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California GAMA Program: A Contamination Vulnerability Assessment for the Bakersfield Area



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California GAMA Program: A Contamination Vulnerability Assessment for the Bakersfield Area

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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 basin that underlies Bakersfield, in the southern San Joaquin Valley. 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.

The metropolitan Bakersfield area, with a population of over 260,000, and average annual rainfall of less than 6 inches, experiences high water demand that is increasing by roughly 3% annually. Over 200 public drinking water wells supply up to 60% of municipal demand. Bakersfield is situated at the base of the Sierra Nevada, where relatively coarse-grained sediments and ample historical recharge from the Kern River made possible copious groundwater extractions for agriculture over the past several decades. Under current groundwater management, unlined irrigation canals traverse the growing urban area, and provide the major route for groundwater recharge, while the natural flow in the Kern River is almost entirely diverted upstream of Bakersfield. Forty-three active public supply wells are included in the GAMA susceptibility study.

Mean groundwater ages in several wells in the center of the study area and near irrigation canals are less than 7 years, indicating very recent connection with the surface, and high contamination vulnerability. It is not surprising, then, that the frequency of VOC occurrence is high – 81% of wells included in the study had detections of more than one class of compounds (trihalomethanes, solvents, or gasoline compounds). Perchloroethylene (PCE or tetrachloroethylene) is particularly widespread at very low concentrations in drinking water wells. Seventy four percent of wells had PCE detections – the highest occurrence frequency of any area examined so far using ultra low-level techniques. The highest concentration found is still nearly 10 times below the Maximum Contaminant Level (MCL) for PCE, and 20 detections (63% of detections) are below the Public Health Goal (PHG) of 56 ng/L. These results are therefore not relevant with

respect to regulatory limits or even with regard to potential health effects in most cases. They rather offer evidence for vertical transport to deep groundwater, and confirm the susceptibility evidence offered by groundwater ages, which indicate relatively high vulnerability.

Mean groundwater ages reflect the recharge pattern in the area, where unlined canals are the major route for recharging the heavily exploited basin. The youngest groundwater ages occur in wells along the main canals that are supplied with Kern River, imported, and other water sources. The presence of a large component of Kern River water, derived from very high elevation meltwater from the slopes of Mt. Whitney, is evidenced by highly depleted $\delta^{18}\text{O}$ values found in all of the wells included in the study. Spatial variability in $\delta^{18}\text{O}$ is likely related to varying proportions of imported and captured water sources, all of which are isotopically enriched compared to the Kern River. A small fraction of water from sources other than Kern River water is indicated in wells near the center of the study area.

On the margins of the study area, especially in downgradient areas to the west, southwest, and northwest of the urban center, significantly older ages are observed, although only 2 wells in the study area produce groundwater with tritium concentrations below the detection limit (indicating groundwater ages of greater than 50 years). The wells in outlying areas are characterized by old groundwater ages and high fractions of pre-modern water, $\delta^{18}\text{O}$ values that match the range for Kern River water, and a low frequency of VOC occurrence. These wells also have very low concentrations of 'excess air' indicating recharge under natural conditions, before canal recharge became dominant. A significant concentration of radiogenic ^4He (which indicates the presence of a groundwater component with a subsurface residence time of thousands of years or more) is found in only well. Overall, a dynamic recharge and flow system is indicated for this urbanized basin, with areas of intense pumping and active artificial recharge resulting in rapid turnover of groundwater. Old groundwater that is free of VOCs is present only in the downgradient, outlying areas.

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 GAMA Program is to assess the water quality and to predict the relative susceptibility to contamination of groundwater resources throughout the state of California. Under the GAMA program, scientists from Lawrence Livermore National Laboratory (LLNL) collaborate with the SWRCB, the U.S. Geological Survey (USGS), 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 groundwater basin that underlies Bakersfield, in the southern San Joaquin Valley. 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:

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

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

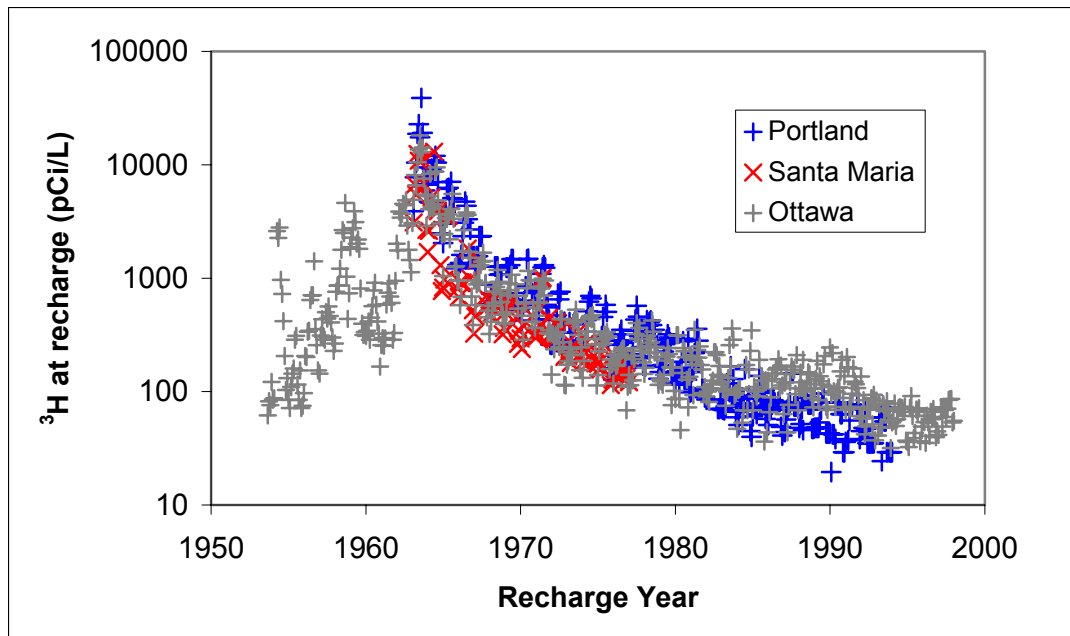


Figure 1. The tritium concentration measured in precipitation at three North American locations. Nuclear weapons testing introduced a large amount of tritium into the atmosphere in the 1960's, peaking in 1963.

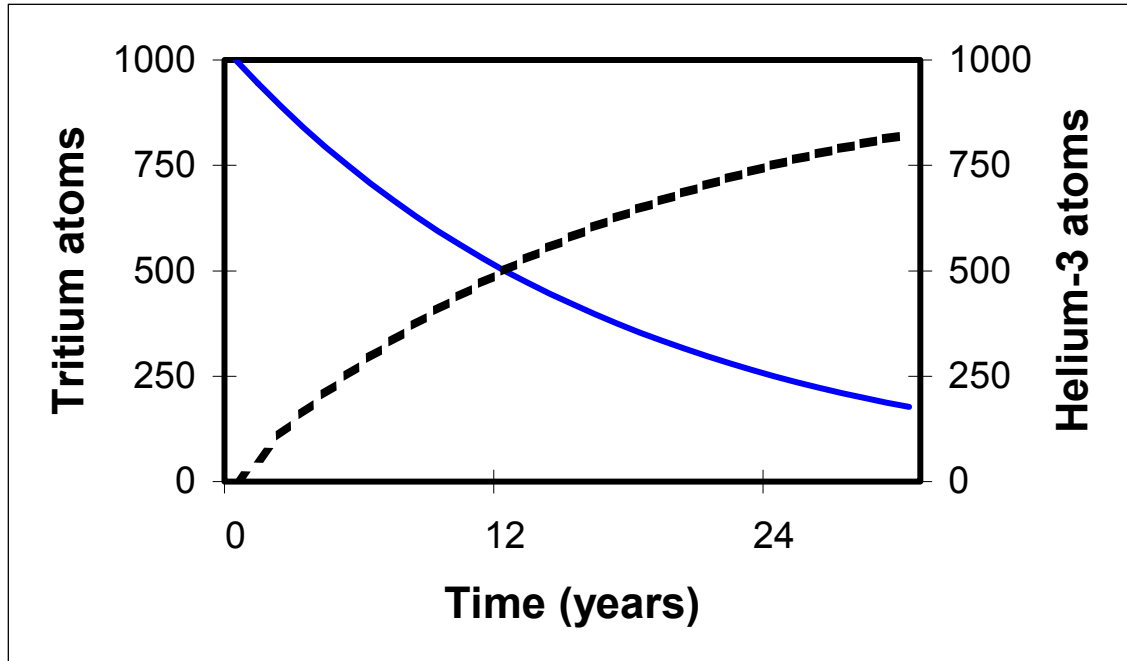


Figure 2. Solid line shows the decay of tritium, with a half-life of 12.34 years, while the dashed line shows the growth of the daughter product, ^3He . The sum of tritium and ^3He is the same at any time, and equal to the initial tritium value. This is the basis for the groundwater age-dating technique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

