

These elements have contributed to relatively large uncertainties in mass-balance estimates of sediment export. To improve mass-balance estimates, the Grand Canyon Monitoring and Research Center is field testing new and existing technologies to develop a continuous suspended-sediment transport protocol.

A recent innovation includes use of optical forward-scattering instruments, LISST, in combination with programmable pumping samplers. The LISST-100 (Laser In-Situ Scattering and Transmissometry) is both a particle-size analyzer (size range 2.5 to 500 microns) and a transmissometer capable of measuring variable concentrations, depending on particle size. A second innovation, the LISST-25X, is a recently developed variation of the instrumentation that allows sand to be measured separately from finer particles. This is achieved by use of shaped focal plane detectors that compute 2 distinct weighted sums of angular scattering by suspended particles. The LISST-25X currently collects volume-concentration and grain size (Sauter-mean-diameter) data for suspended particles at four sites below the dam. Unit values are derived by averaging 1000 individual measurements every 15-minutes (sampling about 1.1 liters of water per hour). The volume-to-mass conversion is made once average particle density has been gravimetrically determined through conventional methods.

During high-concentration conditions, laser-transmission values (T) can fall outside of the user-defined minimal threshold ( $20 < T < 99$  is acceptable range). During these periods, the LISST-25X is designed to electronically enable its pump-sampler counterpart, ensuring that point samples are physically collected when the LISST detectors are subject to bias from multiple scattering caused by the abundance of fines. As with any point-data set, the LISST point values must be calibrated to cross-sectionally integrated samples collected using isokinetic samplers. The increased temporal and spatial resolution, and continuous nature of these in-situ measurements, is a significant advance over previous methods for monitoring suspended-sediment mass balance of the Colorado River.

Recent work by Rubin and Topping (2001), has shown that suspended-sediment concentration and grain-size data can be used to back-calculate grain size of sediment on the bed upstream (a surrogate for how enriched the river is in fine sediment, and thus an indirect measure of the mass balance). Preliminary results indicate that bed-sediment grain size mimics the sediment balance (fining during depositional events and coarsening by winnowing during intervening periods). Results also suggest that LISST data will be suitable for tracking beta values in real time. Field testing of these combined technologies and others is scheduled to continue through 2004.

Rubin, D.M., and Topping, D.J., 2001, Quantifying the relative importance of flow regulation and grain size regulation of suspended sediment transport (*alpha*) and tracking changes in grain size of bed sediment (*beta*): *Water Resources Research* vol. 37, no. 1, p. 133-146.

#### H72B-0861 1330h POSTER

##### Water Follies: Groundwater Pumping and the Fate of America's Fresh Waters

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The next time you open a bottle of spring water, consider that it may have come from a well that is drying up a blue-ribbon trout stream. The next time you super-size a meal at McDonald's, note that the fries are all the same length. That's because the potato farmers irrigate their fields with groundwater from wells, some adjacent to nearby rivers. The next time you purchase gold jewelry, consider that it may have come from a mine that has pumped so much groundwater to de-water the gold-bearing rock that 60 to 100 years will pass before the water table recovers. The next time you water your suburban lawn, pause to reflect on what that's doing to the nearby wetland. And the next time you visit Las Vegas and flip on the light in your hotel room, consider that the electricity may have been generated by a coal-fired power plant supplied by a slurry pipeline that uses groundwater critical to springs sacred to the Hopi people.

These and countless other seemingly innocuous activities reflect our individual and societal dependence on groundwater that is hydrologically connected to surface water. Hydrologists understand that ground and surface water are interconnected, but frequently the legal rules governing water distinguish between ground and surface water. This has led to groundwater pumping that has dried up many rivers, particularly in the arid West. In Arizona, many once verdant streams have become desiccated sandboxes as city, mines, and farms pumped groundwater to such an extent that surface flows were totally depleted.

The problem of the impact of groundwater pumping on the environment, however, is not confined to the arid West. It is an enormous national, indeed international problem. This presentation will focus on the United States and illustrate with examples from around the

country the array of environmental problems caused by excessive groundwater pumping. The locations of these case studies range from Maine to California, from Minnesota to Florida, and from Texas to Massachusetts. Indeed, a river in Massachusetts - the Ipswich River - has gone dry in three of the last six years due to groundwater pumping.

This presentation will also explore our cultural uses of water and supposed "solutions" that can actually worsen environmental consequences. It will also offer alternative solutions that would prevent some of the most severe environmental consequences. One problem, as a matter of public policy, we have treated water as a public resource that is free for the taking, creating what economists call the tragedy of the commons. It is essential that we begin to price water more in line with its true economic value. Any meaningful reform must combine principles of water marketing together with meaningful government regulation. This presentation will outline the steps that states should take if we are to prevent further degradation of our rivers, streams, wetlands, and estuaries.

