

GROUNDWATER AMBIENT
MONITORING AND ASSESSMENT
(GAMA)
Domestic Well Project
Groundwater Quality Data Report
TULARE County focus Area



Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

California State Water Resources Control Board
Groundwater Protection Section
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ABBREVIATIONS AND ACRONYMS

CDPH	California Department of Public Health
DWR	California Department of Water Resources
EC	Electrical Conductivity
GAMA	Groundwater Ambient Monitoring and Assessment
LLNL	Lawrence Livermore National Laboratory
MCL	Maximum Contaminant Level
NL	Notification Level
SMCL	Secondary Maximum Contaminant Level
SWRCB	State Water Resources Control Board
TDS	Total Dissolved Solids
VOCs	Volatile Organic Compounds
µg/L	Micrograms per Liter
mg/L	Milligrams per Liter

ABSTRACT

The State Water Resources Control Board (State Water Board) established the Groundwater Ambient Monitoring and Assessment (GAMA) Program in 2000. Private domestic wells in Tulare County were sampled in 2006 as part of the GAMA Domestic Well Project. Tulare County was selected for sampling due to the large number of domestic wells located within the county and the availability of well-owner data. A total of 181 wells were sampled by Water Board staff, primarily in the valley and foothill areas of the county.

Groundwater samples were analyzed by an accredited environmental laboratory for commonly observed chemical constituents such as bacteria (total and fecal coliform), inorganic parameters (metals, major anions and general minerals), and volatile organic compounds (VOCs). Test results were compared against three public drinking water standards established by the California Department of Public Health (CDPH): primary maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and notification levels (NLs). These water quality standards are used for comparison purposes only, since private domestic well water quality is not regulated by the State of California. A total of twenty-two constituents were detected at concentrations above public drinking water standards. Fourteen constituents were detected above a primary MCL, five constituents were above an SMCL, and three were above NLs.

The fourteen constituents were detected above MCLs included total and fecal coliform bacteria, arsenic, beryllium, chromium, nickel, nitrate, nitrite, perchlorate, thallium, 1,2-dibromo-3-chloropropane (DBCP), gross alpha activity, combined radium activity, and uranium activity. Nitrate was the most frequently detected chemical above an MCL, and was detected in 75 wells at concentrations greater than or equal to the MCL of 10 mg/L (nitrate as N). Total coliform bacteria were present in 60 wells, and fecal coliform bacteria were present in 13 wells. DBCP and thallium were detected at concentrations above the MCL in eight and six wells, respectively. All other constituents detected above an MCL were observed in three or fewer wells.

The five chemicals were detected at concentrations above SMCLs, including aluminum, iron, manganese, total dissolved solids (TDS), and zinc. The chemicals detected above an SMCL were all observed in four or fewer wells. Three chemicals were detected above NLs: boron, vanadium, and 1,2,3-trichloropropane. Vanadium was detected in 14 wells at concentrations greater than the NL of 50 µg/L. 1,2,3-trichloropropane and boron were detected above the NL in a single well each.

INTRODUCTION

More than 95 percent of Californians get their drinking water from a public or municipal source - these supplies are typically treated to ensure that the water is safe to drink. However, private domestic wells supply drinking water to approximately 1.6 million Californians. Those served by public or municipal supplies should be concerned about groundwater quality too, as groundwater supplies part or all of the water delivered to approximately 15 million municipal public water supply users. Contaminated groundwater results in treatment costs, well closures, and new well construction, which increases costs for consumers.

Groundwater is also an important source of irrigation and industrial supply water. Reliance upon this resource is expected to increase in the future, in part due to increased agricultural and industrial demand, drought, climate change, and population/land-use changes. Consequently, there are growing concerns regarding groundwater quality in California, and whether decreases in quality will affect the availability of this resource. Since the 1980s, over 8,000 public groundwater drinking water sources have been shut down – some due to the detection of chemicals such as nitrate, arsenic, or methyl tert-butyl ether (MTBE).