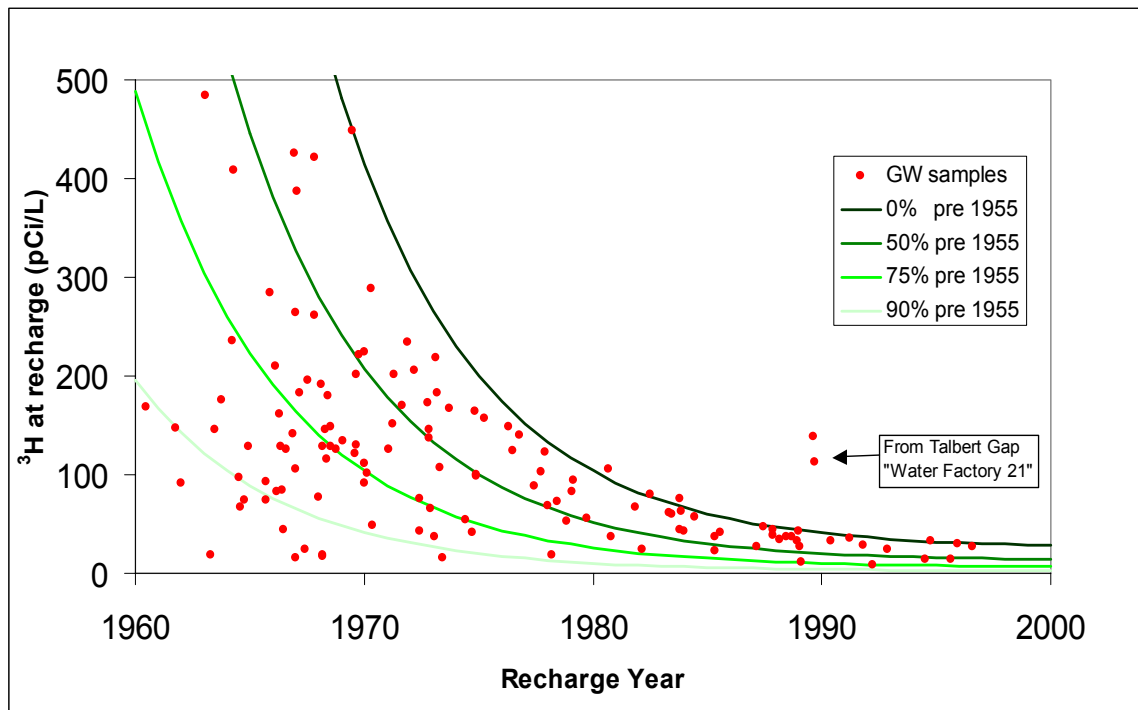


Figure 3. Curves show equal fractions of pre-modern water. The line labeled 0% is an approximation of the tritium in precipitation data from figure 1. Lines below approximate mixtures of pre-modern and post-modern water. Groundwater samples from southern California coastal basins are shown as points.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

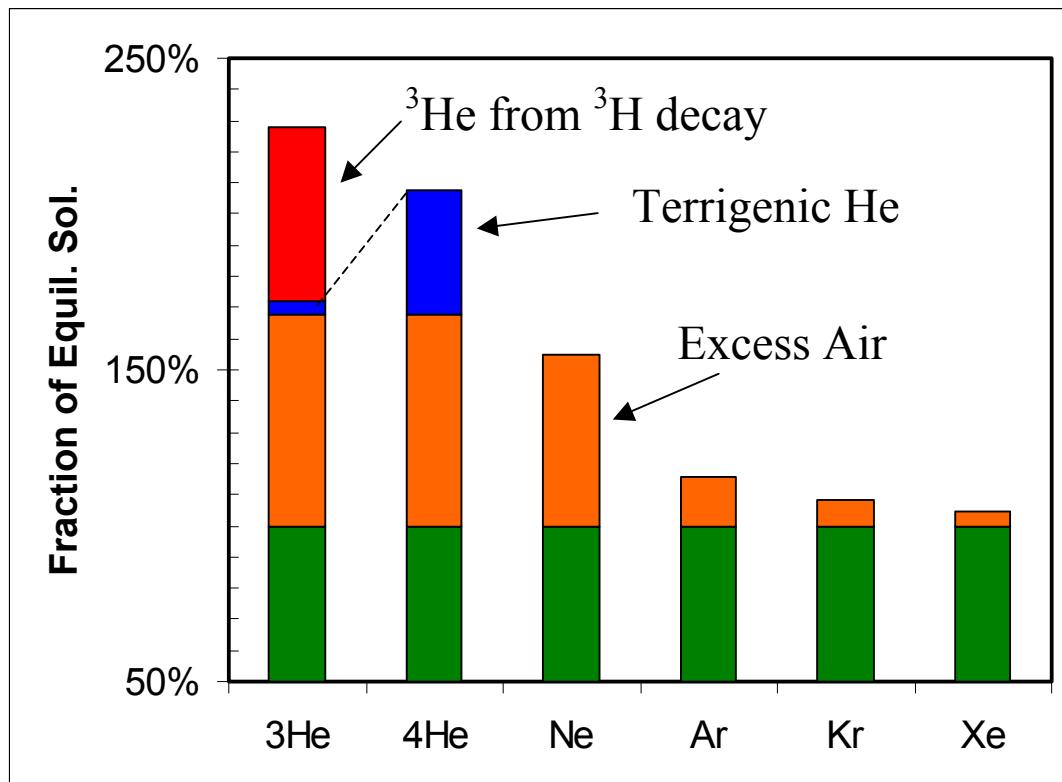


Figure 4. Graphical representation of the various dissolved noble gas components in a typical groundwater sample, relative to equilibrium solubility concentrations. Terrigenous He has a component of radiogenic ^4He from U and Th decay in the earth's crust.

Radiogenic $^4\text{Helium}$

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 ^4He atoms)

are emitted. Thus, ^4He accumulates significantly in groundwater on time scales of hundreds to thousands of years. The ^4He from U and Th decay in the earth's crust is termed 'radiogenic ^4He ', and is expected to increase along a groundwater flow path. Precise age dating using ^4He 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 ^4He (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}C dating of groundwater (Marty et al., 2003, Castro et al., 2000). Radiogenic ^4He 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 ^4He from the earth's crust of $2 \times 10^{-7} \text{ cm}^3 \text{ STP cm}^{-2} \text{ yr}^{-1}$.

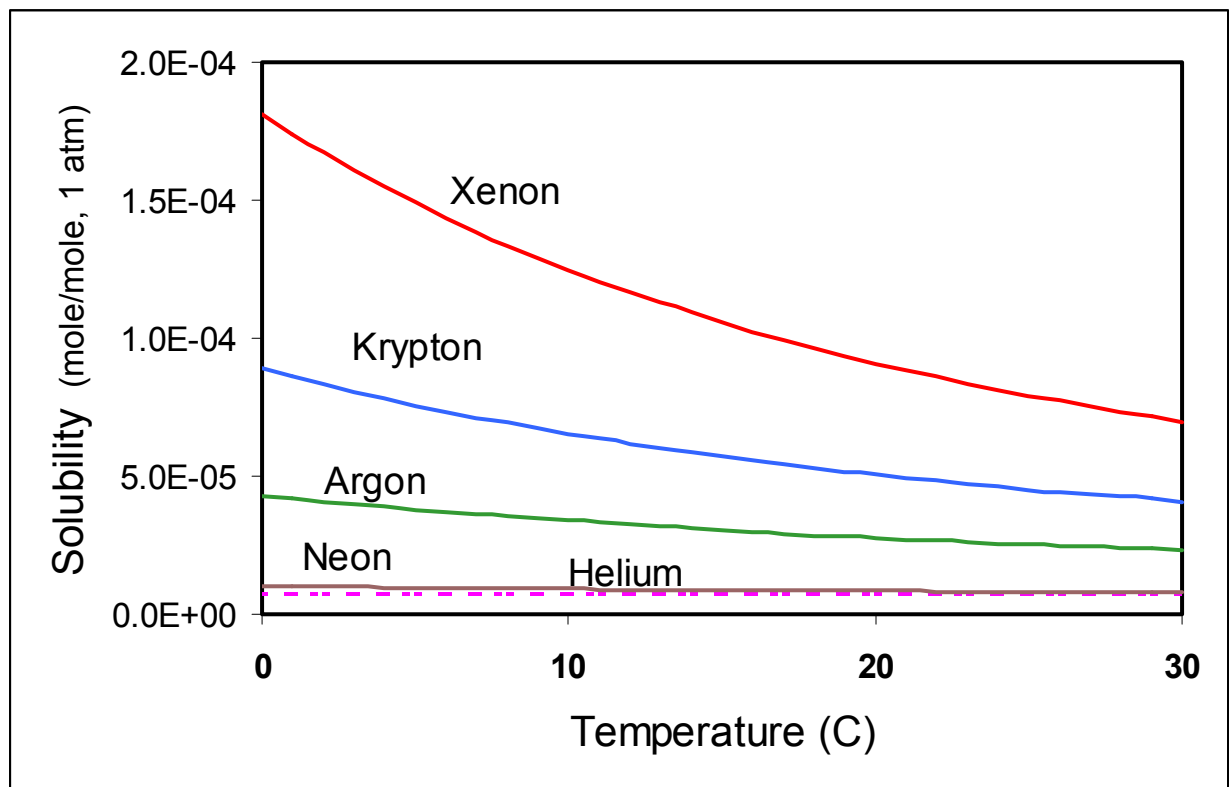


Figure 5. The solubility curves for the noble gases according to water temperature, showing the strongest temperature dependence for Xe. Noble gas recharge temperatures are calculated from these well-established curves.

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 ('sinks'), 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 ^2H (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.