URL: <http://www.islandpress.org/Water>

#### H72C MCC: Hall C Sunday 1330h Isotopic and Chemical Tracers of Groundwater Susceptibility: Linking Science Understanding to Policy Needs Posters (joint with B, PA)

Presiding: T Bullen, U.S. Geological Survey; K Thomasberg, Monterey County Water Resources Agency

#### H72C-0862 1330h POSTER

##### The Effect of 1999 Chi-Chi Earthquake on the Groundwater Flows of Choshuichi Alluvial Fan, Taiwan

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The 1999 Chi-Chi (Mw=7.5) earthquake in central Taiwan stands as one of the most important hydrogeological events in the past century in Taiwan. It has produced profound impacts for the local groundwater hydrology. The monitoring network that completed its emplacement in 1997 in the Choshuichi Alluvial Fan has recorded for the first time detailed and complex variations of groundwater levels of various aquifers during and after the Chi-Chi earthquake. In addition, hydrogen and oxygen isotope compositions for the same set of monitoring wells have been measured in 1999 and 2000 to elucidate the groundwater flow patterns and interactions among aquifers before and after the Chi-Chi earthquake. In general, water levels exhibited relatively higher positive anomalies in the northern (Changhua) section than those of the southern (Yunlin) section during the Chi-Chi earthquake. The water levels showed larger affected area for the lower confined aquifer III and the affected area diminished toward upper unconfined aquifer I. Stable isotopes identified three sources responsible for the groundwater recharging in the Choshuichi Alluvial Fan: the northern Pakua Terrace, the central Choshuichi river and the southern Toliu Terrace. During the Chi-Chi earthquake, the central Choshuichi river expanded its recharging extents primarily in a horizontal propagating way for confined aquifers and mainly flowed toward the northern section. Minor vertical mixing among aquifers were also observed for some monitoring wells implying the ruptures of aquitards. The Choshuichi Alluvial Fan eventually resumed their pre-earthquake groundwater flow patterns in the summer of 2000. We suggest that the expansion of the Choshuichi river recharge following the Chi-Chi earthquake may be due to enhanced

permeability by the earthquake. The eventual resumption of groundwater flow to the pre-earthquake pattern may signify the return of the permeability to its pre-earthquake value.

#### H72C-0863 1330h POSTER

##### Quantification of Natural and Anthropogenic Components in Karst Aquifer Discharge Under Variable Flow Conditions: A Case Study of the Classical Karst (Kras), Southwestern Slovenia

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The groundwater resurgence of the Classical Karst (Kras) aquifer is an internationally shared water resource. The springs of the resurgence zone are located in Italy, while the majority of the recharge area is within Slovenia. In this study, measurements of chemical ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , electrical conductivity) and stable isotopic ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}_{DIC}$ ) parameters of the groundwaters were made in an effort to quantify the contributions of multiple sources to the aquifer discharge under changing hydrologic conditions. Principal components analysis (PCA) and end-member mixing analysis (EMMA) were employed to estimate mixing proportions among three end-members: allogenic surface water recharge from the sinking Soča River, autogenic recharge from local precipitation, and an anthropogenic component characterized by 1) anomalously high  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations, and 2) a  $\text{Cl}^-/\text{Br}^-$  ratio of 460. Water samples were collected on a monthly basis for two years, and daily during storm events. Hydrograph recession analysis of the major spring flow was used to identify four hydrologic flow regimes of the aquifer resurgence. The PCA/EMMA was performed on the mean chemical compositions of the four flow regimes, as well as on the data obtained from the storm sampling.

The results indicate that the three end-member sources mix in varying proportion to give rise to 4 groups of groundwaters. For all of these, the Soča River water is the largest component of flow under all flow conditions. The river provides the majority of the aquifer discharge at low flow, while during high flow there is an increased contribution from autogenic recharge. In addition, an anthropogenic component significantly affects the aquifer discharge under high flow conditions. It affects most the water supply well at Klariči, providing as much 28% of the well discharge under conditions of elevated hydraulic head during storm events.

#### H72C-0864 1330h POSTER

##### Physical and Hydrochemical Evidence of Lake Leakage and Assessment of Karst Features in the Vicinity of Lake Seminole, Southwestern Georgia and Northwestern Florida

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Lake Seminole is the surface manifestation of an interconnected aquifer-stream-reservoir system characterized by a constructed impoundment emplaced in the karst terrain of the lower Apalachicola-Chattoohocchee-Flint River Basin. Physical, chemical, and isotopic constituents of water samples indicate surface water mixing with ground water of the underlying Upper Floridan aquifer, lake leakage beneath Jim Woodruff Dam, and karstic dissolution of the limestone aquifer matrix.

Major ions, nutrients, radon 222, and stable isotopes of hydrogen and oxygen collected in 2000 from 30 wells, 7 lake locations, and 5 springs indicate that in-lake springflow evolves chemically and isotopically along ground-water and surface-water pathways. Although mixing ratios of ground water to surface water in springs varied with location and season, springflow from May to October exhibited more ground-water-like qualities (higher specific conductance, dissolved oxygen, and lower temperature) than surface water. Ratios from November to April were difficult to quantify due to rapid mixing of spring and lake water during sampling and reduced flow from springs.

