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California GAMA Program: Groundwater Ambient Monitoring and Assessment Results for the Sacramento Valley and Volcanic Provinces of Northern California

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January 25, 2005

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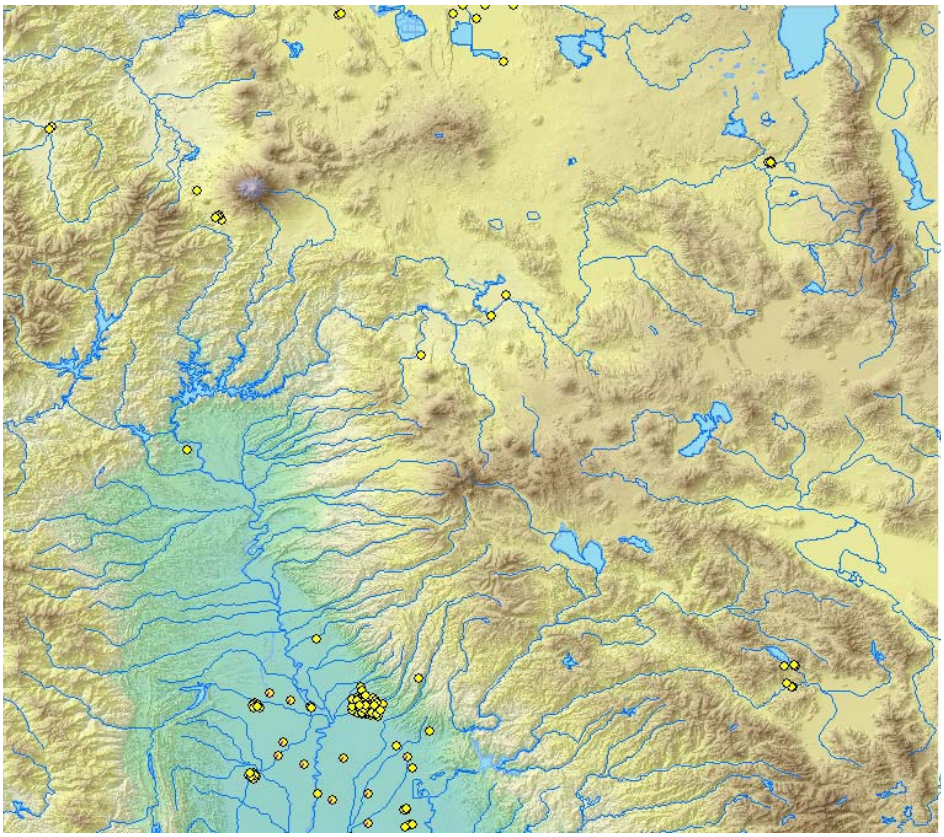

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California GAMA Program: Groundwater Ambient Monitoring and Assessment Results for the Sacramento Valley and Volcanic Provinces of Northern California

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Executive Summary

The Groundwater Ambient 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 2003, Lawrence Livermore National Laboratory (LLNL) completed a vulnerability study of the groundwater basins in the Sacramento Valley including Butte, Glenn, and Tehama counties, and in Volcanic Provinces including Modoc, Shasta, Siskiyou, and Plumas counties. 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 heavily exploited for agriculture in the Sacramento Valley, and while the total volume of groundwater pumped for public drinking water supply is relatively small because of the generally low population density, several towns and small cities are entirely dependent upon groundwater for drinking water. The highest density of wells included in the study area occurs in Chico and surrounding areas, with 62 public supply wells; other smaller towns included in the study have at most 8 wells. Comparisons are drawn between results from cities and towns in the Sacramento valley, where numerous sources of contamination are present and a large volume of groundwater is produced, and results from small population centers in Volcanic Provinces to the north, where contamination sources are fewer in number and a relatively small volume of groundwater is pumped.

Stable isotopes of oxygen provide a useful parameter for identifying the source area of water produced in wells in the Sacramento Valley. The oxygen isotope values ($\delta^{18}O$) delineate regions where groundwater is influenced by recharge of isotopically lighter (^{18}O depleted) Sierran or Coast Range water and other areas where natural recharge introduces isotopically heavier (^{18}O enriched) local water. A major result of this study shows the influence of Big Chico Creek recharge, from which all of the water in wells adjacent to the stream is derived, in decreasing proportions in wells to the north and south. Wells from the outlying areas of Chico have an isotopic signature that is indicative of a local

(valley) water source. Likewise, the spatial pattern in $\delta^{18}O$ in public supply wells from Orland show the influence of Stony Creek, which carries a somewhat depleted Coast Range signature. High elevation volcanic regions to the north and east of the Sacramento Valley have strongly depleted ratios, which is evidence for recharge by locally derived precipitation. Other somewhat depleted ratios observed at wells from low elevations are likely the result of return flow of Sacramento River or Feather River water used for irrigation.

Despite higher precipitation rates, higher river flows, and less municipal pumping than for previously studied areas of California, tritium concentrations in groundwater over a wide region are generally low, and indicate that a large volume of pre-modern (pre-1955 recharge) water is produced from drinking water wells. Overall, 74 of 168 samples (including 39 monitoring wells) have tritium concentrations that are less than 3 pCi/L, indicating that nearly all of the produced water recharged before 1955. The small number of wells in the study area that produce very young groundwater (< 10 years old) are situated close to major rivers and show multiple lines of evidence for river recharge to the well. Eighteen of the 33 wells from high elevation regions north of the Sacramento Valley have dissolved helium ratios that indicate the presence of a component of mantle-derived fluids, as expected in Volcanic Provinces.

One hundred and twenty three public supply wells were tested for a suite of common VOCs. Twenty eight wells (23% of wells) in the entire study area had no detections of any of the VOCs analyzed. Another 16 public supply wells (for a total of 37%) had detections only of trihalomethanes. Fifty one wells (44% of wells) had detections of the gasoline additive methyl *tert* butyl ether (MtBE), but only four of those detections were greater than 50 parts per trillion (ng/L). Chloroform (or trichloromethane) was the most frequently detected VOC in wells from the study area. Seventy-five public supply wells (60% of PWS wells tested) had detections of chloroform above the reporting limit of 5 parts per trillion, but with a median concentration of only 31 ng/L. Other VOC statistics are dominated by results for the Chico area, which has known contaminant plumes, including one designated as a superfund site. Widespread PCE occurrence suggests that its distribution is controlled by more than just point sources. Accordingly, tetrachloroethylene (PCE) was detected in 47 public supply wells in the Chico area; all but 4 detections were at concentrations well below the Maximum Contaminant Level (MCL), which is 5,000 ppt, and 16 were below the public health goal (PHG) of 56 ppt. Nineteen of the Chico wells with PCE detections also had detections of TCE, which likely occurs as a breakdown product. MtBE co-occurred with PCE even more frequently, with 33 PCE-contaminated wells also having MtBE detections, suggesting a high degree of vulnerability to both recently-introduced and decades-old contaminants at those wells.

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 denser that water. The source of the VOCs differs for the different compounds observed. MtBE and chloroform are found in surface 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 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 Valley 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 low, and indicate minimal interaction with vadose zone gases during recharge. Low excess air concentrations are consistent with recharge that is dominated by natural recharge (as opposed to artificial recharge), such as 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 to public supply wells, this report includes results from 39 monitoring wells that are widely spaced across the Sacramento Valley. Eleven sets of nested monitoring wells with relatively narrow well screens provide a more detailed picture of the vertical patterns in isotope tracers, and reveal the presence of paleowater in deep monitoring wells, especially to the west of the Sacramento River. These wells produce groundwater with depleted $\delta^{18}O$ signatures, radiogenic ^{4}He concentrations that are consistent with residence times of 20,000 years or more, and recharge temperatures that are depressed from modern ambient temperatures by approximately 5 degrees C. Shallow monitoring wells on the east side of the valley show evidence for recent recharge of evaporated water from flood irrigation. Isotopic results vary considerably across the Sacramento Valley, and do not offer evidence for long range, continuous cross-valley groundwater flowpaths.

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 Groundwater Ambient Monitoring and Assessment (GAMA) Program. The primary objective of the California Aquifer Susceptibility (CAS) project (under the GAMA Program) is to assess 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 this groundwater assessment program.

In 2003, LLNL carried out this vulnerability study in the Sacramento Valley and Volcanic Provinces. 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 location. 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:

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

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).

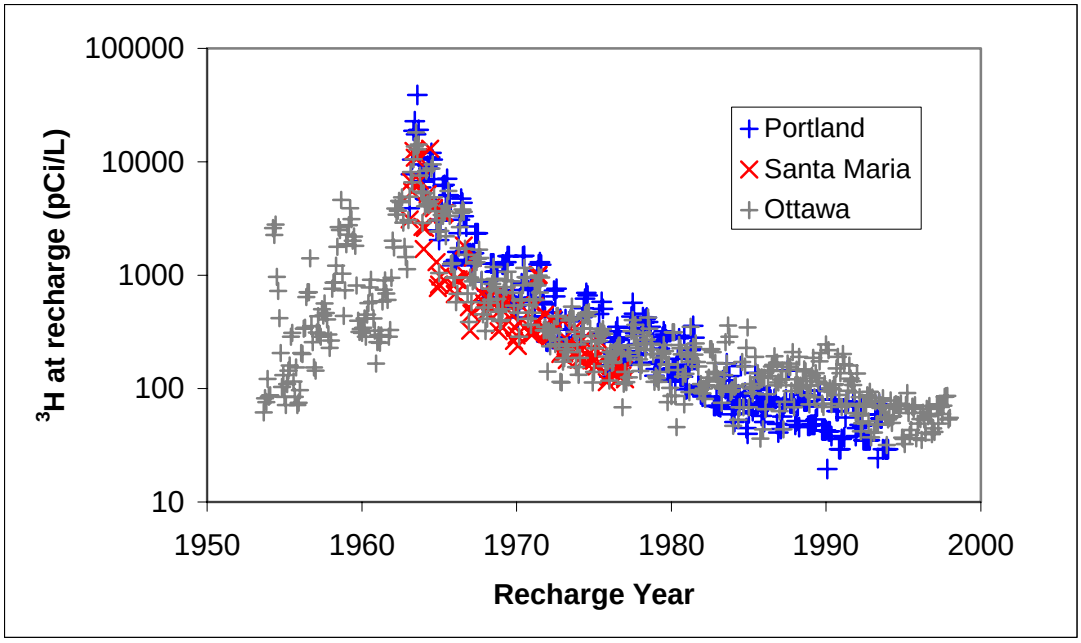

Figure 1. The tritium concentration measured in precipitation at three North American locations. Nuclear weapons testing introduced a large amount of tritium into the atmosphere in the 1960's, peaking in 1963.

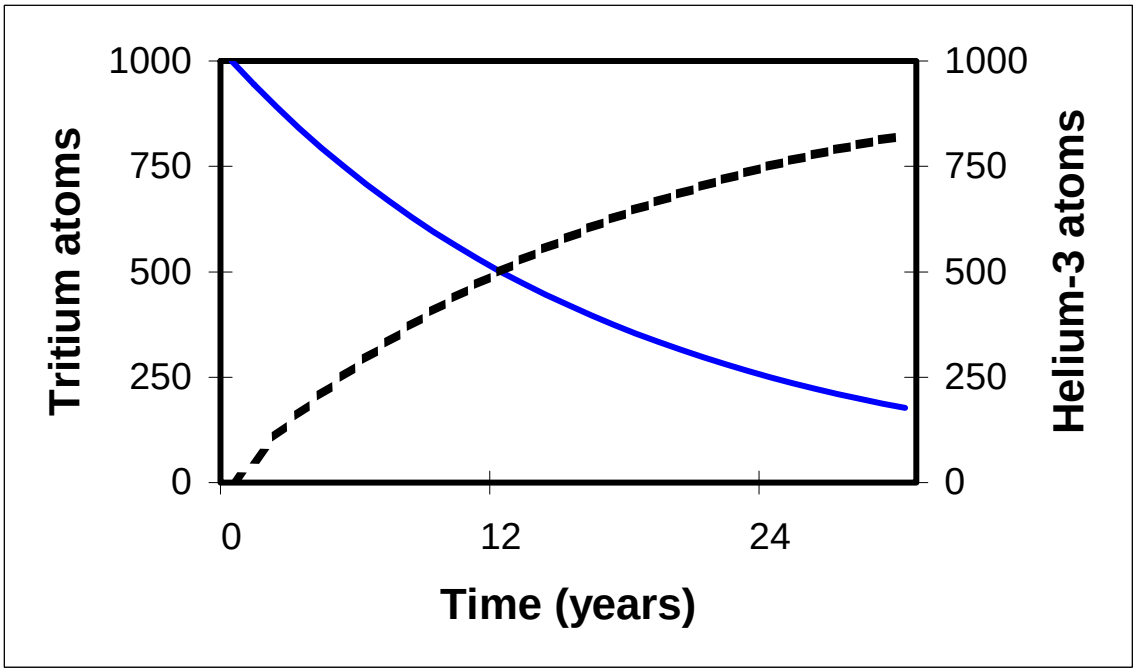

Figure 2. Solid line shows the decay of tritium, with a half-life of 12.34 years, while the dashed line shows the growth of the daughter product, ^{3}He. The sum of tritium and ^{3}He is the same at any time, and equal to the initial tritium value. This is the basis for the groundwater age-dating technique 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). Most long-screened drinking water wells produce a combination of post-modern and pre-modern groundwater (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.

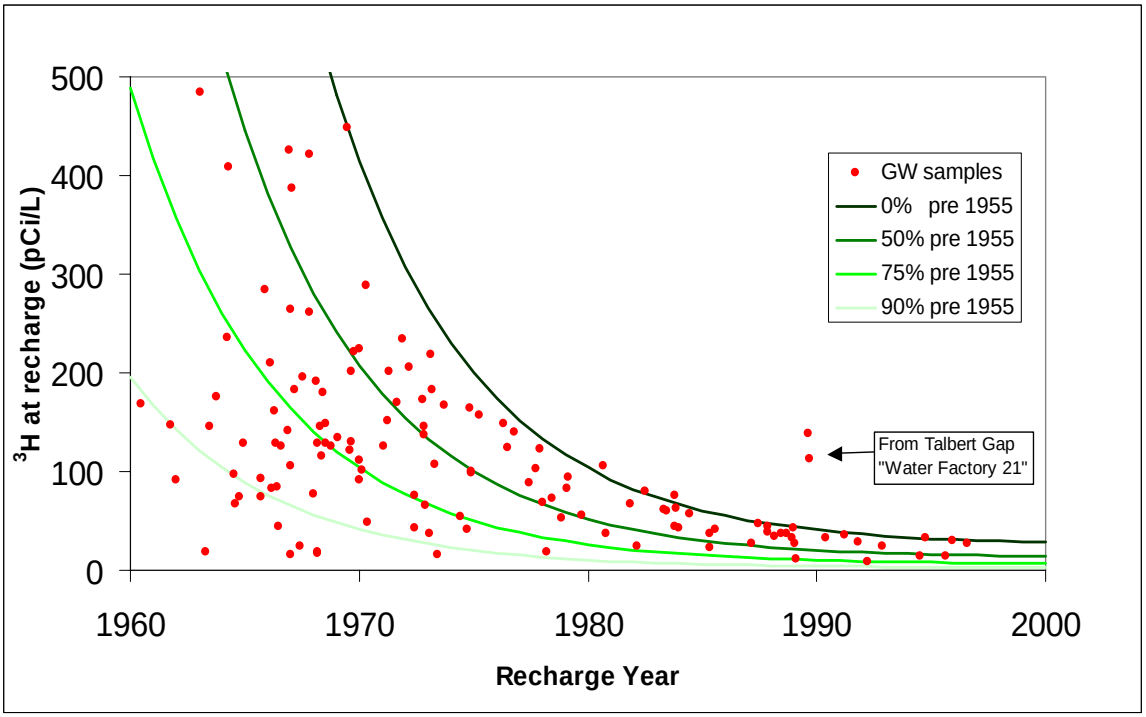

Figure 3. Curves show equal fractions of pre-modern water. The line labeled 0% is an approximation of the tritium in precipitation data from figure 1. Lines below approximate mixtures of pre-modern and post-modern water. Groundwater samples from southern California coastal basins are shown as points.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

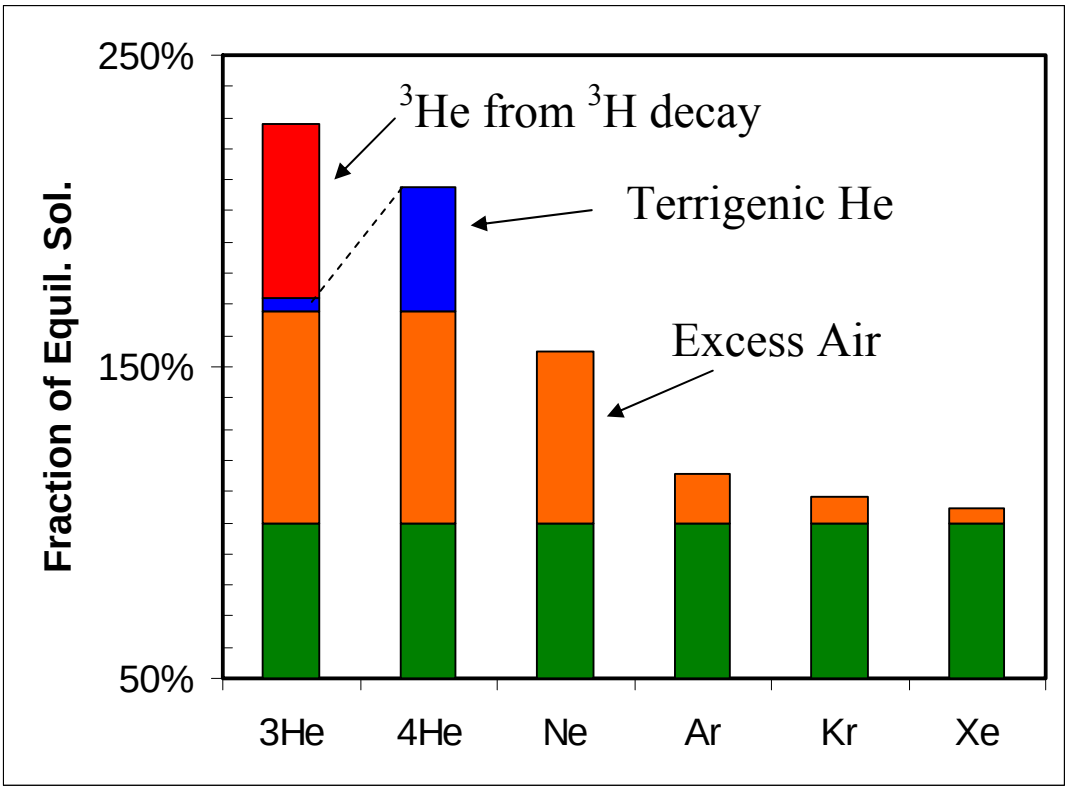

Figure 4. Graphical representation of the various dissolved noble gas components in a typical groundwater sample, relative to equilibrium solubility concentrations. Terrigenic He has a component of radiogenic ^{4}He from U and Th decay in the earth's crust.

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 $2x10^{-7}$ cm^{3} STP cm^{-2} yr^{-1}.

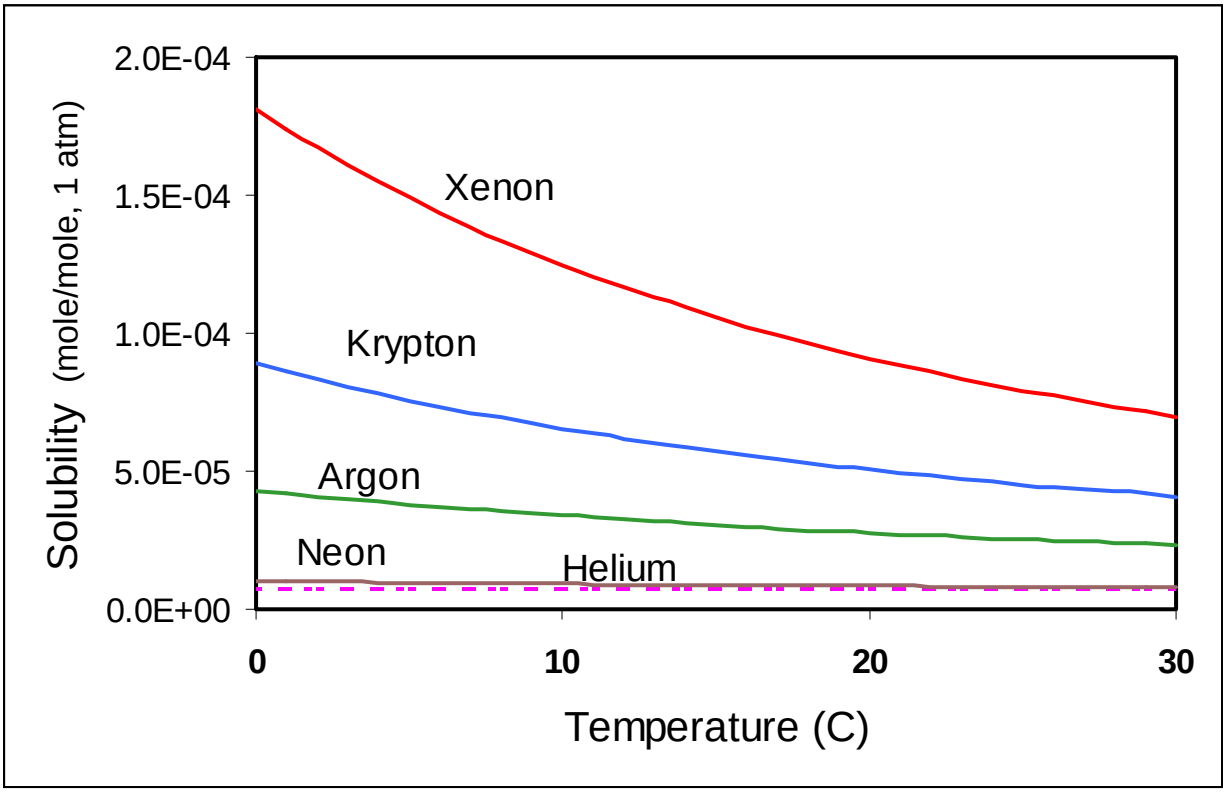

Figure 5. The solubility curves for the noble gases according to water temperature, showing the strongest temperature dependence for Xe. Noble gas recharge temperatures are calculated from these well-established curves.

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, Squillace et al., 2004).

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.

