

A Contamination Vulnerability Assessment for the Livermore-Amador and Niles Cone Groundwater Basins



Report to the
California State
Water Resources
Control Board



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Executive Summary

The Ambient Groundwater Monitoring and Assessment (GAMA) program, sponsored by the California State Water Resources Control Board (SWRCB), aims to assess the water quality and relative susceptibility of groundwater resources throughout the state of California. In 2001, Lawrence Livermore National Laboratory (LLNL) carried out this vulnerability study in the groundwater basins of the Alameda Creek watershed. 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 by 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). These observable parameters help define the flow field of a groundwater basin, and indicate the degree of vertical connection between near-surface sources (or potential sources) of contamination, and deeper groundwater pumped at high capacity production wells.

The spatial pattern in vulnerability indicators (groundwater age and low level contaminants) differs greatly for the western versus the eastern portions of the Livermore-Amador Basin. Tetrachloroethylene (PCE) is nearly ubiquitous in Livermore wells, and may have a distributed source such as leaky sewers in addition to known point sources from dry cleaners. Non-point source methyl *tert* butyl ether (MTBE) frequently occurs in these same wells. Trihalomethanes (THMs) are not useful as tracers of advective transport of 'recycled' treated water in this basin, but MTBE is a good indicator of very recently recharged water. Distributed recharge is inferred from the spatial distribution of ages. Somewhat younger ages, and significantly more widespread VOC occurrence indicates that vertical pathways are present in the eastern side of basin. A striking lack of VOC detections on the western side, and several very old groundwater ages indicate that the confining layer is thoroughly effective in preventing vertical flow in this highly productive part of the basin. In contrast, the area of the Mocho sub-basin (eastern side), which is in active use, has a relatively high degree of vulnerability to contamination from surface sources.

While Niles Cone public supply wells produce a large volume of very young water (70% of CY99 production had a mean age of less than ten years), the lack of contaminant sources in the small area between the recharge ponds and wellfields results in no detections of solvents or gasoline (BTEX) compounds. The likely source for the very low-level detections of MTBE is the atmospheric-derived component from the recharging pond water. In fact, the MTBE concentrations measured in production wells suggest that subsurface degradation of MTBE is taking place during transport from the recharge ponds to the wells. The observed low-level THMs are likely residual from on-site disinfection. The very young water ages measured for Above Hayward Fault (AHF) sub-basin wells indicate rapid, unimpeded, vertical and lateral transport, and a high degree of vulnerability. The Below Hayward Fault (BHF) sub-basin wells in the shallow Newark Aquifer likewise yield young water and have higher vulnerability than the deeper Centerville-Fremont and Deep Aquifer wells. The narrow age range observed in each of the three aquifers in the BHF sub-basin, and the good agreement with the predicted initial tritium value, indicate little mixing of water of different ages in the layered BHF aquifer system.

1. Introduction

The State Water Resources Control Board (SWRCB), in response to concerns expressed by the California Legislature and private citizens, has implemented a program to assess groundwater quality, and provide a predictive capability for identifying areas that are vulnerable to contamination. The program was initiated because of concern about recent public supply well closures due to the presence of chemicals, such as MTBE from gasoline, and various solvents from industrial sources. As a result of this increased awareness regarding groundwater quality, the Supplemental Report of the 1999 Budget Act required the SWRCB to develop a comprehensive ambient groundwater-monitoring plan. To meet this mandate, the SWRCB created the Ambient Groundwater Monitoring and Assessment (GAMA) Program. The primary objective of the GAMA Program is to assess the water quality and relative susceptibility 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 to implement this groundwater assessment program.

In 2001, Lawrence Livermore National Laboratory carried out this vulnerability study in the groundwater basins of the Alameda Creek watershed, located east of the San Francisco Bay. 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 isotopes of oxygen are measured to help determine 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 connection between near-surface sources (or potential sources) of contamination, and deeper groundwater pumped at high capacity production wells.

1.1. Background and Theory

1.1.1. Groundwater Age-Dating Technique

Tritium (^3H) is a very low abundance (around 1 part in 10^{17} of total hydrogen), radioactive isotope of hydrogen with a half-life of 12.34 years. 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 (which results from cosmic ray interaction with isotopes in the atmosphere). This atmospheric tritium enters groundwater (as HTO, with one hydrogen atom as tritium) during recharge. Its concentration in groundwater decreases by radioactive decay, dilution with non-tritiated groundwater, and dispersion. While the presence of tritium is an excellent indicator of water that recharged less than about 50 years ago, age dating groundwater using tritium alone results in large uncertainties due to spatial and temporal variation in the initial tritium at recharge. Measurement of both tritium and its daughter product helium-3 (^3He)

allows calculation of the initial tritium, and ages can be determined from the following relationship:

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

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

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 (see discussion below). 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 groundwater with a relatively rapid vertical connection with the surface has a younger age. Since most contaminants are present near the earth's surface, younger groundwater is therefore more vulnerable. Old groundwater is more likely to be isolated from the contaminating activities that are ubiquitous in urban environments.

1.1.2. 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 materials 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. 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. Thus, the interpretation of VOC detections is not with regards to health or regulatory concerns, but rather as another tracer of recent groundwater recharge. Detection of these compounds in drinking water wells may also provide early warning of an approaching plume.

1.2. Stable Isotopes as Tracers of Recharge Source

The minor stable isotopes of water molecules ${}^2\text{H}$ (deuterium, denoted as *D*) and ${}^{18}\text{O}$ vary in precipitation as a function of temperature, elevation and latitude (Craig, 1961; Ingraham & Taylor, 1991). In California, extreme changes in elevation occur over a relatively short distance. The net effect is that surface water from mountain watersheds has a significantly lower abundance of ${}^{18}\text{O}$ and *D* than coastal water. The abundance of these isotopes in groundwater samples can provide clues as to the origin of the source water from which the groundwater is derived.

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 -5‰ along the Pacific coast to -15‰ in the Sierra Nevada Mountains.

1.3. Hydrogeologic Setting

The 600 mi² Alameda Creek watershed comprises two major groundwater basins that are used for public water supply: the Livermore-Amador groundwater basin, and downstream, the Niles Cone groundwater basin. While experiencing similar water supply demands, and similar climatic controls, these two basins will be described separately in this report, because they differ in geologic setting and in their engineered facilities.

2. Livermore-Amador Groundwater Basin

In an average water year, groundwater from the Livermore-Amador basin is used to supply approximately one-third of the potable water (total annual potable supply is roughly 40,000 acre-ft, or about 13 billion gallons) to the population centers of Livermore, Pleasanton, and Dublin (approximately 210,000 people). Twenty-two of the twenty-seven ‘active’ (DHS definition) public supply wells in the basin were sampled for this study (Figure 1). In addition, six monitoring wells were included to provide increased spatial coverage. The City of Pleasanton, underlain by the Bernal and Amador sub-basins, is home to fourteen public water supply wells, while Livermore, underlain by the Mocho II sub-basin, has thirteen public water supply wells. Hundreds of potentially contaminating activities are present in these two cities, including forty-seven and ninety leaking underground fuel tank sites, respectively. One EPA-listed national priority superfund site (Lawrence Livermore National Laboratory) sits on the eastern edge of Livermore, over the Mocho I and Spring sub-basins. The reliance on groundwater, especially during drought conditions, and the increasing urbanization that is taking place, were factors in choosing this area as among the first where the vulnerability assessment has been carried out.

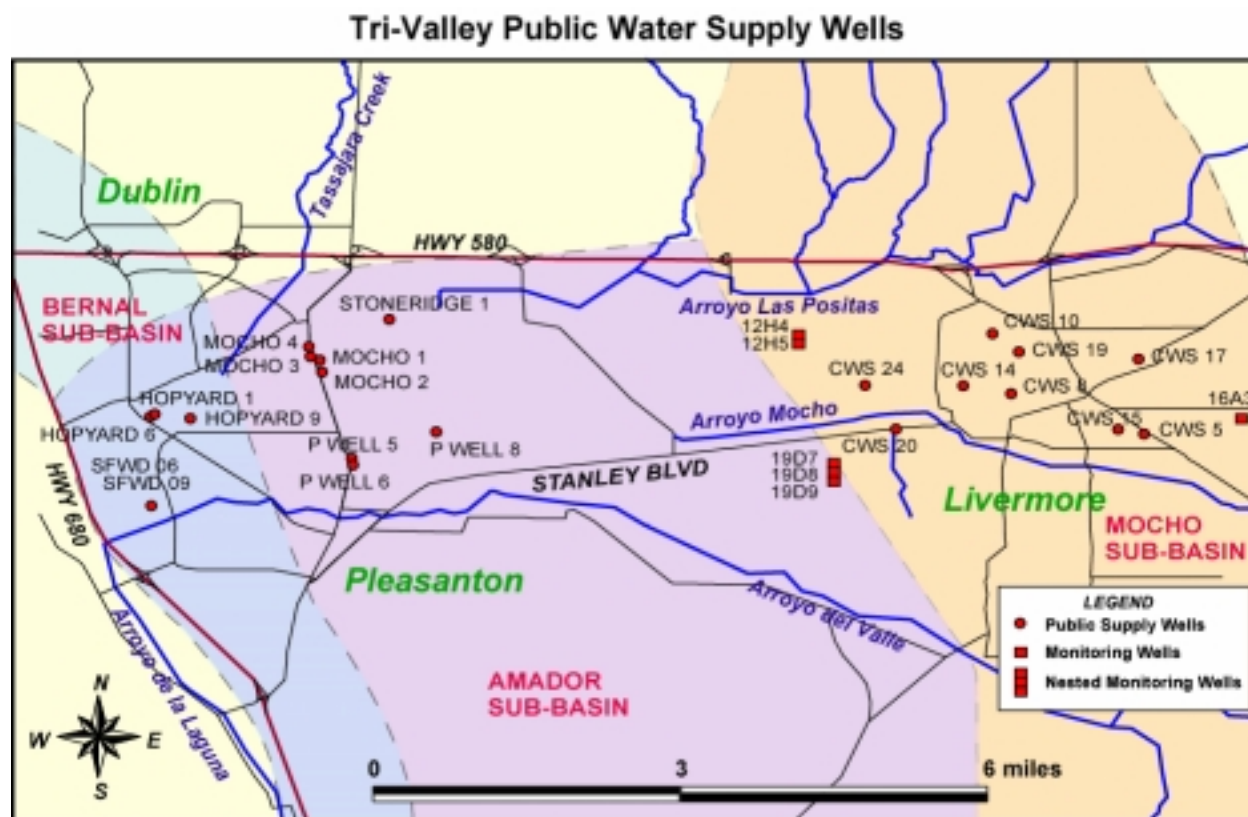


Figure 1. Study location map, showing well locations and sub-basin outlines.

