



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Intrinsic and Extrinsic Chemical and Isotopic Tracers for Characterization Of Groundwater Systems

J. E. Moran, M. J. Singleton, S. F. Carle, B. K. Esser

September 17, 2007

3D Geological Mapping for Groundwater Applications  
Denver, CO, United States  
October 28, 2007 through October 28, 2007

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

# INTRINSIC AND EXTRINSIC CHEMICAL AND ISOTOPIC TRACERS FOR CHARACTERIZATION OF GROUNDWATER SYSTEMS

Jean E. Moran, Lawrence Livermore National Laboratory, U.S.A., [moran10@llnl.gov](mailto:moran10@llnl.gov), Michael J. Singleton, Lawrence Livermore National Laboratory, [singleton20@llnl.gov](mailto:singleton20@llnl.gov), Steven F. Carle, Lawrence Livermore National Laboratory, [carle1@llnl.gov](mailto:carle1@llnl.gov), and Bradley K. Esser, Lawrence Livermore National Laboratory, [esser1@llnl.gov](mailto:esser1@llnl.gov)

## Introduction

In many regions, three dimensional characterization of the groundwater regime is limited by coarse well spacing or borehole lithologic logs of low quality. However, regulatory requirements for drinking water or site remediation may require collection of extensive chemical and water quality data from existing wells. Similarly, for wells installed in the distant past, lithologic logs may not be available, but the wells can be sampled for chemical and isotopic constituents. In these situations, a thorough analysis of trends in chemical and isotopic constituents can be a key component in characterizing the regional groundwater system.

On a basin or subbasin scale, especially in areas of intensive groundwater management where artificial recharge is important, introduction of an extrinsic tracer can provide a robust picture of groundwater flow. Dissolved gases are particularly good tracers since a large volume of water can be tagged, there are no real or perceived health risks associated with the tracer, and a very large dynamic range allows detection of a small amount of tagged water in well discharge. Recent applications of the application of extrinsic tracers, used in concert with intrinsic chemical and isotopic tracers, demonstrate the power of chemical analyses in interpreting regional subsurface flow regimes.

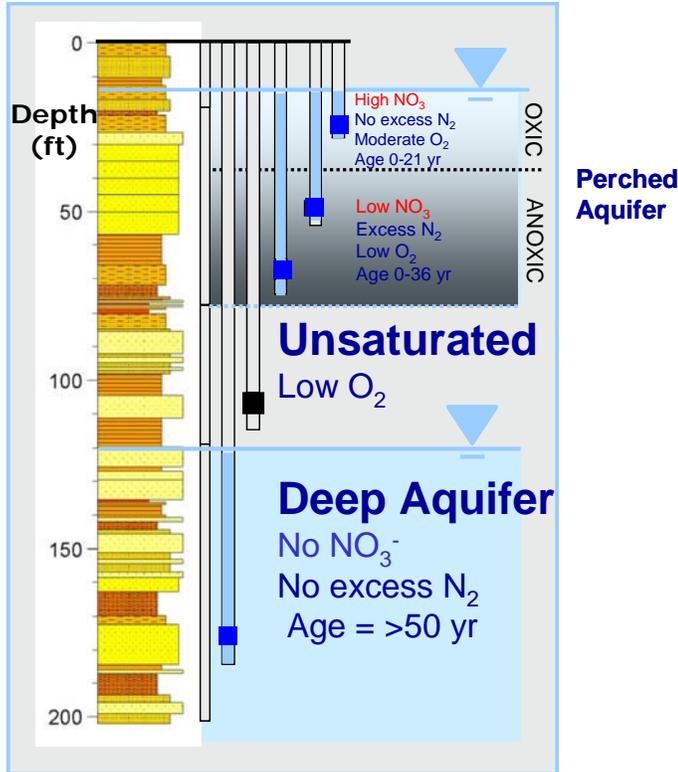
## Examples

The combination of groundwater age and basic chemical composition can be especially useful for determining the degree of groundwater stratification in a multi-aquifer system. The following examples illustrate this point.

