

## **GAMA Special Studies: The impact of groundwater banking and septic effluent on California groundwater quality**

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This presentation will survey two special projects being conducted by Lawrence Livermore National Laboratory (LLNL) in the Groundwater Ambient Monitoring and Assessment (GAMA) program for the California EPA State Water Resources Control Board (SWRCB). These special studies address the need to better understand the impact of wastewater and groundwater basin management on groundwater quality.

***Arsenic contamination induced by groundwater banking:*** To understand water quality changes associated with groundwater banking, we are conducting two tracer studies of surface recharge in San Joaquin County near Stockton, California. Both naturally occurring (e.g.  $\delta^{18}\text{O}\text{-H}_2\text{O}$ ) and introduced ( $\text{SF}_6$ ) tracers are being used to tag large volumes of artificially recharged water, and a number of water quality parameters (including major and trace elements, nutrients, and disinfection byproducts) are being analyzed in surface water and groundwater. In addition, tritium and helium-3 contents by noble gas mass spectrometry are being used to calculate an apparent groundwater age and to estimate the fraction of “pre-modern” water recharged prior to atmospheric nuclear testing in a given groundwater sample. Tracer data, groundwater apparent ages and mixing ratios between modern and pre-modern groundwater allow identification of recently recharged and of ambient groundwater in the subsurface and allow delineation of recharge flow paths. Geochemical modeling using PHREEQC is being used to understand the evolution of water quality during recharge.

The major geochemical trends observed at the most intensively studied site are 1) an increase in TDS, including conservative ions such as  $\text{Cl}^-$ , and in dissolved inorganic carbon during recharge; 2) relative enrichment in monovalent cations ( $\text{Na}^+$  and  $\text{K}^+$ ) relative to divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) during recharge; and 3) elevated concentrations for the oxyanions As, V, and Mo in waters impacted by recharge. Both recently recharged groundwaters and shallow ambient groundwaters are oxidic at this site. These trends are consistent with 1) mixing between low-TDS recharge water and higher-TDS ambient groundwater, and 2) ion exchange of recharge and mixed water with aquifer solids (modeled as having ion exchange sites and having both strongly and weakly complexing HFO sites). Carbonate mineral equilibration is not indicated.

The elevation in arsenic concentrations in groundwater impacted by recharge cannot be explained by simple mixing between surface waters and ambient groundwaters. This trend, however, is consistent with displacement of oxyanions from aquifer sediment HFO binding sites by hydroxyl ions in recharging waters that have slightly higher measured pH than observed in ambient groundwaters. The modeled sediment

concentration of As used to simulate this trend is 15 mg/kg, and is comparable to sediment concentrations measured in other Central Valley locations (e.g. 24 mg/kg in Tulare Lake Bed sediment; Gao et al., 2006, *Chemical Geology* 228:33-43).

**Strong attenuation of organic compounds during infiltration of septic effluent:** To assess the impact of septic systems loading to drinking water aquifers and to identify robust tracers for septic effluent components in drinking water aquifers, we have introduced a  $\delta D$ -enriched water into two septic systems (a residential site and a commercial site); and measured a large number of analytes (including nutrients, major and trace elements, volatile and semi-volatile organic compounds, and stable isotopes of water and nitrate) in both septic effluent and in local groundwater in order to track transport of water and contaminants from individual systems to the local groundwater system. Both sites are in the same hydrogeologic setting (poorly-sorted alluvial sediments), have similar septic systems (two-chamber non-recirculating tank with subsurface leach lines), and both were instrumented with first-encounter and multi-level monitor wells, during which depth-discrete water and soil samples were collected.

The most promising inorganic tracer for septic effluent impact on local groundwater is boron. Regionally, groundwater boron is high (1-2 ppm) in deep (>60') groundwater and low (500 ppb) in shallow groundwater. Septic site groundwaters have high boron concentrations that decrease with depth and distance from the leach field. Furthermore, on a plot of boron versus sodium, septic site groundwaters define a mixing line between septic effluent and shallow ambient groundwater that is distinct from the mixing line between shallow and deep ambient groundwater. Similar shallow groundwater depth profiles are observed for chloride and sulfate, and these profiles are distinct from soil leachate profiles from a local non-septic site. The isotopic composition on nitrate-N and nitrate-O is consistent with a mixture of soil nitrate (as determined from soil leachate at a local non-septic site) and manure or septic nitrate, and indicates some denitrification.

Septic effluent collected from between the septic tank and the leach field at the residential site contains a number of organic compounds, including reduced sulfur compounds (e.g. carbon disulfide, dimethyl sulfides), pharmaceuticals (e.g. ibuprofen), steroids (e.g. androstane), and fragrance and cleaning compounds (e.g. triclosan; terpenes and sesquiterpenes, including limonene). First-encounter groundwater (15-20' bgs) directly beneath the septic leach field contains much lower concentrations of reduced sulfur compounds and unidentified terpenes and sesquiterpenes, and does not contain detectable concentrations of the other identified compounds. Deeper groundwaters beneath the septic leach field (27-32' bgs) and groundwaters down-gradient from the leach field do not contain detectable concentrations of these compounds. A similar pattern was seen at the commercial restaurant site: septic effluent contained large concentrations of caffeine, which was not detected in site groundwater.

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