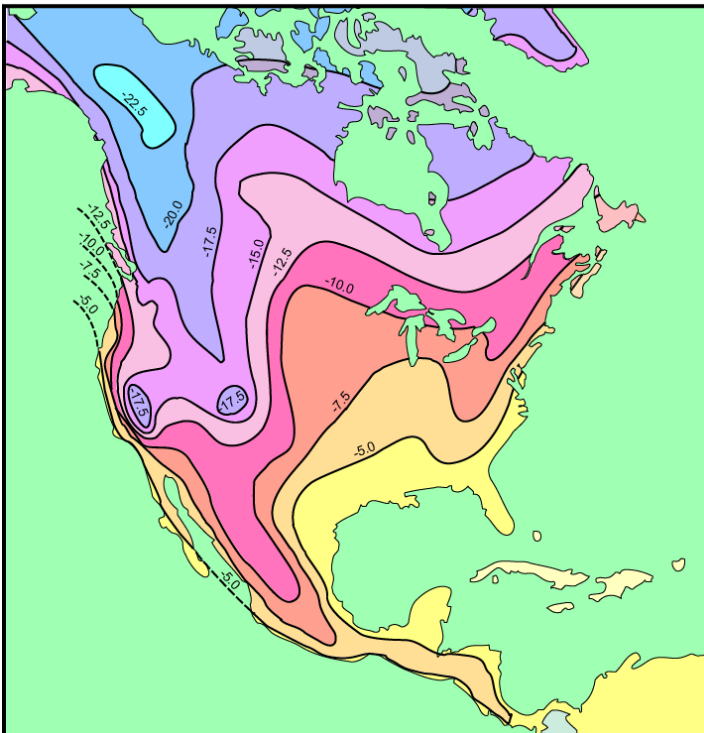


Figure 6. Contour map of $\delta^{18}\text{O}$ (SMOW) showing tight contours and lighter, depleted values at high elevation in California. (after Taylor, 1974)

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:

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

where R_x is the $^{18}\text{O}/^{16}\text{O}$ ratio of the sample and R_{std} is the $^{18}\text{O}/^{16}\text{O}$ ratio of the standard. The conventional standard reference material for oxygen isotopes is Standard Mean Ocean Water (SMOW; Craig, 1961). Using the delta notation, $\delta^{18}\text{O}$ in precipitation varies from approximately -4‰ along the Pacific coast to -15‰ 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 $\delta^{18}\text{O}$ 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

Groundwater is a crucial part of the municipal supply

The metropolitan Bakersfield area, with a population of over 260,000, and average annual rainfall of less than 6 inches, has high water demand, which is supplied by surface water and groundwater. Surface water from the Kern River, CA State Water Project (CWP), and Central Valley Project (CVP) supplies a little over one quarter of the total demand of about 100,000 to 150,000 acre-ft. Groundwater pumping, excluding extraction from the ‘2800 Acre Bank’, accounts for about 60% of the municipal supply, and is therefore a crucial resource. Municipal well production averages approximately 70,000 acre-ft per year, and is increasing by approximately 2,000 acre-ft/yr. Agricultural pumping in surrounding areas is roughly ten times the level of urban extraction. The largest source of recharge to the groundwater basin in the Bakersfield urban area is by canal and river seepage, which is estimated to be 106,000 acre-ft per year (City of Bakersfield Water Balance Report; <http://www.bakersfieldcity.us/cityservices/water/pdfs/2000waterrpt-1.pdf>). A series of unlined canals traverses the city and carries irrigation water to agricultural areas to the south and west. The canals are fed by Kern River, CWP, and CVP allotments. Infiltration of river water, local runoff, and imported water through the canals, then, is the most significant mechanism for groundwater recharge in Bakersfield. Other sources of recharge are from storm water, which is collected in drainage basins (24,000 acre-ft per year), and reclaimed water used for irrigation (20,000 acre-ft per year). In surrounding agricultural areas, recharge of irrigation water occurs on a large scale, but cannot be quantified. Groundwater banking

extractions (averaging 22,000 acre-ft per year) occur to the west of the study area, in the 2800 Acre recharge facility.

The study area is within the Kern County Groundwater subbasin, which is bounded on the east and southeast by the Sierra Nevada foothills and Tehachapi Mountains, on the north by the Tule subbasin, and on the west by the marine sediments of the San Emigdio Mountains and Coast ranges (DWR Bulletin 118). Significant water-bearing deposits in the groundwater subbasin include the Plio-Pleistocene Kern River Formation, which includes the Corcoran Clay Member, below which groundwater is confined. Sediments in this formation comprise clay, silt, sand and gravel from the Sierra Nevada, and yield moderate to large quantities of water to wells. Overlying alluvium and flood basin deposits of Holocene age vary in character and thickness and can yield significant quantities of groundwater (DWR Bulletin 118). The fluvial-deltaic sediments of the Kern River fan, west of Bakersfield have high specific yield, and represent the greatest thickness of unconfined aquifer. DWR reports that groundwater levels have decreased by more than 25 feet in the Bakersfield area over the period 1970-2000.

Overall, groundwater quality in the subbasin is good, with areas of impairment due to MCL exceedances of nitrate, and the pesticides DBCP and ethylene di-bromide (EDB). Fewer than 10 percent of over four hundred public supply wells in Bakersfield and surrounding areas tested over the period 1980-2000 had a concentration above an MCL in any of the major water quality categories (inorganics, radiological, nitrate, pesticides, or VOCs). Forty three public supply wells, which were in regular operation during the course of sampling, were included in the GAMA study. The major private retailer of groundwater, along with the City of Bakersfield participated in the CAS study. Hundreds of potentially contaminating activities exist in the Bakersfield urban area, including 8 open SLIC sites and approximately 493 LUFT sites (39 open; GeoTracker).

Sampling and Analysis Procedures

LLNL personnel collected well water samples from 43 public water supply wells in Bakersfield, with the assistance of well owners, during the spring of 2003 (figure 7). Wells were sampled according to the procedures outlined in Appendix A. Sampled constituents include oxygen isotopes, tritium and dissolved noble gases for groundwater age, and low-level VOCs. 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.

Four different analyses are performed on each well water sample: 1) A set of VOCs (shown in Table 1, Appendix B) is measured using purge and trap gas chromatography-mass spectrometry, with a reporting limit of 5 parts per trillion. 2) The $^{16}\text{O}/^{18}\text{O}$ ratio is analyzed by stable isotope mass spectrometry. 3) The concentration of tritium is measured by the ^3He -ingrowth method (Clark et al., 1976, Surano et al., 1992, Beyerle et al., 2000). 4) The ratio of $^3\text{He}/^4\text{He}$ and the concentrations of all of the dissolved noble gases are measured by noble gas mass spectrometry. The tritium and

noble gas analyses are used together to calculate the groundwater age, and the temperature at which recharge took place is determined from the noble gas concentrations. A summary of analytical methods is given in Appendix A.

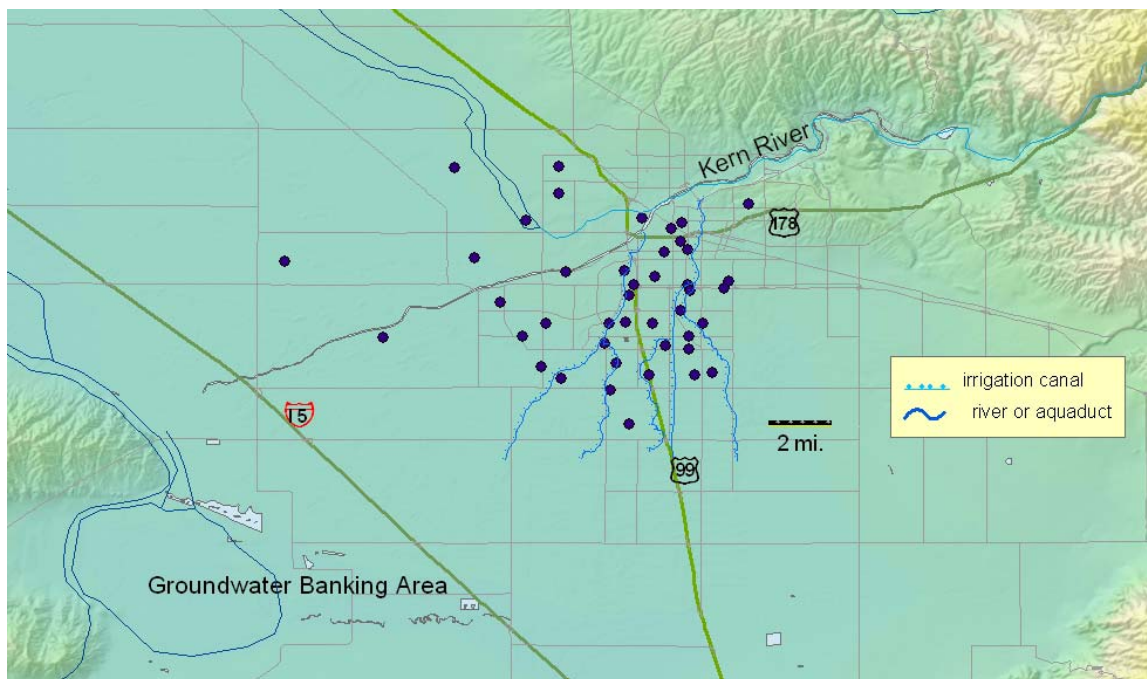


Figure 7. Location map showing public supply wells included in the Bakersfield area study.

Results

Analytical results for the Bakersfield wells are shown on figures 8 through 18. 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. Four ‘trip’ blanks (VOAs filled with laboratory-prepared deionized, distilled water that are carried around during field sampling but not opened) and twenty-four ‘transfer’ blanks (laboratory-prepared deionized, distilled water that is poured over into a VOA at the well location) were analyzed for all of the compounds in Table 1. As described in Appendix A, these QA samples test the cleanliness of the sampling equipment and containers, of the laboratory-prepared blank water and of the analytical equipment. In addition, the transfer blanks test the possibility that VOCs are transferred from the atmosphere to the sample vial during sampling. In previous GAMA study areas, transfer blanks were infrequently found to contain toluene and MtBE, and well sample results were screened accordingly, at a higher level than the analytical reporting limit of 5 ng/L. However, there were no detections of any VOC in any of the blanks from Bakersfield area sampling. No screening of results was necessary and all results have a reporting limit of 5 ng/L.

Discussion of VOC Occurrence

Overall frequency of VOC occurrence is similar to other Central Valley basins

Only four wells from the Bakersfield area had no detections above the report limit of 5 ng/L for all of the target analytes. Another 3 wells had detections only of THMs, which may occur as residuals of on-site disinfection. All of these wells produce very old groundwater, dominated by pre-modern recharge, and are near the outer margins of the study area. Regulatory analyses of VOCs for wells from the study area, from the DHS database, show infrequent detections of VOCs in wells not included in the study. Except for one MtBE detection discussed below, none of the wells have had detections of any of the compounds included in the study above the DHS reporting limit, which is typically 0.5 ppb ($\mu\text{g/L}$). Concentrations reported here do not represent concentrations in water supplied to the distribution system, which has contributions from multiple wells and surface water sources.

