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AMBIENT GROUNDWATER MONITORING AND ASSESSMENT

A Contamination Vulnerability Assessment for the Sacramento Area Groundwater Basin

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Executive Summary

The Ambient Groundwater Monitoring and Assessment (GAMA) program, sponsored by the California State Water Resources Control Board (SWRCB), aims to assess water quality and to predict relative susceptibility of groundwater resources to contamination throughout the state of California. In 2001 and 2002, Lawrence Livermore National Laboratory (LLNL) completed a vulnerability study of the groundwater basins in the Sacramento suburban area. The goal of the study was to provide a probabilistic assessment of the relative vulnerability of groundwater used for public water supply to contamination by surface sources. This assessment of relative contamination vulnerability was made based on the results of two types of analyses that are not routinely carried out at public water supply wells: ultra low-level measurement of volatile organic compounds (VOCs), and groundwater age dating (using the tritium-helium-3 method). These analyses provide observable parameters that help define the flow field of a groundwater basin, and indicate the degree of vertical connection between near-surface sources (or potential sources) of contamination, and deeper groundwater pumped at high capacity production wells.

Groundwater is an essential resource in the Sacramento suburban area where more than 300 wells supply up to 40% of the public drinking water supply for over 600,000 people. While the natural groundwater flow pattern is dominated by topographic flow in the west-southwesterly direction away from the Sierra Nevada, intense pumping in Sacramento and surrounding areas has resulted in a distinct groundwater level depression that extends well below sea-level east of the Sacramento River. Overdraft in the areas adjacent to the American River has altered the natural recharge pattern, and induced formation of losing reaches over a large part of the study area. A major result of this study shows the influence of American River recharge, from which all of the water in wells adjacent to the river is derived, in decreasing proportions in wells to the north, all the way to Interstate 80.

Stable isotopes of oxygen provide a useful parameter for delineating the flow field of the main groundwater basin in the Sacramento suburban area north of the American River. The oxygen isotope values ($\delta^{18}O$) delineate regions where groundwater is influenced by recharge of isotopically lighter (^{18}O depleted) American River water and other areas where natural recharge introduces isotopically heavier (^{18}O enriched) local water. Wells from the northern-most part of the Sacramento suburban area have an isotopic signature that is indicative of a local water source. The zone of influence of American River water extends from the areas adjacent to the river, where wells produce 100% recently recharged river water northward to Interstate 80. In contrast, the natural recharge of local water is evident in wells north of Interstate 80, and in a small number of wells that were tested south of the river, in the Florin area.

Tritium concentrations in groundwater over a wide region of the Sacramento suburban area are strikingly low, and indicate that a large volume of pre-modern (pre-1955 recharge) water is being produced from these drinking water wells. Only a small number of public supply wells (17 of 108, mainly relatively near the American River) have tritium concentrations that indicate the presence of a significant component of young or 'post-modern' groundwater. This result has major implications for groundwater management, since artificial recharge may not reach capture zones of production wells for long time periods.

Chloroform (or trichloromethane) was the most frequently detected VOC in wells from the study area. Seventy-five public supply wells (71% of PWS wells tested) had detections of chloroform above the reporting limit of 5 parts per trillion. The gasoline additive methyl *tert* butyl ether (MtBE) was detected

above the reporting limit in eighteen public supply wells, with a maximum concentration of only 53 ppt and a median value of only 10 ppt. Most significantly, tetrachloroethylene (PCE) was detected in 45 public supply wells (44%), albeit nearly always at extremely low concentrations. All of the PCE detections are well below the Maximum Contaminant Level (MCL), which is 5,000 ppt, and 32 of the 44 detections are below the public health goal (PHG) of 56 ppt. In fact, almost half of the detections (19) are between 5 and 20 ppt, a level not previously quantifiable by any laboratory. Twenty-seven public supply wells (or 26% of those tested), mainly from the northwest portion of the study area (north of Interstate 80, in Rio Linda and surrounding suburbs) had no detections of any of the VOCs analyzed. Another 25 public supply wells (for a total of 50%) had detections only of trihalomethanes. The analyte suite included dibromochloropropane (DBCP), benzene, toluene, ethylbenzene and xylene, but these were not detected above the reporting limit in any public supply well.

While a large fraction of drinking water wells have detections of VOCs, the very low levels observed are likely the result of considerable mixing and dilution, either in the well bore or by dispersion in the aquifers. The large volume of old groundwater observed in these wells is not likely to have carried advectively transported post-modern contaminants. The semi-confined aquifers that comprise the basin sediments likely allow limited vertical non-advective transport of VOCs from near surface sources, especially of solvents, which are more dense than water. In particular, the presence of PCE in wells where the tritium concentration is less than 1 picoCurie per liter indicates VOC transport via 'short-circuiting'. The source of the VOCs differs for the different compounds observed. MtBE is found in American and Sacramento River water at concentrations that are consistent with those observed in well water, when significant dilution with uncontaminated ambient groundwater is taken into account. In contrast, the frequent detections of PCE are not consistent with a river source, but rather are likely due to mobilization of numerous point sources from spills or leaks at dry cleaners or other businesses, or possibly, from leaky sewer lines that hold small amounts of PCE.

The dissolved noble gas concentrations observed in wells from the Sacramento area are useful for establishing the dominant recharge mechanism for groundwater in the basin. In particular, the dissolved 'excess air' concentrations observed in all of these samples are exceedingly low, and indicate minimal interaction with vadose zone gases during recharge. Low excess air concentrations are consistent with recharge that is dominated by infiltration of river water. The fact that very low excess air is observed even in wells where oxygen isotope ratios indicate the presence of locally-derived water, indicates that there is minimal vadose zone interaction and minimal fluctuation in the water table, even in areas away from the main rivers. In addition, dissolved noble gas concentrations allow calculation of groundwater recharge temperatures. Recharge temperatures in the Sacramento area show the same spatial pattern as oxygen isotopes, whereby wells close to the American River have low recharge temperatures of about 11 C, and recharge temperatures increase to an average of 18 C in wells to the north of Interstate 80. The low temperatures observed in wells near the American River reflect the average wintertime temperature of the river, while temperatures on the high end reflect the approximate mean annual air temperature for the Sacramento area. Therefore, a decreasing fraction of American River water in wells to the north is confirmed by the pattern in noble gas recharge temperatures. Wintertime recharge is likely, as flows are higher, and infiltration is more likely to take place along the upper banks, where dessication cracks occur and fine-grained sediments are absent.

In addition to public supply wells, this report includes results from 14 monitor wells adjacent to the American River on and near the California State University, Sacramento campus. Data from these wells

provide a more detailed picture of recharge along the American River, including water quality results for very recently recharged water and estimates of groundwater recharge rates. In wells screened at the shallowest depths (30 to 70 feet bgs), groundwater ages are less than one year, $\delta^{18}O$ values match river values, and MtBE concentrations closely match the river water concentration. A slurry wall, emplaced to prevent seepage under levees complicates the recharge pattern and results in significant spatial variability. Results from wells screened over deeper intervals have groundwater ages of 20 years or more, and very low MtBE concentrations. In one area, however, very young groundwater, with an MtBE concentration that closely matches that of the river, is observed at a depth of 200 ft.

Introduction

In response to concerns expressed by the California Legislature and the citizenry of the State of California, the State Water Resources Control Board (SWRCB), implemented a program to assess groundwater quality, and provide a predictive capability for identifying areas that are vulnerable to contamination. The program was initiated in response to concern over public supply well closures due to contamination by chemicals such as MtBE from gasoline, and solvents from industrial operations. As a result of this increased awareness regarding groundwater quality, the Supplemental Report of the 1999 Budget Act mandated the SWRCB to develop a comprehensive ambient groundwater-monitoring plan, and led to the initiation of the Ambient Groundwater Monitoring and Assessment (GAMA) Program. The primary objective of the GAMA Program is to assess the water quality and to predict the relative susceptibility to contamination of groundwater resources throughout the state of California. Under the GAMA program, scientists from Lawrence Livermore National Laboratory (LLNL) collaborate with the SWRCB, the U.S. Geological Survey, the California Department of Health Services (DHS), and the California Department of Water Resources (DWR) to implement the groundwater assessment program in cooperation with local water purveyors.

In 2001 and 2002, LLNL carried out this vulnerability study in the groundwater basin of Sacramento suburban area, located to the north of the American River and to the east of the Sacramento River. The goal of the study is to provide a probabilistic assessment of the relative vulnerability of groundwater used for the public water supply to contamination from surface sources. This assessment of relative contamination vulnerability is made based on the results of two types of analyses that are not routinely carried out at public water supply wells: ultra low-level measurement of volatile organic compounds (VOCs), and groundwater age dating (using the tritium-helium-3 method). In addition, stable oxygen isotope measurements help determine the recharge water source. Interpreted together, and in the context of existing water quality and hydrogeologic data, these observable parameters help define the flow field of a groundwater basin, and indicate the degree of vertical communication between near-surface sources (or potential sources) of contamination, and deeper groundwater pumped at high capacity production wells.

Vulnerability Assessment Tools

Groundwater Age-Dating Technique

Tritium (^3H) is a very low abundance (around 1 part in 10^{17} of total hydrogen), radioactive isotope of hydrogen with a half-life of 12.34 years. Natural tritium is produced in the earth's atmosphere by cosmic radiation. Atmospheric nuclear weapons testing in the 1950's and early 1960's released tritium to the atmosphere at levels several orders of magnitude above the background concentration (figure 1). This atmospheric tritium enters groundwater (as HTO, with one hydrogen atom as tritium) during recharge. Tritium concentration in groundwater is reported in units of picoCuries per liter, and has a regulatory limit (Maximum Contaminant Level or MCL) of 20,000 pCi/L. Its concentration in groundwater decreases by radioactive decay, dilution with non-tritiated groundwater, and dispersion. While the presence of tritium is an excellent indicator of water that recharged less than about 50 years ago, age dating groundwater using tritium alone results in large uncertainties due to spatial and temporal variation in the initial tritium at recharge. Measurement of both tritium and its daughter product helium-3 (^3He) allows calculation of the initial tritium present at the time of recharge (figure 2), and ages can be determined from the following relationship:

$$\text{Groundwater Age (years)} = -17.8 \times \ln\left(1 + {}^3He_{trit}/{}^3H\right)$$

The age measures the time since the water sample was last in contact with the atmosphere. The $^3He_{trit}$ indicated in the equation is the component of ^3He that is due to the decay of tritium. Methodologies have been developed for correcting for other sources of ^3He, such as the earth's atmosphere and potential small contributions from thorium and uranium decay (Aesbach-Hertig et al., 1999; Ekwurzel et al., 1994).

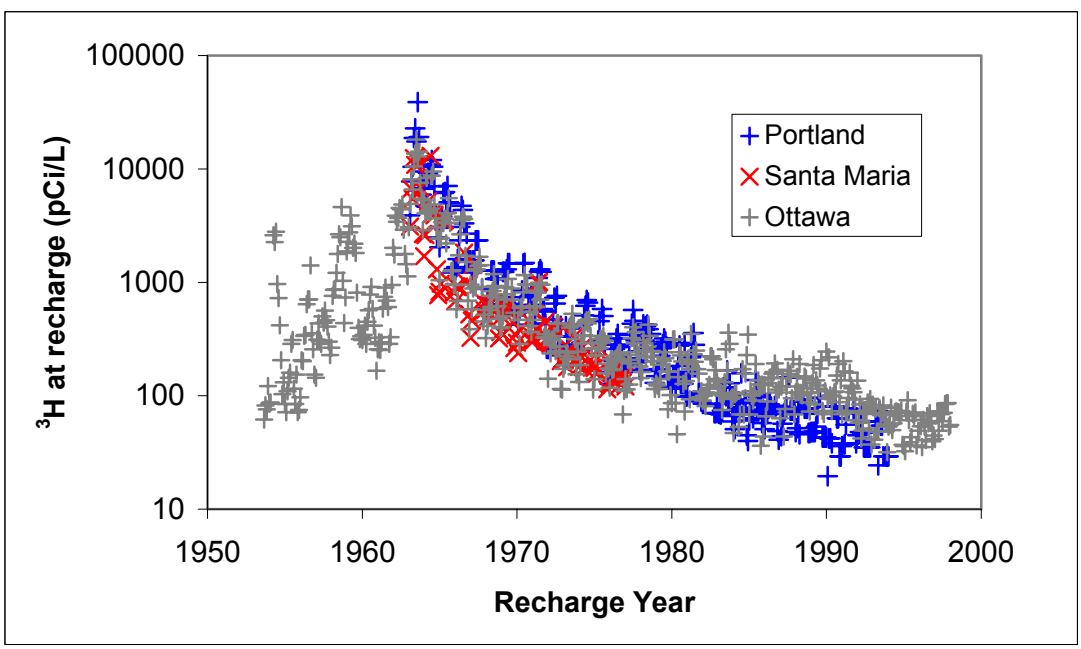

Figure 1. The tritium concentration measured in precipitation at three North American locations. Nuclear weapons testing introduced a large amount of tritium into the atmosphere in the 1960's, peaking in 1963.

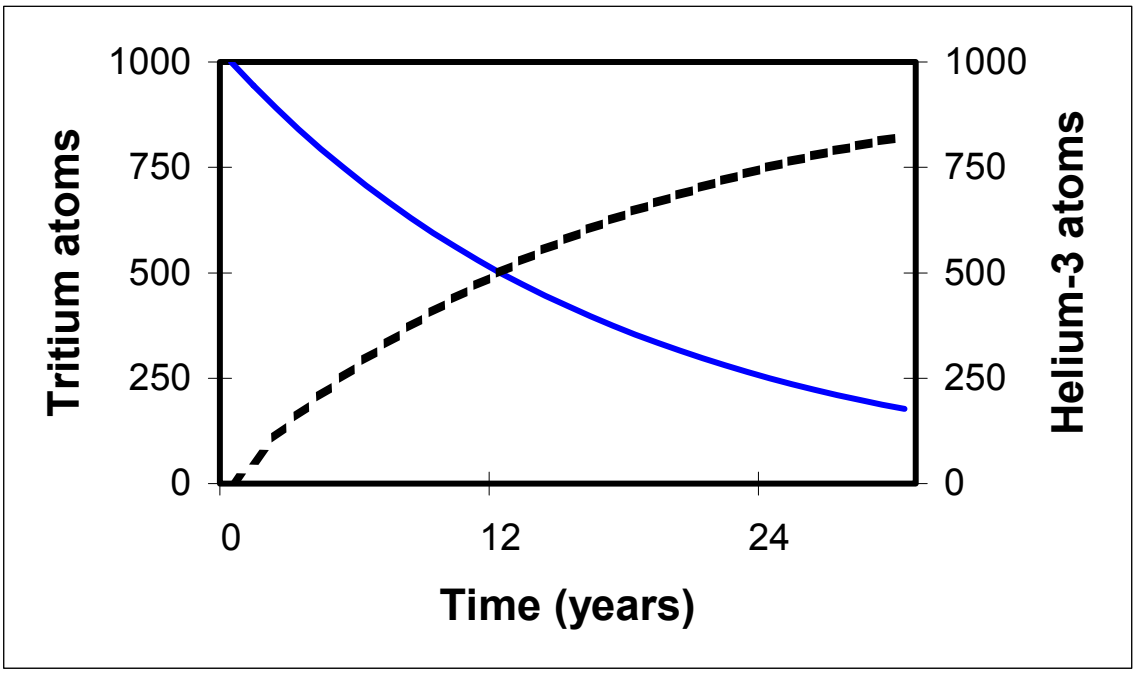

Figure 2. Solid line shows the decay of tritium, with a half-life of 12.34 years, while the dashed line shows the growth of the daughter product, ^{3}He. The sum of tritium and ^{3}He is the same at any time, and equal to the initial tritium value. This is the basis for the groundwater age-dating technique used in this study.

Well water samples are always a mixture of water molecules with an age distribution that may span a wide range. The reported groundwater age is the mean age of the mixed sample, and furthermore, is the age only of the portion of the water that contains measurable tritium. Groundwater age dating has been applied in several studies of basin-wide flow and transport (Poreda et al., 1988, Schlosser et al., 1988, Solomon et al., 1992, Ekwurzel et al., 1994, Szabo et al., 1996). The basic premise for using groundwater age to establish vulnerability is that young groundwater has been transported to a well capture zone relatively rapidly from the earth's surface. Most contaminants have been introduced in shallow zones, by human activity in the past 100 years, so younger groundwater is more likely to have intercepted contamination. On the other hand, old groundwater is likely to be isolated from the contaminating activities that are ubiquitous in modern urban environments.

Characteristics of Groundwater Derived From Dissolved Noble Gases

Fraction Pre-modern

A groundwater sample has an age distribution that is a result of groundwater mixing both during transport and in the well's borehole. Useful information about the groundwater age distribution in a well water sample comes from comparing a sample's measured tritium to the tritium expected in the original recharge water. This data analysis technique is illustrated on a plot of initial tritium versus calculated mean age (or recharge year; figure 3). The tritium that was present at the time of recharge is known from measurements of tritium in precipitation at several sites in North America. The calculated tritium-helium groundwater age is plotted along the x-axis position on figure 3, against the corresponding expected initial tritium value, on the y-axis. Water that recharged before about 1955 now contains extremely low levels of tritium. Samples that fall below the 'initial tritium' curve thus contain a fraction of water that

recharged before 1955 ('pre-modern'). In contrast, a groundwater sample for which the measured age gives a decay-corrected tritium value that falls on or near the curve, is not significantly diluted with a component of pre-1955 water. A coarse estimate of the fraction of pre-modern water that is drawn from a well comes from calculation of the difference between the measured tritium and the 'initial' tritium (figure 3). This technique can be complicated by: scatter in ^{3}H concentrations in precipitation, poor retention of ^{3}He in the vadose zone, and mixing of post-modern aged waters in the modern fraction, especially for waters with ages near the tritium bomb-pulse peak.

