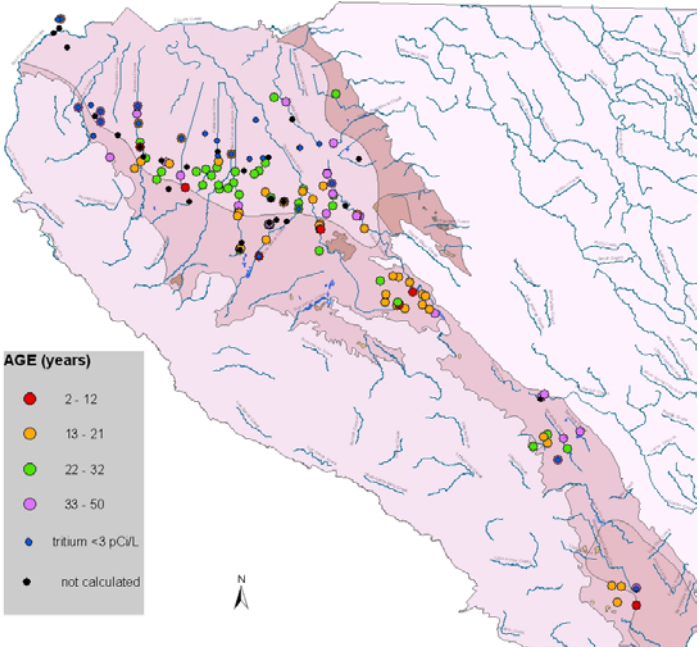


# CALIFORNIA AQUIFER SUSCEPTIBILITY

## A Contamination Vulnerability Assessment for the Santa Clara and San Mateo County Groundwater Basins



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## EXECUTIVE SUMMARY

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

Groundwater is an essential resource in the South Bay, with more than 350 wells supplying up to half the drinking water supply to 1.75 million people. As groundwater management and groundwater remediation have intensified over the past several decades, the groundwater flow field of the Santa Clara Valley Basin is becoming an increasingly engineered system. Historical overdraft that resulted in extensive land subsidence, combined with major threats to water quality posed by numerous contamination sources from industry, have been actively mitigated and managed by the Santa Clara Valley Water District and the San Francisco Bay Area Regional Water Quality Control Board. A major result of this study shows that the frequency of occurrence of VOCs in public supply wells, even at the ultra-low levels tested in this study, is remarkably low. Of the 146 wells where LLNL's analytical methods were employed for VOC analysis (with a reporting limit of 5 parts per trillion), 104, or 68% had no detections for any of the VOCs analyzed. In addition, 14 more (for a total of 77%) had detections of only tri-halomethanes (disinfection by-products that may occur as residuals of groundwater disinfection at the well site). Other important VOCs, MtBE, TCE, and PCE, were detected most frequently in the forebay area of Santa Clara's main subbasin. Low-level MtBE occurred primarily in wells with multiple lines of evidence for the influence of surface water, and likely has a non-point source from atmospheric MtBE dissolved in surface water. The small number of low level solvent occurrences in the forebay, in an area affected by 1,1,1TCA (Department of Health Services Title 22 data), are likely due to mobilization of numerous point sources during natural and artificial recharge.

Stable isotopes of oxygen, groundwater age, and the fraction of pre-modern water are the most useful parameters for delineating the flow field of the main groundwater basin in the Santa Clara Valley. The oxygen isotope values ( $\delta^{18}\text{O}$ ) delineate regions where groundwater is influenced by artificial recharge of isotopically lighter ( $^{18}\text{O}$  depleted) imported water and other areas where natural recharge introduces isotopically heavier ( $^{18}\text{O}$  enriched) local water. The western alluvial apron of the main Santa Clara basin has isotopic signatures that are indicative of a local water source. The zone of influence of water imported from the CA State Water and Federal Water Projects, extends from the major recharge ponds along creeks in the forebay area, across the main subbasin to the north. In contrast, the natural recharge of local water evident in wells from the west side of the main subbasin has features unique to episodic recharge events in a semi-arid Mediterranean-type climate. This recharge scenario, in which episodic recharge occurs along incised ephemeral streams, has implications for water quality, because oxygenated waters, with high 'excess air' concentrations, are efficiently transported into the aquifer. The southern-most area of the forebay, which is

characterized by a local  $^{18}\text{O}$  signature, but not by features of episodic recharge, has historically been artificially recharged with captured, local water. Groundwater age indicators reveal uniformly young groundwater in this somewhat hydrologically isolated area of the forebay.

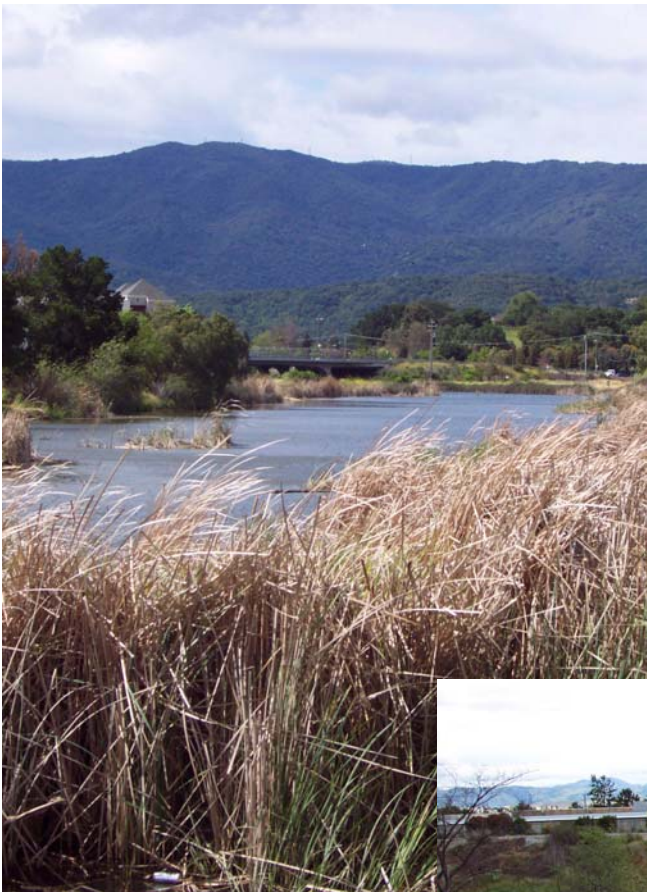
Tritium concentrations in groundwater from the main subbasin of Santa Clara Valley likewise show a clear spatial pattern, with the highest concentrations recorded in wells in recharge areas in the south/southeast, decreasing to non-detectable levels in wells located in the confined zone near San Francisco Bay. As expected, younger aged groundwater is found in the forebay area in the southern part of the main subbasin, and this is the area of the main subbasin that is most vulnerable to vertical transport of contaminants. It is important to note that complex capture zones, influenced by pumping patterns in wellfields in and near the forebay, complicate the interpretation of flow and vulnerability indicators with depth. Furthermore, the long-screened production wells produce water of mixed age, and some wells, even in the forebay, draw water without detectable tritium that has in large part recharged more than 50 years ago, as determined by the fraction of pre-modern water. However, tritium concentrations in depth specific samples (collected by the USGS), age results from multi-level monitoring wells, and examination of age versus depth to top perforations all indicate a sharp contrast in age above and below the major clay confining units of the main subbasin. The sum of evidence indicates that there is a lack of vertical transport between the shallow aquifers where contamination is widespread, and deeper, older groundwater in this part of the basin.

The deep, confined portion of the main subbasin is relatively invulnerable to rapid transport of contaminants from the surface. VOC analyses show only two MtBE detections and four solvent detections in the confined zone that could be related to vertical fast-paths. These sporadic detections of VOCs in the confined part of the basin could be due to abandoned wells, or natural geologic features serving as vertical conduits. The widespread absence of VOC detections in the confined zone may be related to groundwater management practices. After severe overdraft, the large volume of recent recharge in the forebay area and continued intense pumping in the confined zone may have induced an upward gradient in the confined zone that inhibits widespread downward contaminant transport. If that is the case, cessation of current practices may cause unwanted changes in the pattern of contaminant transport. The most distal wells in the confined zone have no measurable tritium in the groundwater, implying groundwater ages greater than 50 years. These distal wells also show isotopic evidence for upwelling of deeply sourced groundwater. The complex tectonic regime of coastal California, dominated by strike-slip faulting with local crustal thinning, allows transport of fluids from the earth's mantle in isolated areas of the basin.

Over and above the widespread resilience of the Santa Clara Valley Groundwater Basin to contamination, areas of vulnerability are identified. The most vulnerable areas in the study area are characterized by relatively young mean groundwater ages, and a somewhat higher frequency of VOC detections. These vulnerable areas are limited to: a) the forebay area of the main subbasin, especially the most southerly group of wells, b) the unconfined area of the Llagas subbasin, and c) the confined area of the Llagas subbasin where young groundwater is prevalent in the shallow aquifer. The Llagas and Coyote subbasins have a significant operational storage capacity (nearly 200,000 acre-ft), and may be used for future increases in groundwater production, but are an area identified by this study as having a relatively high vulnerability to contamination. These vulnerable areas coincide with areas where groundwater is the sole source of drinking water. Based on the results of this study, these areas in particular deserve further study.

A pattern of infrequent VOC occurrence also prevails in San Mateo County public supply wells. Wells from the South San Francisco area are screened over differing intervals, revealing the stratified nature of the groundwater system. The shallow zone contributes 'modern' groundwater, and

contaminants such as industrial solvents, to wells with screens that include a portion of the shallow interval. Wells screened exclusively below the confining layer produce water that has no measurable tritium (>50 years old), and is free of VOCs. In two areas of San Mateo County, the Westside Basin and San Mateo Plain, many of the public supply wells produce old, entirely pre-modern groundwater – a fact that should be considered when water resource managers estimate ‘safe yield’ for these areas. In addition, on the Pacific Coast in San Mateo County, a small number of wells provide the sole source of drinking water for coastal communities. These wells draw from a shallow, unconfined aquifer in the Coastside Basin and have a mean groundwater age of only 4 years. The young age of the water pumped from these wells, and low level non-point source MtBE, indicate that there is rapid recharge of surface water into the aquifer. This shallow, rapid recharge makes these wells highly vulnerable to near-surface contamination sources.



*Artificial recharge operations in Santa Clara County include maintaining flows in creeks and impounding captured and imported water behind dams.*



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## INTRODUCTION

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

In 2001 and 2002, LLNL carried out this vulnerability study in the groundwater basins of Santa Clara County and San Mateo County, located to the south of the city of San Francisco. 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.

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## VULNERABILITY ASSESSMENT TOOLS

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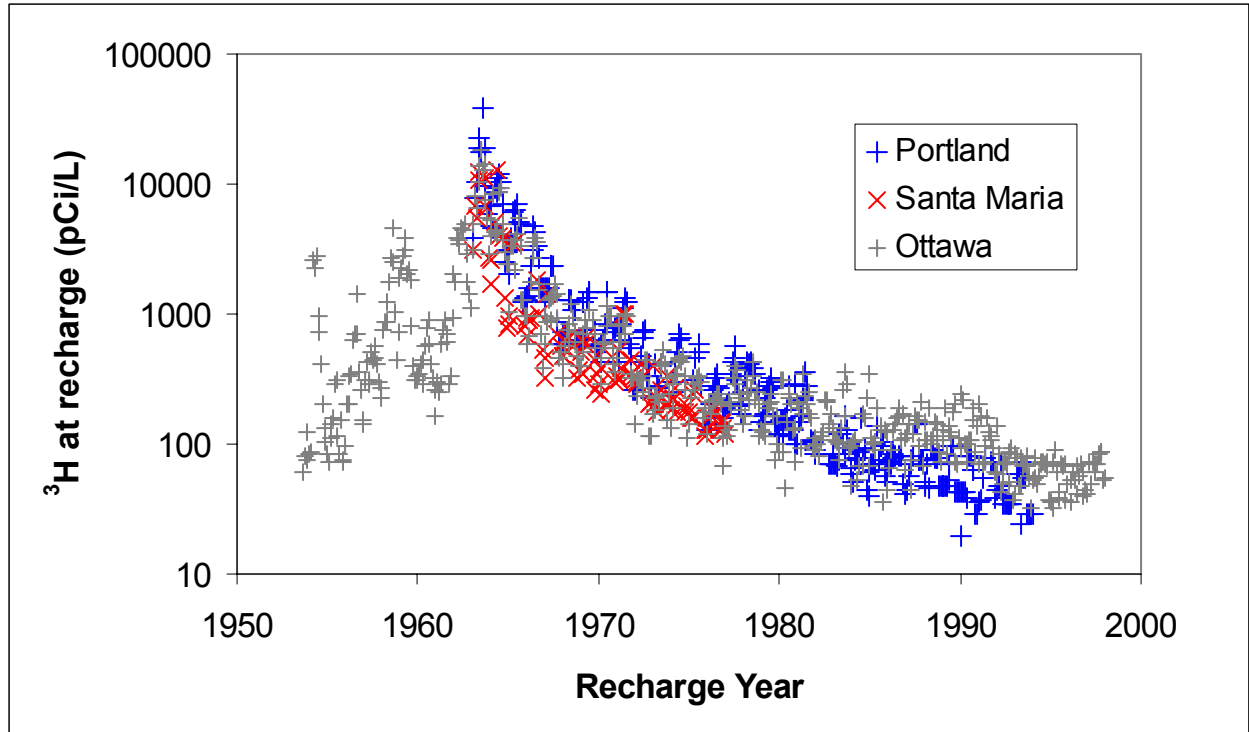
### GROUNDWATER AGE-DATING TECHNIQUE

Tritium ( $^3\text{H}$ ) 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 ( $^3\text{He}$ ) allows calculation of the initial tritium present at the time of recharge (figure 2), and ages can be determined from the following relationship:

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

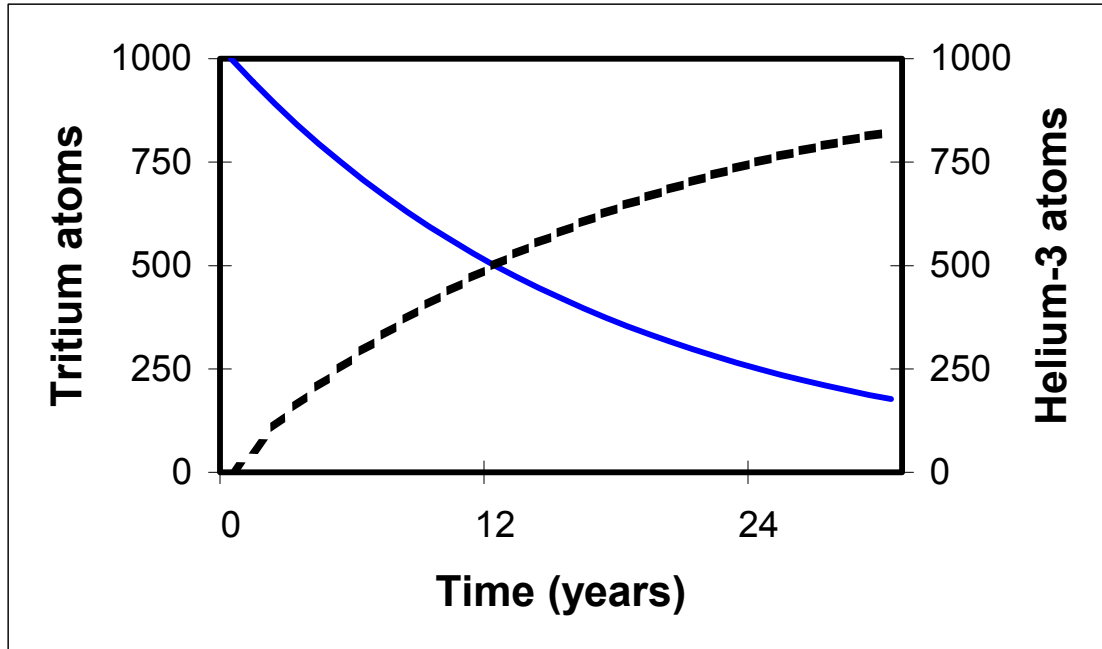
The age measures the time since the water sample was last in contact with the atmosphere. The  $^3\text{He}_{\text{trit}}$  indicated in the equation is the component of  $^3\text{He}$  that is due to the decay of tritium. Methodologies have been developed for correcting for other sources of  $^3\text{He}$ , such as the earth's atmosphere and potential small contributions from spontaneous fission of  $^6\text{Li}$ , and 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 1964.

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 (Ekwurzel et al., 1994, Schlosser et al., 1988, Poreda et al., 1988, Szabo et al., 1996, Solomon et al., 1992). 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.