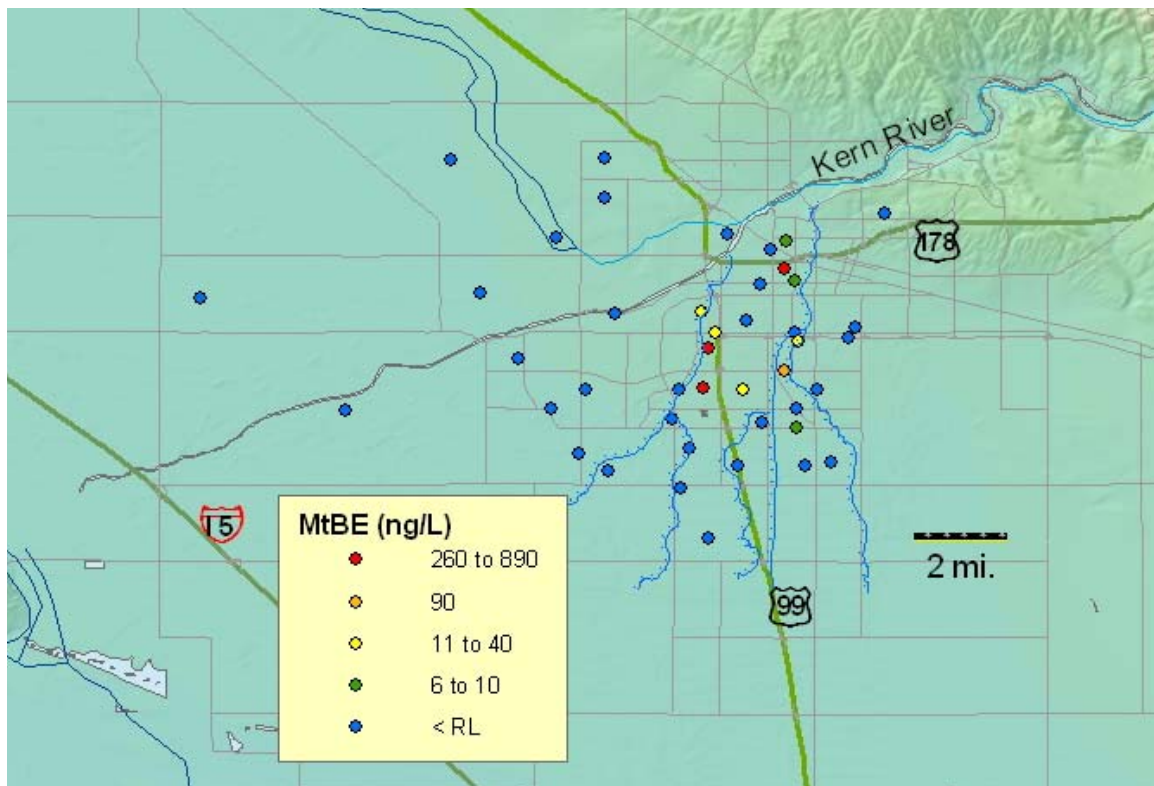


Figure 8. MtBE is found in 11 wells in the central part of the study area. Wells colored red have relatively high concentrations, and may be affected by point-source MtBE from leaking underground fuel tanks.

Eleven wells (or 26%) included in the study had detections of MtBE above the reporting limit of 5 ng/L (figure 8). A similar percentage of public water supply wells have been found to contain very low level MtBE in other Central Valley areas where the low-level analytical method was applied (Moran et al., 2003). MtBE occurs in wells with evidence for recent recharge, most likely

from the unlined irrigation canals that traverse the City of Bakersfield en route to agricultural areas to the south. The Kern River and canals are likely to contain MtBE at low concentrations, from atmospheric MtBE, and from inputs from recreational boating on Isabella Lake. The MtBE observed in the public supply wells, therefore, could come exclusively from surface water. However, three MtBE concentrations greater than 250 ng/L are higher than typically observed in public supply wells with surface water MtBE sources. A significant fraction of the water produced at these wells is old groundwater, so the MtBE measured is likely diluted to some degree by water not containing MtBE. In these wells, point source MtBE, from a leaking underground fuel tank (LUFT) or refinery leak ([http://yosemite.epa.gov/r9/r9coract.nsf/0/67ea2cbe99a9d02188256acc0082e33a/\\$FILE/Texaco%20Bakersfield%20087-%20769%20+%2003.pdf](http://yosemite.epa.gov/r9/r9coract.nsf/0/67ea2cbe99a9d02188256acc0082e33a/$FILE/Texaco%20Bakersfield%20087-%20769%20+%2003.pdf)) may contribute, although no detections of other gasoline compounds (BTEX) were observed. Compared to BTEX compounds, MtBE is more soluble and less labile. One of these three wells has had MtBE detections at concentrations between 1 and 14 ug/L (a level clearly indicating point source MtBE), during bi-weekly sampling from 2002 through 2004 (www.dhs.ca.gov/ps/ddwem/chemicals/MTBE/MTBEforweb.XLS).

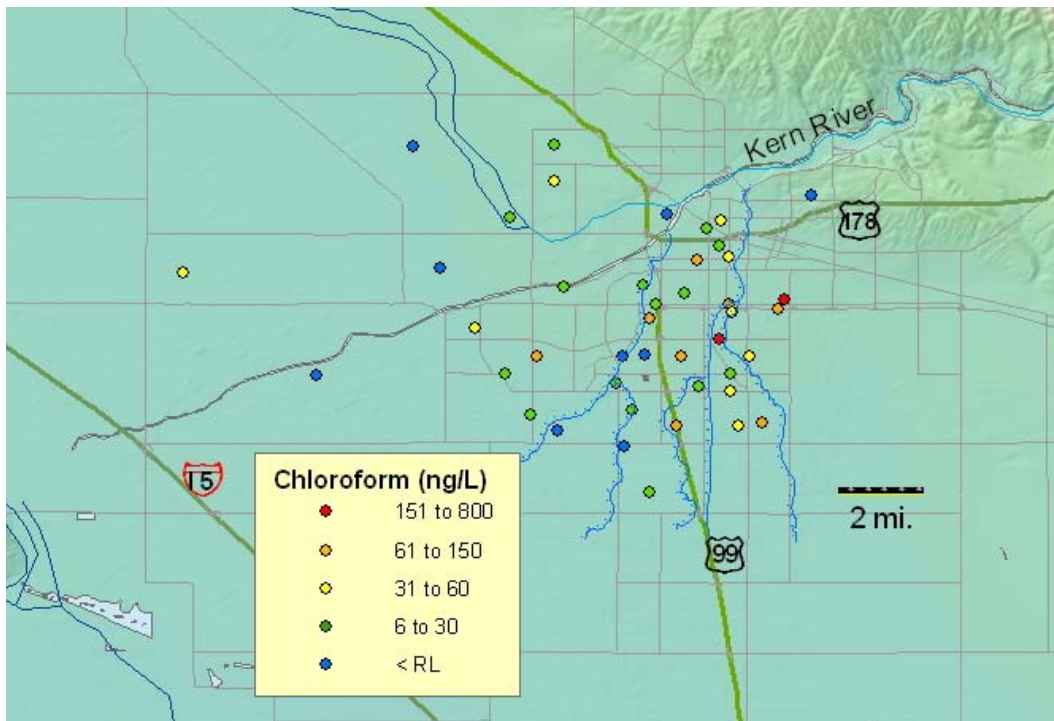


Figure 9. Chloroform is the most frequently detected VOC, with the highest concentrations found in the eastern and central portions of the study area.

Chloroform, a THM, was found in 32 wells (79%), a proportion similar to that observed in other Central Valley study areas (figure 9; Moran et al., 2003, Wright et al., 2004). Chloroform was detected with another THM (bromodichloromethane, chlorodibromomethane, bromoform) in 13 wells, and with PCE but not another THM in 16 wells. In general, relatively high concentrations of chloroform are accompanied by other THMs, and these detections are likely the result of residuals from on-site disinfecting and well maintenance operations. However, three chloroform detections above 100 ng/L are accompanied by relatively high concentrations of PCE and TCE. The

co-occurrence of the solvents may indicate that the source of chloroform is industrial, since chloroform is widely used in the manufacture of plastics, and in other industrial processes. Low concentrations of chloroform that occur without another THM may come from an advectively transported surface source or from a residual on-site source.

The frequency of PCE occurrence is high in Bakersfield wells

Tetrachloroethylene was detected above the reporting limit in 32 of 43 wells (74 %), a higher proportion of wells than in any area studied previously using low-level methods (figure 10). However, the highest concentration detected, 580 ng/L, is still almost ten times below the MCL for PCE. Twelve detections are above the PHG, which is 56 ng/L. Twelve are below 20 ng/L, a level not previously reported in the literature. Of the thirteen detections of TCE, 12 occur in wells with PCE detections, with TCE nearly always occurring at a lower concentration. In these cases, TCE likely occurs as a breakdown product of PCE. PCE does not co-occur in the well with the highest TCE concentration (450 ng/L, which is 64% higher than the next highest TCE detection), and in that case TCE was likely introduced on its own. The widespread occurrence of low-level PCE is common in Central Valley basins (Moran et al., 2003, Wright et al., 2004), but not in coastal basins (Shelton et al., 2001, Moran et al., 2002), probably because the semi-confined aquifers of the Central Valley allow vertical transport of contaminants to deep portions of the aquifer that are tapped by public supply wells.