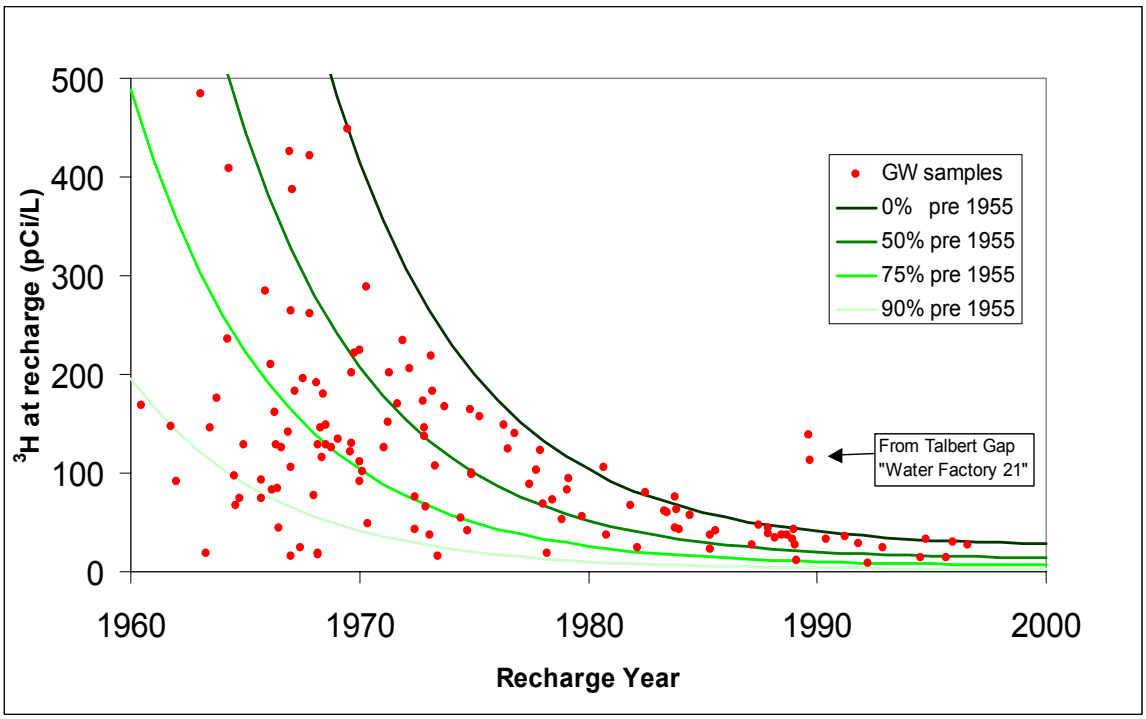

Figure 3. Curves show equal fractions of pre-modern water. The line labeled 0% is an approximation of the tritium in precipitation data from figure 1. Lines below approximate mixtures of pre-modern and post-modern water. Groundwater samples from southern California coastal basins are shown as points. Most samples have a large component of pre-modern groundwater.

Excess Air

During transport through the vadose zone, infiltrating water may entrain or trap air bubbles that subsequently dissolve in groundwater. Air bubbles may also become trapped in groundwater during fluctuations in the water table. This dissolved gas component is termed 'excess air' (Aesbach-Hertig et al., 2000, Holocher et al., 2002). The concentration of excess air provides valuable information about the recharge process, and is an important consideration during reduction of dissolved noble gas data to the calculated age (figure 4). For example, each measured ^{3}He concentration must be apportioned between the equilibrium solubility, excess air, and tritiogenic components. Excess air concentrations are derived from the measurement of excess Neon concentration because Neon can be assumed to derive solely from the atmosphere. Excess air is reported in units of cm^3 at standard temperature and pressure (STP) per gram of water.

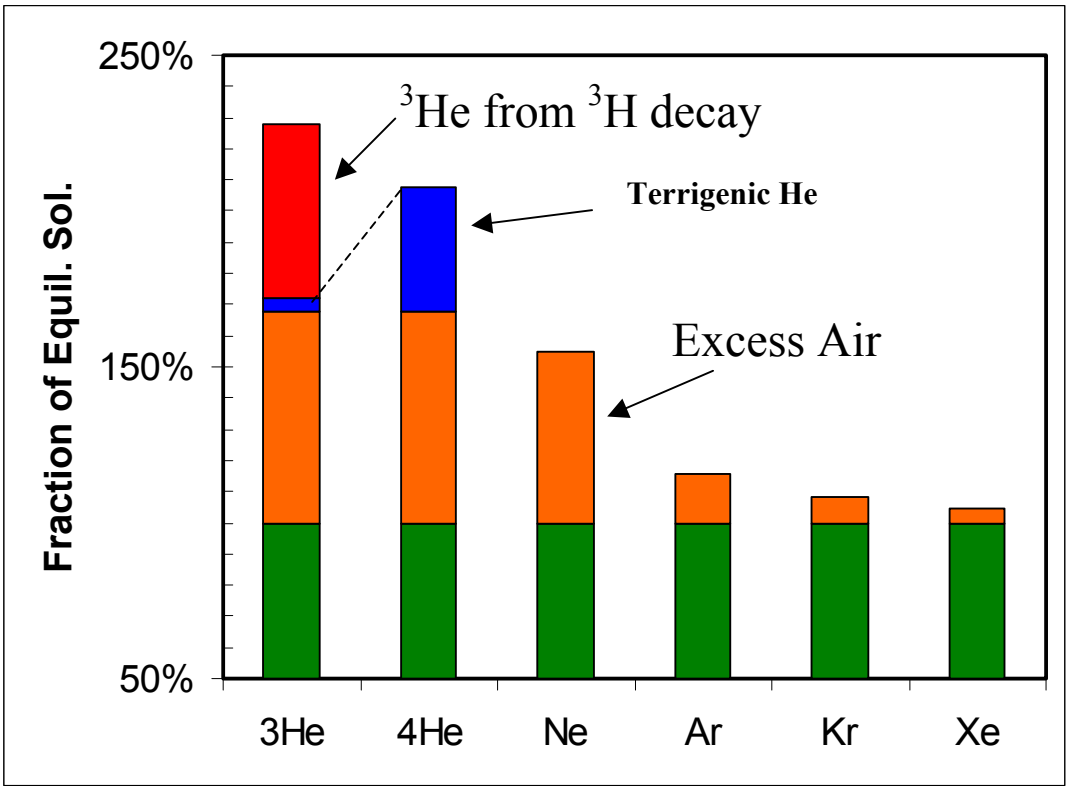

Figure 4. Graphical representation of the various dissolved noble gas components in a typical groundwater sample, relative to equilibrium solubility concentrations.

Radiogenic ^{4}Helium

The tritium-helium age dating method provides a mean age for the portion of groundwater that contains tritium (the post-modern or post-1955 portion). In many wells, a large component of pre-modern water is present, as determined by the fraction pre-modern (described above). A qualitative estimate of groundwater age for this old groundwater component comes from the in-growth of helium due to radioactive decay of uranium and thorium in crust. During the decay of naturally occurring uranium (^{238}U decaying to ^{206}Pb), alpha particles (which, after picking up electrons, become ^{4}He atoms) are emitted. Thus, ^{4}He accumulates significantly in groundwater on time scales of hundreds to thousands of years. The ^{4}He from U and Th decay in the earth's crust is termed 'radiogenic ^{4}He', and is expected to increase along a groundwater flow path. Precise age dating using ^{4}He is not possible because the accumulation rate depends on poorly known factors such as host rock U and Th concentrations and rock porosity (Solomon et al., 1996; Castro et al., 2000), but groundwater with a subsurface residence time greater than a few hundred years usually contains detectable radiogenic ^{4}He (Moran et al., 2002, Hudson et al., 2002). This technique has been applied in deep groundwater basins in France and in Sweden and has been compared with ^{14}Carbon dating of groundwater (Marty et al., 2003, Castro et al., 2000). Radiogenic ^{4}He has units of cm^3 (STP) per gram of water, and these concentrations are converted to an apparent "age" using an assumed, constant flux of ^{4}He from the earth's crust of 2×10^{-7} cm^3 STP cm^{-2} yr^{-1}.

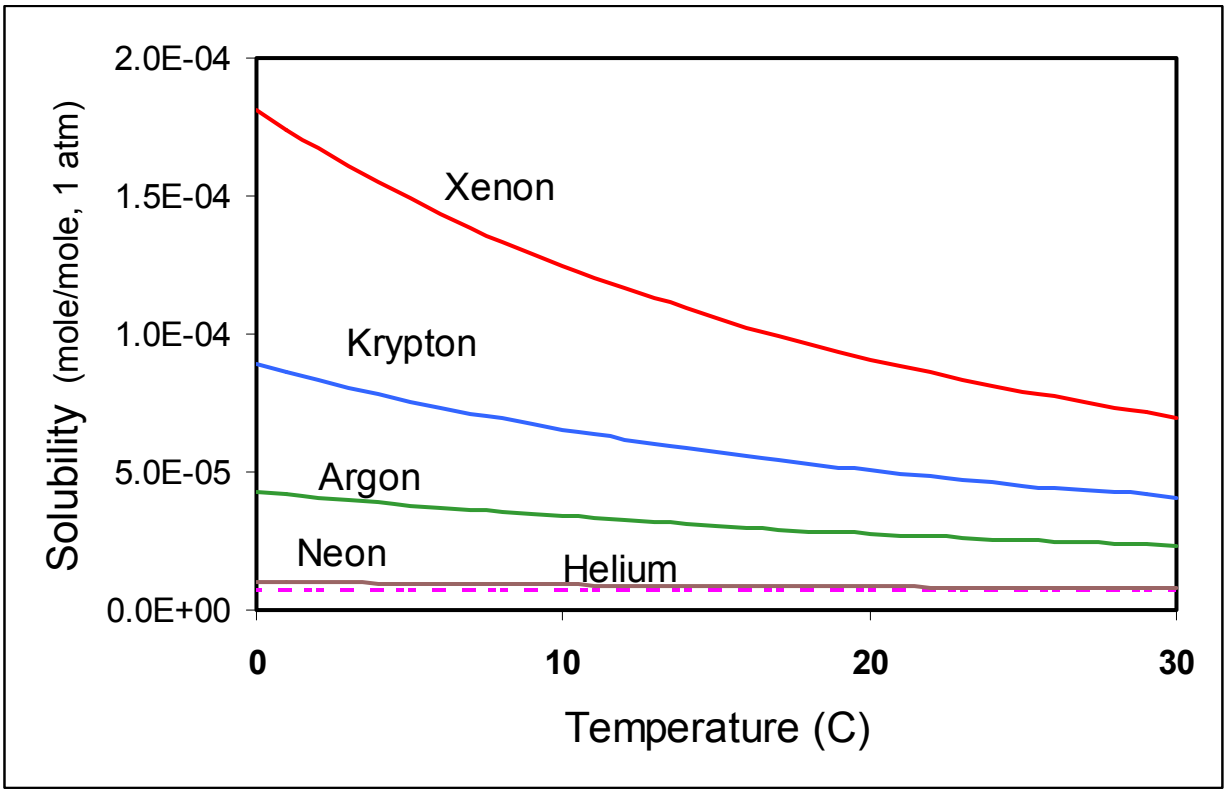

Figure 5. The solubility curves for the noble gases according to water temperature, showing the strongest temperature dependence for Xe. Noble gas recharge temperatures are calculated from these well-established curves.

Noble Gas Recharge Temperature

The solubilities of the noble gases in water vary as a function of temperature and pressure and are well known from theoretical and empirical studies (figure 5; Andrews, 1992). A robust estimate of the temperature at which recharge took place is determined by measuring the concentrations of all of the dissolved noble gases, and comparing the results to the solubility curves. The temperature determination is weighted by the dissolved xenon concentration since it is most strongly dependent upon temperature. Under natural conditions, the temperature of recharge is strongly dependent upon the altitude of recharge, and noble gas recharge temperatures have been used successfully to determine recharge elevation in mountainous regions (Manning and Solomon, 2003). Another application of this technique has been in studies of paleoclimate, in which groundwater recharged under significantly colder conditions is identified (Andrews and Lee, 1979, Aesbach-Hertig et al., 2002, Clark et al., 1997). In the intensively managed groundwater basins of the coastal plain in southern California, high noble gas recharge temperatures demarcate the region affected by artificial recharge. Variation in recharge temperature occurs because natural recharge in southern California takes place in cold, high elevation areas that surround the groundwater basin, while recharging water in low elevation artificial recharge facilities equilibrates at higher temperatures (Hudson et al., 2002).

Low-level VOCs as Environmental Tracers

Just as tritium provides a time marker for groundwater recharge, so can chemicals that have been widely used only in post-industrial times. The presence of volatile organic compounds such as gasoline compounds, organic solvents, and applied agricultural chemicals is an indication that the sampled water recharged since the onset of intense human development. In this study, these compounds are measured with a reporting limit of 5 parts per trillion – well below routine monitoring and regulatory limits. The basic properties, reporting, and regulatory limits of these compounds are given in Table 1 (Appendix B). This short list of compounds was chosen because they have the highest frequency of occurrence of the approximately 100 organic compounds in the DHS drinking water well database.

When examined at sub-part-per-billion concentrations, these VOCs serve as useful environmental tracers, since they have a near ubiquitous presence at low concentrations near the earth's surface due to common human activities. Their presence in groundwater is indicative of a component of post-industrial aged water. Thus, the interpretation of VOC detections in this study is not with regards to health or regulatory concerns, but rather as another tracer of recent groundwater recharge. And, since the number of years the different VOCs have been in common use differs – over 100 years for disinfection by-products, 50 to 60 years for heavy use of the solvents, and only 10 to 15 years for the gasoline additive MtBE, their presence or absence can be used to mark the time since recharge. Detection of these compounds in drinking water wells may also provide early warning of an approaching plume.

The potential sources for MtBE, BTEX, TCE, and PCE encompass activities that number in the thousands in the study area. Furthermore, previously existing facilities, that are no longer in operation, are perhaps more likely sources of VOC plumes than existing facilities. In addition to point source releases directly into groundwater, VOCs may be released into the air, surface water, or vadose zone. Subsequent transport to groundwater may take place by infiltration followed by advection, or by non-advective transport (e.g., a structurally compromised well casing). Numerous small, point sources can be mobilized by large-scale artificial recharge, as occurs in the forebay of the Los Angeles and Orange County Basins (Shelton et al., 2001). Furthermore, these compounds can have a dispersed source from damaged infrastructure such as leaking sewer pipes. At joints, or places where sewer lines turn or have low points, solvents may accumulate and subsequently leak into groundwater. PCE and TCE are more dense than water ('sinkers'), unlike MtBE and gasoline compounds (Table 1), which are less likely to be transported from the vadose zone to the saturated zone.

Several factors may be considered to explain spatial disparities in the occurrence of VOCs. They include population density (because the number of sources of VOCs generally increases with increasing population density), leaking underground fuel tank (LUFT) density (relevant for MtBE and BTEX compounds), the proximity of wells to sources, and the presence or absence of vertical transport pathways that allow near surface sources to reach deeper wells. These factors have been found, in some cases, to correlate with VOC detections in ambient groundwater in other suburban areas (Squillace et al., 1999; Squillace and Moran, 2000).

Stable Isotopes as Tracers of Recharge Source

The minor stable isotopes of water molecules ^{2}H (deuterium, denoted as *D*) and ^{18}O vary in precipitation as a function of temperature, elevation and latitude (Craig, 1961; Ingraham & Taylor, 1991). In California, extreme changes in elevation occur over relatively short distances. The net effect of isotopic

fractionation during evaporation and condensation is that surface water from mountain watersheds has a significantly lower abundance of ^{18}O and D than coastal water (figure 6). The abundance of these isotopes in groundwater samples provides a fingerprint of the origin of the source water.

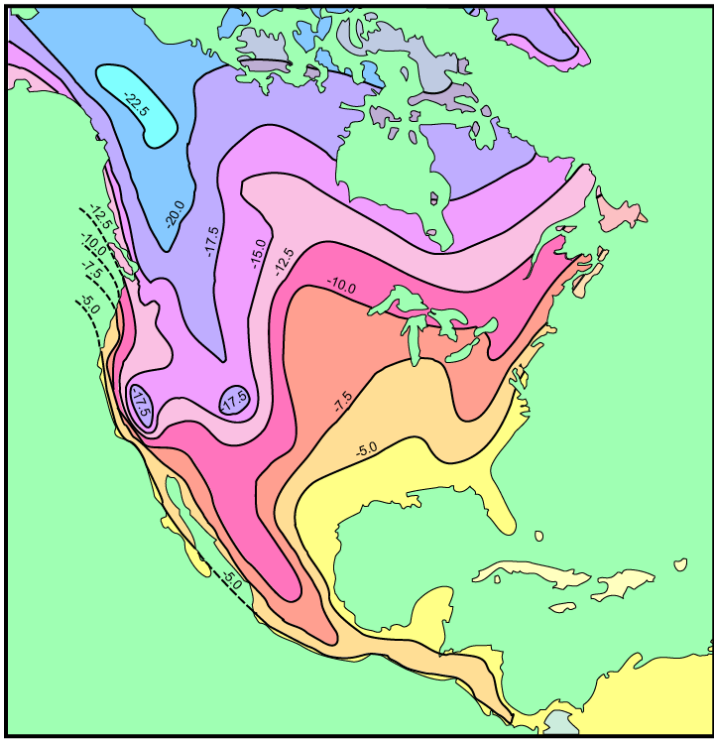

Figure 6. Contour map of $\delta^{18}O$ (SMOW) showing tight contours and lighter, depleted values at high elevation in California. (after Taylor, 1974)

Oxygen isotope ratios are reported in the standard delta (δ) notation as parts per thousand (per mil or ‰) variations relative to a reference material of known composition and defined by the following equation:

$$\delta_x = 1000 \frac{R_x - R_{std}}{R_{std}} \qquad (1)$$

where R_x is the $^{18}O/^{16}O$ ratio of the sample and R_{std} is the $^{18}O/^{16}O$ ratio of the standard. The conventional standard reference material for oxygen isotopes is Standard Mean Ocean Water (SMOW; Craig, 1961). Using the delta notation, $\delta^{18}O$ in precipitation varies from approximately -4$^{o}/_{oo}$ along the Pacific coast to -15$^{o}/_{oo}$ in the Sierra Nevada mountains. Imported water used to supplement water supplies in areas of high water demand nearly always comes from colder and/or higher elevation sources, and thus has a distinctly lighter $\delta^{18}O$ signature than local water from within the water-poor watershed. Oxygen isotopes in groundwater can thus provide a signature that identifies the source water location.

