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California GAMA Special Study:
Examination of Water Quality in “Tritium-Dead” Drinking Water Wells

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March, 2013

**Final Report for the California
State Water Resources Control Board**

GAMA Special Studies Task 11.3: *Examination of Water Quality
in “Tritium-Dead” Drinking Water Wells*

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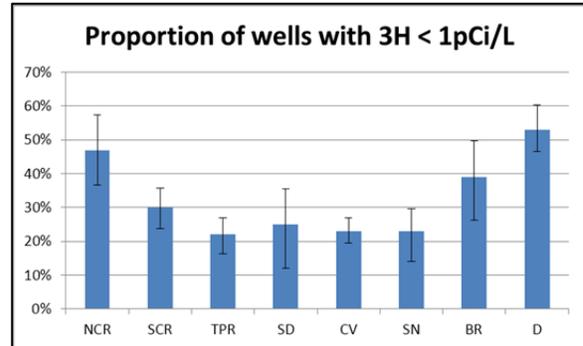
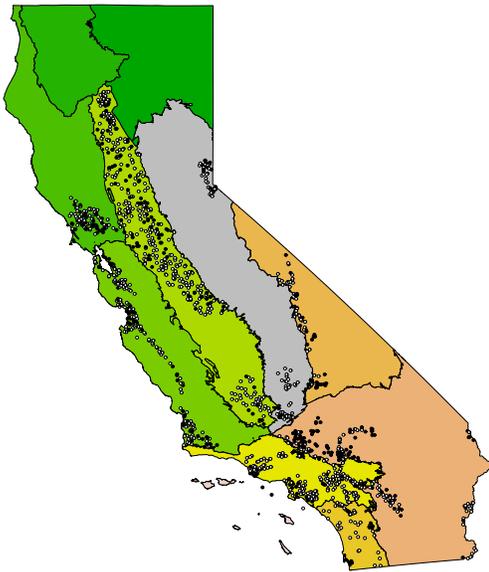
GAMA: AMBIENT GROUNDWATER MONITORING & ASSESSMENT PROGRAM SPECIAL STUDY



California GAMA Special Study: Examination of Water Quality in “Tritium-Dead” Drinking Water Wells

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California GAMA Special Study: Examination of Water Quality in “Tritium-Dead” Drinking Water Wells

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EXECUTIVE SUMMARY

The Groundwater Ambient Monitoring and Assessment (GAMA) Program is a comprehensive groundwater quality monitoring program managed by the California State Water Resources Control Board (SWRCB). Under the GAMA program, Lawrence Livermore National Laboratory carries out special studies that address groundwater quality issues of statewide relevance. The GAMA Special Studies Project provides analysis and interpretation of constituents of concern, as described in the AB 599 Report, which will allow assessment of current groundwater conditions. In addition, the GAMA Special Studies Project includes analyses that will enhance the monitoring and assessment effort by focusing on specific constituents of concern and water quality parameters, such as waste water indicators, emerging contaminants and nitrate. LLNL designs and carries out these Special Studies in coordination with the Water Board.

In order to assess and manage contamination of groundwater supplies caused by human activity, it is critically important to have a quantitative estimate of natural, background conditions based on measured water quality parameters. The goal of this GAMA Special Study is to examine water quality in California drinking water wells classified as producing “pre-modern” (or “pre-industrial”) water, in order to estimate background conditions. We use the tritium concentration to categorize samples as pre-modern or modern, defining samples with < 1 pCi/L (< 0.3 TU) tritium (“tritium-dead” herein) as “pre-modern”. The presence of tritium in a groundwater sample is a good indicator of water that entered the saturated zone in the last 55 years, roughly coinciding with the time period during which human activity has had a significant effect on water quality in California.

Groundwater samples collected under the GAMA Priority Basin Project (PBP) provide a large, spatially distributed, consistently sampled and analyzed set of water quality and tritium data upon which we base our analysis of pre-modern water quality. Results are compared within and among geographic provinces, highlighting differences in the portion of wells producing pre-modern water, as well as differences related to climate and aquifer characteristics. For example, major anion and cation patterns show the influence of marine solute sources in Transverse and Peninsular Range, South Coast Range, and San Diego provinces, of volcanic host rocks in the North Coast Range province, and of an arid climate in Desert and Basin and Range provinces. In 124 wells of the 469 tritium-dead wells studied (26%) concentrations of regulated constituents are found above the Maximum Contaminant Level (MCL), Notification Level (NL) or Secondary MCL (SMCL). Shared geologic, climatic, and geochemical conditions lead to elevated concentrations of multiple constituents in individual samples. For example, iron and manganese frequently co-occur above the SMCL under anoxic conditions, and concentrations of the regulated constituents arsenic, fluoride, boron and vanadium above the MCL co-occur in more than half of the wells where at least one is found above its MCL.

Arsenic (As) is a common naturally occurring regulated constituent that is detected above the MCL of 10 µg/L in >20% of the tritium dead wells in 5 of the 8 provinces studied. The North Coast Ranges, Desert, and Basin and Range provinces are most affected.

Nitrate and perchlorate are important constituents that have both natural and anthropogenic sources, so determination of the natural component is critical for guiding management and remediation efforts. The 95th percentile concentrations of nitrate in oxic or suboxic, tritium-dead samples vary among provinces and some are greater than the nominal natural concentration of 13 mg/L (as nitrate); however, all samples (but one) have concentrations less than the MCL of 45 mg/L. Provinces where land use is dominated by irrigated agriculture and presently are affected by widespread nitrate contamination, such as the Central Valley and South Coast Range provinces, exhibit very low nitrate levels in pre-modern groundwater. Perchlorate most frequently occurs below the detection limit, and is not found above the MCL of 6 µg/L.

In evaluating natural background for redox-sensitive elements such as nitrate, arsenic and perchlorate, groundwater redox state must be considered. A complication associated with establishing natural background concentrations is that some constituents may be affected by water-rock interaction or biogeochemical reactions during subsurface transport. Observed concentrations of these constituents under certain conditions may not be indicative of the presence or absence of anthropogenic impact. As an example, nitrate is denitrified in reducing water, and nitrate concentration in low-oxygen groundwater may not accurately reflect pre-modern "background" concentration. In this study, we examine the redox conditions of the well water samples as a way of assessing the possibility that significant changes have occurred in redox-sensitive constituents, especially nitrate.

Pesticides and volatile organic compounds (VOCs) do not occur naturally (except in rare instances for certain VOCs), and their occurrence is not expected in tritium dead groundwater. However, either pesticides or VOCs are detected in 41 of the 469 tritium-dead wells of the PBP data available for this study. Excluding wells with occurrences of trihalomethanes (THMs) only (since THMs may be present as a result of well maintenance activities), the detection frequency for these compounds is about 4% (i.e., 19 of 469 wells have detections of a solvent (PCE and/or TCE), fuel oxygenate (MTBE), or pesticide (simazine or atrazine)). This compares to typical detection frequencies in the entire set of PBP wells of about 10% for VOCs other than the THM chloroform and 10% for pesticides, and occasional detection frequencies for these compounds of up to 30% for certain study units.

The occurrence of anthropogenic compounds in these samples is evidence for a small modern water component or a non-advective transport mechanism for the detected compounds. One limitation of using the tritium concentration to categorize water as pre-modern is that even water with less than 1 pCi/L tritium may contain a small portion of modern water, which may have a significant effect on water quality. In this study, we set model limits on the proportion of model water that may be contained in a "tritium-dead" groundwater sample.

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**California GAMA Special Study:
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(LLNL-TR-548931)**

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1 INTRODUCTION

The goal of this study is to examine water quality in California drinking water wells classified as producing pre-modern water. The primary rationale for examining pre-modern water quality is to establish natural background water quality conditions, for eventual comparison with water quality in more recently recharged groundwater, the latter being more likely to have been affected in some way by industrial, agricultural, or other human activity. Although groundwater systems in certain remote areas of California are unlikely to be measurably affected by human activity, the vast majority public drinking water wells are in populated areas with potentially contaminating activities close to wells and in recharge areas (Belitz et al., 2003).

Compared to other freshwater reservoirs that make up the hydrosphere, groundwater exhibits a very wide range in residence times. At the extremes, water in the hyporheic zone of a stream may flow through porous media for less than a day, while in deep sedimentary basins water may be trapped in sedimentary sequences for millions of years. Even in the groundwater reservoirs typically tapped for drinking water by production wells, residence times may range from months to tens of thousands of years. Drinking water wells may therefore tap water that recharged before human activity significantly affected the groundwater system, potentially providing an archive that represents the "pre-modern" or "pre-industrial" state of the system.

Several methods have been proposed to select water quality data that represents pre-modern groundwater or natural background levels. Griffioen et al. (2008) compare three selection methods:

- 1) Use of historical water quality data (from before 1945; arguing that industrial and agricultural activity intensified strongly after 1945),
- 2) Selection of water samples having an oxidizing capacity (for agricultural areas where nitrate and sulfate concentrations indicate agricultural influence), and
- 3) Selection of water samples with low tritium concentrations.

The tritium concentration of a groundwater sample is a good indicator of the presence/absence of water that entered the saturated zone in the last 55 years. The time period covered by the presence of tritium roughly coincides with the time period during which human activity has had a significant effect on water quality and on the scale of groundwater use. Both industrial and agricultural activity (including the use of synthetic nitrogen fertilizer and the expansion of animal populations) significantly increased in California and in the nation after World War II (Burow et al., 2007; Puckett et al., 2010).

In previous GAMA studies, GAMA PBP wells have been categorized as 'young' or 'old' based in part on tritium activity, with either 1 tritium unit (3.2 pCi/L) or 1 pCi/L serving as the benchmark

(Bennett et al., 2010; Landon et al., 2010). In these studies, age is considered as a contributing factor to explain the distribution of various natural and non-natural constituents. Similarly, Kulongoski et al. (2010) use a combination of tritium, radiogenic helium-4, and carbon-14 to discriminate between 'young', 'old', and 'mixed' aged groundwater (Belitz, 2011), and find statistically significant correlations between groundwater age and several individual water quality indicators.

In this study (GAMA Special Study Task 11.3: Examination of Water Quality in "Tritium-Dead" Drinking Water Wells), we use tritium concentration to categorize samples as pre-modern or modern, with a pre-modern cutoff value of <1 pCi/L (called 'tritium dead'). The advantages of using tritium as a marker are:

- 1) As part of the water molecule, tritium is a robust tracer of advective-dispersive transport of water, without the complications associated with potentially non-conservative constituents;
- 2) Tritium is measured in nearly all PBP wells; and
- 3) When tritium is detected above 1 pCi/L, it indicates that a well produces some water that recharged in the last 55 years, which covers much of the time period of potential alteration of water quality by human activity.

Although water quality data from samples taken decades ago, say before 1945, is a more direct measure of past water quality, few such samples exist, techniques for measuring many constituents were less reliable for analyses done at the time of sample collection, and preservation issues preclude accurate analysis of archived samples using modern methods decades after collection.

The use of tritium alone to evaluate background water quality has certain limitations. The first limitation is that water with measured tritium activity below 1 pCi/L (a common detection or reporting limit) may contain a small portion of "modern" water and even a small portion of "modern" water can have a significant impact on water quality and could lead to a detection of an anthropogenic constituent in what appears to be pre-development groundwater. This would be a "quasi false positive" detection of an anthropogenic constituent in pre-development groundwater. The second limitation is that certain anthropogenic contaminants pre-date nuclear weapons testing so that tritium-dead groundwater containing only "pre-modern" recharge may, nonetheless, be affected by anthropogenic activities. For example, while the use of synthetic nitrate fertilizer increased dramatically after 1960, and while MTBE was added to gasoline in large quantities only in the 1990s, drinking water in California has been disinfected using chlorine (potentially producing trihalomethanes) for at least 100 years. In these examples, nitrate and MTBE concentrations in tritium-dead groundwater are more likely to be true background values than THM concentrations in tritium-dead groundwater.

A major complication associated with establishing natural background concentrations is that many constituents are affected by water-rock interaction or biogeochemical reactions during subsurface transport. In groundwater, acid-base, solution-precipitation, and oxidation-reduction reactions are particularly important over decadal and longer time periods. Alkalinity and total dissolved solids typically increase along groundwater flow paths as the result of acid-base and solution-precipitation reactions, while conditions typically become progressively more reducing as dissolved oxygen is consumed and microbes utilize subsequent electron donors. Observed concentrations of some constituents in pre-modern groundwater may therefore reflect the product of geochemical reactions and not 'background' concentrations. One important example is that a low or non-detectable nitrate concentration may be the result of denitrification (which occurs under reducing conditions), masking the original 'background' nitrate level. In this study, we examine the redox

conditions of the well water samples as a way of assessing the possibility that significant changes have occurred in redox-sensitive constituents.

The constituents analyzed in California's drinking water wells for research and to comply with Federal and State regulations can be categorized by source as anthropogenic or naturally-occurring. Certain constituents are purely anthropogenic with no known natural sources – examples include volatile organic compounds (VOCs) such as tetrachloroethylene (PCE) and trichloroethylene (TCE), and pesticides such as atrazine and simazine. Naturally-occurring constituents include iron and manganese, while nitrate may have both natural and anthropogenic components. This method of categorization is imperfect in that some constituents may be overwhelmingly but not exclusively from one source. Arsenic, uranium and chromium-6 are predominantly natural in origin but may have localized anthropogenic sources. Chloroform and hydrocarbons such as benzene are predominantly anthropogenic but may have natural sources in specific hydrogeologic settings (Albers et al., 2011; Landon and Belitz, 2012).

Furthermore, constituents with natural sources may be redistributed under conditions affected by human activity. For example, chemical equilibria and redox conditions are typically altered during application of water via artificial recharge or irrigation, sometimes causing non-natural mobilization or sorption of a native constituent. This concept is used to describe mobilization of naturally occurring radioactive material by human activity; T-NORM refers to Technologically mobilized Naturally Occurring Radioactive Material. Still, anthropogenic vs. natural is a useful categorization in the present context, because waters classified as pre-modern rarely contain anthropogenic compounds (Moran et al., 2004) and are reasonably expected to contain only natural constituents. Therefore, key applications of the results of the current study are to:

- 1) Assess the geographic variability in background concentrations of various constituents of interest in California basins used for drinking water supply;
- 2) Estimate natural background concentrations of constituents that have both natural and non-natural components (for example, nitrate), so that source control management practices address non-natural inputs;
- 3) Identify settings where modern contaminants are found in pre-modern groundwater in order to assess possible non-advective modes of transport of the contaminant and/or the history of use of the compounds in the area, and
- 4) Provide the basis for comparing pre-modern water quality with modern water quality for assessment of groundwater management and groundwater protection practices.

2 METHODS

To reach the task objective for GAMA Special Study Task 11.3: Examination of Water Quality in “Tritium-Dead” Drinking Water Wells, the following steps were carried out:

1. Acquire data from the GAMA Priority Basin project through the GeoTracker database (September, 2011).
2. Establish the threshold in tritium concentrations for defining “pre-modern” groundwater.
3. Assess redox state for redox sensitive constituents (nitrate, manganese, iron)
4. Calculate the frequency of detections above maximum contaminant level (MCL), notification level (NL) or secondary MCL (SMCL) for constituents of interest in tritium dead samples.
5. Calculate the frequency of VOC and pesticide detections (of any concentration above reporting limits) in tritium dead wells.
6. Calculate 95th percentile of constituent concentrations in tritium dead groundwater.
7. Report results for 8 “groundwater provinces” in California (Belitz et al., 2003)

2.1 Data acquisition

Once a list of PBP samples had been compiled, the following 45 groundwater quality variables (valid values) were requested for download:

Table 1: Analytes included in this study.

Analyte*	units	Analyte*	units	Analyte*	units
AL	UG/L	DO	MG/L	PCATE	UG/L
ALKB	MG/L	EDB	UG/L	PCE	UG/L
AS	UG/L	F	MG/L	PH	PH UNITS
ATRAZINE	UG/L	FE	UG/L	SC	UMHOS/CM
B	MG/L	H-3	pCi/L	SIMAZINE	UG/L
BDCME	UG/L	I	MG/L	SO4	MG/L
BR	MG/L	K	MG/L	TBME	UG/L
C-14	PCT MODERN	MG	MG/L	TCA111	UG/L
CA	MG/L	MN	UG/L	TCE	UG/L
CD	UG/L	MTBE	UG/L	TCLME	UG/L
CL	MG/L	NA	UG/L	TEMP	CELSIUS
CR	UG/L	NH3NH4N	MG/L	THM	UG/L
CU	MG/L	NI	UG/L	U	pCi/L
DBCME	UG/L	NO3	MG/L	V	UG/L
DBCP	UG/L	PB	UG/L	ZN	MG/L

*A complete list of valid values and names corresponding to abbreviations may be found at: http://geotracker.waterboards.ca.gov/gama/translation_table.asp

This data set was not supplemented by additional data from earlier GAMA studies under the California Aquifer Susceptibility (CAS) Project (2000-2002).