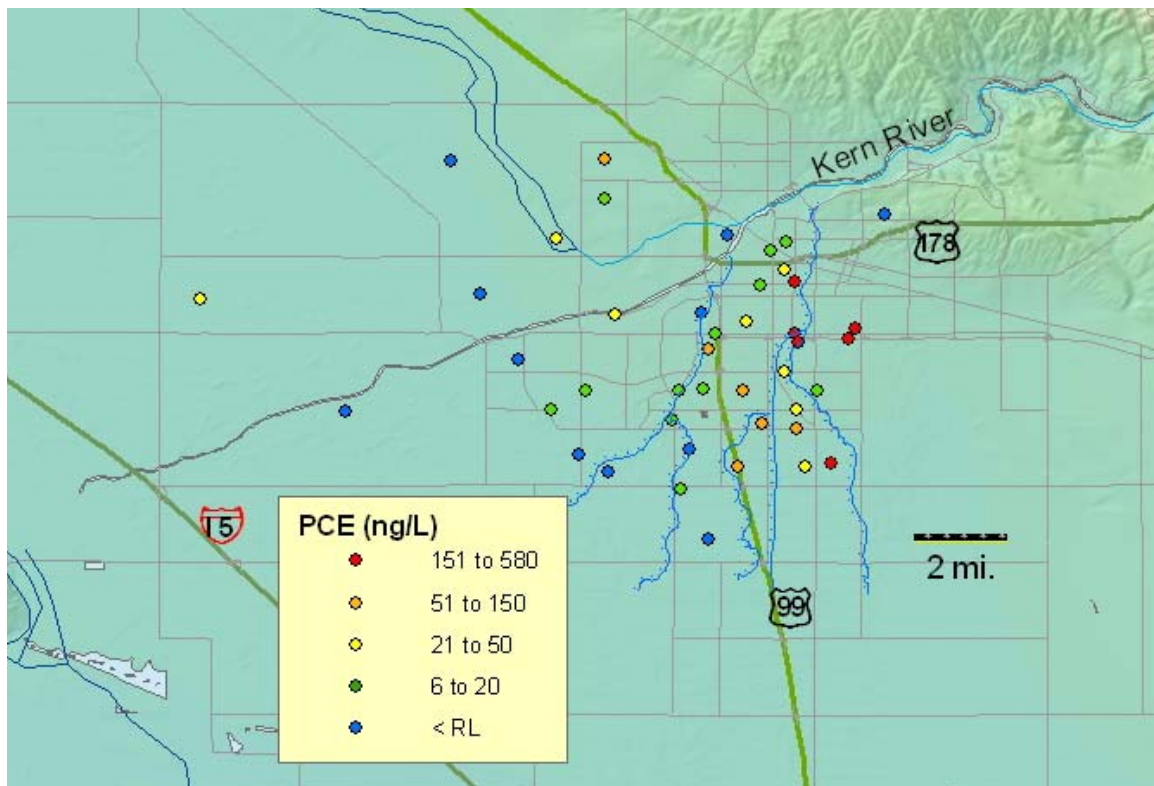


Figure 10. PCE is found in a high proportion of wells in Bakersfield, but concentrations are most commonly below 50 ng/L.

The frequency of occurrence of PCE is especially high in the Bakersfield area, even compared to other Central Valley Basins, where previous studies showed that up to half of the drinking water wells are affected by PCE occurrence (Moran et al., 2003, Wright et al., 2004). The combination of unconfined conditions resulting in areas of relatively young groundwater, and numerous sources, leads to a high frequency of PCE occurrence in Bakersfield. A plot of PCE concentrations versus groundwater age (figure 11) reveals that while PCE (greater than 15 ng/L) is not found in wells with groundwater ages greater than about 35 years, wells producing very young groundwater are just as likely to have significant PCE concentrations as wells with mean ages of 20 to 30 years. As discussed below, the same wells with relatively old calculated ages also produce a large component of pre-modern (tritium dead) groundwater. PCE concentrations are likely diluted by this pre-modern component. As in other areas of widespread PCE occurrence, discharge from dry cleaning operations to sewers with leaky joints is a likely route to groundwater (http://www.swrcb.ca.gov/rwqcb5/available_documents/site_cleanup/DryCleanerReport.pdf). The relatively low concentrations observed over a widespread area suggest that wells are affected by numerous, low level point sources that are entrained during recharge.

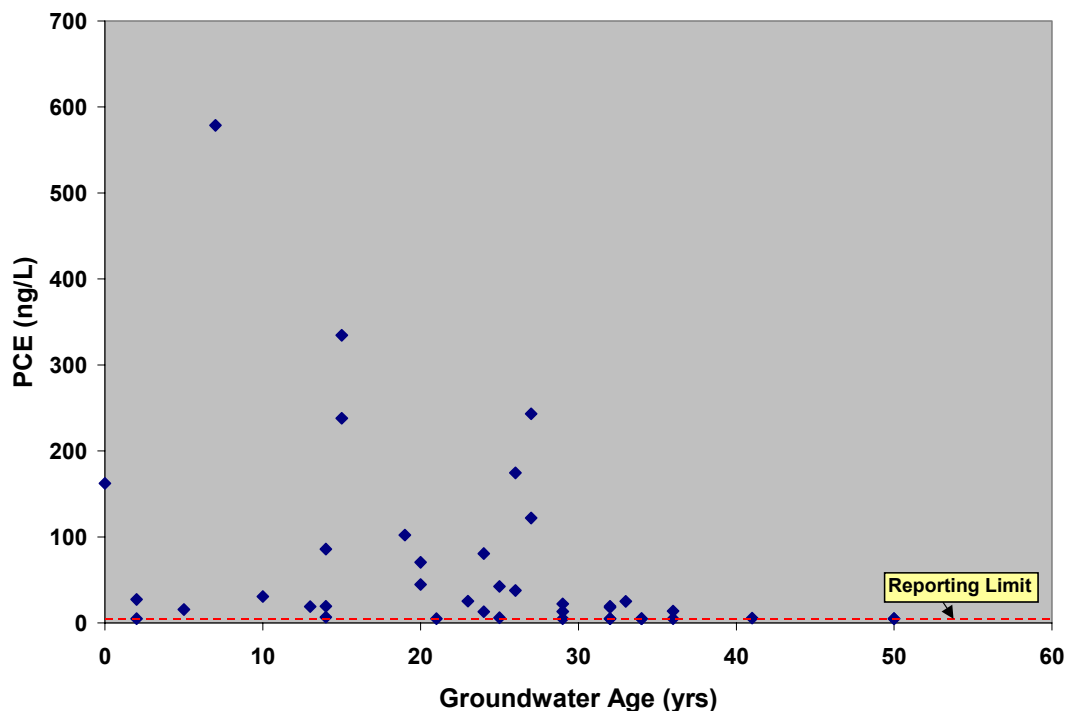


Figure 11. PCE concentration versus groundwater age shows that wells with the ages greater than 35 years do not have detections above 15 ng/L, but wells with mean ages younger than 35 years have a wide range in concentrations.

Two wells in the outlying area to the southwest of the urban center have extremely low-level DBCP detections, at 7 and 23 ng/L. DBCP is unlikely to become a water quality concern in Bakersfield because use of DBCP was banned in 1970, and because the areas potentially affected have changed from agricultural to suburban land use. Nitrate,

another contaminant that can be an indicator of agricultural pollution, is found at low concentrations in these two wells, and in the Bakersfield area in general (DHS database). The area to the north of the Kern River in Bakersfield (North Garden) is affected by high nitrate concentrations in some drinking water wells. Given that groundwater ages in that area are 20 to 40 years, with high fractions of pre-modern water, nitrate concentrations are likely much greater in shallow zones, and increasing nitrate concentrations may be expected in drinking water wells.

Discussion of Isotopic and Groundwater Age Results

Isotopic tracers indicate a high Sierran water source

Results of analyses of stable isotopes of oxygen are shown in figure 13. Compared to other major groundwater basins in California's Central Valley, wells from the Bakersfield area have a lighter (more depleted) range overall. The Kern River headwaters form at high elevation, on the slopes of Mt. Whitney, and the Kern River has one of the most depleted isotopic signatures of any major river in California (the mean value of 15 analyses of Kern River water $\delta^{18}\text{O}$ from 1984 to 1987 was -13.7‰ ; USGS Open File Report 00-160, Kendall and Coplen, 2001). The lightest (most negative) values recorded in wells are from outlying areas, especially to the south of the main urban area – these results are in a range that matches the range in river values. Tritium concentrations and groundwater ages indicate that these wells produce water that recharged 40 or more years ago, as described in the next section. Groundwater produced at these wells was recharged by Kern River water, before major imports to the area, when recharge to fan sediments was primarily from river water.

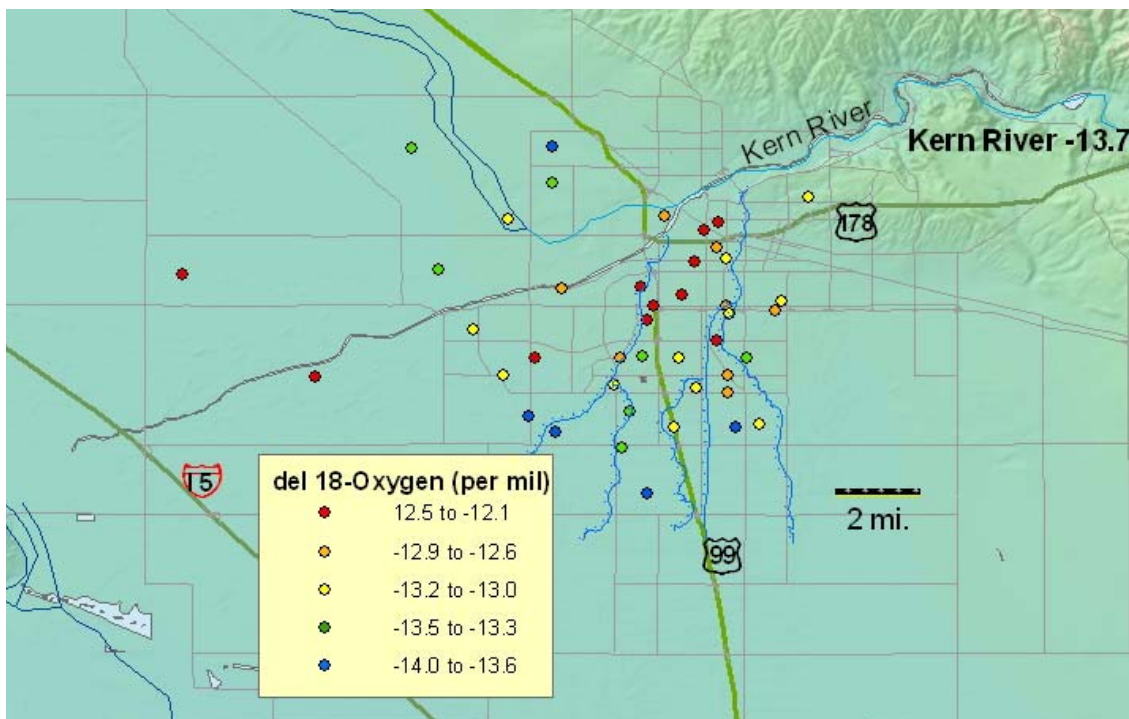


Figure 13. To the south and north of the urban area, $\delta^{18}\text{O}$ values from wells match the range observed in the Kern River. Heavier $\delta^{18}\text{O}$ values are observed in the central area.