Lake leakage is evidenced in the bottom of the Apalachicola River about 300 yards downstream of the dam, where lake water boils up from a limestone ledge at rates of about 140-220 cubic feet per second. Dye tracing by the U.S. Army Corps of Engineers indicates that the river boil also receives water from a similar boil on land, which discharges to a sinkhole adjacent to the river. Isotopic data indicate about a 13 to 1 mixing ratio of lake water to ground water.

Calcite saturation indices of ground-water samples indicate a higher potential for karstic dissolution from late fall through early spring than in the summer. The relatively short residence time (5-7 hours) and rapid flow velocity (nearly 500 feet per hour) for lake water to leak into the aquifer and exit at the boil suggests that this water would not reach equilibrium while in transit.

#### H72C-0865 1330h INVITED POSTER

##### Sources and Chronology of Nitrate Contamination of Spring Waters: Integrating Science and Policy Decisions

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Human health and ecological concerns have arisen regarding spring waters in Florida as a steady increase in nitrate concentrations has been observed during the past 30 years. The extensive aesthetic, cultural, and recreational value of these springs, which also supply water for human consumption and support critical ecological habitats, could be threatened by the presence of nitrate. As part of the response to these concerns by the State of Florida, several research studies have used various chemical and isotopic tracers to determine sources of nitrate contamination and age of ground water discharging from springs. Since 1997, 60 water samples have been collected from 44 springs and analyzed for isotopic (<sup>15</sup>N, <sup>3</sup>H/<sup>3</sup>He, <sup>18</sup>O, <sup>2</sup>H, <sup>13</sup>C) and other chemical tracers (CFCs, major ions, dissolved gases, SF<sub>6</sub>). Delta <sup>15</sup>N values of nitrate ranged from 2.6 to 12.9 per mil (median = 5.8 per mil) and indicated that nitrate in most spring waters originated from synthetic fertilizers. CFCs, <sup>3</sup>H/<sup>3</sup>He, and SF<sub>6</sub>, used to estimate the residence time of ground water discharging from springs, indicated that spring-water ages ranged from 5 to 39 years. Concentrations of these multiple transient tracers are consistent with a two-component hydrologic model with mixtures of varying proportions of young water (less than 8 years) from the shallow part of the aquifer system and older water (20-50 years) from the deeper part of the flow system. Given residence times of 20-40 years for ground water discharging from most springs, it could take decades for nitrate concentrations to decrease to near background levels, even with immediate reductions in nitrogen inputs to the land surface. These research results are being used by the State of Florida to inform elected officials, water-resource managers, and planners that decisions about land use today will affect the quality of ground water in springs for decades.

#### H72C-0866 1330h POSTER

##### Nitrate Source, Transport and Fate in Ground Water Near La Pine, Oregon

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A shallow, sandy aquifer serves as both the source of drinking water and the receptor of septic tank effluent for most residents in the vicinity of La Pine, Oregon. High concentrations of NO<sub>3</sub><sup>-</sup> (>10 mg NO<sub>3</sub><sup>-</sup>-N/L) first were observed in study area ground water in the early 1980s. A framework for understanding NO<sub>3</sub><sup>-</sup> dynamics and a conceptual model in support of a numerical NO<sub>3</sub><sup>-</sup> transport model are described here.

Geochemical and hydrogeologic data were collected at a variety of scales to develop an aquifer scale (640 km<sup>2</sup> area, 37-m thickness) understanding of NO<sub>3</sub><sup>-</sup> source, advection, dispersion, and fate. A network of 193 existing wells, two transects of monitoring wells installed along ground-water flowpaths, a dense array of direct-push wells installed perpendicular to one of the

transects, and three wells installed in septic tank effluent plumes were sampled and variously analyzed for common ions, nutrients, dissolved organic carbon, field parameters, dissolved gases, isotopes of water and nitrogen, and age-dating tracers (CFCs, <sup>3</sup>H, <sup>3</sup>H/<sup>3</sup>He).

Nitrogen isotopes, N/Cl<sup>-</sup> relations, age gradients, and hydraulic considerations indicate that septic tank effluent is the dominant source of NO<sub>3</sub><sup>-</sup> in the aquifer. Most NO<sub>3</sub><sup>-</sup> currently resides within the upper 5 m of the aquifer, due in large part to low recharge rates (CFC-based ground-water age gradients indicate a median recharge rate of 5.1 cm/y) and low hydraulic gradients that limit advection. High concentrations of NH<sub>4</sub><sup>+</sup> (up to 39 mg NH<sub>4</sub><sup>+</sup>-N/L) were observed in deep (generally > 37 m) ground water (water that, for the most part, resides beneath the primary aquifer). Nitrogen isotopes, N/Cl<sup>-</sup> and N/C relations, <sup>3</sup>H data, and hydraulic considerations point to a natural, sedimentary organic matter source for this NH<sub>4</sub><sup>+</sup>. Relations between NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and geochemical indicators of redox conditions, and relations between concentrations and isotopes of N<sub>2</sub>, indicate that denitrification is extensive in the study area. Denitrification occurs near the oxic/suboxic boundary. Laboratory denitrification experiments with aquifer sediments confirm the existence of a denitrification capacity in sediments currently exposed to NO<sub>3</sub><sup>-</sup>, and also demonstrate a latent denitrification capacity in sediments collected from what is currently NO<sub>3</sub><sup>-</sup>-free ground water.

