating oils. The ^{14}C contents of a limited number of CO_2 samples were also analyzed. Several of the samples from the southeast part of the SCA were significantly elevated above atmospheric levels as a result of buried reactor shields. However, a couple of samples from the northwest part of the SDA had very low ^{14}C contents (<15% of atmospheric CO_2), indicating that the CO_2 was derived from fossil carbon sources (i.e., the contaminants).



^{13}C values of subsurface CO_2 samples collected from in and around the RWMC plotted versus the inverse of the CO_2 concentration. The estimated ^{13}C value of the source is offset by 4.4‰ to account for isotopic fractionation caused by diffusion of the CO_2.

Approach

One of the primary products of aerobic microbial metabolism of organic compounds is CO_2. To determine whether there was evidence of increased subsurface biologic activity in the vicinity of the burial pits, the CO_2 concentrations of subsurface gas samples collected from monitoring wells at the RWMC were monitored over a 2-year period. In addition, the stable carbon isotope ratios (^{13}C values) and radiocarbon (^{14}C) contents of the CO_2 were measured to distinguish CO_2 produced from the contaminants from other potential sources of subsurface carbon (e.g., root respiration, carbonate dissolution).

Results

CO_2 Data - The subsurface CO_2 concentrations were clearly elevated in the northern part of the Subsurface Disposal Area (SDA). Between 10 and 25 m depth, the CO_2 concentrations exceeded 1% (versus ~0.2% in background wells). At greater depths, the CO_2 concentrations decreased, but were still 2-3 times higher than background.

Significance of Findings

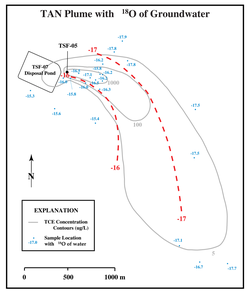
The CO_2 concentrations in the subsurface in the northern section of the RWMC are elevated by 3- to 5-fold relative to background. The low ^{14}C concentrations in CO_2 from several of these samples also indicate that it was derived from degradation of contaminants produced from fossil fuels. It is not clear, however, whether this CO_2 is produced from degradation of the chlorinated solvents, the lubricating oils, or some combination of both (or some other, undetermined organic waste buried at the site).

The Test Area North (TAN) Site

Between 1955 and 1972, a wide variety of waste materials, including low-level radioactive isotopes, sewage and chlorinated solvents, were injected into the upper, unconfined aquifer at the TAN site through a 95 m deep well (TSF-05). The result of this activity is a 2 km plume. The primary contaminant of concern is trichloroethene (TCE). The regulatory goals for the site are to eliminate the source of contamination, defined as the 5000 mg/liter concentration isograd for TCE, and to decrease the remaining contamination to below 5 mg/liter. During the first two years of this project, the primary remediation technique utilized at the site was pump-and-treat. However, because of the low solubility of TCE, the rate of removal was slow and an enhanced bioremediation system was tested during FY99.

Our research at the TAN site had three primary objectives. These were:

- *Determine the primary factors affecting regional groundwater flow at the TAN site*
- *Evaluate the potential for natural degradation of TCE in the TAN plume*
- *Monitor enhanced bioremediation experiment.*



^{18}O values of groundwater samples collected from the upper aquifer at the TAN site. Also shown are the concentration contours for TCE and the locations of TSF-05 (the injection well) and TSF-07 (the process water infiltration pond).

Results and Discussion

The ^{18}O values of groundwater samples from the TAN plume are plotted in the figure above. The ^{18}O values clearly increase towards the west. The D values of the waters also increase, forming a linear array of data with a slope of approximately 5 (see the figure to the right), indicating that the shift in isotopic composition is caused by mixing with evaporated water from the west originating to the west of the TAN site. It is possible that a small fraction of the evaporated water is derived from the wastewater injected into TSF-05 or dumped in the TSF-07 disposal pond, but these sources were not big enough to produce the overall shift in ^{18}O values observed in the plume. The only potential source of evaporated water large enough explain the observed shift is the playa lake that was located to the west of the site.

The figure at the top of the next column shows the TAN plume relative to the former location of Playa 4. Also plotted on this figure are the ^{18}O values of regional water samples collected from water wells in the area. Several of these waters also have a significant evaporated signal.

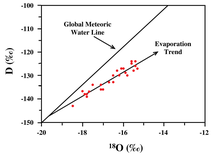
Regional Groundwater Flow

The general direction of groundwater flow in the Snake River Aquifer is from the northwest to the southeast. At the TAN site, however, groundwater flow (as defined by the shape of the contaminant plume) is roughly perpendicular to the regional flow direction. One factor that could be affecting groundwater flow is the significant amount of process water that was dumped into the evaporation pond (TSF-07) to the northwest of the injection well (TSF-05). Another potential influence is the playa lake that was located to the west of the TAN site (the playa has been dry since the early part of the 20th century when much of the water in its tributary, the Big Lost River, was diverted for agricultural purposes). It is also possible that anisotropic permeability in the aquifer (e.g., due to precipitation of secondary minerals beneath the playa) could be affecting flow.

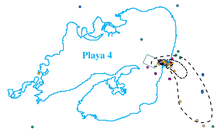
Determining the importance of these factors is critical for the long-term remediation plan for the site. If it is a transitory effect caused by infiltration of the process waters, then potential changes in the shape and direction of the plume need to be taken into account, especially if any downstream barriers or treatment systems are deemed necessary to control the plume. To address these questions, we analyzed the isotopic compositions of water samples from the potential sources of the groundwater, from monitoring wells in the TAN area and regional wells.