In the central, heavily urbanized portion of the study area, more isotopically enriched (heavier, less negative) values are observed, indicating another recharge source. All of the other potential sources of water to the unlined canals – Central Valley Project, State Water Project, local precipitation including captured stormwater, and reclaimed water, have significantly heavier isotopic signatures than Kern River water (e.g., State Water Project water has a $\delta^{18}\text{O}$ range of -9 to -10 compared to -13 to -14 for river water). The observed spatial distribution in $\delta^{18}\text{O}$, and negative correlation with groundwater age (figure 14), suggest that sources other than Kern River water have become increasingly significant recharge water sources in the urban area. (A few measurements of δD were carried out to rule out evaporation as the main influence on the variability in stable isotope results – evaporative enrichment was not indicated.) Most wells show intermediate values, between enriched sources and Kern River end members, due to mixing in the aquifer and/or in the wellbore. In contrast to previously studied Central Valley Basins, a clear river water signature is not observed in wells near the Kern River. However, unlike rivers in the northern San Joaquin Valley which flow perennially, the Kern River does not flow through the study area west of the canals except on rare occasions, due to diversions in and upstream of Bakersfield. Stable isotope results illustrate that the major area of recent recharge is the unlined canals, which are fed by a combination of Kern River water and other water sources.

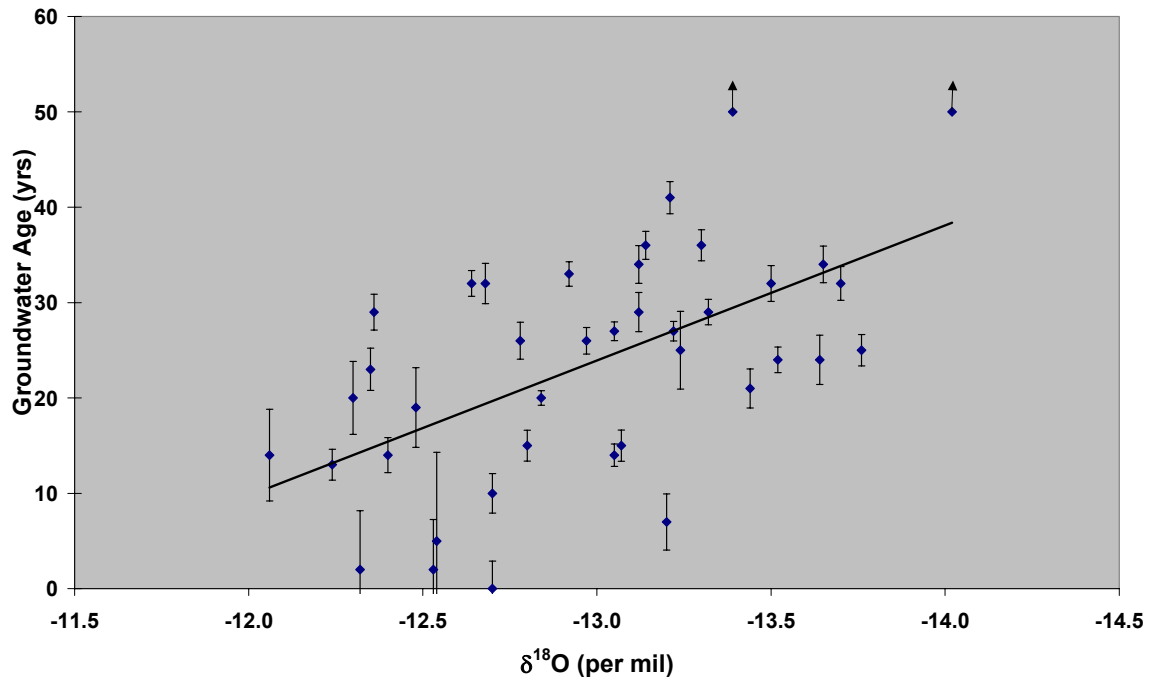


Figure 14. Wells that produce young groundwater have heavier $\delta^{18}\text{O}$ values than wells that produce old groundwater (linear correlation coefficient 0.32). Younger water is more likely to be influenced by other water sources, which are all isotopically enriched compared to than Kern River.

Very young groundwater is found in wells along canals

Groundwater ages, as calculated from tritium concentrations and tritiogenic ^3He , are shown in figure 15. Groundwater ages in the study area cover the entire range of the tritium-helium method, from one well with a calculated age of less than 1 year to two wells with tritium concentrations less than 1 pCi/L, indicating an age of greater than 50 years. The overall pattern in age reveals older ages in wells from the margins of the study area, and younger ages toward the urban center, especially along the canals that traverse Bakersfield. Some young ages have large error bars, as shown in figure 14, because of high excess air concentrations, which make determination of tritiogenic ^3He more uncertain. Based on results from previous GAMA studies, ages of less than 10 years are uncommon in production wells. The group of wells in the center of the study area in Bakersfield, which have ages of less than 10 years, must therefore be classified as highly vulnerable to contamination. These wells produce groundwater that has recently recharged from the unlined canals, and contains a component of isotopically enriched water. In contrast, many wells to the south, west, and northwest of the urban area produce old groundwater and are less vulnerable to contamination.

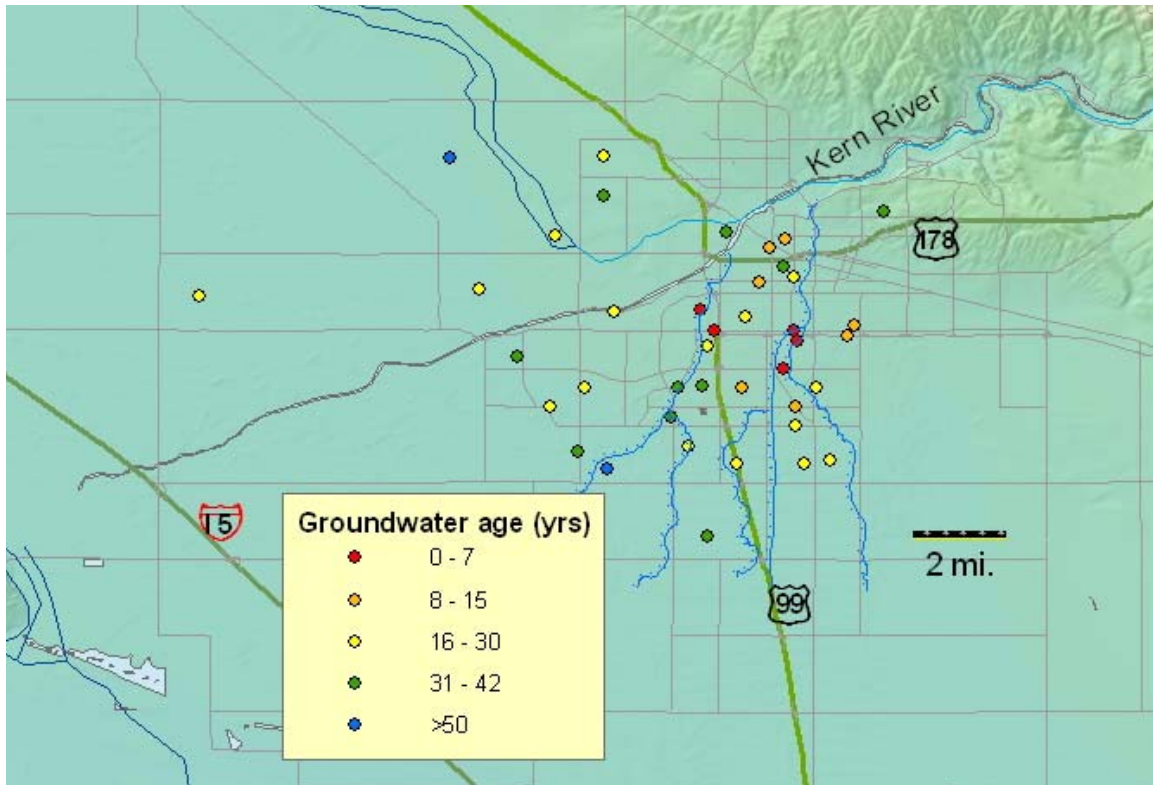


Figure 15. Tritium-helium groundwater ages show a pattern of increasing age toward the margins of the study area. Very recently recharged groundwater is produced at several wells along canals, in the center of the study area.

More than half of the wells (25 of 43) have calculated groundwater ages between 20 and 40 years. In this group of wells, groundwater ages for the post-modern component are relatively precise (errors of < 1 to 2 years), and indicate that these wells produce water

that may have encountered surface contaminants in the past 2 to 4 decades. Of these 25 wells, 16 have tritium concentrations significantly greater than present-day tritium concentrations, indicating the presence of ‘bomb pulse’ tritium (fig. 1). The nine remaining wells in the group, while having post-modern components in the same age range, have depressed tritium concentrations, indicating the presence of a large component of pre-modern (tritium-free) groundwater (fig. 3). As shown on figure 16, some of these wells produce up to 90% pre-modern groundwater, and only a small fraction of groundwater 20 to 40 years old. The relative proportions of pre-modern versus post-modern groundwater likely affect contaminant concentrations. Because pre-modern groundwater is less likely to contain contaminants, wells with high fractions of pre-modern water likely have contaminant concentrations that are diluted by at least the ratio of post-modern to pre-modern water. In general, upgradient wells, and wells in the urban center have smaller fractions pre-modern than downgradient wells on the outskirts of the study area.