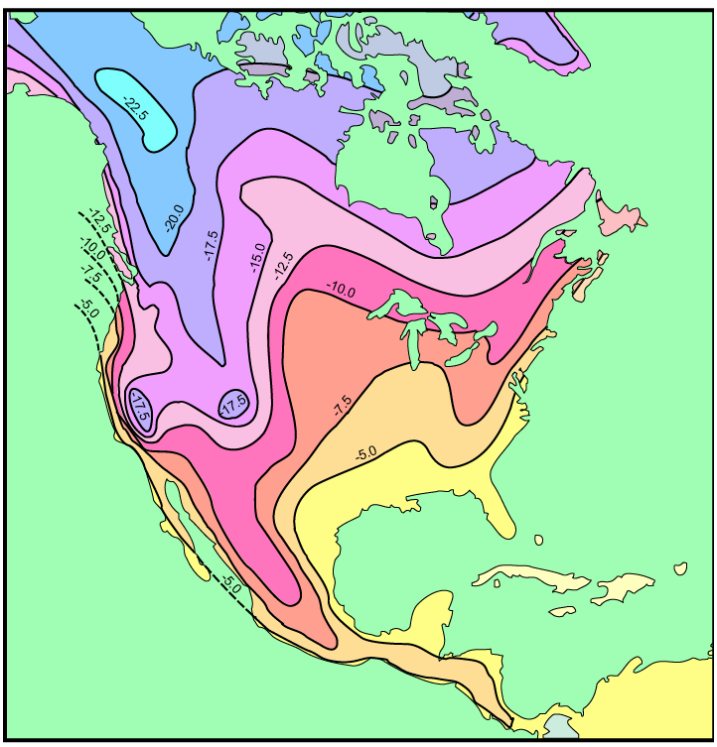

Figure 6. Contour map of $\delta^{18}O$ (SMOW) showing tight contours and lighter, depleted values at high elevation in California. (after Taylor, 1974)

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 Valley is briefly described, so that results from vulnerability parameters can be interpreted in the context of known groundwater flow patterns in this large basin. A smaller number of wells from the Volcanic Provinces to the north of the Sacramento Valley are also included in the study. Hydrogeologic conditions in the small basins from Volcanic Provinces vary widely, and little information is available for each.

Vina and West Butte Subbasins of the Sacramento Valley Groundwater Basin

The Vina and West Butte subbasins lie in the northeastern portion of the Sacramento Groundwater Basin – one of the largest and most productive groundwater basins in the state. Big Chico Creek divides the two subbasins at the surface, but the hydrogeologic conditions are similar across the two subbasins. The water-bearing units of the subbasin are dominated by unconsolidated continental deposits of Tertiary and Quaternary age. Quaternary deposits include Holocene stream and channel deposits, and the Pleistocene Modesto Formation, Riverbank Formation, and Sutter Buttes alluvium (DWR Bulletin 118, 2004). Tertiary deposits comprise the Pliocene Tehama Formation, consisting of sediments originating from the coastal mountains, and the Tuscan Formation, a series of volcanic mudflows, tuff breccia, tuffaceous sandstone, and volcanic ash layers. The Tuscan Formation is 800 to 1250 ft thick, and is broken up into 4 subunits, consisting of similar sediment types and separated in some areas by ash layers.

The natural groundwater flow direction is to the southwest, away from the Sierra Nevada to the Sacramento River, but alteration is observed in the Chico area, where year-round pumping results in groundwater depressions of up to 16 ft. Spring-to-spring water levels decreased by up to 30 ft or more during the droughts of the late 70's and early 90's, while the long-term trend indicates a 10 to 15 foot decline since the 1950's (DWR Bulletin 118, 2004). Natural recharge to the two subbasins has not been estimated but applied water recharge is estimated 156,000 at acre-ft. Municipal and industrial extraction is approximately 30,000 acre-ft and agricultural extraction is 320,000 in the two subbasins in a normal water year (http://www.buttecounty.net/waterandresource/GWmgmtPlan/Section%202%20Physical%20Setting%20bv%20041904%20JA.pdf).
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. Natural recharge takes place along streams and outcrops of the Tuscan

Formation to the east of the study area. Rainfall averages approximately 18 inches per year in the valley floor to 27 inches in the foothills to the east. 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 most significantly, net irrigation return flows. The Feather River, Sacramento River and several perennial creeks drain the foothills and Sierra Nevada, and traverse the valley. While some subbasins in the study area have large surface water allotments from the Feather River and Sacramento River for agriculture (East Butte, Plumas), others rely almost exclusively on groundwater pumping for irrigation (Colusa, Vina, West Butte).

Groundwater Management and Historical Water Quality

Butte, Glenn and Colusa counties have adopted groundwater ordinances. Butte County uses a Basin Management Objectives (BMO) approach to groundwater management, which allows representatives from 18 subareas to participate on the Water Advisory Committee and carry out public outreach. Glenn County takes a similar BMO approach, in which the County Board of Supervisors has ultimate authority. A 51% increase in water demand is expected Butte County by 2030, and a 96% increase in demand in Chico alone. In Volcanic Provinces, Siskiyou, Shasta, Tehama, and Modoc counties all have groundwater ordinances, while the Scott River Valley is an adjudicated basin. Plumas County, where municipal and industrial extraction is only 200 acre-ft per year, has no groundwater management plan. Likewise, Lassen County and the Fall River Valley have no plan, although industrial extraction (paper mills) is 13 MGD in the Fall River groundwater basin. Brief descriptions of some of the groundwater basins and water-bearing units in Volcanic Provinces are available in DWR Bulletin 118 (2003).

Groundwater quality in the study area is generally good, as evidenced by widespread low total dissolved solids, although some localized contamination has taken place. Sites with significant groundwater contamination occur in Chico, as described below. Solvent plumes have been identified in Chico and Orland, and landfill leachate contaminates groundwater in Plumas County. The most ominous water quality problem in several of the subbasins included in the study is nitrate contamination by septic leachate and by agricultural activities. Septic systems are suspected to contribute to high nitrate concentrations in Chico/Butte County, Tehama County, Glenn County, and locally in several of the counties where a high proportion of residences use septic systems. Geotracker (the SWRCB on-line database for tracking MtBE/LUFT sites) lists 119 LUFT sites in Chico, 30 of which are open, 19 in Glenn County, 14 in Plumas County (4 open), 319 in Shasta County (most in Redding) and 15 in Modoc County (9 of those are in Alturas with 5 open). http://www.waterboards.ca.gov/centralvalley/available_documents/ug_tanks/mtbe.pdf. However, according to the DHS database, only 5 public water supply wells in the entire study area had detections of VOCs above MCLs from 1994 through 2000 (4 in the Vina subbasin and 1 in the West Butte subbasin), and none have had MtBE concentrations above the detection limit for reporting for Title 22 water (5 ppb). MCL exceedences of nitrate are reported in 4 PWS wells in the Vina subbasin, 2 in the East Butte subbasin, and 2 in the Colusa subbasin. Nitrate contamination is more commonly found in shallow private wells rather than in the long-screened production wells included in this study.

Groundwater is a Crucial Resource

Population centers served by wells sampled for this study include Chico, Gridley, Paradise, and Biggs in Butte County, Orland and Willows in Glenn County, Fort Jones, Tulelake, Mt. Shasta, and Weed in Siskiyou County, Alturas and Dorris in Modoc County, Portola in Plumas County, and Burney and Fall River Mills in Shasta County. Groundwater provides the sole source of the public supply to over 100,000 people Chico. Other areas that rely solely on groundwater are Willows, Orland, the City of Portola, the City of Alturas, the City of Fort Jones, the City of Mt. Shasta, the City of Tulelake, Dorris, Weed, Maxwell, and Fall River Mills. Two private retailers, two irrigation districts, and 11 public agencies participated in the CAS study.

Sampling and Analysis Procedures

Department of Water Resources (Northern District) personnel collected well water samples from 121 public water supply wells in the Sacramento Valley and Volcanic Provinces, with the assistance of well owners, during the summer and fall of 2003 (figure 7a and 7b). In addition, DWR personnel collected samples from 39 monitoring wells (figure 7a) using a gas-powered generator and submersible pump. Two spring water sources that are used as public supply are also included. Well identification information is given in Appendix B, Table 2. Each sample was collected directly at the sampling port, located upstream of 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.

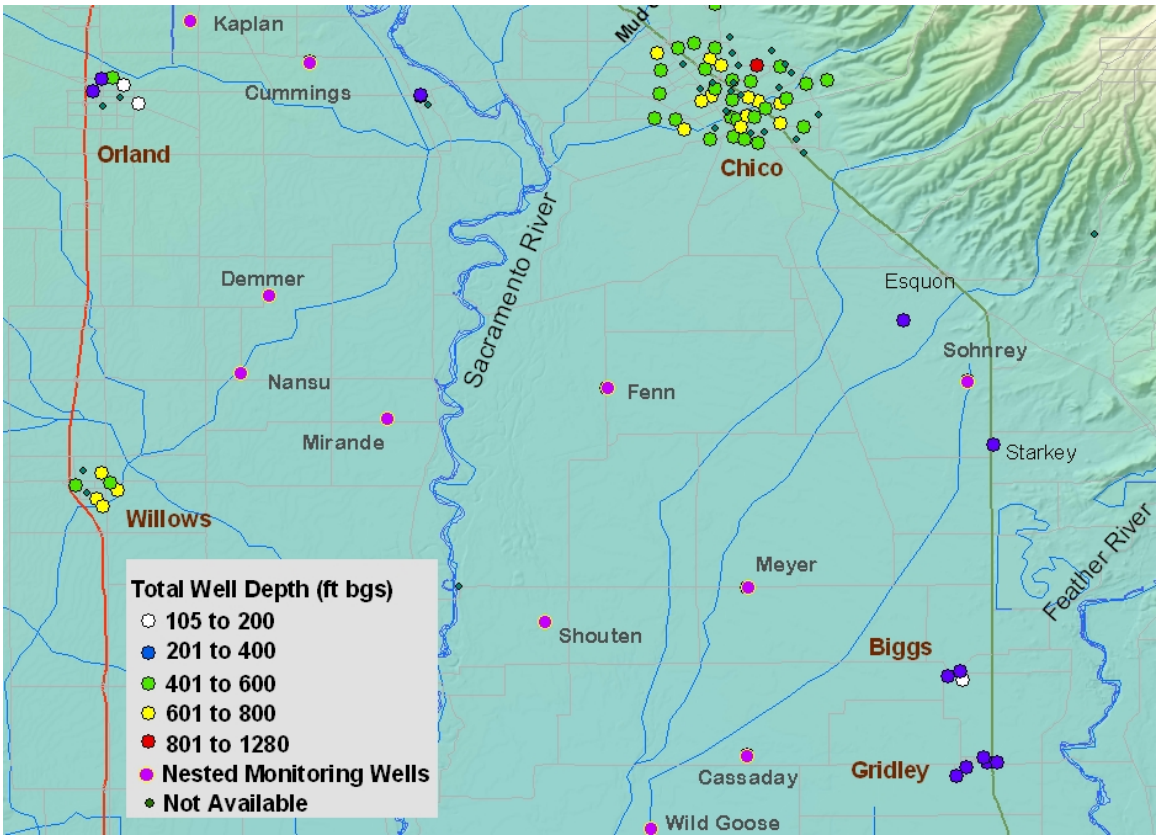

Figure 7a. Shown are sample locations for the Sacramento Valley, including the locations of nested monitoring wells and individual monitoring wells, identified by name.

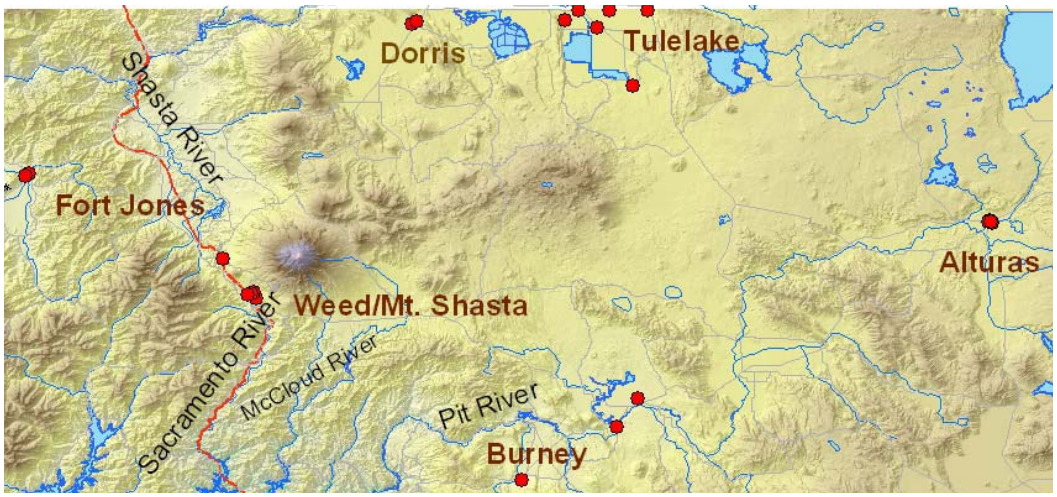

Figure 7b. Well locations for 'Volcanic Province' wells. Wells from Portola/Lake Davis are not shown.

Four different analyses are performed on each well water sample: 1) A set of VOCs (shown in Appendix B, 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.

Results

Compared to previous GAMA study areas, a huge geographic area is covered in this report. Only the Chico area has a high density of wells, where statistical analysis and interpretation of results can be carried out in detail. The other, smaller towns in the Sacramento Valley where wells were sampled (including Biggs, Hamilton City, Gridley, Willows, and Orland) will be discussed in the same sections as wells from Chico. Wells in Volcanic Provinces will be discussed separately in each section, as they have little in common hydrologically or geologically with wells from the valley areas. Towns and communities included under the Volcanic province designation include the City of Alturas, the City of Dorris, Burney Falls, the City of Weed, Fall River Mills, the Tulelake area, and the City of Portola near Lake Davis in Plumas county. The City of Fort Jones, with three public supply wells included in the study, is to the west of the Volcanic Province, in a small alluvial valley surrounded by granitic terrain. Results from Fort Jones wells are discussed in sections with Volcanic Province wells. Analytical results for the Sacramento Valley and Volcanic Province wells are shown in Table 3 and Table 4, Appendix B.

Uncertainties shown 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, p,m-Xylene, and toluene, were detected in VOC transfer and trip blanks over the course of sampling. MtBE was detected in 1 trip blank and 9 transfer blanks, with a maximum concentration of 49 ng/L; toluene was detected in 5 trip blanks and 35 transfer blanks with a maximum concentration of 32 ng/L; p,m-xylene was detected in 3 trip blanks and 7 transfer blanks, with a maximum concentration of 32 ng/L. Detections of these compounds occurred somewhat more frequently in blanks in this sampling campaign than in previous CAS sampling campaigns. 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 VOA vial. Because of the greater distances between sampling sites in this CAS area, blanks were held longer (up to 4 weeks), and leaching from the septum likely increases with a greater holding time in vials. 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 from the same sampling day. This raised the reporting limit above 5 ppt for 12 MTBE results, 8 p,m-xylene results, and 29 toluene results. If the result of a well water analysis is less than 5 ng/L, that result is retained, even if a corresponding blank had a detection of the reporting limit. The observed detections in transfer blanks are a testament to 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 where the possibility for contaminating a sample is minimal.

In the monitoring well sampling campaign, a submersible pump and gasoline-powered generator were used to collect samples. In previous studies where low-level techniques were employed, equipment blanks and 'transfer' blanks from monitoring well operations had detections of BTEX compounds, MtBE, and THMs. Transfer of the gasoline compounds from the exhaust of the gas generator to transfer blanks and well samples has been documented during sampling of monitoring wells. For this reason, and because a high degree of importance was placed on avoidance of reporting of 'false positives', low-level VOCs were not analyzed at monitoring wells. Results for low-level VOCs from private wells are likewise not reported because sampling conditions are not uniform or controlled.

Discussion of VOC Occurrence

Overall VOC occurrence is dominated by a high detection frequency in wells from the Chico area

The distribution of VOCs in the public water supply (PWS) and monitoring wells is shown in Figures 8-12. All of the compounds that were analyzed had at least two detections above the reporting limit. Twenty-eight wells (23% of those tested) delivered raw water that was below the reporting limit for all the compounds monitored. Eighteen more public supply wells (for a total of 37%) 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 in Dorris (1 of 2), Burney (3 of 3), Chico (11 of 62), Biggs (2 of 3), Gridley (1 of 5), Portola (1 of 4), Weed (4 of 6), Fort Jones (1 of 3), and Tulelake (4 of 6). Five wells in Orland, six in Willows, one in Tulelake, three in Chico, and all three wells in Hamilton City had detections of THMs only.

Fifty-one wells (41% of 123 public supply wells) had low level detections above the reporting limit of MTBE, with a maximum of 840 ppt, but only 4 wells had detections greater than 50 ppt. Thirty of the 51 detections are in Chico. Twenty-three wells had low level detections above the reporting limit of the solvent trichloroethylene (TCE), 19 of which are in Chico (figure 8), with a maximum concentration of 3300 ppt. Most significantly, 55 wells (45% of those tested, 45 detections from 62 wells in Chico) had PCE detections. The maximum concentration in a well was 580 ppb, while two more wells in Chico had PCE concentrations greater than 10 ppb, and three more had concentrations greater than 1 ppb. Outside of Chico, however, most detections were at concentrations more than two orders of magnitude below regulatory limits. In fact, twenty-six of the 55 detections were less than 56 ppt (the public health goal; PHG), and fourteen were less than 20 ppt, a level not previously quantifiable, even by specialized research analytical laboratories. 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. In Chico, treatment for chlorinated solvents takes place at drinking water wells with MCL exceedences.

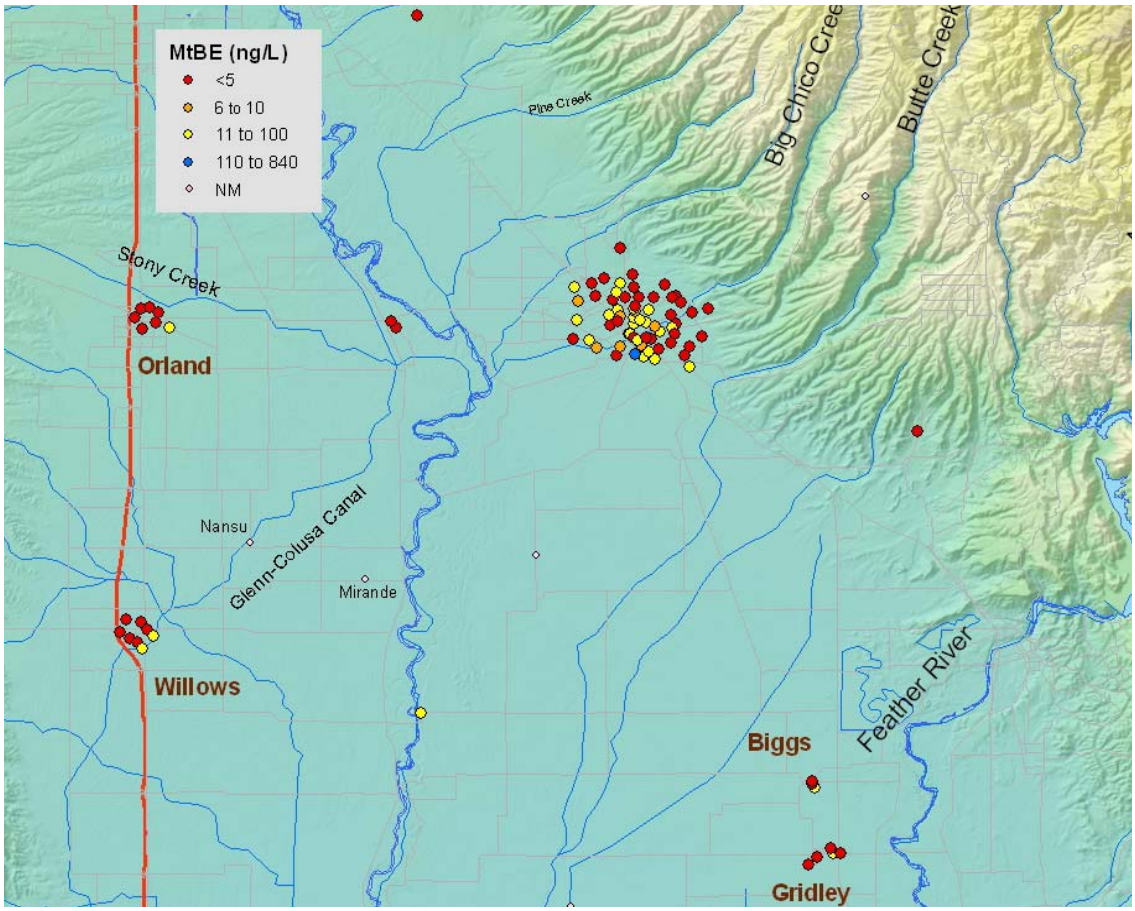

Figure 8. Non-point sources (precipitation, runoff, and boating) could explain MTBE concentrations below about 100 ng/L in drinking water wells. At least one detection in Chico is likely due to a point source (LUFT).

Low-level MTBE is frequently from non-point sources

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). 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 could explain the MTBE detected in nearly all of the wells where MTBE was found in the study area (figure 8). These 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). The occurrence of MtBE at concentrations of less than 100 ng/L can therefore be explained by recharge of water containing non-point source MtBE, including precipitation (MtBE in equilibrium solubility with MtBE in the atmosphere) and streams (runoff and recreational boating contributions). However, at least one detection in Chico, with a concentration of 840 ppt, is almost certainly the result of transport from a LUFT site. GeoTracker lists 110 LUFT

sites in Chico, 30 of which are open cases. Overall, 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.

Chloroform has multiple potential sources

THMs are by-products of the disinfection of drinking water. The source of low-level THMs can be advective transport of 'recycled' treated water, or residual from water treatment at or near the wellhead (fig. 8). At many of the public supply wells in the the study areas, 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 28 wells of the 75 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 all but one well (in Orland) 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. In addition, the Sacramento River consistently has low level chlorofrom detections and river water may be a source of chloroform in wells with a significant component of river water (e.g., in Maxwell). In that case, the THM is likely present due to advective transport of young water containing THMs. In 29 wells from Chico, chloroform was not accompanied by another THM, but did co-occur with PCE. In these cases, chloroform may be present as a solvent from industrial sources.