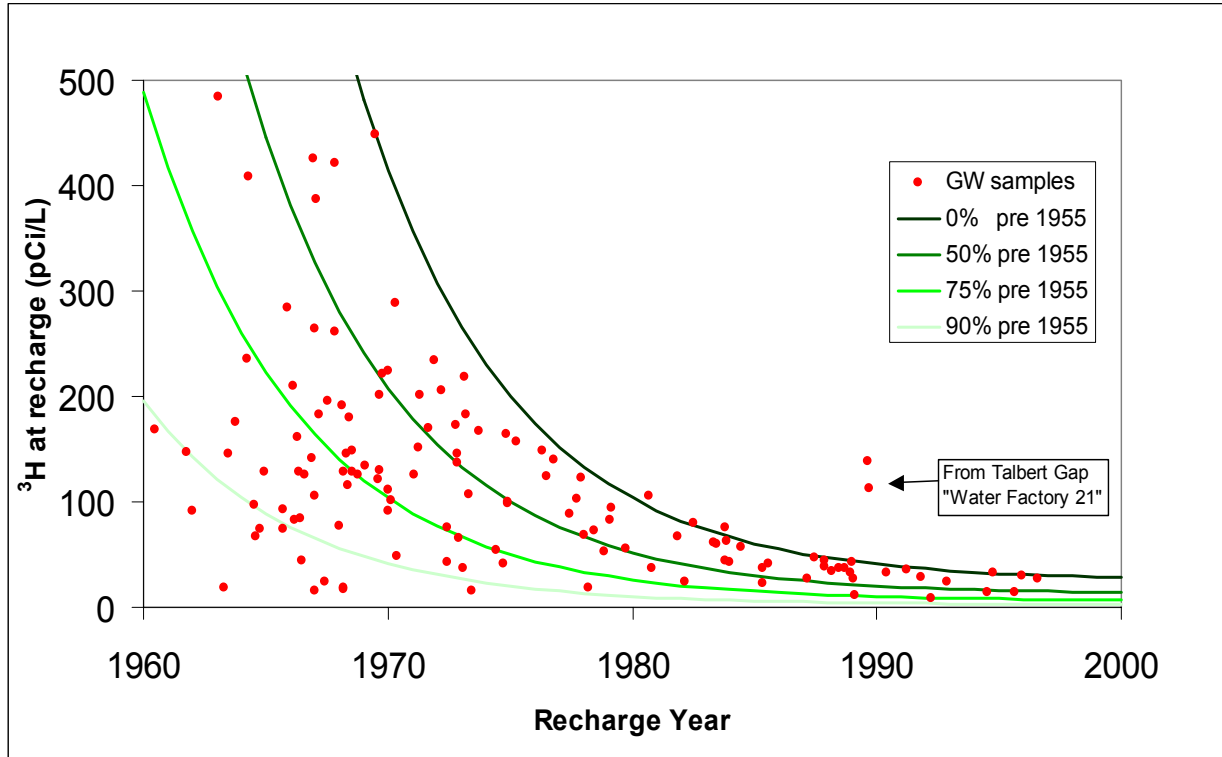


**Figure 2.** Solid line shows the decay of tritium, with a half-life of 12.34 years, while the dashed line shows the growth of the daughter product,  $^3\text{He}$ . The sum of tritium and  $^3\text{He}$  is the same at any time, and equal to the initial tritium value. This is the basis for the groundwater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

## CHARACTERISTICS OF GROUNDWATER DERIVED FROM DISSOLVED NOBLE GASES

### *Fraction Pre-modern*

A groundwater sample has an age distribution that is a result of groundwater mixing both during transport and in the well's borehole. Useful information about the groundwater age distribution in a well water sample comes from comparing a sample's measured tritium to the tritium expected in the original recharge water. This data analysis technique is illustrated on a plot of initial tritium versus calculated mean age (or recharge year; figure 3). The tritium that was present at the time of recharge is known from measurements of tritium in precipitation at several sites in North America. The calculated tritium-helium groundwater age is plotted along the x-axis position on figure 3, against the corresponding expected initial tritium value, on the y-axis. Water that recharged before about 1955 now contains extremely low levels of tritium. Samples that fall below the 'initial tritium' curve thus contain a fraction of water that recharged before 1955 ('pre-modern'). In contrast, a groundwater sample for which the measured age gives a decay-corrected tritium value that falls on or near the curve, is not significantly diluted with a component of pre-1955 water. A coarse estimate of the fraction of pre-modern water that is drawn from a well comes from calculation of the difference between the measured tritium and the 'initial' tritium (figure 3). This technique is complicated by: scatter in  $^3\text{H}$  concentrations in precipitation, poor retention of  $^3\text{He}$  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.

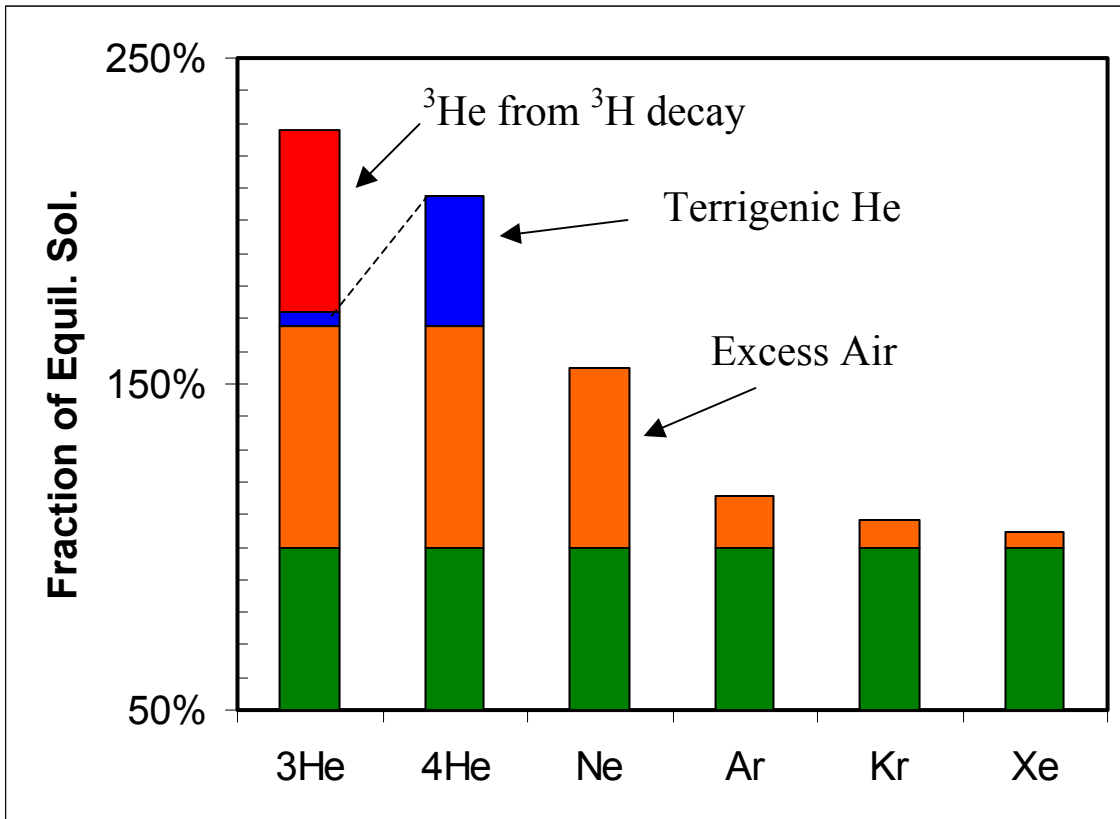


**Figure 3.** Curves show equal fractions of pre-modern water. The line labeled 0% is an approximation of the tritium in precipitation data from figure 1. Lines below approximate mixtures of pre-modern and post-modern water. Groundwater samples from southern California coastal basins are shown as points. 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 depth to 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  $^3\text{He}$  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  $\text{cm}^3$  at standard temperature and pressure (STP) per gram of water.





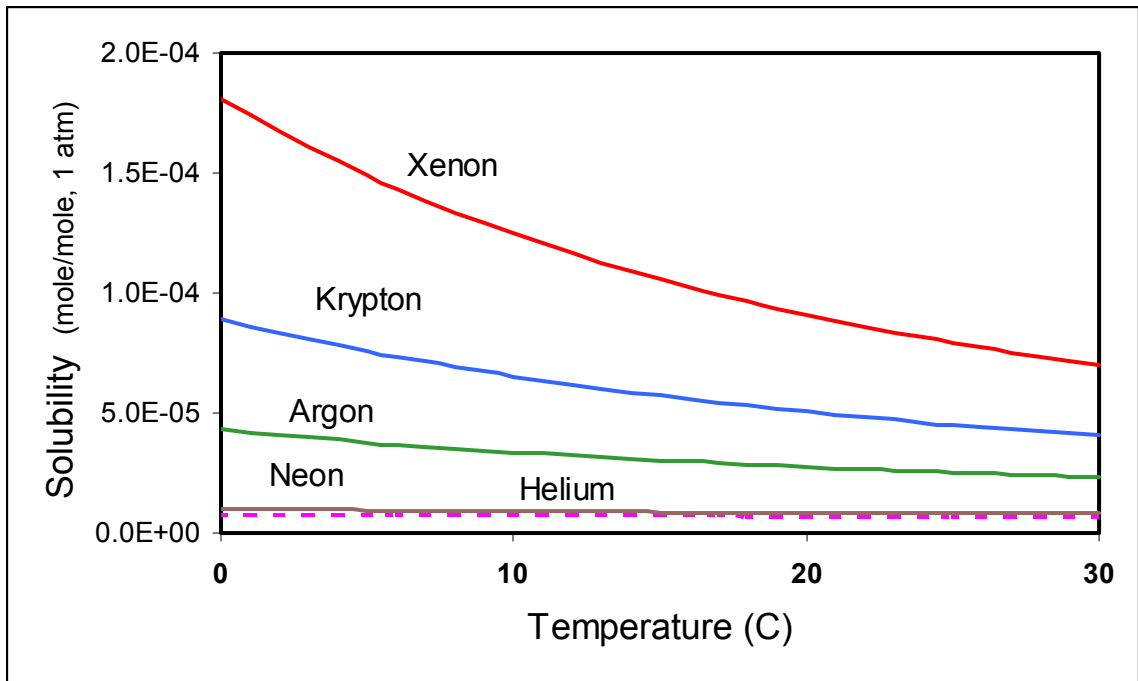
**Figure 4.** Graphical representation of the various dissolved noble gas components in a typical groundwater sample, relative to equilibrium solubility concentrations.

#### *Radiogenic <sup>4</sup>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 ( $^{238}\text{U}$  decaying to  $^{206}\text{Pb}$ ), alpha particles (which, after picking up electrons, become  $^4\text{He}$  atoms) are emitted. Thus,  $^4\text{He}$  accumulates significantly in groundwater on time scales of hundreds to thousands of years. The  $^4\text{He}$  from U and Th decay in the earth's crust is termed 'radiogenic  $^4\text{He}$ ', and is expected to increase along a groundwater flow path. Precise age dating using  $^4\text{He}$  is not possible because the accumulation rate depends on poorly known factors such as host rock U and Th concentrations and rock porosity (e.g., 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  $^4\text{He}$  (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  $^{14}\text{C}$  dating of groundwater (Marty et al., 2003, Castro et al., 2000). Radiogenic  $^4\text{He}$  has units of  $\text{cm}^3$  (STP) per gram of water, and these concentrations are converted to an apparent "age" using an assumed, constant flux of  $^4\text{He}$  from the earth's crust of  $2 \times 10^{-7} \text{ cm}^3 \text{ STP cm}^{-2} \text{ yr}^{-1}$ .

### *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).



**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.

## *Mantle Helium*

Primordial helium trapped in the earth's mantle is enriched in helium-3, and fluids emanating from the mantle thus have high  $^3\text{He}/^4\text{He}$  ratios (Craig et al., 1975). Windows to the mantle, such as hot spots and mid-ocean ridges emanate fluids with  $^3\text{He}/^4\text{He}$  ratios of up to 8 times the atmospheric  $^3\text{He}/^4\text{He}$  ratio ( $8R_a$  or  $8 \times 1.4 \times 10^{-6}$ ). In groundwater samples, this component may contribute to the measured, integrated  $^3\text{He}/^4\text{He}$  ratio (Marty et al., 2003, Mahra and Igarashi, 2003, Lesniak et al., 1997). When a component of mantle helium is present, as evidenced by a measured  $^3\text{He}/^4\text{He}$  ratio in excess of the atmospheric ratio, and too little tritium to support the  $^3\text{He}$  observed, groundwater age dating by the tritium-helium method is not reliable. (Age dating depends upon being able to accurately quantify the  $^3\text{He}$  that comes from tritium decay as shown in figure 4.) Helium isotope determinations in groundwater have been used to identify mantle fluids in the San Andreas Fault system (Kennedy et al., 1997), and along faults in Japan (Mahara and Igarashi, 2003). The tectonic regimes where mantle He can be sampled at the surface are typically characterized by crustal thinning, or by deep vertical conduits that traverse the crust.

## 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. 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 urban areas (Squillace et al., 1999; Squillace and Moran, 2000).

Table 1. Listing of VOCs analyzed using the low-level technique established by LLNL, along with regulatory and reporting limits.

Constituent	PHG (ppb)	MCL (ppb)	DLR (ppb)	LLRL (ppb)
<b>Methyl tert-Butyl Ether (MTBE)</b>	13	5	3.0	0.005
<b>Benzene</b>	0.14	1	0.5	0.005
<b>Toluene</b>	0.15	150	0.5	0.005
<b>Ethylbenzene</b>	300	700	0.5	0.005
<b>Xylene</b>	1800	1750	0.5	0.005
<b>Tetrachloroethylene (PCE)</b>	0.056	5	0.5	0.005
<b>Trichloroethylene (TCE)</b>	0.8	5	0.5	0.005
<b>Trihalomethanes (THMs), Chloroform Bromodichloromethane Chlorodibromomethane</b>		(Total THMs) 100	0.5 0.5 0.5	0.005 0.005 0.005
<b>Dibromo-3-chloropropane (DBCP)*</b>	0.0017	.2	.01	0.005

PHG=Public Health Goal (CalEPA suggested)

MCL=Maximum Contaminant Level (Dept. of Health Services)

DLR=Detection Limit for Reporting (commercial analytical labs)

LLRL=Livermore Lab Reporting Limit

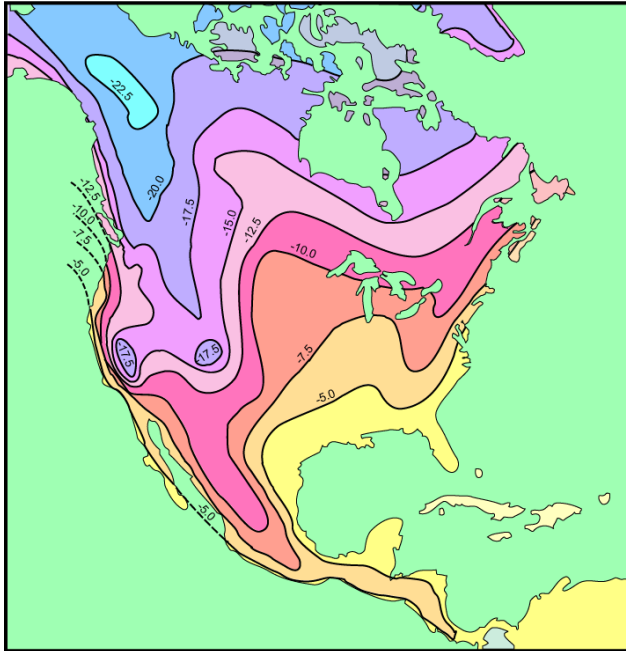
#### STABLE ISOTOPES AS TRACERS OF RECHARGE SOURCE

The minor stable isotopes of water molecules <sup>2</sup>H (deuterium, denoted as *D*) and <sup>18</sup>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 <sup>18</sup>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.

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  $-4\text{‰}$  along the Pacific coast to  $-15\text{‰}$  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.