Two major sources of groundwater are tapped in the Livermore-Amador basin (Figure 2). The Livermore Formation is a Plio-Pleistocene bedded sandy gravel with thin aquitards of silty clay, which occurs beneath the floor of the Livermore valley at depths ranging from a few tens of feet to over 400 ft. Overlying the Livermore Formation are alluvial fill materials, composed of unconsolidated sand, gravel, and clay, of Holocene age. The public supply wells sampled for this study tap both of these formations, with higher yields observed in the alluvial deposits. The specific capacity of wells is significantly greater for wells in the Bernal and Amador sub-basins, compared to those in the Mocho sub-basin; the western portion of the basin having the greater thickness of alluvial fill. On average, about 70% of the total volume of groundwater extracted from the basin comes the western sub-basins. Groundwater flow is toward the longitudinal axis of the valley, then westerly toward the Western Amador sub-basin. The major municipal well fields in the Western Amador and Bernal sub-basins, as well as the dewatering pits for gravel mining activity in the southern Amador sub-basin, are the major sinks for groundwater in the basin.

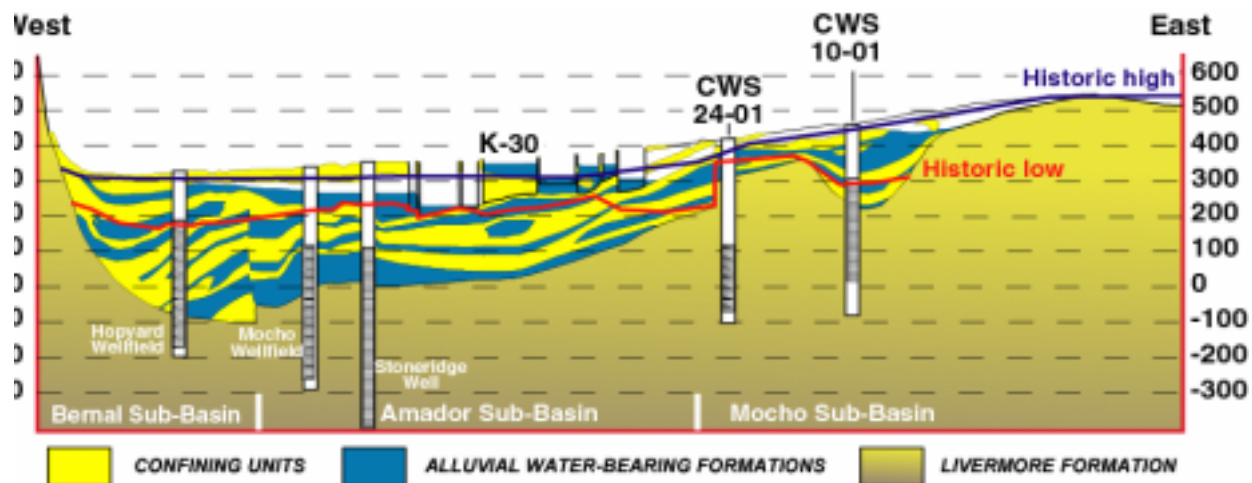


Figure 2. Cross-section of Livermore-Amador Groundwater Basin showing main water-bearing units, aquitards, and examples of public supply wells (courtesy of Zone 7 Water Agency).

The sub-basins are defined and separated by major faults, some of which are barriers to horizontal groundwater flow. Vertical transport between the two water bearing formations is limited to areas where the Livermore Formation is in contact with overlying stream channel deposits along Arroyo Valle and Arroyo Mocho. An upper aquiclude caps nearly the entire western portion of the Livermore Valley, and ranges in thickness up to 70 ft (Figure 2). Recharge to the Livermore Formation occurs primarily along the southern margin of the basin, where outcrops are present, by percolation of rainfall. Leakage from the overlying alluvial aquifers in the southeastern area of the basin is another source of recharge to the deeper aquifer. Significant recharge to both water-bearing units occurs through coarse-grained sediments in the Arroyo del Valle and Arroyo Mocho creek beds, with much of the water flow in the creeks coming from diversions of imported water from the South Bay Aqueduct. The other creeks crossing the basin are less important sources of recharge. Subsurface inflow along the major faults is a major source of subsurface recharge to the alluvial aquifers in the western part of the basin.

The basin is managed for conjunctive use by the Zone 7 Water Agency, a water wholesaler and flood control management agency. Zone 7 supplies treated surface water for blending and for supply, surface water for recharge along Arroyo Valle and Arroyo Mocho, and groundwater from its eight high capacity production wells. One well included in the study, Hopyard 6, was tested for aquifer storage and recovery (ASR) prior to sampling. A nearby well, Hopyard 1, is known to be under the influence of the ASR well.

2.1. Water Quality History

In general, the two main water-bearing units generally produce good quality sodium, magnesium, or calcium bicarbonate water, but poor quality sodium chloride water occurs in the northeastern part of the valley, where little recharge takes place. Increasing total dissolved solids (TDS) is a pressing water quality issue in the Livermore-Amador basin. Other water quality

problems include locally high nitrate concentrations (exceeding the MCL of 45 mg/L), and several VOC plumes, including an extensive TCE plume emanating from the LLNL site (Hoffman, 1992). There are one hundred and thirty-seven LUFT sites, including an MTBE plume in downtown Livermore that stretches some 1,500 ft (Happel et al., 1998). The present study does not address the TDS or nitrate issues directly, except in providing information related to the basin flow field, and to water balance. The question of occurrence and transport of anthropogenic contaminants is directly addressed in the discussion below.

2.2. Methods

LLNL personnel collected well water samples, with the assistance of well owners, during the summer and fall of 2001. Well locations and identification information are given in Tables 1a and 1b. 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 2) are measured using purge and trap gas chromatography-mass spectrometry, with a reporting limit of 5 parts per trillion. (2) The $^{16}\text{O}/^{18}\text{O}$ ratio is analyzed by stable isotope mass spectrometry. (3) The concentration of tritium is measured by the ^3He -ingrowth method (Clark et al., 1976; Surano et al., 1992; Beyerle et al., 2000). (4) The ratio of $^3\text{He}/^4\text{He}$ and the concentrations of all of the dissolved noble gases are measured by noble gas mass spectrometry. The tritium and noble gas analyses are used to calculate the groundwater age, and the temperature at which recharge took place is determined from the noble gas concentrations. A discussion of analysis methods is given in Appendix A and Hudson, 2002.

2.3. Results and Discussion

Analytical results for the twenty-two public supply wells and five monitoring wells from the Livermore-Amador Basin are shown in Tables 1a and 1b. Uncertainties shown in Appendix A are analytical errors only – uncertainty in the age estimate is discussed below. All results are fully quantitative, as described in Appendix A. Two compounds, MTBE, and toluene, were detected (one and six times, respectively) in transfer blanks taken during public supply well sampling. 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. Unlike the public supply wells, which have dedicated pumps, monitoring wells were sampled using a submersible pump and a gasoline-powered generator, and corresponding transfer blanks had positive detections of MTBE and all of the BTEX compounds. These are likely due to atmospheric transfer of exhaust from the generator to the blank water. These observed detections are a testament to the extreme sensitivity of the analytical method used for VOC determinations. 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 for four MTBE results and twenty-three toluene results.

Table 1a. Analytical data for VOCs from wells sampled in the Alameda Watershed.