VOCs in Chico drinking water wells

VOC contamination of soil and groundwater in the Chico area was first reported in 1984 (DTSC Fact Sheet, March, 2004). Eventually 8 major plumes were defined, 6 of which are shown in figure 9 (those shown have PCE or TCE as the major contaminant). The Central Plume is known to affect drinking water wells included in the study, and is known to have migrated to the Deep Aquifer at concentrations of 20 ppb PCE. The North Central and Southwest Plumes are also known to affect active drinking water wells included in the study, where treatment now takes place before the water enters the distribution system. The purpose of the present study is not to track contamination back to individual plumes or to investigate migration of the contaminants from individual releases in detail. However, some useful information is added to that gathered during ongoing regulatory and cleanup studies through the use of the ultra-low analytical method employed here. Not surprisingly, a high frequency of occurrence and high concentrations are observed in raw water from wells downgradient of the major plumes (figure 9). Several occurrences that appear to be just upgradient of plumes may result from upgradient migration due to pumping. Very low level PCE detections in wells significantly upgradient (to the east/northeast) of the major plumes is evidence for other, smaller point sources, or for releases to groundwater from a distributed source such as sewer lines. Dense liquids like PCE are known to accumulate in at joints and low points

in sewer lines, where they may subsequently leak through cracks to the subsurface and into groundwater. Furthermore, the spatial extent of contamination from PCE is better defined by the ultra low level analytical method; only 12 wells, all in outlying areas, are not affected by PCE contamination. In particular, wells in the southeastern portion of the study area are not affected by either point sources or by distributed sources.

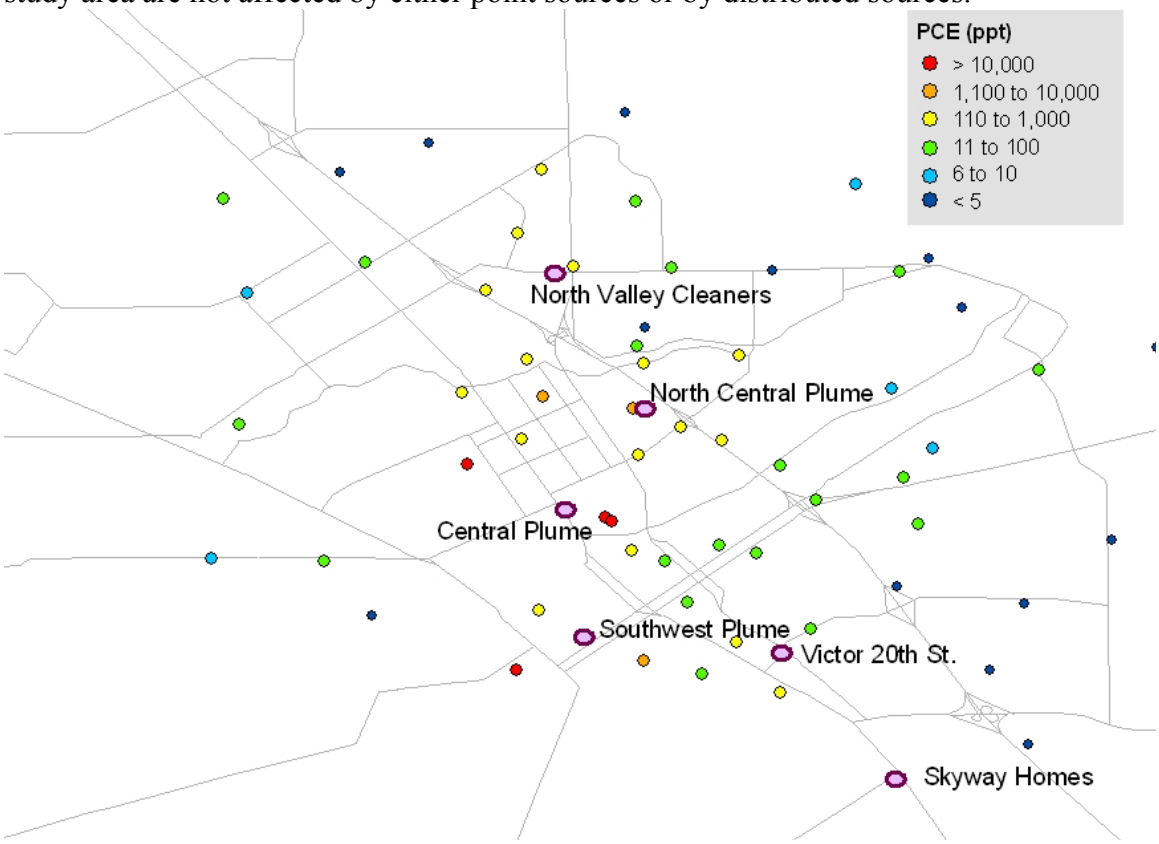

Figure 9. Results of low-level PCE analysis in Chico drinking water wells. The approximate location of the source areas for the major mapped PCE contamination sites (DTSC Fact Sheet, March, 2004) are shown as filled ovals. PCE detections upgradient of the major plumes suggest that there are other, distributed sources of low-level contamination.

TCE occurs in Chico wells less frequently than PCE, and often presumably as a PCE breakdown product. Breakdown of PCE to TCE is a likely explanation for the detections near the Central, North Central, and North Valley Cleaner plumes (figure 10). Four detections downgradient of the Victor 20th Street plume are from direct releases of TCE, the main contaminant identified for that plume (DTSC Fact Sheet, March, 2004).

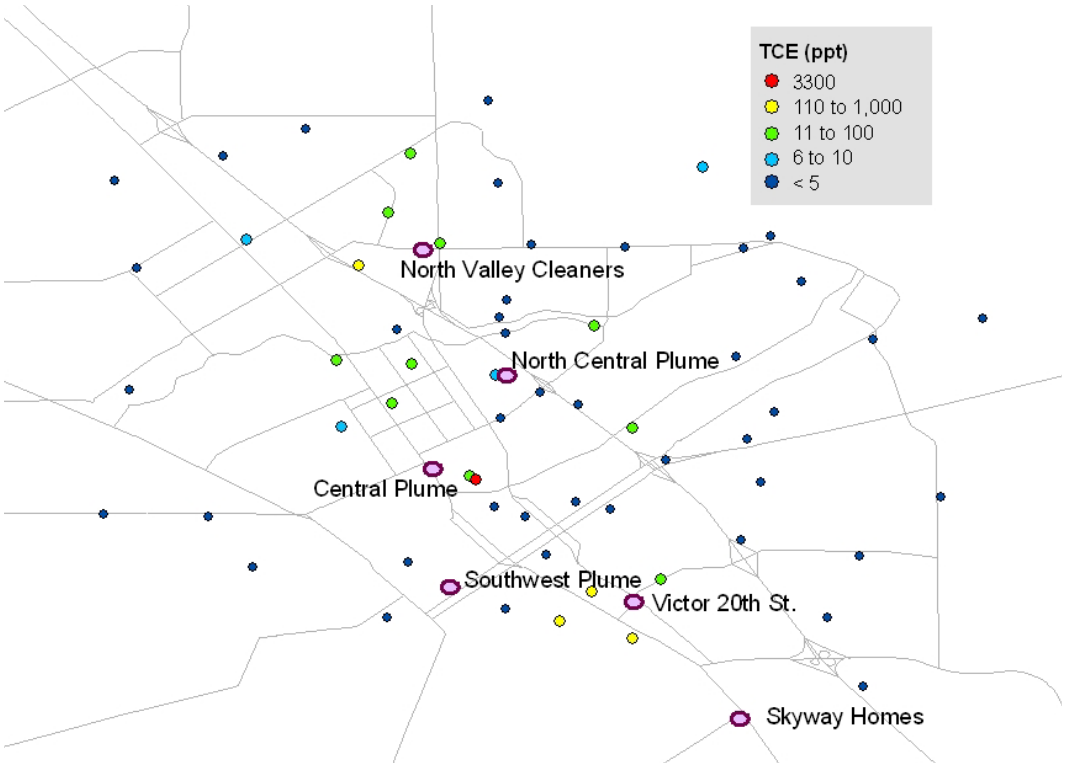

Figure 10. Results of low-level TCE analysis in Chico drinking water wells. The spatial distribution indicates that TCE occurs as a breakdown product of PCE, except in the vicinity of the Victor 20th St. plume.

While the frequency of occurrence of the chlorinated solvents is high in the Chico area, a similar detection frequency has been reported for other CAS areas (figure 11). For example, 72% of public supply wells in Bakersfield had detections above 5 ng/L PCE (Moran et al., 2004). The contrast between detection frequencies in coastal versus Central Valley areas is likely due to differing hydrogeologic conditions. (In addition to frequency of occurrence, the relationship between PCE occurrence and groundwater age differs for the two regimes. In coastal basins with significant artificial recharge, PCE is most commonly found in young groundwater near recharge areas, and is likely due to mobilization of numerous point sources in the recharge areas (Shelton et al., 2001; Moran et al., 2002). In contrast, PCE is found ubiquitously, and frequently in old groundwater in Central Valley basins (Wright et al., 2004; Moran et al., 2003)). Continuous clay confining units in Coastal basins seem to provide an effective barrier to downward migration of contaminants, while the semi-confined aquifers prevalent in Central Valley basins allow some vertical transport of contaminants. Infrequent, low-level PCE detections in Orland, Gridley, Portola, and Dorris are a testament to the ubiquity of this chemical in modern-day environments.

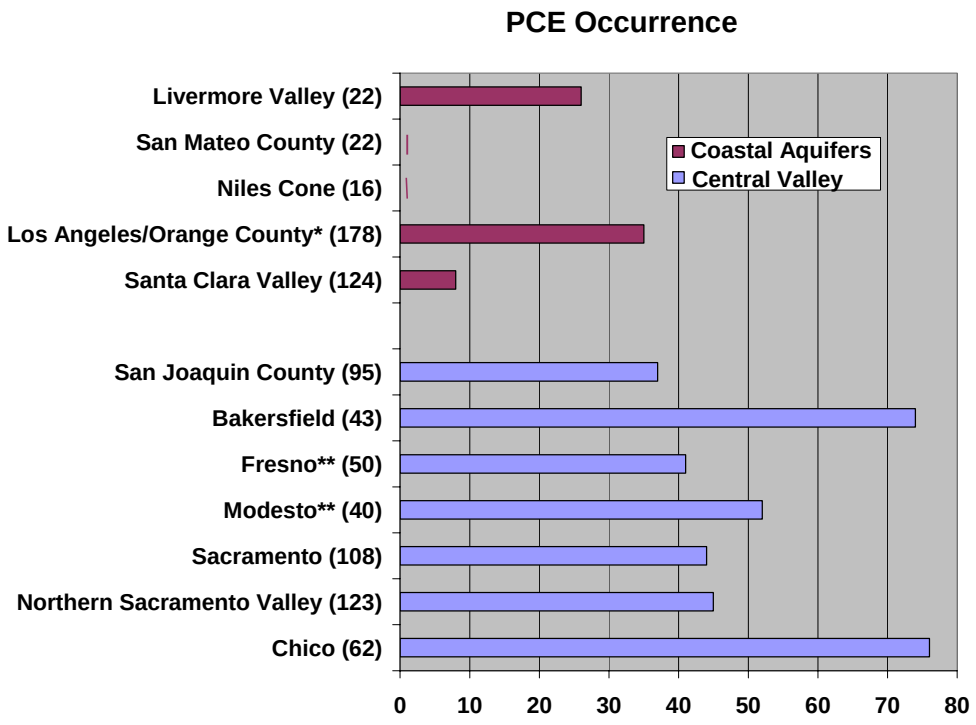

Figure 11. A comparison of percent of wells with PCE occurrence in GAMA focus areas reveals the ubiquity of low-level PCE in public supply wells in Central Valley study areas. Numbers in parentheses are the number of public supply wells sampled and analyzed for low-level PCE in the study area. Chico results are included in the overall results shown for the northern provinces. *USGS results from Shelton et al., 2001, with a lower reporting limit of 10 ng/L. **USGS results from Wright et al., 2004, with a lower reporting limit of 10 ng/L.

VOCs in Volcanic Provinces

VOCs were detected infrequently in wells from the Volcanic Provinces. Extremely low-level MtBE was found in two production wells from Tulelake, 3 wells from Portola, all 4 wells in the City of Alturas, one well in Dorris, two wells in Fort Jones, and one in the City of Weed (39% of PWS wells from Volcanic Provinces; figure 12). Groundwater ages could not be determined at many of these wells (see discussion below), but measured tritium concentrations are consistent with recent recharge (except in two Tulelake wells which have extremely low tritium concentrations). The presence of MtBE is therefore likely due to non-point, surface sources that contain MtBE at very low concentrations from recreational boating sources (atmospheric deposition is expected to be a minor contributor in these rural areas). Concentrations in one well from Alturas (130 ppt), and three in Portola (51, 83, and 110 ppt) are somewhat higher than levels expected for precipitation or runoff in these non-urban settings, and a point source such as a leaking underground fuel tank (LUFT) may contribute MtBE. Low-level chloroform was detected in 8 of the 31 PWS wells from Volcanic Provinces – in all but one of those wells, MtBE was also detected, suggesting that chloroform may also have a surface water/recent recharge source. In the three wells with the highest chloroform

concentrations (> 350 ppt), the other THMs co-occurred at similar concentrations, which points to their presence as residuals from on-site operations.

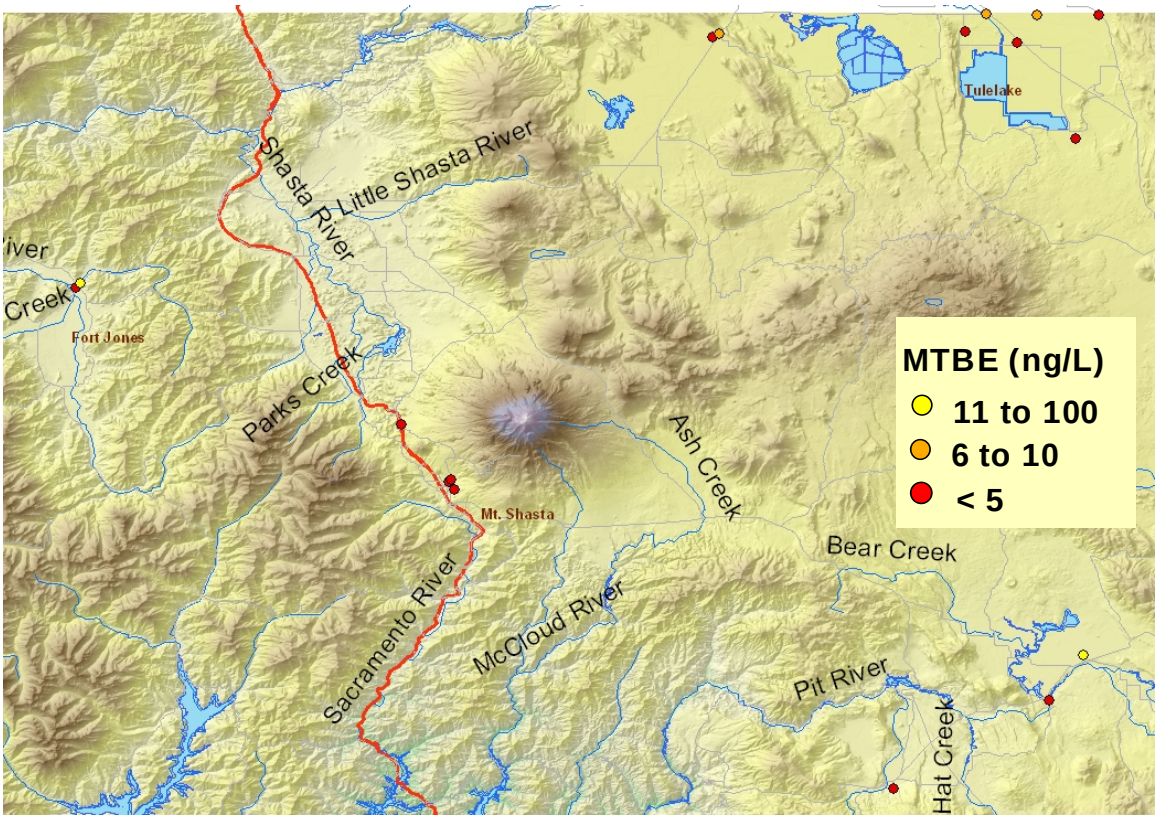

Figure 12. Results of MtBE analyses for Volcanic Province wells.

In addition to detections of MtBE and THMs, one PWS well in Dorris had detections of BTEX, PCE, and TCE, at very low concentrations. Interestingly, this well is one of the few wells from the Volcanic Provinces that does not tap a mantle helium component of the groundwater, and had a higher tritium concentration (with a calculated age of 23 years) than other wells from the same area. Another well from the City of Weed had a low level BTEX detection, and no other VOCs, while 3 PWS wells in Portola had PCE detections (1 with a TCE co-occurrence and 2 with 1,1,1 TCA co-occurrences).

Discussion of Isotopic and Groundwater Age Results

Isotopic tracers indicate river water recharge and pre-modern groundwater

The ratio of oxygen isotopes in the water molecule ($\delta^{18}O$) is a useful isotopic tracer for determining recharge water source in the areas studied. As seen in figures 13-16, $\delta^{18}O$ values recorded in wells from the study area range from -14.7‰ in Weed to -6.0‰ in a shallow monitoring well in the southeastern portion of the study 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 low-lying Sacramento Valley's geographic location, adjacent to the foothills and mountains of the Sierra Nevada. $\delta^{18}O$ values in the range -

7.5‰ to –8.5‰ are expected for locally-derived water (precipitation) from the Sacramento Valley. 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 5, Appendix B gives $\delta^{18}O$ values for some major northern California rivers and surface water bodies, measured over the last few years at LLNL. River 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‰), thus allows the possibility of tracing river water recharge in groundwater.

Stable Isotopes Mark Recharge from Perennial Streams

The pattern observed in the wells tested in Chico clearly shows that wells closest to Big Chico Creek have $\delta^{18}O$ values that are depleted compared to locally-derived water. $\delta^{18}O$ values steadily become more enriched in wells further from the creek to the north and south (figure 13). Several wells with $\delta^{18}O$ values between –8.3‰ and –8.7‰ in the Sacramento Valley delineate the range observed for locally-derived water. Long losing reaches along Big Chico Creek are likely induced by the large-scale pumping that has resulted in water level depressions to the north and south of the creek. Recharge of surface water streams draining the Sierra Nevada occurs in several Central Valley groundwater basins where groundwater is heavily exploited. This phenomenon is observed in previous CAS study areas (e.g., Moran et al., 2003). With a much smaller sample set, the same pattern is evident in the six wells from Orland, to the south of Stony Creek. The effect is less pronounced on the western side of the valley, with a smaller range observed, because Stony Creek has its headwaters in the Coast Range, which has significantly lower elevations than the Sierras. Recharge of Stony Creek water carries a $\delta^{18}O$ signature of approximately –9.5‰, and wells further from the creek have more enriched values. In Willows, at least two wells show evidence for recharge from the unlined Glenn-Colusa canal, which carries Sacramento River water. Similarly, wells in Gridley have $\delta^{18}O$ values that are too depleted to reflect exclusively local water, and Feather River water likely provides a component of recharge.

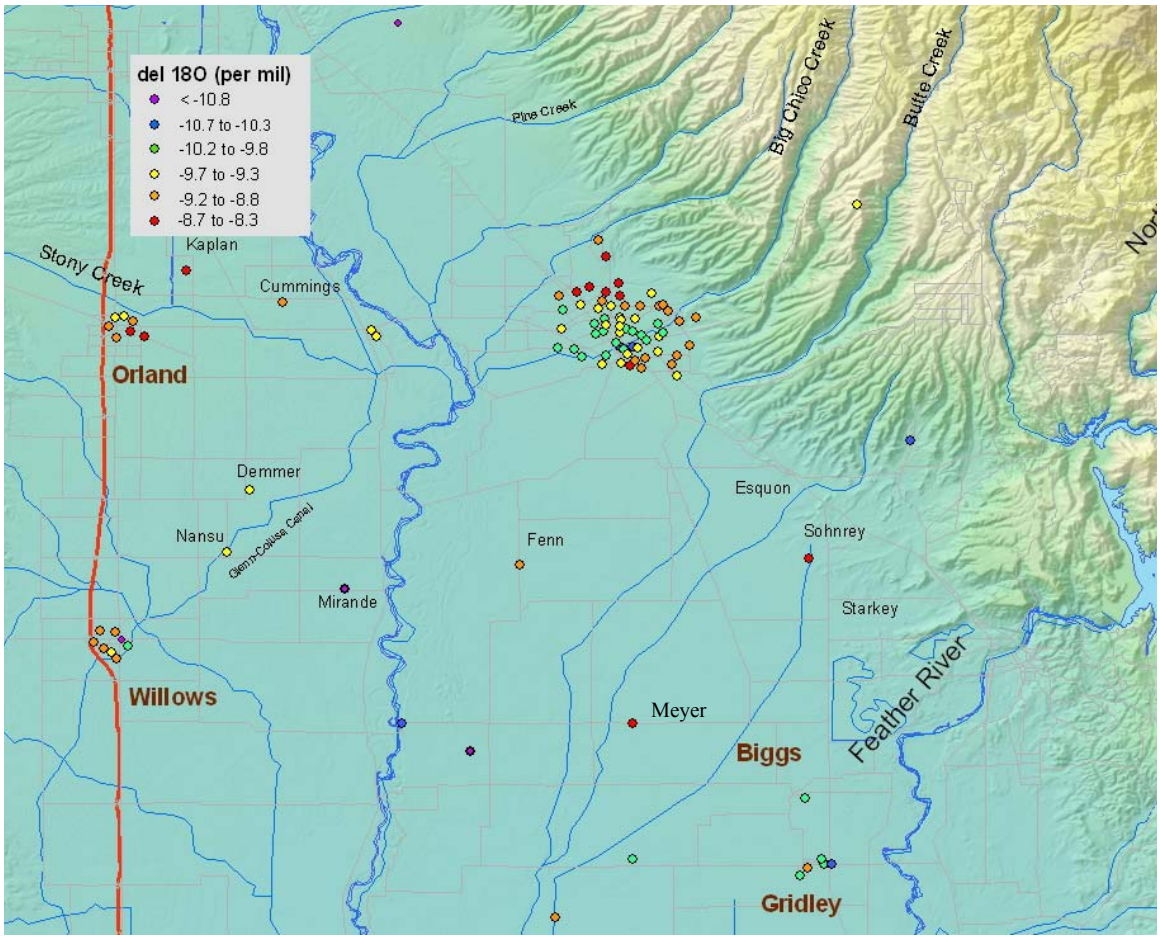

Figure 13. Oxygen isotope ratios reveal the influence of Big Chico Creek on recharge in Chico, and of Stony Creek in Orland. Other depleted ratios reflect recharge from the large rivers, either directly or via irrigation return flow.