The State Water Board created the Groundwater Ambient Monitoring and Assessment (GAMA) Program to address public concerns over groundwater quality. The primary objectives of the GAMA Program are to improve comprehensive statewide groundwater monitoring and to increase the public availability of groundwater quality information. The data gathered by GAMA highlight regional and local groundwater quality concerns, and may be used to evaluate whether there are specific chemicals of concern in specific areas throughout the state. The GAMA Program consists of four current projects:

- **Domestic Well Project:** A voluntary groundwater monitoring project that provides water quality information to private (domestic) well owners. To date, the Domestic Well Project has sampled over 1,000 private domestic wells in five county focus areas: Yuba (2002), El Dorado (2003-2004), Tehama (2005), Tulare (2006), and San Diego (2008-2009). State Water Board staff sample the participants' well at no cost to the well owner.
- **Priority Basin Project:** A comprehensive, statewide groundwater monitoring program that primarily uses public groundwater supply wells in high-use, or "priority," groundwater basins. These high-use basins contain more than 95% of all public groundwater supply wells. As of April 2009, the Priority Basin Project has sampled over 1,700 wells in over 90 different groundwater basins. The United States Geological Survey (USGS) is the project technical lead, with support from Lawrence Livermore National Laboratory (LLNL).
- **Special Studies Project:** Focuses on identification of contaminant sources and assessing the effects of remediation in private domestic and public supply wells. The Special Studies Project also studies aquifer storage and recovery projects. LLNL is the project technical lead.
- **GeoTracker GAMA:** A publicly-accessible, map-based on-line query tool that helps users find useful groundwater quality data and information.

This Data Summary Report summarizes Domestic Well Project results from 181 domestic wells sampled in the Tulare County Focus Area collected during 2006. Sampled well locations are shown in Figure 1.

Domestic Well Project Overview

Domestic wells differ from public drinking water supply wells in several respects; domestic wells are generally shallower, are privately owned, supply a single household, and tend to be located in more rural settings where public water supply systems are not available. Census data indicate that there are over 600,000 private domestic wells in California, supplying water to approximately 1.6 million Californians. Tulare County has more than 20,000 domestic wells alone. Due to low pumping rates, the volume of

groundwater use by domestic well owners is estimated at 2 percent of the total groundwater volume used in California. The State of California does not regulate water quality in private domestic wells. As a result, many well owners do not have an accurate assessment of their own well water quality.

Domestic well owners are responsible for testing the water quality of their well to know if it is safe for consumption. Domestic wells typically produce very high quality drinking water. However, poor well construction or placement close to a potential source of contamination can result in poor water quality. Chemicals from surface-related activities such as industrial spills, leaking underground fuel tanks, and agricultural applications can impact groundwater. Biological pathogens from sewers, septic systems, and animal facilities can infiltrate into groundwater. Naturally-occurring chemicals can also contaminate groundwater supplies.

Water quality testing results from the Domestic Well Project are compared to existing groundwater information and public supply well data to help assess California groundwater quality and to better identify issues that may impact private domestic well water.