Well owner	LLNL ID	State Well ID	Well name	Sample date	Concentrations in parts per trillion (ppt)											
					MTBE	CHCl ₃	Benzene	TCE	BDCM	Toluene	PCE	DBCM	Ethylbenzene	p,m-Xylene	o-Xylene	DBCP
(units)																
Livermore-Amador Groundwater Basin																
Zone 7 public supply wells	100791	3S/1E-18A01	HOPYARD 1	20010216	270	8,400	<5	<5	150	<5	<5	110	<5	<5	<5	<5
	100792	3S/1E-18A06	HOPYARD 6	20010216	250	10,000	<5	<5	3,300	<5	<5	1,200	<5	<5	<5	<5
	100799	3S/1E-17D12	HOPYARD 9	20010307	<5	510	<5	<5	23	<100	<5	5.0	9.4	41	17	<5
	100793	3S/1E-09M02	MOCHO 1	20010216	<5	380	<5	<5	19	<5	<5	6.0	<5	<5	<5	<5
	100794	3S/1E-09M03	MOCHO 2	20010216	<5	6.6	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
	100790	3S/1E-09M04	MOCHO 3	20010208	<5	7,800	<5	<5	420	<100	<5	160	<5	<5	<5	<5
	100800	3S/1E-08H18	MOCHO 4	20010314	<5	19,000	<5	<5	680	<100	<5	250	<5	<5	<5	<5
City of Pleas.	100795	3S/1E-09B01	STONERIDGE 1	20010216	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
	100797	3S/1E-16L05	CP W-5	20010223	<8	230	<5	<5	140	<5	<5	92	<5	<5	<5	<5
	100798	3S/1E-16L07	CP W-6	20010223	<5	89	<5	<5	22	<5	<5	11	<5	<5	<5	<5
California Water Service	100796	3S/1E-16A02	CP W-8	20010223	23	860	<5	<5	1,000	<5	<5	790	<5	<5	<5	<5
	100906	3S/2E-16B01	CWS 5-01	20010620	<5	300	<5	<5	59	200	6.8	55	<5	<5	<5	<5
	100908	3S/2E-08P01	CWS 8-01	20010620	9.6	160	<5	84	46	<5	550	28	<5	<5	<5	<5
	100868	3S/2E-08F01	CWS 10-1	20010503	23	75	<5	<5	11	<100	8,700	7.1	<5	<5	<5	<5
	100867	3S/2E-08N02	CWS 14-1	20010503	<8	67	<5	12	11	<100	650	5.1	<5	<5	<5	<5
	100869	3S/2E-16C01	CWS 15-1	20010503	<5	21	<5	<5	9.9	<100	<5	21	<5	<5	<5	<5
	100905	3S/2E-09L01	CWS 17-01	20010620	89	190	15	220	12	24	9.4	<5	7.6	26	15	<5
	100907	3S/2E-08G01	CWS 19-01	20010620	33	190	<5	<5	20	6.4	3,300	9.4	<5	<5	<5	<5
	100865	3S/2E-18B01	CWS 20-1	20010503	<5	39	<5	<5	9.0	<100	<5	6.6	<5	<5	<5	<5
SFWD	100866	3S/2E-07P03	CWS 24-1	20010503	<5	18	<5	<5	9.4	<100	<5	<5	<5	<5	<5	<5
	100977	3S/1E-19A03	SFWD-06	20010808	<5	10	<5	<5	<5	<15	<5	<5	<5	<5	<5	<5
Zone 7 monitor wells	100978	3S/1E-19A02	SFWD-09	20010808	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
	101191	3S/2E-19D07	19D7	20011018	<10	11	<10	<5	5.3	<110	5.9	19	<23	<110	<30	<5
	101192	3S/2E-19D09	19D8	20011018	<10	46	<10	<5	<5	<110	<5	<5	<23	<110	<30	<5
	101193	3S/2E-19D08	19D9	20011018	<10	210	<10	<5	23	<110	<5	<5	<23	<110	<30	<5
	101195	3S/1E-12H05	12H5	20011018	<10	55	<5	<5	<5	<100	95	<5	<10	<45	<20	<5
	101194	3S/1E-12H04	12H4	20011018	<10	16	<5	<5	<5	<100	5.3	<5	<10	<45	<20	<5
101196	3S/2E-16A03	16A3	20011018	27	447	<5	<5	10	<5	<5	<5	<5	<45	<5	<5	

Table 1a. Analytical data for VOCs from wells sampled in the Alameda Watershed. (Cont.)

Well owner	LLNL ID	State Well ID	Well name	Sample date	Concentrations in parts per trillion (ppt)												
					MTBE	CHCl ₃	Benzene	TCE	BDCM	Toluene	PCE	DBCM	Ethylbenzene	p,m-Xylene	o-Xylene	DBCP	
(units)																	
<i>Niles Cone Groundwater Basin</i>																	
ACWD	100892	4S/1W-28C01	MOWRY 1	20010607	<5	19	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
		4S/1W-28C14	MOWRY 2	19970429	<15 ^a	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	
	100893	4S/1W-28C15	MOWRY 3	20010607	13	19	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	
	100894	4S/1W-28C16	MOWRY 4	20010607	9.4	8.1	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
	100891	4S/1W-28C18	MOWRY 6	20010607	<5	100	<5	<5	13	<30	<5	10	<5	<5	<5	<5	
	100902	4S/1W-28C19	MOWRY 7	20010607	6.0	31	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
	100901	4S/1W-28C20	MOWRY 8	20010607	9.9	7.2	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
		4S/1W-28C21	MOWRY 9	19990608	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
		4S/1W-21P06	PT W-1	19970416	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	100895	4S/1W-21P07	PT W-2	20010607	<5	67	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
	100900	4S/1W-21P09	PT W-4	20010607	<5	110	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
	100896	4S/1W-21P10	PT W-5	20010607	5.2	15	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	
	100897	4S/1W-21P11	PT W-6	20010607	12	5.5	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5	
	100898	4S/1W-21P12	PT W-7	20010607	11	9.9	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	
100899	4S/1W-21P13	PT W-8	20010607	27	5.5	<5	<5	<5	<30	<5	<5	<5	<5	<5	<5		

Notes:

ACWD = Alameda County Water District

BDCM = Bromodichloromethane.

CHCl₃ = Chloroform.

DBCM = Dibromochloromethane.

DBCP = 1,2-Dibromo-3-chloropropane.

MTBE = Methyl-*tert*-butyl-ether.

nm = Not measured.

PCE = Tetrachloroethylene.

SFWD = San Francisco Water Department

TCE = Trichloroethylene.

^a Sample date: 19990608

Table 1b. Analytical data for stable isotopes and noble gases from wells sampled in the Alameda Watershed.

Well owner	LLNL ID	Statewell ID	Well name	Sample date	$\delta^{18}\text{O}_{\text{SMOW}}$	Tritium	Age (years)	Recharge temperature	Excess air concentration	% pre-modern	Radiogenic ^4He concentration	Radiogenic ^4He age	χ^2
(units)					(‰)	(pCi/L)	(years)	(°C)	(cc-STP/g)		(cc-STP/g)	(kyr)	
Livermore-Amador Groundwater Basin	100791	3S/1E-18A01	HOPYARD 1	20010216	-7.8	12.7	33	nc	0.036	87	2.69E-08	5.E+02	4.5
	100792	3S/1E-18A06	HOPYARD 6	20010216	-8.4	10.8	14	11.6	0.002	58	1.16E-08	2.E+02	1.2
	100799	3S/1E-17D12	HOPYARD 9	20010307	-6.8	1.6	>50	nc	0.013	100	1.63E-08	3.E+02	5.9
	100793	3S/1E-09M02	MOCHO 1	20010216	-7.2	22.4	33	14.7	0.009	77	6.94E-09	1.E+02	1.1
	100794	3S/1E-09M03	MOCHO 2	20010216	-6.5	23.1	29	nc	0.010	68	3.48E-09	7.E+01	3.8
	100790	3S/1E-09M04	MOCHO 3	20010208	-7.2	2.3	33	13.4	0.008	98	7.22E-09	1.E+02	0.1
	100800	3S/1E-08H18	MOCHO 4	20010314	-7.4	2.1	37	15.0	0.015	99	1.98E-08	4.E+02	3.2
Zone 7 public supply wells	100795	3S/1E-09B01	STONERIDGE 1	20010216	-7.3	6.9	31	15.8	0.011	92	3.71E-09	7.E+01	4.7
	100797	3S/1E-16L05	CP W-5	20010223	-6.0	26.2	15	nc	0.009	-2	1.25E-09	2.E+01	3.0
	100798	3S/1E-16L07	CP W-6	20010223	-6.8	23.5	22	nc	0.010	38	3.43E-10	7.E+00	0.5
City of Pleas.	100796	3S/1E-16A02	CP W-8	20010223	-6.5	18.8	23	nc	0.010	56	3.11E-09	6.E+01	4.9
	California Water Service	100906	3S/2E-16B01	CWS 5-01	20010620	-7.9	15.2	28	nc	0.010	76	7.89E-10	2.E+01
100908		3S/2E-08P01	CWS 8-01	20010620	-8.3	27.3	18	15.0	0.012	10	1.38E-08	3.E+02	1.6
100868		3S/2E-08F01	CWS 10-1	20010503	-7.8	35.9	21	16.8	0.013	2	7.54E-09	2.E+02	1.2
100867		3S/2E-08N02	CWS 14-1	20010503	-8.0	18.6	22	16.3	0.013	52	2.72E-08	5.E+02	4.1
100869		3S/2E-16C01	CWS 15-1	20010503	-7.8	13.3	20	13.9	0.009	60	3.82E-08	8.E+02	0.1
100905		3S/2E-09L01	CWS 17-01	20010620	-7.6	36.0	14	15.2	0.011	-42	1.24E-08	2.E+02	0.3
100907		3S/2E-08G01	CWS 19-01	20010620	-7.5	46.2	21	16.7	0.012	-28	7.4E-09	1.E+02	0.8
100865		3S/2E-18B01	CWS 20-1	20010503	-7.4	9.3	10	nc	0.010	60	1.24E-08	2.E+02	10.1
SFWD	100866	3S/2E-07P03	CWS 24-1	20010503	-6.8	1.5	>50	13.6	0.008	100	5.14E-08	1.E+03	2.0
	100977	3S/1E-19A03	SFWD-06	20010808	-6.1	26.4	16	13.7	0.019	3	2.7E-09	5.E+01	2.5
Zone 7 monitor wells	100978	3S/1E-19A02	SFWD-09	20010808	-6.2	30.7	14	13.7	0.022	-23	0	0.E+00	1.9
	101191	3S/2E-19D07	19D7	20011018	-6.9	0.6	>50	nc	0.007	100	0	0.E+00	30.1
	101192	3S/2E-19D09	19D8	20011018	-7.0	3.9	nc	nc	0.014	91	0	0.E+00	10.9
	101193	3S/2E-19D08	19D9	20011018	-6.8	17.0	17	16.3	0.009	40	1.3E-09	3.E+01	3.9
	101195	3S/1E-12H05	12H5	20011018	-8.4	19.6	9	16.0	0.012	17	0	0.E+00	1.4
	101194	3S/1E-12H04	12H4	20011018	-8.1	16.1	11	13.5	0.018	31	0	0.E+00	4.5
	101196	3S/2E-16A03	16A3	20011018	-7.7	48.7	12	18.5	0.017	-103	0	0.E+00	0.6

Table 1b. Analytical data for stable isotopes and noble gases from wells sampled in the Alameda Watershed. (Cont.)