In general, wells from Volcanic Provinces have highly depleted $\delta^{18}O$ signatures that reflect locally derived, high elevation recharge sources (figure 14). In particular wells in Weed, on the southwestern flank of Mt. Shasta, and wells in Alturas, in the Pit River watershed, have the most depleted signatures; <-14‰. Other wells have $\delta^{18}O$ values of less than about –13‰. Two wells near Tulelake stand out in this subset of wells. Water likely has a long residence time in the lake (sump) and becomes significantly evaporated, which causes enrichment in $\delta^{18}O$. The well just to the south of the lake, and one well to the north of lake (figure 14), with $\delta^{18}O$ values greatly enriched compared to wells in surrounding areas (-6.6‰ and –10.6‰, respectively, compared to –13‰ to –14‰ for other wells) produce a significant component of (evaporated) Tulelake water. The same phenomenon occurs in Lake Davis, where lake water has an observed $\delta^{18}O$ of –5.6‰, due to significant isotopic fractionation during evaporation. Public supply wells in the City of Portola, however, have $\delta^{18}O$ values between –13.7‰ and –14.3‰, and show no evidence for a contribution of Lake Davis water. A greater spatial and temporal coverage in both surface water and well water $\delta^{18}O$ and δD data is necessary to allow more detailed interpretation of surface water – groundwater interaction near mountain lakes.

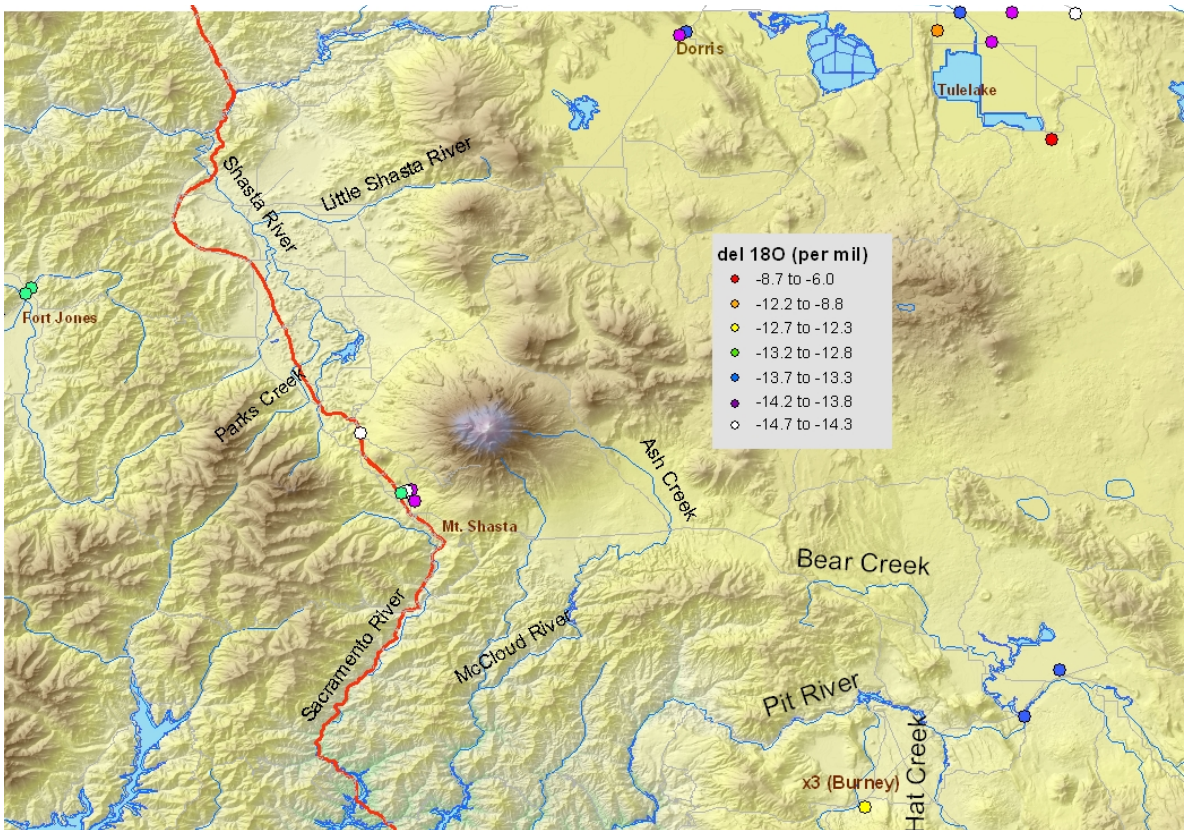

Figure 14. Oxygen isotope results for Volcanic Province wells are highly depleted in general, but enriched values are evidence for recharge of evaporated water in the Tulelake area.

Monitoring wells spaced across the Sacramento Valley display a large range in measured $\delta^{18}O$. Two shallow wells on the eastern flank of the valley (Starkey and Esquon) have enriched $\delta^{18}O$ values compared to other wells, and fall below the trend of the local meteoric water line on a plot of $\delta^{18}O$ versus δD (figure 15). These wells are in an area where flood irrigation is practiced on a large scale, and thus produce water that has been evaporated, as evidenced by an enrichment of heavy stable isotopes (to a greater degree for δD than for $\delta^{18}O$). Other nested monitoring wells on the eastern side of the valley (Sohnrey and Meyer - shallow) have $\delta^{18}O$ signatures that indicate recharge of locally derived water, in the range –8.2‰ to –8.7‰.

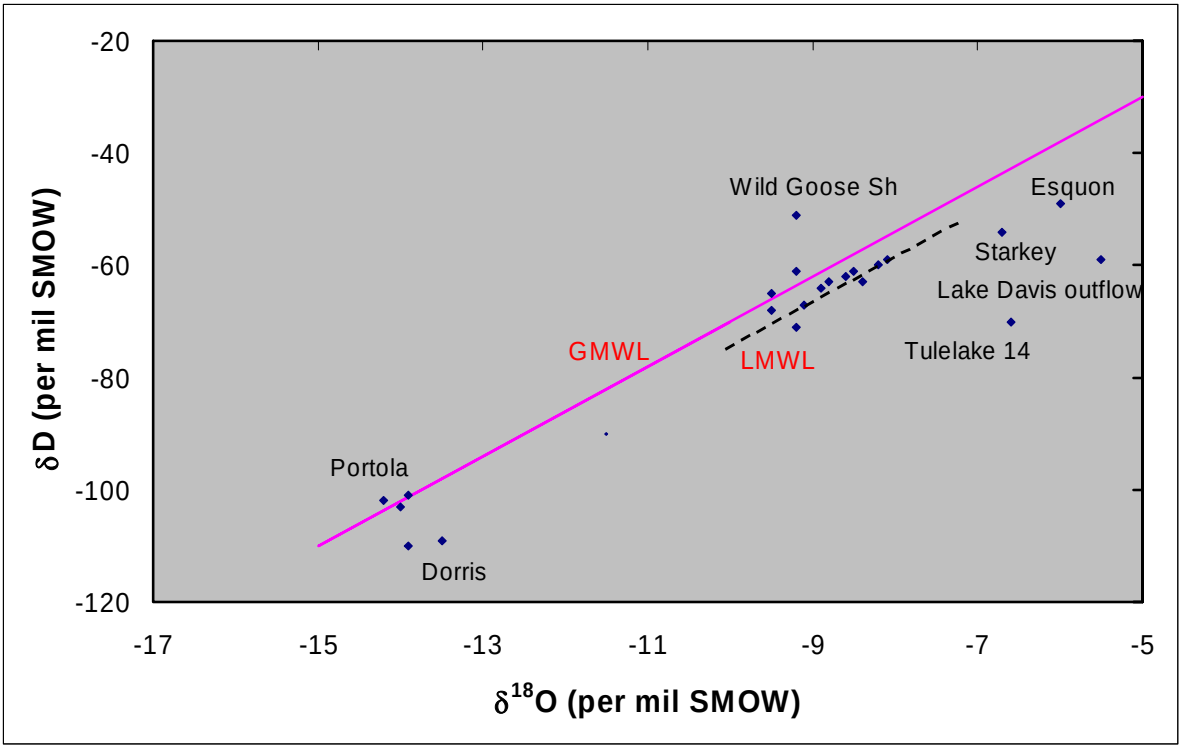

Figure 15. Plot of $\delta^{18}O$ vs. δD for a subset of samples analyzed for δD. Evaporation is indicated by points that fall below the local meteoric water line (LMWL), which is typically somewhat below the global meteoric water line (GMWL).

To the west, somewhat more depleted values are observed in shallow monitoring wells, while the deepest monitoring wells have very depleted values. Wild Goose monitoring wells are likely influenced by recharge from the adjacent Cherokee Canal ($\delta^{18}O$ = -10.6‰), or by recharge of irrigation water diverted from the canal. The $\delta^{18}O$ values recorded in monitoring wells in the central and western parts of the valley therefore likely reflect the main source of irrigation water, which is the Sacramento River. Direct recharge from the Sacramento River, or recharge of applied irrigation water from the Sacramento River also accounts for the $\delta^{18}O$ values observed in wells in Maxwell, Hamilton City, and Butte City. Relatively young groundwater ages (discussed below) in production wells in Hamilton and Butte City support the direct-river recharge interpretation. Deep wells from the Mirande, Demmer, Nansu, and Shouten nested sets have highly depleted values (down to –11.6‰), and multiple lines of evidence for the presence of paleowater (see discussion below under radiogenic ^{4}He heading). This water recharged ten to twenty thousand years ago, when a cooler climate gave rise to depleted $\delta^{18}O$ values (Clark et al., 1997; Andrews and Lee, 1979).

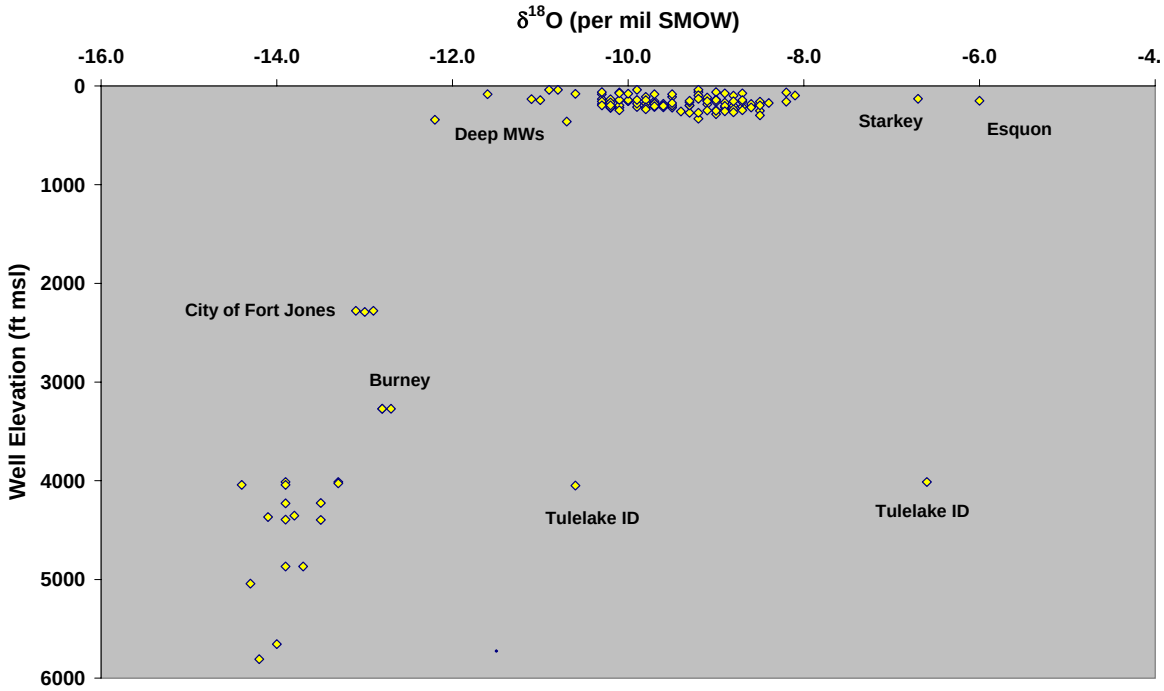

Figure 16. Comparing measured $\delta^{18}O$ with the elevation of the sampled well shows the range observed in valley wells, including evaporated signatures in at least two monitoring wells on the eastern side of the valley, and enriched signatures in deep monitoring wells, where there are multiple lines of evidence for the presence of paleowater.

A plot of measured $\delta^{18}O$ versus well elevation illustrates the effects of evaporation on high elevation samples (such as those from the Tulelake area), and reveals the presence of paleowater in deep monitoring wells from the valley (figure 16). The bimodal distribution in well elevations (valley wells versus wells from areas at elevations over 2500 ft), results in a clear separation of wells from outside the valley in the lower left-hand corner, with depleted $\delta^{18}O$ signatures indicating locally-derived waters. The two Tulelake samples fall off the trend due to the evaporative enrichment of lake water described above. A few deep monitoring wells from within the valley have very depleted $\delta^{18}O$ values due to the presence of paleowater, as described above. The range observed in wells from the valley (-8‰ to –10.5‰) reflects the range in the two important source components – local precipitation, and streams that carry water from higher elevations, which enter the groundwater system via percolation of irrigation water and direct recharge from rivers and streams.

Tritium Concentrations and Groundwater Ages Reveal a Dynamic Shallow System and a Slow Flow Regime at Depth

A histogram of tritium concentrations measured in groundwater samples from the Sacramento Valley and Volcanic Provinces is shown in figure 17. Seventy four samples (44% of samples) have tritium concentrations of less than 3 pCi/L – a level that indicates that more than approximately 80% of the groundwater produced from the well recharged before 1950. Forty-seven of those wells (28% of wells) have tritium concentrations of

less than 1 pCi/L, indicating that more than 90% of the groundwater recharged before 1950. Twenty of the 'tritium dead' (< 1 pCi/L) wells are monitoring wells, which are more likely to have very low tritium concentrations because they draw water from a shorter vertical interval, and do not mix water from shallow zones. Figure 18 illustrates the effect of the depth to the top perforation on the tritium concentration. While some wells with a top perforation depth of less than 300 ft bgs have very low tritium concentrations, nearly all wells with top perforation depths below about 300 ft have extremely low tritium concentrations. Still, 26 long-screened production wells (16 in Chico) produce tritium-dead groundwater (<1 pCi/L), and 48 production wells (26 in Chico) produce groundwater with a tritium concentration less than 3 pCi/L. This result has major implications for groundwater management since recharge to these wells takes place on a time scale of at least several decades, and continued high volume extraction is probably not sustainable without mitigation measures such as large-scale artificial recharge.

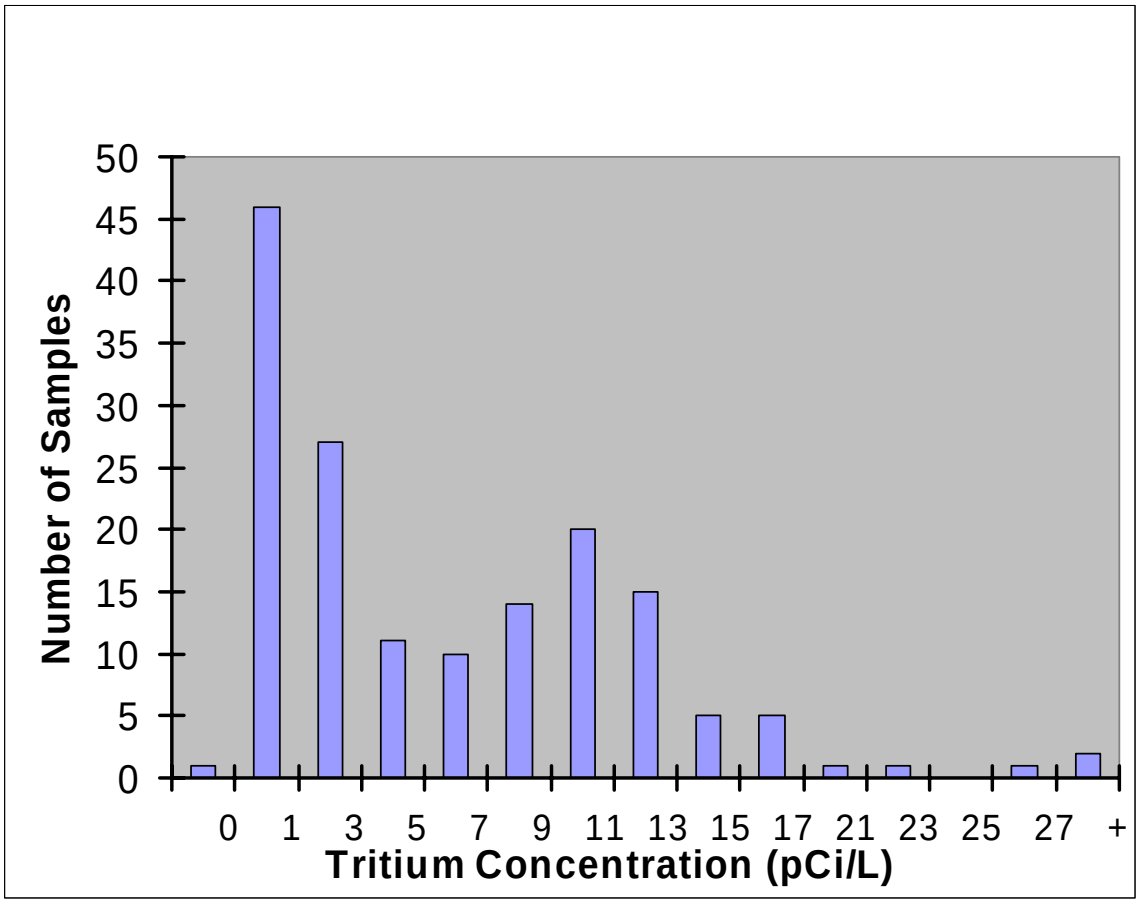

Figure 17. The histogram of tritium concentrations for all wells in the study area reveals the large number of low-tritium samples, and few wells containing 'bomb pulse' tritium at the upper range of measured values.

Samples with tritium concentrations greater than 3 pCi/L have a roughly normal distribution about 11 pCi/L – the approximate concentration of tritium in present-day

precipitation and surface water (figure 17). The presence of 'bomb-pulse' tritium (figure 1) is evident in samples with tritium concentrations at the upper range of observations. Lower tritium concentrations are the result of radioactive decay or of mixing with low-tritium groundwater, or both. Analysis of ^{3}He, and quantification of tritiogenic ^{3}He (figure 3) distinguishes decay from dilution of tritium, and allows determination of groundwater age. The spatial pattern in groundwater age is related to the pattern in tritium concentration (figures 19 and 20), but gives a direct measure of the residence time for the post-modern (tritium-containing) portion of the groundwater.

Very few young groundwater ages are observed in Sacramento Valley wells. One well in Hamilton City, adjacent to the Sacramento River, has a groundwater age of 10 years, and one well in northernmost Chico, adjacent to Mudd Creek, has a groundwater age of 8 years. Relatively young groundwater ages (13 to 20 years) are observed in three other wells in Chico, adjacent to Big Chico Creek, in one well in Butte City adjacent to the Sacramento River, in two wells in Orland, and one in Willows. (As noted below in the volcanic province results, wells in Burney and Fort Jones produce uniformly young groundwater (8 to 10 years), three wells in Portola/Lake Davis produce young groundwater, and tritium concentrations in wells from Weed are close to the present-day atmospheric concentration, and hence likely indicate very young groundwater.)

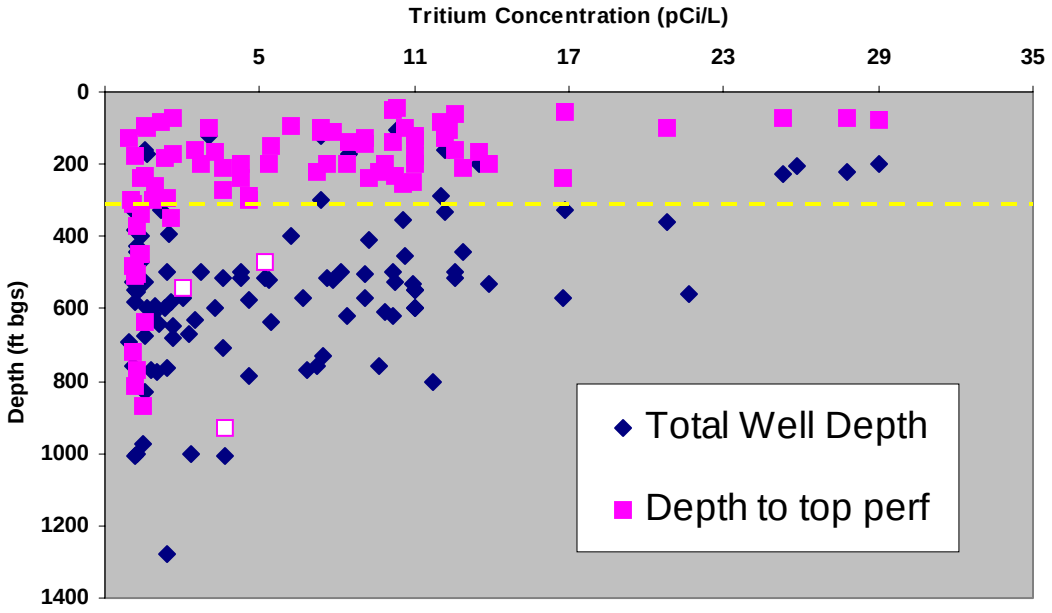

Figure 18. Except for three monitoring wells in the western portion of the study area (shown by open symbols), significant tritium concentrations occur only in wells with top perforations shallower than 300 ft bgs. Tritium concentrations are not a clear function of total well depth.

Overall, relatively young groundwater is produced from Orland, Willows, and Hamilton City drinking water wells. Orland's location, on the Stony Creek fan, is an area of relatively rapid recharge of Coast Range drainage in unconsolidated, coarse-grained fan sediments. While VOC observations are few in number, these wells should be considered relatively vulnerable to contamination. In Willows, VOC detections are limited to two low-level MTBE occurrences. Three wells have very low tritium concentrations, produce old groundwater, and have low vulnerability to contamination. Four more wells in Willows produce younger groundwater and have higher vulnerability. Hamilton City wells have shallow top perforations, relatively young ages with low fractions pre-modern, and stable isotope signatures that are consistent with Sacramento River water recharge. These three wells are therefore relatively vulnerable to contamination. However, other than very low-level THMs, VOCs were not detected in these wells.