An intensively studied agricultural site is located in the Kings River alluvial fan, a sequence of fluvial sediments deposited by the Kings River from the Sierra Nevada to the low lying southern San Joaquin Valley of California (Weissman 1999; Weissman, 2002). The site overlies an unconfined aquifer, which has been split into an upper aquifer to 24m below ground surface (BGS) and a lower aquifer (>40 m BGS) separated by a gap of unsaturated sediments. Both aquifers are predominantly composed of unconsolidated sands with silty and clayey interbeds. The unsaturated gap between the unconfined aquifers was likely caused by intense regional groundwater pumping of the lower unconfined aquifer. Wells completed in this unsaturated gap have very low gas pressures, indicating continuing water table decline in the lower unconfined aquifer.

This study focuses on the upper unconfined aquifer, where water table levels are about 5 m BGS across the site with no persistent hydraulic gradients. In general, regional groundwater flow is NW to SE due to recharge from canal leakage from unlined canals and irrigation return. Transient cones of depression are induced during groundwater pumping from shallow irrigation wells. regional groundwater quality is highly impacted by agricultural activities and contains elevated concentrations of nitrate and pesticides (Burrow, 1998). The site was instrumented with five sets of multi-level monitoring wells and one "up-gradient" well near an irrigation canal (Singleton et al., 2006). The multi-level wells have short, 0.5m screened intervals in order to detect heterogeneity and stratification in aquifer chemistry. In addition, there are eight dairy operation wells that were sampled over the course of this study, which are screened over a broad interval, generally between 9 to 18 meters below ground surface (BGS).

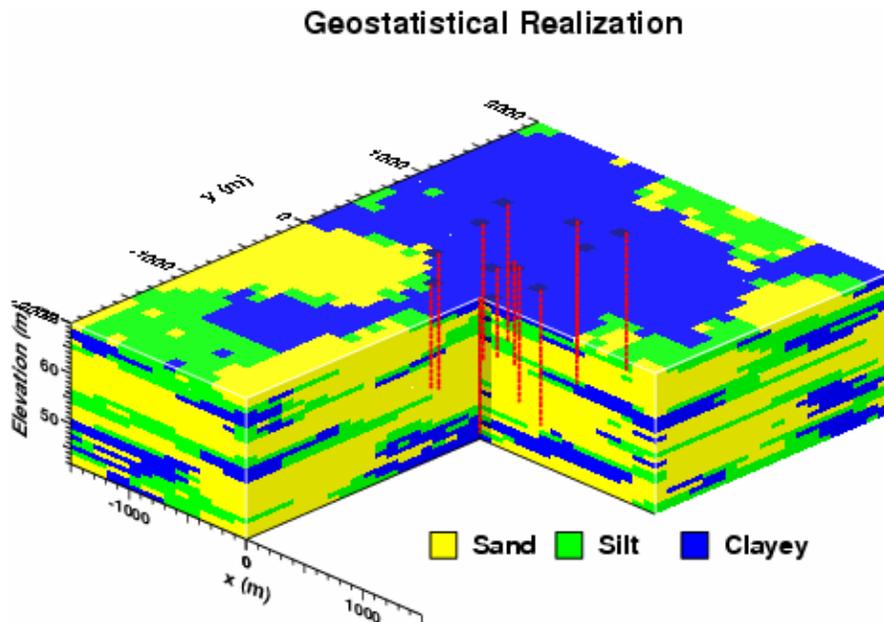
Mean tritium-helium ( $^3\text{H}/^3\text{He}$ ) apparent groundwater ages are determined for water produced from 20 monitor wells at depths of 6m to 54m. The lower unconfined aquifer has no measurable  $\text{NO}_3^-$  and no detectable tritium, indicating a recharge age of more than 50 years. Modern water (i.e. water containing measurable tritium) is found at all multi-level wells completed in the upper unconfined aquifer, with  $^3\text{H}/^3\text{He}$  apparent ages ranging from 1 to 35 years. In general, apparent ages are lowest near the water table and increase regularly with depth in the monitoring wells (Figures 1 and 3), consistent with recharge from infiltration of irrigation water. Some wells are seasonally influenced by recharge from unlined irrigation canals, and have young apparent ages. Another area has an observed high vertical flow rate