Our data allowed development of a framework and a conceptual model for the NO<sub>3</sub><sup>-</sup> transport model. Septic tank effluent is the dominant NO<sub>3</sub><sup>-</sup> source term; census data were combined with study area septic tank effluent data to estimate NO<sub>3</sub><sup>-</sup> loading terms. Concentration data from a dense array of wells facilitated estimation of dispersion. Advection of NO<sub>3</sub><sup>-</sup> occurs until NO<sub>3</sub><sup>-</sup> reaches the oxic/suboxic boundary, at which point denitrification quickly results in reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub>. Age-dating data were combined with hydraulic head, slug test, and ground-water/surface-water interactions data to constrain and calibrate the transport model. Results from the transport model are being presented by Morgan et al. in a separate Fall, 2002 AGU session.

#### H72C-0867 1330h POSTER

##### Isotopic Evidence for the Impact of Playa Water on Shallow Groundwater Flow in the Snake River Aquifer Beneath the INEEL

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The Idaho National Engineering and Environmental Laboratory (INEEL) is located on the Snake River Plain in eastern Idaho. At Test Area North (TAN) on the INEEL, waste consisting of low-level radioactive isotopes, sewage and chlorinated solvents was injected into the upper aquifer through a 95 m well, resulting in a 2 km plume of TCE in the groundwater. The geology consists of fractured basalt flows separated by sedimentary interbeds. The depth to groundwater at the site is 65 m. At 120-160 m depth, a continuous interbed (the Q-R) acts as a confining layer between the upper and lower aquifer. The primary direction of flow in the Snake River Aquifer is NE to SW, but flow at TAN (as defined by the TCE plume) is perpendicular to the regional flow, starting out to the east and bending to the SE. Possible causes of this anomalous flow include injection and/or infiltration of wastewater, infiltration of water from ephemeral playa lakes (dry for the last 50 years due to agricultural diversion), or heterogeneous permeability due to subsurface geological features. Understanding this flow is critical for determining the risk factors associated with the contamination.

We have measured the isotopic compositions of surface and groundwater from TAN. Water above the Q-R interbed is evaporated ( $\delta^{18}O$  values shifted up to 3‰/‰). The degree of evaporation increases towards the edge of outline of the closest playa. The <sup>87</sup>Sr/<sup>86</sup>Sr values are very uniform (0.71035±0.0001) and are equal to samples from the playa system. Conversely, water beneath the Q-R is not contaminated and is isotopically distinct from the water above the interbed (no evaporation, <sup>87</sup>Sr/<sup>86</sup>Sr values >0.711). The playa water is the primary factor producing the flow patterns observed in the TAN area. Radiocarbon ages calculated from the <sup>14</sup>C of DIC are 1800 to 2800 years BP, giving infiltration rates of 2-3 cm/yr. Given the possibility of subsurface DIC exchange with carbonates, these ages should be considered minimum ages, however, they suggest that the playas will affect groundwater flow directions well into the future.

#### H72C-0868 1330h POSTER

##### Chemical and Isotopic Tracers of Groundwater Sustainability: an Overview of New Science Directions

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Groundwater sustainability is an emerging concept that is rapidly gaining attention from both scientists and water resource managers, particularly with regard to contamination and degradation of water quality in strategic aquifers. The sustainability of a groundwater resource is a complex function of its susceptibility to factors such as intrusion of poor-quality water from diverse sources, lack of sufficient recharge and reorganization of groundwater flowpaths in response to excessive abstraction. In theory the critical limit occurs when degradation becomes irreversible, such that remediation efforts may be fruitless on a reasonable human time scale. Chemical and isotopic tracers are proving to be especially useful tools for assessment of groundwater sustainability issues such as characterization of recharge, identification of potential sources, pathways and impacts of contaminants and prediction of how hydrology will change in response to excessive abstraction. A variety of relatively cost-efficient tracers are now available with which to assess the susceptibility of groundwater reserves to contamination from both natural and anthropogenic sources, and may provide valuable monitoring and regulatory tools for water resource managers. In this overview, the results of several ongoing groundwater studies by the U.S. Geological Survey will be discussed from the perspective of implications for new science directions for groundwater sustainability research that can benefit water policy development. A fundamental concept is that chemical and isotopic tracers used individually often provide ambiguous information, and are most effective when used in a rigorous "multi-tracer" context that considers the complex linkages between the hydrology, geology and biology of groundwater systems.