Well owner	LLNL ID	Statewell ID	Well name	Sample date	$\delta^{18}\text{O}_{\text{SMOW}}$	Tritium	Age (years)	Recharge temperature	Excess air concentration	%pre-modern	Radiogenic ^4He concentration	Radiogenic ^4He age	chi^2
(units)					(‰)	(pCi/L)	(years)	(°C)	(cc-STP/g)		(cc-STP/g)	(kyr)	
ACWD	100892	4S/1W-28C01	MOWRY 1	20010607	-6.3	21.5	9	nc	0.007	8	2.81E-09	6.E+01	18.8
		4S/1W-28C14	MOWRY 2	19970429	-7.0	94	31	nc	nc	nc	nc	nc	nc
	100893	4S/1W-28C15	MOWRY 3	20010607	-6.1	29.5	22	14.4	0.004	24	0	0.E+00	0.4
	100894	4S/1W-28C16	MOWRY 4	20010607	-6.0	23.5	10	15.7	0.008	-1	3.38E-10	7.E+00	0.6
	100891	4S/1W-28C18	MOWRY 6	20010607	-6.8	36.9	26	14.2	0.009	33	5.31E-09	1.E+02	0.2
	100902	4S/1W-28C19	MOWRY 7	20010607	-6.1	18.7	9	14.1	0.006	19	2.7E-09	5.E+01	4.5
	100901	4S/1W-28C20	MOWRY 8	20010607	-6.0	20.3	8	14.2	0.005	13	0	0.E+00	1
		4S/1W-28C21	MOWRY 9	19990608	nm	nm	20	nc	nc	nc	nc	nc	nc
		4S/1W-21P06	PT W-1	19970416	-6.1	48	9	15.8	nc	nc	nc	nc	nc
	100895	4S/1W-21P07	PT W-2	20010607	-6.7	22.9	17	15.2	0.007	17	5.27E-09	1.E+02	0.9
	100900	4S/1W-21P09	PT W-4	20010607	-6.4	19.7	8	14.8	0.008	15	7.94E-11	2.E+00	1.8
	100896	4S/1W-21P10	PT W-5	20010607	-6.5	19.4	4	13.2	0.006	22	4.69E-10	9.E+00	1.4
	100897	4S/1W-21P11	PT W-6	20010607	-6.5	19.9	3	15.2	0.005	23	0	0.E+00	0.5
	100898	4S/1W-21P12	PT W-7	20010607	-6.6	17.6	3	14.3	0.005	30	0	0.E+00	1
100899	4S/1W-21P13	PT W-8	20010607	-6.8	19.9	5	12.9	0.005	18	1.29E-10	3.E+00	0.2	

Notes:

ACWD = Alameda County Water Department.

nc = Not calculated.

nm = Not measured.

SFWD = San Francisco Water Department.

Table 2. Basic properties, regulatory, and reporting limits for VOCs included in this study.

Compound type/ Chemical name (units)	Common name	Sources	Key properties	MCL (ppb)	PHG (ppb)
Gasoline oxygenate Methyl tert-Butyl Ether	MTBE	LUFTs, non- point source	highly soluble in water	5	13
Gasoline compounds		petroleum products, industrial solvents			
Benzene	B		less dense	1	0.14
Toluene	T		than water	150	0.15
Ethylbenzene	E			700	300
Xylene	X			1,750	1,800
Solvents					
Trichloroethylene	TCE	Industrial cleaning	more dense than water	5	0.8
Tetrachloroethylene	PCE	dry cleaning		5	0.056
Trihalomethanes	THMs			total	na
Trichloromethane	Chloroform	disinfection	present in environment for >100 years	THMs	
Bromodichloromethane	BDCM	by-products		100	
Chlorodibromomethane	CDBM				
Volatile pesticide	DBCP	agricultural application	now banned	0.2	.0017
Dibromo-3-chloropropane					

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

PHG = Public Health Goal (CalEPA suggested).

2.3.1. VOC Occurrence

The distribution of VOCs in the public water supply (PWS) and monitoring wells is shown in Figure 3 (a–c). The basic properties, reporting, and regulatory limits of these compounds are given in Table 2. This short list of compounds was chosen because they showed the highest frequency of occurrence of the approximately 100 organic compounds in the DHS drinking water well database.

The only compound that was monitored and had no detections above the reporting limit was DBCP (a volatile pesticide). Only two wells delivered water that was below the reporting limit for all the compounds monitored (SFWD-09 and Stoneridge). Nine more public supply wells and two of the five monitoring wells had positive detections of trihalomethanes (THMs) only, and were below the reporting limit for all the other compounds analyzed. THMs are by-products of the disinfection of drinking water. The source of low-level THMs can be advective transport of ‘recycled’ treated water, or residual from water treatment at or near the wellhead (see discussion below). Three wells (all PWS) had low level detections above the reporting limit of the solvent trichloroethylene (TCE), while six PWS wells and three monitoring wells had detections of tetrachloroethylene (PCE). Only one of the PCE concentrations (CWS 10-1)

exceeded the state and federal maximum contaminant level (MCL) of 5 g/L for drinking water (U.S. Environmental Protection Agency, 1996). The water purveyor was aware of this MCL exceedance from routine monitoring, and the water was being blended (with water below the reporting limit for PCE) to bring the delivered water into compliance with the DHS drinking water standard. The PCE occurrences in CWS 8-01, CWS 19-01 and CWS 14-01, and the TCE occurrence in CWS 8-01, had likewise been detected during routine monitoring for several years prior to this study. It should be emphasized that this study sampled raw water, and reported concentrations do not represent the concentrations entering the drinking water distribution system. Delivered water is treated, and may be blended with surface water or with water from other PWS wells.

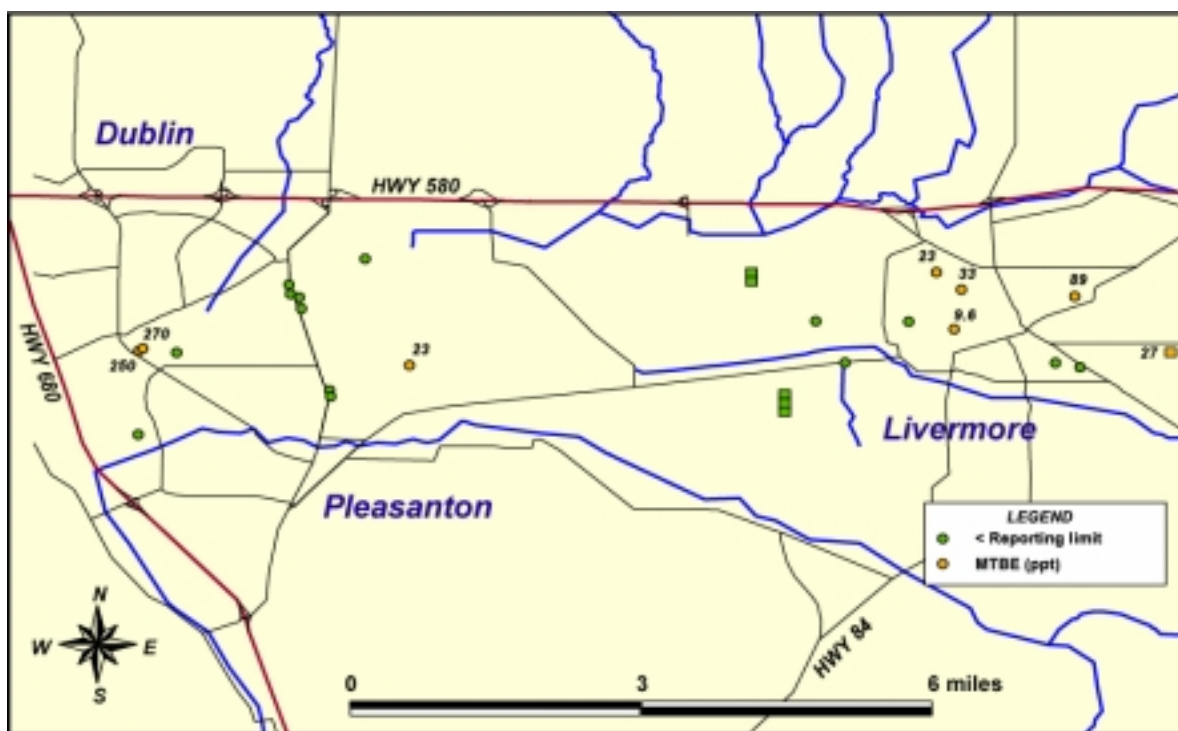


Figure 3a. Map of MTBE concentrations in wells in the Livermore-Amador Groundwater Basin. Sampling sites shaded in green indicate wells with MTBE concentrations below the reporting limit. Sampling sites denoted by squares indicate monitoring wells, while circles indicate public supply wells.

The CA state public health goal (PHG), which is the concentration at which the risk of developing cancer by drinking two liters of the affected water per day is 1 in 1 million, is especially low for PCE (Table 2), and is exceeded in four PWS wells (including those mentioned above) and in 1 monitoring well. For all of the other compounds tested, the concentrations are well below regulatory limits, and most often more than 1,000 times below MCLs. The concentrations found in these wells are not, for the most part, a public health concern. Their presence in groundwater is indicative of a component of post-industrial aged water. 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 demarcate the time since recharge.