Groundwater ages in Chico span a wide range, from 8 to greater than 50 years, but only 5 wells in the main urban area (and 2 others to the north, near the airport) have calculated ages of less than 25 years. Most wells, 29, have calculated ages between 25 and 45 years, and produce large proportions of pre-modern water. The groundwater age reported for these wells is the age of the small fraction of water in the sample that contains tritium. Many of these wells have VOC detections, especially of PCE, and the concentrations observed are likely depressed by the pre-modern groundwater component, which likely contributes little or no PCE. The spatial pattern in both tritium concentration, and groundwater age (figure 19 and figure 20) shows very old groundwater in wells that form a semi-circle that is open to the west/southwest. Drinking water wells that back up to the foothills to the east, and wells to the north of Lindo Channel produce almost exclusively pre-modern groundwater. While 12 of the very low tritium wells do not have PCE detections, 14 of the wells producing old groundwater (<3 pCi/L tritium) do have low-level PCE detections. This is in sharp contrast to results from coastal alluvial basins in California (Shelton et al., 2001, Moran et al., 2003), where wells producing old groundwater are nearly always free of VOCs. 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 DNAPL or along a continuous vertical geologic feature, can be inferred in the vicinity of those wells.

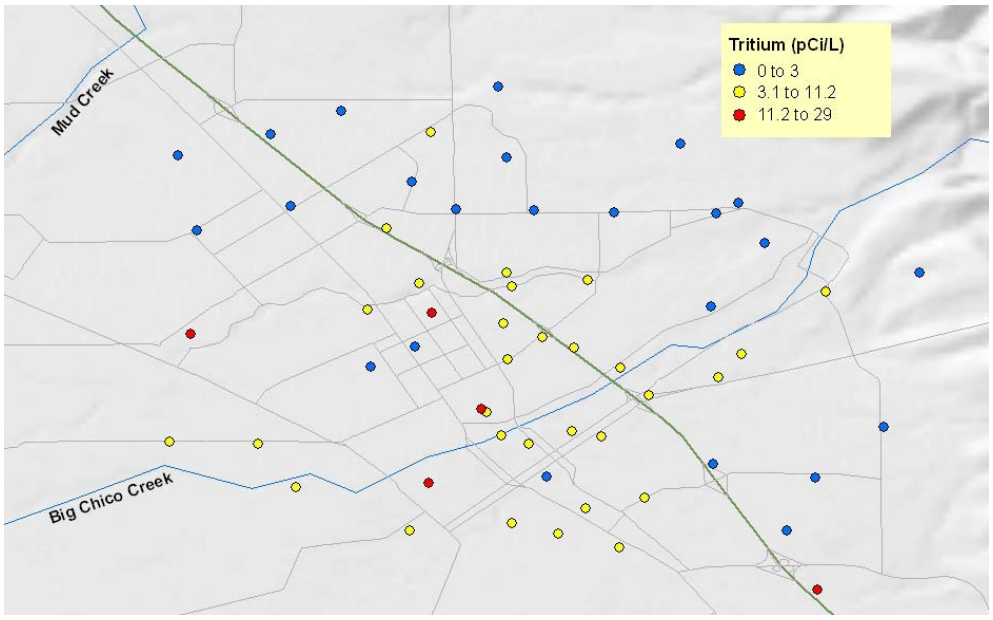

Figure 19. Tritium concentrations are shown in wells from the Chico area, with low concentrations occurring in an arc along the foothills.

Groundwater flow direction and bulk groundwater flow rate can be inferred from a collection of groundwater ages. This analysis is complicated, however, by the characteristic long screened interval of production wells, which draw groundwater from different aquifers, over a wide range of depth, usually with a broad age distribution. In Chico, where the sampling density is highest, well depth and screened intervals are similar for many of the wells included in the study, so a comparison of groundwater ages is useful in determining the pattern of *relative* ages between wells. If the major source of recharge to Chico wells were the foothill areas to the east, one would expect to observe decreasing groundwater ages in an east to west pattern. However, almost exclusively pre-modern groundwater dominates the age distribution in groundwater to the east, while somewhat younger ages are observed in wells close to Big Chico Creek in central and western Chico, and in two wells close to Mud Creek, to the north of Chico. This pattern suggests that Big Chico Creek is a major source of recharge, and has been for at least three decades. Overall, relatively old ages and low tritium concentrations (indicating large fractions of pre-modern water drawn at individual wells) indicate relatively low recharge rates and slow groundwater flow, at least over the intervals sampled by production wells. As noted above, more rapid flow and recent recharge is indicated in Hamilton City, Butte City, Maxwell, and in Orland (and for some wells in Willows), where younger groundwater ages and a clear link to surface water are observed.

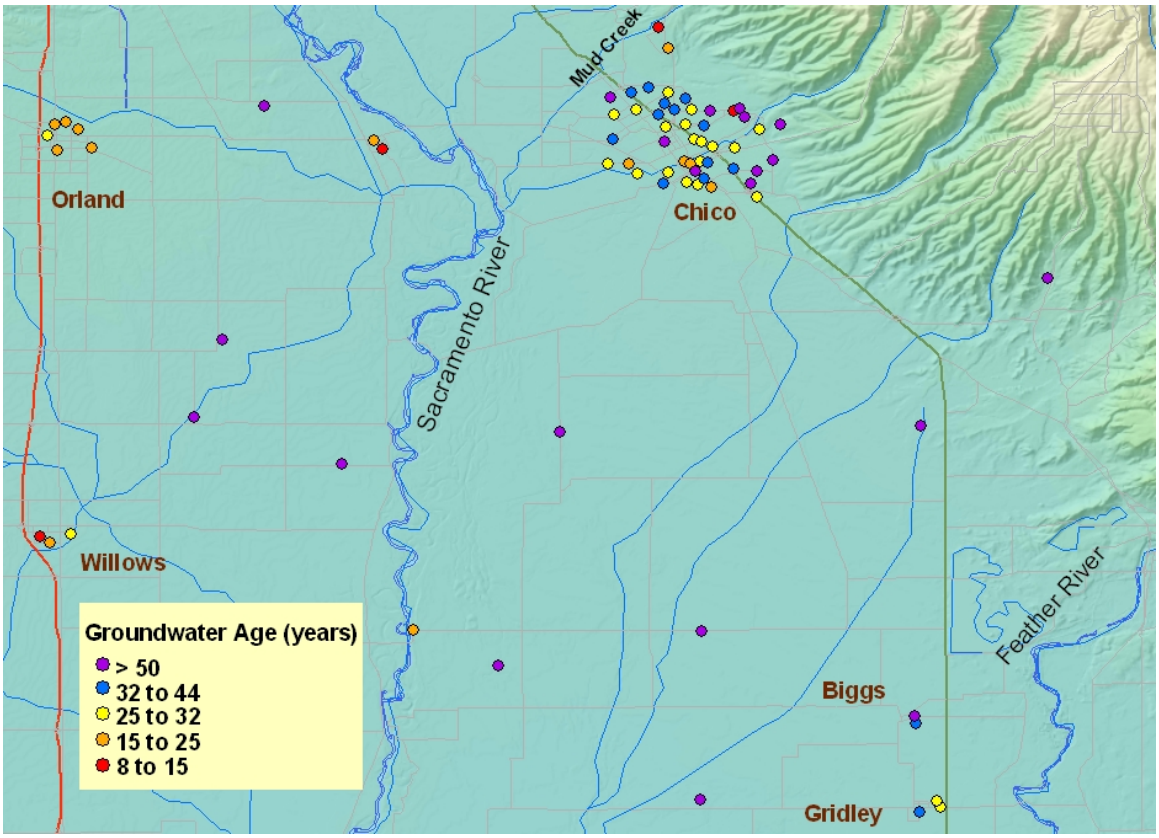

Figure 20. Calculated mean groundwater ages from tritium-helium analyses. Wells with tritium concentrations below 1 pCi/L have purple symbols and produce >90% pre-modern groundwater. For nested monitoring wells, results from the well with the deepest screened interval are displayed.

Mantle Helium is Prevalent in Public Supply Wells from Volcanic Provinces

As discussed in the background section above, primordial fluids that emanate from the earth's mantle have distinct $^{3}He/^{4}He$ ratios. The presence of mantle helium in a dissolved gas sample complicates (and sometimes precludes) the calculation of groundwater age by the tritium-helium method. In this study area, a significant component of mantle helium is found in 16 public supply wells from northern counties. For example, all four drinking water wells in Alturas, all 7 production wells in the Tulelake area, one well in Dorris, and both production wells in Fall River Mills have strong mantle signatures. The strongest mantle signal of all is from a drinking water well in Weed, where all four wells sampled show evidence for mantle helium. (Two spring sources sampled in Weed show evidence for gas loss, so a determination of a mantle component cannot be made.) A mantle signature is expected in Weed, situated on the western flank of Mt. Shasta, where volcanic activity brings mantle fluids close to the surface. Similarly, the Medicine Lake volcano and lava beds – part of a large volcanic region that encompasses northeastern California and southeastern Oregon, affect wells in Alturas, Tulelake, and Dorris. In the Fall River Valley groundwater basin, major springs are points of discharge for a flow system that is postulated to originate at the Tulelake basin and flow beneath and through the Medicine Lake Highlands (DWR Bulletin 116, Rose et al., 1996). Two wells in Fall

River Mills, in the distal portion of the flow field, have substantial mantle helium components that show the affect of the volcanic activity to the north.

Three wells in Burney and three in Fort Jones, however, do not show evidence for mantle helium. In Burney, shallow public supply wells presumably tap only Quaternary lake deposits or underlying colluvium where groundwater is not influenced by deeper volcanic formations (Rose et al., 1996). Groundwater ages and tritium concentrations indicate uniformly young groundwater, and $\delta^{18}O$ values indicate local recharge, so a localized flow system with the Quaternary unit may provide all of the groundwater to these 3 wells. Similarly, public supply wells in Fort Jones are at most 159 ft deep, and are situated in a narrow alluvial floodplain deposited by the Scott River and its tributaries. Recharge to the water-bearing alluvium is via underflows and surface runoff originating from southern and western tributaries (DWR, Bulletin 118). Groundwater ages of less than 10 years and low-level MtBE detections indicate rapid turnover of groundwater, and no contribution from deep-seated fluids. In Portola/Lake Davis, two public supply wells have ages of 7 and 14 years, and should be considered vulnerable to contamination. Isotopic results for a spring used for public water supply suggest a short subsurface residence time for that groundwater as well.

Newly installed, high capacity irrigation wells in the Tulelake area, and two City of Tulelake drinking water wells deserve further discussion because of the recent water crisis in the Klamath Basin. Historically, groundwater use in the basin has been minor. The irrigation wells were constructed as emergency back-up for the Tulelake Irrigation District as alternate water supply for agriculture, in the face of reduced surface water deliveries (DWR, Bulletin 118). Two of the 7 production wells sampled for the present study are relatively shallow, with top perforations above 300 ft bgs. These two wells (one to the north and one to the south of the Tulelake sump) have highly enriched $\delta^{18}O$ values that clearly indicate evaporated sump water as their main recharge source. The 5 deeper wells are producing groundwater with depleted $\delta^{18}O$ signatures, indicating an unevaporated, local, high elevation source of recharge. Interestingly, all 7 wells produce 'tritium dead' (pre-modern) groundwater - even shallow wells with lake recharge signatures. Despite evidence for local recharge to these wells, a long turnover time and slow flow regime are indicated by the lack of tritium.

Radiogenic ^{4}Helium Concentrations Give Additional Information about the 'Pre-modern' Groundwater Component

Calculated concentrations of radiogenic ^{4}He are shown on figure 21. Radiogenic ^{4}He concentrations in the basin give additional information about the pre-modern component of groundwater that is present in many wells in the study area. Conversion of these concentrations to groundwater residence times is highly inexact, as noted in the background section, and subject to uncertainties in the distribution of U and Th in host aquifers, and in mixing with more recently recharged groundwater. Still, the observed spatial pattern gives some information about where very old groundwater is being produced at wells. Drinking water wells in Chico, Orland, Willows, and Gridley, and wells north of Stony Creek produce water with uniformly low radiogenic ^{4}He concentrations, indicating an insignificant contribution from groundwater more than a

few hundred years old. Accordingly, the age distribution in most of these wells is dominated by a component that has an aquifer residence time of greater than 50 years but less than a few hundred years. In contrast, deep monitoring wells, especially in the southern and western parts of the study area produce groundwater with very high radiogenic ^{4}He concentrations, indicating groundwater residence times greater than 10,000 years.

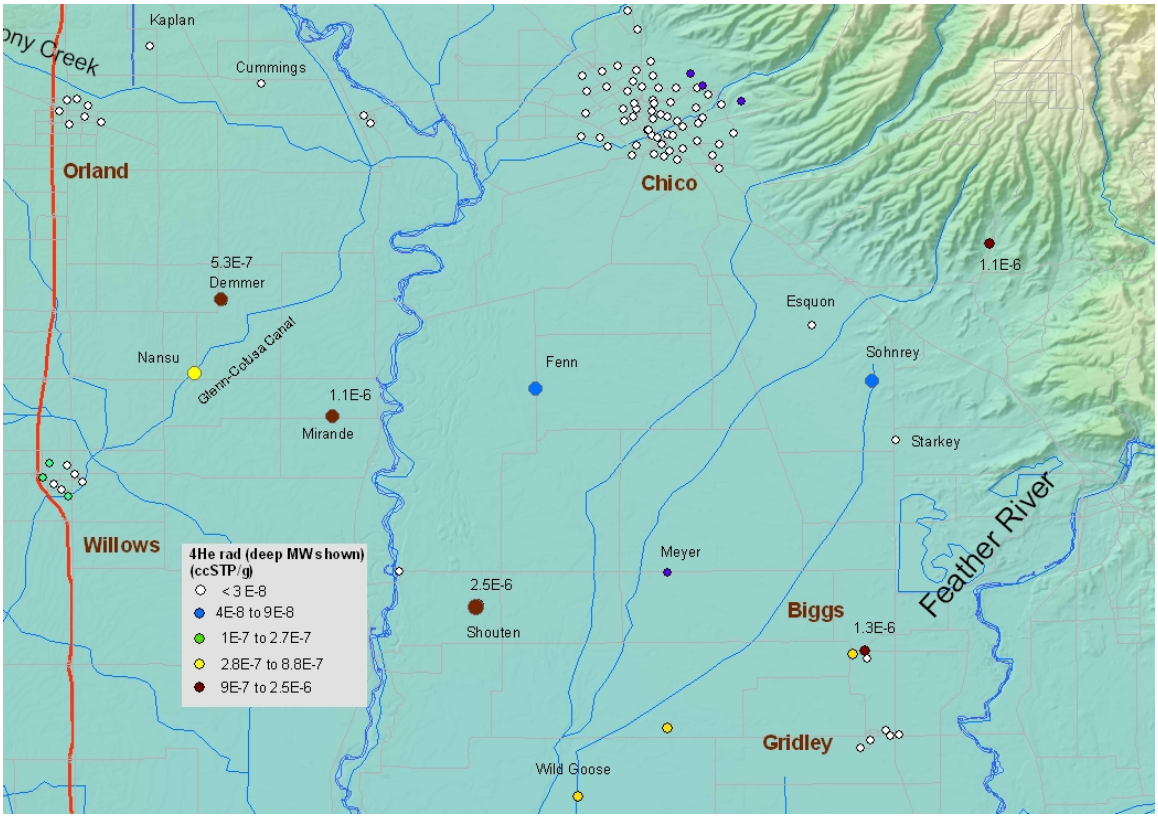

Figure 21. High radiogenic ^{4}He concentrations indicate the presence of groundwater with residence times greater than a few thousand years. (For nested monitoring wells, results from the well with the deepest screened interval are shown.) Deep monitoring wells, especially in the western part of the study area produce paleowater that recharged more than 10,000 years ago, when a cooler climate prevailed.

The nested monitoring wells provide valuable information on patterns in isotopic and water quality indicators with depth, on stratification of groundwater, and on vertical flow in the areas examined. Figure 22a,b are schematic cross sections that are intended to highlight the variation in observed parameters with depth to well screens. Significant tritium is found only in the shallow intervals in three well sets (Demmer, Mirande, Shouten and Meyer). Tritiated water reaches depths of at least 200 ft in the vicinity of Demmer and Mirande and 100 ft at Shouten. In the other areas, significant downward vertical transport of recently recharged water is very limited and has not occurred over at least the last 50 years. (Even in wells where calculated ages are shown (figure 21a), the

fraction of pre-modern groundwater greater than 75%.) The prevalence of $\delta^{18}O$ values that are depleted compared to local precipitation (except in Sohnrey, which exhibits an evaporated signature (figure 14)), is likely due to the contribution of a significant component of recharge from the major rivers that carry water from higher elevations. Highly depleted signatures observed in the deep Nansu, Demmer, and Mirande wells are evidence for the presence of paleowater, as noted below. (Explain Shouten) Stratification of groundwater is evidenced by $\delta^{18}O$ values that differ by greater than 1 per mil (e.g., from Fenn shallow to Fenn middle, and from Wild Goose shallow to Wild Goose middle), which in turn is likely because the aquifers tapped carry water from different recharge sources. Except for Nansu, Demmer, and Mirande, for which the parameters are similar in a lateral sense, lateral continuity is not a prevalent feature. In particular, Meyer, Shouten, Wild Goose, and Fenn, on the East side of the valley, exhibit considerable variability in the parameters examined, and are probably not hydrologically connected. The prevalence of pre-modern groundwater, which cannot be dated using the tritium-helium method, precludes the possibility of identifying flowpaths across the valley using increasing tritium-helium ages. The highest radiogenic ^4He concentrations are found in the middle of the valley, in the deep Shouten and Mirande wells.

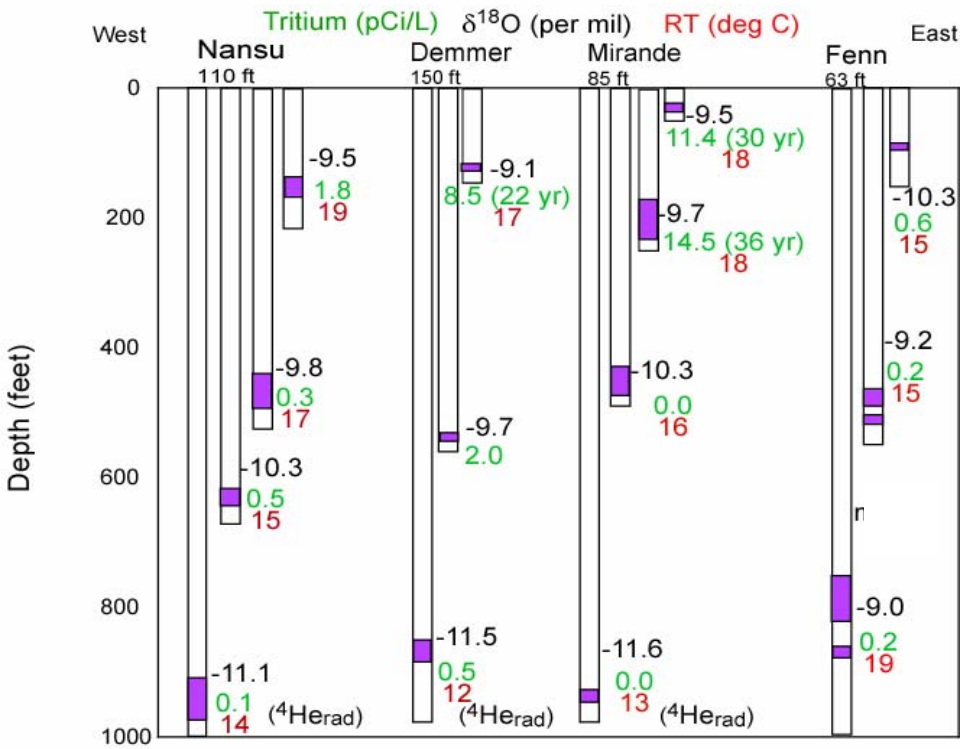

Figure 22a. Schematic cross section showing the relative depths to screened intervals (shaded purple) in nested monitoring wells along a northerly roughly W-E section. Approximate well elevations are given below well names. Tritium concentrations (in green, with calculated groundwater ages where ages could be determined), stable oxygen isotope results (in black), noble gas recharge temperatures (in red), and an indication for radiogenic ^{4}Helium concentrations greater than $3x10^{-7}$ ccSTP/g, are shown adjacent to the screen.

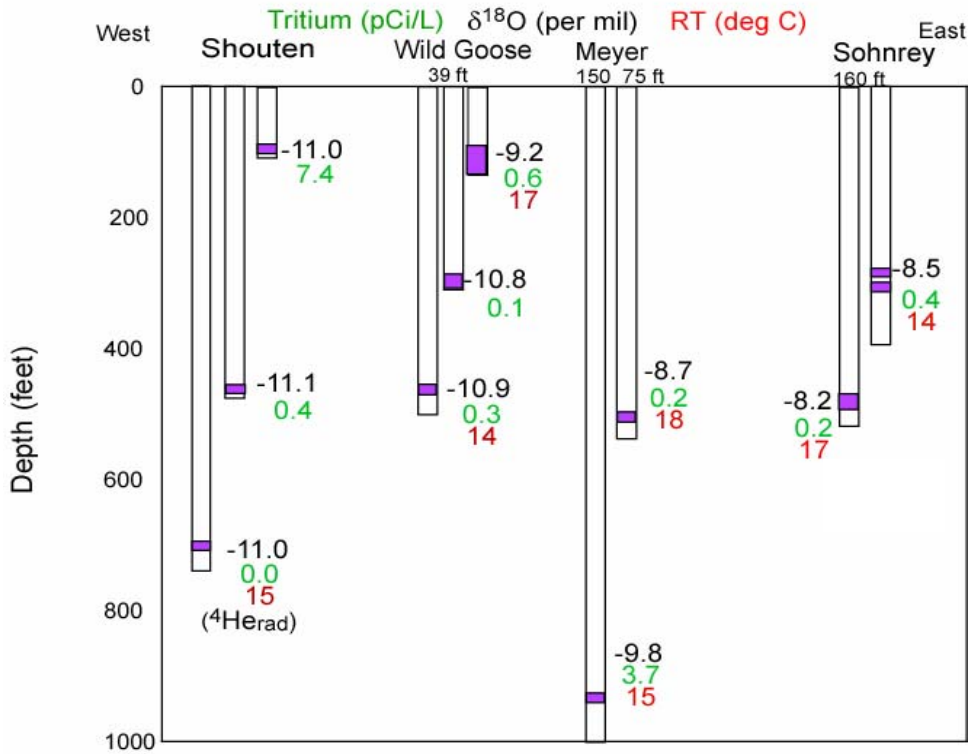

Figure 22b. Schematic cross section showing the relative depths to screened intervals (shaded purple) in nested monitoring wells in the southern portion of the Sacramento Valley. Approximate well elevations are given below well names. Tritium concentrations (in green, with calculated groundwater ages where ages could be determined), stable oxygen isotope results (in black), noble gas recharge temperatures (in red), and an indication for radiogenic ^{4}Helium concentrations greater than $3x10^{-7}$ ccSTP/g, are shown adjacent to the screen.