**Multi-level wells:**

Excess N<sub>2</sub> by MIMS, Age by <sup>3</sup>H-<sup>3</sup>He

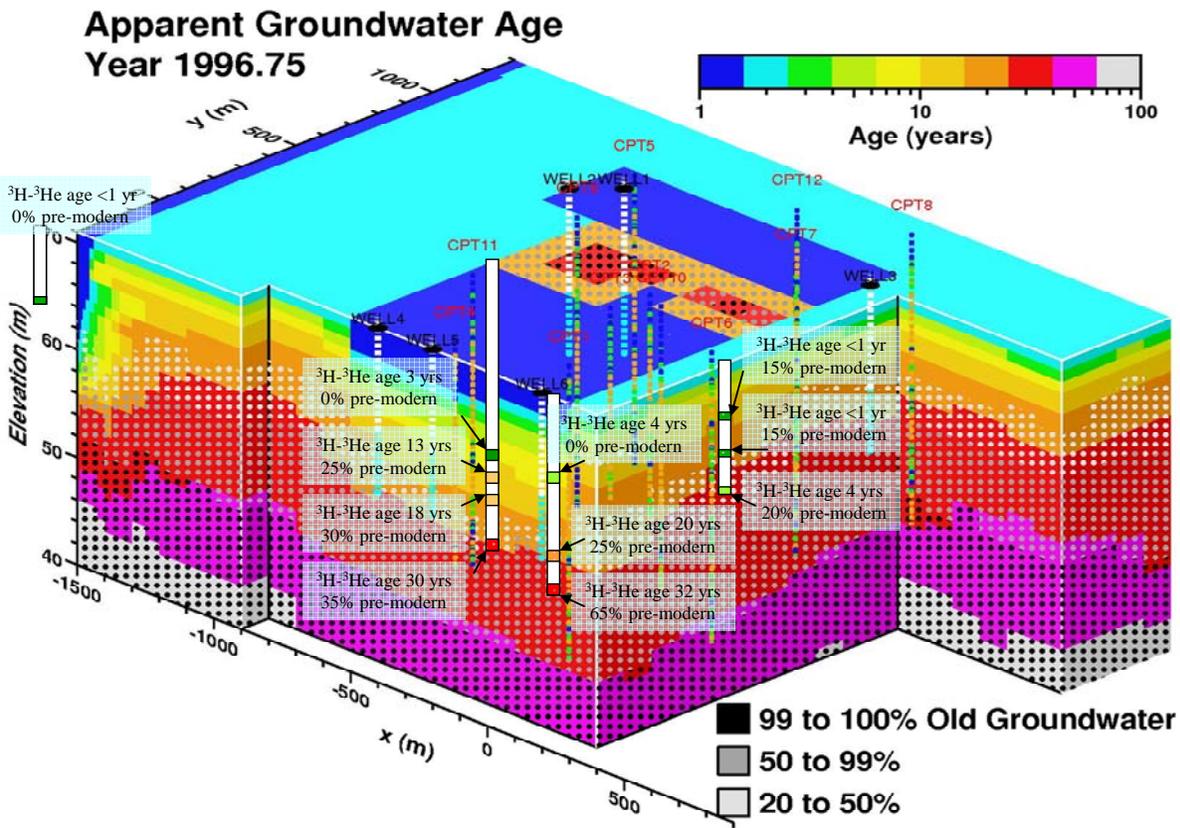
**Figure 1.** Lithologic log at one of the agricultural site nested monitoring wells. Screened intervals shown by shaded squares. Groundwater is strongly chemically stratified.