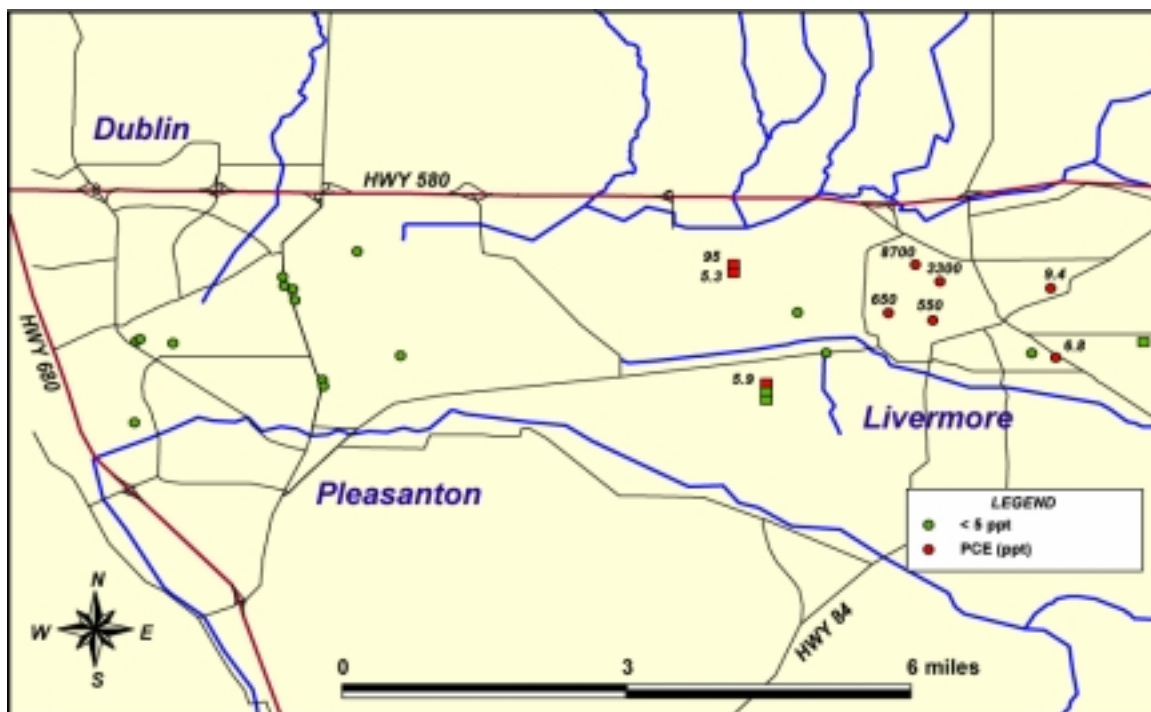


Figure 3b. Map of PCE concentrations in wells in the Livermore-Amador Groundwater Basin. Sampling sites shaded in green indicate wells with PCE concentrations below the reporting limit.

The potential sources for MTBE, BTEX, TCE, and PCE encompass activities that number in the hundreds in the study area. For example, there are thirty-two dry cleaners (nineteen in Pleasanton and thirteen in Livermore) among the two hundred and sixty-two Environmental Protection Agency (EPA) regulated facilities in the study area (one hundred and twenty-three in Pleasanton and one hundred and thirty-nine in Livermore). Furthermore, previously existing facilities, that are no longer in business, are perhaps more likely sources of e.g., PCE plumes, than existing facilities. VOCs may be released into the air, surface water, vadose zone, or directly into groundwater from these facilities. Subsequent transport to groundwater may take place by infiltration followed by advection, or by non-advective transport (e.g., a structurally compromised well casing). Furthermore, leaking sewer lines, carrying wastewater contaminated with these compounds, can result in unintentional releases into the vadose or saturated zone.

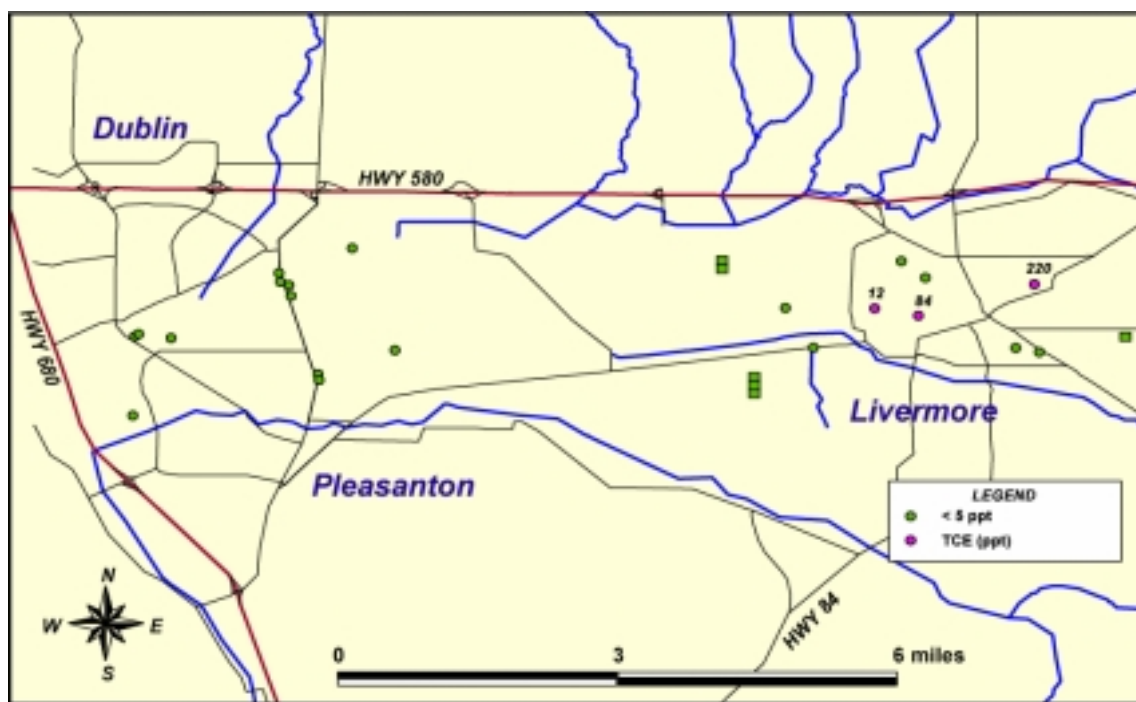


Figure 3c. Map of TCE concentrations in wells in the Livermore-Amador Groundwater Basin. Sampling sites shaded in green indicate wells with TCE concentrations below the reporting limit.

2.3.1.1. THMs

Water from the public supply wells in the Livermore-Amador Groundwater Basin is chlorinated or chloraminated at the well site (sometimes just downstream from sampling port). Some CWS wells are treated using down-hole chlorination devices. Also, during pump maintenance and well development, pump parts and well casing are treated in order to disinfect the well. For instance, Mocho 4 was newly drilled and pump tested at the time of sampling and Mocho 3 had been active only for several months, which likely explains the relatively high levels of disinfection byproducts found in these wells. These activities suggest that THMs can be present as residuals, rather than from advective transport of treated surface water to the well capture zone. Treated surface water at the del Valle treatment plant, which serves the area, has approximately equal, or sometimes more, BDCM compared to chloroform (and total THMs of approximately 100 ppb). In general, groundwater has a much lower proportion of brominated THMs than chlorinated surface water, corroborating the evidence that the THMs have a local origin. In contrast, Hopyard 6 well has THM ratios that reflect the surface water that has been injected there. The Pleasanton W-8 also has relatively more of the brominated forms, and may be an exception in having a recycled surface water source. However, the THM pattern may also be explained by groundwater that is locally higher in Br^- .

The most striking feature of Figure 3 (a-c) is that the detections of VOCs above the reporting limit (other than THMs) occur almost exclusively in the eastern portion of the basin, beneath the City of Livermore. Several factors may be considered to explain the spatial disparity in occurrences 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).

2.3.1.2. MTBE and BTEX

California surface waters and precipitation contain MTBE due to equilibrium solubility with MTBE in the atmosphere, at concentrations of 50 to 1,000 ppt (Ekwurzel et al., 2001). Since MTBE has been in heavy use beginning 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 Pleasanton W-8, CWS 10-1, CWS 8-01, and CWS 19-01. These wells therefore have a component of water that recharged in the last decade or so. Pleasanton W-8, the only well on the western side of the basin with recent water indicators, is a higher capacity well (4,000 gpm) than the other wells in the area, and may have a more shallow capture zone.

The data suggest that only two wells are affected by point source MTBE/gasoline leaks. Hopyard 9 has extremely low concentrations of E and X only – perhaps from a leak that pre-dates use of MTBE. In CWS 17-01, low level BTEX accompanies MTBE, and the MTBE concentration is higher than observed in other wells. This is likely a very early warning of a LUFT plume, however, the plume may continue to be diluted to levels below concern because of the radial capture zone and high degree of dilution characteristic of long-screened production wells (Einarson and Mackay, 2001). So, while there are more LUFTs, and a higher LUFT density, in areas closer to wells in Livermore than in Pleasanton, LUFT density and proximity explains only one MTBE detection.

Treated water from the South Bay Aqueduct was injected at Hopyard 6, and pumped out 3 months later. At the time of sampling, it is estimated that $\frac{3}{4}$ of the injected water had been recovered (David Lunn, Zone 7 Water Agency, personal communication). Previous water quality tests have shown that Hopyard 1, located just tens of feet away, is influenced by the injection well, and a fraction of the water pumped from it is injected water. The surface water used for injection, from the South Bay Aqueduct, had an MTBE concentration of approximately 1 $\mu\text{g/L}$ (David Lunn, Zone 7 Water Agency, personal communication), so the measured MTBE concentration of 250 ppt agrees well with the estimated recovery of injected water. Our own measurements of MTBE in State Project Water at a surface water treatment plant in the study area over the course of the study ranged from a low value of 60 ng/L in April, 2001 to a high of 240 ng/L in October 2001.

2.3.1.3. TCE and PCE

Detections of TCE and PCE are all on the eastern side of the basin, beneath Livermore. There are nineteen SLIC (Spills, Leaks, Investigations and Cleanup) sites (Region 2 RWQCB database) in Livermore and ten SLIC sites in Pleasanton. Several of these sites are the sources of TCE and PCE plumes. The TCE plume that has its source on the LLNL site is well characterized (Hoffman, 1992) and does not reach any of the wells sampled in this study. Many of the SLIC sites in Livermore are located near the town's center and up-gradient of the PWS

wells. In contrast, the majority of the SLIC sites in Pleasanton are located to the southwest of the town's center and down-gradient of the PWS wells. Two dry cleaner plumes are known from RWQCB investigations (which affect wells CWS 14-01 and CWS 8-01) but these known plumes do not account for all the PCE detections. PCE was detected in nine out of fifteen wells in Livermore. One possibility for its widespread occurrence is that at joints, or places where sewer lines turn or have low points, PCE may accumulate and subsequently leak into groundwater. Furthermore, 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.