#### H72C-0869 1330h POSTER

##### Assessing Contaminant Susceptibility Near Artificial Recharge Operations by Imaging Flowpaths and Transport Times With Geochemical Tracers

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Critical for assessing the potential impacts of artificial recharge operations on water quality is detailed knowledge of groundwater dynamics near spreading areas. Geochemical tracer techniques including tritium/helium-3 (T/<sup>3</sup>He) dating and the addition of trace gases in controlled experiments are ideally suited for these investigations. A series of experiments were conducted using these tracers near the artificial recharge facilities in Northern Orange County, CA. Here, approximately 2.5 x 10<sup>8</sup> m<sup>3</sup> of surface water are recharged annually to the groundwater basin. T/<sup>3</sup>He ages show that most of the relatively shallow groundwater within 3 km of the recharge facilities have ages less than 4 years; further down gradient ages increase, reaching >20 years at distances more than about 6 km. Far from the spreading area in the confined portions of the aquifer there is little evidence for young groundwater (<50 years). Gas tracer experiments using sulfur hexafluoride and xenon isotopes were conducted from two spreading basins and the Santa Ana River. These tracers were followed in the groundwater for up to 4.5 years, allowing subsurface flow patterns and flow times to selected wells to be quantified. Results demonstrate that the mean horizontal flow velocity range between 0.4 and 2.9 km yr<sup>-1</sup>. It is likely that the gas tracers were moving primarily through the most conductive layers and thus these velocities do not represent bulk flow within all layers. The leading edge of the tracer plume moved at velocities about twice as fast as the center of mass. The latter velocities are important when considering the potential transport of microbes and other "time sensitive" contaminants because they reflect the fastest paths in the aquifer. These velocities can not be easily determined with other methods showing the importance of geochemical methods for artificial recharge site evaluation.

H72C-0870 1330h POSTER

### Comparing Groundwater Contamination Vulnerability in Large, Urbanized Basins of California

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We have sampled over 700 public drinking water wells as part of a study to assess relative contamination susceptibility of the major groundwater basins in California. The parameters used to rank wells according to vulnerability are groundwater age dates (using the tritium-3helium method), stable isotopes of the water molecule (for water source determination), and occurrence of low level Volatile Organic Compounds (VOCs). Long-screened production wells supply clean, high quality samples, and sample the resource that is being used. However, the groundwater age distribution from production wells may be quite broad, and comparisons to the predicted initial tritium value for the measured mean age, along with analysis of radiogenic 4Helium are used to de-convolute the mixed age.

Results from the Los Angeles and Orange County Basins, and Santa Clara Valley, will be presented. A large volume of both imported and locally captured water is artificially recharged in these intensively managed basins. An effective confining unit in the Santa Clara Valley basin prevents widespread vertical transport of contaminants down to drinking water wells. In the southern California basins, groundwater age and the frequency of occurrence of low-level VOCs are spatially correlated, with more recently recharged water likely to have VOC detections. 'Pre-modern' water is nearly always free of VOCs, except when a suspected 'short circuit', (e.g., loss of integrity in well casing) allows near surface contamination to reach 'old' water. Methyl-tertiary-Butyl Ether (MTBE) can be a useful time marker in groundwater basins, with water recharged after the 1980's showing traces of MTBE. Water resource managers can use these vulnerability assessments to focus monitoring efforts, site new wells, plan land use, and evaluate remediation activities. 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.

URL: <http://www.swrcb.ca.gov/cwphome/land/gama/webpages/gamahome.htm>

H72C-0871 1330h INVITED POSTER

### Characterizing Saline Waters with Isotopes in the Coastal Alluvial Aquifers of Monterey Bay, California

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A multiple-well monitoring site completed in the deep-aquifer system in the Salinas Valley, California, is used to characterize the source of saline water in the layered coastal alluvial aquifers. One well is completed at the base of the upper-aquifer system that extends to a depth of 955 feet below land surface (bls) and three wells are completed in the deep-aquifer system that extends to depths of 2,000 feet bls. Water levels at the monitoring sites, if the aquifers are hydraulically connected with submarine outcrops in Monterey Bay, are about 10 to 30 feet below the level necessary to prevent seawater intrusion.

Geophysical logs indicate that saline water is present in water-bearing zones throughout most of the upper-aquifer system and at depths ranging from 1,025 to 1,130 feet bls in the deep-aquifer system. Numerous thick fine-grained units retard the vertical movement of ground water between aquifers and may restrict the movement of saline water to narrow water-bearing zones in the upper-aquifer system.

Boron concentrations and isotopes in samples from the deep aquifer system indicate that the saline water is not seawater and carbon-14 analyses indicate that the water was recharged thousands of years ago. The saline ground water may be related to the dissolution of salts from the saline marine clays that surround the water-bearing zone. Understanding the potential for seawater intrusion of the deep-aquifer system requires a better understanding of its extent and characteristics.

URL: <http://water.usgs.gov/pubs/wri/wri024003/>

H72C-0872 1330h POSTER

### Volatile Organic Compounds and Stable Isotopes in Groundwater as Tracers of Industrial-Age Recharge in the Southern California Coastal Plain

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The USGS, in collaboration with the California Water Resources Control Board, is using volatile organic compounds (VOCs) and stable isotopes to assess the susceptibility of California aquifers to contamination from land surface activities. One of the areas studied is the 2700 square kilometer coastal plain of southern California, where we have sampled more than 200 public supply and monitoring wells.