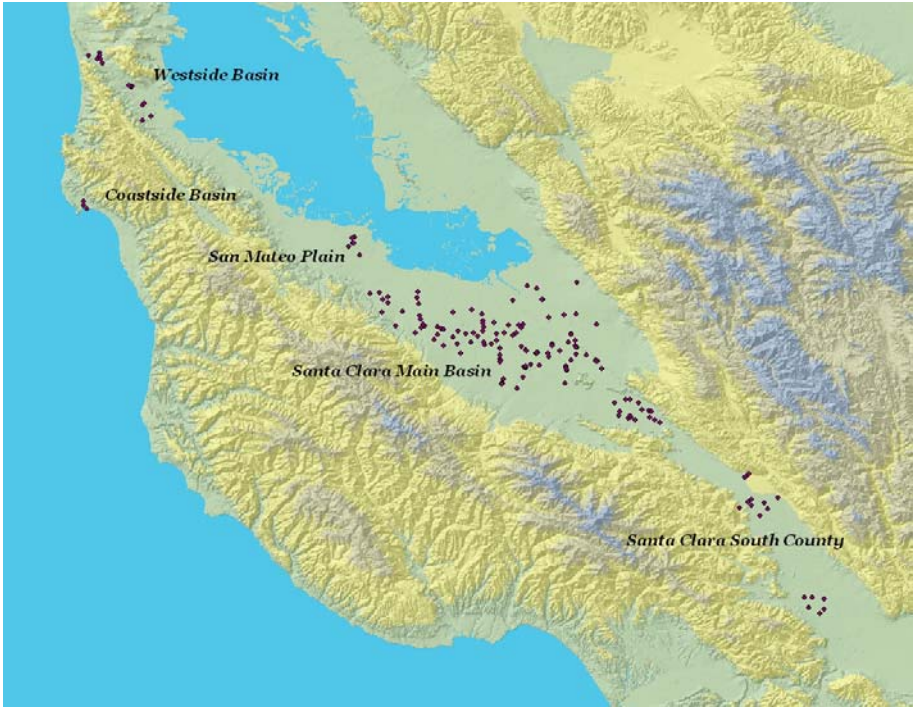
**Figure 6.** Contour map of  $\delta^{18}\text{O}$  (SMOW) showing tight contours and lighter, depleted values at high elevation in California. (after Taylor, 1974)

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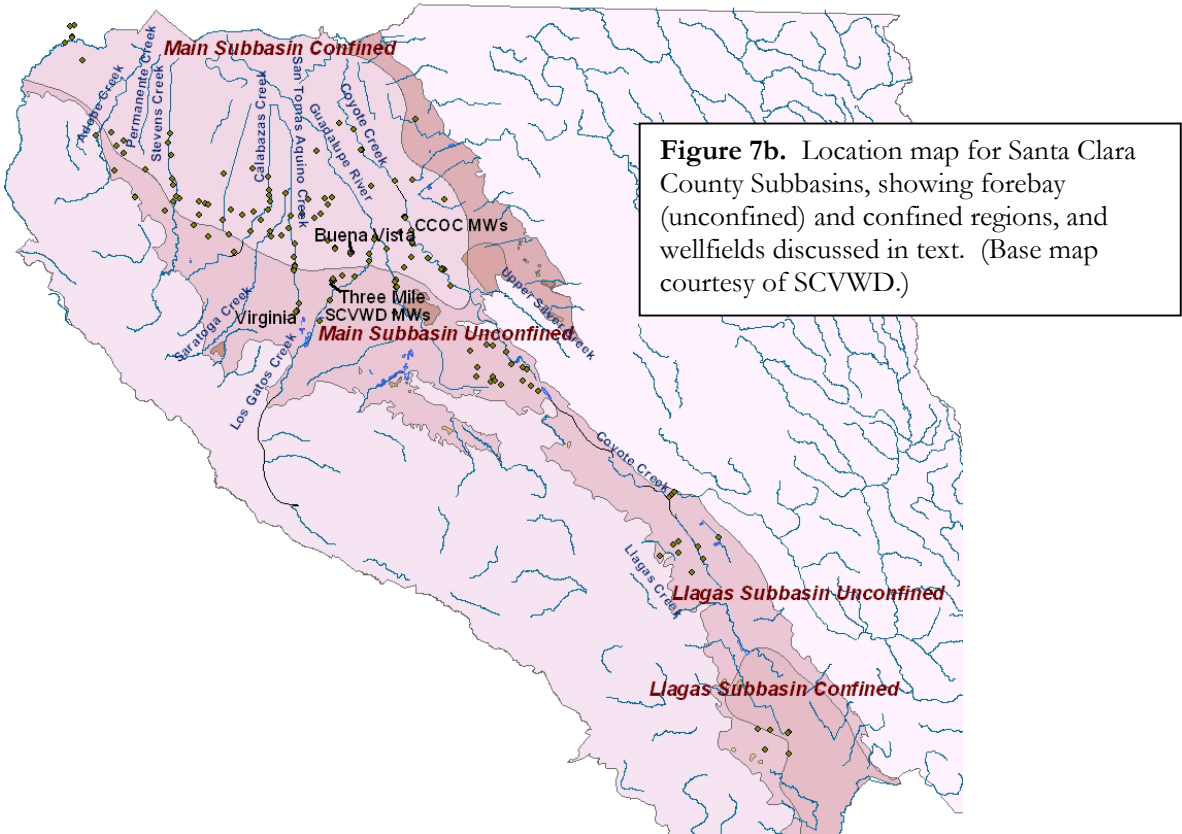
## GROUNDWATER BASIN CHARACTERISTICS

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In this section, the hydrogeologic setting of the Santa Clara Valley, including the San Mateo Plain, and of the Westside Basin, are briefly described, and results from vulnerability parameters are interpreted in the context of known groundwater flow patterns in these basins. Demand and production are lower in the San Mateo County portion of the study area than in the Santa Clara Valley portion. Likewise, the water management practices and infrastructure for recharge and pumping differ, with Santa Clara Valley (especially the main part of the basin north of Coyote Narrows) being much more intensively managed. For these reasons, the isotopic and age results from the basins are discussed separately. However, the low frequency of occurrence of VOCs throughout the study area, and the similarity in the density of sources, evokes direct comparison of VOC results.



**Figure 7a.** Sample location map, showing the 191 active drinking water wells included in this study. Each point represents a groundwater well, or in some cases, multiple, closely spaced wells that were sampled for the vulnerability assessment.



**Figure 7b.** Location map for Santa Clara County Subbasins, showing forebay (unconfined) and confined regions, and wellfields discussed in text. (Base map courtesy of SCVWD.)



## SANTA CLARA VALLEY GROUNDWATER BASIN

The groundwater basins of Santa Clara County lie in an alluvial trough between the Santa Cruz Mountains on the west and the Diablo range to the east (figure 7a and 7b). The Santa Clara Valley Basin fills the southern end of the structural trough containing San Francisco Bay. South of the main subbasin, the Santa Clara Valley Basin narrows through Coyote Valley. The Coyote sub-basin includes the area along Coyote Creek south of Metcalf Rd., and has a boundary with the Llagas Groundwater Basin at Cochran Rd. in Morgan Hill. Public supply wells from the Santa Clara (main) subbasin, the Coyote subbasin, and the Llagas subbasin are included in this report.

Three primary geologic units comprise the main Santa Clara subbasin, which are from oldest to youngest: the Franciscan Formation, Santa Clara Formation, and quaternary to recent-aged alluvial sediments. The two younger units lie unconformably on the consolidated basement rocks of the Franciscan Formation, and are primarily unconsolidated to partially-consolidated sands and gravels which are part of a network of gravel-filled, high permeability, stream channels punctuated by layers of more consolidated, low-permeability marine silts and clays. These silt and clay layers form aquicludes that separate and confine aquifers both vertically and laterally. The area of greatest groundwater production in the Santa Clara Valley is in the region just south of the San Francisco Bay, underlying the city of San Jose. This area is made up of thick sequences of recent alluvial sediments, and to a lesser extent, Santa Clara Formation sediments. More than 1500 feet thick, these sediments contain aquifers of high transmissivity, and are confined (DWR Bulletin 118, 2003; Fio and Leighton, 1995). Along the elevated margins of the basin are alluvial fan areas where the sediments are unconfined, and where active recharge occurs. Recharge is by stream infiltration, applied irrigation waters, rainfall, percolation ponds, and injection wells. A small amount of recharge occurs via subsurface inflow from the Coyote Valley subbasin through Coyote Narrows (SCVWD, 2002). Recharge to the Coyote subbasin is by infiltration of runoff and artificial flows along Coyote Creek and by rainfall, as the subbasin is essentially unconfined.

The basin is managed for conjunctive use by the Santa Clara Valley Water District. In 2000, the groundwater basin supplied 165,000 acre-ft for municipal and industrial use, while in 2001, 115,400 acre-ft came from the main subbasin, and 53,900 acre-ft from the Llagas and Coyote subbasins. The district operates 18 major recharge systems, which are a combination of off-stream and in-stream facilities (SCVWD, 2002). The total average annual capacity of these systems is 157,200 acre-ft. Forty five percent of the total recharge is controlled in-stream recharge (mainly behind temporary dams), while 20% is uncontrolled in-stream recharge. Off-stream recharge in ponds that are either continuously recharged, or in ponds that are periodically dried out, accounts for 35% of the total. Natural recharge from rainfall (average annual rainfall in San Jose is 14.5 inches) and runoff occurs throughout the basin, and sources of non-natural uncontrolled recharge include leakage from pipelines, seepage through the boundaries of the groundwater basin, and net irrigation return flows. Beginning in the 1930's groundwater overdraft caused inelastic land subsidence of up to 13 feet in the main subbasin of Santa Clara Valley and historical lows in groundwater elevation were up to 160 ft. below the present-day elevation. Through intense groundwater management, and with the benefit of an imported supply, SCVWD has been successful in mitigating subsidence (to a rate of .01 ft/yr) and in returning groundwater elevations to pre-development levels (SCVWD, 2002).

## SAN MATEO COUNTY GROUNDWATER BASINS

The San Mateo Plain, along the southwestern edge of the San Francisco Bay, is the northern continuation of the Santa Clara Basin. (To the east, the northern continuation includes the Alameda Plain and Niles Cone, discussed in a previous GAMA report; Moran et al., 2002.) Studies of the San Francisquito Cone, part of the San Mateo Plain, identify two main aquifers, a lower formation composed of Plio-Pleistocene Santa Clara sands and gravels, and an upper unit comprising late Pleistocene and Holocene alluvium (DWR Bulletin 118, 2003). Pleistocene Bay Mud, a thick continuous clay layer that pinches out to the west, separates upper and lower alluvial deposits. The San Francisquito Cone contains both unconfined and confined aquifers, but wells sampled for this study are all from the confined zone.

Also included in this report are wells from the Westside Basin, an alluvial trough to the northwest of the San Mateo Plain, and wells from a perched coastal aquifer west of the Coast Range, on the Pacific Coast. The Westside Groundwater Basin is located on the San Francisco peninsula and extends from a bedrock ridge in Golden Gate Park in the North to Hillsborough and Burlingame in the South. To the northeast, the basin is bounded by bedrock outcrops of Mount Davidson, Twin Peaks and San Bruno Mountain, while the southwestern boundary is defined by the San Andreas Fault in Daly City, South San Francisco and San Bruno. The groundwater basin is open to the west under the Pacific Ocean and to the east under San Francisco Bay (Rogge, 2003). The most important water-bearing formation in the Westside Basin is the Merced Formation (Pliocene-Pleistocene), followed by the overlying Colma Formation (Pleistocene) and Holocene sand dunes. The sediments of the Merced Formation are primarily composed of sands and clays, and to a lesser degree, gravel. Sands predominate in the upper portion of the formation where the sediments are mainly terrestrial in origin (Clifton and Hunter 1991). The thickness of the silt and clay units ranges from about 4 to 100 ft. (Phillips et al., 1993).

Although not all clay layers are shown as continuous in the cross sections, water quality parameters provide clues supporting the presence of distinct hydrostratigraphic units. In particular, chloride and nitrate data show a sharp contrast depending on the depth to the top of the wellscreen. Wells that have the shallowest top of screen show the lowest chloride concentration and the highest nitrate concentration (Rogge, 2003). The observed increase in chloride concentration with depth may be due to connate water found at greater depths. Loading of nitrate from the surface has affected the shallow aquifer, while deeper water bearing zones have not yet been affected. High total dissolved solids concentrations and locally high nitrate concentrations are the major water quality concerns in the Westside Basin.

### *Groundwater is a Crucial Resource*

Population centers served by wells sampled for this study include San Jose, Palo Alto, Santa Clara, Mountain View, Sunnyvale, Los Altos, Morgan Hill and Gilroy in Santa Clara County, and South San Francisco, Daly City, San Bruno, East Palo Alto, and Half Moon Bay in San Mateo County. For Half Moon Bay, the Great Oaks area, Morgan Hill and Gilroy, groundwater is the sole source of public drinking water. One hundred and ninety one of the approximately 242 'active' (DHS Title 22 definition) public supply wells in the study area were sampled for this study (figure 7b). In Santa Clara County, three private retailers and five public agencies participated in the CAS study. In San Mateo County, participating well owners include three private retailers and two public agencies.

Thousands of potentially contaminating activities exist in these urban areas, including 491 open SLIC sites in Santa Clara Valley and 66 in the San Mateo Plain, approximately 2000 LUST sites (75% closed; SF Bay Regional WQ Control Board et al., 2003) in Santa Clara Valley and approximately 3000 in the San Mateo County (70% closed; SF Bay Regional WQ Control Board et al., 2003). Santa

Clara Valley has over 100 mapped solvent plumes and the largest number of federal Superfund sites of any county in the United States. However, only 4 public water supply wells have had detections of VOCs above MCLs, and these have been destroyed. While large plumes from semi-conductor and chemical plants are relatively well characterized, numerous leaks from e.g., dry cleaning facilities and sewers are largely unmapped. Other major water quality threats in the study area include nitrate concentrations in public supply wells above the MCL (in the Los Altos and Mountain View areas, in the Llagas subbasin, and in the Westside Basin), and high TDS in wells near the bay, and in Palo Alto. Most recently, an extensive perchlorate plume in the Llagas subbasin has resulted in closures of public supply wells in Morgan Hill and San Martin. The reliance on groundwater, especially during drought conditions, and the large number of contamination sources present, were factors in choosing this area as among the first where the vulnerability assessment has been carried out.

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## **SAMPLING AND ANALYSIS PROCEDURES**

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LLNL personnel collected well water samples from 154 public water supply wells in Santa Clara County (a subset of wells in the main subbasin were collected by SCVWD personnel) and San Mateo County, with the assistance of well owners, during the summer and fall of 2001 (figures 7a and 7b). In addition, the USGS collected approximately 55 samples in Santa Clara Valley, 22 of which were duplicates of samples collected by LLNL. The USGS and LLNL use somewhat different sampling and analytical techniques for low level VOC measurements, and the goal was to compare outcomes (see discussion below). The USGS used a discrete depth sampling apparatus on three production wells (Mountain View 20 at 2 levels plus a composite sample, Williams W-3 at 2 levels plus a composite sample, and California Water Service 17 at 5 levels plus a composite), and sampled two sets of multi-level monitoring wells for an additional 8 samples. In all, 262 samples were collected at 173 different wells in the area covered by SCVWD, 165 of which are public water supply wells. LLNL personnel sampled twenty-four active public supply wells, two monitoring wells, and one private well in San Mateo County. 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) is measured using purge and trap gas chromatography-mass spectrometry, with a reporting limit of 5 parts per trillion (ppt). 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  $^3\text{He}$ -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 excess air concentration and temperature at which recharge took place are determined from the noble gas concentrations. A summary of analytical methods is given in Appendix A.

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## RESULTS

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Analytical results for VOCs,  $\delta^{18}\text{O}$ , age, and related parameters in Santa Clara Valley and San Mateo County wells are shown in Figures 8 through 28. Uncertainties discussed 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 compounds - MTBE, PCE, Xylene, and toluene, were detected in blanks over the course of Santa Clara Valley sampling. For well water samples that had detections of a VOC compound, that were collected on a day when any transfer blank also had a detection, the results were screened at the value of the highest concentration measured in a sample or blank that day. This raised the reporting limit above 5 ppt for 18 MTBE results, 17 PCE results, 17 xylene results, and 73 toluene results. In the San Mateo County sampling campaign, MTBE was detected in one transfer blank and toluene was detected in the transfer blanks on two days, which resulted in screening 5 MTBE and 5 toluene well results at levels higher than 5 ppt. The likely source of MTBE is transfer from the atmosphere during collection or storage, while the likely source of toluene is leaching of the rubber septum in the cap of the VOA vial. The observed detections in transfer blanks are a testament to the extreme sensitivity of the analytical method used for VOC determinations.

Of the 22 wells that were sampled by both LLNL and the USGS, and VOC analyses carried out independently using somewhat different protocols, only eight wells had a detection of any kind. In four wells, only THMs were detected, and the results differ by less than 20% except for one chloroform detection, which differs by 30%. The LLNL analysis found one chloroform, one bromodichloropropane, and two MTBE detections that are below the detection limits for the USGS lab. The USGS laboratory found one PCE detection (Koch 1) at 0.1  $\mu\text{g/L}$  where the LLNL result was <5 ng/L. While the overall agreement between analyses from the two labs is good, the total number of VOC detections is too small for a more meaningful statistical comparison.

## DISCUSSION OF VOC OCCURRENCE

### *Overall Frequency of VOC Occurrence is Remarkably Low*

The distribution of VOCs in the public water supply (PWS) and monitoring wells is shown in Figures 8-11. Compounds that were monitored and had no detections above the reporting limit include benzene, ethylbenzene, xylene, and 1,2-dibromo-3-chloropropane. Toluene was detected above the reporting limit in only one well (in the Coastside Basin). One hundred and four wells delivered raw water that was below the reporting limit for all the compounds monitored. Fourteen more public supply wells had positive detections of trihalomethanes (THMs, including trichloromethane, dibromochloromethane, bromodichloromethane, and tribromomethane) only, and were below the reporting limit for all the other compounds analyzed. Thirty-eight wells had detections of chloroform, the most abundant of the THMs.

Fifteen wells had low level detections above the reporting limit of MTBE, with a maximum of only 69 ppt. Eight wells (all PWS) had low level detections above the reporting limit of the solvent trichloroethylene (TCE), six of which were less than or equal to 50 ppt. Twelve PWS wells had

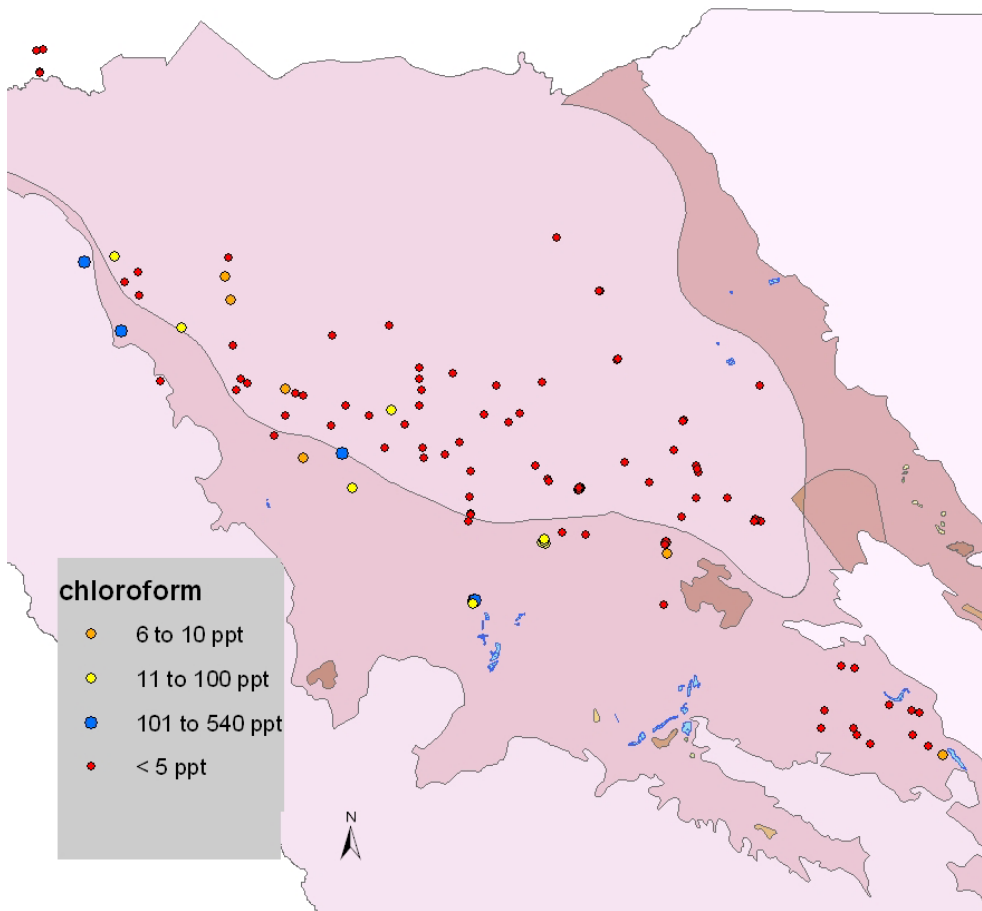
detections of tetrachloroethylene (PCE), 10 of which were less than or equal to 58 ppt (the public health goal; PHG). The other two PCE concentrations were greater than 0.5 ppb (both in the Llagas subbasin), but none exceeded the state and federal maximum contaminant level (MCL) of 5 ppb for drinking water (U.S. Environmental Protection Agency, 1996). The PHG for TCE is exceeded in one well (in South San Francisco), and the PHG for toluene is exceeded in one well (in Half Moon Bay). For all of the other compounds tested, the concentrations are well below regulatory limits, and most often more than 1000 times below MCLs. 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.