2.3.2. Mean Groundwater Ages and Dissolved Noble Gas Results

Mean groundwater ages vary from 9 years to greater than 50 years for Livermore-Amador Basin wells. In general, younger mean ages are found on the eastern side of the basin (Figure 3d), and in wells with shallower top-of-screens. The lack of a clear spatial pattern in the mean groundwater ages determined for water samples from Livermore-Amador basin wells indicates that recharge is distributed over a large area (Figure 3d). This is in contrast to e.g., the

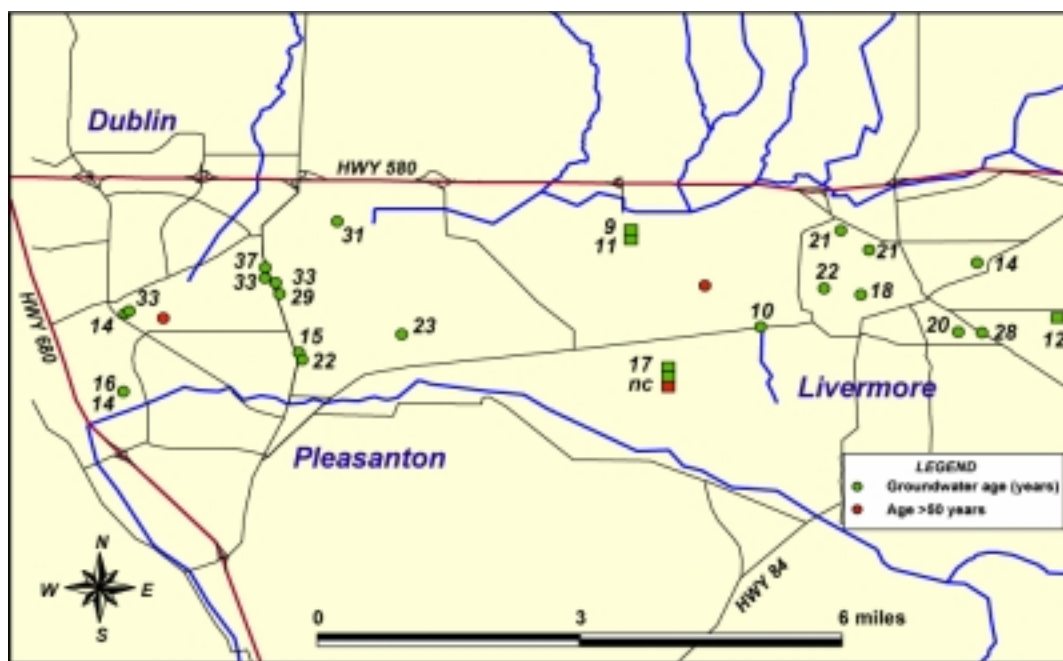


Figure 3d. Map of groundwater ages determined using the ^3H - ^3He method for wells in the Livermore-Amador Groundwater Basin. Numbers adjacent to well sites indicate mean groundwater age in years. Sampling sites shaded in red indicate groundwater devoid of tritium, and hence greater than 50 years old. NC denotes where the age was not calculated.

intensively managed groundwater basins of the Los Angeles Basin, where recharge is intensely focused at engineered facilities (Shelton et al., 2001). In the Livermore-Amador basin, significant recharge takes place along Arroyo del Valle and Arroyo Mocho, but also in higher elevation areas that surround the basin. $\delta^{18}\text{O}$ patterns corroborate the notion of distributed recharge for this basin. The mean $\delta^{18}\text{O}$ for Livermore wells is -7.7‰ , while for Pleasanton wells (excluding Hopyard 1 and Hopyard 6 which are affected by State Project water with a $\delta^{18}\text{O}$ of -9

to -10‰) $\delta^{18}\text{O}$ averages -6.9‰. This difference reflects the gradient in $\delta^{18}\text{O}$ for precipitation as clouds move further inland, and indicates that these wells derive water from local recharge.

There is a gradient in groundwater age from young to old on the western side of the basin, away from Arroyo del Valle, northward. An area of significantly older water exists in the north-central part of Bernal sub-basin (Hopyard and Mocho wellfields). This older water is free of VOC detections (except THMs as noted above). A large fraction of the total groundwater extracted from the basin comes from these wells. It seems likely that the confining layer that exists in the western portion of the basin effectively isolates these wells from vertical transport (Figure 2). The two Hopyard wells are a complex mixture of injected surface water and ambient groundwater, and the tritium-helium ages are not meaningful for the goals of the present study.

The youngest age in a production well is observed in CWS 20-1, which is close to Arroyo Mocho Creek where recharge in coarse-grained creek bed sediments takes place. In general, wells situated near the creeks that drain the valley record younger ages. These wells may be considered vulnerable even though no VOCs (other than THMs) were detected. Sources for VOCs are likely not present in the subsurface between the recharge areas and the well capture zones. Likewise, vertical transport from the surface to CWS 17-01 is evidenced by its younger age, but in this case, local VOC sources result in the presence of 8 VOCs, excluding THMs. In contrast, well CWS 24-01, located on the western edge of the Mocho sub-basin has no detectable tritium (age >50 years), and a high radiogenic ^4He concentration (indicating the presence of a component thousands of years old), but also by far the deepest top-of-screen (Figure 2). The total depth for wells in Pleasanton is on average 50-ft greater than for Livermore wells, and depth to the top of first screened interval is on average 10-ft deeper for Pleasanton wells. However, the younger average age for groundwater sampled from the eastern side of the basin is more likely due to the presence of unconfined aquifers on the eastern side, which allow more rapid vertical transport of water and contaminants.

Additional information about the distribution that results from the mixture of ages present in water drawn from a well comes from the plot of initial tritium versus mean age (Figures 4a and 4b). The tritium that was present at the time of recharge is well known from measurements of tritium in precipitation at several sites in North America. Water that recharged before about 1955 now contains extremely low levels of tritium. 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 'older' water. Samples that fall below the 'initial tritium' curve contain a fraction of water that recharged before 1955 ('pre-modern'). An estimate of the fraction of pre-modern water that is drawn from a well can be derived from the difference between the measured tritium and the 'initial' tritium. The fact that many of the Livermore-Amador samples fall well below the initial tritium curve indicates that a significant component of older water reaches these wells, and that the mean ^3H - ^3He age that is reported really represents a broad age distribution. In particular, Hopyard, Mocho, and the Stoneridge wells draw high percentages of pre-modern water. In contrast, the two eastern-most wells (CWS-17 and monitoring well 16A3), where relatively young ages are recorded, also have very low fractions of pre-modern water, corroborating the notion there is a zone of significant vertical transport in the eastern portion of the basin. (As shown in Figure 4b, well 16A3, the well closest to the LLNL site, has a tritium level somewhat greater than the predicted level based on precipitation measurements. This slightly elevated concentration is likely due to tritium releases from LLNL.)

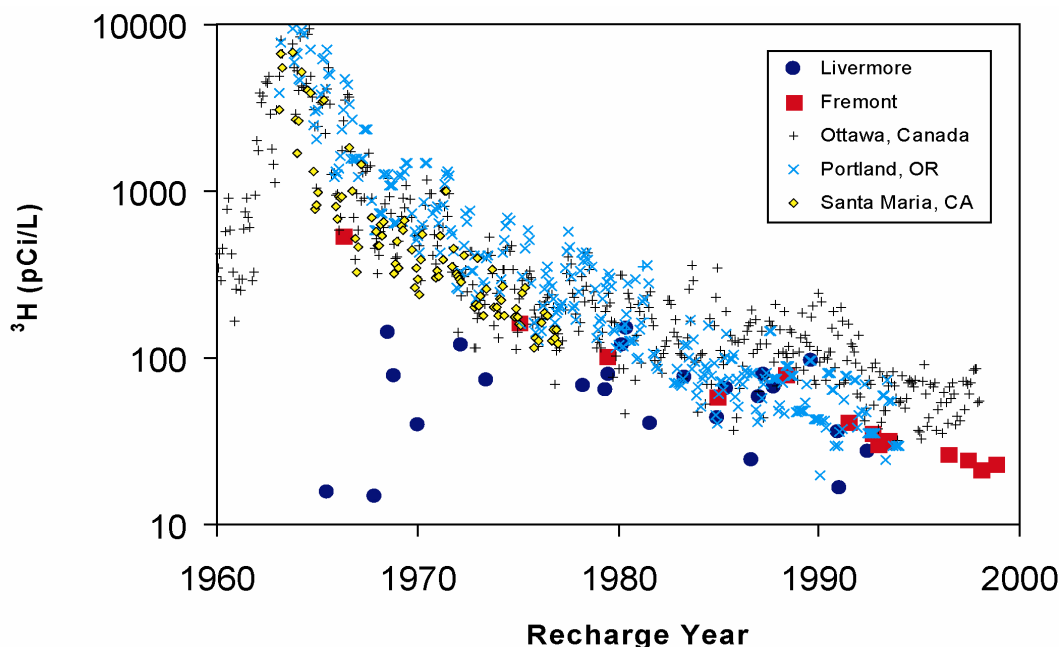


Figure 4a. Small symbols show tritium measured in precipitation over the last several decades at the location indicated. Larger symbols are for wells from this study and show recharge year (groundwater age) vs. decay-corrected ^3H concentration at the time of recharge. Samples that fall below the curve indicate wells where a component of 'pre-modern' groundwater is present.