Groundwater Basin Characteristics

In this section, the hydrogeologic setting of the Sacramento suburban area, which lies in the North American Subbasin of the Sacramento Valley Groundwater Basin is briefly described, and results from vulnerability parameters are interpreted in the context of known groundwater flow patterns in this subbasin. A small number of wells from the South American Subbasin are also included in the study.

North American Subbasin

The North American subbasin lies in the eastern central portion of the Sacramento Groundwater Basin – one of the largest and most productive groundwater basins in the state. The water-bearing materials of the subbasin are dominated by unconsolidated continental deposits of Late Tertiary and Quaternary age. An upper aquifer system, comprising alluvial flood basin and stream channel deposits, occurs over the top 100 feet in areas along and adjacent to the Sacramento and American Rivers. Sand and gravel zones, along with dredger tailings that occur sporadically along the American River are highly permeable and yield significant quantities of water to wells. Older alluvium, deposited during Pliocene and Pleistocene times and occurring over the area between the Sierra foothills and the valley axis, consists of loosely to moderately compacted sand, silt and gravel. Permeability varies considerably in these alluvial deposits, which occupy the upper 200 to 300 feet of the aquifer system (DWR, 2003). Underlying the alluvial formations are Miocene/Pliocene volcanics of the Mehrten Formation, which is composed of intervals of "black sands", stream gravels, silt, and clay, interbedded with intervals of dense tuff breccia. While sand and gravel intervals are highly permeable and productive, tuff breccia intervals act as confining layers. The thickness of this unit varies between 200 and 1,200 feet.

Groundwater levels in Sacramento County north of the American River have generally decreased, with many wells declining at a rate of one and a half feet per year in the center of the basin for the last 50 years through the late 1990s, but have recently stabilized largely due to the recent availability of surface water deliveries into the central part of the basin. Historically, the central and northern parts of the basin were fully reliant on groundwater for supply (DWRSGA, Bulletin 1182003). However, wells in the city of Sacramento, which have historically had access to surface water and are more adjacent to surface water channels, have fluctuated less than 10 feet overall since the mid-1970's. Natural recharge to the subbasin is estimated at 83,800 acre-ft and applied water recharge at 29,800 acre-ft. Artificial recharge does not contribute significantly to total recharge, although several new artificial recharge projects are currently underway. Suburban extraction was approximately 109,900 acre-ft and agricultural extraction was 289,100 in the subbasin in 1990. A groundwater model developed for Sacramento County (Montgomery Watson, 1993), which represented an average yearly budget for 1970 to 1995 used a total recharge of 257,000 acre-ft, a net subsurface outflow of 29,676 af, suburban extraction of 68,058 af, and agricultural extraction of 162,954 af. Natural recharge in this part of the Sacramento Valley is a combination of subsurface flow that originates in the Sierra Nevada and foothills, and infiltration of local precipitation. Rainfall averages 18 inches per year in the Sacramento area. Runoff occurs throughout the basin, and sources of non-natural uncontrolled recharge include leakage from pipelines, seepage through the boundaries of the groundwater basin, and net irrigation return flows. The Sacramento and American Rivers are major, perennial rivers that create a groundwater divide in the shallow subsurface. However, there is interaction between groundwater of adjacent subbasins at greater depths (DWR, 2003). The

natural recharge pattern, in which significant reaches of the major rivers were likely gaining streams, has been altered by large scale pumping, resulting in increasingly longer losing reaches.

Groundwater management in the basin is under direction of the Sacramento Groundwater Authority (SGA), a joint powers authority responsible for managing the regional groundwater basin underlying Sacramento County north of the American River. A feasibility report for establishing a program of conjunctive use in the North American subbasin was published by DWR in 1997, and some projects that involve subsurface storage of excess wintertime surface flows are underway, mainly to the north of the study area (Tim Parker, DWR, personal communication, 2003). Groundwater quality in the study area is generally good, although some localized contamination is present. Three sites with significant groundwater contamination issues are the former McClellan Air Force Base, United Pacific Roseville Rail Yard, and the Aerojet Superfund Site. The Aerojet site is south of the American River, but a contaminant plume (including PCE and TCE) extends north under the American River into the North American subbasin (Montgomery Watson, 2000). Many smaller areas of contamination exist throughout the basin. The Regional Water Quality Control Board for Region 5 lists 120 Spills, Leaks, Investigations, Cleanup (SLIC) sites in Sacramento County for 2001, 25 of which have PCE identified as a constituent of concern. Geotracker (the SWRCB on-line database for tracking MtBE/LUFT sites) lists 786 LUFT sites in the city of Sacramento, 297 of which are open. However, according to the DHS database, only 6 public water supply wells had detections of VOCs above MCLs from 1994 through 2000 and only 2 have had MtBE concentrations above the detection limit for reporting for Title 22 water (5 ppb). While large plumes from the superfund sites and military facilities are relatively well characterized, numerous leaks from smaller sources (e.g., dry cleaning facilities and sewers) are largely unmapped.

Groundwater is a Crucial Resource

Population centers in the study area include the city of Sacramento, Rio Linda, Orangevale, and Florin- all in Sacramento County. Groundwater provides over 40% of the public supply to over 600,000 people. One hundred and eight of the approximately 300 'active' (DHS Title 22 definition) public supply wells in the study area were sampled for this study (figure 7). Two private retailers and four public agencies participated in the CAS study. In addition, 14 monitor wells on and near the CSUS campus, adjacent to the American River, were sampled for the CAS suite of analytes. Surface waters from the American and Sacramento Rivers were also sampled and analyzed for oxygen isotopes and low level VOCs. The reliance on groundwater, the planned increase in conjunctive use projects, and the large number of contamination sources present were factors in choosing this area as among the first where the vulnerability assessment has been carried out.

Sampling and Analysis Procedures

LLNL personnel collected well water samples from 108 public water supply wells in the Sacramento suburban area, with the assistance of well owners, during the fall and winter of 2001/2002 (figure 7). In addition, DWR and CSUS personnel collected samples from 14 monitor wells using a gas-powered generator and submersible pump. Each sample was collected directly at the sampling port, prior to any treatment, during well operation. Collection of 'transfer' and trip blanks for low level VOC quality assurance is described in Appendix A. The sampling procedure for dissolved noble gases, which involves sealing water in a copper tube without exposure to the atmosphere, is also described in Appendix A.

Four different analyses are performed on each well water sample: 1) A set of VOCs (shown in Table 1) is measured using purge and trap gas chromatography-mass spectrometry, with a reporting limit of 5 parts per trillion. 2) The $^{16}O/^{18}O$ ratio is analyzed by stable isotope mass spectrometry. 3) The concentration of tritium is measured by the ^{3}Helium-ingrowth method (Clark et al., 1976, Surano et al., 1992, Beyerle et al., 2000). 4) The ratio of $^{3}He/^{4}He$ and the concentrations of all of the dissolved noble gases are measured by noble gas mass spectrometry. The tritium and noble gas analyses are used together to calculate the groundwater age, and the temperature at which recharge took place is determined from the noble gas concentrations. A summary of analytical methods is given in Appendix A.

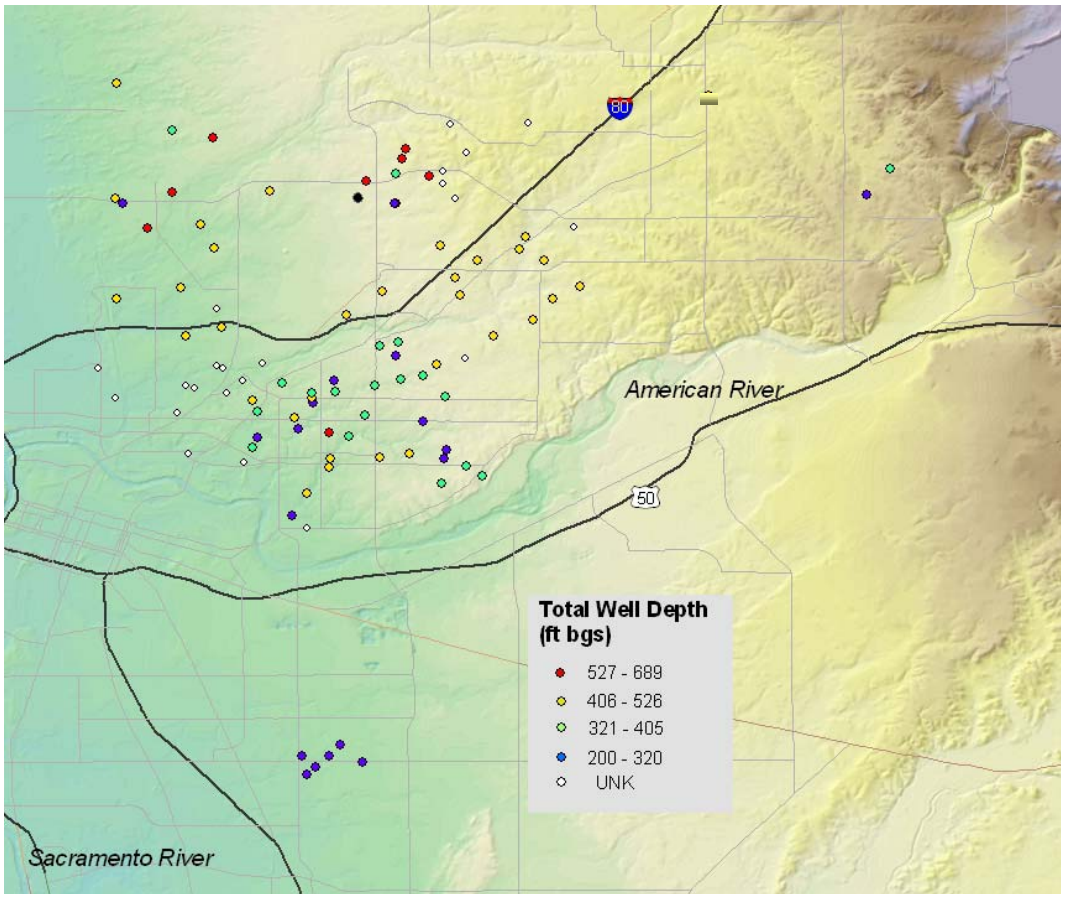

Figure 7. Sample location map, showing the 108 active drinking water wells included in this study. Each point represents a public water supply well, or in some cases, multiple, closely spaced wells that were sampled for the vulnerability assessment.

Results

Analytical results for the Sacramento suburban area wells are shown in figures 8-21. Uncertainties given in Appendix A are analytical errors only – uncertainty in the age estimate is discussed below. All results are fully quantitative, as described in Appendix A. Three compounds - MtBE, o-Xylene, and toluene, were detected in VOC transfer blanks over the course of sampling. The likely source of MtBE is transfer from the atmosphere during collection or storage, while the likely source of toluene and xylene is leaching of the rubber septum in the cap of the Volatile Organic Analysis (VOA) vial. For well water samples that had detections of a VOC compound, that were collected on a day when any transfer blank also had a detection, the results were screened at the value of the highest concentration measured in a sample or blank that day. This raised the reporting limit above 5 ppt for 11 MtBE results (maximum 15 ppt), 2 o-

xylene results (maximum 25 ppt), and 68 toluene results (maximum 110 ppt). The observed detections in transfer blanks at public supply wells demonstrate the extreme sensitivity of the analytical method used for VOC determinations, and highlight the advantage of carrying out the sampling at well-maintained, high capacity drinking water wells with dedicated pumps.

In the monitor well sampling campaign, a submersible pump and gasoline-powered generator were used to collect samples. An 'equipment' blank was collected by drawing several tens of liters of CSUS laboratory de-ionized water through the submersible pump. All of the VOCs analyzed (except DBCP, 1,1,1 TCA, PCE, and TCE) were detected in the equipment blank. The trihalomethanes are likely from the laboratory water, while MtBE and the BTEX compounds are likely present due to transfer from the generator exhaust to the sample during sample collection. While the equipment blank thus had detections of several VOCs, the transfer blanks (LLNL-supplied ultra-clean water poured over into a clean VOA in the vicinity of the wells to be sampled), as well as a trip blank (LLNL-supplied ultra-clean water in a VOA that travels with samplers but is unopened) had no VOC detections. The extraction well on the CSUS campus has a dedicated pump and was the only well water sample in which MtBE was not detected. All other monitor well results were screened at a higher reporting limit and with a greater uncertainty than the 5 ppt +/- 1 ppt (2 sigma) reporting limit/uncertainty applied at drinking water wells. Results are shown in figure 23 and Table 2 (Appendix B). Only MtBE results are used in the interpretation section (below).

Discussion of VOC Occurrence

While One Quarter of the Wells had no VOC detections, Occurrence of Low-level PCE is Widespread

The distribution of VOCs in the public water supply (PWS) wells is shown in Figures 8-11. Compounds that were monitored and had no detections above the reporting limit include benzene, ethylbenzene, toluene, xylene, and the volatile pesticide 1,2dibromo-3,chloropropane. Twenty-seven wells (26% of those tested) delivered raw water that was below the reporting limit for all the compounds monitored. Twenty-five more public supply wells (for a total of 50%) had positive detections of trihalomethanes (THMs) only, and were below the reporting limit for all the other compounds analyzed. Wells that are completely free of VOCs occur almost exclusively in the northern part of the subbasin, especially in the Rio Linda area. Seventy-five public supply wells had detections of chloroform, the most abundant of the THMs.

Nineteen wells had low level detections above the reporting limit of MtBE, with a maximum of only 59 ppt (figure 8). Twenty-two wells (all PWS) had low level detections above the reporting limit of the solvent trichloroethylene (TCE), four of which were greater than 100 ppt, with a maximum concentration of 940 ppt. Most significantly, 45 wells (44% of those tested) had PCE detections, with a maximum concentration of 3000 ppt (figure 9). The two PCE detections above 1000 ppt (1 ppb) were from wells where the occurrence of PCE was previously known and reported to DHS. However, most detections were at concentrations more than two orders of magnitude below regulatory limits. In fact, thirty-two of the detections were less than 57 ppt (the public health goal; PHG), and nineteen were less than 20 ppt, a level not previously quantifiable, even by specialized research analytical laboratories. While 10 wells had concentrations between 100 and 3000 ppt, none exceeded the state and federal maximum contaminant

level (MCL) of 5 µg/L (5000 ppt) for drinking water (U.S. Environmental Protection Agency, 1996). It should be emphasized that this study sampled raw water, and reported concentrations do not represent the concentrations entering the drinking water distribution system. Delivered water is treated, and may be blended with surface water or with water from other PWS wells.

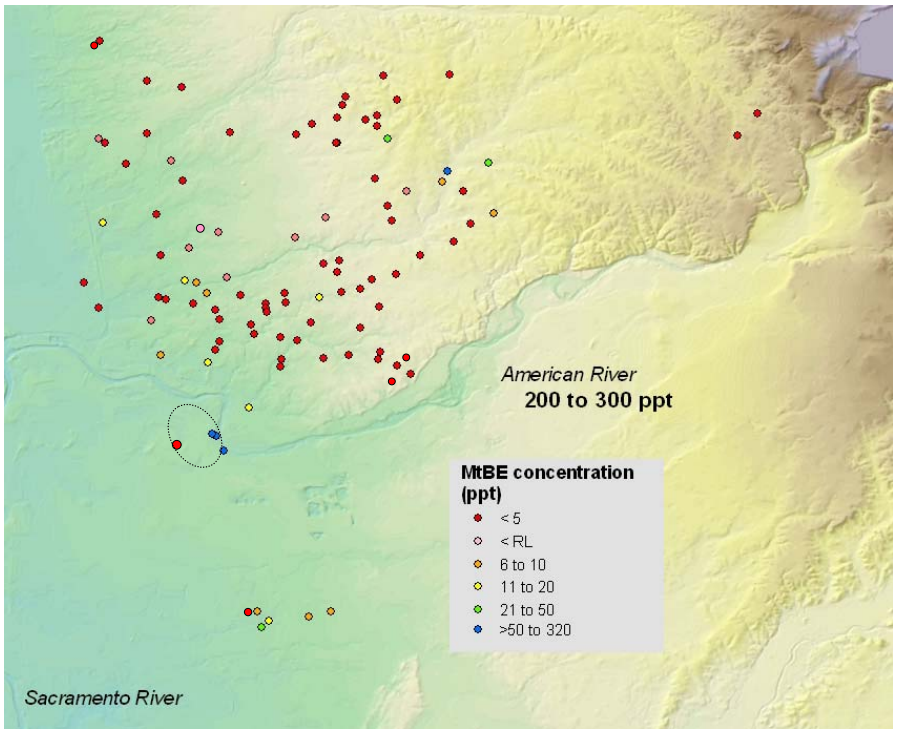

Figure 8. MtBE is observed in monitor wells near the American River, and at very low levels in a small number of wells scattered throughout the study area. (Nested monitor wells are shown in dashed oval and are not included in VOC statistics in text.)

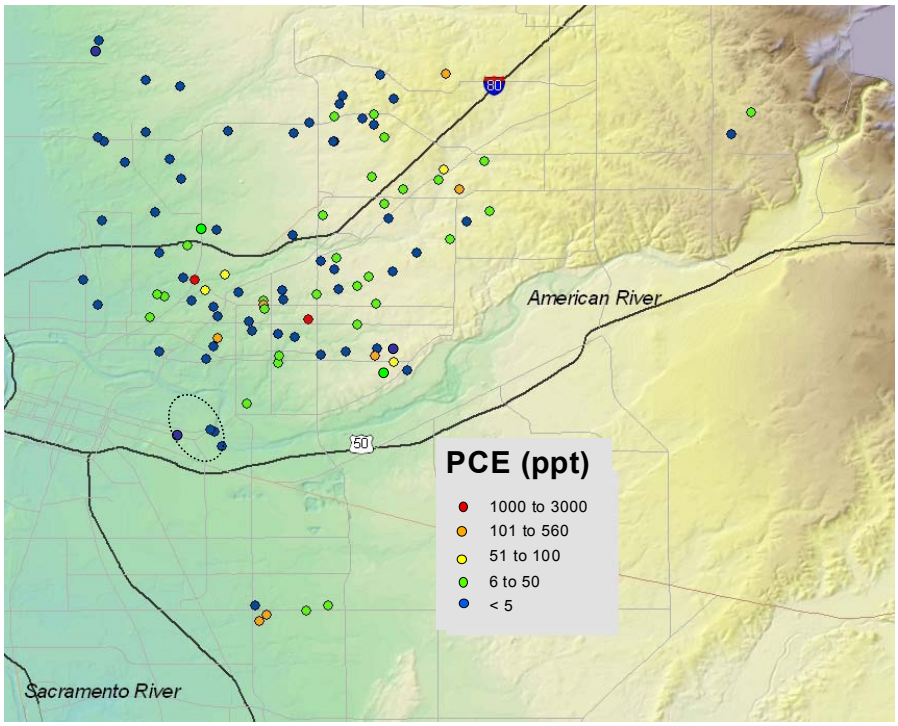

Figure 9. Tetrachloroethylene (or perchloroethylene; PCE) occurs in nearly half of the public supply wells in the Sacramento area, but nearly always at levels 2 orders of magnitude below the regulatory limit of 5000 ppt (5 ppb).