The ground-water hydrologic cycle in the southern California coastal plain is dominated by human activity. Engineered recharge facilities along the Rio Hondo, San Gabriel River, Santa Ana River, and Santiago Creek are the primary sources of ground-water replenishment for the regional aquifer system. During the past 50 years, approximately 20 cubic kilometers of water have been recharged through these facilities. The primary source of ground-water discharge is from hundreds of production wells that are generally perforated at depths ranging from 150 to 300 meters. Currently, the rates of recharge and discharge are approximately equal.

VOCs in ground-water can be used to demarcate water that has entered the flow system within the past 50 years. Associated with each of the recharge facilities is a radial wedge: within the wedge ground-water contains one or more VOCs at concentrations above the USGS laboratory reporting limits (LRL); outside the wedge there are no detections above LRL. The distribution of specific VOCs in ground-water reflects the historical usage of those compounds. For example, MTBE, which was introduced within the past decade, is only present in ground water within a few kilometers of the recharge facilities. In contrast, chloroform, which has been used or generated for more than 50 years, is present in ground water more than 20 kilometers from the larger recharge facilities.

The distribution of stable isotopes can also be used to demarcate water that has entered the flow system within the past 50 years. Within the radial wedges, the isotopes of oxygen and hydrogen are lighter than outside the wedges. The depletion in stable isotopes reflects the importation of relatively light Colorado River and Northern California water into the basin. Overall, the distribution of VOCs and stable isotopes documents the regional-scale displacement of native ground water by industrial-age ground water introduced to the system at the engineered recharge facilities.

H72C-0873 1330h POSTER

### A Tracer investigation Into the Importance of Diffusive Exchange in the Unsaturated Zone of the British Chalk

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The Chalk is an economically and ecologically important aquifer in England and in other countries of North-West Europe. Its susceptibility to pollution is a source of ongoing concern and the pathway of pollutants through the unsaturated zone is not fully understood. The chalk medium is characterized by a fine-grained porous matrix intersected by extensive fractures. An important question is whether in the unsaturated zone the water flow and transport passes through the fractures or through the intergranular pores in the matrix. In general it is assumed that a substantial part of the flow goes through the matrix pores as piston displacement and that fracture flow is only generated during periods of high recharge rates. During fracture flow there is diffusion of contaminants between the mobile fracture-water and the nearly static matrix-water. The extent of the diffusive exchange between fractures and matrix is largely determined by the fracture flow velocity, ranging from complete diffusive equilibrium between fractures and matrix for low velocities to an effective bypass of the matrix for high fracture flow velocities.

A comparative tracer test is being carried out on the Middle Chalk in Cambridgeshire, Eastern England, to analyze the conditions that trigger fracture flow and diffusive exchange between fractures and matrix. The experiment runs under natural rainfall conditions on a large (5x5m), grass-covered lysimeter and the tracers used are deuterium and bromide. After one winter recharge season, none of the tracer has penetrated to any great depth. Vertical core profiles show that the bulk of the tracer has migrated very little but there is some evidence of fracture flow with partial diffusion into the surrounding matrix. The experiment highlights the high attenuation capacity of the soil cover and the chalk unsaturated zone but demonstrates that even for moderate rainfall conditions some rapid bypass flow is possible. The results of the tracer test will aid in the development of a modelling tool to address the vulnerability of the Chalk aquifer.

H72C-0874 1330h POSTER

### Using Environmental Isotopes to Determine Groundwater Flowpaths in a Mountain Range in NE Spain

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Groundwater systems in crystalline mountain areas can not be adequately described using conventional hydrological data because of the lack of observation points and the usual preferential flow through main fractures. The use of environmental isotopes is then appropriate to infer the origin, evolution and flowpaths of ground-water. In our study area, the Gavarres range in NE Spain, <sup>18</sup>O and D indicate recharge water altitude, mixing between waters of distinct origin (i.e., rainfall-infiltrated groundwater, sea water, or surface river water), and the main period of recharge. Regional system flow paths are thus established using potentiometric, geochemical, and isotope data.

In its northern limit, the Gavarres crystalline range is surrounded by tectonic basins filled by highly fractured carbonated and detritic aquifers. In the southern area, regional faults control the depth of the granitic basement, which is overlaid by non-consolidated sedimentary deposits. A divergent flow from the range, suggested by potentiometric and isotope data, shows that it acts as the recharge area of the surrounding aquifers. It also suggests a good hydraulic connection between different aquifers through vertical ascendent flow lines along fractures. Furthermore, sea water intrusion and river leakage caused by intensive withdrawals are also inferred from isotope data in the deepest alluvial aquifers of the northern basin. In the southern area, differences between the isotope contents of the granitic basement groundwater and that of the overlying sedimentary aquifer suggest the existence of deep regional groundwater flows at a larger scale than the studied mountain range. Finally, the isotope content of existing thermal and CO<sub>2</sub> rich waters is integrated in the hydrogeological conceptual model of the area.