Approach

Samples of groundwater and potential source waters for the groundwater were collected. To distinguish the sources of the groundwater, the stable hydrogen (D) and oxygen (^{18}O) isotope compositions of the waters, the stable carbon (^{13}C) and radiocarbon (^{14}C) isotope compositions of dissolved inorganic carbon compounds (DIC) in the groundwater and the $^{87}Sr/^{86}Sr$ ratios of dissolved strontium in the water were all analyzed.



Plot of D versus ^{18}O values of groundwater samples from the TAN area. The data form a distinctive trend characteristic of evaporation.



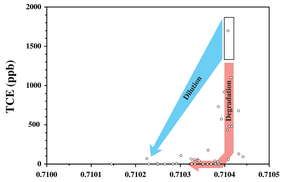
Map showing the location of the TAN plume relative to the former location of Playa 4. Also plotted are the ^{18}O values of water samples from the area.

Natural Attenuation

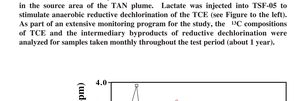
The rate of growth of the TCE plume at the TAN site is less than predicted based upon hydrologic models of groundwater flow. There are several processes that could be retarding the spread of TCE, including sorption on sediments, volatilization and natural biodegradation. If these processes are occurring, they will have significant implications for management of the plume. One of the primary goals of this project was to use natural isotopic tracers to assess the nature and extent of natural attenuation that is occurring in the plume.

The $^{87}Sr/^{86}Sr$ ratios in the TAN plume vary from ~0.7104 near the injection well to ~0.7102 at the distal end of the plume. The figure to the right is a plot of the concentrations of TCE in samples from the plume versus their $^{87}Sr/^{86}Sr$ ratios. The TCE concentrations decrease much more quickly than the strontium isotope ratios, suggesting that significant natural attenuation of TCE is occurring in the plume.

We also have independent evidence that biodegradation of organic matter is occurring in the TAN plume. The ^{14}C values of organic matter tend to be lower than most other sources of subsurface carbon. There is a small, but significant decrease in the ^{14}C values of the DIC in the plume, suggesting that some biodegradation of organic matter is occurring in the plume. It is not clear whether this is due to biodegradation of TCE or the sewage injected into TSF-05, but it does confirm that there is significant subsurface biologic activity.



TCE versus strontium isotope ratios for groundwater samples from the TAN plume showing expected trends for dilution and natural degradation.



Reductive dechlorination pathway for TCE

A recent study found that reductive dehalogenation of chlorinated solvents results in large shifts in the stable carbon isotopic ratios of the compounds, causing the products to have significantly lower ^{13}C values than the substrate. In addition, as the substrate is consumed, the residual becomes enriched in ^{13}C. These isotopic shifts are diagnostic of these processes and can be used to estimate the degree of degradation.

The concentrations and ^{14}C values of TCE and its byproducts from monitoring well TAN-26 (~5 m from TSF-05) are plotted on the Figure to the right. The concentrations of cis-DCE increased as TCE disappeared. However, commensurate increases in vinyl chloride and/or ethene were not observed when the concentrations of cis-DCE decreased. This could be an indication that significant biodegradation of cis-DCE was not occurring.

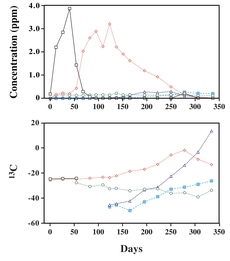
The ^{14}C values of cis-DCE, however, increase significantly as it's concentration decreases. At the same time, the ^{13}C values of vinyl chloride are much lower than those of the cis-DCE. This is a clear indication that the cis-DCE is being biologically degraded to vinyl chloride. Similar trends were seen with ethene. Further, the final ^{14}C value of ethene is approximately equal to the initial ^{14}C value of the TCE, demonstrating that lactate is stimulating complete reductive dechlorination of the TCE.

Estimating Infiltration Rates

The ^{14}C contents of DIC in three water groundwater samples with strongly evaporated signals from groundwater wells near the edges of Playa 4 were measured. The radiocarbon ages of these samples were between 1800 and 2800 years old. For an average depth to groundwater of ~60 m, this gives an infiltration rate of 2-3 cm per year. This is relatively slow and should be taken as a minimum estimate. There are certainly fast paths (e.g., fractures) with much higher infiltration rates. In addition, it is possible that there has been some exchange of DIC with subsurface carbonates (which would tend to increase the radiocarbon age). However, this does help explain why infiltration from the playa is still dominating the regional hydrology of the site.

Enhanced Bioremediation

During the final year of this project (FY99), a field-scale pilot study was conducted to evaluate the potential for enhanced, in situ bioremediation of TCE in the source area of the TAN plume. Lactate was injected into TSF-05 to stimulate anaerobic reductive dechlorination of the TCE (see Figure to the left). As part of an extensive monitoring program for the study, the ^{14}C compositions of TCE and the intermediary byproducts of reductive dechlorination were analyzed for samples taken monthly throughout the test period (about 1 year).



Concentration and ^{13}C data for groundwater samples collected from monitoring well TAN-26 during the enhanced bioremediation experiment conducted at the TAN site.