THMs Occur More Frequently than Other VOCs

THMs are by-products of the disinfection of drinking water. The source of low-level THMs can be advective transport of 'recycled' (previously disinfected) treated water, or residual from water treatment at or near the wellhead (figure 10). At some of the public supply wells in the Sacramento suburban area, groundwater is chlorinated or chloraminated at the well site (sometimes just downstream from the sampling port), and a small amount of back-flushing may occur at valves that separate raw and treated water. Also, during pump maintenance and well development, pump parts and well casing may be treated in order to disinfect the well. These activities allow for the possibility that THMs are present as residuals, rather than from advective transport of treated surface water to the well capture zone. In 25 wells where chloroform was detected, another THM was also detected (most frequently bromodichloromethane). Furthermore, the three other THMs analyzed, viz., bromodichloromethane, chlorodibromomethane, and bromoform, are accompanied by chloroform in every well where they were detected. In those wells, THM occurrence may not be dictated by transport in aquifers, but rather by operating conditions at the wellhead.

The American and Sacramento Rivers have low-level chlorofrom detections (46 ppt and 1400 ppt respectively in December, 2001), and river water may be a source of chloroform in wells with a significant component of river water. In that case, the THM is likely present due to advective transport of young water containing THMs. This is likely the case for the detections of chloroform in the monitor wells along the Sacramento River, as well as for wells near the river, in the area where tritium concentrations and groundwater ages show a component of recently recharged groundwater (discussed below).

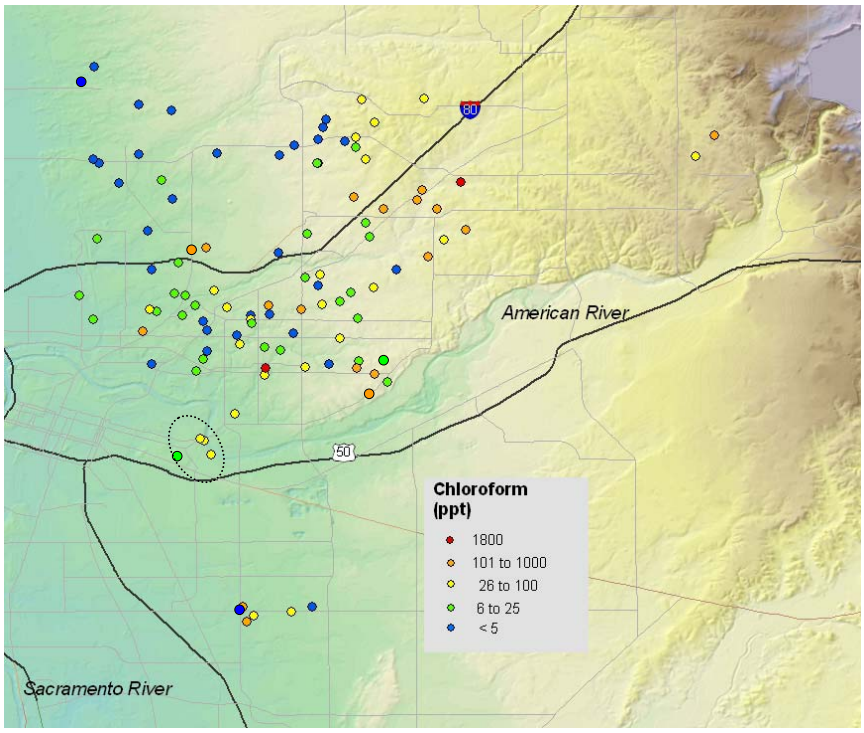

Figure 10. Occurrence of chloroform (trichloromethane) in wells from the Sacramento area. Occurrence is related to either operating conditions at wellheads (as residual from on-site disinfection) or to the presence of advectively transported, previously treated water. American and Sacramento River water may also be a source of low level chloroform to groundwater.

The American River is a Source of MtBE to Groundwater

California surface and meteoric waters contain MtBE due to equilibrium solubility with MtBE in the atmosphere, at concentrations of 50 to 1000 ppt (Ekwurzel et al., 2001). In addition, recreational boating on upstream reservoirs contributes MtBE to the American Sacramento Rivers, especially during summer months. Since MtBE has been in heavy use beginning only 10 to 15 years ago, this non-point source MtBE provides a time marker, indicating a component of groundwater that recharged less than 15 years ago. The very low concentrations measured, and lack of BTEX co-contaminants suggest that this non-point source component explains the MtBE detected in all of the wells where MtBE was found in the study area (figure 8). These 18 wells therefore likely have a component of water that recharged in the last decade or so. This modern water 'signal' is likely to be diluted to very low levels because of the radial capture zone and high degree of dilution characteristic of long-screened production wells (Einarson and Mackay, 2001). While contributions of MtBE from LUFTs cannot be ruled out at individual wells, these data do not support the idea of widespread contamination to public supply wells from LUFTs. Because most of the water drawn from these wells recharged greater than fifty years ago, and because MtBE is not likely to be transported non-advectively, the lack of MtBE detections in most of these wells is expected.

VOC Co-occurrence Gives Insight into Sources

The types of VOCs that co-occur at wells with multiple VOC detections offer clues to their sources and to their mode of transport to well capture zones (figure 11). For example, of the 75 wells with chloroform detections, 52 have detections of a solvent or another THM or of both a solvent and another THM. Both PCE and/or TCE and another THM are found in 17 wells where chloroform was also detected, while PCE and/or TCE occurs in 27 wells where chloroform was detected, and another THM occurs in 8 wells with chloroform. Occurrences of chloroform without other THMs, at wells where PCE and/or TCE were detected (which occurs in 27 wells, as noted above), could be evidence for a chloroform source other than as a disinfection by product. This combination of chloroform and solvent occurrence is observed less frequently in areas previously studied using ultra low-level methods (Moran et al., 2002, Moran et al., 2004) than it is in the Sacramento area. Chloroform is used in the manufacture of fluorocarbons for refrigerants, propellants, and plastics, as an industrial solvent, and in industrial dry cleaning. These potential industrial sources are likely for the chloroform occurrences in the wells where other solvents are observed, but other disinfection by-products are absent.

Co-occurrence of MtBE and other VOCs offers insight into the transport mechanism for VOCs to deep wells, since MtBE was introduced into the environment more recently than the other VOCs analyzed. At all but 5 of the 18 wells where MtBE was detected, PCE was also found. MtBE is also likely to co-occur with chloroform (chloroform was detected in all but one well where MtBE was detected). Furthermore, chloroform is found at relatively high concentrations at the three wells where the MtBE concentration is greater than 20 ppt. All three compounds occur together in 10 wells. Because the presence of MtBE indicates a component (however small) of water that has recharged in the last decade or so, the contaminants present in these wells may have been transported to the capture zone in the recently recharged component. Although this pattern of VOCs co-occurs infrequently in the Sacramento area, it is the dominant pattern in the major coastal basins studied previously using low level methods (Shelton et al., 2000; Moran et al., 2004).

PCE was detected in all but four of the 22 wells where TCE was detected, usually at a higher concentration than TCE. TCE can occur as a breakdown product of PCE, or in its originally-introduced form. The solvent stabilizer 1,4 dioxane (identified at a screening level of greater than 200 ppt) was detected in three wells, all of which have relatively high concentrations of PCE (figure 11). Two of these three wells also have relatively high concentrations of both TCE and MtBE. The co-occurrences of 1,4 dioxane and PCE/TCE suggest that these are areas affected by industrial solvent releases rather than dry cleaning sources. When multiple classes of VOCs (gasoline, solvent, disinfection by-product) are detected in a single well, it suggests that the well is in an area where vertical transport is greater than at surrounding wells. Groundwater ages and tritium concentrations support this conclusion since the affected wells have somewhat younger ages and higher tritium concentrations than wells in the nearby area (see discussion below). Two of the wells are in the upstream area of Arcade Creek, which has multiple lines of evidence for enhanced vertical transport of water and contaminants.

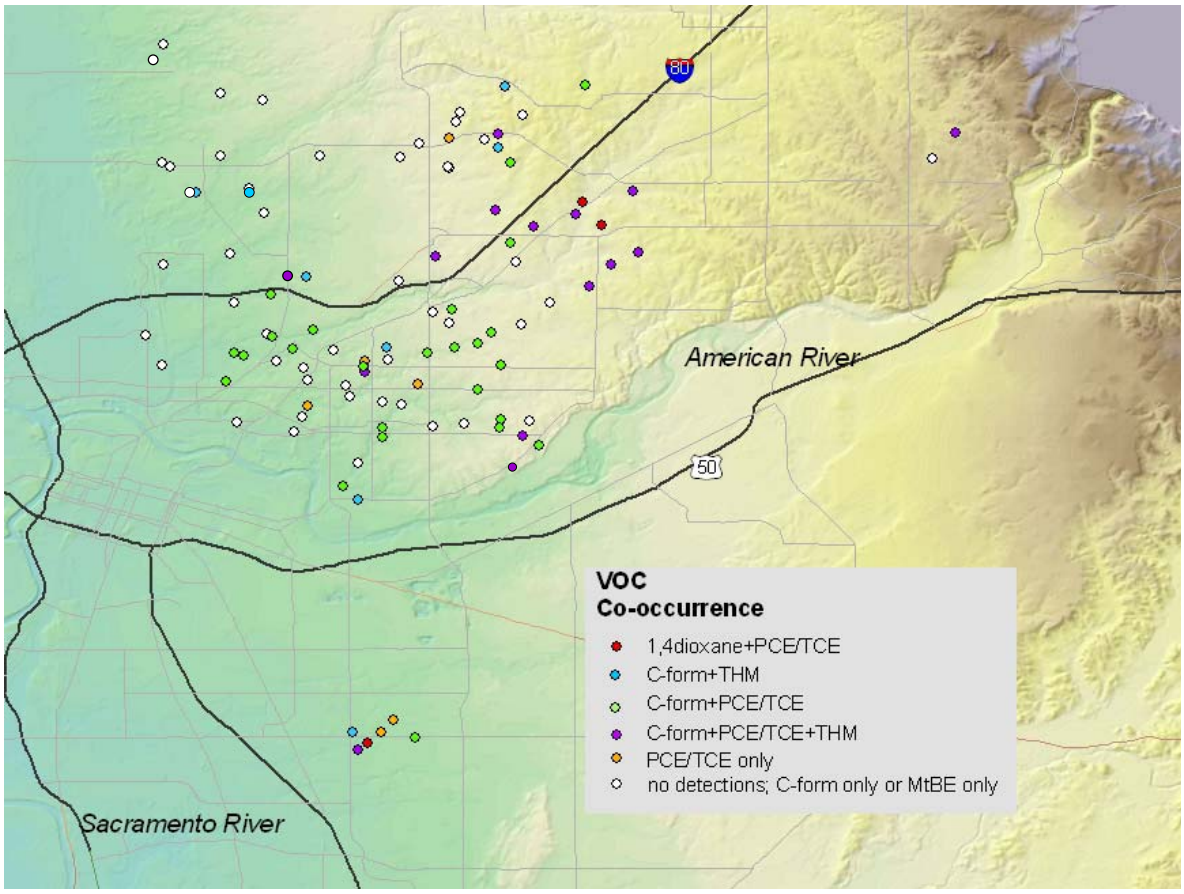

Figure 11. VOCs are grouped and co-occurrence is compared in order to gain insight into sources and transport properties. In the legend, PCE/TCE means PCE and/or TCE was detected; C-form stands for chloroform and THM indicates a trihalomethane in addition to chloroform was detected. See text for interpretation of co-occurrence.

Discussion of Isotopic and Groundwater Age Results

Isotopic tracers indicate river water recharge and pre-modern groundwater

The most useful isotopic tracers for determining water source and groundwater age in this groundwater basin are stable isotopes of the water molecule (viz. $\delta^{18}O$), and tritium concentrations. As seen in figure 12, $\delta^{18}O$ values recorded in wells from Sacramento range from –11.5 per mil in wells nearest the American River to -7 per mil in the northern-most group of wells, in the Rio Linda area. The relatively large range observed in this area is due to the presence water from two disparate sources, which in turn is a result of the subbasin's geographic location in the large, low-lying Central valley, adjacent to the foothills and mountains of the Sierra Nevada. $\delta^{18}O$ values in the range -7 to -8 are expected for locally-derived water from this part of the Central Valley (Kendall and Coplen, 2001). Criss and Davisson (1996) report a volume-weighted average of -7.5 per mil for precipitation in the Sacramento area. In contrast, water in the major rivers that drain the Sierra Nevada is derived mainly from snowmelt that is formed at a higher elevation and colder temperature. Table 3 (Appendix B) gives $\delta^{18}O$ values for the major Central Valley rivers, measured over the last few years at LLNL. These values are all significantly isotopically depleted in upstream as well as downstream reaches, year-round, because most of the water is from high elevation runoff. The large contrast in the $\delta^{18}O$ values of locally-derived versus river water sources (especially given the analytical uncertainty of 0.1 per mil), thus allows the possibility of tracing river water recharge in groundwater.

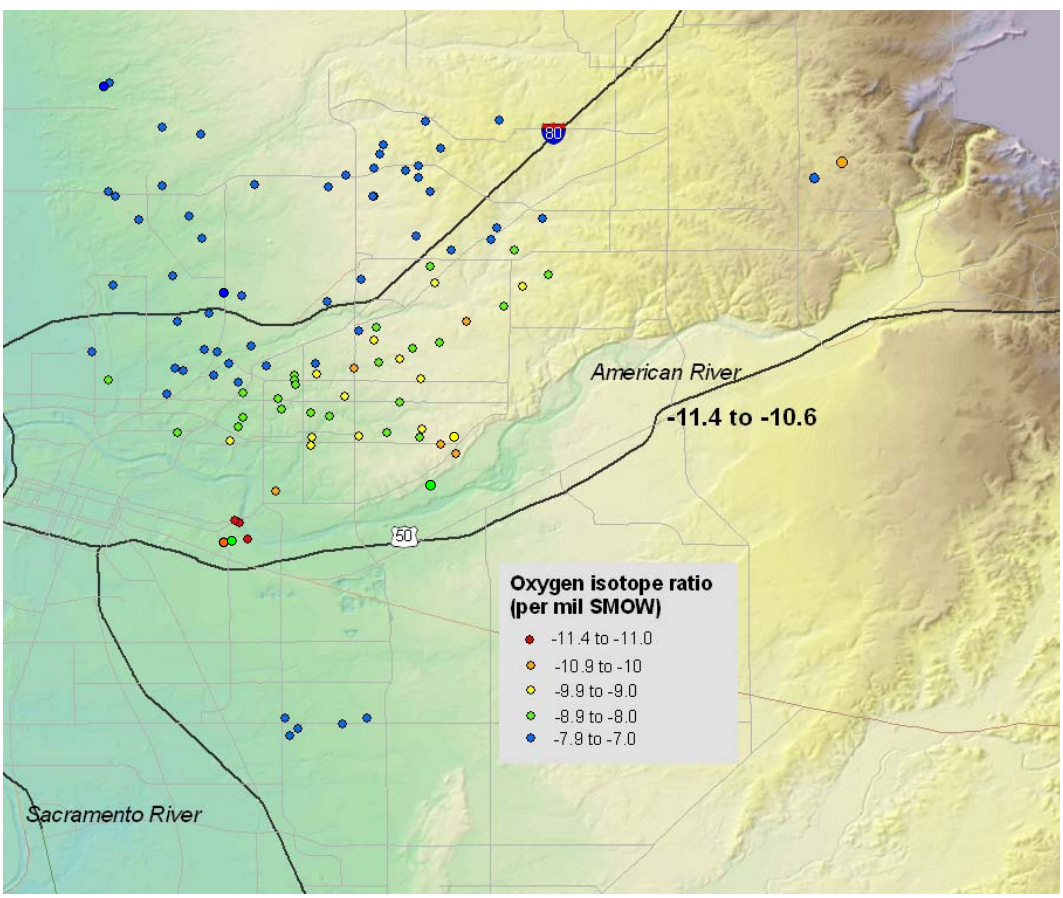

Figure 12. The pattern in $\delta^{18}O$ shows the influence of American River recharge on wells between the river and Highway 80. A lighter oxygen isotope signature is observed in the rivers draining the Sierra Nevada because the water is derived at a colder temperature (higher elevation). Local precipitation in the Sacramento area has a $\delta^{18}O$ value that averages approximately –7.5‰.

Stable Isotopes Mark the Zone of Influence of American River Water

The pattern observed is that wells closest to the American River have $\delta^{18}O$ values that closely match the values recorded for river water. Shallow monitor wells adjacent to the riverbanks are nearly exact matches (figure 23), while production wells within a few miles of the river are significantly depleted. $\delta^{18}O$ values steadily become more enriched in wells further from the river (figure 12). Using representative end member values of -11 for the American River and -7.5 for 'local recharge' water, one can calculate the approximate fraction of American River water produced at the sampled wells (figure 13). While wells within roughly 3 miles of the river produce greater than 80% river water, the proportion of river water quickly decreases to less than 50% in many wells just 6 or more miles from the river. Long losing reaches along the American River may be induced by the large-scale pumping that has resulted in the major depression to the north of the river. Wells with $\delta^{18}O$ values heavier than about -7.9 are likely producing water that recharged within the low-lying region, albeit more than several decades ago.