This research is funded by CICYT project HID980366.

H72C-0875 1330h POSTER

### Use of Naturally Occurring Noble Gas Tracers to Evaluate the Freshwater/Saline Water Interface of the Edwards Aquifer, South-Central Texas.

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The Edwards Aquifer currently is the primary source of water in south central Texas for agriculture, municipal, industrial, and ecological needs, supplying

over 1.5 million people and supporting unique habitats for endangered species. The aquifer consists of limestone with some dolostone members of the Edwards Group that dip in a southeasterly direction. The up-dip freshwater zone of the aquifer is recharged with fresh water along the northern area of the outcropping Edwards Group. Adjacent to the freshwater zone is the saline-water zone that forms an interface at the down-dip limit of the fresh water. Though the freshwater/saline-water interface is spatially defined within the aquifer, little is known about the nature of groundwater flow between and along its surface. Structural, lithologic and hydrologic features may influence the possible up-dip migration of the saline water into the freshwater zone and may adversely affect current freshwater supplies. Freshwater/saline-water monitoring well transects were sampled for dissolved gas using both conventional and un-conventional methods to establish vertical profiles across the aquifer. Data revealed two highly distinct gas compositions between the zones. The upper freshwater zone is characterized by normal, atmospherically saturated water gas concentrations with slight enrichments due to excess air ( $^4\text{He}$  60  $\mu\text{cc}/\text{kg}$ ). The lower saline zone displayed a very different gas composition, highlighted by extremely high concentrations of radiogenic  $^4\text{He}$  (>20,000  $\mu\text{cc}/\text{kg}$ ) and minor amounts of excess  $^{40}\text{Ar}$  contained in a gas composition rich in  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and other hydrocarbons. Vertical profiles of dissolved gas compositions across the interface show active flowing water along the interface, and sluggish, stagnant flow within the saline zone. These sharply contrasting zones are strongly influenced by the faulting in the aquifer and by the hydrostatic head within the freshwater zone. Both the faulting and the hydrostatic head in the freshwater zone of the aquifer appear to exert a major influence on the regional groundwater flow patterns.

## H72D MCC: Hall C Sunday 1330h

### Elucidating the Fate of Emerging Contaminants in Groundwater and Surface-Water Systems Posters (joint with B)

Presiding: J Landmeyer, U.S.

Geological Survey; P Bradley, U.S.

Geological Survey

## H72D-0876 1330h INVITED POSTER

### Emerging Water Contaminants: Technical, Legal and Policy Challenges

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Approximately 120 new chemicals are created each year due to ever-improving industry and technology markets. Releases of new contaminants into the environment can occur during production, use and disposal of these chemicals thereby leading to potential contamination of water supply sources. Very few emerging contaminants are regulated. In addition, knowledge gaps regarding emerging contaminants include lack health effects, occurrence (either because these compounds are not measured or because concentrations are below detection limits of readily available analytical techniques) and fate and transport in the environment especially with regards to mobility and persistence. The sources of these compounds are numerous. One source is treated wastewater, which is re-injected into groundwater aquifers for indirect potable reuse purposes. Emerging compounds of concern can be classified in various classes. This presentation will focus on contaminants, which have emerged in the last 10 years including pharmaceuticals (antibiotics/drugs), personal care products (polycyclic musks), pesticides/herbicides, industrial solvents (1,4-dioxane), gasoline additives (MTBE), disinfection byproducts such as NDMA (N-nitrosodimethylamine), and inorganic compounds such as perchlorate and arsenic. This presentation will present technical, legal and legislative challenges posed by the presence of these contaminants in water. Background information including chemicals history of use, sources in the environments, nationwide occurrence, physical and chemical properties, behavior in the environment and technologies for removal from soil and water will be presented.

In addition, case studies on MTBE, pharmaceuticals and personal care products, 1,4-dioxane, arsenic and NDMA will be discussed.

## H72D-0877 1330h POSTER

### Attenuation of Selected Emerging Contaminants During River Transport

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The ubiquitous occurrence of emerging (non-regulated) contaminants in the aquatic environment is of concern because some of these chemicals are biologically active at low concentrations and a potential threat to wildlife and human health. Emerging contaminants include a diverse range of chemicals, including pharmaceuticals, natural and synthetic hormones and industrial surfactants, such as alkylphenol ethoxylates (APEO) and their metabolites. To address the ecotoxicological impact of these chemicals, it is necessary to know their sources, removal efficiencies during wastewater treatment, and their behavior in the environment.

In this study, the fate of selected emerging contaminants in the Santa Ana River (SAR) in Southern California was investigated. The SAR originates in the San Bernardino Mountains and flows 80 miles into the Pacific Ocean. The SAR flow stems mainly from storm runoff, wastewater treatment effluents and several other minor sources. During the dry season, SAR flow is dominated by effluent from public wastewater treatment plants. Input into the SAR was studied by analyzing samples from four major treatment plants that employ different tertiary treatment processes. To assess the fate during river water transport and during wetland treatment, samples from six sites along the river were analyzed.