A significant concentration of radiogenic ^4He , indicating the presence of groundwater with a residence time of about 1000 years, was found in only one well (the well with non-detectable tritium to the north of the Kern River). The age distribution at all the other wells does not include this very old component, indicating a relatively dynamic flow system, characteristic of coarse-grained fan material.

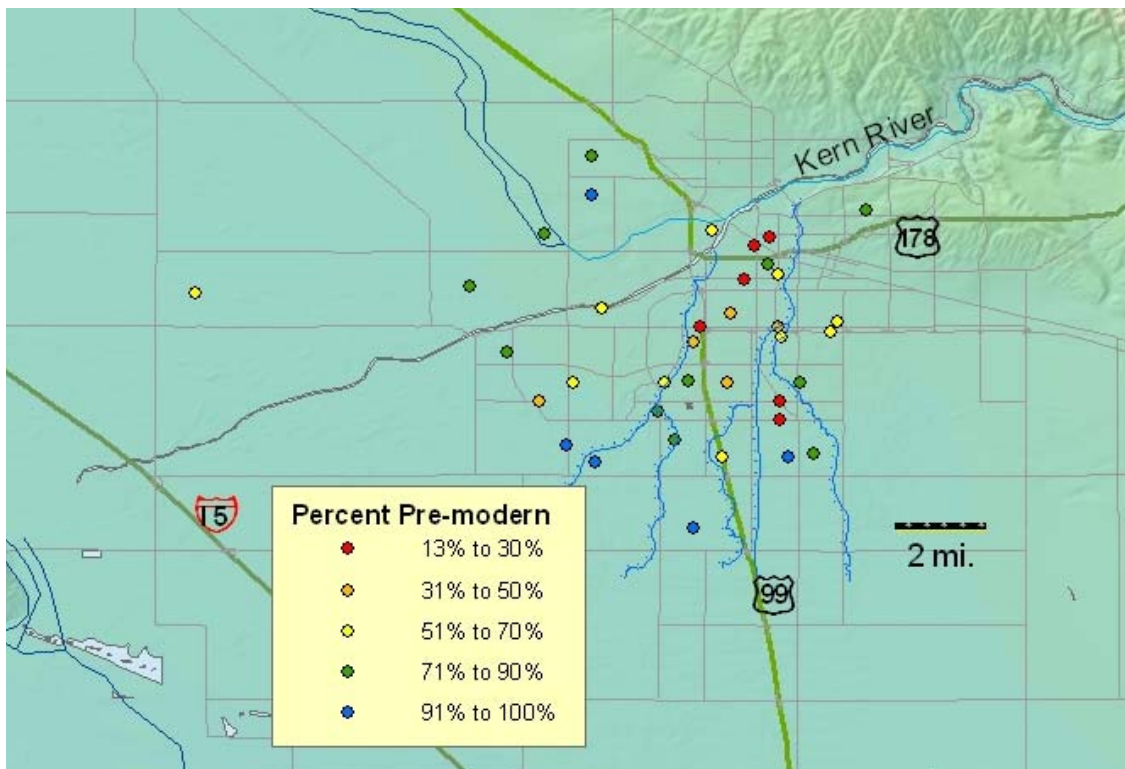


Figure 16. The fraction of pre-modern water at each well is calculated from the measured tritium concentration and the calculated tritium-age. Wells with large proportions of pre-modern water are less likely to have significant contaminant concentrations.

Excess air concentrations from Bakersfield wells are shown in figure 17. A large range in excess air is observed, from values at the low end that are characteristic of natural recharge conditions where little vadose zone interaction is indicated, to quite high concentrations of excess air that are characteristic of artificial recharge (wet/dry cycles) and significant air entrainment. The overall pattern is that high excess air concentrations are observed in wells in the urban center, where canal recharge is indicated, and lower in outlying areas, especially in the southeastern portion of the study area. Lower excess air concentrations in wells along the main eastern canal compared to the main western canal may be the result of a more continuous flow in the first diversion from the river.

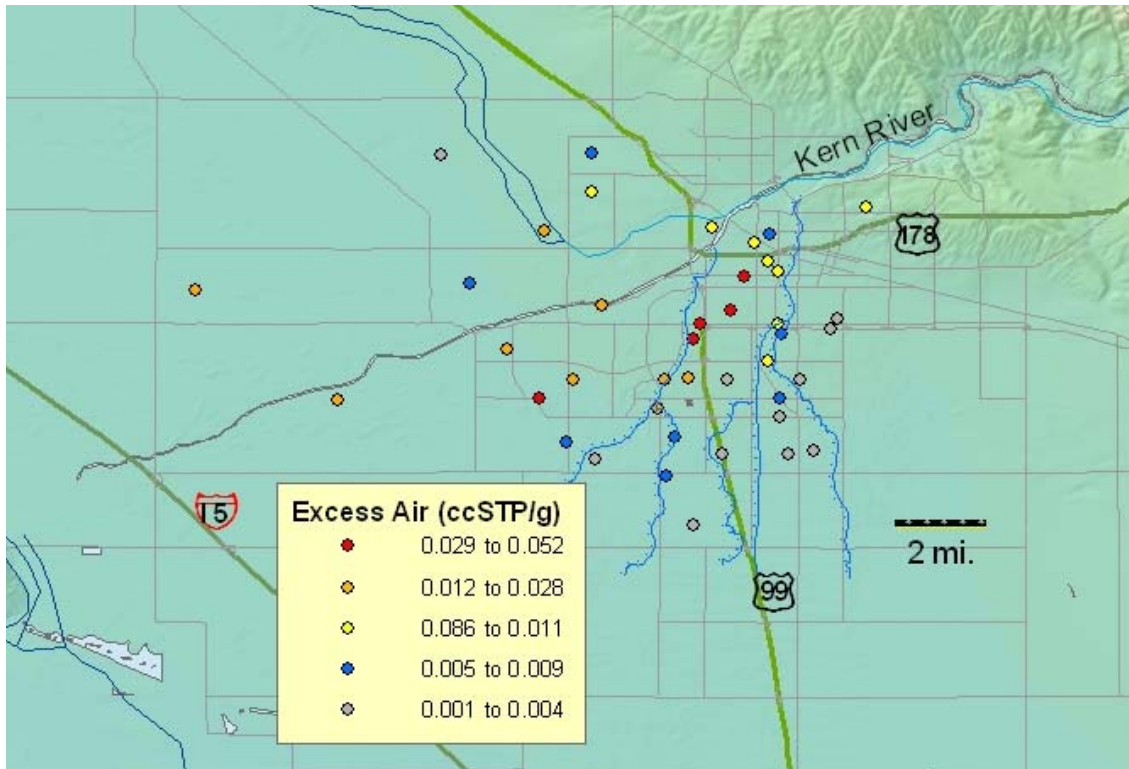


Figure 17. Excess air concentrations are generally higher in wells affected by recent canal recharge. Wells with gray symbols have excess air concentrations that are consistent with natural recharge and little vadose zone interaction.

Noble gas recharge temperatures for Bakersfield wells vary significantly around the mean annual air temperature for the area of 18.5C (<http://www.giss.nasa.gov/cgi-bin/update/gistemp/>). The spatial distribution in recharge temperatures (figure 18) reflects the pattern in groundwater age, with older groundwater having lower recharge temperatures. Recharge temperatures below about 16 C are likely the result of natural recharge of Kern River water during high runoff periods (late winter and early spring), when the water temperature is much lower than the ambient air/vadose temperature. Higher recharge temperatures, close to the mean annual air temperature are observed in

wells in the eastern and southern portions of the study area, where canal water and agricultural return water have likely equilibrated at a higher temperature, before recharge.

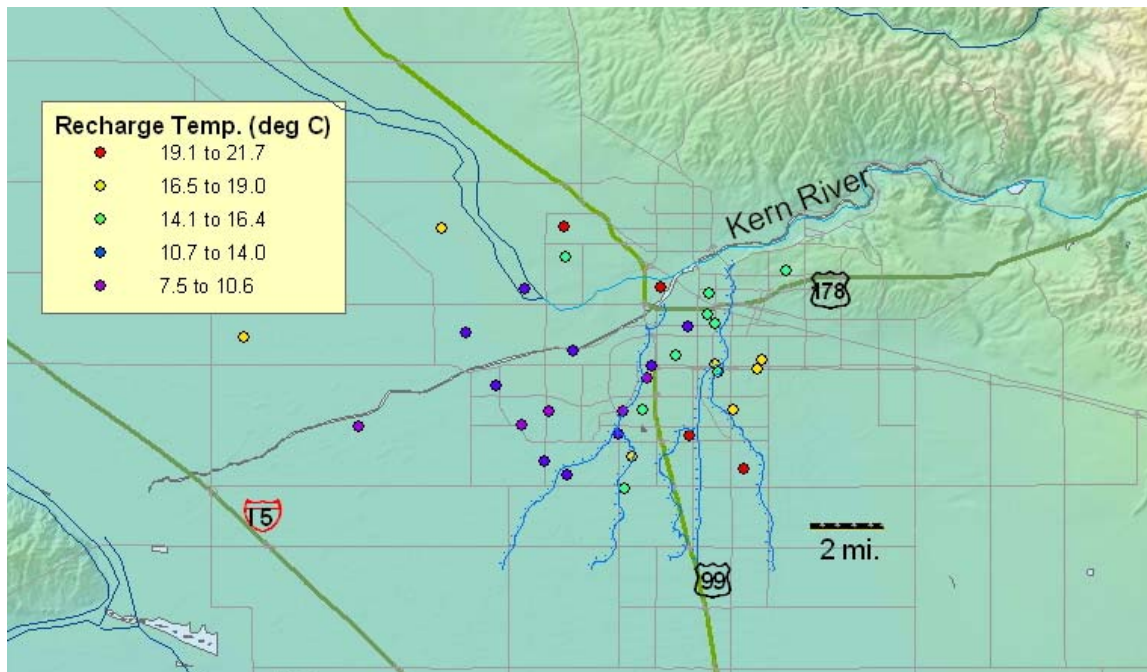


Figure 18. Calculated noble gas recharge temperatures have a wide range around the mean annual air temperature for the Bakersfield area. Lower temperatures in downgradient regions likely reflect recharge of cold Kern River water under natural conditions.