The PBP wells were selected using a randomized grid-based method to provide statistical representation of the study area (Belitz et al., 2003). Additional wells were selected by the USGS to evaluate changes in water chemistry along ground-water flow paths (“Flow Path” wells) and for a better understanding of the groundwater system (“Understanding” wells). While the “Understanding” and “Flow Path” wells were not included in the statistical characterization of water quality in USGS data summary reports, they are included in this study of the water quality of tritium-dead groundwater. The randomized grid-based approach required for the purpose of making robust statistical comparisons between study units is less important when only a sub-set of the data (tritium-dead wells) is analyzed. Including these additional wells provided more data and a better statistical characterization of water quality in this subset of wells. Also, data obtained from public supply wells may be biased towards higher quality because wells that are abandoned or become inactive due to water quality concerns are not among the sampled wells, and are removed from the CDPH water quality database. Moreover, these wells are typically drilled in areas known to have high quality groundwater, suitable for drinking water (Mendizabal and Stuyfzand, 2009).

Analytical results (Table 2, as of September, 2011) were obtained from 1366 samples collected from a total of 2102 wells studied in the PBP. For 1563 wells, a tritium measurement is available. 1111 of these analyses were analyzed at LLNL by the 3-Helium ingrowth method (Eaton et al., 2003), and 453 at the USGS (Menlo Park) by tritium enrichment followed by liquid scintillation counting (Michel, 1989).

Table 2: Summary of wells included in the analysis of water quality in tritium-dead samples

Priority Basin wells		2102
Wells with ³H analysis		1563
³ H analyzed by LLNL	1111	
³ H analyzed by USGS	453	
Wells with water quality data		1366
Wells with ³H and water quality data		1355

2.2 Selection of pre-modern groundwater samples using measured tritium concentration

2.2.1 Reconstruction of tritium in historical precipitation in California

In order to put limits on the proportion of modern water that might be present in samples with very low tritium concentrations, we derive functions that represent the historical input of tritium to groundwater in California. Under natural recharge conditions, precipitation is the dominant source of tritium in groundwater. The tritium concentration in natural historical recharge in California (Figure 1) is reconstructed from monthly time series of tritium measurements from the IAEA Global Network of Isotopes in Precipitation (GNIP) program (IAEA/WMO, 2006). Data for this study were obtained from the GNIP Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER) database on February 15, 2011 (<http://nds121.iaea.org/wiser/index.php>). Time-series from Ottawa (Canada), Portland (OR), and Menlo Park (CA) were combined, by cross-correlation of overlapping time periods and exponential fitting to extrapolate to 2010. Figure 1 shows monthly data for all three stations combined with the precipitation-weighted annual average concentrations. Ottawa ($^3\text{H}_\text{O}$) is the only station where data was acquired prior to 1961, and while it does provide a complete series from 1953 to 2007, the closer Portland station ($^3\text{H}_\text{P}$) provides a more reliable estimate of tritium concentrations in California precipitation. For the period 1961 to 1975, the Menlo Park station ($^3\text{H}_\text{MP}$) offers a reliable time series for coastal California. For the period prior to 1961, a linear regression with the Ottawa time series was derived as $^3\text{H}_\text{MP} = 0.20 * ^3\text{H}_\text{O}$, based on the overlapping period. For the period between 1975 and 2002, a linear regression with the Portland time series was derived as $^3\text{H}_\text{MP} = 0.67 * ^3\text{H}_\text{P}$, based on the period 1968 to 1974. Prior measurements (near the peak of tritium concentrations) caused the regression to deviate from the more relevant recent period and were excluded. The most recent period (2003 to 2010) was based on an exponential regression model fitted through the Portland data since 1970. The model equation is $^3\text{H}_\text{MP} = a + b * \exp(c * y)$, with y the number of years since 1970 and fitted parameters $a=8.1$ pCi/L, $b=170$ pCi/L and $c=-0.186 \text{ y}^{-1}$.

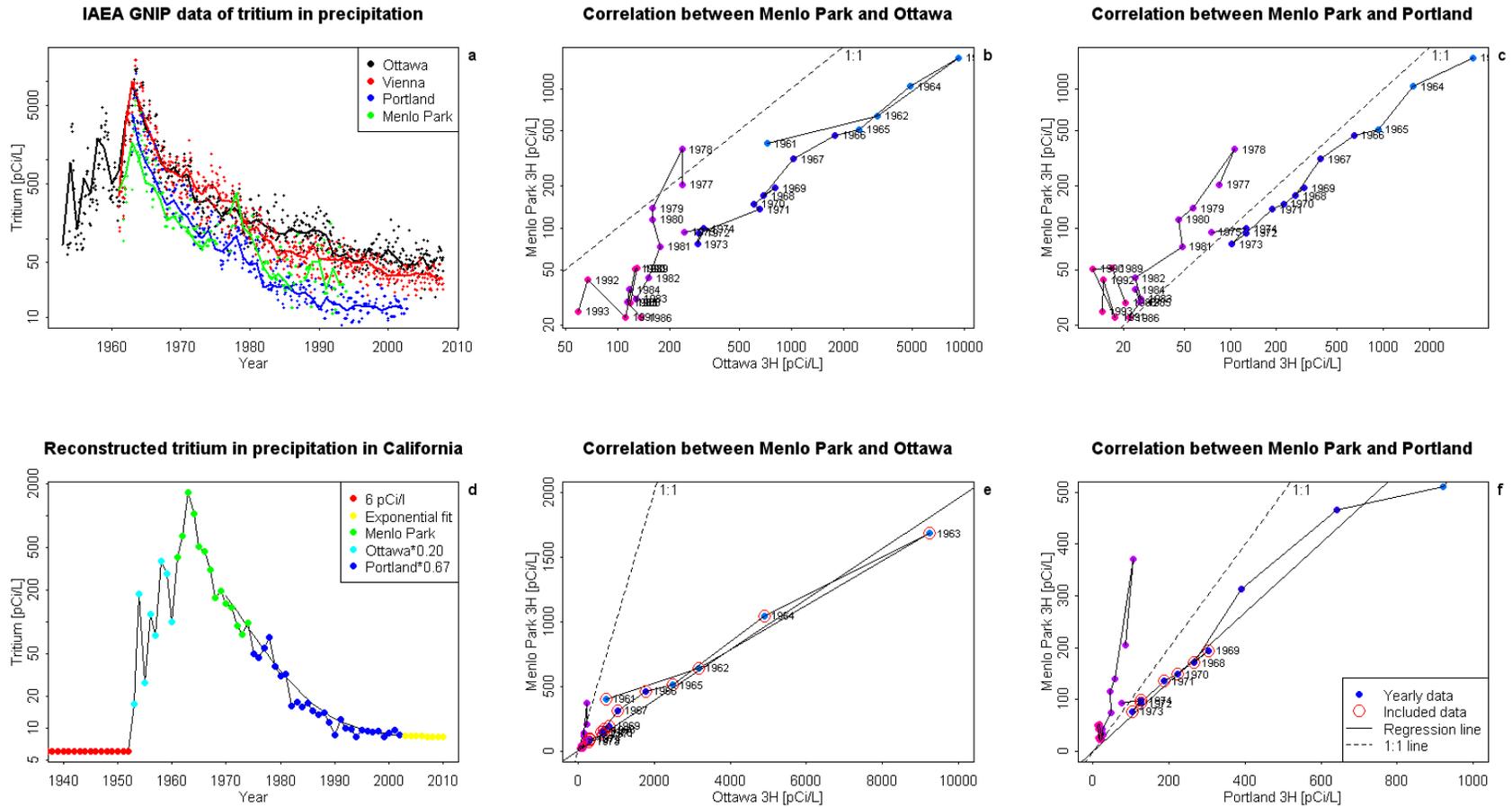


Figure 1: Reconstruction of tritium in historical precipitation in California. Measured tritium concentrations in Ottawa, Vienna, Portland and Menlo Park (a), correlation between Menlo Park and Ottawa (b (log scale), e (linear scale)) and Portland (c (log scale), f (linear scale)) and the reconstructed tritium curve for California (d).

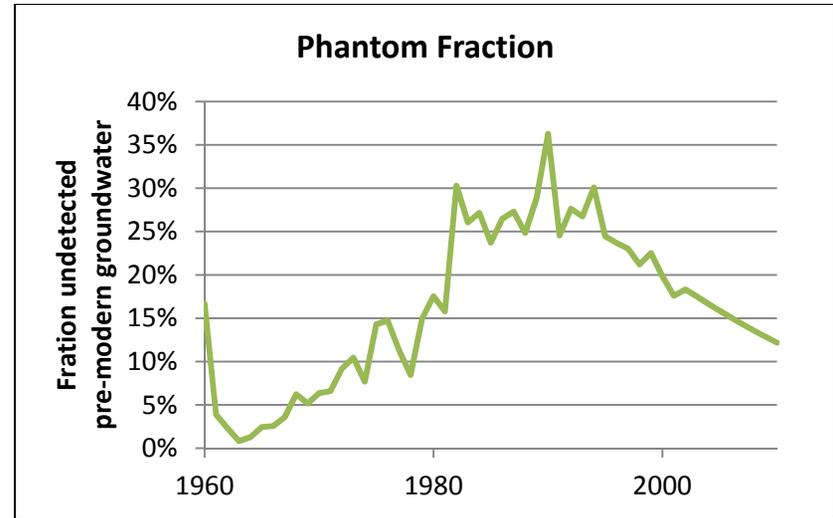
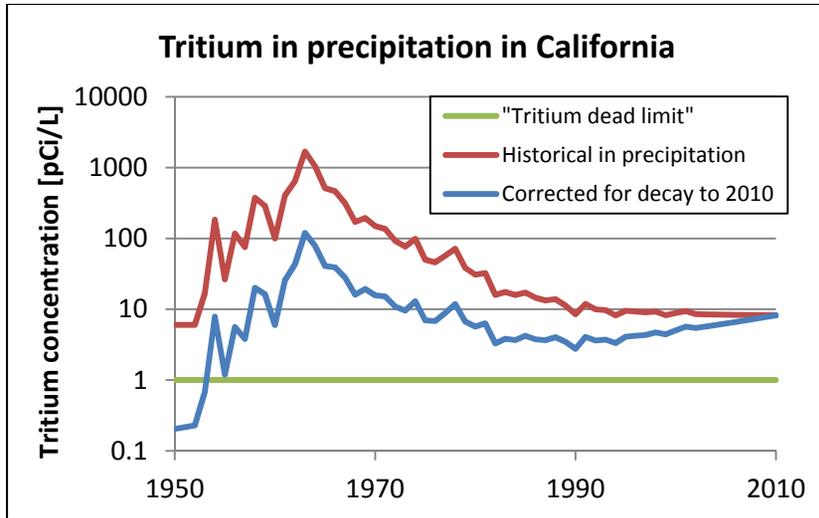


Figure 2: Tritium in precipitation and the *phantom fraction*

2.2.2 Present day tritium concentrations in groundwater

Present day concentrations of tritium in naturally recharged groundwater are what remains of the initial tritium in precipitation after radioactive decay, and can be calculated based on the reconstructed tritium levels in historical precipitation. Groundwater recharged before 1950 contains no detectable tritium in 2012, due to decay (62 years is approximately five tritium half-lives). Because of atmospheric nuclear weapons testing and natural cosmogenic production of tritium in the atmosphere, groundwater that recharged after 1950 presently contains at least 3 pCi/L. However, there are two conditions that could lead to modern water not being detected by the tritium content of a well water sample: mixing of modern groundwater with pre-modern groundwater (either in the aquifer or in the wellbore) resulting in dilution to a tritium concentration below 1 pCi/L, or recycling of tritium dead water by groundwater pumping and irrigation return flow.

Samples collected from long screened production wells – including most public supply wells – contain a mixture of pre-modern and modern groundwater. Such a mixture may contain no detectable tritium if the fraction of modern water is small, or may contain concentrations well above the detection limit if the fraction of "bomb pulse" recharge is large or if the water is mostly recent recharge.

Present day tritium concentrations in groundwater that recharged between 1982 and 1994 in California are below 4 pCi/L. With a detection limit of 1 pCi/L (consistently achieved for the analytical techniques used by the USGS and LLNL) a mixed groundwater sample can therefore contain as much as 25% of "modern" groundwater without being detected. Hydrogeologically, such a binary mixture of pre-modern groundwater and groundwater that recharged between 1982 and 1994 is not likely, yet it cannot be ruled out. The fraction of modern groundwater in a mixed groundwater sample with a bulk tritium concentration of ≤ 1 pCi/L may be considered the phantom fraction (Figure 2).

The tritium content of recharging groundwater is only constrained by the above analysis if the source of recharge is exclusively precipitation. In California, river infiltration (losing streams), irrigation return flow, and managed aquifer recharge can also contribute to groundwater recharge.

River infiltration could recharge water with low tritium contents after 1950 if the water has a considerable subsurface or surface residence time since it originated as precipitation. For example, if the river drained a large groundwater basin or if water has a long residence in an in-stream reservoir before reaching the losing reach and recharging groundwater, its tritium content would reflect tritium concentrations from an earlier time period. In California, this situation is not likely prevalent.

Return flow from groundwater irrigation is potentially a more likely source of low tritium concentrations in recent groundwater in agricultural areas where a major source of recharge is irrigation return flow. The tritium content of recharging groundwater (both natural precipitation and irrigation return flow) depends on the fraction of irrigation return flow and the groundwater age distribution of irrigated water. If the groundwater used to irrigate recharged before 1950, it would contain negligible tritium and would dilute the tritium in recharging return flow, by a factor defined by the ratio of return flow to natural recharge.

For these two reasons, additional tracer information is desirable. Additional tracers of modern water are available, such as CFCs, SF6 or 85Kr. With these tracers it might be possible to detect a smaller fraction of modern groundwater in a mixed – mostly pre-modern – groundwater sample. Because these are all environmental gaseous tracers, they would also detect recent irrigation return flow because they would dissolve in the water according to equilibrium solubility while the water is in contact with the atmosphere. However, analyses for these tracers are not available for the PBP dataset. A follow up special studies project could be to revisit wells with no detectable tritium but with detections of anthropogenic constituents.

If, for this study, a lower tritium concentration for selecting pre-modern groundwater were chosen, the number of water quality analyses would be reduced and the statistics of pre-modern groundwater would be more uncertain. Instead, the tritium concentration for defining pre-modern groundwater was set at <1 pCi/L. Considering this discussion, it should be noted that a detection of an anthropogenic constituent in “pre-modern” groundwater does not necessarily imply a natural source, but may rather indicate the presence of a small modern fraction of groundwater affected by human activity..

2.3 Redox classification

Common groundwater constituents, such as oxygen, nitrate, iron, manganese and sulfate, are subject to chemical reduction or oxidation (redox) reactions in aquifers. For example, natural nitrate in recharging groundwater can be reduced to N_2 if electron donors such as organic matter or pyrite are available in the aquifer. To assess natural, background concentrations of redox sensitive constituents, it is important to examine samples in the context of the groundwater redox state, and consider the predicted speciation for the constituent of interest. Following the example of nitrate, if reduced groundwater samples were to be included in the characterization of natural nitrate levels, these would bias the estimated nitrate levels downward because nitrate may have been removed by geochemical redox processes.

For this study the redox-classification scheme developed by McMahon and Chapelle (2008) was adopted, with two modifications (Table 3). First, the original redox categories “suboxic” and “anoxic – nitrate reducing”, were renamed to “oxic or suboxic” and “suboxic – nitrate reducing”, respectively. With this modification, anoxic categories now start when all dissolved electron acceptors (oxygen, nitrate) have been depleted and aquifer materials (Mn, Fe) are being reduced. Second, a distinction is made between “anoxic – sulfate reducing” and “anoxic – methanogenic/ CO_2 reducing”. The criterion for “sulfate reducing” is that the SO_4/Cl ratio is below 0.128, which represents 90% of the seawater ratio.

Furthermore, criteria are applied as leniently as possible in the case of missing values. For example, when oxygen is present above 0.5 mg/L and data for Mn and Fe are missing, the sample is classified as “oxic”, while it could technically also be “mixed” between oxic and anoxic, if Mn or Fe were present. Other cautionary notes related to redox classification are pointed out by Green et al. (2010) and apply to these data as well. As one example, mixing during transport or in the wellbore may result in a groundwater sample with a relatively high field measured dissolved oxygen concentration, when in fact a portion of the water came from a highly reduced zone, where denitrification was active or where iron was mobilized. Furthermore, high pumping rates, common

in public supply wells, alter the flow field within the radius of influence, and may draw in water with redox characteristics that differ from those prevalent in the regional aquifer.