### *THMs Occur More Frequently than Other VOCs*

THMs are by-products of the disinfection of drinking water. The source of low-level THMs can be advective transport to the aquifer of previously treated water, or on-site residual from water treatment at or near the wellhead (fig. 8a, 8b). Chloroform (trichloromethane) is nearly always accompanied by very low levels of the other THMs (dibromochloromethane, bromodichloromethane, and bromoform). Treated water can enter the groundwater system via infiltration of potable irrigation water or recycled water, or from leakage out of treated water distribution lines. However, at some of the public supply wells in the Santa Clara basins and San Mateo basins, groundwater is chlorinated or chloraminated at the well site (sometimes just downstream from 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 to the aquifer of treated surface water to the well capture zone. In general, wells owned and operated by the California Water Service Company (South San Francisco-fig. 8a and Los Altos on the western apron of the main subbasin-fig. 8b) are more likely to have THM detections than wells owned by other retailers (52% of CWS wells have a THM detection, while 25% of wells overall have a THM detection). This disparity in occurrence is presumably due to differences in operating procedures or conditions, and these detections are therefore likely to be from a residual source.



**Figure 8a.** Chloroform, or trichloromethane (a THM) occurrence in San Mateo County wells.



**Figure 8b.** Occurrence of chloroform, or trichloromethane in wells from the Santa Clara main subbasin and San Mateo Plain. Occurrence is related to either operating conditions at wellheads (as residual from on-site disinfection) or to the presence of advectively transported, previously treated water.

Excluding CWS wells, there is a relatively high likelihood that wells having a VOC detection of any compound other than a THM, will have a THM (especially chloroform) detection (19 wells with MtBE, TCE, or PCE detections also have a THM detection, while 12 wells with MtBE, TCE or PCE detections do not have a THM detection). The source of THMs that are accompanied by other VOCs is more likely to be previously treated water than residual from on-site activity. In some cases, such as the wells in the forebay area of the main Santa Clara subbasin and the Denniston wells, the THM is likely present due to advective transport of young water containing THMs. The Virginia St. wells (figure 7b and figure 12) have the highest THM concentrations, and are under the influence of the nearby San Tomas injection well, where a small volume of imported, treated water was injected in a pilot project. Chloroform levels reached a maximum of 10 ppb in the San Tomas injection well (DHS Title 22 database) in October 1997. These wells are likely also influenced by regional artificial recharge in the ponds and creeks in the forebay area. The Virginia wells stand out in having the highest concentrations of all 4 THM compounds measured.

Occurrences of chloroform without other THMs, at wells where PCE, TCE, and/or 1,1,1TCA (from DHS database) were detected could be evidence for a chloroform source other than as a disinfection by product. Chloroform is used in the manufacture of fluorocarbons for refrigerants, propellants, and plastics, as an industrial solvent, and in industrial drycleaning. These potential sources are likely



for the chloroform occurrences in the deep, confined part of the basin (Mountain View and City of Santa Clara wells), where old groundwater is prevalent and other disinfection by-products are absent.

*MTBE Likely has a Non-point Source*

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 water that recharged less than 15 years ago. The very low concentrations measured, and lack of BTEX co-contaminants suggest that this non-point source component explains the MTBE detected in all but 2 of the 15 wells where MTBE was found in the study area (figure 9a, 9b). These 13 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).



**Figure 9a.** Methyl *tert* butyl ether occurrence in wells from San Mateo County. In these wells, MtBE occurrence is associated with recently recharged groundwater.

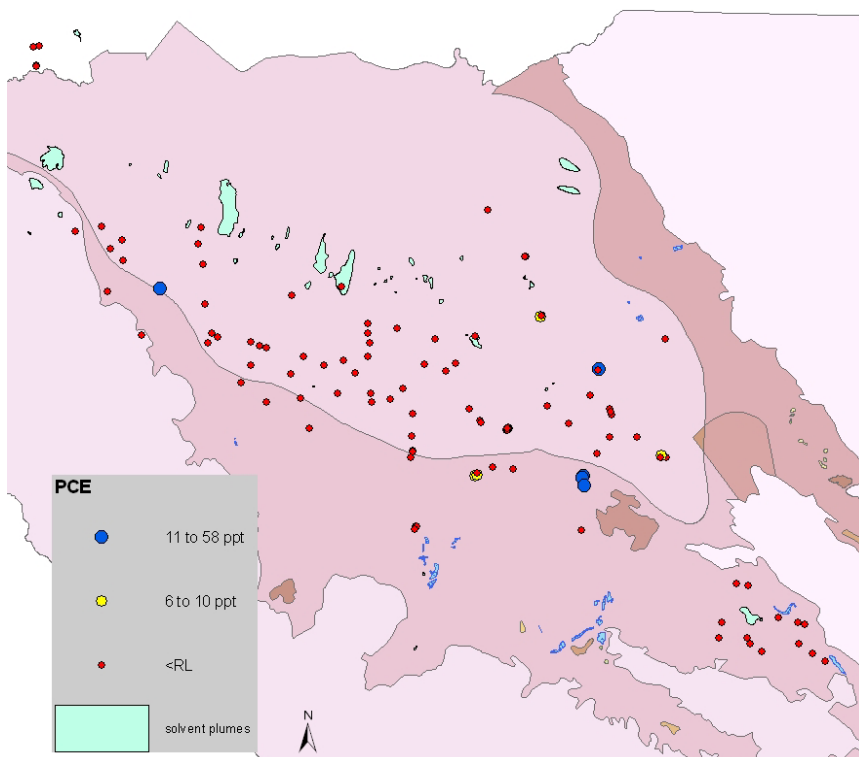
The detections of MtBE in Santa Clara Valley wells are clustered in wellfields near artificial recharge areas (figure 9b). For example, the highest MTBE levels were found in the Virginia Street wells, which are under the influence of the nearby San Tomas injection well and/or other artificial recharge facilities. The low levels observed in the wells influenced by the large ponds along Los Gatos Creek are also consistent with likely surface water MtBE concentrations diluted with groundwater recharged before extensive use of MtBE. Similarly, the low level detection in a well from Morgan



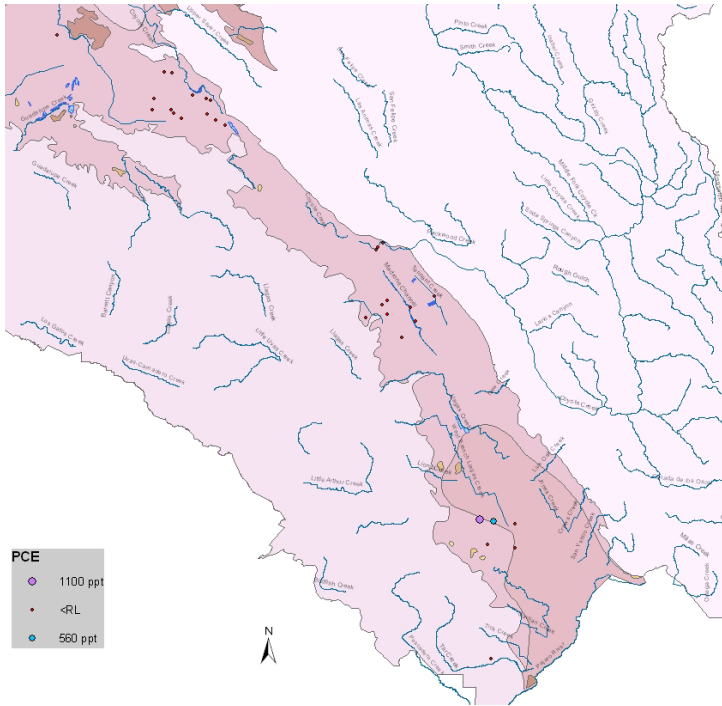
Two public supply wells along Stevens Creek in Mountain View have low level MtBE detections that may or may not be due to subsurface point sources. Oxygen isotope and age dating results (described in detail below) show evidence for naturally-recharged, ‘old’ groundwater in that area of the basin, with a large fraction of the water recharged before 1950. In this area, MtBE occurrences may have a LUFT source, and transport to deep groundwater may be facilitated by coarse-grained streambed sediments that provide a vertical conduit. Eleven LUFTs are located within ½ mile of MV-19 (2 cases open), while 8 LUFTs are located within ½ mile of MV-21 (2 open, 1 overlapping). MTBE concentrations measured in monitoring wells from these LUFT sites are three or more orders of magnitude higher than concentrations measured in public supply well water (30 to 400 parts per billion).

#### *Chlorinated Solvents Occur More Frequently in the Forebay Area*

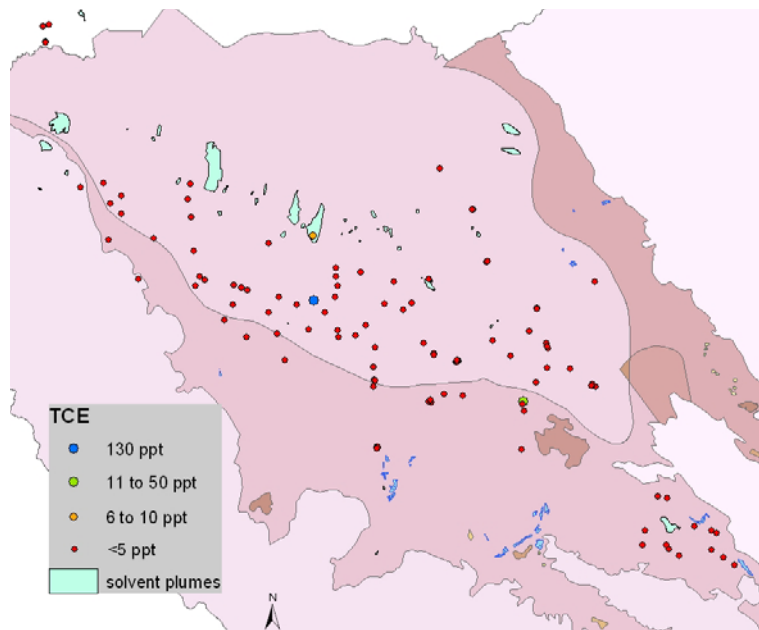
Detections of TCE and PCE are extremely few in number and low in concentration compared to other major, urbanized groundwater basins in California (Shelton et al., 2001; Moran et al., 2002). This striking lack of solvent occurrences is especially notable considering the very large number of sources, which occur over large areas and have been present for decades, in some cases. The PCE and TCE occurrences cannot readily be traced to the known, mapped solvent plumes (SF Bay Regional WQ Control Board et al., 2003), given the very low concentrations observed and high density of (sometimes overlapping) sources.



**Figure 10a.** Tetrachloroethylene (PCE) occurrence in wells from the main basin in Santa Clara County. PCE occurrence is extremely rare, especially in the confined (northern) portion of the basin, despite the large number of solvent plumes there.



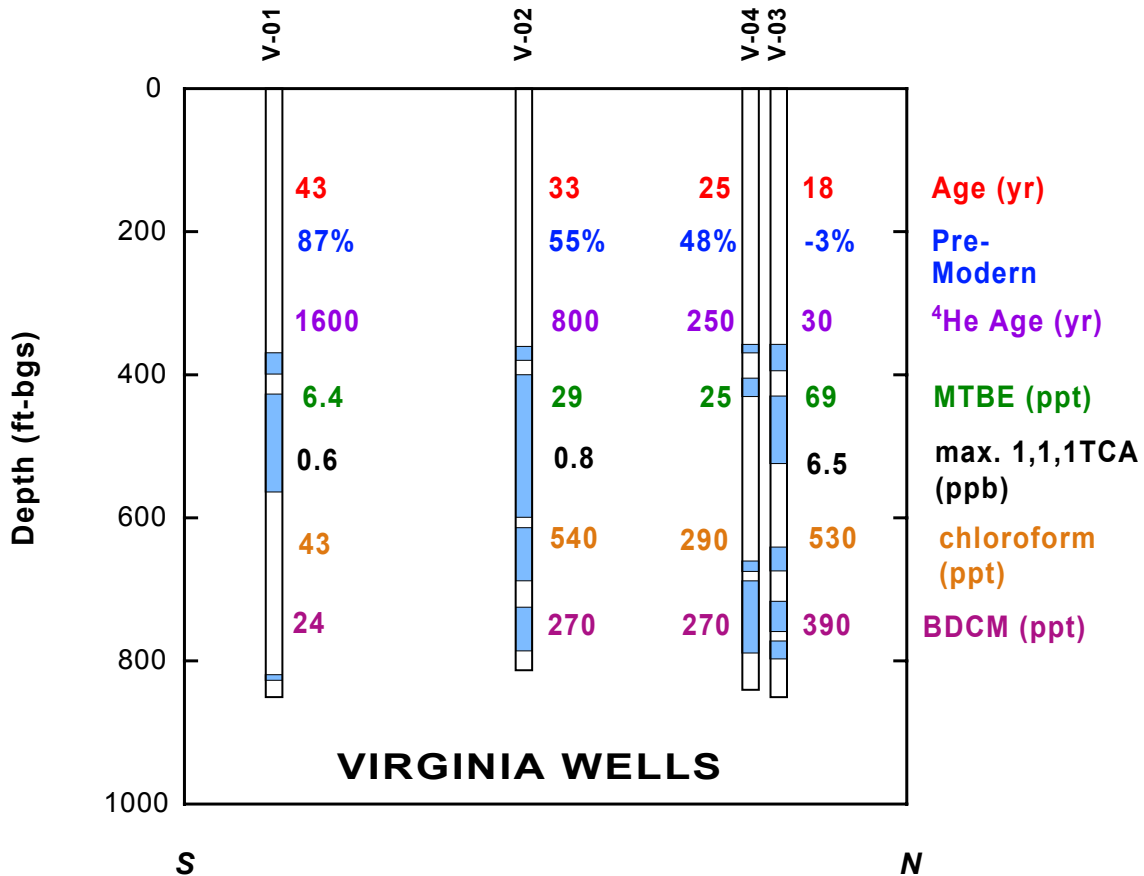
**Figure 10b.** PCE occurrence in wells from southern Santa Clara County shows two (previously known) affected wells in Gilroy.



**Figure 11.** Trichloroethylene (TCE) occurrence in wells from the main subbasin in Santa Clara County. Although TCE can occur as a degradation product of PCE, the two compounds co-occur in only one well. Green-filled symbol represents two closely-spaced wells with TCE in the range indicated.

TCE and PCE detections number 10 in and near the forebay area, and only 4 in the confined zone (fig. 10a, 11). Compared to the forebay region, the confined region is overlain by a high density of solvent plumes, many of which extend thousands of feet from their source. Hence, TCE and PCE occurring in wells in the forebay area of the main subbasin may have numerous, small sources that are mobilized by the large volume of artificially-recharged water that enters the basin there. The area of the forebay where TCE and PCE (and MtBE) occur coincides closely with the area where 1,1,1 TCA is present in several wells (at somewhat higher levels (DHS database)), further indicating that this region is affected by mobilization of low level contamination. 1,1,1TCA may occur at a higher concentration than TCE or PCE in the source areas and thus is observed at higher levels in wells. In

the Virginia St. wells (figure 12), the historical maximum 1,1,1TCA concentration correlates closely with the patterns observed for the different wells in MtBE and in groundwater age, suggesting that these contaminants are present in the young, recently recharged component of the groundwater.



**Figure 12.** Schematic cross section of Virginia St. Wellfield, showing perforated intervals and various constituents at each well. Age increases and VOC concentration decreases from north to south. These wells are influenced by the San Tomas injection well, which lies just to the north of the wellfield, and by artificial recharge areas to the south and southeast. (1,1,1TCA data is from DHS database.)