Overall, public drinking water wells in the central Bakersfield area are at relatively high risk for contamination because groundwater reaches those wells quickly. Numerous sources of VOCs are present as evidenced by the high frequency of observance of e.g., PCE. The irrigation canals provide the main conduit for groundwater recharge and allow continued pumping without significant overdraft, but wells along the canals, especially in the central and eastern part of the study area, are susceptible to contaminants that may be present in the intervening media. Bakersfield shares characteristics of other Central Valley GAMA study areas, including a relatively high occurrence of low-level VOCs, and the predominance of a Sierran water source. It is unique, however, in having areas of very young groundwater, and in having several high excess air concentrations. These two factors are the manifestation of artificial recharge along canals and the hydrogeologic setting on the Kern River fan.

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References

- Aeschbach-Hertig, W., Peeters, F., Beyerle, U., and Kipfer, R. (1999) Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resources Research*, v. 35, p. 2779-2792.
- Aeschbach-Hertig, W., Peeters, F., Beyerle, U., and Kipfer, R. (2000) Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air. *Nature* 405: 1040-1044.
- Aeschbach-Hertig W. Stute M. Clark JF. Reuter RF. Schlosser P. A (2002) paleotemperature record derived from dissolved noble gases in groundwater of the Aquia Aquifer (Maryland, USA). *Geochimica et Cosmochimica Acta*. 66(5):797-817.
- Andrews, J.N. and Lee, D.J., (1979) Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and palaeoclimatic trends. *Journal of Hydrology*, v. 41, p. 233-252.
- Beyerle, U., Aeschbach-Hertig, W., Imboden, D.M., Baur, H., Graf T., and Kipfer R. (2000) A mass spectrometric system for the analysis of noble gases and tritium from water samples, *Environ. Sci. Technol.*, 34 (10), 2042-2050.
- Bulletin 118, CA Department of Water Resources (2003) San Joaquin Valley Groundwater Basin; Tulare Lake Hydrologic Region; Kern County Subbasin. <http://www.waterplan.water.ca.gov/groundwater/118index.htm>
- Castro M.C., Stute M., and Schlosser P. (2000) Comparison of ^4He and ^{14}C ages in simple aquifer systems: implications for groundwater flow and chronologies. *Applied Geochemistry*, v. 15, p. 1137-1167.
- Clark JF. Stute M. Schlosser P. Drenkard S. A (1997) Tracer Study Of The Floridan Aquifer In Southeastern Georgia - Implications For Groundwater Flow And Paleoclimate. *Water Resources Research*. 33(2):281-289.
- Clarke, W. B., W. J. Jenkins and Z. Top (1976) Determination of tritium by spectrometric measurement of ^3He . *International Journal of Applied Radioisotopes*, 27, 515-522.
- Craig, H. (1961) Isotopic variations in meteoric waters. *Science*, v. 133, p. 1702-1703.
- Ekurzel, B., Schlosser, P., Smethie, W.M., Plummer, L.N., Busenberg, E., Michel R.L., Weppernig, R., and Stute, M. (1994) Dating of shallow groundwater - Comparison of the transient tracers $^3\text{H}/^3\text{He}$, chlorofluorocarbons, and ^{85}Kr . *Water Resources Research*, v. 30, p. 1693-1708.

Ekwurzel, B., Moran, J.E., Koester, C.J., Davisson, M.L., and Eaton, G.F. (2001) Nonpoint source Methyl tert-Butyl Ether movement through the environment: Ultra-low level (ppt) measurements in California. in: ACS Symposium Series 799, Oxygenates in Gasoline – Environmental Aspects (A.F. Diaz and D.L. Drogos, Eds.), p. 17-26.

Holocher J. Peeters F. Aeschbach-Hertig W. Hofer M. Brennwald M. Kinzelbach W. Kipfer R. (2002) Experimental investigations on the formation of excess air in quasi-saturated porous media. *Geochimica et Cosmochimica Acta*. 66(23):4103-4117.

Hudson, G.B., Moran, J.E., and Eaton, G.F. (2002) Interpretation of Tritium-³Helium groundwater ages and associated dissolved noble gas results from public water supply wells in the Los Angeles Physiographic Basin. Lawrence Livermore National Laboratory internal report, UCRL-AR-151447, 26 pp.

Ingraham, N.L., and Taylor, B.E. (1991) Light stable isotope systematics of large-scale hydrologic regimes in California and Nevada. *Water Resources Research*, v. 27, n. 1, p. 77-90.

Kendall C. Coplen TB. (2001) Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes*. 15(7):1363-1393.

Mahara Y. Igarashi T. (2003) Changes in isotope ratio and content of dissolved helium through groundwater evolution. *Applied Geochemistry*. 18(5):719-738.

Manning AH. Solomon DK. (2003) Using noble gases to investigate mountain-front recharge. *Journal of Hydrology*. 275(3-4):194-207.

Marty B. Dewonck S. France-Lanord C. (2003) Geochemical evidence for efficient aquifer isolation over geological timeframes. *Nature*. 425(6953):55-58.

Moran J.E., Hudson, G.B., Eaton, G.F., and Leif, R. (2003) A contamination vulnerability assessment for the Sacramento Area Groundwater Basin. Lawrence Livermore National Laboratory internal report, UCRL-TR-203258, 44 pp.

Moran J.E., Hudson, G.B., Eaton, G.F., and Leif, R. (2002) A contamination vulnerability assessment for the Santa Clara and San Mateo County Groundwater Basins. Lawrence Livermore National Laboratory internal report, UCRL-AR-148831, 45 pp.

Poreda, R.J., Cerling, T.E., and Solomon, D.K. (1988) Tritium and helium isotopes as hydrologic tracers in a shallow unconfined aquifer: *Journal of Hydrology*, v. 103, p. 1-9.

Schlosser, P., Stute, M., Dorr, H., Sonntag, C., and Munnich, O. (1988) Tritium/³He dating of shallow groundwater. *Earth, Planetary Science Letters*, v. 89, p. 353-362.

Shelton, J.L., Burow, K.R., Belitz, K., Dubrovsky, N.M., Land, M., and Gronberg, J. (2001) Low-level Volatile Organic Compounds in Active Public Supply Wells as Ground-Water Tracers in the Los Angeles Physiographic Basin, California, 2000. United States Geological Survey Water Resources Investigations Report 01-4188, 29 pp.

Solomon, D.K., Poreda, R.J., Schiff, S.L., and Cherry, J.A. (1992) Tritium and helium-3 as groundwater age tracers in the Borden aquifer. *Water Resources Research*, v. 28, p. 741-755.

Solomon D.K; Hunt A; Poreda R.J. (1996) Source Of Radiogenic Helium 4 In Shallow Aquifers - Implications For Dating Young Groundwater. *Water Resources Research*, v. 32, n. 6, p. 1805-1813.

Squillace, P.J., and Moran, M.J. (2000) Estimating the likelihood of MTBE occurrence in drinking water supplied by ground-water sources in the Northeast and Mid-Atlantic regions of the United States. United States Geological Survey Open-File Report 00-343, 10 pp.

Squillace, P.J., Moran, M.J., Lapham, W.W., Price, C.V., Clawges, R.M., and Zogorski, J.S. (1999) Volatile organic compounds in untreated ambient groundwater of the United States, 1985-1995. *Environmental Science Technology*, v. 33, n. 23, p. 4176-4187.

Surano, K.A., G.B. Hudson, R.A. Failor, J.M. Sims, R.C. Holland, S.C. MacLean, J.C. Garrison (1992) Helium-3 Mass Spectrometry for Low-level Tritium Analysis of Environmental Samples, *J. of Radioanal. and Nuc. Chem.*, 161: 443.

Szabo, Z., Rice, D.E., Plummer, L.N., Busenberg, E., Drenkard, S., and Schlosser, P., (1996) Age dating of shallow groundwater with chlorofluorocarbons, tritium helium 3, and flow path analysis, southern New Jersey coastal plain: *Water Resources Research*, v. 32, no. 4, p. 1023-1038.

Wright, M.T., Belitz, K., and Johnson, T. (2004) Assessing the susceptibility to contamination of two aquifer systems used for public water supply in the Modesto and Fresno metropolitan areas, California, 2001 and 2002: U.S. Geological Survey Scientific Investigations Report 2004-5149, 35 pp.

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 CO₂ equilibration method for ¹⁸O/¹⁶O (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:

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

where R_x is the ¹⁸O/¹⁶O 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 δ¹⁸O = +0.35‰, 2) two isotopically distinct California meteoric water samples δ¹⁸O = -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 δ¹⁸O 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 δ¹⁸O 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)
- ⁴Helium, Neon, Argon, Krypton, Xenon abundances (cm³STP/g)
- Tritium-helium age (in years)
- Radiogenic ⁴Helium (cm³STP/g)
- Excess air (in cubic centimeters at STP per liter)
- Recharge temperature (in °C)

In the laboratory, 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 CO₂. 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 ³He. Helium-4 is measured using a faraday cup with a 10¹¹-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 ⁴He and Ne abundances are measured with an accuracy of 2% and the ratio of ³He/⁴He is measured with an accuracy of 1%.

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

The measured abundances of Ne, Ar, Kr and Xe are used to determine the amount of air-derived He present in the sample. The amount of radiogenic ⁴He and tritiogenic ³He 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 re-frozen and headspace gases are pumped away. In each cycle, approximately 99% of the He is removed. After five cycles, virtually no ³He remains (< 100 atoms). The ³He 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 ³He in-growth. Samples are analyzed in a similar fashion as the dissolved gas samples except that Ne, Kr and Xe are not analyzed.

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

References

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

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

Appendix B

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 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|--------------------------------------------------|---------------------------------------------|-------------------------|-----------------------------|------------------------------|
| <i>(units)</i> | | | | <i>(ppb)</i> | <i>(ppb)</i> | <i>(ppb)</i> |
| 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 | | | | | | |