Table 3: Redox classification scheme

Color Legend	Redox Classification	O ₂ (mg/L)	NO ₃ (mg/L)	Mn (µg/L)	Fe (µg/L)	SO ₄ /Cl	SO ₄ (mg/L)
	● Oxidic (O ₂)	≥ 0.5		< 50	< 100		
	● Oxidic or Suboxidic		≥ 2.25	< 50	< 100		
	● Suboxidic (NO ₃)	< 0.5	≥ 2.25	< 50	< 100		
	● Anoxic (Mn)	< 0.5	< 2.25	≥ 50	< 100		
	● Anoxic (Fe)	< 0.5	< 2.25		≥ 100	≥ 0.128	≥ 0.5
	● Anoxic (SO ₄)	< 0.5	< 2.25		≥ 100	< 0.128	≥ 0.5
	● Anoxic (CO ₂)	< 0.5	< 2.25		≥ 100	< 0.128	< 0.5
	● Mixed	≥ 0.5 or ≥ 2.25	≥ 50 or ≥ 100				

2.4 Geographical classification: Groundwater provinces

It is anticipated that climate, vegetation, hydrology and geology exert primary control on the water quality characteristics of pre-development, tritium-dead groundwater in California. This demands a subdivision of PBP wells into geographic units. These units should include a sufficient number of wells for statistical characterization, yet be somewhat homogeneous with respect to climate and physiographic features. For this study, we adopted the USGS grouping of PBP data into 11 "Groundwater Provinces" (Figure 3). At the time of this study, water quality data from 8 provinces were available. In some provinces, the data were not available for all study units, potentially introducing a small spatial bias. The provinces, study units, number of PBP wells and number of available analysis for this study are listed in Table 4.

Table 4a. Available GAMA PBP water quality analyses in California groundwater provinces.

Province	Province description	Wells	WQ analyses
BR	Basin and Range	74	67
CV	Central Valley	580	397
D	Desert	266	213
KM	Klamath Mountains	39	0
MPC	Modoc Plateau and Cascades	90	0
NCR	North Coastal Ranges	157	97
SCR	South Coastal Ranges	306	226
SD	San Diego	58	52
SN	Sierra Nevada	217	100
TPR	Transverse & Peninsular Ranges	315	214

Table 4b. Available GAMA PBP water quality analyses in GAMA PBP Study Units

Province	Study Unit	Wells	WQ analyses
BR	OWENS	74	67
CV	CE	79	77
CV	KERN	50	49
CV	MIDSAC	86	84
CV	NSAC	66	56
CV	NSJV	70	64
CV	SESJV	99	0
CV	SSAC	87	67
CV	WSJV	43	0
D	ANT	57	56
D	CLUB	52	0
D	COA	35	35
D	COLOR	28	28
D	MADCHOW	35	35
D	MOJO	59	59
KM	KLAM	39	0
MPC	CAMP	90	0
NCR	NOCO	60	0
NCR	NSF	97	97
SCR	MS	97	91
SCR	SCRC	74	58
SCR	SCRI	54	0
SCR	SF	81	77
SD	SD	58	52
SN	CENSI	30	0
SN	SIERRA	85	0
SN	SOSA	50	50
SN	Tahoe	52	50
TPR	Bear	38	0
TPR	CLAB	69	64
TPR	SCRV	57	52
TPR	ULAB	52	0
TPR	USAW	99	98



Figure 3: Map of the California Groundwater Provinces (source: USGS.gov)

2.5 Measures of well vulnerability and ambient concentration levels

The analysis of water quality data from tritium-dead wells can be used to address two questions. The first question relates to the vulnerability of public water supply wells to contamination: What is the chance of detecting a regulated constituent above the MCL in tritium dead groundwater? The second question is: What is the geographic distribution and range of ambient concentrations of naturally occurring regulated constituents in pre-modern groundwater? An accurate estimate of naturally occurring concentrations is crucial for distinguishing anthropogenic sources, especially if no other (e.g. isotopic) discrimination techniques are available.

To answer the first question, we calculated the proportion of tritium-dead wells in which a natural or anthropogenic constituent was detected above a regulatory level. The concentrations of four constituents (arsenic, fluoride, nitrate and perchlorate) were compared to the maximum contaminant level (MCL). Two constituents (boron and vanadium) were compared to the California Notification Level (NL). Four more constituents (chloride, iron, manganese and sulfate) were compared to the California Secondary Maximum Contaminant Level (SMCL), an aesthetic regulatory limit. Additionally, we investigated the proportion of wells in which anthropogenic VOCs or pesticides are detected at any level above the reporting limit.

To answer the second question, the 95th percentile of concentrations of the 10 constituents with both natural and anthropogenic sources was calculated. These may be regarded as the highest concentrations of likely natural origin; above the 95th percentile value, there is a strong indication that an anthropogenic component is present.

The 95th percentile P95 was calculated as:

$$P95 = (1 - g) \times x_j + g \times x_{j+1}$$

where:

p = percentile = 0.95

n = number of measurements

m = 1 - p

j = floor(n*p + m)

g = n*p + m - j

x_j = jth order statistic = value of jth measurement, sorted ascending

The result is a linear interpolation between measured values (sorted ascending) in which the 95th percentile lies. For further chemical characterization, the median and 95th percentile of major and minor cation and anion concentrations were calculated. In addition, "Piper" diagrams (Figures 7 through 10) are presented to compare natural, background concentrations in different groundwater provinces.

3 RESULTS

3.1 Proportion of wells with $^3\text{H} < 1 \text{ pCi/L}$

The total number of available PBP sample results ranges among the provinces between 58 (San Diego) and 517 (Central Valley). The proportion of wells with $^3\text{H} < 1 \text{ pCi/L}$ varies between 22% (Transverse and Peninsular Ranges) and 53% (Desert) (Table 4, Figure 4). The 95% confidence intervals on the proportion (calculated according to Gilbert, 1987) show that the tritium-dead proportions in the South Coast Ranges, Transverse and Peninsular Ranges, San Diego, Central Valley and Sierra Nevada provinces do not differ significantly. Public supply wells in North Coast Ranges, Basin and Range and Desert provinces have a significantly higher proportion of ^3H dead groundwater. The pattern observed in the proportion of tritium-dead wells is likely related to both natural patterns of recharge (whereby more arid provinces are likely to have lower recharge rates and thus a larger proportion of tritium-dead water), and to the prevalence of artificial recharge, imported water application, and large scale irrigation (whereby those process increase recharge rates and decrease the proportion of tritium-dead water compared to what might be expected for the natural system). Basin and Range and Desert provinces experience low natural recharge rates and relatively little artificial recharge, while Transverse and Peninsular Ranges and Central Valley provinces are strongly influenced by artificial recharge and irrigation, respectively. Sierra Nevada province likely experiences a relatively high recharge rate and is probably least altered from the natural condition, with a corresponding low proportion of tritium-dead water. Water is not imported into North Coast Ranges province and some aquifers have relatively low permeability, yet groundwater use is high, resulting in a high proportion of wells producing tritium-dead water. South Coast Ranges province results are strongly influenced by Santa Clara Valley (with extensive artificial recharge of imported water) and Salinas Valley (with no imported water but significant irrigation return flow).

Table 4: Number and proportion of wells with less than 1 pCi/L tritium, per province.

	NCR	SCR	TPR	SD	CV	SN	BR	D
³ H ≥ 1 pCi/L	51	167	189	43	400	95	43	101
³ H < 1 pCi/L	45	71	53	14	117	29	28	112
TOTAL	96	238	242	57	517	124	71	213
Proportion of wells with ³H < 1 pCi/L	47%	30%	22%	25%	23%	23%	39%	53%
Lower Limit	37%	24%	17%	15%	19%	16%	28%	46%
Upper Limit	57%	36%	28%	38%	27%	32%	52%	59%

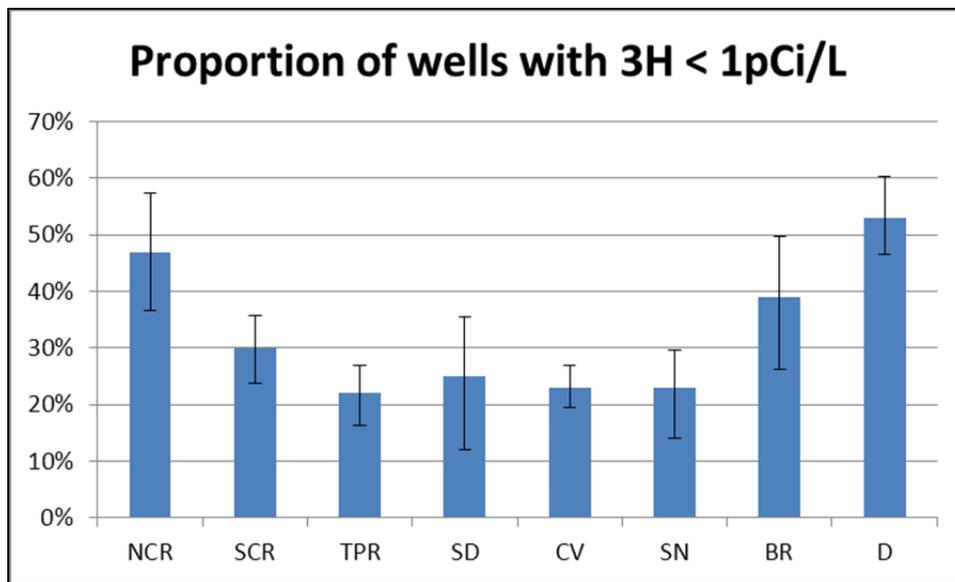


Figure 4: Proportion of wells producing water with less than 1 pCi/L of tritium. Error bars indicate statistical uncertainty based on the number of wells available.

3.2 Available water quality data

The number of tritium-dead wells that are available for water quality assessment (Table 5) is over 25 for each province except San Diego. All wells in the PBP were sampled for VOCs, pesticides and pesticide degradates, pharmaceutical compounds, perchlorate, hexavalent chromium, stable isotopes of water, and dissolved noble gases and tritium/helium age dates (“fast” wells). Only a subset of the wells (“intermediate” wells) was also sampled for nutrients and dissolved organic carbon, major and minor ions and trace elements. Therefore the number of available analyses for nitrate and major chemical composition is lower. Table 5 lists the number of analyses available for each of the 10 constituents that were analyzed, with respect to the relevant MCL, NL or SMCL. Data for the 11 selected pesticides and VOCs are nearly complete for each tritium-dead well. Because the number of available analyses is limited for some analytes and for some provinces, the 95% confidence interval around the proportion is calculated (Gilbert, 1987) to indicate the statistical uncertainty in the reported proportions.

Table 5: Available water quality analyses per province

	NCR	SCR	TPR	SD	CV	SN	BR	D
Wells with ³H < 1 pCi/L	45	71	53	14	117	29	28	112
Available analyses for natural and anthropogenic constituents								
AS	18	40	24	9	76	21	26	61
F	17	40	24	9	76	21	26	61
NO3	11	47	24	9	68	21	26	61
PCATE	39	52	50	10	72	25	26	109
B	18	40	24	9	78	21	26	61
V	18	40	24	9	76	21	26	61
CL	19	40	24	9	78	21	26	61
FE	19	39	24	9	76	21	26	61
MN	18	39	24	9	76	21	26	61
SO4	19	40	24	9	76	21	26	61
Available analyses for Pesticides and VOCs								
SIMAZINE	40	69	48	14	104	25	24	112
BDCME	41	68	50	14	107	25	26	112
DBCME	41	68	50	14	107	25	26	112
DBCP	41	68	50	14	107	25	26	112
EDB	41	68	50	14	107	25	26	112
MTBE	41	68	50	14	107	25	26	112
PCE	41	68	50	14	107	25	26	112
TCE	41	68	50	14	107	25	26	112
TCA111	41	68	50	14	107	25	26	112
TCLME	41	68	50	14	107	25	26	112

3.3 Redox conditions

Proportions of redox classifications vary between the groundwater provinces, as anticipated (**Figure 5**). The uncertainty on the proportions can be relatively large due to the small number of samples for which the necessary constituents for redox classification are available. The North Coast Ranges province has the smallest proportion of oxic or suboxic wells, and the largest proportion of anoxic wells. On the other end of the spectrum, the Desert province is nearly entirely oxic/suboxic, with only two anoxic wells and one mixed redox well. Considering the uncertainty on these proportions, at least 90% of the wells in the Desert province contain sufficient oxygen for nitrate to be stable during transport. All other provinces vary within these extremes, with typically 60% - 70% oxic/suboxic groundwater, 20% - 40% anoxic groundwater and up to 12% groundwater with mixed redox conditions. This redox classification shows that a large proportion of tritium-dead groundwater produced for drinking water is oxic, and potentially vulnerable to nitrate contamination. At present, all of these wells produce tritium-dead groundwater, indicating recharge occurred prior to 1950. Under stable hydrogeological conditions, the age distribution of groundwater is constant, and the time of recharge captured by a well progresses. As a result, in the future these wells may capture post-1950 (“modern”) groundwater carrying anthropogenic contaminants. These contaminants will not be attenuated by anoxic aquifer conditions. Additional groundwater age tracers (e.g. ^{14}C or ^{39}Ar) or groundwater models could be applied to determine the age distribution at longer time periods, and further investigate this vulnerability.

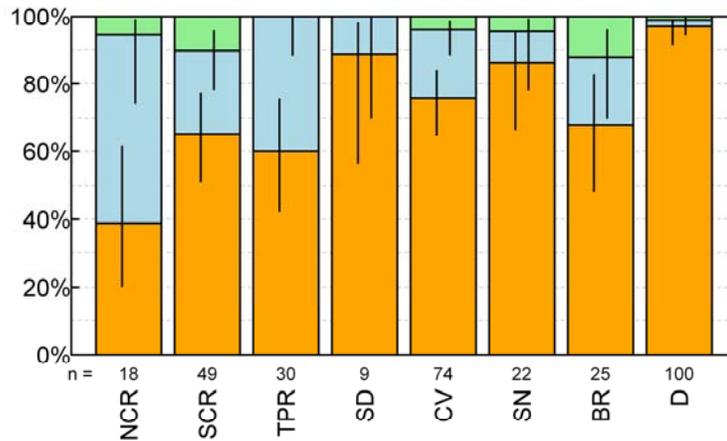


Figure 5: Groundwater redox: Proportions of wells in each study area classified as Oxic/Suboxic (orange), Anoxic (light blue) and Mixed (light green).
 Error bars indicate statistical uncertainty of the proportions based on the number of wells.

3.4 Radiocarbon

As a first indication of the age distribution beyond the range covered by tritium alone, Figure 6 shows the distribution of ¹⁴C contents (expressed as "percent modern carbon", pmC) of inorganic carbon measured in the oxic and suboxic tritium dead groundwater samples collected under the PBP. Red, orange and yellow bars represent the proportion of wells with ¹⁴C ratios of >90pmC, >80pmC and >70pmC, respectively. While these wells are tritium-dead, they produce a large fraction of groundwater younger than the ¹⁴C half-life of 5730 years. Without additional information, these ¹⁴C ratios could be interpreted to represent groundwater with a single "age" of 870 years, 1840 years or 2950 years, respectively; or a mixture of ages with a fraction of very old (> 20,000 years) groundwater. A significant component of post-1950 recharge would result in pmC values >100% (indicating the presence of 'bomb pulse' ¹⁴C). While pmC values >100% are not uncommon among wells with >3 pCi/L tritium, only one well (from the Desert province) with <1pCi/L tritium has a pmC value of 100.3%.

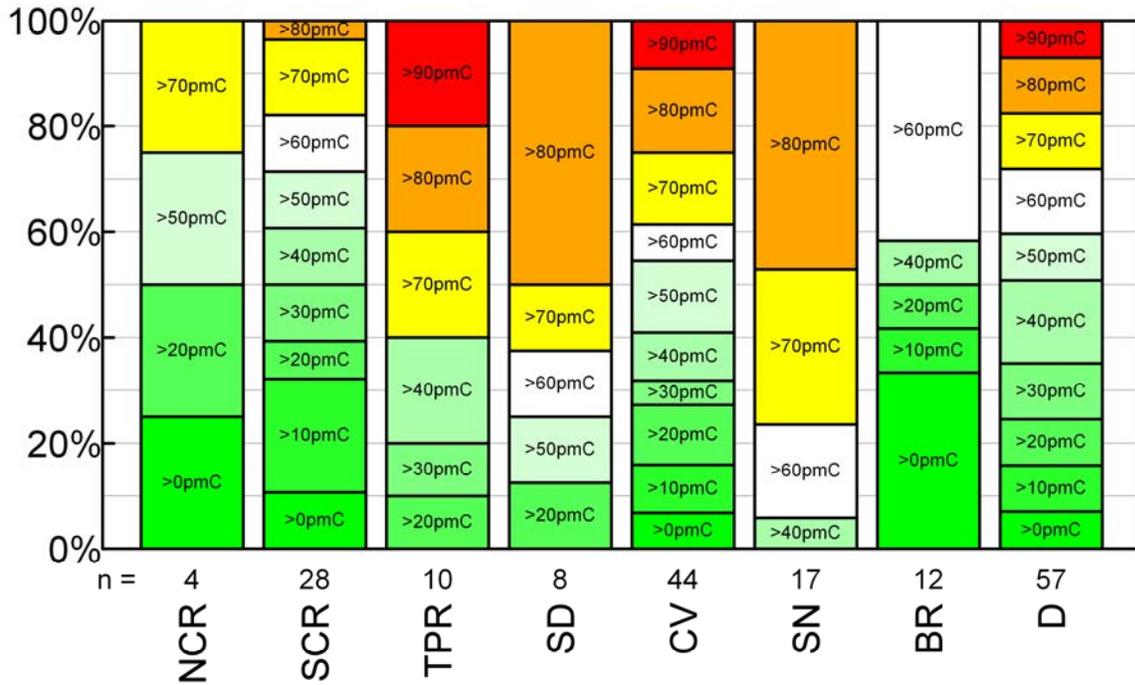


Figure 6: Distribution of 14C contents of oxic/suboxic, tritium-dead groundwater samples. Red, orange and yellow indicate a large fraction of near-modern carbon, potentially vulnerable to future contamination by nitrate and other oxidized contaminants.