**Figure 2.** Geostatistical realization of the heterogeneous lithology at the agricultural site. Locations of Cone Penetrometer Testing holes are shown as vertical dashed lines.

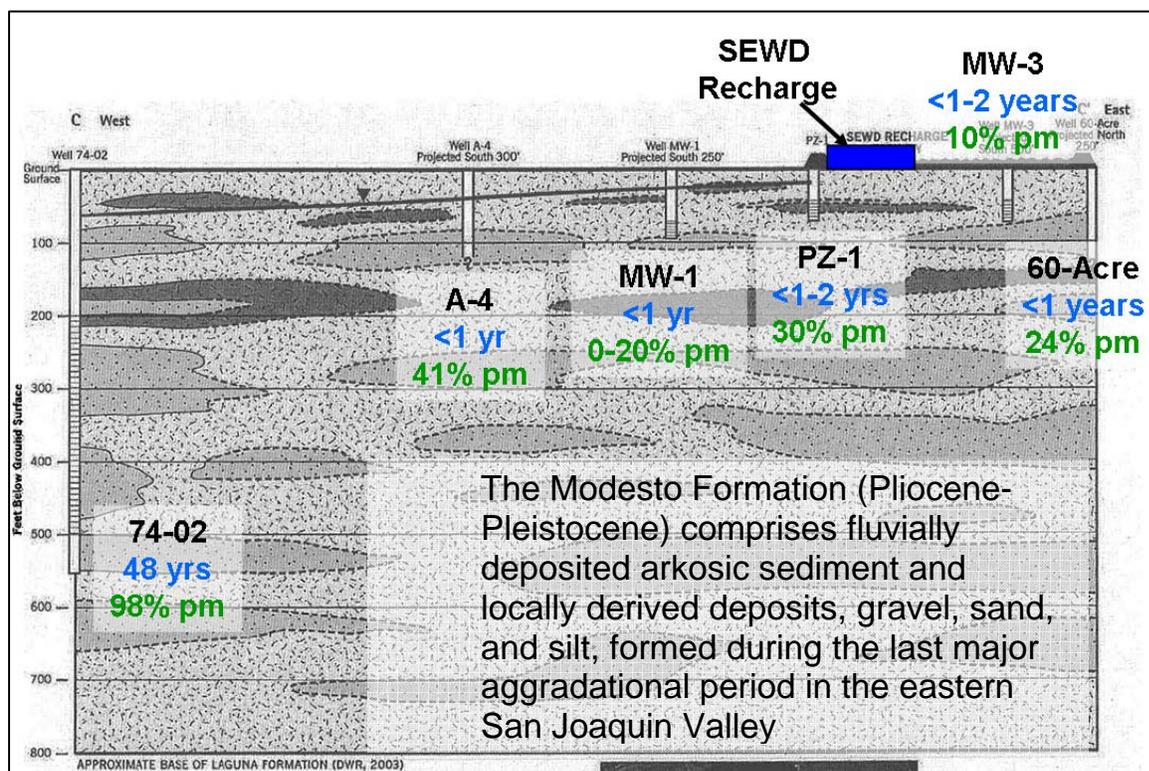
Indicated by no measurable increase in apparent age with depth, except for a localized low-yield clay rich zone at 12m BGS that has an older apparent age than the water sampled at 14 m BGS. The clay rich zone is thought to impede flow around the 12 m monitor well screen, and also has lower nitrate concentrations than samples from surrounding depths. The chemical stratification observed in multilevel wells demonstrates the importance of characterizing vertical variations within aquifers for water quality monitoring studies. Groundwater nitrate concentrations in irrigation wells, which have long screened intervals from 9 to 18 meters BGS, are integrated over the high and low nitrate concentration zones