The very long residence times indicated by radiogenic ^{4}He concentrations for groundwater from the deep monitoring wells in the Nansu, Demmer and Mirande nests are supported by several other measured parameters. For example, the deep Mirande, Nansu, Fenn, and Shouten wells were analyzed for their radiocarbon (^{14}C) contents. While the Mirande and Shouten wells gave calculated ^{14}Carbon ages of 27 and 32 kyr, respectively, the deep Fenn well had a calculated radiocarbon age of 7.5 kyr. The calculated ^{14}C ages are affected by chemical reactions such as dissolution of carbonate, so the reported ages do not have a high degree of accuracy (e.g., Castro et al., 2000), but are useful with regard to the pattern observed (i.e., older ages in deep wells from the western portion of the valley where other indicators suggest long groundwater residence times). Nansu, Demmer and Mirande wells show strongly depleted oxygen isotopes in deep wells compared to shallower wells, indicating a major difference in the recharge water source. Likewise, recharge temperatures observed in the deep Nansu, Demmer, and Mirande wells are about 5 degrees C colder than recharge temperatures observed in the

shallower wells of the same nested set. A noble gas recharge temperature depression of approximately 5 degrees has been observed in other groundwater basins where the presence of paleowater is inferred (e.g., Aeschbach-Hertig et al., 2002). All of the evidence therefore points to the presence of pre-Holocene groundwater in the deep wells. This water recharged under the colder, wetter conditions that were prevalent more than ten of thousand years ago.

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

Recharge temperatures determined from noble gas concentrations measured in groundwater samples over the entire study area show a very wide range, from about 5.5 C to 19 C. As shown on figure 23, recharge temperature correlates weakly with the oxygen isotope composition, and high elevation locations, with very depleted oxygen isotopes, are more likely to have very low recharge temperatures. In particular, recharge temperatures from wells in Portola, Dorris, Weed, Mt. Shasta, and Alturas are 5.5 to 10 C, and springtime recharge of snowmelt is indicated, given mean annual air temperatures of 9 to 12 C (http://www.giss.nasa.gov). Fort Jones has intermediate recharge temperatures of about 12 C, while Tulelake wells exhibit a wide range in recharge temperatures. Wells having an evaporated oxygen isotope signature have low recharge temperatures, indicating that evaporation takes place under cold conditions. Higher recharge temperatures coupled with local oxygen isotope signatures, found in other Tulelake wells, suggest that the regional pattern involves summertime recharge of locally-derived water. Wells from valley locations cluster in the range 11 to 19 C, and have a weak positive correlation with oxygen isotope signature. Many of these recharge temperatures reflect the mean annual air temperature for the recharge region. The mean annual air temperature for the Chico area is approximately 16 C (http://www.giss.nasa.gov station Chico Univ Farm), in reasonable agreement with the recharge temperatures for wells with other lines of evidence for a local recharge source. The spatial pattern exhibited by recharge temperatures (figure 24) mirrors the pattern in oxygen isotopes, with cooler temperatures in wells near Big Chico Creek, and a gradual progression to warmer temperatures in wells away from the creek. Recharge temperatures near the river are approximately 12 to 14 C. Water temperatures in Big Chico Creek fluctuate widely, with temperatures as low as 5 C in December and January, and high temperatures of 25 C in July and August is (www.cdec.ca.gov station BIC). The recharge temperatures observed in wells with multiple lines of evidence for river recharge suggest then that recharge takes place in March and April when natural flows are highest (www.cdec.ca.gov station BIC), and water temperatures are 12 to 14 C.

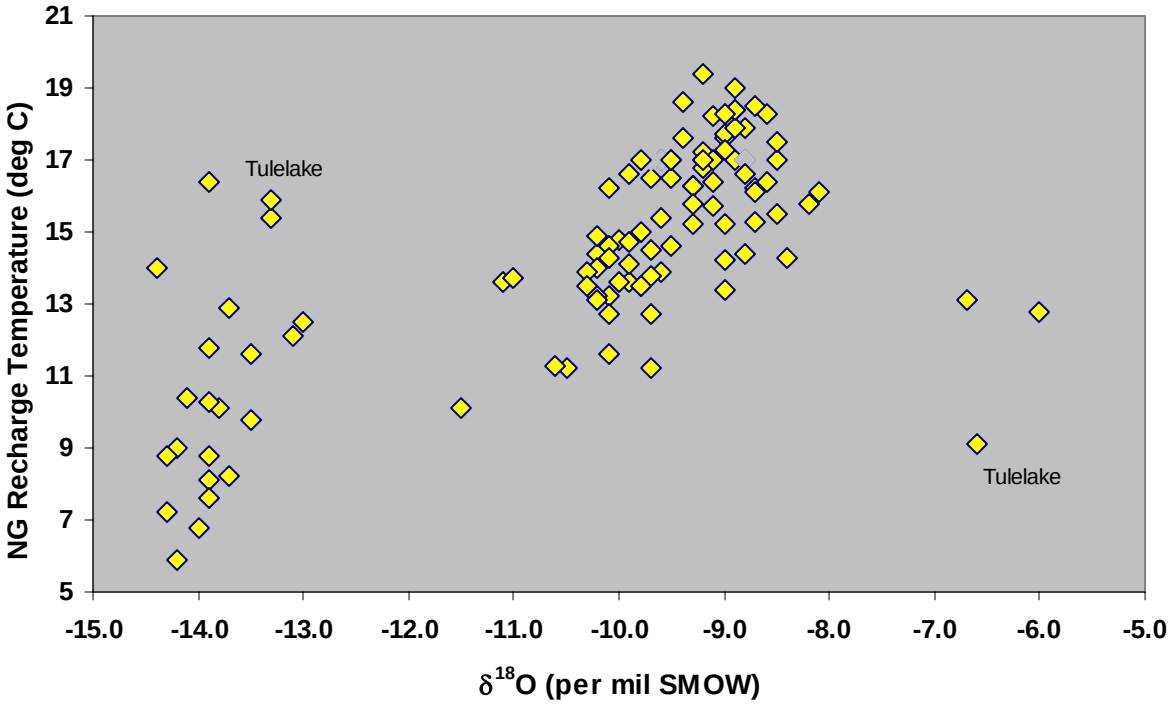

Figure 23. Calculated noble gas recharge temperatures correlate roughly with oxygen isotope ratios, and fall into two distinct fields. Results from wells in Volcanic Provinces fall in the lower left portion of the graph, and very low recharge temperatures are recorded in wells from Portola, Dorris, Alturas, Weed, and Mt. Shasta. Valley wells range between 11 and 19 C, in the range of mean annual air temperatures.

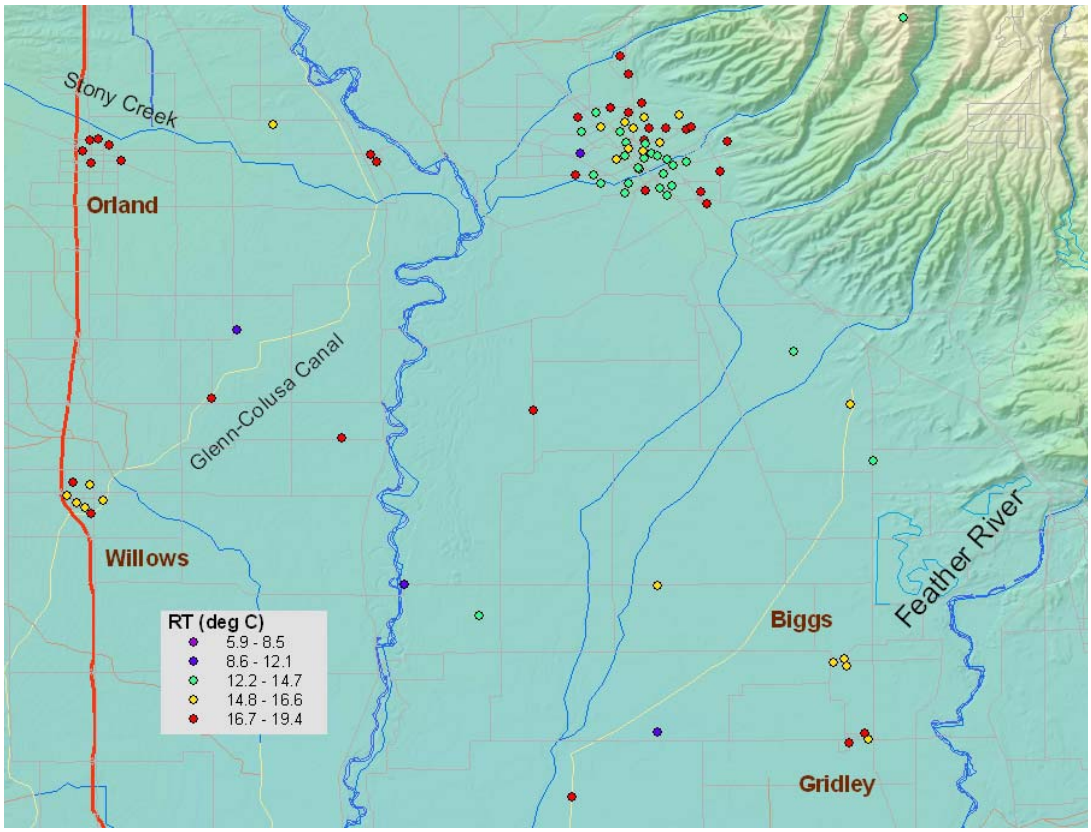

Figure 24. Noble gas recharge temperatures in Chico have a pattern of increasing temperatures away from Big Chico Creek, offering further evidence for the importance of recharge through the creek for nearby wells. Overall, higher temperatures are recorded on the western side, while east side wells show the influence of colder Sierran water. For monitoring wells, the result for the shallow interval is displayed.

Excess air concentrations give an indication of the degree of interaction between infiltrating water and vadose zone gas during recharge. The excess air concentrations observed in Sacramento Valley area wells are low compared to excess air concentrations measured in wells from major coastal groundwater basins in California previously studied using GAMA/CAS techniques (figure 25; Moran et al., 2002; 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. Low excess air concentrations are indicative of limited interaction with vadose zone gas during recharge, and a slow, steady downward movement to the water table. These are the conditions that prevail during river recharge. In contrast, coastal CA aquifers suggest extensive vadose zone interaction and a rapidly fluctuating water table (figure 25). 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. Therefore little gas dissolution during passage through a vadose zone, and minimal fluctuation in the water table can be inferred for most sample locations in the study area.

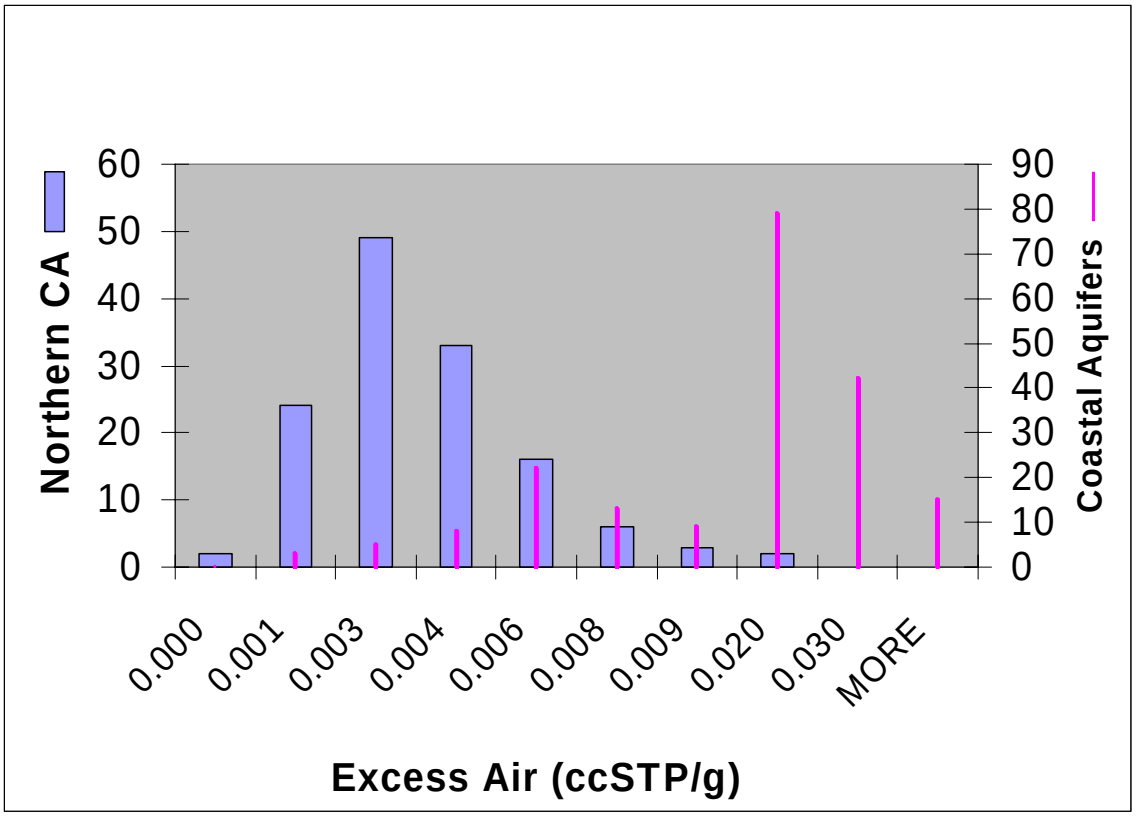

Figure 25. Histogram of excess air concentrations, comparing values from this study (filled blue bars) to values measured in wells in coastal aquifers (including Santa Clara Valley, San Mateo County, the Niles Cone, and the Livermore Valley).

The spatial pattern in excess air concentrations in Sacramento Valley wells (figure 26) shows the influence of river recharge in Chico and Orland, with very low concentrations observed in wells close to Big Chico Creek and Stony Creek, respectively. Somewhat higher concentrations are observed in wells from central Chico, southern Orland, and Willows. Wells closest to the foothills in Chico, where wells are devoid of tritium, and show several lines of evidence for recharge under natural conditions, also have very low excess air concentrations.

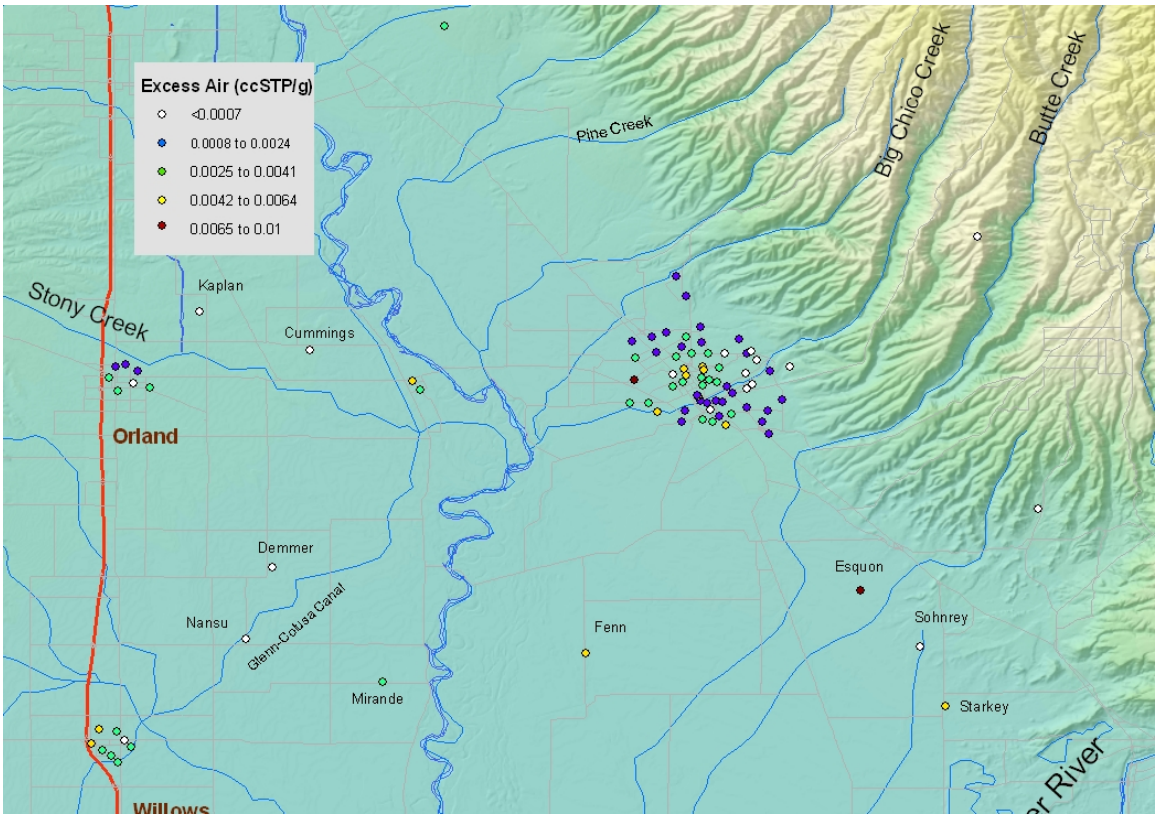

Figure 26. Excess air concentrations are low in general, and especially low in areas where creek recharge is indicated.

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. Groundwater in the Chico area is detrimentally affected by high nitrate concentrations primarily in private drinking water wells. Future research under the GAMA will be directed at determining source attribution for nitrate and whether denitrification is a major factor affecting groundwater nitrate concentrations in the Chico area.

The major conclusions of this study are:

● Low level VOCs occur very frequently in wells from Chico, and PCE is ubiquitous at very low levels in Chico public drinking water wells. MtBE occurs frequently in nearly all areas sampled, but nearly always at extremely low levels, and most commonly from non-point sources.

● Stable isotopes of the water molecule reveal the significance of recharge via creeks in Chico and in Orland. In Volcanic Provinces, recharge of water precipitated in nearby high elevation areas is indicated by highly depleted oxygen isotope signatures.

● Very low tritium concentrations are encountered frequently in Chico and in monitoring wells that traverse the Sacramento Valley. Wells with top perforations below 300 ft bgs do not contain tritium. The large volume of old groundwater produced at drinking water wells has implications for groundwater management since recharge to these wells takes place over periods greater than 50 years. Relatively rapid groundwater flow is limited to the shallow regime in localized areas near the major streams and in fan sediments. Rapid, localized turnover of groundwater is indicated for Fort Jones and Burney wells. Groundwater vulnerability is relatively high in areas of limited geographic extent, where a young groundwater component is produced from drinking water wells, including wells in Orland, Willows, Maxwell, Butte City, Fort Jones, Weed, and Burney.

● Contaminants, especially PCE, are found in 'old' groundwater in the Chico area, and occur at a similar frequency as in other Central Valley study areas where low-level techniques were employed.

● Radiogenic ^{4}Helium concentrations, stable isotope signatures, noble gas recharge temperatures, and ^{14}Carbon concentrations all indicate that deep monitoring wells, especially to the west of the Sacramento River, produce paleowater that recharged more than ten thousand years ago.

Acknowledgements:

The authors are deeply indebted to Debbie Spangler, Seth (?) , and Toccoy Dudley of the Northern district of DWR. Well owners participated voluntarily, and their cooperation is also greatly appreciated. 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 ^{3}He/^{4}He 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.

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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: Well location data.

LLNL ID	State ID	Owner ID	Sample Date	Well Type*	Sampling Agency	City	County	Well Owner
			(yyyy/mm/dd)					
101696	042N012E12M001 M	WELL 05	20030604	PS	DWR	Alturas	Modoc	City of Alturas
101697	042N012E12L001 M	WELL 06	20030604	PS	DWR	Alturas	Modoc	City of Alturas
101698	042N012E12F002 M	WELL 08	20030604	PS	DWR	Alturas	Modoc	City of Alturas
101699	042N012E12Q001 M	WELL 07	20030604	PS	DWR	Alturas	Modoc	City of Alturas
101456	NO STATE ID	HENRY WELL	20030116	PS	DWR	Biggs	Butte	City of Biggs
101460	NO STATE ID	TANK WELL	20030116	PS	DWR	Biggs	Butte	City of Biggs
101461	018N002E13E001M	WILLARD WELL	20030116	PS	DWR	Biggs	Butte	City of Biggs
101709	035N003E20Q001 M	WELL 06	20030609	PS	DWR	Burney	Shasta	Burney Water District
101710	035N003E20Q002 M	WELL 07	20030609	PS	DWR	Burney	Shasta	Burney Water District
101711	035N003E20Q003 M	WELL 08	20030609	PS	DWR	Burney	Shasta	Burney Water District
101455	NO STATE ID	BUTTE CITY WELL	20030108	PS	DWR	Butte City	Glenn	Butte City Water Company
101486	022N001E23A001M	CWS 24-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101487	022N001E13E001M	CWS 32-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101488	NO STATE ID	CWS 70-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101489	022N001E13H004M	CWS 49-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101490	022N001E22A001M	CWS 19-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101491	022N001E15L001M	CWS 52-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101492	022N001E14E005M	CWS 25-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101493	022N001E14C001M	CWS 37-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101494	022N001E11E001M	CWS 62-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101495	022N001E10R001M	CWS 48-01	20030124	PS	DWR	Chico	Butte	California Water Service-Chico
101496	022N001E16C002 M	CWS 69-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101497	022N001E09R001 M	CWS 56-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101498	022N001E15B001 M	CWS 30-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101499	022N001E16H001 M	CWS 27-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101500	022N001E16L002 M	CWS 63-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101501	022N001E33A001 M	CWS 42-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101502	NO STATE ID	CWS 77-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101503	022N001E34G001 M	CWS 46-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101504	022N001E35H002 M	CWS 11-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101505	022N001E36M001 M	CWS 51-01	20030130	PS	DWR	Chico	Butte	California Water Service-Chico
101506	022N001E35A002 M	CWS 05-02	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101507	022N001E25M001 M	CWS 07-04	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101508	022N001E25C001 M	CWS 18-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101509	022N001E22P001 M	CWS 21-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico

Table 2: Well location data con't.