3.5 General Chemistry

Charge balance between major anions and cations in groundwater samples is one measure of the quality of laboratory analyses of those ions. For PBP wells, only about 30% of samples were analyzed for bicarbonate alkalinity, a major anion, so analysis of charge balance was restricted to samples for which all major ions were analyzed. Only eleven samples from the PBP water quality data set of 367 wells (those with values for all major anions and cations) had charge imbalances greater than 5%. Of the 469 tritium-dead samples examined for water quality (many of which were not analyzed for bicarbonate alkalinity), 14 samples may thus have charge imbalances for the same overall proportion of imbalanced samples. However, 9 of the 11 imbalanced samples were from wells with tritium concentrations of <1 pCi/L. Therefore, a greater proportion of tritium-dead samples may have charge imbalances.

Tritium dead samples having data for all major anions and cations are plotted on “Piper” diagrams in Figures 7 through 10, and in box-whisker plots in Figure 11. Provinces sharing Piper diagrams were chosen to show contrasting major ion patterns. Most provinces show predominant cation trends as mixtures between Na and Ca waters, with varying amounts of Mg. This pattern evolves as Ca-rich waters experience cation exchange with aquifer materials such as feldspar minerals. Desert, South Coast Ranges, and Central Valley show mixtures with comparatively high Mg proportions, while North Coast Ranges, Basin and Range, Sierra Nevada, and Transverse and Peninsular Ranges have comparatively low Mg proportions. Tritium dead samples from Desert, Central Valley, Basin and Range and Sierra Nevada provinces show mixing trends between Na-HCO₃ and Ca-HCO₃ waters, with low proportions of Cl and SO₄. In comparing Piper diagrams with absolute concentrations (Figure 11), Sierra Nevada and Central Valley are characterized further by relatively low specific conductance (a measure of total dissolved solids), and low concentrations of Cl, Br, Na, and K. The background water chemistry of Sierra Nevada and Central Valley likely reflects the low TDS of the major water source (Sierra snowmelt carried by large, perennial rivers) and minimal interaction between water and granitic host rock (for Sierra Nevada, and sediments derived from them for Central Valley). The pattern observed in Central Valley samples is particularly significant because it is likely altered in modern water that recharged since the onset of extensive irrigation for agriculture. Burow et al. (1997) find that major ion chemistry is affected in areas dominated by irrigated agriculture as a result of leaching accumulated salts and soil amendments during infiltration. In particular, Ca-Mg-HCO₃ groundwater becomes enriched in Cl and SO₄ under the influence of irrigation. The similarity between Sierra Nevada and Central Valley tritium dead groundwater confirms this water recharged before the onset extensive irrigation. On the other hand, Transverse and Peninsular Ranges, South Coast Ranges, and San Diego (the latter with very few samples), show a pattern typical of waters influenced by marine deposition, with relatively high TDS, Cl, Na, and Br. Desert and Basin and Range provinces show some patterns characteristic of groundwater quality in arid environments, such as higher Cl, Na, and SO₄ concentrations than Sierra Nevada and Central Valley and lower proportions of Mg. North Coast Ranges has a unique water composition that shows the influence of water-rock interaction with volcanic host rocks and reduced waters, which strongly affects trace element composition, as described below.

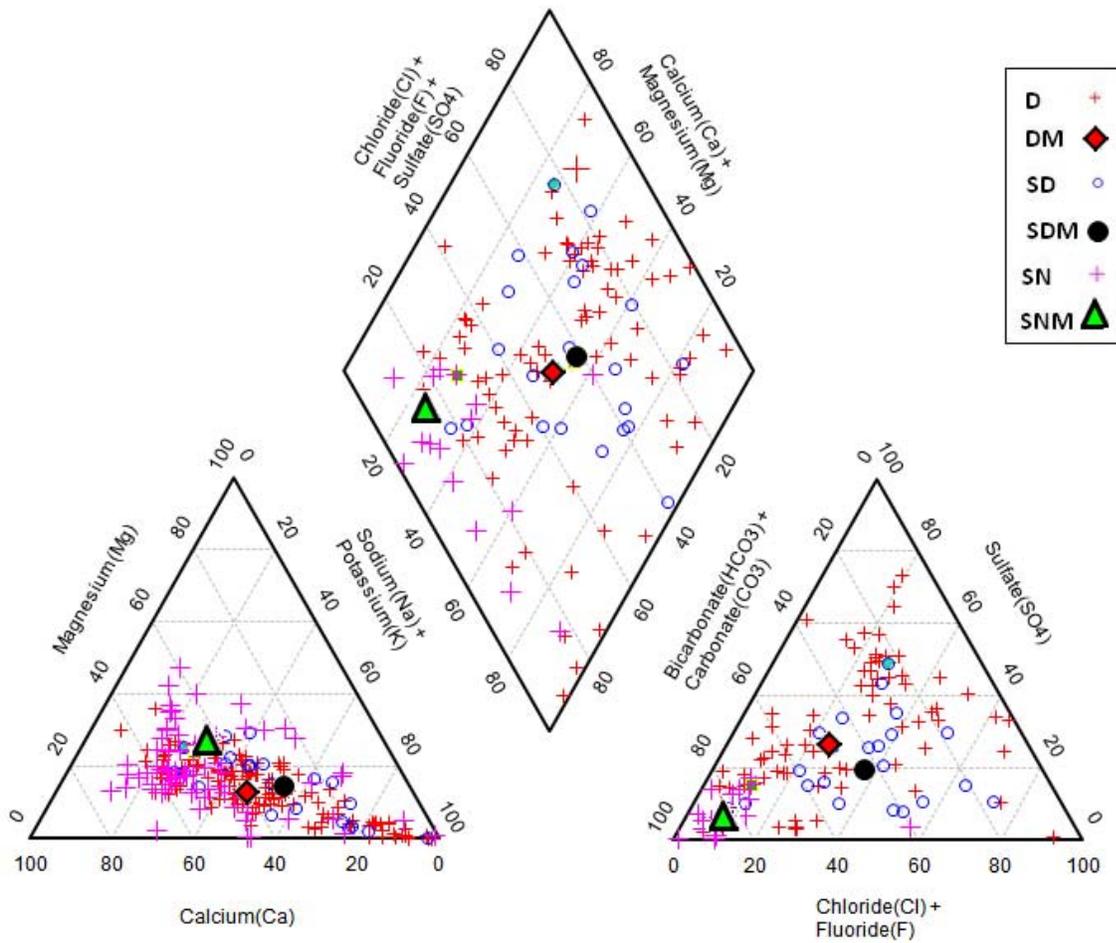


Figure 7: Piper plot of Desert (D), San Diego (SD) and Sierra Nevada (SN) provinces. Median values are labeled DM, SDM, and SNM.

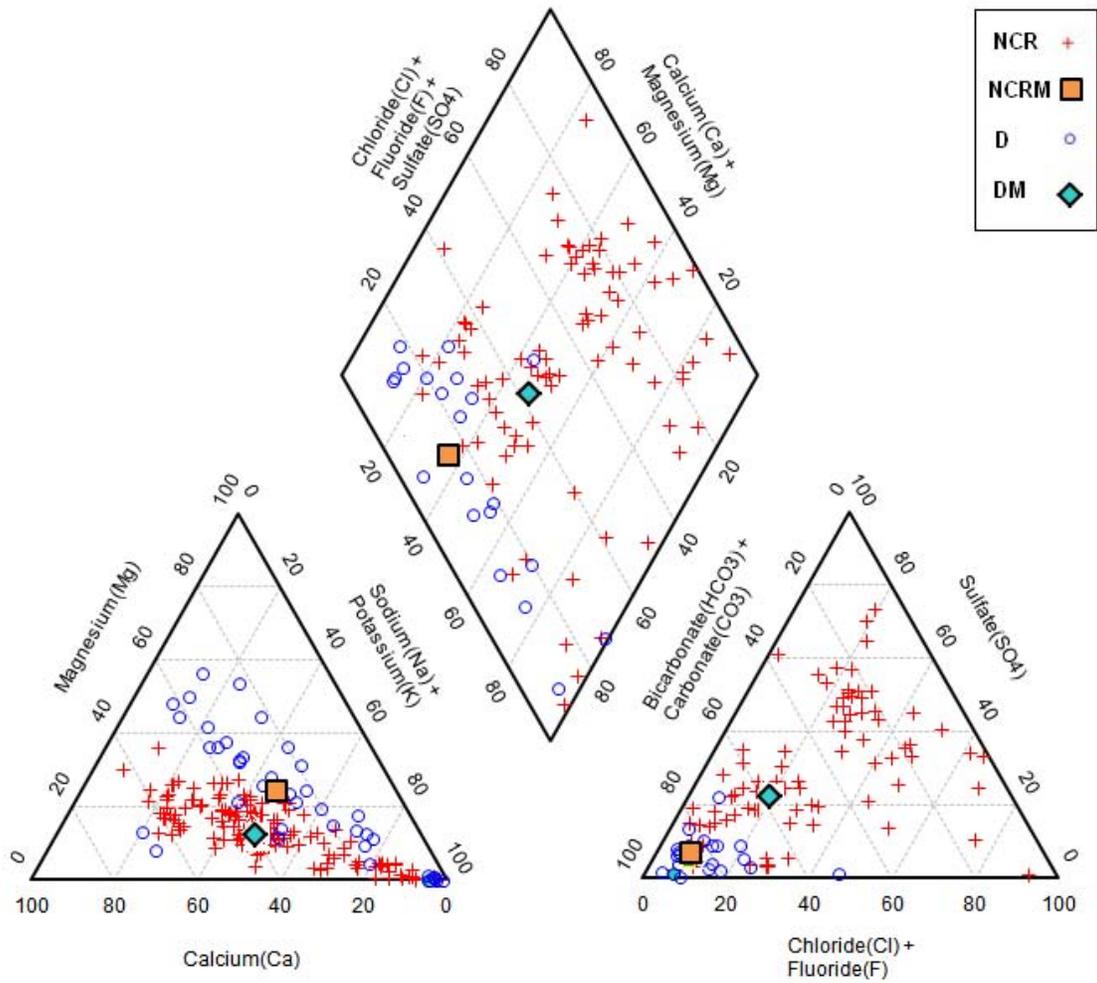


Figure 8: Piper plot of North Coast Ranges (NCR) and Desert (D) provinces.
 Median values are labeled NCRM and DM.

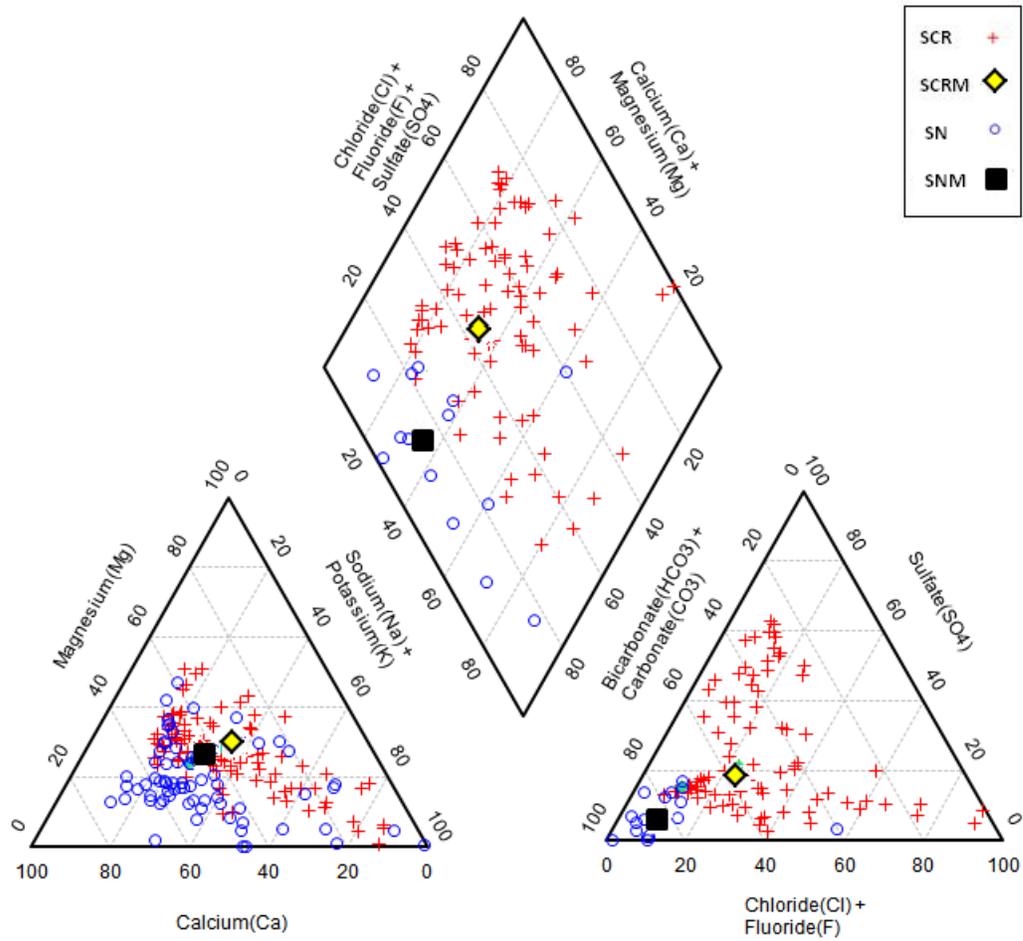


Figure 9: Piper plot of South Coast Ranges (SCR) and Sierra Nevada (SN) provinces. Median values are labeled SCR median and SNM.

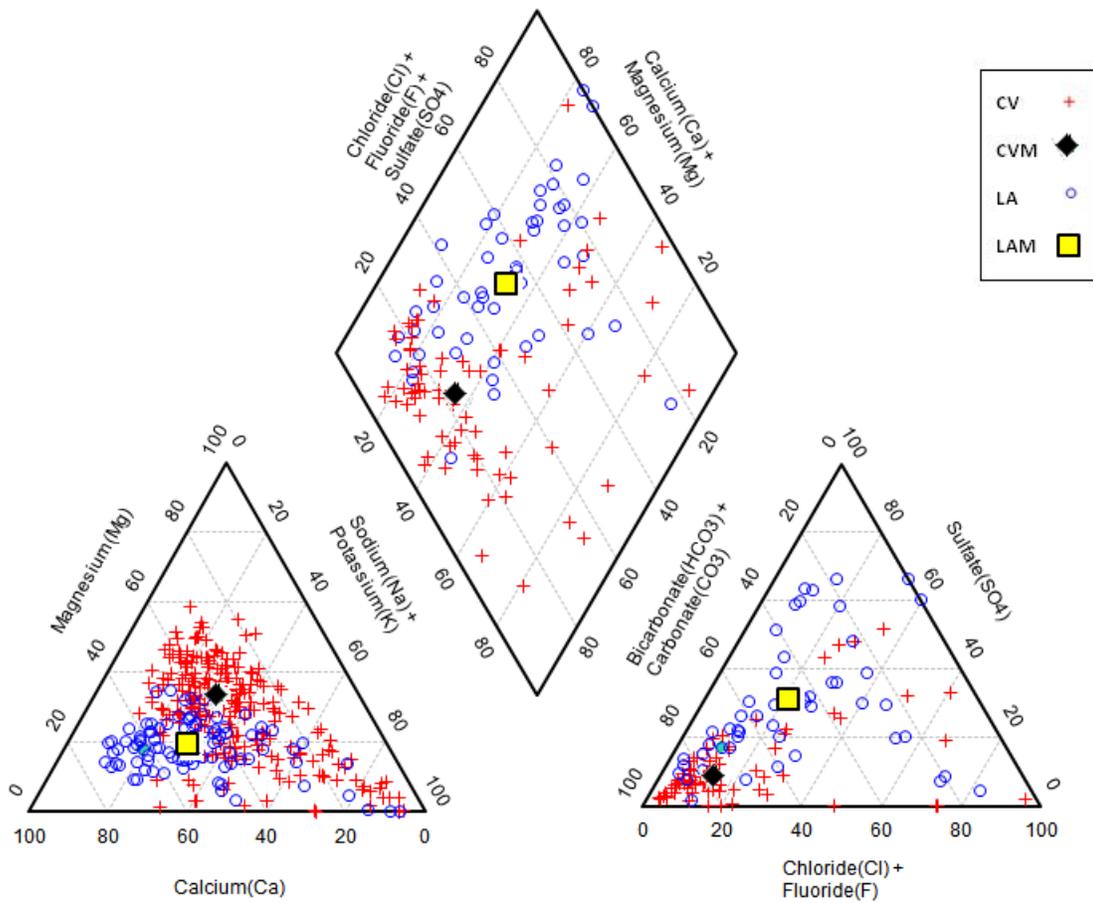


Figure 10: Piper plot of Central Valley (CV) and Transverse and Peninsular Ranges (LA) provinces. Median values are labeled CVM and LAM.

