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

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1. INTRODUCTION

In many regions, three dimensional characterization of the groundwater regime is limited by coarse well spacing or lithologic well 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 well 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 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.

2. EXAMPLES

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

2.1 Example 1 – Kings River Alluvial Fan

An intensively studied agricultural site is located in the Kings River alluvial fan, a sequence of layered sediments transported 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 from 3m to 24m below ground surface (BGS) and a lower aquifer (>40 m BGS) that are separated by a gap of unsaturated sediments. Both aquifers are predominantly composed of unconsolidated sands with minor clayey sand layers. The lower unsaturated gap was likely caused by intense regional groundwater pumping, and wells completed in this unsaturated zone have very low gas pressures. There are no persistent gradients in water table levels across the site, but in general, regional groundwater flow is from the NW to SE due to topographic flow on the Kings River fan. The water table is located about 5 m BGS. Local recharge is dominated by vertical fluxes from irrigation, and to a lesser extent, leakage from adjacent unlined canals. Transient cones of depression are induced during groundwater pumping from dairy operation wells. The regional groundwater 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 apparent ages are determined for water produced from 20 monitor wells at depths of 6m to 54m. The upper aquifer has ³H/³He apparent ages that range 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. The lower aquifer has no measurable NO₃- 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 aquifer. 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 since

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**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.
there is no measurable increase in apparent age with depth, except for a localized low-yield clay rich zone at 12 m 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 are integrated over the high and low nitrate concentration zones by water supply wells, which have long screened intervals from 9 to 18 meters BGS.

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 site. The absolute mean age of groundwater may be obscured by mixing along flow paths due to heterogeneity in the sediments (Weissman, 2002). A key component of this study is development of a highly-resolved model of the heterogeneity in the aquifer system using a new geostatistical technique for simulating hydrofacies architecture that can incorporate 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 introduced in irrigation water, invading native groundwater. For comparison, measured groundwater ages and tritium concentrations allow calculation of the fraction of pre-modern (> 50 year old) groundwater in each well water samples. 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 model results of groundwater age and fraction pre-modern for the block shown in Figure 2.

2.2 Example 2 – Stockton, California

In the second example, we used an inert dissolved gas, sulfur hexafluoride, to tag about 125,000 m³ of surface water at a groundwater banking facility near Stockton, California, and trace its movement in 11 monitoring wells and 4 production wells. The objective of the study was to identify and quantify changes in
water quality during recharge and subsurface transport. In contrast to the very large artificial recharge operations in southern California, where relatively high TDS water is applied at long-established recharge areas, applied water in this study is very low TDS river water from Sierra Nevada runoff, and the facility has only been in operation for about three years. Analysis of tritium-helium groundwater age, fraction pre-modern, and the SF6 tracer allow estimation of the bulk flow rate.

The Modesto Formation (Pliocene-Pleistocene) comprises fluvially deposited arkosic sediment and locally derived deposits, gravel, sand, and silt, formed during the last major aggradational period in the eastern San Joaquin Valley.

Figure 4. Schematic cross-section of artificial recharge site and wells monitored for introduced tracer, groundwater age and chemical constituents.

We also examined 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, and modeled equilibrium reactions. 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 SF6 tracer 2) Shallow groundwater far from ponds; age <1-10 years, 15-40% pre-modern, low concentration SF6 tracer and 3) Deep groundwater; age 30-50 years, >80% pre-modern, no SF6 tracer. The groundwater mound generated by artificial recharge spreads to the east, west, and south, due to 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.

3. REFERENCES


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