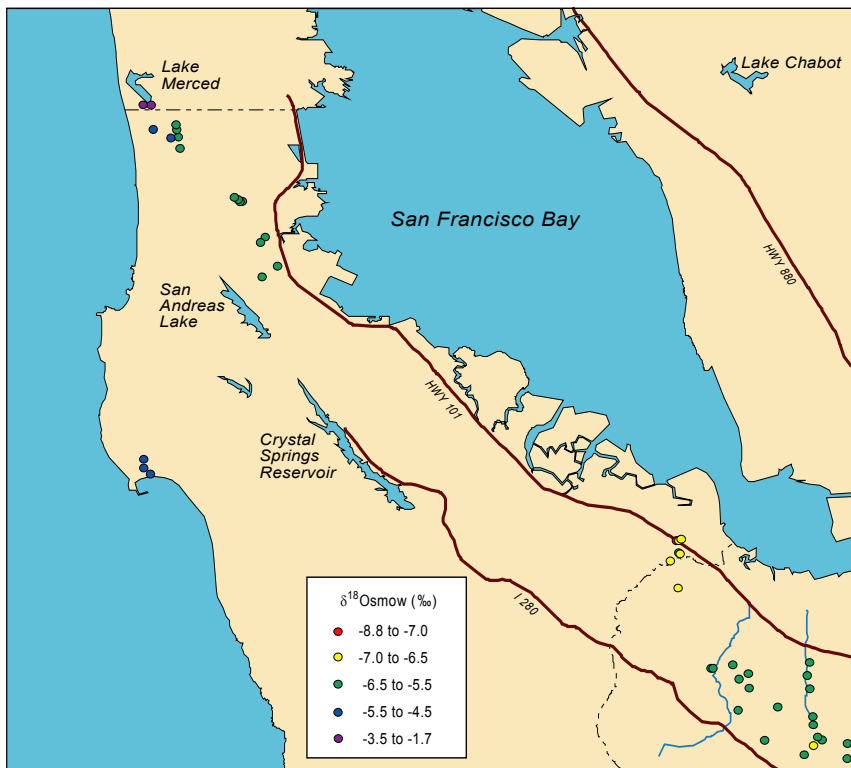
Widespread vertical transport is not evident in the confined zone, and the 4 solvent detections may be related to localized, vertical ‘short circuits’ caused by abandoned wells, compromised well casings, or natural conduits such as faults or buried erosional features. Many wells in the confined zone are situated along creeks (e.g., figure 7b). The high hydraulic conductivity of the sediments encountered by drillers that results in the choice of a well location may also provide a conduit for vertical transport of VOCs. Although abandoned and destroyed wells number in the thousands over the study area (SF Bay Regional WQ Control Board et al., 2003), the VOC data presented here do not provide direct evidence for widespread short-circuiting via abandoned wells.

## DISCUSSION OF ISOTOPIC AND GROUNDWATER AGE RESULTS

### SAN MATEO COUNTY

#### *Isotopic tracers indicate local recharge and pre-modern groundwater*

As seen in figure 13,  $\delta^{18}\text{O}$  values recorded in wells from San Mateo follow the gradient predicted for meteoric water values, with the Denniston wells along the coast having  $\delta^{18}\text{O}$  values of -5, progressing to lighter  $\delta^{18}\text{O}$  values eastward from Coastside Basin wells to Westside Basin wells to the San Mateo Plain (East Palo Alto) where the lightest  $\delta^{18}\text{O}$  is observed, -7.0. In these areas, the recharge water source is likely precipitation that falls in the local watershed. Lake Merced has a  $\delta^{18}\text{O}$  value of +0.6, indicating a high degree of evaporation. Nearby monitoring wells likewise show highly evaporated  $\delta^{18}\text{O}$  signatures, and indicate direct communication between surface water and groundwater.



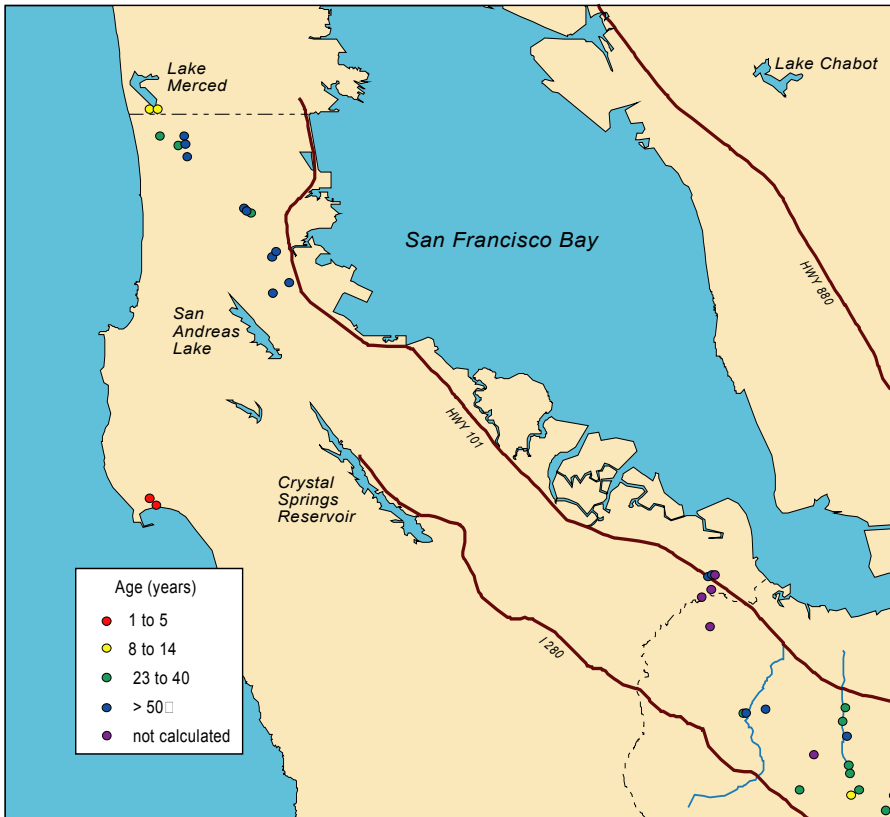
**Figure 13.** Oxygen isotope results for wells from San Mateo County showing trend toward depleted  $\delta^{18}\text{O}$  values from west to east. Shallow monitoring wells adjacent to Lake Merced suggest that evaporated water from the lake is a source of recharge.

**Coastside Basin:** Three public supply wells from the Coastside Basin have mean groundwater ages of only 4 years (at a fourth well an age could not be determined but the observed tritium concentration suggests an age similar to the three other wells; figure 14). The wells have total depths of only about 100 ft, and are screened in a shallow, sandy, unconfined aquifer. This aquifer likely has a relatively small recharge area, and rapid turnover of water. All of the vulnerability indicators point to rapid groundwater transport to the capture zone of these wells, and these are among the most vulnerable wells in the study area. Given the high vulnerability for the groundwater wells, and proposed increase in groundwater production in the Coastside Basin, a more detailed study of recharge sources and transport pathways is called for. An important consideration is to distinguish

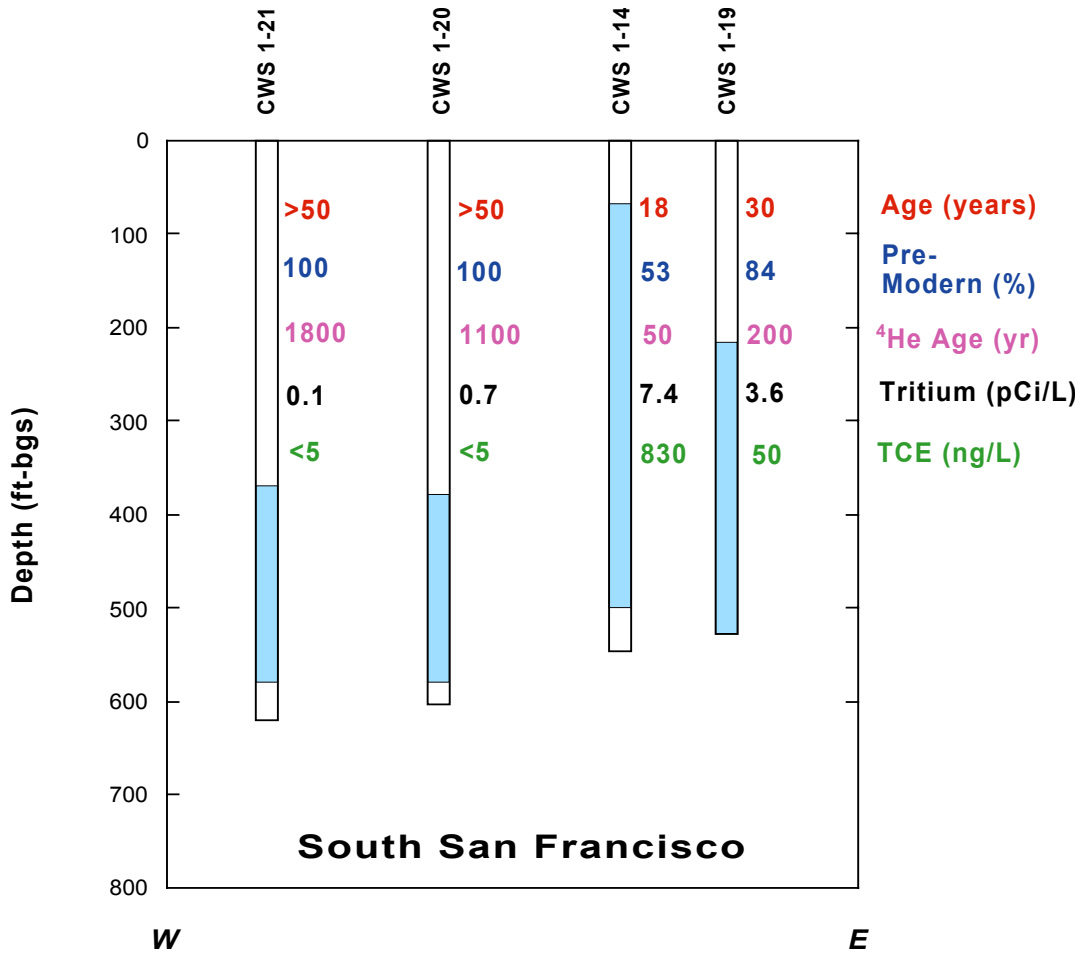


recharge via small streams, and dispersed rainwater recharge, so that these public supply wells can be protected from non-point source or point source contamination to the greatest extent possible.

**Westside Basin:** A relatively large number (8 of 14) of Westside Basin wells are devoid of tritium (<1 pCi/L), and another two Daly City wells have tritium values between 1 and 2 pCi/L, for a total of 10 wells with groundwater ages that indicate that the groundwater was recharged more than 50 years ago (figure 14). Three wells in South San Francisco and two in Daly City have detectable tritium, but these wells produce water that is largely greater than 50 years old as well, as determined by the fraction pre-modern. The slightly younger ages in Daly City are in the western-most wells, which have shallower top perforations than the wells to the east. A wellfield in South San Francisco illustrates the effect that well screens have on the distribution in water ages that are drawn at a well (figure 15). One well, with a screened interval that begins at a depth of only 70 ft below ground surface (compared to other wells in the basin with top perforations at >200 ft bgs) has the highest recorded tritium value, the youngest groundwater age (18 years), the smallest fraction pre-modern water (53%), and the highest concentration of a VOC (TCE at 830 ppt) in the Westside Basin. Another well with a slightly deeper top perforation shows intermediate age indicators and a lower TCE concentration. The wells with deeper screens draw an older groundwater component, and are free of VOCs. In this basin, vulnerability of groundwater is dictated by depth, and wells that tap deeper aquifers are apparently protected from the widespread contamination present at the surface. Nearly all of the wells in the Westside Basin have detectable levels of radiogenic <sup>4</sup>Helium, indicating the presence of a component of water at least hundreds of years old.



**Figure 14.** Tritium-helium groundwater age results for wells from San Mateo County.

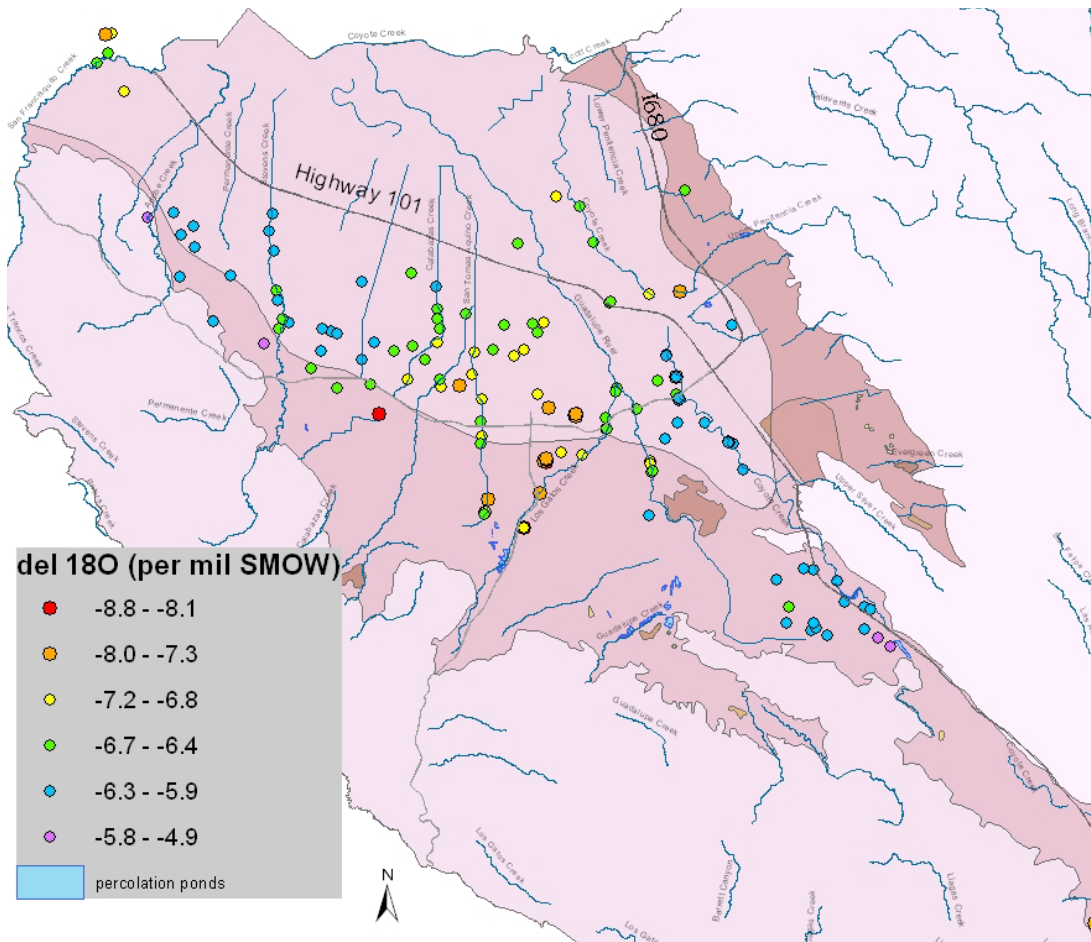


**Figure 15.** Schematic cross section of a South San Francisco wellfield, showing effect of perforated interval on groundwater age and related properties, including TCE concentration.

**San Mateo Plain:** Nine wells in Palo Alto and East Palo Alto produce mostly pre-modern groundwater, and stand out in having high concentrations of radiogenic  $^4\text{He}$  (fig. 14 and 23). The stratified nature of the groundwater is evident in the East Palo Alto wellfield, where a single well (Well 2), screened across a very shallow interval, has a mean groundwater age of only 12 years, a tritium value of 14.6 pCi/L, and produces no pre-modern water, while another well (Well 7), screened over a much deeper interval, produces groundwater with an age of greater than 50 years, a significant radiogenic  $^4\text{He}$  concentration, and a distinct  $\delta^{18}\text{O}$  signature. In general, the groundwater produced from deep-screened wells in this part of the basin is 10's to 100's of thousands of years old, and likely has a very deep source. Two lines of evidence support the idea that deeply sourced fluids are transported upward in this part of the basin: the major ions present are Na and Cl, whereas Ca and bicarbonate waters dominate throughout most of the main subbasin underlying San Jose (SCVWD, 2001), and two wells show evidence of a component of He from the Earth's mantle (figure 25), as described above.

*Stable Isotopes in the Main Subbasin Mark Artificially Recharged Imported Water*

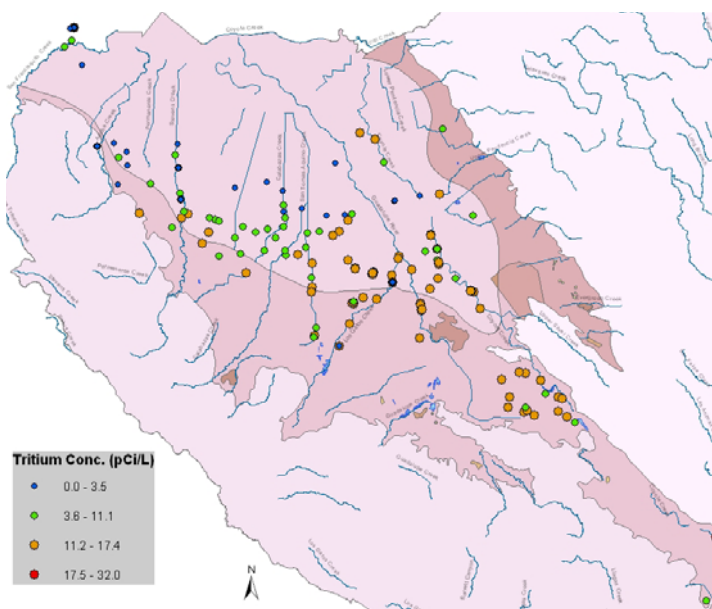
$\delta^{18}\text{O}$  values for Santa Clara main subbasin wells are shown in figure 16, and are an excellent marker of the influence of imported water in the main subbasin. Imported water used for artificial recharge in the SCV Basin is from the State Water Project (SWP), which comes from the Sacramento-San Joaquin Delta (comprised of 80% Sacramento River water), or from the Central Valley Project (CVP; San Luis reservoir), which is also comprised of Sacramento River watershed water. Sacramento River  $\delta^{18}\text{O}$  varies seasonally, from -12 to -10, and State Project water, which contains a component of isotopically lighter San Joaquin River water, ranges between -9 and -10 (Table 2). Water from the Hetch-Hetchy system, which is used for water supply in Palo Alto, San Jose, Sunnyvale, Mountain View, Milpitas, and Santa Clara, has a  $\delta^{18}\text{O}$  signature of approximately -14. Hetch-Hetchy water is not intentionally applied for groundwater recharge, but may enter groundwater when pipes leak or when water is applied for irrigation. Sources of artificially recharged water are therefore a complex combination of imported and locally-captured supplies, the proportions of which vary seasonally.