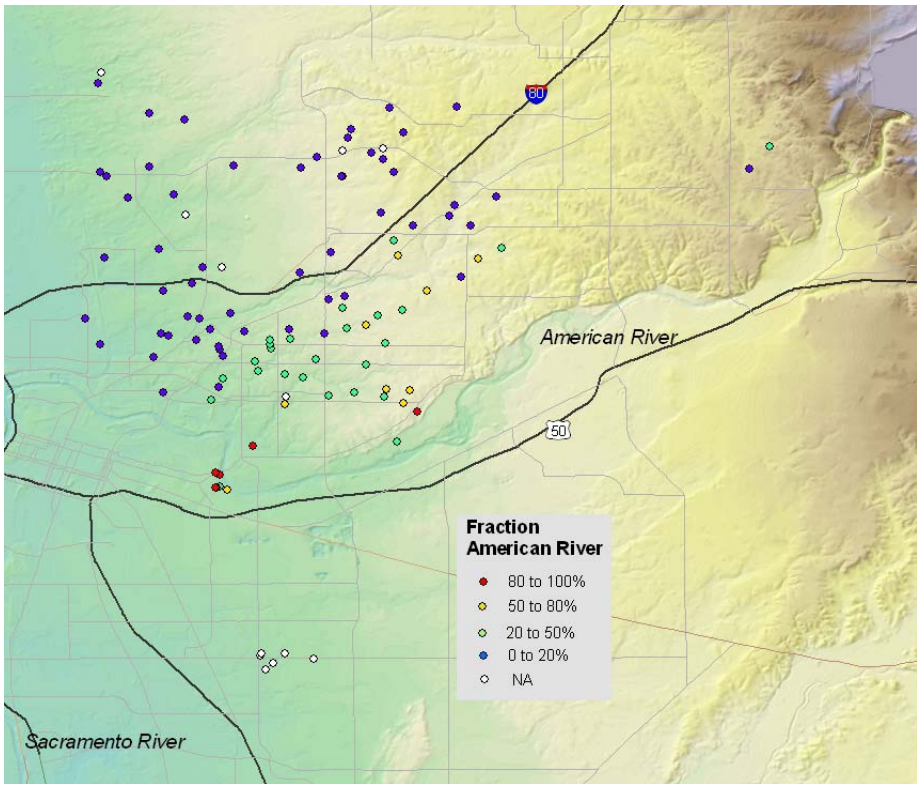

Figure 13. The fraction of American River water in well samples is determined using $\delta^{18}O$ of –11 ‰ as the river end member and –7.5 ‰ for the 'locally-derived' end member. The fraction of river water in wells falls off rapidly with distance from the river. (Wells marked NA have small negative fractions river water.)

Tritium Concentrations are Uniformly Low over a Large Part of the Subbasin

Tritium concentrations measured in groundwater samples from the Sacramento suburban area are very low – lower than those recorded in other major groundwater basin around the state (Moran et al., 2002, Hudson et al., 2002, Moran et al., 2004). While the American River, and monitor wells near the American River have tritium concentrations of approximately 11 pCi/L, a value that is likely close to the

mean concentration in present-day precipitation, 91 out of 108 public drinking water well water samples have tritium concentrations of less than 3 pCi/L (figure 14). Forty-six samples have tritium concentrations of less than 1 pCi/L. In many of these samples, a lower detection limit than the typical 1 pCi/L limit was achieved by allowing the ^{3}He daughter to accumulate longer than 2 weeks; a 1 sigma uncertainty of approximately 50% is associated with tritium values of <1 pCi/L. Nineteen wells have tritium concentrations of less than 0.25 pCi/L, a level at which <2.5% of the groundwater could have a tritium concentration >10 pCi/L. Another 20 wells have between 0.25 and 1 pCi/L, and a corresponding maximum 10pCi/L component of 10%. (In general 'post-modern' groundwater contains more than 10 pCi/L because a small component of bomb-pulse water increases the concentration. These estimates of the modern component in 'dead' waters are therefore maximum estimates.) Even wells with 1 to 3 pCi/L have a very low fraction of post-industrial aged water (Hudson et al., 2002; Moran et al., 2004). Meaningful ages therefore could be calculated at only 12 wells, where the tritium concentration is greater than 3 pCi/L, excess air is sufficiently low and radiogenic ^{4}He is not exceedingly high. These wells are situated in an arc that parallels the American River, along with a small number of wells in the upstream area of Arcade Creek in the eastern portion of the study area.

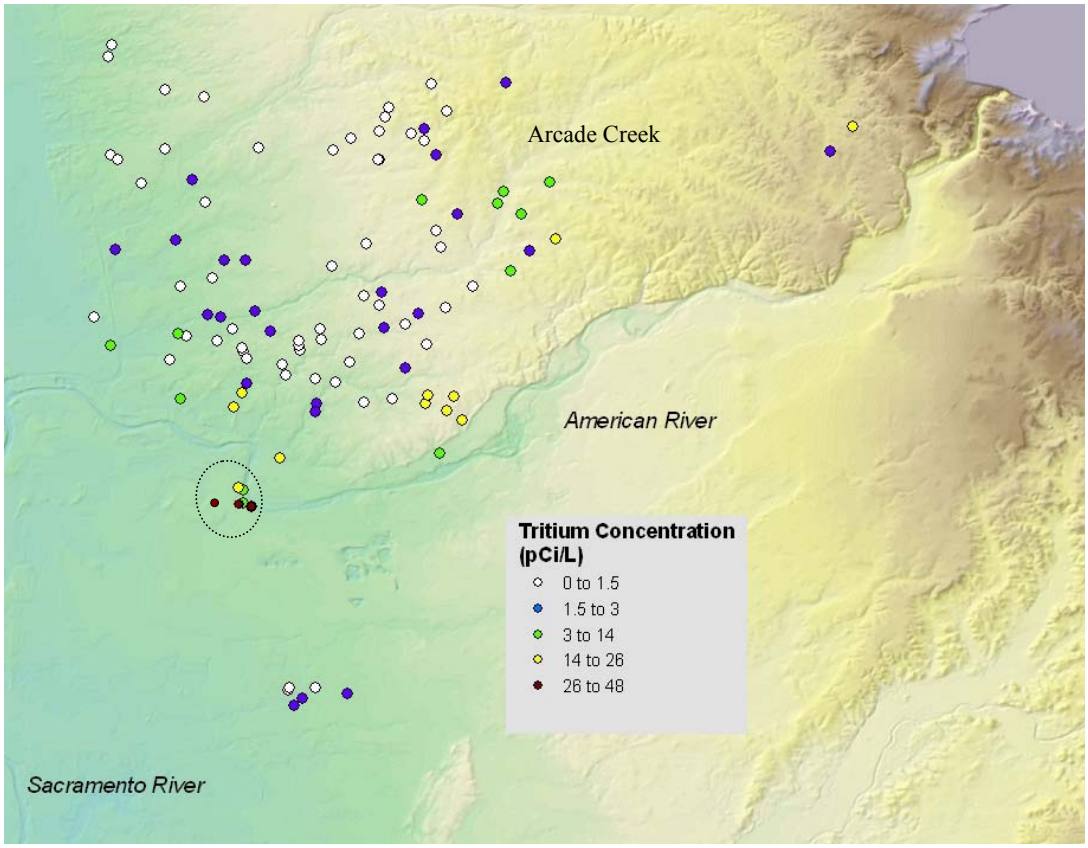

Figure 14. Tritium concentrations in wells from the Sacramento area. Significant tritium concentrations in drinking water wells are observed only in a band near the American River, and in the upstream area of Arcade Creek. (Nested monitor wells are shown in the dashed oval and are not included in the statistics for tritium given in the text.)

While low tritium concentrations are observed in wells over the whole range in total well depth represented in the sample set, higher tritium concentrations are observed only in wells with a total depth of less than 500 ft bgs (figure 15). As is commonly observed in large, exploited groundwater basins (Hudson et al., 2002, Moran et al., 2002, Moran et al., 2004), young groundwater containing significant tritium is generally found at relatively shallow depths and near recharge areas. In distinct contrast with

the patterns observed in coastal alluvial basins (Shelton et al., 2001, Moran et al., 2004), VOCs occur frequently in wells with very low tritium concentrations in the Sacramento area. Only the deep wells in the northern and northwestern part of the study area are devoid of tritium as well as VOCs.

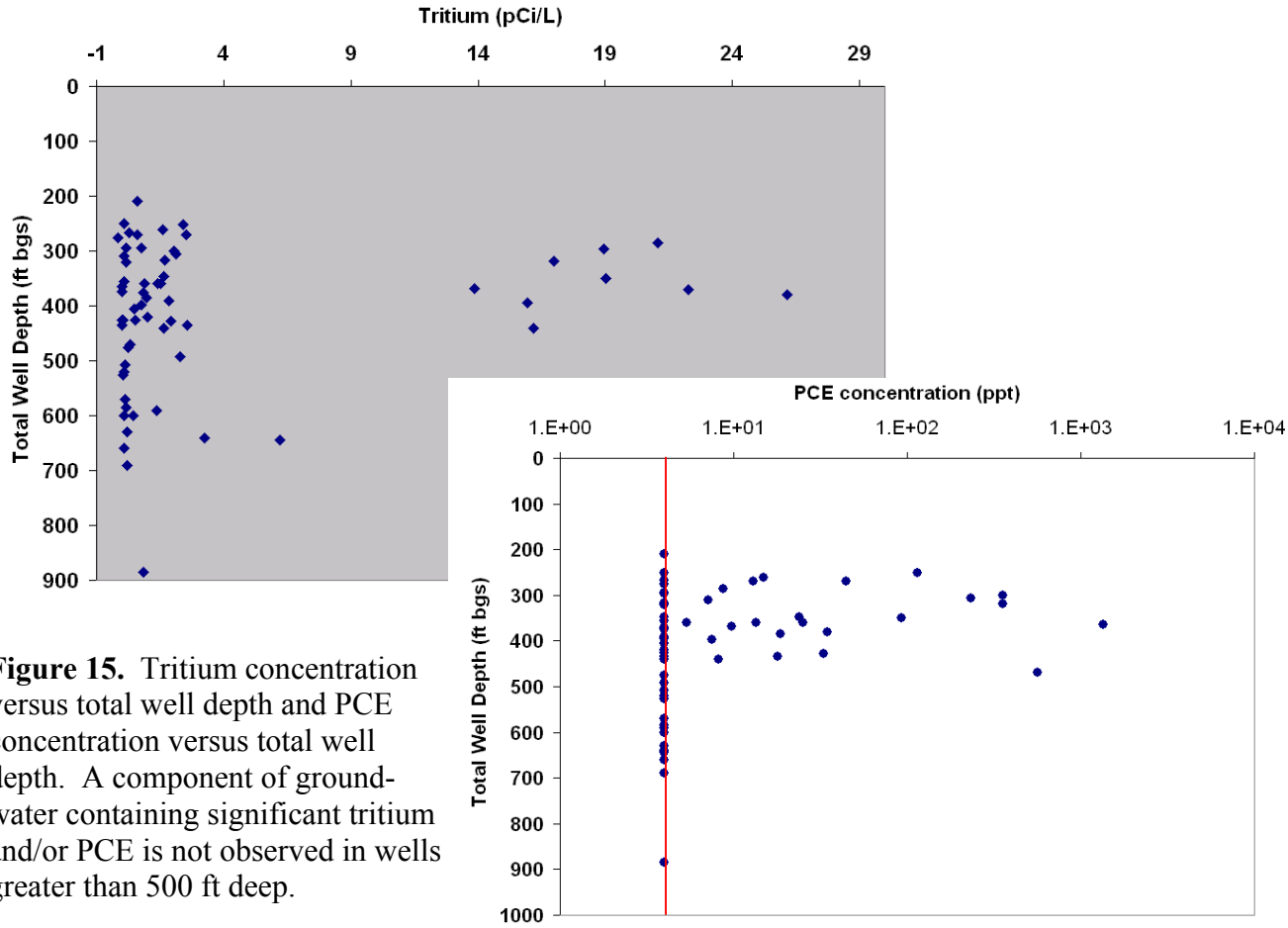

Figure 15. Tritium concentration versus total well depth and PCE concentration versus total well depth. A component of ground-water containing significant tritium and/or PCE is not observed in wells greater than 500 ft deep.

As shown in figure 16, PCE is nearly as likely to be found in wells with very low tritium as it is in wells with relatively high tritium concentrations. Even in the 19 wells with tritium concentrations of less than 0.25 pCi/L, PCE and/or TCE was detected in 6, while PCE and/or TCE was detected in 7 of the 20 wells with tritium concentrations between 0.25 and 1 pCi/L. Thirty-six of 69 wells with tritium concentrations less than 3 pCi/L had PCE and/or TCE detections, while 16 of 25 wells with tritium concentrations greater than 3 pCi/L had PCE/TCE detections. PCE is unlikely to have been transported advectively with the very old groundwater associated with low tritium, since the sources of PCE were likely not present at the time of recharge. Thus, some form of non-advective transport, such as short-circuiting by abandoned wells or compromised well casings, or via fast-path transport as a dense non-aqueous phase liquid (DNAPL) or along a continuous vertical geologic feature can be inferred.

The prevalence of old groundwater (nearly devoid of tritium) over a large part of the basin has major implications for groundwater management, including planned artificial recharge operations. The

overdraft that has produced a major groundwater depression in the south-central portion of the study area leaves room for 'new' storage. However, the fact that these wells produce mainly pre-modern groundwater indicates that groundwater takes more than several decades to reach the capture zone of the wells. Vertical transport of a significant volume of artificially applied water may be quite limited in areas where very low tritium concentrations are observed. The alluvial sediments that occur in a relatively narrow band to the north of the American River, and in the area of higher tritium on the upstream portion of Arcade Creek, do allow recently recharged water to reach deep wells in those areas.

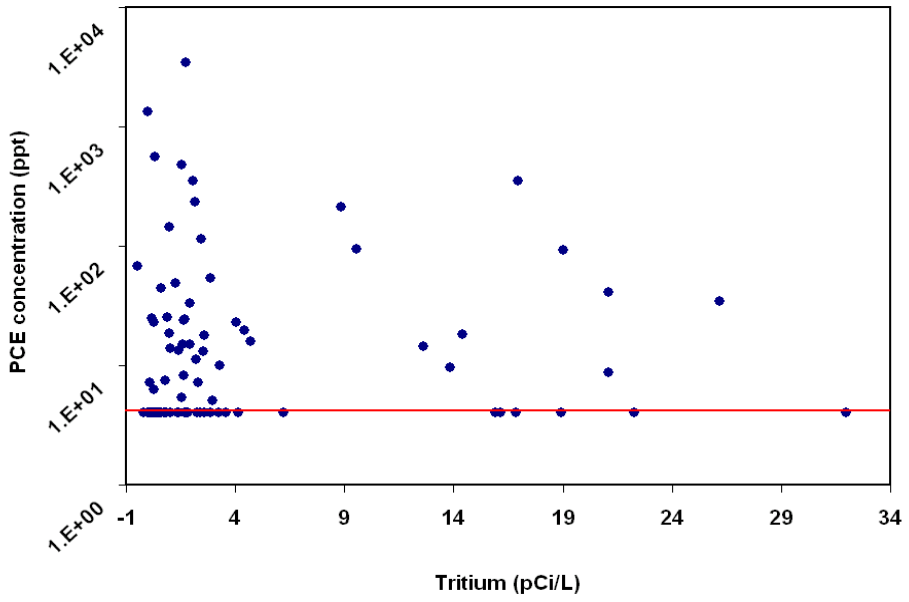

Figure 16. Tritium concentration versus PCE concentration in public supply wells. Note PCE concentration is on a logarithmic scale and the red line is drawn at the reporting limit for PCE. The occurrence of PCE in wells with low tritium concentration suggests non-advective transport of this contaminant.

The spatial pattern in groundwater age mirrors the pattern in tritium concentration (figure 17), but gives a direct measure of the residence time for the post-modern (tritium-containing) portion of the groundwater. Of the 12 drinking water wells where a groundwater age could be determined, 6 have mean ages of less than 20 years. (Five more wells had sufficient tritium to confirm the presence of a post-modern component, but the dissolved noble gas sample was compromised by a relatively high concentration of excess air or high radiogenic ^{4}He so an age could not be determined.) These six wells have somewhat shallower top perforated intervals and/or shallower total depths than wells in the same vicinity, and a young component is likely drawn in at the shallow interval. Another six samples have calculated ages of 20 to 33 years, and have a smaller component of post-modern groundwater.

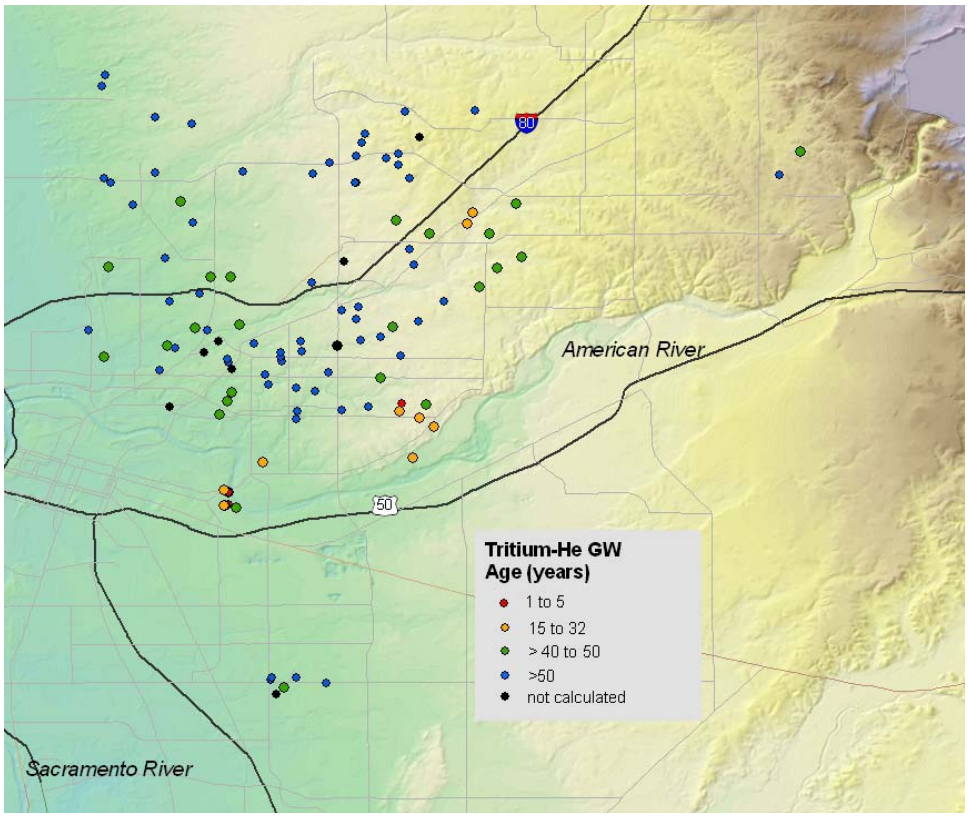

Figure 17. Mean groundwater age as determined using the tritum-helium method. Meaningful ages could be calculated at only a small number of drinking water wells because of the very low tritium concentrations observed over a large part of the study area. Several young ages are observed in wells near the American River.