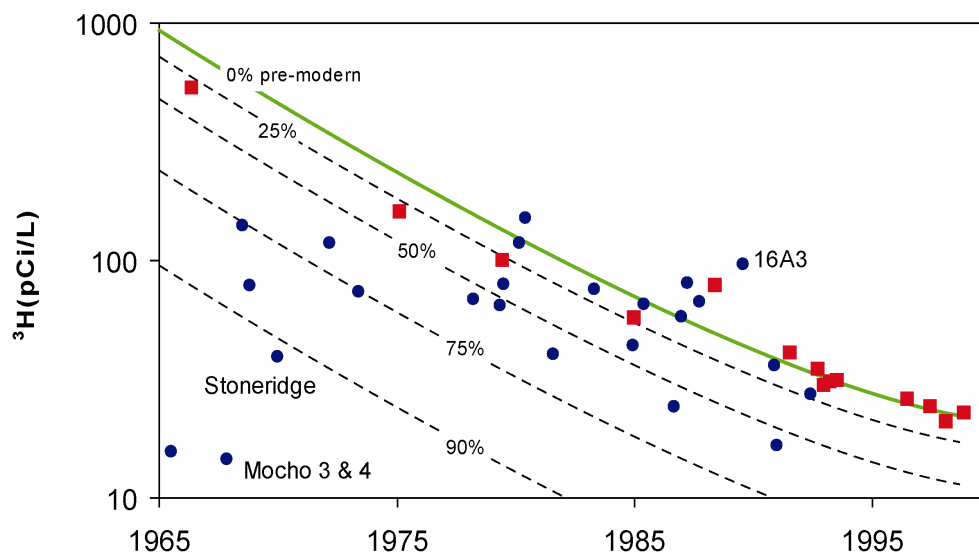


Figure 4b. Expanded view of Figure 4a, including lines of equal percentages of pre-modern water. Sample 16A3 is closest to the Lawrence Livermore Laboratory site and likely has a component of tritium from that local source. Wells falling along lines of high fractions of pre-modern water are those in the Mocho sub-basin, on the western side of the valley.

The concentration of ^4He , a stable isotope of helium, in groundwater, gives additional information on subsurface residence time, at time scales greater than a few hundred years. ^4He accumulates in groundwater due to the decay of uranium and thorium in the earth's crust. Precise age dating using ^4He is not possible because the accumulation rate depends on myriad factors, but samples older than a few hundred years usually have detectable 'excess' ^4He (e.g., Solomon et al., 1996; Castro et al., 2000). ^4He from U and Th decay was found in nearly all the production wells (and especially in the Mocho, Stoneridge, Hopyard, and CWS wells; see Table 2b) at concentrations that indicate the presence of a component of the groundwater that is thousands to hundreds of thousands of years old. These data serve to corroborate the notion that these long-screened wells draw in water with a broad age distribution, which has a long tail toward very old age.

2.4. Summary and Conclusions: Livermore-Amador Groundwater Basin

In summary, the spatial pattern in vulnerability indicators (groundwater age and low level contaminants) differs greatly for the western versus the eastern portions of the Livermore-Amador Basin. PCE is nearly ubiquitous in Livermore wells, and may have a distributed source such as leaky sewers in addition to known point sources. Non-point source MTBE occurs frequently in these same wells. THMs are not useful as tracers of advective transport of 'recycled' treated water in this basin, but MTBE is a good indicator of very recently recharged water. Distributed recharge is inferred from the spatial distribution of ages. Somewhat younger ages, and significantly more widespread VOC occurrence indicates that vertical pathways are present in the eastern side of the basin. A striking lack of VOC detections on the western side, and several very old groundwater ages indicate that the confining layer is thoroughly effective in preventing vertical flow in this highly productive part of the basin. In contrast, the area of the Mocho sub-basin (eastern side), which is in active use, has a relatively high degree of vulnerability to contamination from surface sources.

3. Niles Cone Groundwater Basin

The streams that drain the Livermore-Amador Basin flow into Alameda Creek, through Niles Canyon and discharge to San Francisco Bay. The Niles Cone Groundwater Basin, a coarse-grained, water-bearing alluvial deposit, sits at the western end of Niles Canyon. The Alameda County Water District (ACWD) actively manages the basin for conjunctive use. A key part of basin management is artificial recharge, the volume of which is 40,000 acre-ft of water per year. Recharge facilities consist of several abandoned quarries ranging in volume from 30 to 4,500 acre-ft, and of temporary reservoirs impounded behind inflatable rubber dams, in the Alameda Creek channel, adjacent to recharge ponds (Figure 5).

The groundwater basin comprises alluvial deposits of the Quaternary period. Between periods of alluvial deposition, sea levels in San Francisco Bay rose and fine-grained sediment settled out to form aquicludes, separating the sands and gravels into distinct aquifer layers. The Hayward Fault, part of the San Andreas system, runs in a general north-south direction in the area, and hydraulically divides the groundwater basin into two sub-basins: the "Above Hayward Fault" (AHF) and "Below Hayward Fault" (BHF) sub-basins on the east and west side of the Hayward Fault, respectively (Figure 6).

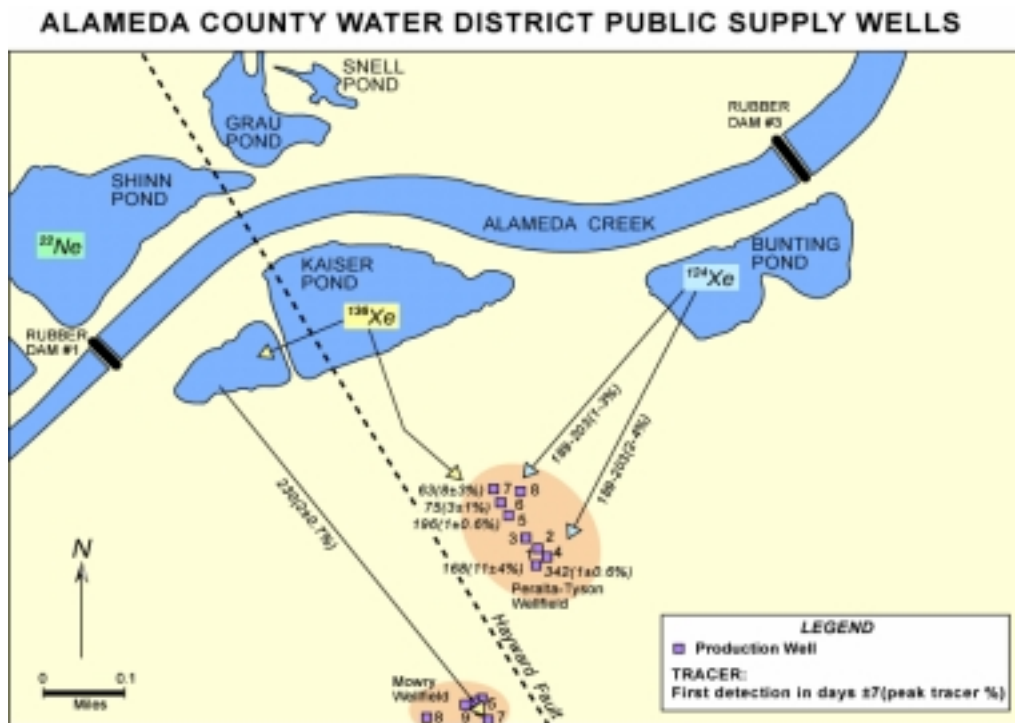


Figure 5. ACWD map showing major recharge facilities and wellfields; also shown are results from an artificial tracer study carried out in 1998 (Moran and Halliwell, in revision).

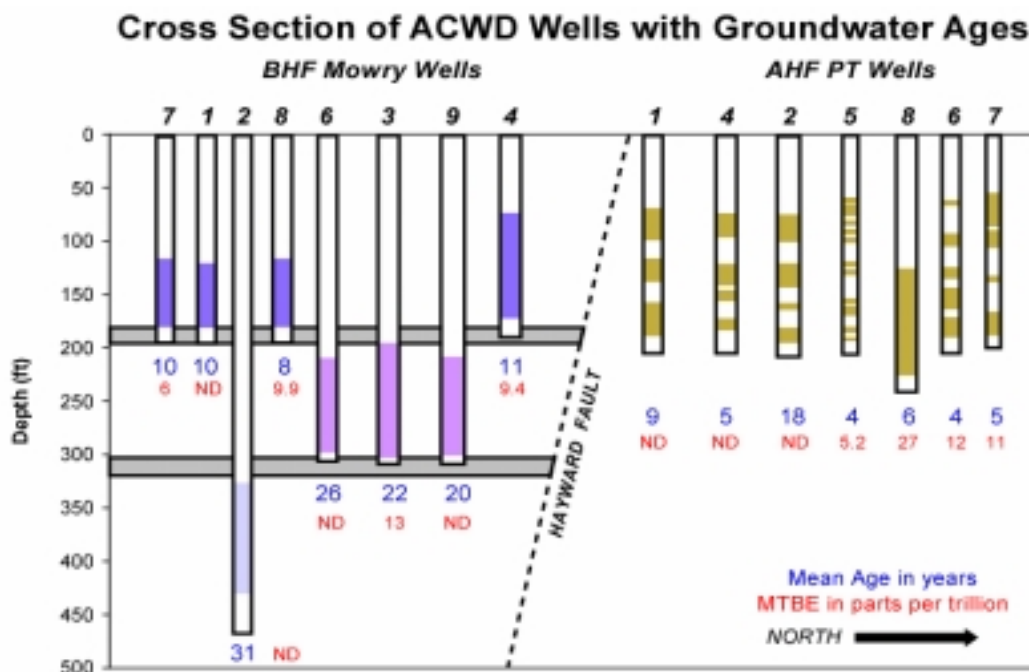


Figure 6. Schematic cross section showing screened intervals in ACWD public supply wells on both sides of the Hayward Fault. Mean $^3\text{H}-^3\text{He}$ ages are shown in blue, MTBE concentrations are shown in red.

With the Hayward Fault to the west, and hills to the north, south, and east, the AHF sub-basin is effectively contained by no-flow boundaries. The aquifer is unconfined throughout the study area, and no major changes in lithology have been observed during drilling of wells. The BHF sub-basin comprises three major regional aquifers, which are separated from each other by clay aquicludes (Figure 6). The aquifers include the shallow Newark Aquifer, the Centerville-Fremont Aquifer and the Deep Aquifer. Throughout the basin, the Centerville-Fremont and Deep Aquifers are confined. The Newark Aquifer is unconfined near the recharge area and the production wellfield but is confined in other areas. All three major aquifers in the BHF sub-basin are hydraulically bounded to the east by the Hayward Fault.