Examination of Water Quality in "Tritium-Dead" Water Well

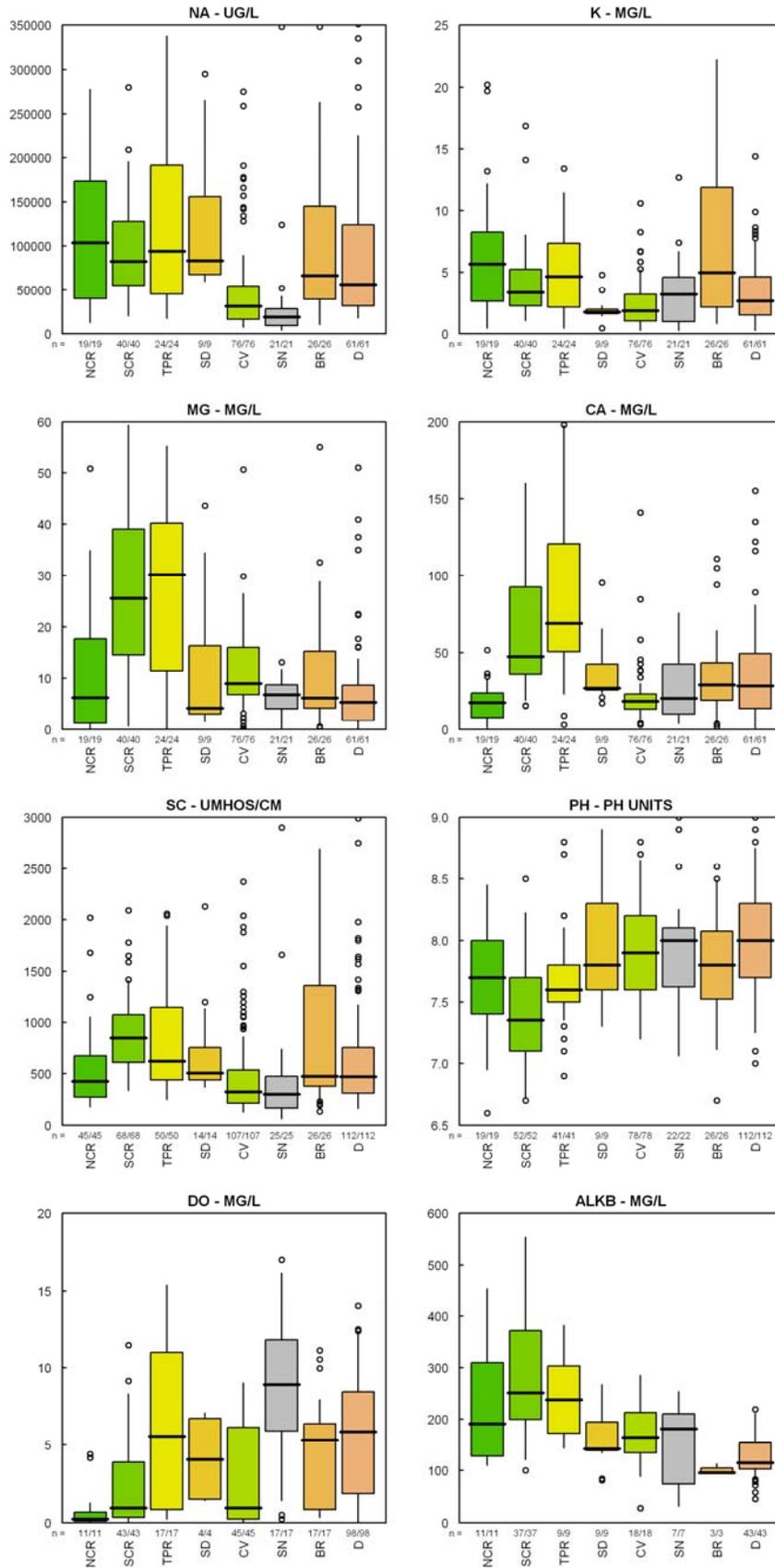


Figure 11: Box-whisker plots of major cations and general water quality parameters for studied groundwater provinces.

The box bounds represent the 25th and 75th percentiles; the median is represented by the bold horizontal line, the whiskers extend to 1.5 times the interquartile range, and data outside of this range are plotted as individual data points.

3.6 Regulated constituents with natural sources

The distribution of regulated constituents (arsenic, fluoride, and nitrate) that can occur naturally is shown for each of the provinces in Figure 12. The box-whisker plots in Figure 12 show for each province the 25th and 75th percentile values for each constituent (box outline); the median value (the bold horizontal line), and either 1.5 times the interquartile (25 to 75%) range or the maximum and minimum values (whiskers). Data beyond 1.5 times the interquartile range are plotted as individual data points. Perchlorate, which is also regulated and can occur naturally, is discussed below.

3.6.1 Arsenic

The highest concentrations of arsenic occurring in tritium-dead groundwater in California are found in the North Coast Ranges (NCR) province (Figure 12). The highest measured concentration is 128 µg/L; the 95th percentile of As concentrations in this province is 74 µg/L: over 7 times the MCL. Arsenic is especially high in the wells of the hydrothermal area of the North San Francisco Bay study unit. Thermal waters were considered as potential explanatory factors in the understanding assessment of water quality in the NSF study unit. The water from the wells in the hydrothermal area is mainly used for recreation (mineral baths), not for drinking-water supply (Kulongoski, 2010 #1360). Six of the eight wells in this area contain arsenic concentrations over the MCL. Excluding those eight wells from the data reduces the 95th percentile to 27 µg/L, still nearly 3 times the MCL, but in line with the other groundwater provinces. The median arsenic concentrations vary from 5.7 µg/L in the North Coast Ranges (including the hydrothermal area) to 0.4 µg/L in the Transverse and Peninsular Ranges provinces. High background concentrations of arsenic are also found in the Central Valley (median of 3.4 µg/L), Basin and Range (4.1 µg/L) and Desert (2.7 µg/L) provinces. The occurrence of naturally-sourced arsenic in California groundwater has been documented, with most studies focusing on As in Central Valley groundwaters (Belitz et al., 2003; Gao et al., 2007; Izbicki et al., 2008; Welch et al., 2000).

Interestingly, Bennett et al. (2010), who define young groundwater as waters having more than one tritium unit (where 1 TU = 3.2 pCi/L) find that in the Northern San Joaquin Basin study unit, “Arsenic concentrations in samples with a groundwater age classified as young and collected from wells with a depth to the top-of-perforation of less than 200 ft were significantly higher than samples with a groundwater age classified as old based on tritium concentrations or samples from wells with a depth to top-of-perforation of greater than 200 ft” A comparison of the exceedance frequency of As between tritium dead wells and wells with tritium >1 pCi/L is outside the scope of this report, but results from the Northern San Joaquin Basin study unit suggest that the relatively high exceedance frequency found in tritium-dead wells may also be observed in younger groundwater.

3.6.2 Fluoride

Like arsenic, fluoride is found in very high concentrations in tritium-dead groundwater from wells in the hydrothermal area of the North Coast Region province. Concentrations range from 1.9 mg/L to 11.3 mg/L. Seven of the eight hydrothermal wells contain fluoride above the California MCL of 2 mg/L. High concentrations of arsenic and fluoride in acidic-volcanic host rocks have been reported elsewhere (Armienta and Segovia, 2008; Farooqi et al., 2007). Excluding these hydrothermal wells, median concentrations of naturally occurring fluoride vary between 0.11 mg/L in the Sierra Nevada and 0.89 mg/L in the Basin and Range province. The 95th percentile of concentrations was above the

MCL in the Basin and Range and Desert provinces, between 2.7 mg/L and 4.5 mg/L. High concentrations of fluoride in groundwater recharged under arid conditions are likewise reported elsewhere (Edmunds and Smedley, 2005).

3.6.3 Nitrate

The lowest nitrate concentrations in tritium-dead groundwater are also found in the North Coast Region province. For nitrate, we have evaluated the concentrations in a selected subset of samples with oxic or suboxic conditions, since nitrate is generally not stable in anoxic groundwater. Of the four samples that qualified in the North Coast Ranges, three did not contain detectable concentrations of nitrate; the fourth had only 0.45 mg/L. In three other provinces, median nitrate concentrations in tritium-dead oxic or sub-oxic groundwater vary from less than 1 mg/L (North Coast Ranges, Sierra Nevada) to over 6.5 mg/L (Transverse and Peninsular Ranges, San Diego) (Figure 12). The criterion used for identifying anthropogenic nitrate is >13 mg/L (Squillace et al., 2002). Nitrate concentrations in tritium-dead groundwater of four other provinces exceeded the 13 mg/L criterion. In the Transverse and Peninsular Ranges, San Diego, Sierra Nevada and Desert provinces, nitrate concentrations up to 65 mg/L were found. Concentrations of nitrate above 13 mg/L were found in South Coast Ranges and Central Valley as well, but only at a proportion of less than 5% of the wells. Yet in the four other provinces, the proportion of wells with nitrate concentrations above 13 mg/L ranges from 16% (Desert, n=9) to 42% (Transverse and Peninsular Ranges, n=5). Because of the small number of wells available for each province (between 8 and 58), there is considerable uncertainty associated with these proportions.

Based on these data, the lowest proportion of wells that contain more than 13 mg/L of nitrate – the lower bound of the 95th percentile confidence interval around the proportion – ranges from 8% (D) to 19% (Transverse and Peninsular Ranges). This shows that in these provinces, a significant proportion of wells that are very unlikely to be affected by anthropogenic inputs of N can contain nitrate concentrations greater than 13 mg/L. Interestingly, some of the provinces with low background concentrations, especially Central Valley and South Coast Ranges, are areas strongly affected by N inputs in the last few decades because of manure from dairy operations, and fertilizer applied to row crops and orchards. For example, Harter and Lund (2012) outlined the extent of the nitrate problem in groundwater in Tulare and Salinas counties and attributed anthropogenic nitrate to these sources. In contrast, the provinces with relatively high background concentrations are not among those dominated by agricultural land use. Desert, San Diego, and Transverse and Peninsular Ranges are all characterized by arid climates, where atmospherically-delivered nitrate may accumulate in the vadose zone, and be flushed into groundwater during wet periods or when irrigation water is applied (e.g. Walvoord et al., 2003).

3.6.4 Perchlorate

A large number of perchlorate analyses were below the detection limit; however the detection limit varies between and within provinces. Perchlorate was detected in 93 samples out of a total of 383 samples (24%, Table 6). With a large proportion of non-detects and a variable detection limit, it is difficult to accurately estimate the 95th percentile of concentrations. However, the large proportion of detections in Desert province is likely due to atmospherically-delivered perchlorate that builds up in the vadose zone under arid conditions and is subsequently transported to groundwater (e.g. Rajagopalan et al., 2006). Perchlorate was not detected at all in the North Coast Ranges or Central Valley provinces. The maximum concentration of perchlorate in other provinces varied between 0.6 µg/L and 3.4 µg/L. A more extensive discussion of perchlorate concentrations in PBP wells is provided by Fram et al. (2011).

Table 6: Detections of perchlorate above a variable detection limit
(varying from 0.1 - 50 µg/L).

	BR	CV	D	NCR	SCR	SD	SN	TPR	Total
Detections	2	0	66	0	9	3	3	10	93
Samples	26	72	109	39	52	10	25	50	383
Proportion	8%	0%	61%	0%	17%	30%	12%	20%	24%

3.6.5 Background levels of regulated constituents with natural sources

To distinguish between anthropogenic and natural sources of regulated constituents, we calculated the 95th percentile of measured concentrations for arsenic, fluoride, nitrate and perchlorate in all provinces (Table 7). A measured concentration above the 95th percentile in a particular province is 5% likely to be natural and 95% likely to be anthropogenic. The 95th percentiles vary strongly between provinces, and exceed the MCL for arsenic and fluoride in several provinces. For strongly heterogeneous provinces that contain hydrothermal areas, like the Northern Coast Ranges, the 95th percentile for the entire province is likely to be higher than the 95th percentile for non-hydrothermal areas of the province and therefore be a conservative indicator of anthropogenic influence in these non-hydrothermal areas.

Table 7: 95th percentile of measured concentrations of As, F and nitrate in the 8 provinces.
Numbers in bold indicate a 95th percentile that is greater than the MCL.

	AS	F	NO3	PCATE
	µg/L	mg/L	mg/L	µg/L
NCR	80.5	10.7	0.5	
SCR	13.6	0.5	12.4	1.5
TPR	26.8	0.7	33.2	3.4
SD	7.6	1.2	24.1	0.9
CV	43.3	0.5	12.7	
SN	31.1	0.7	37.3	1.1
BR	62.5	2.7	11.0	0.6
D	62.2	4.6	20.0	1.2
MCL	10	2	45	6

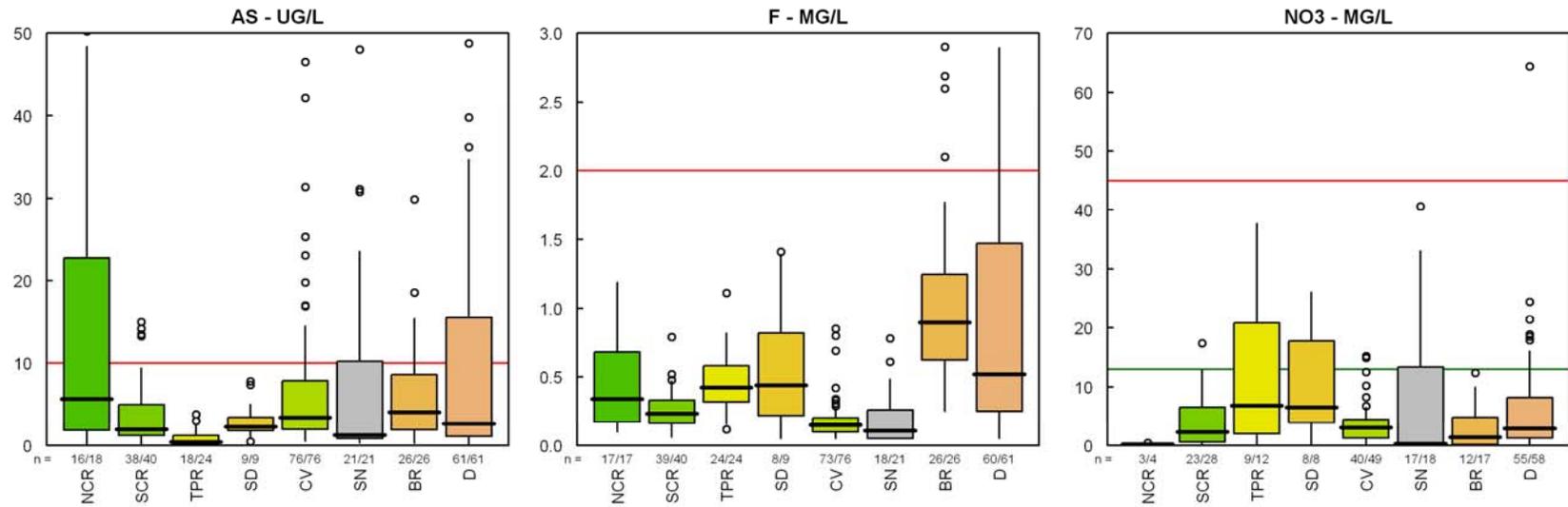


Figure 12: Box-whisker plots for regulated constituents: arsenic, fluoride and nitrate.

The box represents the 25th to 75th percentile; the median is represented by the bold horizontal line, the whiskers extent to 1.5 times the interquartile range outside the box or to the extreme value, data points outside the whiskers are plotted separately. The horizontal red line indicates the MCL. The horizontal green line represents the criterion used for identifying anthropogenic nitrate (>13 mg/L) (Squillace et al., 2002).