Fraction Pre-modern and Radiogenic ^{4}Helium Provide Additional Information about the 'Old' Groundwater Component

Even in wells containing some tritium, produced water is frequently a mixture of mainly pre-modern groundwater with a smaller component of water recharged after 1950 (figure 18). Wells with calculated mean ages younger than about 20 years are more likely to have narrow age distributions than wells with greater ages, with fractions pre-modern of less than 30%. Wells with calculated ages in the 25-33 year range produce water than is more than 50% pre-modern, with some as high as >80% (figure 18).

Radiogenic ^{4}He concentrations in the basin give additional information about the pre-modern component of groundwater that dominates the water produced by drinking water wells in the Sacramento area. Very high radiogenic ^{4}He values are recorded in wells in the north central portion of the basin, and high radiogenic ^{4}He concentrations are also observed in wells in the western portion of the basin, to the northeast of the confluence of the Sacramento and American Rivers (figure 19). These wells are producing a component of water with a residence time in the basin that is on the order of 20,000 years. Similarly, Criss and Davisson (1996) found 'pockets' of Pleistocene-age (8,000 to 16,000 yr) groundwater in wells from the Sacramento area using ^{14}Carbon to estimate groundwater residence time.

In contrast, the northwestern and southeastern portions of the study area are generally low in radiogenic ^{4}He, suggesting that this component is not tapped in those wells.

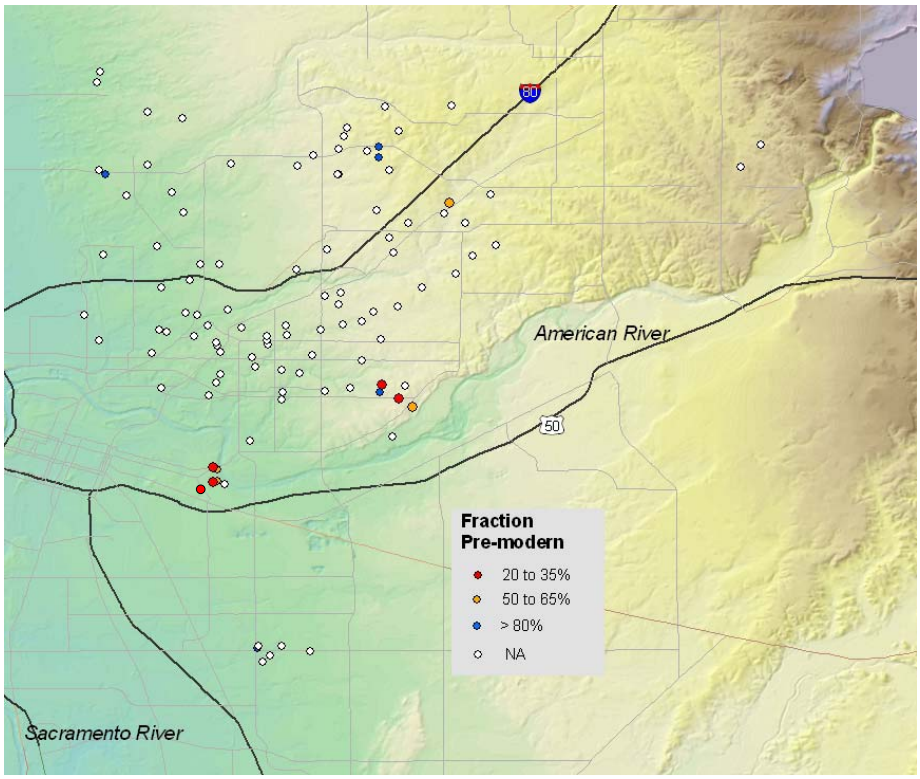

Figure 18. The estimated fraction of groundwater of pre-modern age shows the degree of mixing between post-modern aged water and water that recharged the basin before about 1955.

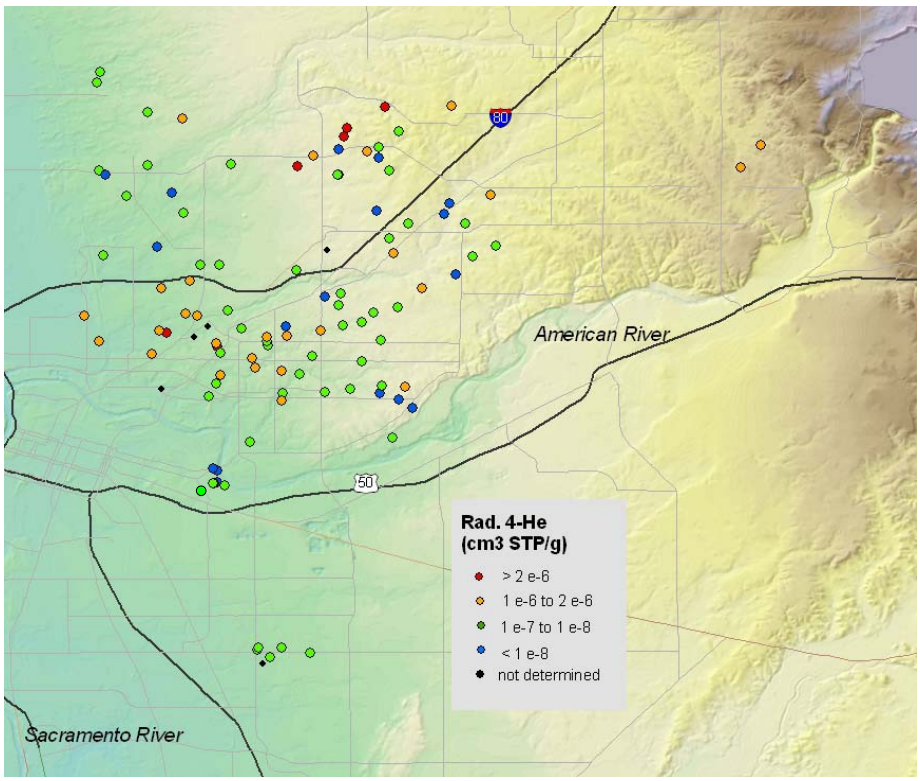

Figure 19. The radiogenic ^{4}He age is a residence time estimate for the groundwater component older than approximately 100 years. Wells with red and orange symbols tap a component of water that has a residence time on the order of 10,000 yrs.

Recharge Conditions are Revealed by Recharge Temperatures and Low 'Excess Air' Concentrations

Recharge temperatures determined from noble gas concentrations measured in groundwater samples are shown in figure 20. The mean annual air temperature for the Sacramento area is approximately 18 C (http://www.giss.nasa.gov), in good agreement with the recharge temperatures for wells with other lines of evidence for a local recharge source – mainly those north of Interstate 80. The spatial pattern exhibited by recharge temperatures mirrors the pattern in oxygen isotopes, with cooler temperatures in wells near the American River, and gradual progression to warmer temperatures in wells to the north of the river. Recharge temperatures near the river are approximately 11.5 C. The water temperature in the American River is 11 to 12 C for the months of January, February, and March, but warms up to temperatures as high as 19 C in the summer months (http://ca.water.usgs.gov/sac_nawqa/gwurblu.html and Table 3). The recharge temperatures observed in wells with multiple lines of evidence for river recharge suggest then that recharge takes place in winter months. Wintertime recharge is likely since river flows are higher, and infiltration likely takes place up on the sides of the river bank, where dessication cracks are present and where fine-grained sediments that inhibit infiltration are absent.

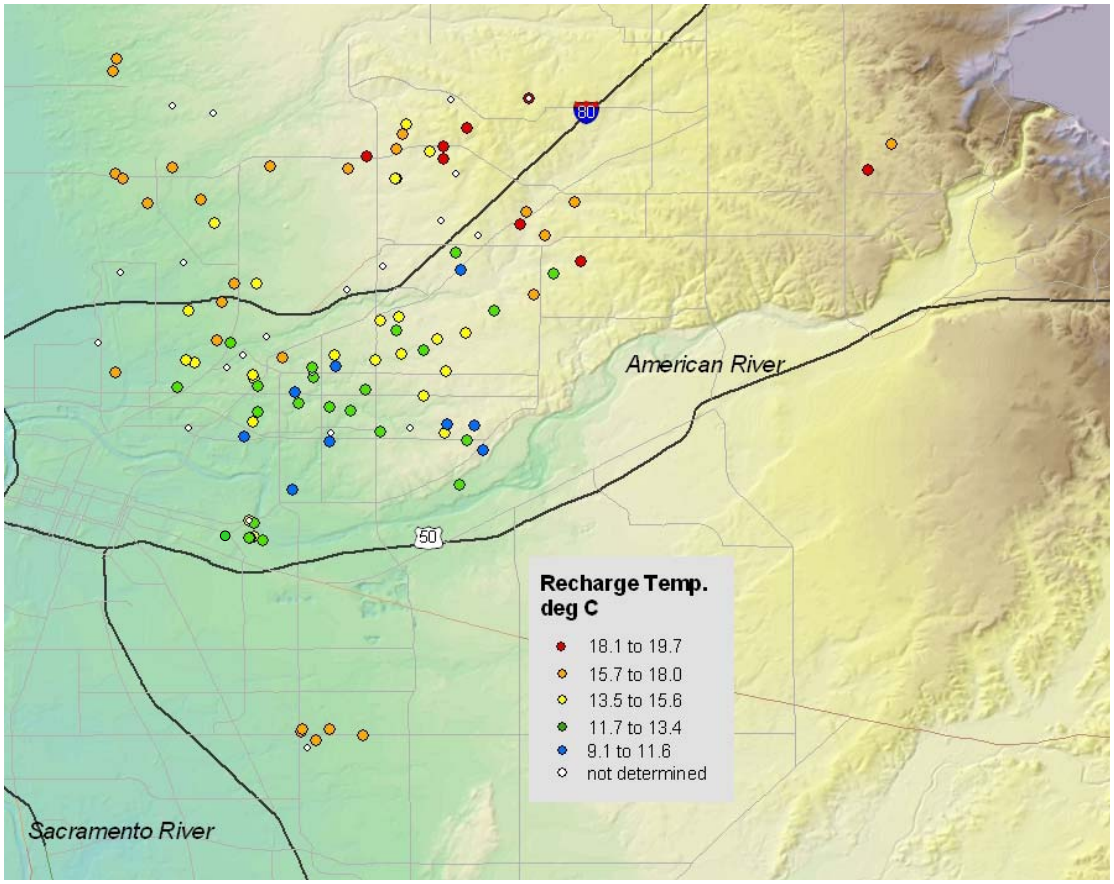

Figure 20. Groundwater recharge temperatures determined from dissolved noble gas concentrations show a pattern of colder temperatures in the region influenced by (wintertime) river recharge, increasing to mean annual air temperatures over the northern portion of the study area.

The excess air concentrations observed in Sacramento area wells are low compared to excess air concentrations measured in wells from major coastal groundwater basins in California previously studied using GAMA techniques (Hudson et al., 2001; Moran et al., 2004), as well as compared to published values. In a survey, Aesbach-Hertig et al. (2000), report values of 0.001 to 0.01 cm^3STP/g, while excess air in this basin is nearly always less than 0.002 cm^3STP/g (figure 21). Low excess air concentrations are indicative of limited interaction with vadose zone gas during recharge, and a slow, steady downward movement of the water table. These are the conditions that prevail during river recharge. The fact that very low excess air is observed even in wells where oxygen isotope ratios indicate the presence of locally-derived water, indicates that there is minimal vadose zone interaction and minimal fluctuation in the water table, even in areas away from the main rivers. In contrast, coastal California aquifers suggest extensive vadose zone interaction and a rapidly fluctuating water table. During passage through the vadose zone, air is trapped as bubbles that subsequently dissolve, and are kept in solution by rapid recharge with a high hydraulic head.

Low concentrations of excess air have water quality implications. Dissolved oxygen concentrations are likely to be low in regions of low excess air. Dissolved oxygen aides in the breakdown of organic matter, and water quality improvement during recharge is expected when dissolved oxygen levels are significant, since a decrease in total organic carbon reduces tri-halomethane formation potential. This phenomenon has been documented at other recharge areas in California (Davisson et al., 1998, Moran and Halliwell, 2002). Low dissolved oxygen may, however, bring about water quality improvements that are associated with reducing conditions. For example, denitrification occurs only when dissolved oxygen concentrations are less than 1-2 mg/L. Nitrate contamination does not occur in Sacramento area wells, as no public supply wells have reported MCL exceedances in the last decade. While nitrate sources are not present in the urban area, sources are likely in the formerly agricultural suburban and outlying areas. Low nitrate concentrations in drinking water wells may be due to denitrification during transport, which is more likely under conditions of low excess air and river recharge. Another factor, however, is the prevalence of old groundwater in potentially affected areas, and the possibility that shallow-sourced nitrate has not yet reached deeper aquifers.

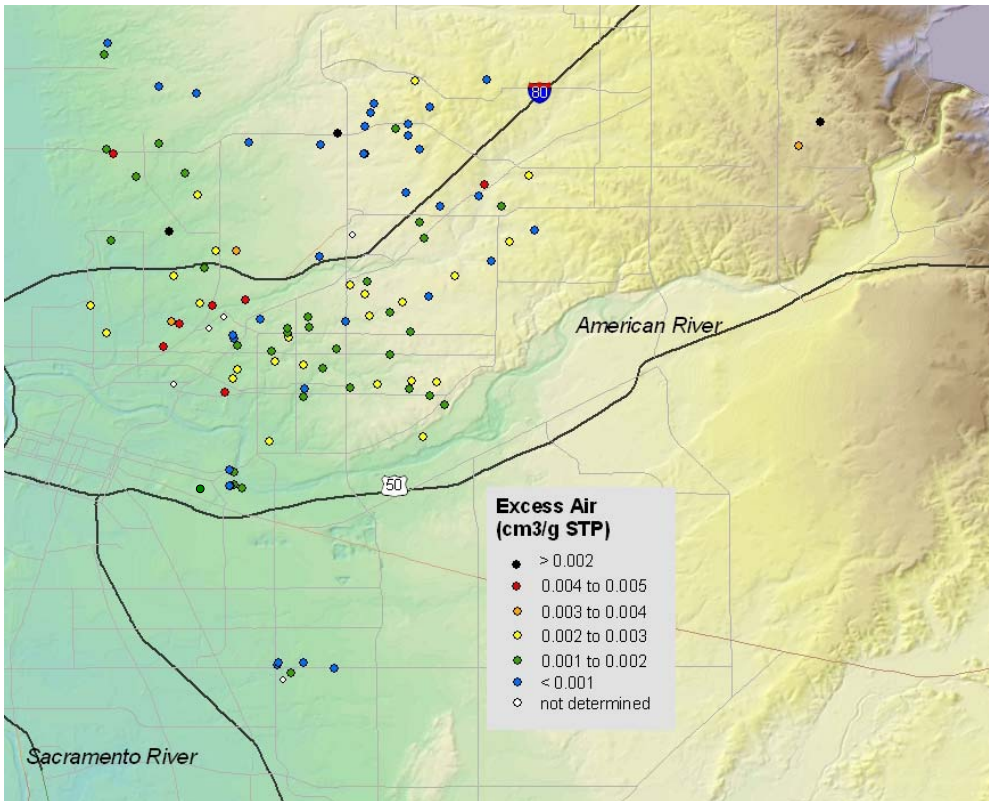

Figure 21. 'Excess Air' concentrations in groundwater samples from the study area are generally very low compared to coastal groundwater basins and suggest recharge conditions with little vadose zone gas/water interaction.

Nested Monitor Wells Offer a Detailed Look at River Recharge

The same suite of parameters measured at the public supply wells discussed above were analyzed in 14 monitor wells along the bank of the American River and on the adjacent campus of CSUS (figure 22). Unlike the public supply wells, the monitor wells have short screened intervals of 10 to 20 feet, and are useful for examining recharge in the vertical dimension and for assessing water quality in very recently recharged groundwater. However, recharge conditions at this location are complicated by the presence of a slurry wall constructed to prevent seepage directly under river levees. The slurry wall runs along the length of the area shown in figure 22, between the riverbank and the wells, to a depth of about 60 ft. In addition, as discussed above, sampling with a gasoline-powered generator and submersible pump results in low-level contamination of groundwater samples, and raises the reporting limit and uncertainty associated with low-level VOC results.