LLNL ID	State ID	Owner ID	Sample Date	Well	Sampling	City	County	Well Owner

				Type*	Agency			
			(yyyy/mm/dd)					
101510	022N001E22H001 M	CWS 14-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101511	022N001E22Q001 M	CWS 08-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101512	NO STATE ID	S-1	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101513	NO STATE ID	S-2	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101514	022N001E23P001 M	CWS 12-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101515	022N001E23L001 M	CWS 16-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101516	022N001E23C002 M	CWS 29-01	20030206	PS	DWR	Chico	Butte	California Water Service-Chico
101517	022N001E36C001 M	CWS 35-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101518	022N001E26Q001 M	CWS 23-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101519	022N001E26L002 M	CWS 01-04	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101520	022N001E27R001 M	CWS 03-03	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101521	022N001E28K001 M	CWS 59-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101522	022N001E22F001 M	CWS 17-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101523	022N001E23R001 M	CWS 38-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101524	022N001E23K003 M	CWS 34-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101525	022N001E24N001 M	CWS 20-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101526	022N001E24B001 M	CWS 28-01	20030220	PS	DWR	Chico	Butte	California Water Service-Chico
101527	022N001E19E001 M	CWS 26-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101528	022N002E18N001 M	CWS 33-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101529	022N002E19N001 M	CWS 54-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101530	022N001E25A001 M	CWS 39-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101573	022N002E29M001 M	CWS 65-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101579	022N001E31Q001 M	CWS 41-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101582	NO STATE ID	CWS 71-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101583	022N002E31B001 M	CWS 53-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101584	022N001E25A002 M	CWS 57-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101585	022N002E19G001 M	CWS 50-01	20030227	PS	DWR	Chico	Butte	California Water Service-Chico
101594	0410002-069	CWS 67-01	20030306	PS	DWR	Chico	Butte	California Water Service-Chico
101595	NO STATE ID	CWS 68-01	20030306	PS	DWR	Chico	Butte	California Water Service-Chico
101596	022N001E14G001 M	CWS 31-01	20030306	PS	DWR	Chico	Butte	California Water Service-Chico
101597	022N001E23C001 M	CWS 22-01	20030306	PS	DWR	Chico	Butte	California Water Service-Chico
101598	023N001E34G001 M	CWS 64-01	20030306	PS	DWR	Chico	Butte	California Water Service-Chico
101600	022N001E04A002 M	CWS 44-01	20030403	PS	DWR	Chico	Butte	California Water Service-Chico
101604	022N001E10K001 M	CWS 58-01	20030403	PS	DWR	Chico	Butte	California Water Service-Chico

Table 2: Well location data con't.

LLNL ID	State ID	Owner ID	Sample Date	Well Type*	Sampling Agency	City	County	Well Owner
			(yyyy/mm/dd)					

101605	022N001E35F001 M	CWS 13-01	20030403	PS	DWR	Chico	Butte	California Water Service-Chico
101606	NO STATE ID	CWS 09-01	20030403	PS	DWR	Chico	Butte	California Water Service-Chico
101607	NO STATE ID	CWS 04-01	20030403	PS	DWR	Chico	Butte	California Water Service-Chico
101608	022N001E25R001 M	CWS 61-01	20030403	PS	DWR	Chico	Butte	California Water Service-Chico
101707	048N001W36A001 M	WELL 06	20030605	PS	DWR	Dorris	Siskiyou	City of Dorris
101708	048N001E30P001 M	WELL 04	20030605	PS	DWR	Dorris	Siskiyou	City of Dorris
101693	043N009W02P001 M	FORT JONES WELL 3	20030520	PS	DWR	Fort Jones	Siskiyou	City of Fort Jones
101694	043N009W02G001 M	FORT JONES WELL 1	20030520	PS	DWR	Fort Jones	Siskiyou	City of Fort Jones
101695	043N009W02G002 M	FORT JONES WELL 2	20030220	PS	DWR	Fort Jones	Siskiyou	City of Fort Jones
101447	NO STATE ID	LITTLE AVE WELL	20021108	PS	LLNL	Gridley	Butte	City of Gridley
101448	017N002E01D001M	PARKSIDE WELL	20021108	PS	LLNL	Gridley	Butte	City of Gridley
101449	018N002E36R001M	WILSON ST WELL	20021108	PS	LLNL	Gridley	Butte	City of Gridley
101450	018N003E32M001M	FAIRVIEW DRIVE WELL	20021108	PS	LLNL	Gridley	Butte	City of Gridley
101451	018N002E36Q002M	SPRUCE AVE WELL	20021108	PS	LLNL	Gridley	Butte	City of Gridley
101601	022N001W29D001 M	CWS 01-01 HAMILTON CITY	20030403	PS	DWR	Hamilton City	Glenn	California Water Service-Hamilton City
101602	022N001W19J001 M	CWS 02-01 HAMILTON CITY	20030403	PS	DWR	Hamilton City	Glenn	California Water Service-Hamilton City
101603	022N001W19J002 M	CWS 02-02 HAMILTON CITY	20030403	PS	DWR	Hamilton City	Glenn	California Water Service-Hamilton City
101589	NO STATE ID	GRIZZLY - CROCKER MTN SYSTEM	20030304	PS	DWR	Lake Davis	Plumas	Grizzly Lake RID (Crocker/Welch)
101690	040N004W10P001 M	HIGH SCHOOL WELL 02	20030513	PS	DWR	Mt. Shasta	Siskiyou	City of Mt. Shasta
101691	037N005E03N002 M	McARTHUR/LEWIS RD	20030516	PS	DWR	Mt. Shasta	Siskiyou	City of Mt. Shasta
101692	NO STATE ID	DEEKNOCH TEST WELL	20030516	PS	DWR	Mt. Shasta	Siskiyou	City of Mt. Shasta
101392	022N003W22D001M	WELL 07 - SUISUN STREET	20021210	PS	DWR	Orland	Glenn	City of Orland
101393	1110001-009	WELL 08 - ROOSEVELT	20021210	PS	DWR	Orland	Glenn	City of Orland
101394	022N003W22G002M	WELL 04 - WOODWARD AVE	20021210	PS	DWR	Orland	Glenn	City of Orland
101395	022N003W27D001M	WELL 02 - RAILROAD AVE	20021211	PS	DWR	Orland	Glenn	City of Orland
101452	022N003W21J001M	WELL 06 - 8th STREET	20021211	PS	DWR	Orland	Glenn	City of Orland
101453	022N003W22Q001M	WELL 01 - CENTRAL STREET	20021211	PS	DWR	Orland	Glenn	City of Orland
101454	022N003W26D001M	WELL 05 - SHOP WELL	20021211	PS	DWR	Orland	Glenn	City of Orland
101391	0410007-004	D TANK WELL	20021209	PS	DWR	Paradise	Butte	Paradise Irigation District
101586	3210003-005	CORPORATION YARD WELL	20030304	PS	DWR	Portola	Plumas	City of Portola
101587	3210003-006	COMMERCIAL STREET WELL	20030304	PS	DWR	Portola	Plumas	City of Portola

Table 2: Well location data con't.

LLNL ID	State ID	Owner ID	Sample Date	Well Type*	Sampling Agency	City	County	Well Owner
			(yyyy/mm/dd)					
101588	023N013E20N0S1 M	WILLOW SPRING	20030304	PS	DWR	Portola	Plumas	City of Portola
101610	NO STATE ID	DEER CREEK TEST PRODUCTION	20030506	PS	DWR	Redding	Shasta	DWR Test Well
101700	048N004E35L001 M	WELL 01	20030604	PS	DWR	Tulelake	Siskiyou	City of Tulelake
101701	048N004E35L002 M	WELL 02	20030604	PS	DWR	Tulelake	Siskiyou	City of Tulelake
101702	NO STATE ID	WELL 01	20030605	PS	DWR	Tulelake	Siskiyou	Tulelake Irrigation District
101703	NO STATE ID	WELL 03	20030605	PS	DWR	Tulelake	Siskiyou	Tulelake Irrigation District
101704	NO STATE ID	WELL 05	20030605	PS	DWR	Tulelake	Siskiyou	Tulelake Irrigation District
101705	NO STATE ID	WELL 07	20030605	PS	DWR	Tulelake	Siskiyou	Tulelake Irrigation District
101706	NO STATE ID	WELL 14	20030605	PS	DWR	Tulelake	Siskiyou	Tulelake Irrigation District
101687	041N005W13E001 M	MAZZEI WELL	20030513	PS	DWR	Weed	Siskiyou	City of Weed
101688	040N004W15L001 M	WELL 01	20030513	PS	DWR	Weed	Siskiyou	City of Weed
101689	040N004W14M001 M	SPRING SOURCE	20030513	SPR	DWR	Weed	Siskiyou	City of Weed
101457	019N003W09D001M	CWS 9-01	20030122	PS	DWR	Willows	Glenn	California Water Service-Willows
101458	019N003W09F001M	CWS 5-01	20030122	PS	DWR	Willows	Glenn	California Water Service-Willows
101459	019N003W04J001M	CWS 6-01	20030122	PS	DWR	Willows	Glenn	California Water Service-Willows
101481	019N003W09K001M	CWS 4-01	20030122	PS	DWR	Willows	Glenn	California Water Service-Willows
101482	019N003W04L001M	CWS 7-01	20030123	PS	DWR	Willows	Glenn	California Water Service-Willows
101483	019N003W10D001M	CWS 2-01	20030123	PS	DWR	Willows	Glenn	California Water Service-Willows
101484	019N003W10F001M	CWS 10-01	20030123	PS	DWR	Willows	Glenn	California Water Service-Willows
101485	019N003W09R001M	CWS 8-01	20030123	PS	DWR	Willows	Glenn	California Water Service-Willows

*PS=public supply well; PV=private/domestic well; SPR=natural spring; MW=monitoring well

Table 3: VOC data.

LLNL ID	MTBE	$CHCl_3$	1,1,1-TCA	Benzene	TCE	BDCM	Toluene	PCE	DBCM	1,2 Dibromo-ethane	Ethylben-zene	p,m-Xylene	o-Xylene	$CHBr_3$	DBCP
	(ng/L)	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*
101696	1.3E+02	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101697	6.4E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101698	8.6E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101699	6.8E+00	<5	<5	<5	<5	<5	<6	<5	<5	<5	<5	<5	<5	<5	<5
101456	1.3E+01	3.8E+01	<5	<5	<5	8.2E+00	<5	<5	<5		<5	<5	<5	<5	<5
101460	<5	<5	<5	<5	<5	<5	<5	<5	<5		<5	<5	<5	<5	<5
101461	<5	<5	<5	<5	<5	<5	<5	<5	<5		<5	<5	<5	<5	<5
101709	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101710	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101711	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101455	1.7E+01	1.4E+02	<5	<5	<5	5.3E+02	<5	<5	1.4E+03		<5	<5	<5	1.6E+03	<5
101486	2.3E+01	3.4E+01	<5	<5	4.3E+01	<5	<5	1.6E+02	<5	<5	<5	<5	<5	<5	<5
101487	<10	<5	<5	<5	<5	<5	<15	<5	<5	<5	<5	<5	<5	<5	<5
101488	<5	<5	<5	<5	<5	<5	<15	<5	<5	<5	<5	<5	<5	<5	<5
101489	<10	1.4E+01	<5	<5	<5	<5	<15	2.1E+01	<5	<5	<5	<5	<5	<5	<5
101490	2.8E+01	7.7E+01	<5	<5	<5	<5	<15	1.2E+02	<5	<5	<5	<5	<5	<5	<5
101491	<10	1.0E+02	<5	<5	1.7E+02	<5	<15	8.2E+02	<5	<5	<5	<5	<5	<5	<5
101492	<10	1.7E+01	<5	<5	1.1E+01	<5	<15	1.6E+02	<5	<5	<5	<5	<5	<5	<5
101493	<5	1.3E+01	<5	<5	<5	<5	<15	4.2E+01	<5	<5	<5	<5	<5	<5	<5
101494	<5	<5	<5	<5	<5	<5	<15	<5	<5	<5	<5	<5	<5	<5	<5
101495	3.6E+01	1.7E+02	<5	<5	2.3E+01	<5	<15	5.0E+02	<5	<5	<5	<5	<5	<5	<5
101496	2.1E+01	3.2E+02	<5	<5	<5	3.8E+02	<10	2.1E+01	4.6E+02	<5	<5	<5	<5	3.2E+02	<5
101497	<5	1.1E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101498	1.3E+01	8.0E+01	<5	<5	2.0E+01	<5	<5	1.2E+02	<5	<5	<5	<5	<5	<5	<5
101499	<5	5.1E+01	<5	<5	5.7E+00	<5	<5	5.8E+01	<5	<5	<5	<5	<5	<5	<5
101500	9.3E+00	2.9E+01	<5	<5	<5	<5	<5	6.5E+00	<5	<5	<5	<5	<5	<5	<5
101501	7.9E+00	8.1E+00	<5	<5	<5	<5	<10	<5	<5	<5	<5	<5	<5	<5	<5
101502	4.5E+01	5.7E+01	1.4E+01	<5	<5	<5	<10	1.2E+01	<5	<5	<5	<5	<5	<5	<5
101503	<5	1.0E+01	<5	<5	<5	<5	<10	2.0E+04	<5	<5	<5	<5	<5	<5	<5
101504	2.7E+01	1.2E+01	<5	<5	4.2E+02	<5	<10	8.1E+01	<5	<5	<5	<5	<5	<5	<5
101505	2.1E+01	6.0E+01	<5	<5	8.6E+02	<5	<10	5.3E+02	<5	<5	<5	<5	<5	<5	<5
101506	2.1E+01	9.9E+00	<5	5.4E+00	1.4E+02	<5	<5	1.3E+02	<5	<5	<5	<5	<5	<5	<5
101507	<5	1.9E+01	<5	<5	<5	3.2E+01	<5	3.2E+01	1.4E+02	<5	<5	<5	4.7E+01	1.1E+03	<5
101508	1.0E+01	1.3E+01	<5	<5	<5	<5	<5	4.2E+01	<5	<5	<5	<5	<5	<5	<5
101509	<5	3.3E+01	<5	<5	7.5E+00	<5	<5	1.1E+04	<5	<5	<5	<5	<5	<5	<5
101510	5.4E+00	2.0E+02	<5	<5	1.6E+01	<5	<5	1.7E+03	<5	<5	<5	<5	<5	<5	<5

Table 3: VOC data con't.

LLNL ID	MTBE	$CHCl_3$	1,1,1-TCA	Benzene	TCE	BDCM	Toluene	PCE	DBCM	1,2 Dibromo-ethane	Ethylben-zene	p,m-Xylene	o-Xylene	$CHBr_3$	DBCP
	(ng/L)	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*
101511	<5	9.0E+00	<5	<5	4.1E+01	<5	<5	3.4E+02	<5	<5	<5	<5	<5	<5	<5
101512	2.7E+01	3.1E+01	<5	<5	7.1E+01	<5	<5	9.3E+04	<5	<5	<5	<5	<5	<5	<5
101513	1.4E+01	2.6E+01	<5	5.4E+01	3.3E+03	<5	6.5E+01	5.8E+05	<5	<5	2.0E+01	1.8E+01	1.2E+01	<5	<5
101514	1.9E+01	1.9E+02	<5	<5	<5	1.1E+01	<5	1.7E+02	1.4E+01	<5	<5	<5	<5	3.5E+01	8.5E+00
101515	1.4E+01	1.9E+02	<5	<5	8.7E+00	1.1E+01	<5	2.9E+03	<5	<5	<5	<5	<5	<5	<5
101516	8.7E+00	3.7E+02	<5	<5	<5	2.2E+01	<5	2.0E+02	9.6E+00	<5	<5	<5	<5	<5	<5
101517	<5	<5	<5	<5	2.2E+01	<5	<5	1.6E+01	<5	<5	<5	<5	<5	<5	<5
101518	9.0E+00	<5	<5	<5	<5	<5	<5	2.0E+01	<5	<5	<5	<5	<5	<5	<5
101519	<5	2.2E+01	<5	<5	<5	1.6E+01	<5	2.5E+02	<5	<5	<5	<5	<5	<5	<5
101520	6.7E+00	<5	<5	<5	<5	<5	<5	1.4E+02	<5	<5	<5	<5	<5	<5	<5
101521	1.7E+01	2.0E+01	<5	<5	<5	<5	<5	5.0E+01	<5	<5	<5	<5	<5	<5	<5
101522	3.5E+01	3.3E+03	<5	<5	2.3E+01	1.3E+01	<5	3.8E+02	<5	<5	<5	<5	<5	<5	<5
101523	1.0E+01	8.4E+02	<5	<5	<5	8.5E+02	<5	1.4E+02	7.8E+02	<5	<5	<5	<5	1.6E+02	<5
101524	1.6E+01	1.3E+02	6.1E+00	<5	<5	1.4E+01	<5	1.5E+02	<5	<5	<5	<5	<5	<5	<5
101525	9.5E+00	3.3E+01	<5	<5	1.2E+01	<5	<5	2.9E+01	<5	<5	<5	<5	<5	<5	<5
101526	<5	1.7E+01	<5	<5	7.8E+00	<5	<5	6.3E+00	<5	<5	<5	<5	<5	<5	<5
101527	<5	2.3E+01	<5	<5	<5	<5	<5	8.4E+00	<5	<5	<5	<5	<5	<5	<5
101528	<5	1.8E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101529	<5	<5	<5	<5	<5	<5	<5	8.1E+00	<5	<5	<5	<5	<5	<5	<5
101530	1.7E+01	<5	<5	<5	<5	<5	<5	1.6E+01	<5	<5	<5	<5	<5	<5	<5
101573	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101579	8.3E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101582	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101583	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101584	<5	8.2E+00	<5	<5	<5	<5	<5	1.3E+01	<5	<5	<5	<5	<5	<5	<5
101585	<5	9.0E+02	<5	<5	<5	2.4E+02	<5	2.4E+01	3.5E+02	<5	<5	<5	<5	4.2E+02	<5
101594	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101595	<6	3.2E+01	<5	<5	<5	5.0E+01	<5	6.3E+00	1.7E+02	<5	<5	<5	<5	6.5E+02	<5
101596	<10	3.0E+01	<5	<5	<5	<5	<5	3.9E+01	<5	<5	<5	2.5E+01	2.6E+01	<5	<5
101597	1.3E+01	8.1E+01	<5	<5	<5	<5	<5	8.8E+01	<5	<5	<5	<5	<5	<5	<5
101598	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101599	<5	4.6E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101600	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101604	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101605	8.4E+02	<5	<5	<5	<5	<5	<5	1.0E+03	<5	<5	<5	<5	<5	<5	<5
101606	2.0E+01	5.1E+00	<5	<5	<5	<5	<5	4.6E+01	<5	<5	<5	<5	<5	<5	<5

Table 3: VOC data con't.

LLNL ID	MTBE	$CHCl_3$	1,1,1-TCA	Benzene	TCE	BDCM	Toluene	PCE	DBCM	1,2 Dibromo-ethane	Ethylben-zene	p,m-Xylene	o-Xylene	$CHBr_3$	DBCP
	(ng/L)	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*
101607	<5	<5	<5	<5	<5	<5	<5	1.2E+01	<5	<5	<5	<5	<5	<5	<5
101608	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101707	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101708	8.0E+00	1.7E+03	<5	7.7E+00	5.1E+01	1.8E+01	3.8E+01	9.3E+00	6.3E+00	<5	<5	<15	<6	<5	<5
101693	<10	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101694	7.6E+01	7.6E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101695	5.0E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101447	<5	<5		<5	<5	<5	<11	<5	<5		<5	<7	<5	<5	<5
101448	<5	2.6E+01		<5	<5	6.3E+00	<11	1.4E+02	2.4E+01		<5	<7	<5	9.3E+01	<5
101449	2.8E+01	1.2E+02		<5	1.7E+02	7.8E+00	<11	<5	<5		<5	<7	<5	<5	<5
101450	<5	<5		<5	<5	<5	<11	<5	<5		<5	<7	<5	<5	1.8E+02
101451	<51	1.5E+02		<5	<5	5.2E+00	<11	1.1E+01	<5		<5	<7	<5	<5	<5
101601	<5	1.1E+01	<5	<5	<5	<5	<5	<5	6.0E+00	<5	<5	<5	<5	1.3E+01	<5
101602	<5	6.6E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101603	<5	5.5E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101589	5.1E+01	1.4E+01	<5	<5	4.2E+01	<5	<5	6.0E+02	<5	<5	<5	<5	<5	<5	<5
101590	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101591	2.6E+02	1.6E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101690	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<10	<5	<5	<5
101691	1.3E+01	1.3E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101692	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101392	<5	<5	<5	<5	<5	<5	<5	<5	<6		<5	<5	<5	2.2E+01	<5
101393	<5	4.1E+01	<5	<5	<5	5.1E+01	<5	7.3E+00	1.7E+02		<5	<5	<5	5.0E+02	<5
101394	<5	1.5E+02	<5	<5	<5	6.3E+01	<5	<5	1.8E+02		<5	<5	<5	4.0E+02	<5
101395	<5	2.3E+01	<5	<5	<5	1.1E+02	<5	<5	3.9E+02		<5	<5	<5	9.9E+02	<5
101452	<5	<5	<5	<5	<5	5.0E+00	<5	<5	1.4E+01		<5	<5	<5	3.1E+01	<5
101453	<5	1.4E+01	<5	<5	<5	<5	<5	<5	<5		<5	<5	<5	<5	<5
101454	1.7E+01	8.5E+01	5.7E+00	<5	<5	<5	<5	8.2E+01	<5		<5	<5	<5	<5	<5
101391															
101586	8.3E+01	6.0E+01	1.6E+01	<5	<5	6.0E+00	<5	2.5E+01	<5	<5	<5	<5	<5	<5	<5
101587	1.1E+02	2.3E+02	5.3E+01	<5	<5	2.0E+01	<5	1.9E+01	<5	<5	<5	<5	<5	<5	<5
101588	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101610	<5	<5	<5	<5	9.9E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101700	9.0E+00	4.8E+02	<5	<5	<5	7.7E+02	<15	<5	8.8E+02	<5	<5	<10	<6	3.7E+02	<5
101701	<5	3.5E+02	<5	<5	<5	4.9E+02	<5	<5	5.2E+02	<5	<5	<5	<5	1.9E+02	<5
101702	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101703	5.3E+00	<5	<5	<5	<5	<5	<10	<5	<5	<5	<5	<5	<5	<5	<5

Table 3: VOC data con't.