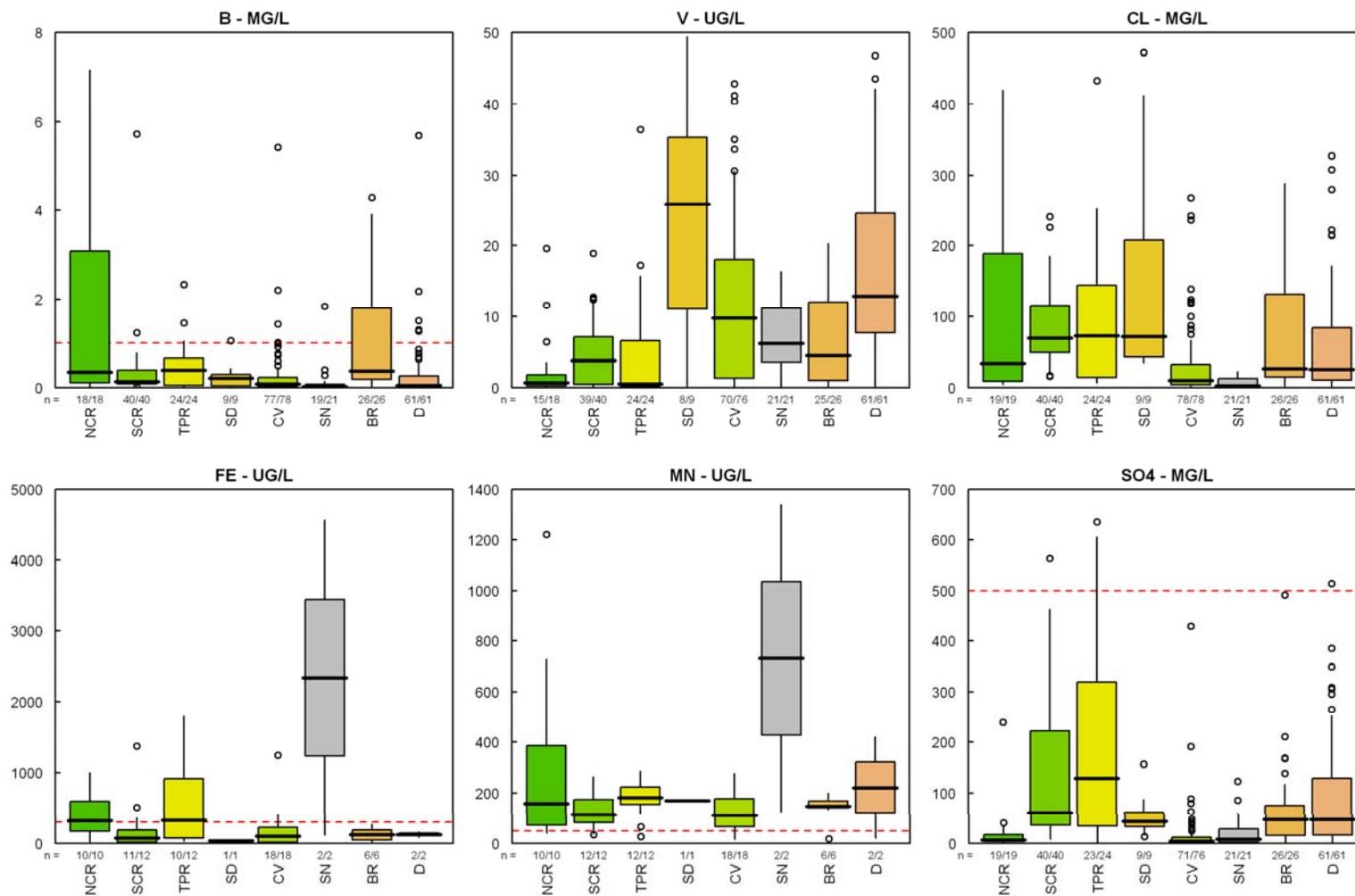


Figure 13: Box-whisker plots for non-regulated constituents: boron, vanadium, chloride, iron, manganese and sulfate.

The box represents the 25th to 75th percentile; the median is represented by the bold horizontal line, the whiskers extent to 1.5 times the interquartile range outside the box or to the extreme value, data points outside the whiskers are plotted separately. The horizontal red line indicates the SMCL.

3.7 Other naturally occurring constituents

The distribution of non-regulated constituents (boron, vanadium, chloride, iron, manganese and sulfate) that can occur naturally is shown for each of the provinces in Figure 13. The box-whisker plots in Figure 12 show for each province the 25th and 75th percentile values for each constituent (box outline); the median value (the bold horizontal line), and either 1.5 times the interquartile (25 to 75%) range or the maximum and minimum values (whiskers). Data beyond 1.5 times the interquartile range are plotted as individual data points.

3.7.1 Boron

High boron concentrations (over 11 mg/L) are measured in the North Coast Ranges and Basin and Range provinces. Like arsenic and fluoride, the high boron concentrations are only found in wells from the hydrothermal areas in the San Francisco Bay study unit. The 95th percentile of boron concentrations in the North Coast Ranges province, excluding the hydrothermal wells, is 1.9 mg/L, similar to the concentrations of 0.4 mg/L to 1.4 mg/L found in other provinces. Two of the three high boron concentrations in the Basin and Range province are associated with the dry Owens Lake playa. As in the hydrothermal wells, they coincide with high arsenic and fluoride concentrations.

3.7.2 Vanadium

Ambient vanadium concentrations in North Coast Ranges, South Coast Ranges, Sierra Nevada and Basin and Range provinces are below 20 µg/L, well below the California Notification Level (NL) of 50 µg/L. Ambient concentrations in Transverse and Peninsular Range, San Diego and Central Valley provinces are mostly below the NL, but concentrations slightly above the NL do occur. In the Desert province, extremely high vanadium concentrations of up to 190 µg/L (nearly 4 times the NL) occur. Wright and Belitz (2010) found high vanadium concentrations associated with mafic and andesitic host rocks, and especially in association with oxic and alkaline geochemical conditions.

3.7.3 Chloride

Chloride concentrations in tritium-dead wells are below the SMCL in most provinces. Concentrations of more than two times the MCL of 500 mg/L rarely occur. Extremely high chloride concentrations (4000 – 6000 mg/L) are measured in three monitoring wells in the Santa Clara River Valley study unit (Transverse and Peninsular Ranges province) near the Pacific Ocean, indicating sea water intrusion.

3.7.4 Iron

The 95th percentile of iron concentrations exceeds the SMCL in all but three (San Diego, Basin and Range, Desert) provinces. High concentrations are to be expected in provinces with a large proportion of anoxic (iron reducing) groundwater, such as the North Coast Ranges. Extremely high iron concentrations are found in the wells that show sea water intrusion in the Santa Clara River Valley and also in one well in the Sierra Nevada, where it is associated with high Mn and SO₄ concentrations.

3.7.5 Manganese

High manganese concentrations are even more common than high iron concentrations, since manganese is reduced before iron. Concentrations of Mn above the SMCL are found in all provinces.

3.7.6 Sulfate

Sulfate concentrations in most provinces are below 200 mg/L, well below the SMCL of 500 mg/L. South Coast Ranges, Transverse and Peninsular Range and Desert provinces are exceptions. The 95th percentile of sulfate concentrations in these provinces is close to the SMCL, at 570, 700 and 514 mg/L, respectively. Exceptionally high sulfate concentrations are found in wells associated with sea water intrusion in the Transverse and Peninsular Ranges and South Coast Ranges provinces. The Sierra Nevada well containing high manganese and iron concentrations also contains a sulfate concentration of 1390 mg/L.

3.8 MCL detections and co-occurrences

In 124 wells of the 469 tritium-dead wells studied (26%) concentrations of regulated constituents are found above the MCL, NL or SMCL. In 67 of the 124 wells a constituent was detected above the MCL. Most of those instances involve arsenic (57), or fluoride (19). Nitrate is detected above the MCL in only one well. Manganese is the constituent most commonly detected above the SMCL.

A small number of wells show exceptionally high concentrations for several constituents. For example, wells showing signs of seawater intrusion, such as along the shore of the San Francisco Bay or in the Santa Clara River Valley, often exceed the SMCL for both, Cl and Mn, and occasionally B, Fe or SO₄. Wells in hydrothermal areas in the North San Francisco study area (North Coast Ranges province) often exceed the MCL for As and F, and the NL for B.

Arsenic (As) is a common naturally occurring regulated constituent that is detected above the MCL of 10 µg/L in >20% of the tritium dead wells in 5 of the 8 provinces. The North Coast Ranges, Desert, and Basin and Range provinces are most affected. These are also the three provinces in which fluoride (F) is commonly detected above the MCL of 2 mg/L in at least 15% or more of the wells. These occurrences are only weakly correlated ($r^2 = 0.24$), meaning that fluoride is detected in only one-third of the wells where arsenic is detected, and arsenic is detected in only half of the wells where fluoride is detected (above the regulatory limit). Still their co-occurrence suggests that a common geochemical environment hosts water with these two constituents or that they have a common source.

Table 8: Probability matrix of co-occurrence above a regulatory limit

		the chance (%) of detecting compound B is given below										
		AS	F	NO3	PCATE	B	V	CL	FE	MN	SO4	n =
If you detect compound A above a MCL, NL or SMCL,	AS	-	18	0	0	28	12	11	9	40	9	57
	F	53	-	0	0	63	0	26	0	11	21	19
	NO3	0	0	-	0	0	0	0	0	0	0	1
	PCATE	0	0	0	-	0	0	0	0	0	0	0
	B	52	39	0	0	-	0	35	3	32	19	31
	V	88	0	0	0	0	-	0	0	0	0	8
	CL	40	33	0	0	73	0	-	20	60	33	15
	FE	25	0	0	0	5	0	15	-	90	20	20
	MN	33	3	0	0	14	0	13	26	-	12	69
	SO4	42	33	0	0	50	0	42	33	67	-	12

Detections of regulated constituents above the MCL often co-occur and are correlated. The matrix in Table 8 shows the chances of detecting a constituent in one of the columns, if a constituent on a particular row has been detected above an MCL, SMCL, or NL. For example, if arsenic is detected above the MCL, the chance of detecting fluoride above the MCL is 18%. Conversely, if fluoride, boron or vanadium is detected above the MCL or NL, the chance of detecting arsenic in the same well is 53%, 52% and 88%, respectively. Other strong correlations are detections of manganese above the SMCL in wells with iron above the SMCL (90%) or boron in wells with chloride (73%). On the other hand, in the one ³H dead well with nitrate above the MCL, none of the other constituents shown on the table is detected above its limit. As another example, when As is detected above its MCL, sulfate is rarely found above its SMCL (9%).

3.9 Pesticides and VOCs

Pesticides and VOCs do not occur naturally, and their occurrence is not expected in tritium dead groundwater. However, either pesticides or VOCs are detected in 41 of the 469 tritium-dead wells of the PBP data available for this study (Table 9). In total, the dataset contains 54 detections, indicating coincidences of detections at the same well. In 9 of the 41 wells, 2 pesticides or VOCs were detected together, in 2 wells three pesticides or VOCs were detected together. The table below shows the correlation between the detections of pesticides and VOCs. For example, simazine was detected in 2 of the 3 wells in which atrazine was detected. Vice versa, atrazine was detected in 2 of the 9 wells in which simazine was detected.

Table 9: Probability matrix of co-occurrences of pesticide and VOC detections

		The chance (%) of detecting compound B is given below											
		ATRAZINE	SIMAZINE	DBCP	EDB	BDCME	DBCME	TCLME	MTBE	PCE	TCE	TCA111	n=
If you detect compound A,	ATRAZINE		67	0	0	0	0	0	0	0	0	0	3
	SIMAZINE	22		0	0	0	0	11	11	11	0	0	9
	DBCP	0	0		0	0	0	0	0	0	0	0	0
	EDB	0	0	0		0	0	0	0	0	0	0	0
	BDCME	0	0	0	0		0	0	0	0	0	0	0
	DBCME	0	0	0	0	0		83	0	0	0	0	6
	TCLME	0	5	0	0	0	23		0	5	5	0	22
	MTBE	0	50	0	0	0	0	0		50	0	0	2
	PCE	0	12	0	0	0	0	12	12		25	0	8
	TCE	0	0	0	0	0	0	25	0	50		0	4
	TCA111	0	0	0	0	0	0	0	0	0	0		0

Of note are the detection frequencies for the Trihalomethanes (THMs) dibromochloromethane (DBCP) and trichloromethane (TCLME, or chloroform). Five of the six samples in which DBCP was detected also contain TCLME. TCLME is the most frequently detected VOC, with 22 detections in total. TCLME is by far the most frequently detected VOC in PBP wells (http://www.waterboards.ca.gov/gama/report_depot.shtml). Trihalomethanes are disinfection byproducts that are formed when chlorine or chloramine interacts with natural organic matter. Because chlorine or chloramine is used during installation and maintenance of drinking water wells, THMs may not have been transported through the porous medium and should not be interpreted in the same way as other anthropogenic constituents (Moran et al., 2004). The presence of THMs in tritium dead groundwater is not a good indicator of the presence of a component of modern water or of well vulnerability.

Excluding tritium dead wells with occurrences of only THMs, the detection frequency for anthropogenic compounds is quite low – about 4% (i.e., 20 of 469 wells have detections of a solvent

(PCE and/or TCE), fuel oxygenate (MTBE), or pesticide (simazine or atrazine)). This compares to typical detection frequencies in the entire set of PBP wells of about 10% for VOCs other than chloroform and 10% for pesticides (http://www.waterboards.ca.gov/gama/report_depot.shtml), and occasional detection frequencies for these compounds of up to 30% for certain study units. Certain compounds appear to co-occur, e.g. the chance of detecting the pesticide simazine when the pesticide atrazine is detected is 2/3 (Table 9). And in half the wells where MTBE is detected, PCE is also detected; similarly in half the wells where TCE is detected, PCE is also detected (Table 10). The number of detections on which to base the probability of co-occurrence, however, is very low. The occurrence of MTBE in two tritium-dead wells (one at a comparatively high concentration of 0.76 µg/L) is particularly difficult to explain if only advective-dispersive transport is considered, given that MTBE only came into widespread use after 1990. The remaining detections of anthropogenic constituents are concentrated in three study units – Salinas Monterey Bay (MSMB), Upper Santa Ana Watershed (USAW), and Upper Los Angeles Basin (ULAB). These are all coastal areas where the initial tritium values are low and groundwater with 1 pCi/L ³H may contain a modern component of as much as 20%. Furthermore, USAW and ULAB are highly urbanized areas with long histories of relatively high VOC detection frequencies in the larger data set, high rates of pumping, and active remediation. These conditions may lead to transport of ubiquitous anthropogenic constituents to deep portions of the aquifer system, facilitated by widespread pumping and artificial recharge.

The list of wells with pesticide or VOC detections was scrutinized for exceptionally large uncertainties in the tritium measurement, consistently high tritium contents (close to 1 pCi/L), the source of tritium data and the ¹⁴C ratio (if available). None of these parameters appears to explain the occurrence of pesticides or VOCs in these samples. Most interestingly, the ¹⁴C ratio of these wells varies between 2.2 pmC and 85.8 pmC and the statistics of the ¹⁴C distribution of this subset is not different from the entire tritium-dead groundwater dataset. If these wells were to be revisited to confirm the constituent detection and low tritium content, additional age tracers that could detect a smaller fraction of recent groundwater (e.g. CFCs, SF₆, or ⁸⁵Kr) should be included in the sampling. If no evidence for a modern component is found, these wells could be scrutinized with respect to well construction and operation/maintenance and land use history within the well capture zone.

4 CONCLUSIONS

Background, or “pre-modern” water quality conditions are revealed through examination of several constituent concentrations in GAMA PBP wells with tritium concentrations <1pCi/L. The proportion of tritium dead wells varies among the geographic provinces and is related to climate and groundwater management practices. About half of the wells sampled in the Desert and North Coast Range provinces produce tritium dead water, while only 22% of wells in the Transverse and Peninsular Range province produce tritium dead water. Close scrutiny of hypothetical mixtures of samples in which tritium dead water is combined with more recent recharge containing tritium above 1 pCi/L reveals that as much as 25% of a sample measuring <1 pCi/L may actually be of modern origin.

Analysis of GAMA PBP water quality data in tritium dead water reveals that 26% of wells have concentrations of regulated constituents above the MCL, NL or SMCL. Median manganese concentrations are well above the SMCL in all provinces, and iron likewise has a high frequency of occurrence above the SMCL. Iron and manganese have a natural source in *anoxic* aquifers, which comprise between 5% and 55% of samples in the different geographic provinces. Arsenic is detected above the MCL of 10 µg/L in >20% of the tritium dead wells in 5 of the 8 provinces studied. The North Coast Ranges, Desert, and Basin and Range provinces are most affected. Concentrations of the regulated constituents As, F, B, and V, when found above the MCL, often coincide.

Ambient concentrations of nitrate and perchlorate do not exceed the MCL, but both occur at concentrations greater than background levels established in previous studies. For example, a significant proportion (18-42%) of tritium-dead wells in the Transverse and Peninsular Ranges, San Diego, Sierra Nevada and Desert provinces contain nitrate concentrations greater than the anthropogenic limit of 13 mg/L reported in literature. Since nitrate is a redox sensitive anion, only oxic samples were considered in the analysis.