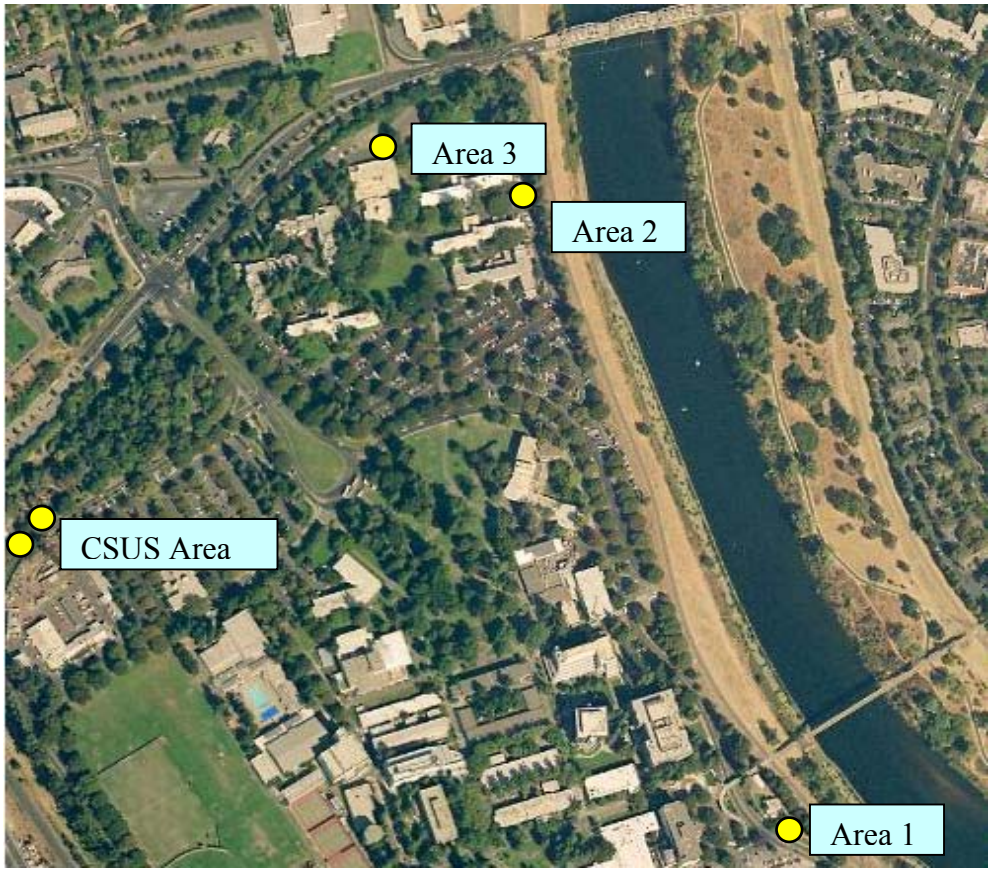

Figure 22. Aerial photograph showing locations of monitor wells on and near the CSUS campus that were included in the study.

Results from oxygen isotope and low level MtBE analyses are shown in figure 23. For comparison, MtBE analyses from American River water grab samples from the same day are shown in figure 23, along with median values of $\delta^{18}O$ from 5 previous sampling events of the American River in Table 3 (Appendix B). Temporal variation in $\delta^{18}O$ and MtBE in the American River is due to seasonal variation, and to releases from upstream reservoirs. For example, recreational boating, which likely contributes a significant fraction of the total MtBE observed is higher in summer months, while direct runoff in winter months is likely lower in MtBE (Ekwurzel et al., 2000). Shallow-screened wells close to the river invariably have $\delta^{18}O$ and MtBE values that closely match those of the river water samples, except for the shallowest well in area 2 (figure 23). The three CSUS wells, set back from the river by 1,200 m (4,000 ft)

have distinct isotopic and chemical signatures, with the shallow-screened well showing evidence for a significant non-river component in its heavier $\delta^{18}O$ value and much lower MtBE concentration. Groundwater ages and tritium concentrations in the shallow wells close to the river, however, confirm that these wells tap very recently recharged American River water (< 1 year ages), with no significant change in any of the parameters measured during infiltration (figure 24).

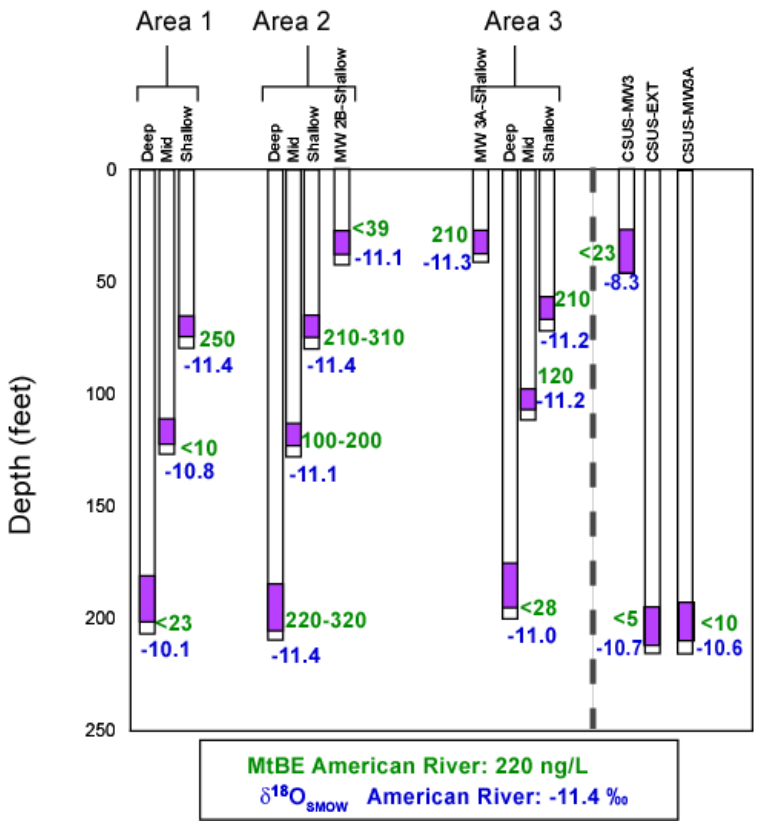

Figure 23. Oxygen isotope results show a strong signal of American River water throughout the monitor well section. MtBE results are screened at a higher level and have greater uncertainty than results from public supply wells because some contamination is introduced from the sampling equipment. Interpretation of MtBE results is given in the text. Dashed line separates wells close to the riverbank (left side) from those set back by about 1200 ft.

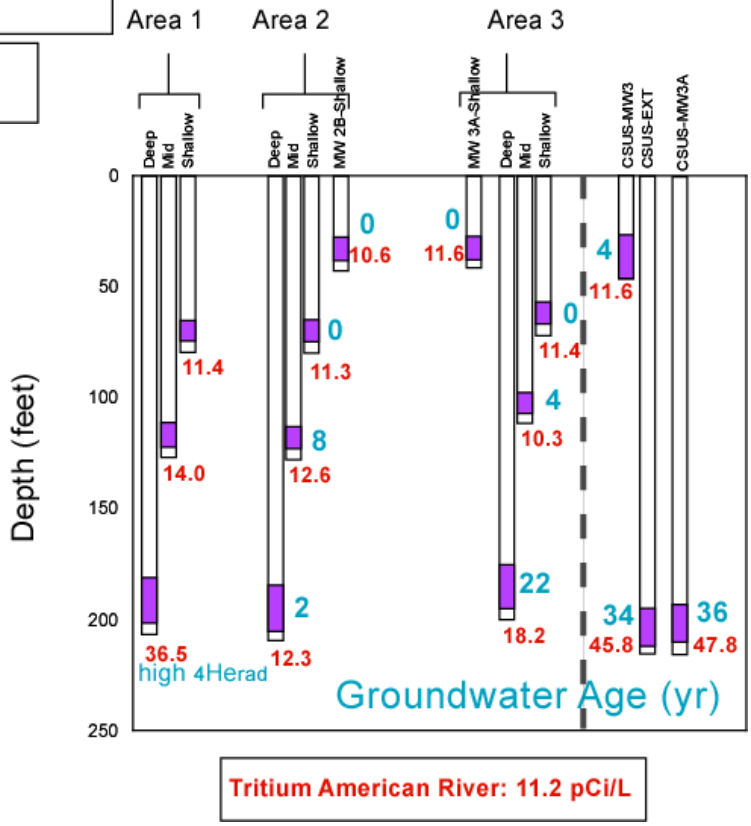

Figure 24. Tritium concentrations and calculated tritium-helium groundwater ages show zero ages in the shallow section and increasing age and tritium concentration with depth at all areas except Area 2. Recharge rates calculated from ages are given in the text.

Groundwater ages increase and MtBE concentrations decrease with depth in areas 1 and 3 near the river, and relatively old (appx. 35 yrs), MtBE-free groundwater is found at depth in the CSUS wells. The steady increase in tritium concentration with depth in these areas is evidence for piston-flow, with the deeper groundwater showing the influence of the 'bomb-pulse', i.e. a steady downward infiltration of groundwater that moves back and up on the curve shown in figure 1. For example, the two deep CSUS wells have the highest tritium concentrations measured in the study area, and tap a volume of water that recharged 35 years ago when tritium concentrations were higher. More subtle differences are seen when comparing depth-dependent results from areas 1 and 3. In area 3, a steady decrease in MtBE concentration, increase in groundwater age, and no change in $\delta^{18}O$ is observed, suggesting that river water moves steadily downward but that MtBE is likely degraded during transport (dilution or significant change in the source term is unlikely with a 4 yr groundwater age). At area 1, heavier $\delta^{18}O$ in the middle and deeper zones is evidence for mixing with ambient groundwater, while very low MtBE concentrations in the middle and deep zones are likely due to both mixing and significantly older water at depth. (Groundwater ages could not be calculated at area 1 but tritium concentrations suggest a steady increase in age from 0 in the shallow zone to approximately 10 years in the middle zone to 30 years in the deep zone.)

Spatial variability in recharge at different points along the river is evidenced by the differences in results between areas 1 and 3, but especially in the large discrepancy between results from areas 1 and 3 versus area 2. At area 2, all the parameters analyzed indicate that young water with a river source is found at all levels, with a groundwater age of only 2 years in the deep zone and a correspondingly high MtBE concentration. At this location, a vertical transport path is present and active, perhaps because of leakage at a break in the slurry wall or because of compromised well construction. The middle zone shows mixed indicators, including an age of 8 years and an MtBE concentration that is half of that observed at the zones above and below. The very shallow well in area 2 has a low MtBE concentration, which is likely related to the complex hydraulics associated with the slurry wall.

Recharge Rates Determined from Groundwater Ages

Several geochemical methods have been used to determine groundwater recharge rates including environmental tracers such as stable isotopes of oxygen and hydrogen and solute profiles. Solomon et al., (1993) determine recharge rates using tritium-helium groundwater ages in an area of nearly vertical recharge, and discuss in detail the limitations of the method with regard to dispersive effects of mixing and molecular diffusion, and with regard to complications posed by samples that come from near and before the tritium bomb pulse peak. In this sample set, all samples are post bomb peak, and the other isotopic and chemical tracers suggest that mixing with non-river sources is minimal. Area 3 is an especially good profile for the purpose of estimating the long-term recharge rate, given the steadily increasing age and consistent $\delta^{18}O$ values that indicate a river source. A vertical recharge rate is calculated using a simple distance/time formula, and a recharge rate of 5.7 ft/yr (1.7 m/yr) is determined for the shallow zone to the deep zone. The recharge rate over the shallow zone to middle zone is 10 ft/yr, while the middle zone to deep zone rate is 4.7 ft/yr. Similar rates can be calculated at area 1 (4.7 ft/yr shallow to middle; 3.8 ft/yr middle to deep; 4.1 ft/yr shallow to deep), and at the CSUS area (5.4 ft/yr).

The rates determined here are estimates of the bulk, long-term recharge rate, and considerable variation is expected on daily and seasonal time scales. The calculated rates are somewhat higher than those observed

by Solomon et al., 1995 for a shallow unconfined aquifer on Cape Cod (2.3 to 3.7 ft/yr), and by Szabo et al., (1996) for a shallow unconfined aquifer on the New Jersey plain (1.5 ft/yr), but similar to those determined at the River Glatt in Switzerland (6-7 ft/yr; Santschi et al., 1987) where significant extraction takes place in wells alongside the river. The large depression in groundwater levels to the north of the American River and groundwater production near the American River induce recharge at a higher rate than what would be expected in the natural system. Away from the river, given the mean annual rainfall in the Sacramento area (18 inches/yr) and relatively high evapotranspiration rate for the Central Valley climate (65%), an infiltration rate about 10 times lower than the rates calculated for river recharge is expected.

Acknowledgements:
This study would not have been possible without the voluntary participation of the well owners who allowed LLNL to sample their wells. Tim Parker and Tanya Meeth of the Department of Water Resources coordinated the sampling of the monitor wells on and near the CSUS campus, and Tim Horner of the Dept. of Geology at California State University, Sacramento generously provided well construction information as well as technical details, which aided in the interpretation of results from those wells. We are indebted to Brenda Ekwurzel of the University of Arizona for developing an automated data reduction system for noble gas data. We are also extremely grateful to Wayne Culham for his careful, hard work in the noble gas lab at LLNL.

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Appendix A: Sampling and Analysis Plan – Lawrence Livermore National Laboratory

Environmental Sample and QA Sample Collection

1. VOCs

After the well is purged, the sampling port is opened and water is allowed to pass through the port for two or more minutes, to allow purging of the sampling port. Vials are filled directly from the sampling port, without touching the bottle to the sampling port. A total of three samples, each in 40 ml VOA vials (VWR TraceClean™, amber borosilicate; 0.125-in septa liner), are collected, with zero head-space. Non-volatile plastic or rubber surgical gloves are worn by the sampler. Sample bottles are opened and filled away from any nearby exhaust from combustible engine sources, or open bottles of solvent. Emissions from regular street traffic are unavoidable in some cases, but should be noted by the sample collector. Two field blanks in 40 ml VOA vials are provided for each well sampled. One of the field blanks is topped-off by the other and capped with zero headspace. The field blanks provide some measure of potential atmospheric contamination. Filled VOA vials are stored refrigerated at all times.

2. Stable Isotopes

A 30 ml glass bottle (clear, French-square type) with Qorpak™ polyseal-lined cap is triple rinsed with water directly from the sampling port, then filled just below the threads on the bottle. No preservatives or refrigeration are required, but the cap should be tightly closed.

3. Tritium

A 1-liter glass bottle (e.g., Pyrex with orange polypropylene plug seal cap) is filled directly from the sampling port to just below the threads. No preservatives are required.

4. Dissolved Noble Gas

Two clamped copper tubes for dissolved noble gas analysis are collected. Reinforced tygon tubing is attached to the well sampling port, with a copper tube dissolved gas sampling assembly connected by hose clamps. The assembly is purged of air by running well water through for several minutes. The sample is collected at the pressure of the distribution system (typically around 100 psi). The tube or assembly is tapped lightly to knock any trapped bubbles free. Any air bubble that is sealed in the copper tube sample will compromise the sample. The downstream clamp is tightened first using a socket wrench. The bolts on either side of the clamp are tightened alternately so the copper is pinched evenly. The metal clamps are completely closed. There will be a small gap in the center section of the clamp to prevent pinching off the copper tube completely. This center portion of the metal clamp is precisely designed for the correct gap on the copper tube when the outer portions of the clamps are in complete contact with each other. Samples are stored at room temperature.

Analytical Method - VOCs

The analytical technique of purge and trap gas chromatography-mass spectrometry (GC-MS) has been optimized to obtain low part per trillion reporting limits for several selected volatile organic compounds: MtBE (Methyl tert-Butyl Ether) [5 ppt], Toluene [5 ppt], PCE (Tetrachloroethylene) [5 ppt], TCE (Trichloroethylene) [5 ppt], DBCP (1,2-Dibromo-3-chloropropane) [5 ppt], Trihalomethanes - Chloroform [5 ppt], Bromodichloromethane [5 ppt], Chlorodibromomethane [5 ppt]. Method detection limits (three times the standard deviation of seven replicate analyses of the blank) are between 0.3 and 1.2

ppt. The low detection limits are achieved, in part, by employing a heated purge to maximize the recovery of target analytes from the water samples, primarily needed for methyl *tert*-butyl ether (MtBE) which has a relatively high aqueous solubility, and by operating the mass spectrometer in selected ion monitoring mode, an operating parameter which substantially increases the signal to noise ratio.

In this method, the target analytes are purged from 25 mL water samples and preconcentrated on a sorbent trap using a Hewlett Packard Model 7965 purge and trap concentrator equipped with a Vocarb™ 3000 trap. A 40°C heated purge is used and the samples are purged with a stream of ultra pure helium at a flow rate of 40 mL/min for a duration of 11 min., followed by a 3 min. dry purge. The analytes are desorbed from the trap at 260°C to a Hewlett Packard 6890 gas chromatograph equipped with a DB-624 column (60 m x 0.32 mm ID, 1.8 μm film thickness), coupled to a Hewlett Packard 6890 mass spectrometer. The trap continues to bake at 260°C for an additional 20 minutes after desorption. The GC oven is temperature programmed as follows: 35°C held constant for 2 min., ramped at 10°C/min. to a final temperature of 225°C, and held constant for 4 min. The mass spectrometer is operated in selected ion monitoring mode and three ion fragments are monitored for each compound, a primary ion used for quantitation and two secondary ions used for compound confirmation. The target analytes are identified by matching the retention times and the relative ratios of the three ion fragments to authentic standards and the compounds are quantified using the internal standard method. For MtBE, masses 43, 57, 73 are used for quantification. Neat standards of MtBE (spectroscopic grade @99.7%) are used for calibration, as well as a 4-bromofluorobenzene internal standard. Matrix blanks are prepared in the laboratory and analyzed periodically bi-weekly as part of sample handling and analytical performance. Duplicate samples are analyzed with a frequency of 10%. Surrogate recovery (Toluene-d8 and 4-BFB) must be between 80 and 120%.

Analytical Blanks are prepared by boiling double distilled water for 30 minutes and syringing into a VOA vial. The syringe is rinsed three times before use. This same blank water is used to prepare field blanks, by filling 40ml VOA vials and capping with zero headspace.

Analytical results greater than 5 ppt are reported to two significant figures. Well sample results for each compound are censored if field blanks from the same day have detections greater than 5 ppt. In that case, results are reported as ”<X”, where X is the highest value measured for the given compound on the given day.