**Figure 16.**  $\delta^{18}\text{O}$  (per mil relative to SMOW) shows the extent of influence of imported water, which has an isotopically depleted (negative) signature. Areas in the western and southern portions of the main basin are recharged by local sources.

Ambient, native groundwater in the Santa Clara valley, recharged from local precipitation and ephemeral or intermittent streams in unconfined regions has an average, time-integrated range in  $\delta^{18}\text{O}$  of -5 to -6.5 (Kendall and Coplen, 2001). A relatively large isotopic contrast is therefore expected between locally-derived water and imported water from the SWP or the CVP. Figure 16 shows that isotopically-lighter water is not randomly distributed in this basin, but rather demarcates the zones influenced by artificial recharge of imported water. An extensive area that shows a gradual mixing of imported water to ambient water goes from wells near the recharge facilities along the Guadalupe River, San Tomas Aquinas Creek, and Los Gatos Creek, across the forebay, extending northward to Highway 101. This area of intensive basin management is also affected by low level MtBE from recharging surface water, and perhaps by mobilization of solvents between the recharge area and wells. There are two factors that may explain why values lighter than -8.8 are not observed: one is that in every well, imported water is mixed to a greater or lesser extent with ambient, locally-derived water, and the other is that prior to recharge, the water is evaporated to some degree, which shifts the  $\delta^{18}\text{O}$  value toward heavier  $\delta^{18}\text{O}$ . Furthermore, the water supplied to SCVWD recharge facilities is a combination of imported and local supplies. These factors combine to dilute the imported water signature in artificially-recharged surface water. Imported water is not diverted to the creeks west of Calabazas Creek, and this is reflected in  $\delta^{18}\text{O}$  results from wells in the western portion of the basin, where the local signature is observed.

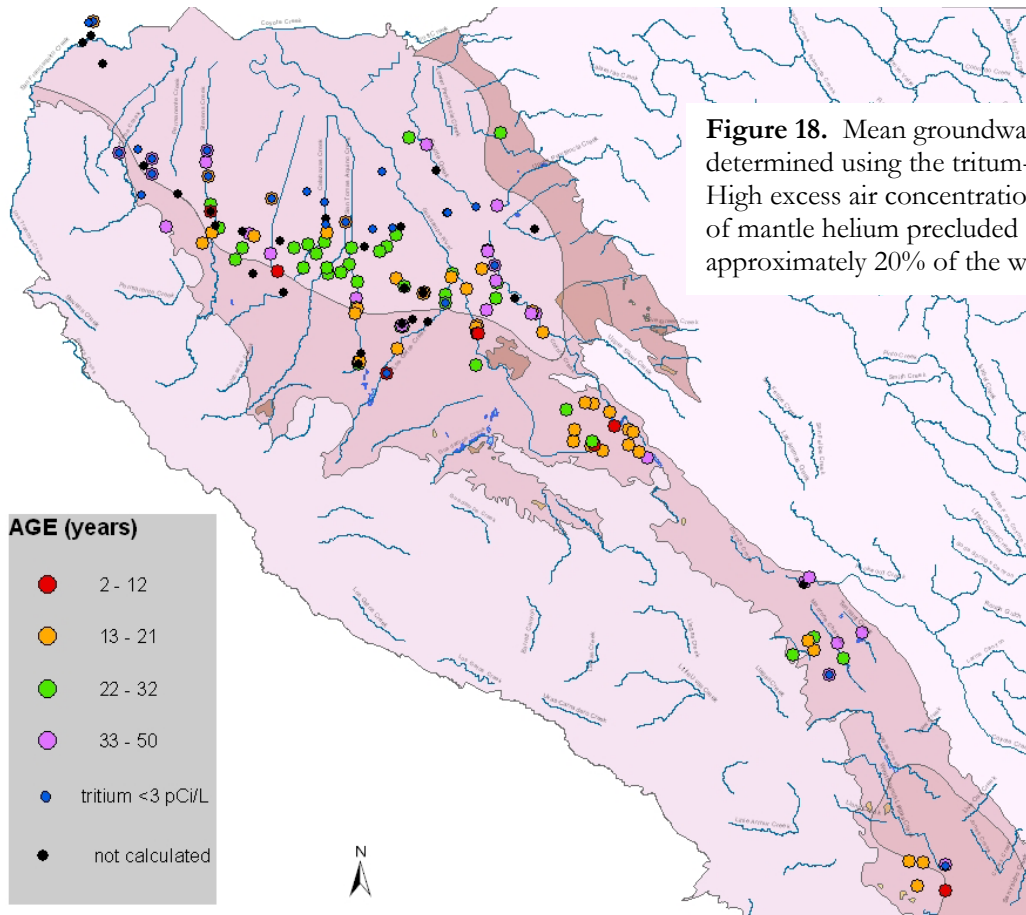
Tritium concentrations measured in groundwater samples from the main subbasin show a spatial distribution that is related to the flow field, and therefore useful for assessing contamination susceptibility. Nearly all samples in the main subbasin have detectable tritium concentrations (>1 pCi/L), but nearly all are significantly lower than the expected range for modern-day precipitation (figure 17). There is a clear spatial pattern in tritium concentration in the main subbasin, with the highest concentrations in the wells in the unconfined region south of Highway 280, especially in the wells along Los Gatos Creek and San Tomas Aquinas Creek. These are the same wells affected by artificial recharge of imported water, and tritium and  $\delta^{18}\text{O}$  maps show similar spatial patterns (figures 16 and 17). The wells along the Guadalupe River are likely influenced by groundwater recharged in Almaden Lake, Guadalupe Ponds, and in the creek beds, but the effect is dampened by the greater distance between these wells and the recharge area. Tritium concentrations decrease to the north and to the west, with the lowest values found in the confined region under northern San Jose, the City of Santa Clara and Los Altos. These wells, situated along an arc that parallels the bay, have tritium concentrations of less than 3.5 pCi/L (figure 17).



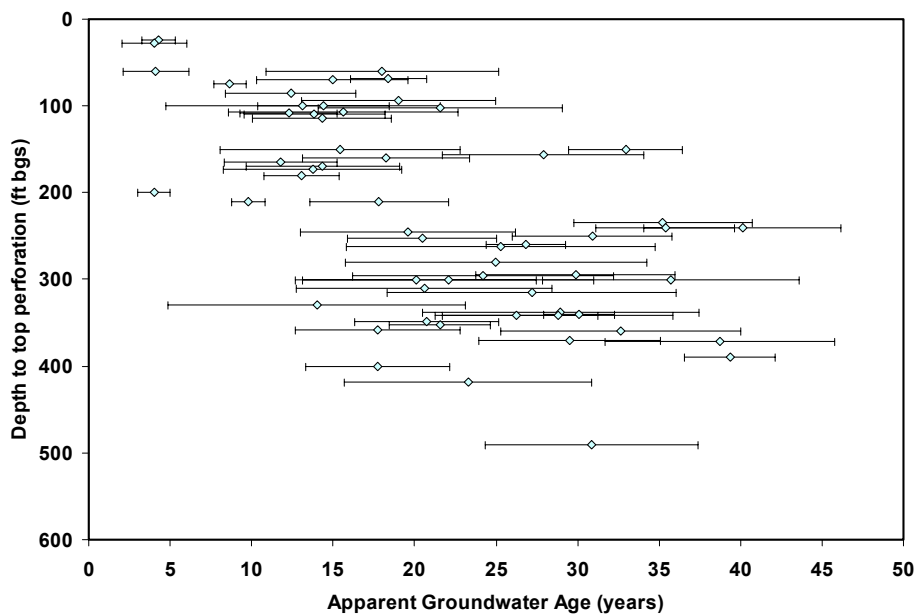
**Figure 17.** The tritium concentration in wells from the Santa Clara main basin shows a generally decreasing pattern away from recharge areas in the forebay, as expected.

The spatial pattern in groundwater age mirrors the pattern in tritium concentration (fig. 18), but gives a direct measure of the residence time for the post-modern portion of the groundwater. Many wells in the main subbasin have groundwater ages of 20 to 40 years, with scattered younger ages along creeks and close to recharge areas. Increasing groundwater age is positively correlated ( $R^2 = 0.4$ ) with depth to the top screen perforation (figure 19). A pattern of increasing groundwater age with depth is typically observed in large groundwater basins (Moran et al., 2002; Hudson et al., 2002).

The groundwater age dates allow estimation of flow rates for the portion of the water dateable by the tritium-helium method. A rough estimation of the horizontal groundwater flow rate is made using a transit time of 50 years and the approximate distance from the recharge area (roughly near the Three Mile wellfield adjacent to Los Gatos Creek) to the band of wells in Santa Clara with mean ages of >50 years that are just downgradient of wells with ages of <50 years (figure 19). The resulting flow rate of approximately 500 ft/yr represents an estimate of the bulk flow rate for the post-modern fraction of the groundwater. Except for a small handful of scattered younger ages (with large error bars due to high excess air concentrations – see next section) along Stevens Creek and Calabasas Creek, the distance between wells with young ages in the forebay and the band of very low tritium wells is roughly the same across the main subbasin. The depressed tritium concentrations observed throughout the basin are indicative of a highly dispersive hydrogeologic regime, and both horizontal and vertical flow rates almost certainly vary widely over short distances (Weissman et al., 2002, Clark et al., 2003). Groundwater flow velocity is likely highest in the shallow zone, and may be significantly greater than 500 ft/yr in the shallow sediments of the forebay (Clark et al., 2003).



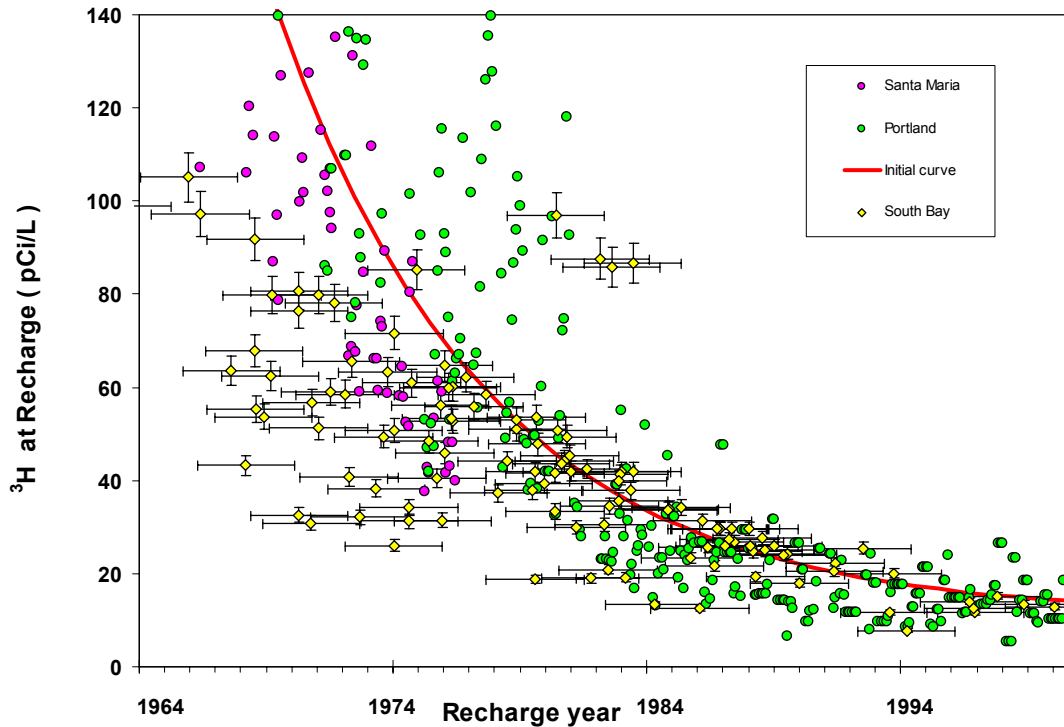
**Figure 18.** Mean groundwater age as determined using the tritium-helium method. High excess air concentrations or the presence of mantle helium precluded age determination in approximately 20% of the wells.



**Figure 19.** Groundwater age versus depth to top perforation for a subset of wells from Santa Clara, showing an overall trend toward older ages in wells with deeper top perforations.

The age, or mean residence time, of groundwater in the basin also allows independent estimation of the storage capacity of the basin, using estimated recharge and extraction rates. The operational storage capacity of the main subbasin was evaluated (SCVWD, 1999) using a numerical groundwater flow model, and historical water levels, and determined to be 350,000 acre-ft. Further analysis indicated that with a subsidence tolerance of 0.01 ft/yr, and an estimated annual recharge capacity of approximately 160,000 acre-ft, the rate of withdrawal from the basin should not exceed 200,000 acre-ft/yr, and accordingly, recent annual withdrawals have been 100,000 to 130,000 acre-ft. An inventory of 350,000 acre-ft, and an annual flux of 120,000 acre-ft, indicates a mean residence time for the active part of the basin of only about three years, much shorter than the mean age determined from groundwater age dating. Using a mean residence time of 25 years, in accordance with measured ages in wells from the main subbasin, an annual flux of 120,000 acre-ft indicates total storage of 3 million acre-ft. Estimates for gross storage capacity (as opposed to operational storage capacity), based on the volume of water that could be contained between the base of the water-bearing materials and 10 ft. below ground surface range from 1.2 million acre-ft (to 110 ft) to 7.3 million acre-ft (to 1010 ft; DWR Bulletin 118). Three million acre-ft in gross storage capacity is reached at a depth of approximately 310 ft. In all likelihood, there are ‘cells’ in the basin that turn over on different time scales. The ‘cell’ sampled by the PWS wells has a turnover time on the order of decades, while shallower, more active cells may turn over on a shorter time scale, and the large volume that makes up the deep basin turns over on a time scale that is likely two orders of magnitude greater.

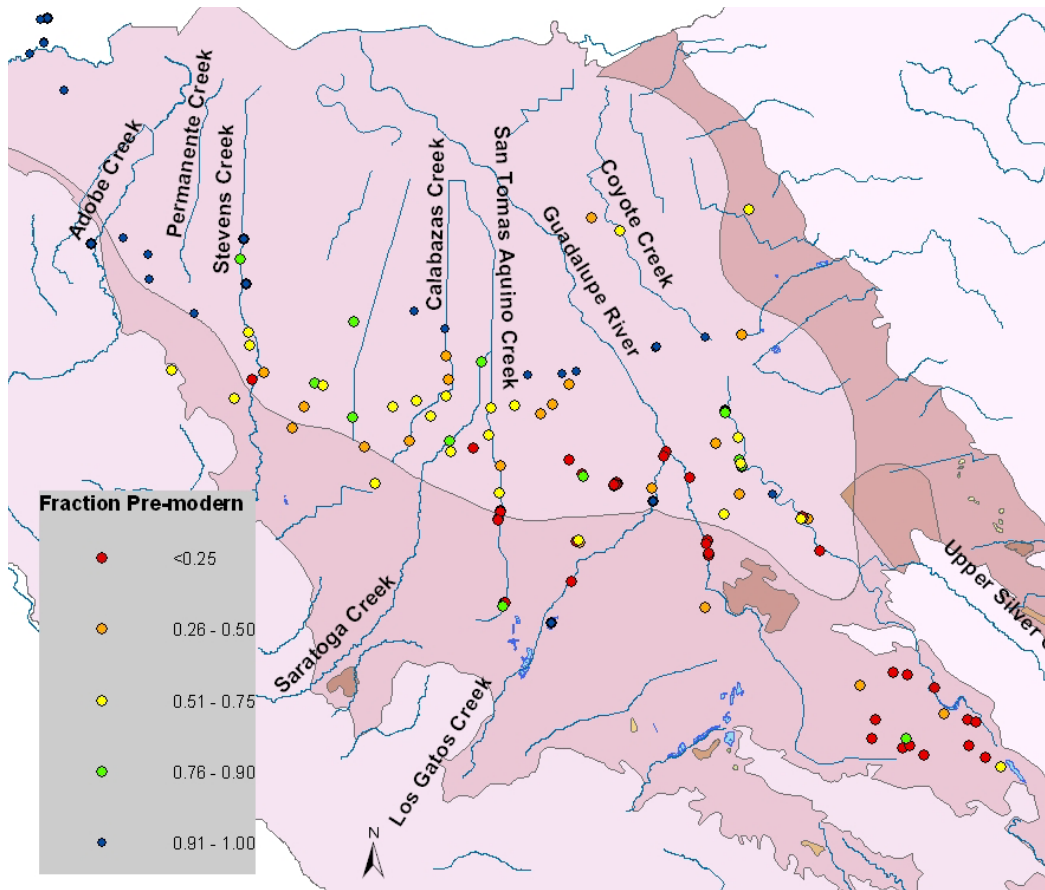




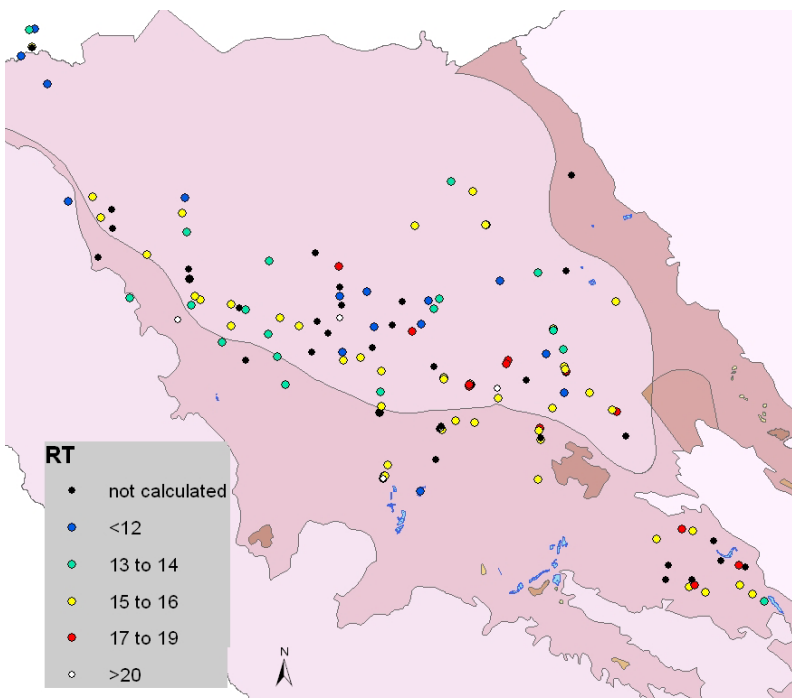
**Figure 20.** The red curved line is an approximation of the tritium-in-precipitation data shown for Portland, OR, and Santa Maria, CA. Yellow symbols are for wells from this study, and are plotted according to the calculated mean groundwater age, and the (decay-corrected) measured tritium concentration. Points that fall below the red line contain a significant fraction of pre-modern groundwater.