These apparent ages give the mean residence time of the fraction of recently recharged water in a sample, and are especially useful for comparing relative ages of water at each monitoring location. The absolute mean age of groundwater may be obscured by mixing along flow paths due to heterogeneity in the sediments (Weissmann, 2002). A key component of this study is development of a highly-resolved model of the heterogeneity in the aquifer system using geostatistical simulation of hydrofacies architecture incorporating uncertain or "soft" data such as well driller logs (Figure 2). The accompanying flow and transport model is validated by measured tritium-helium groundwater ages (Figure 3). In the model, tritium is exchanged into recharge including irrigation return, rainfall, and canal leakage. For comparison, measured groundwater ages and tritium concentrations allow calculation of the fraction of pre-modern (> 50 year old) groundwater in each well water sample. Calculated fractions pre-modern and model results showing native groundwater percentages are also shown in Figure 3. At this site, stratification in groundwater chemistry is the result of biochemical processes, while groundwater flow has a strong vertical component, being dominated by irrigation return and pumping.



**Figure 3.** Values of measured groundwater ages and fraction pre-modern at nested monitoring wells (results shown in test boxes), along with simulated groundwater age and fraction pre-modern for the block shown in Figure 2.

In the second example, movement of an inert dissolved gas, sulfur hexafluoride, applied to about 125,000 m<sup>3</sup> of surface water at a groundwater banking facility near Stockton, California, is traced in 11 monitoring wells and 4 production wells. The objective of the study is to identify and quantify changes in water quality during recharge and subsurface transport. In contrast to the very large and long-established artificial recharge operations in southern California using relatively high TDS water, applied water in this study is very low TDS river water from Sierra Nevada runoff applied in the last three years. Analysis of tritium-helium groundwater age, fraction pre-modern, and the SF<sub>6</sub> tracer allow estimation of the bulk flow rate,



**Figure 4.** Schematic cross-section of artificial recharge site and wells monitored for introduced tracer, groundwater age and chemical constituents (CA DWR, 2003).

dilution of recent recharge with ambient groundwater, and travel time of the most recently recharged water. Major ions, trace metals, volatile and semi-volatile organic compounds, and stable isotope of H, O, C, and N in both surface water and groundwater are examined, and equilibrium reactions are modeled. Groundwater age & tracer arrival define three water types: 1) Shallow groundwater close to ponds, age <1-2 years, 5-35% pre-modern, high concentration of SF<sub>6</sub> tracer; 2) Shallow groundwater far from ponds, age <1-10 years, 15-40% pre-modern, low concentration SF<sub>6</sub> tracer; and 3) Deep groundwater, age 30-50 years, >80% pre-modern, no SF<sub>6</sub> tracer. The groundwater mound generated by artificial recharge spreads to the east, west, and south, as driven by regional pumping. Observations of tracer arrival times and dilution factors, in combination with measured groundwater ages, provide a robust image of subsurface flow and transport in an area where lithologic logs are scarce and of poor quality.

#### References:

- Burrow, K.R., S.V. Stork, and N.M. Dubrovsky, 1998. Nitrate and Pesticides in Ground Water in the Eastern San Joaquin Valley, California: Occurrence and Trends, U.S. Geological Survey Water-Resources Investigations Report 98-4040a.
- California Department of Water Resources, 2003. Bulletin 118.
- Singleton M. J., Esser B. K., Moran J. E., Hudson G. B., McNab W. W., and Harter T. 2007. Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations. *Environ. Sci. Technol.* 41(3), 759-765.
- Weissmann, G.S. J.F. Mount, and G.E. Fogg, 1999. Glacially Driven Cycles In Accumulation Space And Sequence Stratigraphy Of A Stream-Dominated Alluvial Fan, San Joaquin Valley, California, U.S.A., *J. Sed. Res.*, 72 (2), 240-251.
- Weissmann, G.S., Y. Zhang, E.M. LaBolle, and G.E. Fogg, 2002. Dispersion of groundwater age in an alluvial aquifer system, *Water Resources Research*, 38 (10), 1198, doi:10.1029/2001WR000907.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.