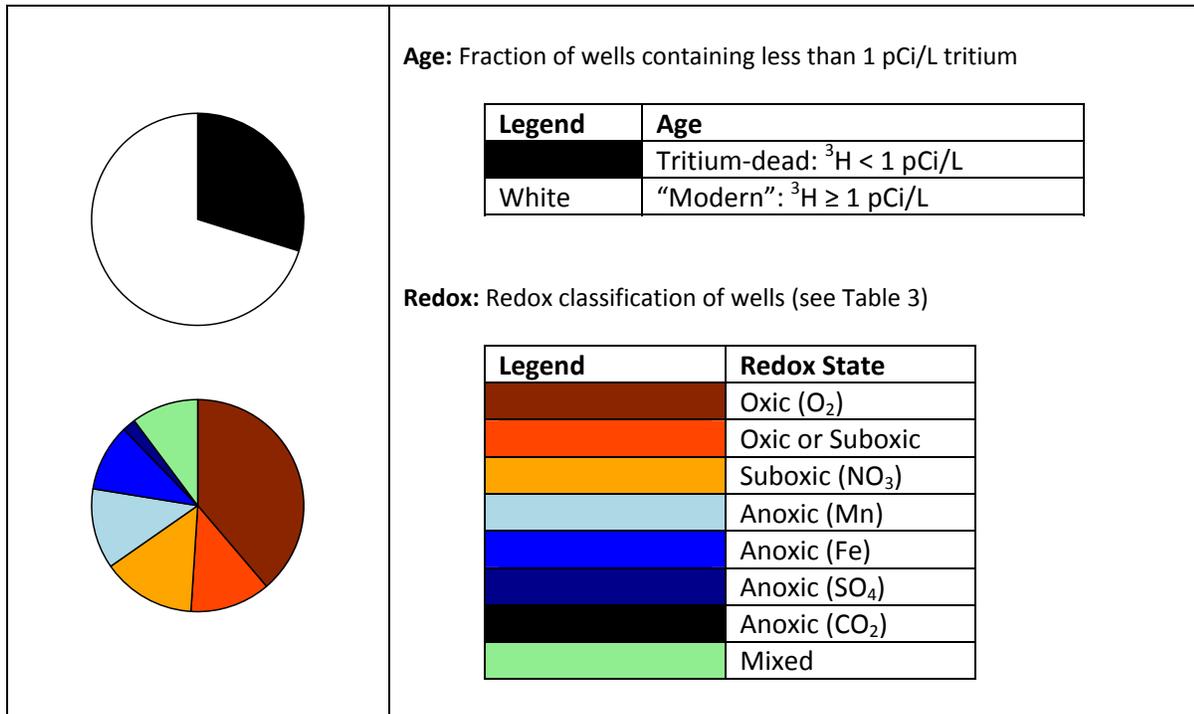
VOCs and pesticides are detected in groundwater with tritium concentrations below 1 pCi/L at a frequency of about 4%, despite their non-natural origin. Chloroform is the most frequently detected compound in this category, and may be related to well maintenance activity rather than transport through porous media. Tritium dead wells with detections of anthropogenic compounds are good candidates for further study, such as analysis of additional isotopic or chemical indicators of a modern component.

5 APPENDICES

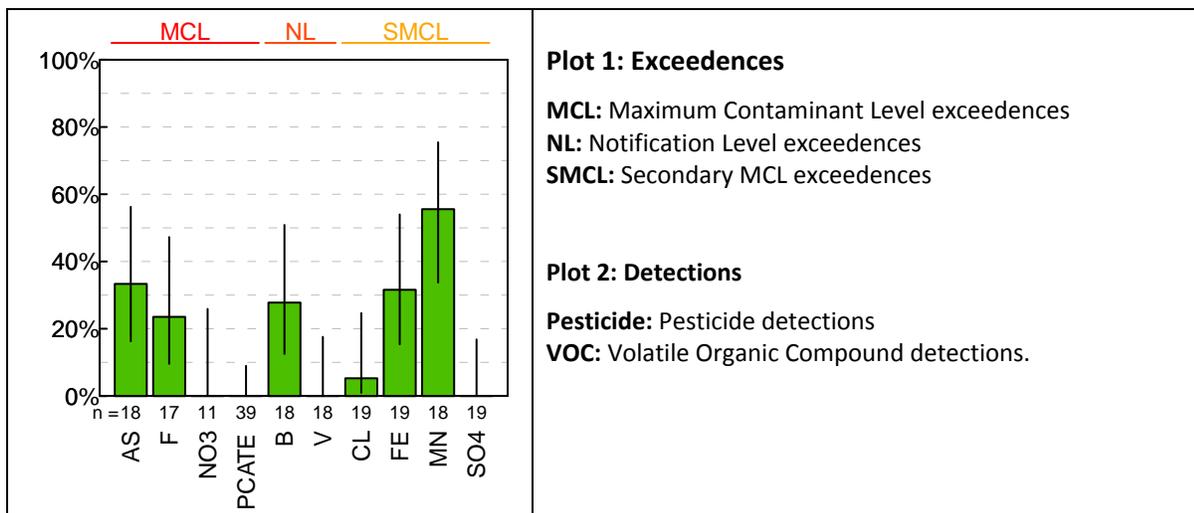
5.1 Results for Individual Provinces

The following sections summarize the findings for the eight groundwater provinces of California for which data were available. The proportion tritium-dead groundwater and redox proportions are presented in pie-charts. Bar-graphs illustrate the number of detections of constituents with natural and anthropogenic sources (including the statistical uncertainty as a result of the sample size), and the number of anthropogenic constituents (VOCs, pesticides) that were detected.

Legend for Groundwater Age/Redox Indices



Legend for Water Quality Indices



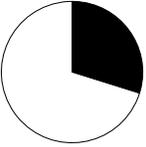
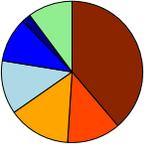
5.1.1 North Coast Ranges

	<p>Age: The North Coast Ranges (NCR) groundwater province includes the Priority Basin study units North Coast Ranges and North SF Bay. Of the 96 ³H analysis, 47% contained less than 1 pCi/L. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 37% and 57%.</p>
	<p>Redox: Relatively few tritium-dead wells in the NCR province (39%) produce oxic or suboxic groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. Anoxic (Mn, Fe, SO₄ or CO₂ reducing) groundwater (56%) is more abundant in this province. One well (representing 6%) produced “mixed” groundwater in terms of redox conditions, containing both indicators of oxic conditions (oxygen or nitrate) and anoxic conditions (Mn, Fe).</p>

	<p>MCL: In over 30% of wells in the NCR province the concentration of arsenic exceeds the MCL of 10 µg/L. In 4 wells (22%) the concentration of fluoride exceeds the MCL of 2 mg/L. All four wells are located in the North San Francisco Bay Hydrothermal Study area (Kulongoski, 2010). Neither nitrate nor perchlorate (PCATE) was detected above the MCL.</p>
	<p>NL: Boron concentrations exceed the NL of 1 mg/L in nearly 30% of wells. Vanadium was not detected above the NL.</p>
	<p>SMCL: Chloride concentrations exceed the SMCL of 500 mg/L in 5% of wells. Due to the large proportion of anoxic groundwater, iron and manganese concentrations are found above the SMCL in 32% and 56% of the wells in this province. Sulfate was not detected above the SMCL.</p>

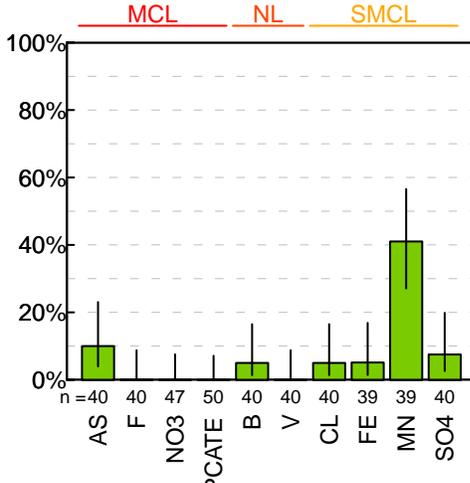
	<p>Pesticide: No pesticides were detected in tritium-dead wells.</p>
	<p>VOC: Only one well had a VOC detection. TCLME was detected above a reporting level of 0.04 µg/L.</p>
	<p><i>Of the 45 tritium-dead wells for which pesticide and VOC analyses were available, only one well had a VOC or pesticide detection.</i></p>

5.1.2 South Coast Ranges

Age: The South Coast Ranges (SCR) groundwater province includes the Priority Basin study units Coastal, Interior, Monterey Bay/Salinas, Santa Cruz Mountains and San Francisco Bay. Of the 238 ³H analyses, 30% contained less than 1 pCi/L. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 24% and 36%. This is significantly lower than the fraction of tritium-dead wells in the North Coast Ranges province.

Redox: A majority of tritium-dead wells in the SCR province produce oxic or suboxic (65%) groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. Anoxic (Mn, Fe, SO₄ or CO₂ reducing) groundwater (24%) is less abundant in this province. Five wells (representing 10%) produced "mixed" groundwater in terms of redox conditions, containing both indicators of oxidic conditions (oxygen or nitrate) and anoxic conditions (Mn, Fe).

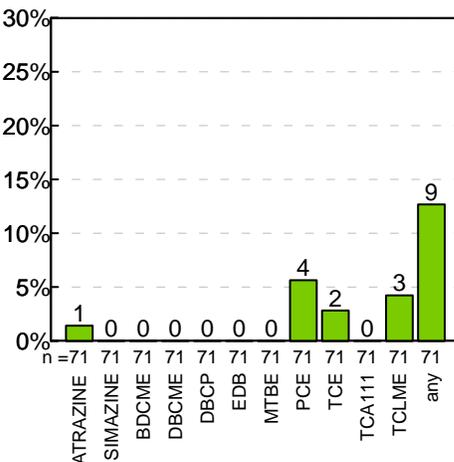


Chemical	n	MCL Exceedance (%)	NL Exceedance (%)	SMCL Exceedance (%)
AS	40	10	0	0
F	40	0	0	0
NO3	47	0	0	0
PCATE	50	0	0	0
B	40	5	5	0
V	40	0	0	0
CL	40	5	0	5
FE	39	5	0	5
MN	39	40	0	40
SO4	40	8	0	8

MCL: Arsenic exceeds the MCL of 10 µg/L in 10% of wells in the SCR province. Neither fluoride, nitrate nor perchlorate was detected above the MCL.

NL: Boron concentrations exceed the NL of 1 mg/L in 5% of wells. Vanadium was not detected above the NL.

SMCL: Chloride concentrations exceed the SMCL of 500 mg/L in 5% of wells. Iron concentrations are found above the SMCL in 5% of the wells in this province, manganese in over 40%. Sulfate was detected above the SMCL of 500 mg/L in 8% of the wells.



Chemical	n	Detection Rate (%)
ATRAZINE	71	1.4
SIMAZINE	71	0
BDCME	71	0
DBCME	71	0
DBCP	71	0
EDB	71	0
MTBE	71	0
PCE	71	5.6
TCE	71	2.8
TCA11	71	0
TCLME	71	4.2
any	71	12.7

Pesticide: Atrazine was detected in 1 well above a reporting level of 0.007 µg/L.

VOC: PCE, TCE and TCLME were detected in 4, 2 and 3 wells, respectively. One PCE detection concurred with a TCE detection. TCLME was detected above a reporting level of 0.04 µg/L in 3 wells.

Either pesticides or VOCs were detected in 9 of the 71 tritium-dead wells (13%) for which pesticide and VOC analyses were available.

5.1.3 Transverse and Peninsular Range

	<p>Age: The Transverse and Peninsular Range (TPR) groundwater province includes the Priority Basin study units Big Bear, San Gabriel Mountains, San Gabriel / San Fernando, Santa Ana, Santa Barbara, Santa Clara River Valley and Southern Coastal Plain. Of the 242 ³H analyses, 22% contained less than 1 pCi/L. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 17% and 28%.</p>
	<p>Redox: A majority of tritium-dead wells in the TPR province produces oxic or suboxic (60%) groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. The remainder of the tritium-dead wells (40%) produce anoxic (Mn, Fe, SO₄ or CO₂ reducing) groundwater. No wells produced “mixed” groundwater in terms of redox conditions.</p>

<table border="1"> <caption>Chemical Concentration Data</caption> <thead> <tr> <th>Chemical</th> <th>n</th> <th>MCL (%)</th> <th>NL (%)</th> <th>SMCL (%)</th> </tr> </thead> <tbody> <tr><td>AS</td><td>24</td><td>4</td><td>0</td><td>0</td></tr> <tr><td>F</td><td>24</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>NO3</td><td>24</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>PCATE</td><td>47</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>B</td><td>24</td><td>0</td><td>8</td><td>13</td></tr> <tr><td>V</td><td>24</td><td>0</td><td>4</td><td>0</td></tr> <tr><td>CL</td><td>24</td><td>0</td><td>0</td><td>13</td></tr> <tr><td>FE</td><td>24</td><td>0</td><td>0</td><td>29</td></tr> <tr><td>MN</td><td>24</td><td>0</td><td>0</td><td>45</td></tr> <tr><td>SO4</td><td>24</td><td>0</td><td>0</td><td>13</td></tr> </tbody> </table>	Chemical	n	MCL (%)	NL (%)	SMCL (%)	AS	24	4	0	0	F	24	0	0	0	NO3	24	0	0	0	PCATE	47	0	0	0	B	24	0	8	13	V	24	0	4	0	CL	24	0	0	13	FE	24	0	0	29	MN	24	0	0	45	SO4	24	0	0	13	<p>MCL: Arsenic was detected above the MCL of 10 µg/L in only 4% of wells. Neither fluoride, nitrate nor perchlorate was detected above the MCL.</p> <p>NL: Boron and vanadium concentrations exceed the NL in 8% and 4% of wells.</p> <p>SCML: Chloride concentrations exceed the SMCL of 500 mg/L in 13% of wells. Iron and manganese concentrations are found above the SMCL in 29% and over 45% of the wells respectively. Sulfate was detected above the SMCL of 500 mg/L in 13% of the wells.</p>
Chemical	n	MCL (%)	NL (%)	SMCL (%)																																																				
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<table border="1"> <caption>Pesticide and VOC Detection Data</caption> <thead> <tr> <th>Chemical</th> <th>n</th> <th>Percentage</th> </tr> </thead> <tbody> <tr><td>ATRAZINE</td><td>53</td><td>2%</td></tr> <tr><td>SIMAZINE</td><td>53</td><td>3%</td></tr> <tr><td>BDCME</td><td>53</td><td>0%</td></tr> <tr><td>DBCME</td><td>53</td><td>1%</td></tr> <tr><td>DBCP</td><td>53</td><td>0%</td></tr> <tr><td>EDB</td><td>53</td><td>0%</td></tr> <tr><td>MTBE</td><td>53</td><td>1%</td></tr> <tr><td>PCE</td><td>53</td><td>3%</td></tr> <tr><td>TCE</td><td>53</td><td>2%</td></tr> <tr><td>TCA111</td><td>53</td><td>0%</td></tr> <tr><td>TCLME</td><td>53</td><td>3%</td></tr> <tr><td>any</td><td>53</td><td>9%</td></tr> </tbody> </table>	Chemical	n	Percentage	ATRAZINE	53	2%	SIMAZINE	53	3%	BDCME	53	0%	DBCME	53	1%	DBCP	53	0%	EDB	53	0%	MTBE	53	1%	PCE	53	3%	TCE	53	2%	TCA111	53	0%	TCLME	53	3%	any	53	9%	<p>Pesticide: Atrazine was detected in 2 wells above a reporting level of 0.007 µg/L. Simazine was detected in the same wells above a reporting level of 0.006 µg/L, and in one additional well.</p> <p>VOC: Other VOC detections included DBCME, MTBE, PCE, TCE and TCLME in up to 3 wells.</p> <p><i>Either pesticides or VOCs were detected in 9 of the 53 tritium-dead wells (17%) for which pesticide and VOC analyses were available</i></p>
Chemical	n	Percentage																																						
ATRAZINE	53	2%																																						
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TCE	53	2%																																						
TCA111	53	0%																																						
TCLME	53	3%																																						
any	53	9%																																						

5.1.4 San Diego

	<p>Age: The San Diego (SD) groundwater province includes the Priority Basin study units San Diego and San Diego Mountains. Of the 57 ³H analysis, 25% contained less than 1 pCi/L. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 15% and 38%.</p>
	<p>Redox: Nearly all tritium-dead wells in the San Diego province for which sufficient water quality data were available to classify the redox conditions (n=9) produce oxidic or suboxic (89%) groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. One well (11%) produced anoxic (Mn reducing) groundwater. The uncertainty of these proportions is very large (56% - 98% for the proportion oxidic/suboxic groundwater), due to the limited number of analyses.</p>

	<p>MCL: Neither fluoride, nitrate nor perchlorate was detected above the MCL in any of the tritium-dead wells in the San Diego Province. However, the 95% confidence interval of the proportion (0%) extends to 30% of the wells.</p> <p>NL: Boron and vanadium are detected above the NL in two different wells.</p> <p>SMCL: Chloride, iron and sulfate concentrations are not found above the SMCL in the San Diego Province. Manganese was detected above the SMCL of 50 µg/L in the one Mn-anoxic well.</p>
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	<p>Pesticide: Simazine was detected in three wells above a reporting level of 0.006 µg/L (21%).</p> <p>VOC: In a different well, MTBE was detected above the reporting limit of 0.2 µg/L.</p> <p><i>Because of the low total number of wells, these four detections add up to a proportion of 29%.</i></p>
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5.1.5 Central Valley

Age: The Central Valley (CV) groundwater province includes the Priority Basin study units Central East Side, Central Sacramento, Kern, Madera/Chowchilla, North Sacramento, North San Joaquin, South Sacramento, Southeast San Joaquin and Western San Joaquin Valley. Of the 517 ³H analyses, 23% contained less than 1 pCi/L (n=117). Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 19% and 27%.