Many wells in the middle of the basin fall in an age range between 20 and 50 years, and are clearly a mixture of mainly pre-modern groundwater with a smaller component of water recharged after 1950 (figure 20). Wells with calculated mean ages younger than about 20 years are more likely to have narrow age distributions than wells with greater ages. Only 4 Santa Clara County wells have mean ages of less than 10 years, and another 32 have ages between 10 and 20 years. It is somewhat unusual for long-screened production wells to produce groundwater with a mean age of less than 10 years (Hudson et al., 2002; Moran et al., 2002), even near recharge areas, because older water is typically drawn in through deeper intervals of the well. The younger ages occur mainly in wells along the creeks in or near the forebay where recharge occurs (fig. 18, 21). The spatial pattern in the fraction pre-modern mirrors the patterns described previously for  $\delta^{18}\text{O}$ , tritium, and groundwater age (fig. 21).

Recharge temperatures determined from noble gas concentrations measured in groundwater samples are shown in figure 22. The mean annual air temperature for the San Jose area is approximately 15.5C (<http://www.giss.nasa.gov>), in good agreement with the mode of the data shown in figure 22. The spatial pattern exhibited by recharge temperatures is somewhat noisy, but in general warmer temperatures are prevalent in areas of artificial recharge in the forebay. Cooler temperatures occur in the center of the confined area of the main subbasin. This pattern is likely the result of groundwater management, whereby captured or imported water is allowed to warm at higher ambient air temperature in recharge ponds or behind temporary dams. Natural recharge takes place during winter months, and at somewhat higher elevations, which gives rise to lower recharge temperatures.



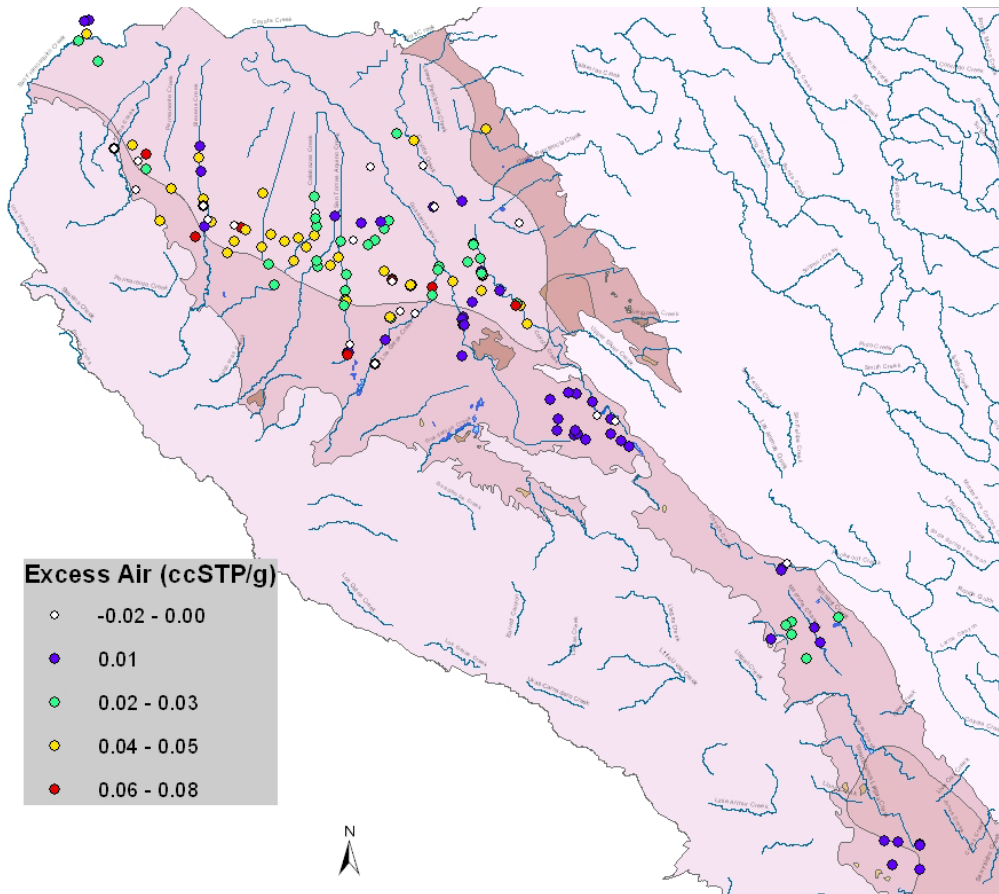
**Figure 21.** The estimated fraction of groundwater of pre-modern age shows the degree of mixing between post-modern aged water and water that recharged the basin before about 1955.



**Figure 22.** Noble gas recharge temperatures in the main subbasin show a rough pattern of warmer recharge temperatures in the artificially-recharged forebay area and cooler temperatures in the northern and western regions.

*Recharge Conditions are Revealed by High 'Excess Air' Concentrations*

Scattered younger mean ages in the deeper, confined parts of the basin (e.g., along Stevens Creek in Los Altos and Mountain View) have consistently large error bars. This area of the basin coincides with an area of extremely high 'excess air' concentration (calculated from dissolved Ne concentrations in groundwater samples; fig. 23). The combination of low tritium concentrations and high excess air concentrations in these wells from the western part of the main subbasin precludes the possibility of precise age dating. The excess air concentrations observed in these wells are exceedingly high compared to published values. In a survey, Aesbach-Hertig et al. (2000), report values of 0.001 to 0.01 cm<sup>3</sup>STP/g, while excess air in this part of the basin is in the range 0.02 to 0.05 cm<sup>3</sup>STP/g. A high hydraulic head, a high rate of infiltration through the vadose zone, extreme vertical fluctuation in the water table, and highly episodic recharge are required to preserve the levels of trapped air that are observed. This may be an expression of the natural recharge pattern in this Mediterranean climate, whereby incised, ephemeral streams are infrequently flooded, and a tall column of water is piled on a thick vadose zone. During passage through the vadose zone, large amounts of air are trapped as bubbles that subsequently dissolve, and are kept in solution by rapid recharge with a high hydraulic head.



**Figure 23.** 'Excess Air' concentrations in groundwater samples from the study area give insight into recharge conditions. Extremely high excess air, observed in the western portion of the main basin may be related to natural, episodic recharge in incised streams.

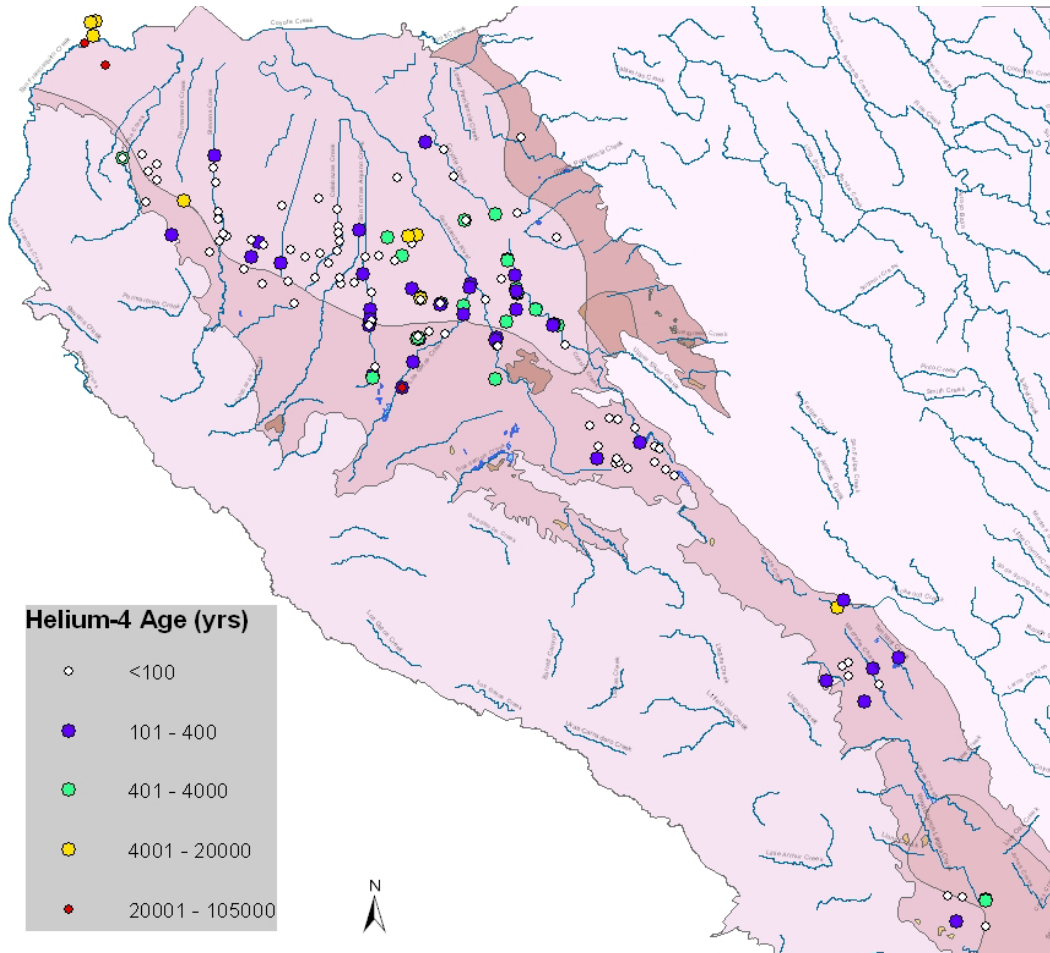
This phenomenon is more pronounced in the western part of the basin for several reasons. There is a steep gradient in precipitation from the Santa Clara-Santa Cruz county line in the west, where annual precipitation averages more than 40 inches, to the area of downtown San Jose in the east, where annual precipitation averages only 12 inches. Natural, episodic recharge during flooding events is therefore more likely to occur in the western region. The streambeds, where natural flows and sand and gravel deposits allow recharge, are more deeply incised in the western part of the basin compared to the valley streams in the central part of the main subbasin. Furthermore, rather than recharging the alluvium, streams in this area recharge the Santa Clara formation, which outcrops in the Los Altos hills and along San Franciscito Creek, Permanente Creek, and Adobe Creek. These creeks are not supplied with artificial flows, so the natural recharge pattern is in effect. These are also areas where extensive coarse-grained deposits, or other vertical conduits, may allow relatively rapid transport of water to deeper parts of the basin.

High concentrations of excess air have water quality implications. In addition to the noble gases, reactive gases such as oxygen are entrained, and affect the water chemistry in the region. If dissolved oxygen is consumed during breakdown of organic matter, water quality improvement during recharge is expected, 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). However, if aerobic conditions persist in groundwater well downgradient of recharge, water quality improvements that are associated with reducing conditions are not realized. For example, denitrification occurs only when dissolved oxygen concentrations are less than 1-2 mg/L. As evidence for this effect on water quality, relatively high nitrate concentrations are observed in the same part of the basin where excess air concentrations are elevated (SCVWD, 2001), compared to areas of the main subbasin where excess air concentrations are lower.

#### *Young Groundwater is Produced in the Southeastern Forebay Area*

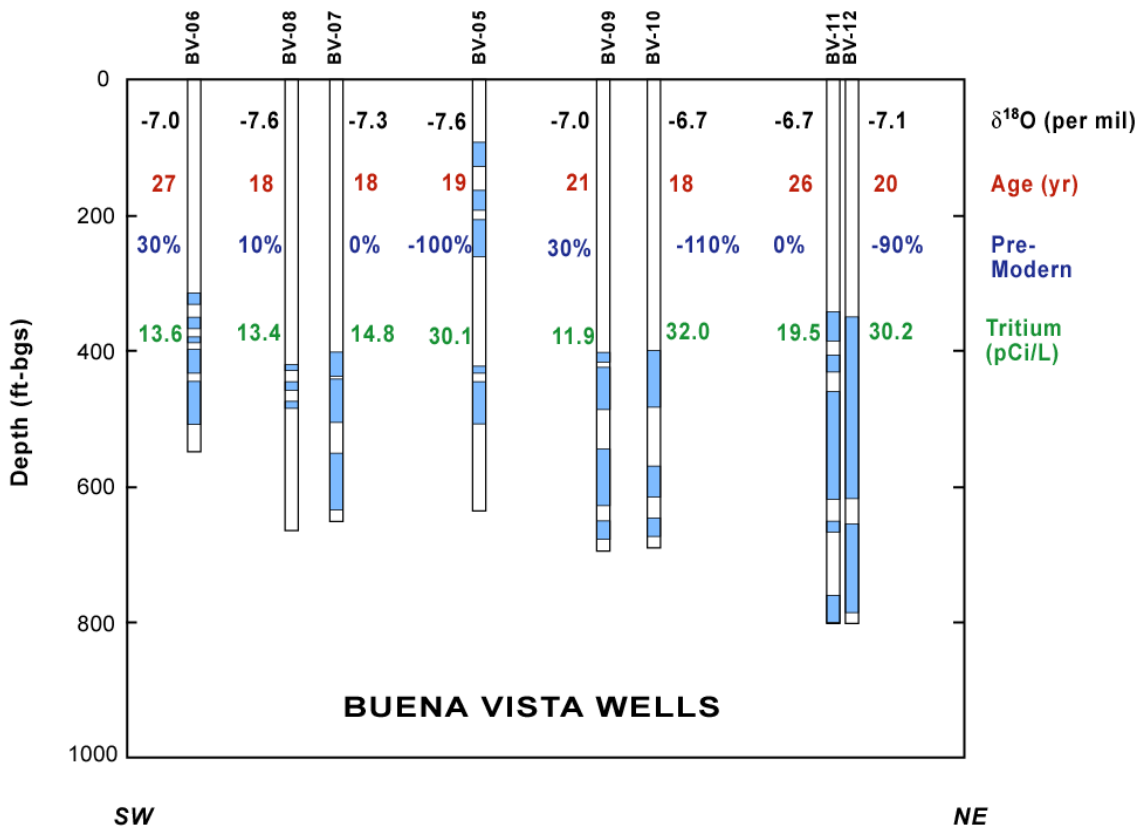
The southeastern forebay (Santa Teresa) area, represented by Great Oaks Water Company wells and one City of San Jose well, is also home to artificial recharge facilities. Although some of the wells from this study are just downgradient from artificial recharge ponds (e.g., GOWC 7, GOWC 16 and GOWC 19 near Coyote Pond),  $\delta^{18}\text{O}$  signatures for these wells cluster tightly around -6.0, indicating the predominance of locally-sourced water (figure 16). Historically, only locally captured water has been delivered to the Ford Rd and Coyote ponds, in this part of the basin. This is in contrast to all of the other recharge facilities in the basin, where either a combination of local and imported water, or exclusively imported water is recharged.

All of the parameters used to estimate groundwater age and groundwater age distribution indicate that young groundwater is produced in the wells from this part of the forebay (figures 18 and 21). This group of 16 wells is evidently part of a more localized, dynamic system, without a strong connection to the rest of the main subbasin. A topographic barrier at the Edenvale Gap (Oak Hill and Edenvale Ridge), and/or the Edenvale Thrust Fault may inhibit transport from the southeastern part of the forebay to the rest of the main subbasin. Hydrogeologic conditions in this part of the basin (DWR Bulletin 118, 2003) support the interpretation based on isotopic evidence, that active recharge takes place, but transport to the north is limited. Except for the most southerly well, tritium-helium ages cluster fairly tightly around 15 years, and the fraction of pre-modern water produced is uniformly low. Radiogenic  $^4\text{He}$  is also uniformly low (fig. 24) in these relatively shallow wells (most have total depths of about 200 ft). Low concentrations of excess air suggest that recharge takes place at a constant rate, and without extensive interaction with vadose zone gas. These wells are classified as relatively vulnerable, given the comparatively young ages observed. Significant, localized VOC occurrence in wells in this area is evident in DHS data, but no VOCs were detected during the present study.