The water district operates seventeen high volume production wells that are situated between 1,200 and 2,500-ft from the recharge ponds (Figure 5). Twelve were sampled for the vulnerability assessment study, and data for three more, tested for similar analytes for the tracer study, are also included. In an average year, production wells in the AHF sub-basin yield 14,000 acre-ft of water, and provide the main sink for water in the sub-basin. BHF wells produce on average 6,000 acre-ft of water, with flow toward distal parts of the basin and up into creeks providing other sinks for water in the sub-basin. Approximately 40% of all of the water delivered to the residents of Fremont, Newark, and Union City (population 330,000) is groundwater.

3.1. Water Quality History

As is the case for the Livermore-Amador Basin, the most pressing and intractable water quality issue for the Niles Cone Basin is relatively high, and slowly but steadily increasing TDS. Groundwater is blended with surface water to reduce the TDS that is delivered to consumers. The two wellfields that comprise the district's groundwater production capacity are adjacent to railroad tracks and industrial facilities. In the relatively small area between the artificial recharge ponds and production wells, there are seven EPA regulated facilities that discharge hazardous waste or have air emissions, four leaking underground fuel tank sites, and two SLIC sites (United States Gypsum and a Union Pacific train derailment which resulted in a spill into the creek in 1995). Water quality issues that are related to artificial recharge are the potential for contamination from spills into the creek that supplies the recharge ponds, changes to water quality during recharge and subsurface flow, and future compliance with proposed regulations related to the use of recycled wastewater. A study in which the recharge ponds were tagged with an artificial tracer, and several water quality parameters were monitored as tracer moved through the basin, addressed these water quality and transport issues (Moran and Halliwell, in review).

3.2. Results and Discussion

Analytical results for ACWD public supply wells are shown in Tables 1a and 1b. Low-level toluene was detected in some of the VOC QC transfer blanks, and well data were screened accordingly, at <30 ppt. Ancillary data, including additional groundwater ages, water quality data for the recharge ponds, and low-level MTBE analyses for monitoring wells can be found in Moran and Halliwell, (in review).

3.2.1. VOC Occurrence

Chloroform was detected at very low concentrations in all of the wells sampled, and the other two THMs in the analyte suite were detected at even lower concentrations in just one well. The likely source of THMs is a small amount of back-flushing of treated water. Water treatment takes place at the wellfield.

Extremely low MTBE concentrations were found in eight out of thirteen wells. MTBE was measured in ACWD's recharge ponds using the same low-level analytical technique and was found to be 100 to 250 ppt (Moran and Halliwell, in review). Rainwater samples from Fremont had concentrations of approximately 100 ppt (Ekwurzel et al., 2001). The MTBE detected in wells is therefore likely to have been transported from recharge ponds. However, monitoring wells just adjacent to ponds had only 20-90 ppt MTBE and production wells have, on average, even lower concentrations, with a maximum concentration of only 27 ppt. Given the young groundwater ages in the AHF wellfield, which do not have broad age distributions (see discussion below), and therefore little dilution with water that pre-dates the use of MTBE, degradation of MTBE must be taking place during transport to the wellfield. Interestingly, while MTBE was detected in all of the wells in the northern part of the AHF wellfield, it was not detected in the two wells from the southern group. The southern group of wells had later arrivals and greater dilution of tracer compared to the northern group (Moran and Halliwell, in review).

No solvents, BTEX compounds, or DBCP were detected in the wells tested. This is likely because no sources are present in the subsurface between the ponds and wellfield, but also indicates that these compounds are not transported from (and likely not present in) the recharge pond or creek water.

3.2.2. Groundwater Ages

The age range observed for Niles Cone production wells nearly spans the applicable range of ^3H - ^3He method. Ten of fifteen wells, all screened in the Newark Aquifer of the BHF sub-basin, or in the AHF sub-basin, have mean ages of ten years or less (Figure 6). Thus, a large volume of the water pumped from the Niles Cone is <10 years old (e.g., in CY 1999 this young water was 70% of total production). Rapid turnover of the entire volume of the AHF sub-basin is indicated by the observed ages. Indeed, Hudson and Moran (in review) found that a small fraction of the water produced at the PT wells travels from the recharge ponds in only 60 days. Tracer results gave a maximum travel rate of 7,000 ft/year, while the mean age of 5 years gives a bulk travel rate of about 250 ft/year. The greater age of 18 years found in well PT-2 is anomalous for the sub-basin. The well log for PT-2 shows a localized confining clay layer just above the top screen (Mikel Halliwell, personal communication), which may create a deeper capture zone for that well.

In the three aquifers of the BHF sub-basin, groundwater ages increase with depth, with the Newark Aquifer producing water with a mean age of 8.7 years, the Centerville-Fremont aquifer producing water with a mean age of 23 years, and the Deep aquifer with one well, and a mean groundwater age of 31 years (Figure 6). The tritium concentration measured in the Deep aquifer, 94 pCi/L, is high for ambient groundwater and indicates relatively little dilution with younger or older water. Most of the ages measured in Niles Cone wells fall close to the predicted initial tritium curve, which indicates that the distribution in ages captured by the wells is rather narrow

(Figure 4a). Addition of older water, which has little or no tritium, would shift those points down, below the initial tritium curve. Accordingly, these wells draw relatively small fractions of pre-modern water, although it is interesting to note that even the wells with mean age results of 3 to 5 years draw component of pre-modern water. Only two wells have high radiogenic ^4He concentrations – Mowry 6, the oldest of the Centerville-Fremont-screened wells, and PT-2, already identified as an outlier, perhaps with a deeper capture zone.

3.3. Summary and Conclusions: Niles Cone Groundwater Basin

While the Niles Cone PWS wells produce a large volume of very young water, the lack of contaminant sources in the small area between the recharge ponds and wellfields results in no detections of solvents or BTEX compounds. The likely source for the very low-level detections of MTBE is the atmospheric-derived component from the recharging pond water. In fact, the MTBE concentrations measured in production wells suggest that subsurface degradation of MTBE is taking place during transport from the recharge ponds to the wells. The observed low-level THMs are likely residual from on-site disinfection. The very young water ages measured for AHF wells indicate rapid, unimpeded, vertical and lateral transport, and a high degree of vulnerability. The BHF wells in the Newark Aquifer likewise yield young water and have higher vulnerability than the Centerville-Fremont and Deep Aquifer wells. The narrow age range observed in each of the three aquifers in the BHF sub-basin, and the good agreement with the predicted initial tritium value, indicate little mixing of water of different ages in the layered BHF aquifer system.

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Appendix A
Sampling and Analysis Plan—Lawrence
Livermore National Laboratory

Appendix A

Sampling and Analysis Plan Lawrence Livermore National Laboratory

A-1. Environmental Sample and Quality Assurance Sample Collection

A-1.1. 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-milliliters (mL) volatile organic analysis (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.

A-1.2. 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.

A-1.3. 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.

A-1.4. 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 pounds per square inch). 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.

A-2. 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 (ppt) 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 and by operating the mass spectrometer in selected ion monitoring mode. A heated purge is primarily needed for methyl *tert*-butyl ether (MTBE) which has a relatively high aqueous solubility, and the mass spectrometer in selected ion monitoring mode 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 Vocab™ 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 × 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 min. 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 min. 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 40-mL 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.

A-3. Analytical Method—Stable Isotopes

Oxygen isotope analyses are conducted using the CO₂ equilibration method for ¹⁸O/¹⁶O (Epstein and Mayeda, 1953) and analyzed with an automated water equilibration unit. Isotope ratio measurements are performed on a VG PRISM isotope ratio mass spectrometer housed in the Analytical and Nuclear Chemistry Division at Lawrence Livermore National Laboratory. Oxygen isotope ratios are reported in the standard delta (δ) notation as parts per thousand (per mil or ‰) variations relative to a reference material of known composition and defined by the following equation:

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

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

Analyses in the Stable Isotope Laboratory are calibrated to internal standards referenced against National Institute of Standards & Technology (NIST) standard reference materials. Internal standards consist of 1) Pacific Ocean water sample δ¹⁸O = +0.35‰, 2) two isotopically distinct California meteoric water samples δ¹⁸O = -9.78 and -14.62‰, and 3) Alaskan Tap Water (-21.02‰). The composition and isotopic values of these internal standards span the range of natural waters typically observed in potable groundwater of California. For each 24 δ¹⁸O analyses, 2 each of 3 internal standards are also analyzed and used for calibration.

The internal standards are periodically compared to the three NIST reference standards: SMOW, Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP). The analytical precision for these δ¹⁸O measurements, from one run to the next, is ± 0.10‰, which is defined in terms of the difference of the internal standard from the precisely known NIST standards. One duplicate is analyzed for every eighteen samples. These duplicates are not "blind" however, but are typically samples from the previous run. If this duplicate varies by more than ± 0.10‰, the sample is run for a third time. If this duplicate is not within the 0.10‰ precision, the entire set of eighteen samples is re-analyzed.

A-4. Analytical Method—Tritium and Dissolved Noble Gases

The following analyses are reported for each groundwater well:

- Tritium (³H in picoCuries per liter; pCi/L)
- ⁴Helium, Neon, Argon, Krypton, Xenon abundances (cm³STP/g)
- Tritium-helium age (in years)
- Radiogenic ⁴Helium (cm³STP/g)
- Excess air (in cubic centimeters at STP per liter)
- Recharge temperature (in °C)
- "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 CO₂. The dissolved gases are released into the previously evacuated headspace in this process.

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

The mass spectrometer uses a conventional 17-stage electron multiplier and a SR400 pulse counting system for measuring ³He. Helium-4 is measured using a faraday cup with a 10¹¹-Ohm feedback resistor. The procedure is calibrated using water samples equilibrated with the atmosphere at a known temperature (21°C). These calibration samples are processed along with regular samples with a frequency of 10%. Duplicate samples are analyzed with a frequency of 10%. The ⁴He and Ne abundances are measured with an accuracy of 2% and the ratio of ³He/⁴He is measured with an accuracy of 1%.

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

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

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

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

A-5. References

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