LLNL ID	MTBE	$CHCl_3$	1,1,1-TCA	Benzene	TCE	BDCM	Toluene	PCE	DBCM	1,2 Dibromo-ethane	Ethylben-zene	p,m-Xylene	o-Xylene	$CHBr_3$	DBCP
	(ng/L)	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*	*(ng/L)*
101704	6.9E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101705	<5	<5	<5	<5	<5	<5	<10	<5	<5	<5	<5	<5	<5	<5	<5
101706	<5	<5	<5	<5	<5	<5	<10	<5	<5	<5	<5	<5	<5	<5	<5
101687	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101688	<5	<5	<5	9.1E+00	<5	<5	3.3E+01	<5	<5	<5	9.0E+00	3.6E+01	1.8E+01	<5	<5
101689	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101457	<10	9.9E+00	<5	<5	<5	1.1E+01	<5	<5	4.7E+01	<5	<5	<5	<5	4.5E+02	<5
101458	<10	2.2E+01	<5	<5	<5	<5	<15	<5	5.6E+01	<5	<5	5.9E+00	<5	6.2E+02	<5
101459	<5	9.1E+00	<5	<5	<5	1.5E+01	<15	<5	5.9E+01	<5	<5	<5	<5	2.6E+02	<5
101481	<10	3.5E+01	<5	<5	<5	1.2E+01	<15	<5	6.2E+01	<5	<5	<5	<5	5.8E+02	<5
101482	<5	2.7E+01	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	8.4E+00	<5
101483	<10	1.5E+02	<5	<5	<5	5.1E+01	<15	<5	5.9E+01	<5	<5	<5	<5	5.0E+01	<5
101484	1.3E+01	7.5E+00	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
101485	1.3E+01	1.5E+01	<5	<5	<5	2.1E+01	<15	<5	6.9E+01	<5	<5	<5	<5	3.2E+02	<5

MTBE=methyl-*tert*-butyl ether; TCA=trichloroethylene; TCE=trichloroethane; BDCM= bromodichloroethane; PCE=perchloroethylene (tetrachloroethylene); DBCM= dibromochloromethane; DBCP=dibromochloropropane

Table 4. Groundwater ages, noble gas and stable oxygen results.

LLNL ID	Elevation	Total Depth	Depth to Perforation 1 Top	$\delta^{18}O_{SMOW}$	Tritium	$^{3}He/^{4}He$	Excess Air from Ne	Radiogenic ^{4}He	Ground-water Age	Ground-water Age Error	Percent pre-modern	Recharge Temp	Recharge Temp Error
	(ft)	*(ft bgs)*	*(ft bgs)*	*(‰)*	*(pCi/L)*		*(ccSTP/g)*	*(ccSTP/g)*	*(years)*	*(years)*	*(%)*	*(°C)*	*(°C)*
101391		680	70	-9.7	1.66	1.50E-06	0.0002	1.67E-10	31.6	0.9	0.98	12.7	0.9
101392		400	95	-9.4	6.25	1.50E-06	0.0018	1.41E-08	24.3	2.5	0.86	18.6	1.0
101393	257.6	410	240	-9.4	9.22	1.65E-06	0.0016	2.72E-09	21.5	1.1	0.75	17.6	1.0
101394	257.2	160	100	-8.9	12.20	1.89E-06	0.0015	-8.38E-10	24.1	0.9	0.73	18.4	1.0
101395	272.3			-9.2	9.17	1.55E-06	0.0025	6.77E-09	19.4	1.5	0.72	19.4	1.1
101447	78.7	355	255	-10.0	10.56								
101448	75.5	300	108	-8.9	7.35	1.88E-06	0.0025	1.29E-08	37.2	1.3	0.95	17.9	1.1
101449	39.4	328	56	-9.9	16.86	2.21E-06	0.0019	9.76E-10	27.1	0.9	0.71	16.6	1.0
101450	80.4	331	130	-10.6	12.18								na
101451	74.2	360	102	-10.1	20.81	2.49E-06	0.0031	5.18E-09	30.8	0.9	0.75	17.1	1.1
101452	251.6	287	85	-9.0	12.07	2.02E-06	0.0036	-6.84E-11	29.9	1.1	0.84	18.3	1.1
101453	297.9			-8.5	15.63	2.09E-06							
101454	246.1	160	105	-8.7	12.36	1.69E-06	0.0032	6.82E-10	20.1	1.1	0.63	18.5	1.1
101455				-10.5	11.34	1.53E-06	0.0078	9.42E-09	19.5	2.0	0.65	11.2	1.2
101456	65.6	200	165	-10.1	13.49	2.05E-06	0.0048	1.88E-08	35.4	1.2	0.90	16.2	1.2
101457	99.1	600	180	-8.8	1.34	5.15E-07	0.0047	1.42E-07				16.6	1.2
101458	118.1			-9.1	3.70	1.28E-06	0.0030	3.01E-08			0.85	15.7	1.1
101459	138.8	650	173	-9.0	1.64	1.24E-06	0.0031	1.70E-08				15.2	1.0
101460	65.6	327	84	-8.2	1.14	7.52E-07	0.0018	4.33E-07				15.8	1.0
101461	97.4	381	175	-8.1	0.14	5.70E-07	0.0023	1.30E-06	>50		1.00	16.1	1.0
101481		730		-9.7	7.48	1.34E-06	0.0039	3.01E-08	16.0	5.6	0.72	16.5	1.1
101482	147.3			-9.1	1.84	4.97E-07	0.0046	1.36E-07				18.2	1.2
101483	144.4	559		-11.0	21.64								
101484	134.6	617	197	-10.2	8.38	1.70E-06	0.0029	1.17E-08	29.5	1.5	0.89	14.9	1.0
101485	95.1	710	212	-9.2	3.58	6.01E-07	0.0036	1.20E-07	13.6	2.4		17.2	1.1
101486	236.2	600	176	-9.8	10.99	2.17E-06	0.0036	1.93E-09	35.1	1.1	0.91	15.0	1.1
101487	213.3	828		-8.9	0.55	1.32E-06	0.0006	6.06E-09	>50		1.00	19.0	1.0
101488	285.4			-9.0	0.07	9.49E-07	-0.0002	5.04E-08	>50		1.00	17.7	1.0
101489	236.2	500	200	-8.8	2.74	1.37E-06	0.0011	6.61E-09	15.1	5.1	0.89	17.9	1.0
101490	180.5			-9.9	10.43	1.92E-06	0.0045	1.44E-09	30.9	1.2	0.87	13.6	1.1
101491	177.2	516	200	-9.7	4.28	1.79E-06	0.0032	2.04E-09	39.4	1.5	0.98	14.5	1.0
101492	200.1	616	300	-9.3	0.83	1.49E-06	0.0028	-1.91E-10	44.2	1.0	1.00	16.3	1.1
101493	210.0			-8.7	1.28	1.50E-06	0.0017	4.75E-09	42.2	1.0	0.99	16.2	1.0
101494	210.0		300	-8.6	0.04	1.37E-06	0.0018	2.89E-09	MH			18.3	1.0
101495	196.9	516	200	-8.5	7.59	1.63E-06	0.0038	3.08E-09	25.1	1.5	0.85	17.5	1.1
101496	169.0	640		-8.9	1.09	1.27E-06	0.0012	9.76E-09	>50		1.00	18.4	1.0

Table 4. Groundwater ages, noble gas and stable oxygen result con't.

LLNL ID	Elevation	Total Depth	Depth to Perforation 1 Top	$\delta^{18}O_{SMOW}$	Tritium	$^3He/^4He$	Excess Air from Ne	Radiogenic ^4He	Ground-water Age	Ground-water Age Error	Percent pre-modern	Recharge Temp	Recharge Temp Error
	(ft)	*(ft bgs)*	*(ft bgs)*	*(‰)*	*(pCi/L)*		*(ccSTP/g)*	*(ccSTP/g)*	*(years)*	*(years)*	*(%)*	*(°C)*	*(°C)*
101497	173.9	526	234	-8.4	0.53	1.41E-06	0.0021	2.29E-09	40.5	1.0	1.00	14.3	1.0
101498	185.4	764	291	-9.1	1.37	1.47E-06	0.0021	1.72E-09	35.0	0.0	0.99	16.4	1.0
101499	182.1			-9.6	1.08	1.43E-06	0.0021	1.96E-10	30.8	1.0	0.99	15.4	1.0
101500	154.2	590	260	-10.0	0.97	1.42E-06	0.0028	1.56E-10	28.2	1.0	0.99	13.6	1.0
101501	141.1	610	200	-10.1	9.85	1.74E-06	0.0051	-2.96E-09	25.4	1.5	0.81	14.6	1.2
101502	205.7	530	200	-9.7	13.88	2.15E-06	0.0070	-7.87E-09	32.2	1.4	0.85	11.2	1.2
101503	180.4	520	200	-9.7	5.38	1.83E-06	0.0020	-1.81E-09	34.4	1.3	0.95	13.8	1.0
101504	160.8	550	120	-8.7	11.04	2.12E-06	0.0030	-4.10E-09	31.5	1.1	0.88		
101505	155.8	528	230	-8.8	10.26	1.77E-06	0.0045	-7.15E-09	24.4	1.8	0.78	14.4	1.1
101506	163.3			-9.0	8.04	2.10E-06	0.0019	-2.32E-09	34.9	1.0	0.93	14.2	1.0
101507		502	142	-9.8	9.09	2.42E-06	0.0019	-3.39E-09	38.3	1.0	0.95	13.5	1.0
101508	216.5	578	290	-10.2	4.56	1.65E-06	0.0019	-3.84E-09				14.0	1.0
101509	154.2	630	158	-10.0	2.47	1.63E-06	0.0026	-2.60E-09				14.8	1.0
101510	165.7	500	160	-9.3	12.60	5.99E-06	0.0046	-5.51E-09				15.2	1.1
101511	147.6	777		-10.1	1.00	6.84E-06	0.0029	-5.50E-09	>50		1.00	13.2	1.0
101512	246.1			-10.1	11.88	7.85E-06	0.0019	-5.89E-09				14.3	1.0
101513	196.9			-10.3	9.52	4.42E-06	0.0058	-8.83E-09				13.5	1.2
101514	196.9	550	131	-9.6	11.01	2.05E-07	0.0033	-8.66E-09				13.9	1.0
101515	196.9			-9.3	9.96	6.48E-06	0.0041	-5.28E-09				16.3	1.1
101516	196.9			-9.5	7.66	1.81E-06	0.0054	-1.01E-08				14.6	1.2
101517				-9.0	8.46		0.0031	-7.76E-09				13.4	1.0
101518	177.2	689	125	-9.8	-0.04	1.08E-05			>50		1.00		
101519	157.5	498		-10.3	8.15	1.61E-06	0.0015	-3.86E-09	18.5	1.3	0.73		
101520	196.9			-10.2	12.39	2.01E-06	0.0019	-4.16E-09	26.1	1.0	0.77	14.4	1.0
101521	141.1	532	250	-9.9	10.91	1.60E-06	0.0037	3.81E-09	19.6	1.4	0.67	14.7	1.1
101522	147.6			-10.0	6.44	4.45E-06							
101523	196.9	784	300	-10.1	4.58	1.67E-06	0.0029	-6.60E-09	30.1	1.8	0.94	12.7	1.0
101524	213.3			-9.9	4.18	1.56E-06	0.0038	-6.83E-09	26.0	2.2	0.92	14.1	1.1
101525	223.1	635	150	-10.2	5.47	1.69E-06	0.0020	-4.13E-09	28.3	1.5	0.92	13.2	1.0
101526	272.3			-9.3	2.26	1.08E-06	0.0019	3.96E-08				15.8	1.0
101527				-10.0	2.92								
101528				-9.2	0.51				>50		1.00		
101529	219.8	500	240	-10.1	4.27								
101530	216.5	757	222	-10.2	9.64	2.01E-06	0.0023	-5.68E-09	29.7	1.1	0.87	13.1	1.0
101573	246.0			-9.0	0.19	1.09E-06	0.0010	2.48E-08	>50		1.00	17.0	0.8
101579	203.4			-9.6	15.07	2.32E-06	0.0024	-3.71E-09	29.6	1.0	0.79	17.1	0.8
101582	201.8			-8.8	0.01	1.29E-06	0.0014	5.16E-09	>50		1.00	17.0	0.8

Table 4. Groundwater ages, noble gas and stable oxygen results con't.

LLNL ID	Elevation	Total Depth	Depth to Perforation 1 Top	$\delta^{18}O_{SMOW}$	Tritium	$^{3}He/^{4}He$	Excess Air from Ne	Radiogenic ^{4}He	Ground-water Age	Ground-water Age Error	Percent pre-modern	Recharge Temp	Recharge Temp Error
	(ft)	*(ft bgs)*	*(ft bgs)*	*(‰)*	*(pCi/L)*		*(ccSTP/g)*	*(ccSTP/g)*	*(years)*	*(years)*	*(%)*	*(°C)*	*(°C)*
101583	239.5	525	240	-8.9	0.43	1.18E-06	0.0011	1.50E-08	>50		1.00		
101584	216.5	757	222	-9.8	7.21	2.01E-06							
101585	249.3	600	200	-9.1	11.00	2.08E-06	0.0015	-1.13E-09	29.5	1.0	0.85		
101586	4868.8	453	100	-13.9	10.64	3.91E-07	0.0035	3.52E-07	14.0	1.5		8.8	0.8
101587	4868.8	618	51	-13.7	10.18	3.38E-07	0.0046	8.84E-07	37.0	1.4		8.2	0.8
101588	5042.7			-14.3	6.98	1.40E-06	0.0008	-9.95E-10	NA			7.2	0.7
101589	5656.1	520	110	-14.0	7.88	1.29E-06	0.0064	8.14E-09	7.0	2.0		6.8	0.8
101594	332.0	600		-9.2	0.64	8.65E-07	0.0005	7.34E-08	>50		1.00	17.0	0.8
101595	144.4	570		-10.0	6.67	1.79E-06	0.0035	-3.83E-09	30.9	1.7	0.92	17.0	0.9
101596	203.4			-8.9	2.97	1.51E-06	0.0025	-3.24E-09	26.5	2.6	0.95	17.0	0.8
101597	216.5	600	168	-9.6	3.29	1.56E-06	0.0062	-8.89E-09	31.2	3.0	0.96	17.0	0.9
101598	267.3	570	240	-8.8	16.79	1.52E-06	0.0014	5.73E-10	8.1	1.2	0.28	17.0	0.8
101599	360.9			-10.7	0.45	3.13E-07	-0.0081	1.05E-06	>50		1.00		
101600	252.6	428		-8.5	0.27	1.38E-06	0.0016	-4.64E-09	22.1	0.0	0.99	17.3	0.8
101601	173.9			-9.5	12.77	1.40E-06	0.0041	1.42E-08	9.6	2.8	0.45	14.1	0.8
101602	150.9	228	70	-9.3	25.28	2.22E-06	0.0051	-7.31E-09	23.0	1.2	0.40	14.3	0.9
101603	131.2	220	71	-9.2	27.78	2.17E-06	0.0056	-8.81E-09	21.2	1.5	0.24	12.2	0.9
101604	183.7	580	350	-8.6	1.57	1.37E-06	0.0014	-4.24E-09	40.0	2.0	0.94	17.0	0.8
101605	196.9	500	138	-9.5	10.14	2.08E-06	0.0026	-4.71E-09	31.2	1.2	0.88	17.0	0.8
101606	167.3	572	128	-10.2	9.10	1.80E-06	0.0017	-3.90E-09	24.8	1.2	0.81		
101607	183.7	770		-10.3	6.81	1.79E-06	0.0018	-4.56E-09	28.4	1.3	0.90		
101608	213.3	770		-9.7	0.78	1.44E-06	0.0022	-4.30E-09	34.4	1.0	0.99		
101609	63.0	173	99	-10.3	0.61	1.98E-06	0.0048	-7.80E-09	MH				
101610	342.2			-12.2	0.81	1.47E-06	0.0034	-6.87E-09	40.8	1.0	0.99		
101611	39.4	556	505	-10.9	0.25	8.83E-07	0.0003	3.77E-07	>50		1.00	17.1	0.8
101612	39.4	326	312	-10.8	0.08				>50		1.00		
101613	39.4	160	92	-9.2	0.57				>50		1.00		
101615	218.2	515	60	-8.6	12.61								
101616	218.2	515	270	-9.5	3.59								
101617	218.2	515	470	-9.5	5.22								
101618	143.1	444	370	-9.8	0.28				>50		1.00		
101619	143.1	444	210	-9.0	12.85								
101650	63.0	581	509	-9.2	0.17	4.09E-06	0.0036	2.17E-09	MH			16.8	0.9
101651	63.0	1000	767	-9.0	0.23	1.07E-06	0.0063	5.48E-08	>50		1.00	16.7	0.9
101652	110.7			-9.5	1.83	6.09E-07	0.0003	1.16E-07					
101653	110.7			-9.8	0.27	2.55E-07	0.0014	1.05E-07	>50		1.00	16.2	0.8
101654	85.3			-11.6	0.27	2.77E-07	0.0029	1.13E-06	>50		1.00		

Table 4. Groundwater ages, noble gas and stable oxygen results con't.

LLNL ID	Elevation	Total Depth	Depth to Perforation 1 Top	$\delta^{18}O_{SMOW}$	Tritium	$^3He/^4He$	Excess Air from Ne	Radiogenic ^4He	Ground-water Age	Ground-water Age Error	Percent pre-modern	Recharge Temp	Recharge Temp Error
	(ft)	*(ft bgs)*	*(ft bgs)*	*(‰)*	*(pCi/L)*		*(ccSTP/g)*	*(ccSTP/g)*	*(years)*	*(years)*	*(%)*	*(°C)*	*(°C)*
101655	85.3			-10.3	0.16	5.35E-07	0.0041	1.33E-07	>50		1.00	17.2	0.9
101656	85.3			-9.7	14.52	2.21E-06	0.0107	-7.46E-09	36.0	1.7	0.89	17.0	1.1
101657	85.3			-9.5	11.41	2.08E-06	0.0029	-3.94E-09	30.1	1.0	0.85	17.0	0.8
101658	155.8	571	540	-9.7	1.99				50.0				
101659	155.8	171	140	-9.1	8.45	1.55E-06	0.0072	-2.43E-09	20.0	2.2	0.75	17.0	0.9
101685				-14.7	6.46	1.47E-06	-0.0005	-1.23E-09					
101686				-13.2	13.42	1.91E-06							
101687				-14.5	0.35	6.85E-06	0.0012	1.22E-07	MH				
101688				-14.3	7.67	6.33E-06	0.0009	7.81E-08	MH			8.8	0.8
101689				-13.9		1.36E-06	-0.0002	-2.68E-09				8.1	0.8
101690				-14.2		2.71E-06	0.0004	6.76E-09	MH			9.0	0.8
101691				-13.6	1.30	3.06E-06	-0.0001	1.84E-07	MH				
101692				-13.7	-0.10	2.70E-06	0.0009	6.66E-08	>50		1.00	12.9	0.9
101693	2290.5			-13.0	15.92	1.26E-06	0.0051	5.83E-08	8.3	6.5	0.32	12.5	1.1
101694	2278.8			-13.1	11.81	1.31E-06	0.0032	-3.83E-10	5.6	2.1		12.1	1.0
101695	2278.8			-12.9	13.16	1.32E-06	0.0039	8.01E-09	8.1	2.0			
101696	4396.3	392		-13.5	1.46	1.85E-06	0.0013	1.74E-07	MH			11.6	0.8
101697	4353.7			-13.8	1.39	1.63E-06	0.0015	1.51E-07	MH			10.1	0.8
101698	4393.0	500		-13.9	1.41	1.75E-06	0.0014	6.96E-08	MH			10.3	0.8
101699	4366.8	670		-14.1	2.23	1.71E-06	0.0013	7.30E-08	MH			10.4	0.8
101700	4012.5			-13.9	-0.01	1.75E-06	0.0018	3.80E-09	>50		1.00	16.4	0.9
101701	4012.5			-13.3	0.15	1.75E-06	0.0013	6.15E-09	MH			15.4	0.8
101702	4048.6			-10.6	0.40	1.73E-06	0.0023	1.46E-09	MH			11.3	0.8
101703	4025.6			-13.3	0.25	1.44E-06	0.0011	4.28E-09	MH			15.9	0.8
101704	4042.0			-13.9	0.13	2.08E-06	0.0032	1.02E-08	MH			11.8	0.9
101705	4042.0			-14.4	1.16	1.43E-06	0.0023	2.73E-09	32.1	1.0	0.99	14.0	0.9
101706	4012.5			-6.6	0.65	3.41E-06	0.0035	1.24E-08	MH			9.1	0.8
101707	4229.0	1280		-13.9	1.44	2.61E-06	0.0025	2.54E-08	MH			7.6	0.7
101708	4225.7			-13.5	6.01	1.58E-06	0.0056	-4.26E-09	23.3	2.2	0.86	9.8	0.9
101709	3271.0			-12.8	8.51	1.42E-06	0.0014	-3.31E-09	9.1	1.1			
101710	3271.0			-12.8	9.39	1.45E-06	0.0013	-3.14E-09	8.3	1.2			
101711	3271.0			-12.7	9.47	1.43E-06	0.0014	-3.73E-09	8.5	1.1			
101712	143.1	800	760	-8.7	11.69	1.53E-06	0.0031	-1.90E-09				15.3	1.0
101713	133.5	1000	920	-11.1	2.37	1.99E-07	0.0008	1.26E-06				13.6	0.9
101714	133.5	675	635	-10.3	0.55	2.65E-07	0.0035	1.35E-07	>50		1.00	13.9	1.0
101748		470	450	-11.1	0.31				>50		1.00		

Table 4. Groundwater ages, noble gas and stable oxygen results con't.

LLNL ID	Elevation	Total Depth	Depth to Perforation 1 Top	$\delta^{18}O_{SMOW}$	Tritium	$^{3}He/^{4}He$	Excess Air from Ne	Radiogenic ^{4}He	Ground-water Age	Ground-water Age Error	Percent pre-modern	Recharge Temp	Recharge Temp Error
	(ft)	*(ft bgs)*	*(ft bgs)*	*(‰)*	*(pCi/L)*		*(ccSTP/g)*	*(ccSTP/g)*	*(years)*	*(years)*	*(%)*	*(°C)*	*(°C)*
101749		120	100	-11.0	7.38								
101750		760	719	-8.9									
101751		495	462	-11.0									
101752		277	174	-9.0									
101753		813	730	-10.0									
101811	160.0	526	484	-8.5	0.07	1.20E-06	0.0003	5.83E-08	MH			15.5	0.9
101812	160.0	399	336	-8.2	0.36				>50		1.00		
101813		974	869	-11.5	0.49	2.60E-07	0.0033	5.33E-07	>50		1.00	10.1	0.9
101814		120	100	-10.5	3.04								
101815		470	450	-11.1	0.42				>50		1.00		
101816		760	719	-11.0	0.07	6.09E-07	-0.0010	2.47E-06	>50		1.00	13.7	0.9
101817	130.0	203	130	-6.7	13.71	2.17E-06	0.0052	-6.10E-09				13.1	1.1
101818	75.0	550	490	-8.7	0.15	1.11E-06	0.0007	9.14E-08	>50		1.00	16.1	1.0
101819		1006	930	-9.8	3.69	9.79E-07	0.0098	2.71E-07				13.5	1.5
101820		1006	816	-10.1	0.17	9.80E-07	0.0013	4.36E-07	>50		1.00	11.6	0.9
101821	150.0	203	130	-6.0	25.82	2.91E-06	0.0074	-7.66E-09				12.8	1.3
101822				-10.2	2.09								
101822				-10.2	2.09								
101823				-8.8	1.00				>50		1.00		
101824				-8.9	0.36				>50		1.00		

MH=mantle helium