**Figure 24.** The radiogenic  $^4\text{He}$  age is a residence time estimate for the groundwater component older than approximately 100 years. The red symbol in the forebay area of the main basin is from a very deep monitoring well.

The complexity introduced by groundwater pumping patterns at wellfields where pumping at one well influences the capture zone of other wells in the wellfield, is evident in the ages and other parameters measured in wellfields in the forebay area. Here it must be emphasized that the data in this report represent a snapshot in time, and that the well owner's normal operations were not significantly altered for sampling. For example, while several indicators point to relatively young, imported water in the Buena Vista wells (figure 25), a component of much older water is produced in some wells from the Buena Vista wellfield and not others. Age-related parameters vary considerably, but not in a pattern that might be predicted based on screened intervals. One well in this wellfield (BV-05) is screened over a significantly shallower interval than the others in the wellfield, but does produce significantly younger groundwater. On the other hand, two other wells from the Buena Vista wellfield stand out from all other wells in the basin as having the highest tritium concentrations, and producing groundwater that is entirely post-modern. Similarly, in the Virginia wells, age, fraction pre-modern, radiogenic  $^4\text{He}$  age, MtBE concentration, and 1,1,1TCA concentration (maximum that appears in the DHS database) all co-vary, indicating that Virginia 3 has the largest young water component. The pattern does not seem to be related to the screened intervals of the wells but rather to the relative proximity of each well to the injection well, located just to the north of the wellfield (figure 12).



**Figure 25.** The Buena Vista wellfield stands out as having some tritium concentrations greater than modern-day precipitation, which leads to fraction pre-modern results that are negative. In this wellfield, the depths of the perforated intervals do not correlate with age-related parameters.

*Confined Zone of Main Subbasin is Area of Lower Vulnerability*

Mean groundwater age, in combination with the calculated fraction pre-modern water (figures 18 and 21), show that the most vulnerable areas of the main subbasin are the southern and south-eastern portions, in the forebay area, where transit times for recharge water (and soluble, non-reactive contaminants) for a major portion of the groundwater are less than twenty years. In contrast, large areas of the basin to the north and west produce groundwater that has largely been isolated from surface sources for more than 50 years. Widespread ‘short-circuiting’ via vertical conduits might be expected in the main subbasin, due to the very large number of abandoned wells (SF Bay Regional WQ Control Board et al., 2003), or due to natural geologic features in this tectonically active region. However, with the exceptions related to VOC detections noted above, there is little evidence for rapid vertical transport in the confined region of the main subbasin, where the age distribution in wells is dominated by pre-modern water. The predominance of pre-modern water, combined with patchy evidence for upwelling of deeply sourced water, might be explained by the effects of groundwater basin management. Mitigation of historical overdraft required that a huge volume of water be artificially recharged in the forebay area of the main subbasin. Water loading in the recharge area (and intense pumpage in the confined zone) may result in vertically upward flow in the confined area. This effect may play a role in preventing transport of contaminants from shallow to deep zones over a large area of the basin. The type of data needed to confirm that an upward gradient is widespread in the confined zone is not available.

Radiogenic  $^4\text{He}$  concentrations in the main subbasin offer further evidence for isolated groundwater, and extensive mixing of groundwater across long-screened wells, resulting in very broad age distributions for individual wells. In addition to very high radiogenic  $^4\text{He}$  values recorded in wells in the northwestern portion of the basin in the San Mateo plain, high radiogenic  $^4\text{He}$  concentrations are recorded in wells at the distal end of the area influenced by artificial recharge, in the eastern portion of the main subbasin (figure 24). In fact, some of the same wells that are in an area of relatively young groundwater (as indicated by tritium-helium ages of the component containing tritium), are producing another component of water with a residence time in the basin that is on the order of 10,000 years. In contrast, wells along Stevens Creek and Calabasas Creek are characteristically low in radiogenic  $^4\text{He}$ , suggesting that this component is not tapped (or not present) in wells in the western portion of the main subbasin.

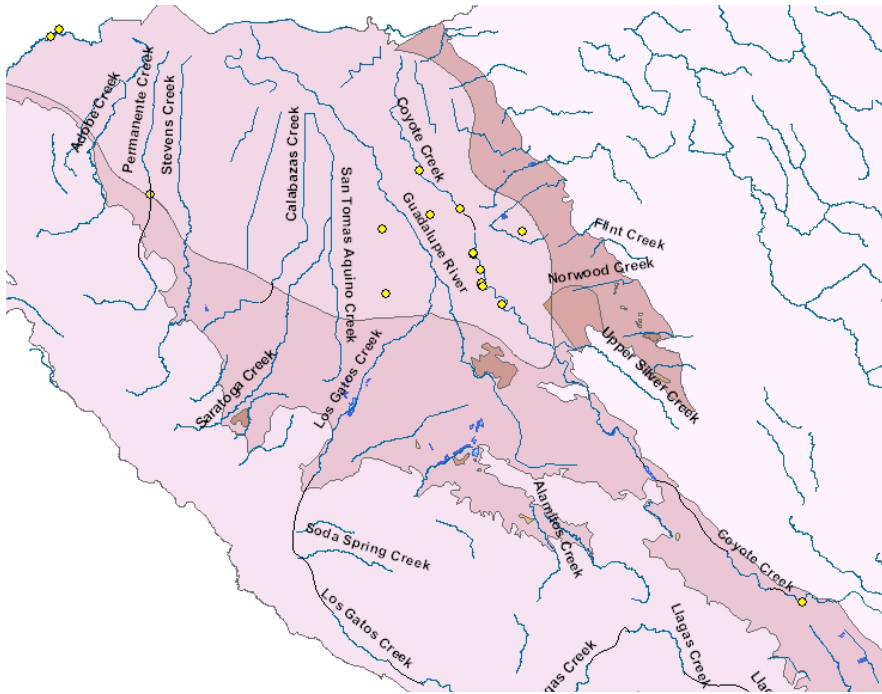
Further evidence for upwelling of deep-seated fluids in the main subbasin comes from 14 wells where  $^3\text{He}/^4\text{He}$  ratios indicate the presence of a component of mantle He (figure 26). These wells are not scattered throughout the basin, but rather are mostly in a northwest trending line along Coyote Creek. Areas of active tectonics provide an opportunity for deep-seated fluids to reach shallower zones along faults and in areas of crustal thinning. The series of right lateral faults in this part of the basin includes the Calaveras and Hayward Faults to the east, and the Silver Creek and Santa Clara Faults to the south-southwest. In the region of the Edenvale Fault and the small thrust fault that runs between the Silver Creek Fault and Santa Clara Fault, a mantle 'window' may be present due to transtensional stress release. In such a tectonic regime, mantle He may emanate along a releasing bend (zone of transtension) within the strike slip system. Zones of transtension are associated with areas of crustal thinning (Van Wijk et al., 2001, Jove and Coleman, 1998, Tenbrink et al., 1999), which could allow mantle material to rise to relatively shallow depths. The major strike slip faults in the San Andreas system are suspected to be conduits for deep-seated fluid migration (Kennedy et al., 1997). Interestingly, deep groundwater wells close to the major strike-slip faults of the San Andreas system, are most often *not* affected by mantle helium. Wells immediately adjacent to the Hayward Fault, in Fremont, CA, are not influenced by mantle helium (Moran and Halliwell, 2002), and wells from the Los Angeles and Orange County areas, near the major strike slip faults, show evidence for mantle helium only in one localized area (Hudson et al., 2002). In the present study, two wells in the Palo Alto area, near the San Andreas fault, have mantle He components (figure 26), but this component is absent in other wells adjacent to the fault, further to the north in Daly City. The tectonic features in the affected areas of the Santa Clara Basin might be identified as areas of transtension in light of this new evidence for facilitated mantle fluid transport.

#### *Llagas Subbasin Wells Show Mixed Vulnerability*

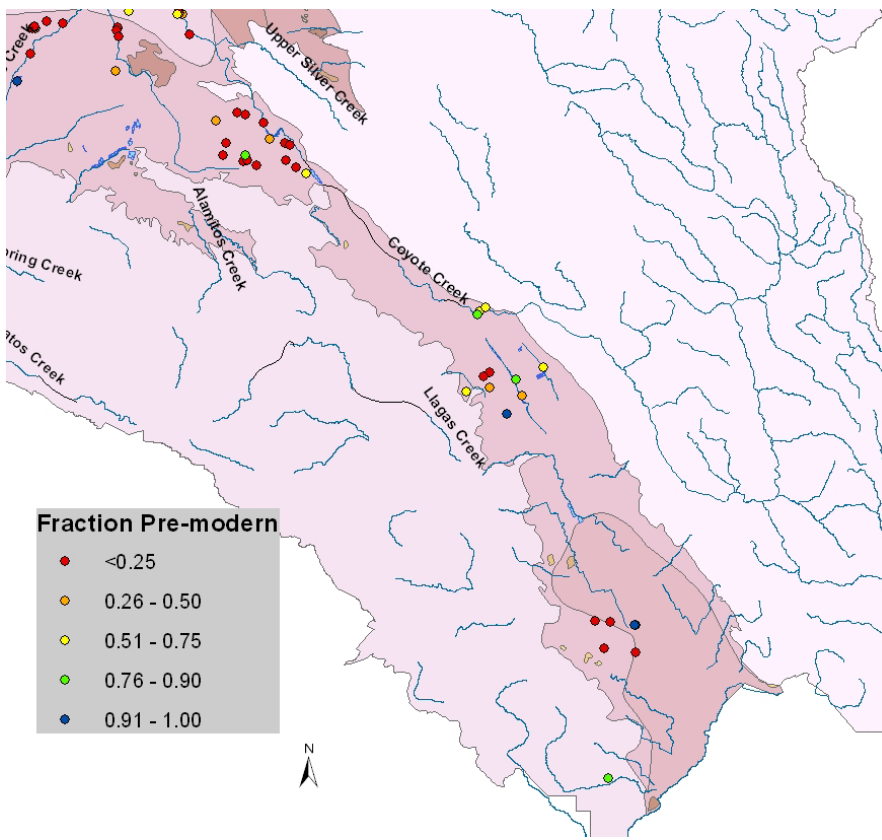
Figures 27 and 28 show age and related results for wells from the Llagas subbasin. The sampling density in this subbasin is much lower than for the main subbasin, so conclusions that can be made regarding basin-wide transport are more limited. A topographic high creates a groundwater divide in Morgan Hill. Groundwater flow is toward San Francisco Bay to the north of the divide, and water flows to Monterey Bay to the south. The Morgan Hill and Gilroy wells sampled in this study are to the south of the divide (except three from the Coyote subbasin described below), in both the confined and the unconfined parts of the basin (figure 7a). Artificial recharge in the northern part of the subbasin occurs in both in-stream (along Cochran Channel and Mardone Channel) and off-stream facilities (Main Avenue, San Pedro and Church Ponds).  $\delta^{18}\text{O}$  results indicate that a component of artificially recharged imported (CVP) water is present in the produced water in the Morgan Hill area of the subbasin. Of the twelve wells tested in the Morgan Hill area, six show evidence for a component of imported water, with a larger component in the wells just to the north of Dunne Avenue. Other wells in the Llagas subbasin have  $\delta^{18}\text{O}$  signatures indicative of a local



water recharge source. A more extensive sample network in the Llagas Basin is needed to better identify the contribution of imported water using isotope tracers.



**Figure 26.** Wells showing evidence for a mantle helium component (yellow symbols) occur most frequently along Coyote Creek. The local tectonic regime, including deep-seated faults and/or a mantle ‘window’ is likely responsible for allowing mantle fluids to reach groundwater in affected areas.

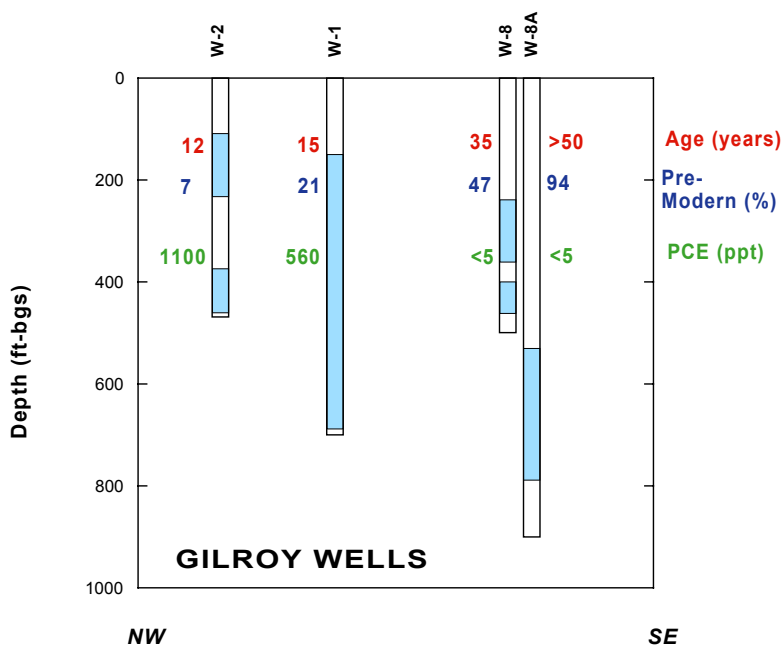


**Figure 27.** The fraction pre-modern (or pre-1955) water in Llagas Basin wells varies over a large range, with a relatively large number of wells exhibiting a narrow age distribution, and low fraction pre-modern.

Groundwater ages in 19 wells located in Morgan Hill and Gilroy span the entire age range of the tritium-helium method. The groundwater divide that exists in the Morgan Hill area, and groundwater age variation with depth are likely responsible for the complex pattern in ages observed in this group of 19 wells. Wells in the downgradient (southeastern) area of Morgan Hill produce water that is older than the northwestern cluster of wells (figures 18 and 27). A few wells from the Llagas subbasin have distinctly young ages (<15 yr), and should therefore be considered vulnerable to contamination. This includes the Diana 1 and 3 wells, and Main Ave. well in Morgan Hill, and Wells 1, 2, 4, and 6 in Gilroy. The Gilroy wells are from the confined zone of the Llagas subbasin, but are very near the boundary between confined and unconfined regions. Groundwater age increases from west to east, indicating that the unconfined region to the west of these wells may be an important source of recharge. A cross sectional view of a subset of the Gilroy wells gives strong evidence for stratified groundwater, with a zone that contributes recently recharged water (and PCE) at less than approximately 200 ft (figure 28). The well with the deepest screened interval presumably draws water exclusively from below the confining layer, and produces water that is almost entirely pre-modern.

As in the main subbasin, tritium concentrations in Llagas subbasin wells are generally below the tritium concentration expected for modern recharge, and the water produced at about half of these wells is largely pre-modern (figure 27). In Gilroy, the fraction pre-modern closely tracks mean groundwater age, suggesting simple mixing of two components of groundwater – a post-modern component that may have a narrow age distribution, and a pre-modern (or “tritium-dead”) component. Radiogenic <sup>4</sup>He “age” also correlates positively with fraction pre-modern, indicating that the pre-modern component likely contributes <sup>4</sup>He at a uniform rate.

The three Boys Ranch wells along Coyote Creek produce old groundwater that is greater than 60% pre-modern. Stable isotopes indicate local water recharge. These are the only samples from the Coyote subbasin, so conclusions about vulnerability of the Coyote subbasin are necessarily limited. The lack of young age indicators indicates that the section along Coyote Creek where the Boys Ranch wells are located is likely a gaining portion of the stream. The deepest well sampled in the Coyote subbasin (Boys Ranch 1) has a helium component indicative of fluid with a mantle source. This well is located on the Coyote Creek Fault, the likely conduit for transport of deep-seated fluids. Interestingly, the other two Boys Ranch wells are situated along the same fault but do not show evidence for a mantle component.



**Figure 28.** Schematic cross section of wells in Gilroy, near the southern boundary of the study area, show stratified groundwater, whereby a shallow screened interval brings in young, contaminated groundwater.

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## **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<sub>2</sub> equilibration method for <sup>18</sup>O/<sup>16</sup>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 ( $\delta$ ) 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. 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 ( $\delta^{18}\text{O} = +0.35\text{‰}$ ), 2) two isotopically distinct California meteoric water samples ( $\delta^{18}\text{O} = -9.78$  and  $-14.62\text{‰}$ ), and 3) Alaskan Tap Water ( $-21.02\text{‰}$ ). 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  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  measurements, from one run to the next, is  $\pm 0.10\text{‰}$ , 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  $\pm 0.10\text{‰}$ , the sample is run for a third time. If this duplicate is not with the  $0.10\text{‰}$  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 ( $^3\text{H}$  in picoCuries per liter; pCi/L)
- $^4\text{He}$ , Neon, Argon, Krypton, Xenon abundances ( $\text{cm}^3\text{STP/g}$ )
- Tritium-helium age (in years)
- Radiogenic  $^4\text{He}$  ( $\text{cm}^3\text{STP/g}$ )
- Excess air (in cubic centimeters at STP per liter)
- Recharge temperature (in  $^{\circ}\text{C}$ )
- ”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  $\text{CO}_2$ . 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  $400^{\circ}\text{C}$ . 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  $^3\text{He}$ . 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 ( $21^\circ\text{C}$ ). These calibration samples are processed along with regular samples with a frequency of 10%. Duplicate samples are analyzed with a frequency of 10%. The  $^4\text{He}$  and Ne abundances are measured with an accuracy of 2% and the ratio of  $^3\text{He}/^4\text{He}$  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  $^4\text{He}$  and tritiogenic  $^3\text{He}$  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  $^3\text{He}$  remains ( $< 100$  atoms). The  $^3\text{He}$  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  $^3\text{He}$  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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