Analytical Method – Stable Isotopes

Oxygen isotope analyses are conducted using the CO_2 equilibration method for $^{18}O/^{16}O$ (Epstein & Mayeda, 1953) and analyzed with an automated water equilibration unit. Isotope ratio measurements are performed on a VG PRISM isotope ratio mass spectrometer housed in the Analytical and Nuclear Chemistry Division at Lawrence Livermore National Laboratory. Oxygen isotope ratios are reported in the standard delta (δ) notation as parts per thousand (per mil or ‰) variations relative to a reference material of known composition and defined by the following equation:

$$\delta_x = 1000 \frac{R_x - R_{std}}{R_{std}} \qquad (1)$$

where R_x is the $^{18}O/^{16}O$ ratio of the sample. The conventional standard reference material for oxygen isotopes is Standard Mean Ocean Water (SMOW; Craig, 1961).

Analyses in the Stable Isotope Laboratory are calibrated to internal standards referenced against National Institute of Standards & Technology (NIST) standard reference materials. Internal standards consist of 1) Pacific Ocean water sample $\delta^{18}O$ = +0.35‰), 2) two isotopically distinct California meteoric water samples $\delta^{18}O$ = –9.78 and –14.62‰), and 3) Alaskan Tap Water (-21.02‰). The composition and isotopic values of these internal standards span the range of natural waters typically observed in potable groundwater of California. For each 24 $\delta^{18}O$ analyses, 2 each of 3 internal standards are also analyzed and used for calibration.

The internal standards are periodically compared to the three NIST reference standards: SMOW, Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP). The analytical precision for these $\delta^{18}O$ measurements, from one run to the next, is ± 0.10‰, which is defined in terms of the difference of the internal standard from the precisely known NIST standards. One duplicate is analyzed for every eighteen samples. These duplicates are not "blind" however, but are typically samples from the previous run. If this duplicate varies by more than ± 0.10‰, the sample is run for a third time. If this duplicate is not with the 0.10‰ precision, the entire set of eighteen samples is re-analyzed.

Analytical Method – Tritium and Dissolved Noble Gases

The following analyses are reported for each groundwater well:

- Tritium (^3H in picoCuries per liter; pCi/L)
- ^{4}Helium, Neon, Argon, Krypton, Xenon abundances (cm^3STP/g)
- Tritium-helium age (in years)
- Radiogenic ^{4}Helium (cm^3STP/g)
- Excess air (in cubic centimeters at STP per liter)
- Recharge temperature (in °C)
- "Goodness of fit" for the equilibrium/excess air model

In the lab, each sample tube is attached to a 250 ml bottle assembly that is part of a multiport gas-handling manifold. The samples are released by unbolting the bottom clamp. The tubes are heated and then the water is frozen using frozen CO_2. The dissolved gases are released into the previously evacuated headspace in this process.

Reactive gases are removed with a SAES Ti-Al getter operated at 400°C. Argon, Kr and Xe are collected on activated charcoal using liquid nitrogen. At this point, a small portion (5%) of the remaining gas phase (He and Ne) is analyzed using a quadrupole mass spectrometer in order to measure the He/Ne ratio and to determine whether excessive He is present in the sample. The remaining He and Ne are then collected at 15K on activated charcoal. The low temperature charcoal trap is then warmed to 35K and the He is released and admitted to the VG 5400 mass spectrometer.

The mass spectrometer uses a conventional 17-stage electron multiplier and a SR400 pulse counting system for measuring ^{3}He. Helium-4 is measured using a faraday cup with a 10^{11}-Ohm feedback resistor. The procedure is calibrated using water samples equilibrated with the atmosphere at a known temperature (21°C). These calibration samples are processed along with regular samples with a frequency of 10%. Duplicate samples are analyzed with a frequency of 10%. The ^{4}He and Ne abundances are measured with an accuracy of 2% and the ratio of $^3He/^4He$ is measured with an accuracy of 1%.

The Ar abundance is determined by measuring its total pressure using a high-sensitivity capacitive manometer. The Kr and Xe abundances are determined using the quadrupole mass spectrometer. The Ar abundance is measured with an accuracy of 2% and the Kr and Xe abundances are measured with an accuracy of 3%.

The measured abundances of Ne, Ar, Kr and Xe are used to determine the amount of air-derived He present in the sample. The amount of radiogenic ^{4}He and tritiogenic ^{3}He are determined by subtraction of the atmospheric component.

For tritium determinations, 500g samples are loaded into stainless-steel bottles and attached to a multiport gas-handling manifold. The samples are chilled with water ice and headspace gases are pumped away. Samples are then heated with valves closed to re-equilibrate the water and the headspace void. Samples are then re-frozen and headspace gases are pumped away. In each cycle, approximately 99% of the He is removed. After five cycles, virtually no ^{3}He remains (< 100 atoms). The ^{3}He from tritium decay is allowed to accumulate for about 10 days. The samples are heated and then frozen and headspace gases are analyzed to determine the amount ^{3}He in-growth. Samples are analyzed in a similar fashion as the dissolved gas samples except that Ne, Kr and Xe are not analyzed.

The procedure is calibrated using samples with known amounts of tritium. The NIST-4361-B tritium standard is used for the calibration standard. These standard tritium samples are processed identically to the well water samples and run with a frequency of 10%. Empty bottle blanks are run with a frequency of 10%. Duplicate samples are analyzed the frequency of 10%. Tritium accuracy is the quadratic sum of 1 pCi/L plus 5%. Tritium detection limit is 1 pCi/L. Groundwater age is calculated using the equation noted above, and reported with a propagated analytical uncertainty.

References

Craig, H. (1961) Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science, v. 133, p. 1833-1834.

Epstein, S. and Mayeda, T. K. (1953) Variation of ^{18}O content of waters from natural sources. Geochimica et Cosmochimica Acta, v. 4, p. 213-224.

Appendix B: Tables

Table 1: Basic properties, regulatory, and reporting limits for VOCs included in this study.

Compound Type Chemical Name	Common Name	Sources	Key Properties	MCL	PHG	LLRL
(units)				*(ppb)*	*(ppb)*	*(ppb)*
Gasoline Oxygenate Methyl tert-Butyl Ether	MTBE	LUFTs, non-point source	highly soluble in water	5	13	.005
Gasoline Compounds Benzene Toluene Ethylbenzene Xylene	 B T E X	petroleum products, industrial solvents	 less dense than water	 1 150 700 1750	 0.14 0.15 300 1800	 .005 .005 .005 .005
Solvents Trichloroethylene Tetrachloroethylene	 TCE PCE	 Industrial cleaning dry cleaning	 more dense than water	 5 5	 0.8 0.056	 .005 .005
Trihalomethanes Trichloromethane Bromodichloromethane Chlorodibromomethane	THMs Chloroform BDCM CDBM	 disinfection by-products	 present in environment for >100 years	total THMs 100	na	 .005 .005 .005
Volatile pesticide Dibromo-3-chloropropane	DBCP	agricultural application	now banned	0.2	.0017	.005

MCL = Maximum Contaminant Level (CA Department of Health Services)

PHG = Public Health Goal (CalEPA suggested)

LLRL = Livermore Laboratory Reporting Limit

Table 2. A subset of the analytical results from monitor wells on and near the California State University at Sacramento campus

LLNL ID	Well Name	$\delta^{18}O$(SMOW)	3H	GW Age	MTBE	CHCL3	Benzene	Ethylbenzene	o-Xylene	Total Depth	casing diam	top perf	bottom perf
units		(‰)	(pCi/L)	(yrs)	(ppt)	(ppt)	(ppt)	(ppt)	(ppt)	ftbgs	inches	ftbgs	ftbgs
101538	Area1-SHALLOW	-11.4	11.4	NC	2.5E+02	<5	<5	<5	<5	80	4	65	75
101539	Area1-MID	-10.8	14.0	NC	6.4E+00	2.1E+01	<5	<5	<5	127	4	112	122
101537	Area1-DEEP	-10.1	36.5	NC	2.3E+01	1.2E+01	<5	<5	6.1E+00	225	4	182	202
101543	Area2-SHALLOW	-11.4	11.3	<1	3.1E+02	<5	<5	<5	<5	80	4	65	75
101541	Area2-MID	-11.1	12.6	8	2.0E+02	1.6E+01	<5	9.5E+01	1.1E+02	128	4	113	123
101540	Area2-DEEP	-11.4	12.3	2	3.2E+02	<5	<5	<5	<5	210	4	185	205
101544	Area2B-SHALLOW	-11.1	10.6	<1	3.9E+01	4.6E+02	1.9E+01	6.2E+00	6.8E+00	43	4	28	38
101542	Area3A-SHALLOW	-11.3	11.6	<1	2.1E+02	7.5E+01	<5	<5	<5	42	4	27	37
101547	Area3-SHALLOW	-11.2	11.4	<1	2.1E+02	6.6E+00	<5	<5	<5	72	4	57	67
101546	Area3-MID	-11.2	10.3	4	1.2E+02	1.1E+01	<5	<5	<5	112	4	97	107
101545	Area3-DEEP	-11.0	18.2	22	2.8E+01	3.5E+02	<5	1.7E+01	1.8E+01	200	4	175	195
101568	CSUS-MW3	-8.3	11.6	4	2.3E+01	6.3E+00	<5	1.9E+01	3.1E+01	47	4	27	47
101569	CSUS-EXT	-10.7	45.8	34	<5	<5	<5	<5	<5	215	8	194	209
101570	CSUS-MW3A	-10.6	47.8	36	6.3E+00	<5	<5	<5	<5	210	2	193	208
101571	CSUS-EQUIPMENT BLANK	-11.4	NA	NA	1.5E+03	2.4E+02	2.2E+01	1.5E+01	2.4E+01				

NC=not calculated
NA=not applicable

Table 3. A subset of field parameters, stable isotope, and MtBE results for river water samples from the northern Central Valley

SAMPLE	DATE	Latitude	Longitude	COND.	T	δD_{smow}	$\delta^{18}O_{smow}$	MtBE
				(µS)	(°C)	(‰)	(‰)	(ppt)
American Rvr								
CSUS site	030113	38°33'52.3"	121°25'23.2"		10.3		-11.40	220
Discovery Park site	011218	38°36'5.8"	121°28'55.6"	82.3	10.8		-10.40	200
AR-1	970905	38°42'18.4"	121°09'32.6"	65.3	18.0	-84	-12.17	
AR-2	970925	38°48'11.9"	120°53'24.8"	34.3	16.0		-12.38	
	971023			33.5	16.0		-12.04	
AR-3	970925	38°54'58.6"	121°02'20.0"	111.3	22.0	-86	-11.13	
AR-3N	970925	38°54'58.6"	121°02'20.0"	161.3	22.0	-83	-10.09	
	971023			144.1	18.0	-81	-10.04	
	971203			113.6	10.5		-12.78	
	980122			68.2	8.0		-10.73	
	980305			89.4	10.2	-79	-11.10	
	980423			64.5	12.0		-11.96	
	980511			52.2	10.5		-12.03	
	980520			66.5	13.0		-11.75	
	980624			45.2	16.0		-12.17	
	980716			64.9	24.0		-11.94	
AR-3M	970925	38°54'58.6"	121°02'20.0"	95.6	22.0		-11.70	
	971023			41.3	16.0		-12.02	
	971203			47.2	10.0		-11.72	
	980122			55.2	8.0	-79	-10.98	
	980305			53.2	8.0	-82	-11.59	
	980423			48.9	11.5		-11.59	
	980511			45.4	9.5		-11.35	
	980520			51.3	13.8		-11.65	
	980624			38.2	18.0		-12.10	
	980716			38.5	17.0		-12.44	
AR-4	971203	38°45'45.9"	120°19'27.2"	61.7	2.0		-11.96	
	980122			50.9	3.2		-12.87	
	980308			78.3	3.0		-12.78	
	980423			36.1	5.5		-14.03	
	980511			33.2	4.0		-13.48	
	980520			35.8	8.0	-69	-13.44	
	980624			24.0	10.0		-13.12	
	980716			23.0	15.5		-13.58	
AR-5	970129	Watt Ave	Bridge	---	---	---	-10.92	
	980119			70.0	10.0	-77	-10.88	
Sacramento River								
SACR-1	970905	38°36'00"	121°32'32.2"	230	23.0	-78	-11.10	
	980113			103.5	11.0		-9.47	
	980119			100	11.5		-9.99	80
	980209			54.1	11.0	-76, -76	-10.52	
	980518			116.5	15.0		-11.33	
	980626			127.5	19.5		-11.33	1200
SACR-2	970905	38°48'08.6"	121°43'15.4"	152.2	22.0	-87	-11.75	

SAMPLE	DATE	Latitude	Longitude	COND.	T	δD_{smow}	$\delta^{18}O_{smow}$	MtBE
				(µS)	(°C)	(‰)	(‰)	(ppt)
SACR-3	971015	38°09'18.6"	121°41'18.3"	178	18.0	-88	-10.99	
	980115			175.5	11.0	-69	-9.55	220
	980517			217.0	15.0		-10.52	
	980626			129.2	19.5		-11.21	890
SACR-4	971015	38°19'16.2"	121°34'38.4"	139.2	17.5		-11.23	
	971114			160.4	15.0		-11.11	
	980119			100	11.0	-73	-10.01	
	980209			44.6	11.0		-10.56	
	980517			109.1	14.5		-11.30	
	980626			124.7	19.0		-11.50	1500
SACR-5	980113			127	11.0	-73, -72	-9.87	260
San Joaquin Rvr								
SJR-1	970129	37°38'22.5"	121°13'42"	---	13.0	---	-10.98	
	970903			867	24.2	-83	-10.34	
	971114			788	16.0	-83	-10.54	
	980114			452	12.0		-8.72	
	980207			276	11.0		-10.35	
	980514				15.5		-11.86	
	980616			141.1	21.0		-12.57	79
	980721			190.1	24.0		-12.68	
SJR-2	970903	37°47.149'	121°18.353'	677	25.0	-78	-10.59	
	971114			687	15.5		-10.73	
	980114			295	12.0		-8.54	280
	980207			109	11.0	-78	-10.53	
SJR-3	970922	37°08'40.7"	119°30'05.2"	56.1	20.5		-14.87	
	971021					-110	-14.60	
SJR-4	970922	36°58'45"	119°43'49.1"	49.8	13.5		-14.04	
SJR-5	970922	36°49'23.3"	120°03'15.4"	107.7	25.0	-101	-13.50	
SJR-6	970922	36°46'55"	120°18'42.6"	54.5	27.5	-100, -96	-12.88	
SJR-7	970922	36°51'22.1"	120°26'48.7"	429	26.1		-10.26	
SJR-8	970922	37°18'33.2"	120°55'41.0	966	26.0	-78	-9.32	
SJR-9	971015	38°02'48.7"	121°43'02.5"	1922	19.5	-78	-10.35	
	980115					-73	-10.02	40
SJR-10	971016	37°59'40.7"	121°24'39.1"	532	20.0	-86	-10.19	
	971114			509	17.0		-10.58	
	980115			499	12.0	-63	-8.41	115
	980207			177	11.0		-9.55	
	980514			230.0	16.0		-11.46	
	980721			185.5	28.3		-12.12	520
Stanislaus Rvr								
SR-1	970903	37°56.944'	120°31.940'	109.7	15.5	-86	-11.82	
SR-2	970903	37°44.523'	120°56.301'	86.6	21.0	-81	-11.67	
SR-3	970903	37°41.627'	120°10.767	118.5	24.0	-86	-11.60	
	980114			86.7	10.5	-80	-10.62	
	980207			109.3	11.0		-10.59	
SR-4	970925	38°16'17.5"	120°16'09.0"	34.3	16.0		-12.90	
	971023			24.7	9.0		-13.25	

SAMPLE	DATE	Latitude	Longitude	COND.	T	δD_{smow}	$\delta^{18}O_{smow}$	MtBE
				(µS)	(°C)	(‰)	(‰)	(ppt)
SR-5	971203	38°08'2.3"	120°22'46.8"	52	10.5		-13.25	
	980122			40.2	5.5		-12.73	
	980305			35.4	6.0		-12.37	
	980520			38.1	9.8		-12.95	
	980624			35.5	13.5		-13.69	220
	980716	---	---	---	---	---	-13.91	
Tuolumne Rvr								
TR-1	970129	37°37.569'	120°59.516'	---	11.0	---	-11.95	
	970903			162	24.0	-92, -91	-11.69	
TR-2	970903	37°40.004'	120°28.238'	97.2	15.0	-89	-12.45	
TR-3*	970925	37°52'38.5"	120°17'35.2"	37.9	17.0		-13.68	
TR-4	971023	37°49'17.3"	120°00'42.3"	105	10.0		-11.34	
	971203			74.5	5.5	-80, -83	-11.63	
	980122			48.2	3.2	-89	-11.98	
	980305			55.3	4.9		-12.08	
TR-5	971203	37°49'41.1"	120°00'8.4"	63.4	4.5		-12.60	
	980122			53.3	2.5		-12.35	
	980305			61.6	4.0		-12.43	
Mokelumne Rvr								
MR-1	970905	38°11'21.3"	121°19'14.4"	59.3	23.0	-82, -85	-11.44	
MR-2	970905	38°12'24.7"	121°03'59.5"	73	15.0	-85	-11.87	
MR-3	970925	38°18'46.1"	120°43'12.7"	52.6	17.5		-13.20	
	971023			38.9	15.5		-12.64	
	971203			65.1	9.0		-11.64	
	980122			48.8	---		-11.72	
	980305			56.6		-86	-12.02	
	980423			50.2	11.8		-12.32	
	980511			41.9	10.5		-12.41	
	980520			41.3	12.5		-12.53	
	980624			24.3	15.0		-13.16	3500
	980716			---	---		-13.05	
MR-4	971015	38°07'38.8"	121°34'42.8"	142.3	18.5		-11.22	
	980115			128	11.5		-9.32	
	980517			125.5	15.5		-11.00	
	980626			115.4	19.0		-11.25	
Feather Rvr								
FR-1	970905	38°48'52.8"	121°38'7.0"	101.7	25.0	-78	-11.14	
FR-2	970129	HWY 99	Nicklaus	---	---		-10.70	
Merced Rvr								
MER-1*	970925	37°36'15.8"	119°57'58.5	84.5	21.5		-12.73	
	971021			91	17.5		-11.92	
MER-2	971203	37°43'24.9"	119°40'47.0"	41.8	3.4		-13.48	
	980122			29.9	2.8		-13.47	
	980305			33	3.5		-13.76	