Redox: A large majority of tritium-dead wells in the Central Valley province produce oxidic or suboxic (73%) groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. 23% of the tritium-dead wells produce anoxic (Mn, Fe, SO₄ or CO₂ reducing) groundwater. Three wells (4%) produced “mixed” groundwater in terms of redox conditions.

Element	n	MCL (%)	NL (%)	SMCL (%)
AS	76	21	0	0
F	76	0	0	0
NO3	68	0	0	0
PCATE	72	0	0	0
B	78	0	5	0
V	76	0	1	0
CL	78	0	0	3
FE	76	0	0	3
MN	76	0	0	24
SO4	76	0	0	1

MCL: Arsenic was detected above the MCL of 10 µg/L in 21% of wells (13% - 31% confidence interval). Neither fluoride, nitrate nor perchlorate was detected above the MCL.

NL: Boron and vanadium concentrations exceed the Notification Level (NL) in 5% and 1% of wells, respectively.

SCML: Chloride and iron concentrations exceed the SMCL in 3% of wells. Manganese concentrations are found above the SMCL of 50 µg/L in 24% of the wells in this province. Sulfate was detected above the SMCL of 500 mg/L in 1% of the wells.

Compound	n	Detection (%)
ATRAZINE	117	0
SIMAZINE	117	2
BDCME	117	0
DBCME	117	1
DBCP	117	0
EDB	117	0
MTBE	117	0
PCE	117	0
TCE	117	0
TCA111	117	0
TCLME	117	3
any	117	5

Pesticide: Simazine was detected in two wells above a reporting level of 0.006 µg/L.

VOC: DBCME and TCLME were detected in 1 and 3 wells, respectively.

Either pesticides or VOCs were detected in 5 of the 117 tritium-dead wells (4%).

5.1.6 Sierra Nevada

	<p>Age: The Sierra Nevada (SN) groundwater province includes the Priority Basin study units Regional, Central Sierra, Southern Sierra and Tahoe/Martis. Of the 124 ³H analyses, 23% were less than 1 pCi/L. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 16% and 32%.</p>
	<p>Redox: Nearly all tritium-dead wells in the SN province produce oxic or suboxic (86%) groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. Two tritium-dead wells (9%) produce anoxic (Fe reducing) groundwater and one well (5%) produced "mixed" groundwater in terms of redox conditions.</p>

<table border="1"> <caption>Ion Concentration Data</caption> <thead> <tr> <th>Ion</th> <th>n</th> <th>MCL (%)</th> <th>NL (%)</th> <th>SMCL (%)</th> </tr> </thead> <tbody> <tr><td>AS</td><td>21</td><td>29</td><td>0</td><td>0</td></tr> <tr><td>F</td><td>21</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>NO3</td><td>21</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>PCATE</td><td>25</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>B</td><td>21</td><td>0</td><td>5</td><td>0</td></tr> <tr><td>V</td><td>21</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>CL</td><td>21</td><td>0</td><td>0</td><td>14</td></tr> <tr><td>FE</td><td>21</td><td>0</td><td>0</td><td>5</td></tr> <tr><td>MN</td><td>21</td><td>0</td><td>0</td><td>14</td></tr> <tr><td>SO4</td><td>21</td><td>0</td><td>0</td><td>5</td></tr> </tbody> </table>	Ion	n	MCL (%)	NL (%)	SMCL (%)	AS	21	29	0	0	F	21	0	0	0	NO3	21	0	0	0	PCATE	25	0	0	0	B	21	0	5	0	V	21	0	0	0	CL	21	0	0	14	FE	21	0	0	5	MN	21	0	0	14	SO4	21	0	0	5	<p>MCL: Arsenic was detected above the MCL of 10 µg/L in 29% of wells. Neither fluoride nor nitrate was detected above the MCL. Perchlorate (PCATE) was not detected above the MCL of 6 µg/L.</p> <p>NL: Boron concentrations exceed the NL in 5% of wells, vanadium is not found above the NL.</p> <p>SCML: Chloride concentrations do not exceed the SCML of 500 mg/L. Iron, manganese and sulfate are found above the SMCL in 5%, 14% and 5% of the wells, respectively.</p>
Ion	n	MCL (%)	NL (%)	SMCL (%)																																																				
AS	21	29	0	0																																																				
F	21	0	0	0																																																				
NO3	21	0	0	0																																																				
PCATE	25	0	0	0																																																				
B	21	0	5	0																																																				
V	21	0	0	0																																																				
CL	21	0	0	14																																																				
FE	21	0	0	5																																																				
MN	21	0	0	14																																																				
SO4	21	0	0	5																																																				

<table border="1"> <caption>Pesticide and VOC Detection Data</caption> <thead> <tr> <th>Compound</th> <th>n</th> <th>Detection (%)</th> </tr> </thead> <tbody> <tr><td>ATRAZINE</td><td>29</td><td>0</td></tr> <tr><td>SIMAZINE</td><td>29</td><td>0</td></tr> <tr><td>BDCME</td><td>29</td><td>0</td></tr> <tr><td>DBCME</td><td>29</td><td>0</td></tr> <tr><td>DBCP</td><td>29</td><td>0</td></tr> <tr><td>EDB</td><td>29</td><td>0</td></tr> <tr><td>MTBE</td><td>29</td><td>0</td></tr> <tr><td>PCE</td><td>29</td><td>9</td></tr> <tr><td>TCE</td><td>29</td><td>0</td></tr> <tr><td>TCA111</td><td>29</td><td>0</td></tr> <tr><td>TCLME</td><td>29</td><td>9</td></tr> <tr><td>any</td><td>29</td><td>18</td></tr> </tbody> </table>	Compound	n	Detection (%)	ATRAZINE	29	0	SIMAZINE	29	0	BDCME	29	0	DBCME	29	0	DBCP	29	0	EDB	29	0	MTBE	29	0	PCE	29	9	TCE	29	0	TCA111	29	0	TCLME	29	9	any	29	18	<p>Pesticide: Pesticides were not detected.</p> <p>VOC: PCE and TCLME were detected above a reporting level of 0.04 µg/L in two different wells</p> <p><i>Either pesticides or VOCs were detected in 2 of the 29 tritium-dead wells (9%) for which pesticide and VOC analyses were available.</i></p>
Compound	n	Detection (%)																																						
ATRAZINE	29	0																																						
SIMAZINE	29	0																																						
BDCME	29	0																																						
DBCME	29	0																																						
DBCP	29	0																																						
EDB	29	0																																						
MTBE	29	0																																						
PCE	29	9																																						
TCE	29	0																																						
TCA111	29	0																																						
TCLME	29	9																																						
any	29	18																																						

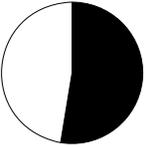
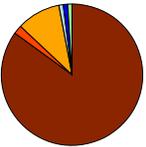
5.1.7 Basin and Range

	<p>Age: The Basin and Range (BR) groundwater province includes the Priority Basin study unit Owens/Indian Wells. A fairly large proportion - 39% -of the 71 ³H results was less than 1 pCi/L. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 28% and 52%.</p>
	<p>Redox: A small majority of tritium-dead wells in the Basin and Range province produces oxic or suboxic (65%) groundwater. These wells contain either dissolved oxygen (>0.5 mg/L), nitrate (>2.25 mg/L) or both. A smaller proportion of tritium-dead wells (23%) produce anoxic (Mn or Fe reducing or methanogenic) groundwater. Three wells (12%) produced “mixed” groundwater in terms of redox conditions.</p>

<table border="1"> <thead> <tr> <th>Chemical</th> <th>n</th> <th>MCL Exceedance (%)</th> <th>NL Exceedance (%)</th> <th>SMCL Exceedance (%)</th> </tr> </thead> <tbody> <tr><td>AS</td><td>26</td><td>23</td><td>0</td><td>0</td></tr> <tr><td>F</td><td>26</td><td>15</td><td>0</td><td>0</td></tr> <tr><td>NO3</td><td>26</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>PCATE</td><td>26</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>B</td><td>26</td><td>0</td><td>38</td><td>0</td></tr> <tr><td>V</td><td>26</td><td>0</td><td>0</td><td>0</td></tr> <tr><td>CL</td><td>26</td><td>0</td><td>0</td><td>12</td></tr> <tr><td>FE</td><td>26</td><td>0</td><td>0</td><td>8</td></tr> <tr><td>MN</td><td>26</td><td>0</td><td>0</td><td>31</td></tr> <tr><td>SO4</td><td>26</td><td>0</td><td>0</td><td>0</td></tr> </tbody> </table>	Chemical	n	MCL Exceedance (%)	NL Exceedance (%)	SMCL Exceedance (%)	AS	26	23	0	0	F	26	15	0	0	NO3	26	0	0	0	PCATE	26	0	0	0	B	26	0	38	0	V	26	0	0	0	CL	26	0	0	12	FE	26	0	0	8	MN	26	0	0	31	SO4	26	0	0	0	<p>MCL: Arsenic was detected above the MCL of 10 µg/L in 23% of wells. Fluoride concentrations exceeded the MCL of 2 mg/L F in 15% of wells. Neither nitrate nor perchlorate was detected above the MCL.</p> <p>NL: In a large proportion of the wells (38%), boron concentrations exceed the NL. Vanadium was not detected above the NL.</p> <p>SMCL: Chloride concentrations exceed the SMCL in 12% of wells, iron in 8%. Manganese concentrations are found above the SMCL in 31% of the wells in this province. Sulfate was not detected above the SMCL of 500 mg/L.</p>
Chemical	n	MCL Exceedance (%)	NL Exceedance (%)	SMCL Exceedance (%)																																																				
AS	26	23	0	0																																																				
F	26	15	0	0																																																				
NO3	26	0	0	0																																																				
PCATE	26	0	0	0																																																				
B	26	0	38	0																																																				
V	26	0	0	0																																																				
CL	26	0	0	12																																																				
FE	26	0	0	8																																																				
MN	26	0	0	31																																																				
SO4	26	0	0	0																																																				

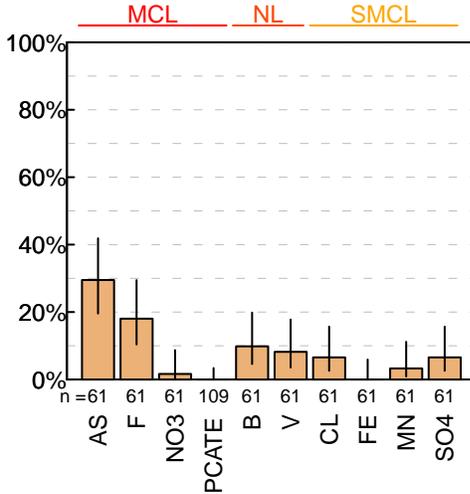
<table border="1"> <thead> <tr> <th>Chemical</th> <th>n</th> <th>Detection (%)</th> </tr> </thead> <tbody> <tr><td>ATRAZINE</td><td>28</td><td>0</td></tr> <tr><td>SIMAZINE</td><td>28</td><td>0</td></tr> <tr><td>BDCME</td><td>28</td><td>0</td></tr> <tr><td>DBCME</td><td>28</td><td>0</td></tr> <tr><td>DBCP</td><td>28</td><td>0</td></tr> <tr><td>EDB</td><td>28</td><td>0</td></tr> <tr><td>MTBE</td><td>28</td><td>0</td></tr> <tr><td>PCE</td><td>28</td><td>0</td></tr> <tr><td>TCE</td><td>28</td><td>0</td></tr> <tr><td>TCA111</td><td>28</td><td>0</td></tr> <tr><td>TCLME</td><td>28</td><td>4</td></tr> <tr><td>any</td><td>28</td><td>4</td></tr> </tbody> </table>	Chemical	n	Detection (%)	ATRAZINE	28	0	SIMAZINE	28	0	BDCME	28	0	DBCME	28	0	DBCP	28	0	EDB	28	0	MTBE	28	0	PCE	28	0	TCE	28	0	TCA111	28	0	TCLME	28	4	any	28	4	<p>Pesticide: No pesticides were detected.</p> <p>VOC: TCLME was the only VOC that was detected, and it was detected in a single well.</p> <p><i>TCLME was the only VOC that was detected, in a single tritium-dead well (4%) in the Basin and Range province.</i></p>
Chemical	n	Detection (%)																																						
ATRAZINE	28	0																																						
SIMAZINE	28	0																																						
BDCME	28	0																																						
DBCME	28	0																																						
DBCP	28	0																																						
EDB	28	0																																						
MTBE	28	0																																						
PCE	28	0																																						
TCE	28	0																																						
TCA111	28	0																																						
TCLME	28	4																																						
any	28	4																																						

5.1.8 Desert

Age: The Desert (D) groundwater province includes the Priority Basin study units Antelope Valley, Borrego, Central Desert, Low Use, Coachella, Colorado and Mojave. With 53% of the 213 wells containing less than 1 pCi/L ³H, the Desert province has the highest proportion of tritium-dead wells of all of the provinces in California. Given the number of analyses, the actual proportion of tritium-dead public supply wells in the entire province could range between 46% and 59%.

Redox: All but three tritium-dead wells in the Desert province produce oxic or suboxic groundwater (97%). Dissolved oxygen was measured above 0.5 mg/L in 85% of all wells, nitrate above 2.25 mg/L in 12%. Two tritium-dead wells (2%) produce anoxic (Mn or Fe reducing) groundwater and one well produced "mixed" groundwater in terms of redox conditions.

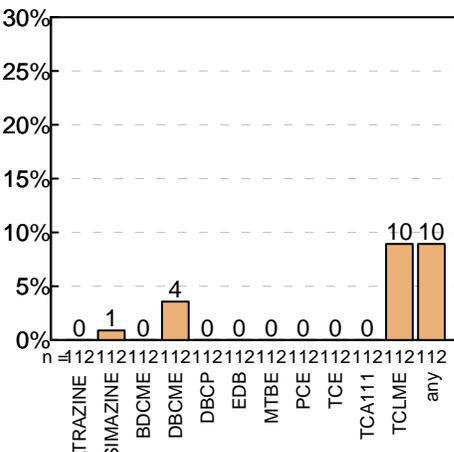


Chemical	n	MCL (%)	NL (%)	SMCL (%)
AS	61	30	0	0
F	61	18	0	0
NO3	61	1	0	0
PCATE	109	0	0	0
B	61	10	0	0
V	61	8	0	0
CL	61	7	0	0
FE	61	0	0	0
MN	61	3	0	0
SO4	61	7	0	0

MCL: Arsenic was detected above the MCL of 10 µg/L in 30% of wells. Fluoride above the MCL of 2 mg/L was found in 18% of wells. This is the only province in which nitrate was measured above the MCL of 45 mg/L (as NO₃) - in one well. Perchlorate (PCATE) was not detected above the MCL.

NL: Boron and vanadium concentrations exceed the NL in 10% and 8% of wells, respectively.

SMCL: Chloride concentrations exceed the SMCL of 500 mg/L in 7% of wells. The iron concentration in the one iron reducing well does not exceed the SMCL of 300 µg/L. Manganese concentrations are found above the SMCL in 3% of the wells in this province. Sulfate was detected above the SMCL of 500 mg/L in 7% of the wells.



Chemical	n	Detection (%)
ATRAZINE	112	0
SIMAZINE	112	1
BDCME	112	0
DBCME	112	4
DBCP	112	0
EDB	112	0
MTBE	112	0
PCE	112	0
TCE	112	0
TCA111	112	0
TCLME	112	10
any	112	10

Pesticide: Simazine was detected in one well above a reporting level of 0.006 µg/L.

VOC: DBCME was detected above a reporting level of 0.12 µg/L in 4 wells (4%), TCLME was detected above a reporting level of 0.04 µg/L in all 10 wells in which pesticides or VOCs were detected.

Either pesticides or VOCs were detected in 10 of the 112 tritium-dead wells (9%) for which pesticide and VOC analyses were available.

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http://www.swrcb.ca.gov/water_issues/programs/gama/report_depot.shtml

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