Effluent samples were analyzed every two months, river water every four months. River samples were taken considering the flow velocity, which is approximately 1 mile per hour. The analytical method involves solid-phase extraction using C-18 cartridges and extraction of three fractions. Samples were analyzed with and without further derivatization using GC/MS and GC/MS/MS.

Results indicate significant contaminant removal during river transport, presumably by photochemical oxidation. Within a distance of nine miles, pharmaceuticals, plasticizers, flame retardants, APEOs and metabolites were attenuated with removal rates ranging from 76% for a flame retardant to up to 97% for some APEO metabolites. The two pharmaceuticals gemfibrozil and ibuprofen were attenuated by more than 90%. Whether photochemical transformations are mainly responsible for the observed removals remains to be investigated.

## H72D-0878 1330h POSTER

### Empirical Models of NAPL Dissolution and Their Applications in Subsurface Contaminant Transport Modeling

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Three simple empirical models of nonaqueous phase liquid (NAPL) dissolution are proposed based on the NAPL mass conservation and the assumption of proportionality between the solute concentration and the remaining residual NAPL mass. The purpose of the proposed models is to predict the solute concentration in the vicinity of the residual NAPL as a result of dissolution. The predicted solute concentration decrease is used to simulate and account for the decrease of dissolution rate with time. The empirical parameters used in the proposed models that were obtained from one-dimensional simulations of water-saturated column are found to be also representative of variably saturated systems with a fairly reasonable success. It is found that the proposed models are fairly good for quantification of non-equilibrium dissolution, which is characterized by tailing of breakthrough curves. The models are especially useful for the situations of small residual NAPL saturation, which are typical for field applications.

## H72D-0879 1330h POSTER

### Compound-Specific Carbon and Hydrogen Isotope Analysis - Field Evidence of MTBE Bioremediation

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Compound-specific stable isotope analysis allows opportunity to determine the isotopic ratios of individual contaminants. The technique has been applied to confirm biodegradation in studies of chlorinated solvents and recently BTEX, MTBE and TBA. Chemical reactions (including bio- and inorganic degradation) tend to favor molecules with the lighter isotopic species (e.g.,  $^{12}\text{C}$ ,  $^1\text{H}$ ), resulting with enrichment of the unreacted substrate in the heavier isotopic species ( $^{13}\text{C}$ ,  $\text{D}$ ), referred to as kinetic isotopic fractionation, so that the extent of fractionation may be used as a proxy for biodegradation. Processes such as volatilization, sorption etc., result in minimal degree of fractionation and do not interfere with the isotopic signal due to biodegradation.

The results presented here show the first successful applications of compound-specific isotope analysis to understanding MTBE biodegradation in the field, at both aerobic and anaerobic sites. Observed fractionations suggest that two different biodegradation pathways may be involved. At a number of anaerobic locations major fractionation effects were observed for both C and H; enrichment factors for both elements were approaching or exceeding -10. A laboratory microcosm study using an enrichment culture yielded similar results (C data only). A characteristic feature of these sites was the presence of high concentrations of TBA.

Conversely, at a number of sites, the C composition remained stable with little fractionation and stayed within the analytical precision range or changed minimally, while H displayed significant fractionation in excess of 60 per mil. Moderate agreement of the data with Rayleigh fractionation model was observed, suggesting that biodegradation effect was distorted by variability at the source or the plume was not homogeneous. The enrichment factor calculated for these data is similar to the one published for aerobic microcosm of MTBE-degrading culture from Vandenberg AFB by Gray et al. (Env. Sci. Tech., 2002, 36, 1931-1938) and appears to be in excess of -60 for H and under -2 for C.

The high H fractionation observed under aerobic conditions may be attributed to the initial, monooxygenase transformation of MTBE (cf., Deeb et al., Biodegradation, 2000, 11, 171-186). The anaerobic enzymatic reactions were not characterized yet, but a hydrolytic process may be responsible. Interestingly, isotopic fractionation at an anaerobic site, which was treated by oxygen injection, did not show differences between aerobic and anaerobic parts of the plume. Despite oxygen addition, there was no evidence for monooxygenase activity.

## H72D-0880 1330h POSTER

### Factors Affecting the Success of Enhanced Aerobic Biodegradation of MTBE and BTEX

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At a gasoline-release site in South Carolina, a proprietary form of  $\text{MgO}_2$  injected into the subsurface in a former underground storage tank (UST) area to increase dissolved oxygen (DO) levels did not elevate low (0 mg/L) DO levels nor decrease concentrations of benzene, toluene, or methyl tert-butyl ether (MTBE). In contrast,  $\text{MgO}_2$  injected less than 200 meters downgradient rapidly increased DO, and benzene, toluene, and MTBE concentrations decreased up to 87%. These different results following oxygen addition to an anoxic fuel-contaminated aquifer can be related to differences in ambient hydrologic conditions