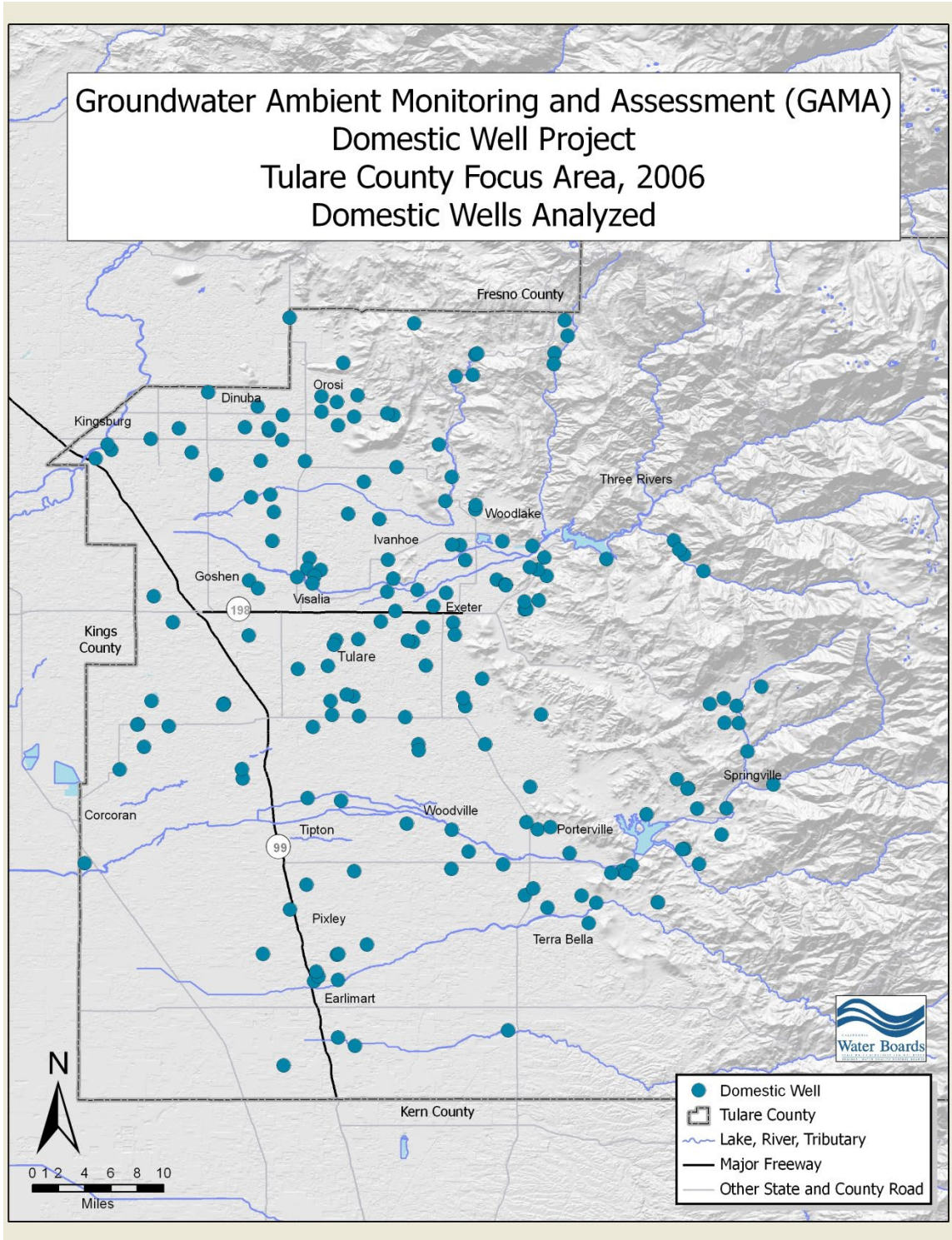


FIGURE 1. LOCATION OF SAMPLED DOMESTIC WELLS

TULARE COUNTY BACKGROUND

Tulare County is part of one of the nation's most productive agricultural regions. The major economic activity in the county is agriculture, and agricultural output from Tulare County alone accounts for approximately 35% of the state's total agricultural economy. With over \$3.5 billion in annual agricultural revenues, Tulare County is the most productive county in the United States in terms of revenue. Tulare has been the number one milk-producing county in the United States since 2003.

HYDROGEOLOGIC SETTING

The western half of Tulare County is comprised of flat valley lands of the southern San Joaquin Valley, while rolling foothills associated with the Sierra Nevada Mountains characterize its eastern half. Topography consists of flat valley land, gently rolling foothills, and canyons of the Sierra Nevada Mountains. Water bearing units within Tulare County include younger and older alluvium, flood-basin deposits, lacustrine, marsh and continental deposits. The older alluvium is moderately to highly permeable and is the major aquifer for Tulare County. Regional groundwater flow is generally southwestward; however, pumping can affect local groundwater flow direction.

Tulare County is located within the San Joaquin Valley Groundwater Basin. The California Department of Water Resources (DWR) Bulletin 118 identifies several groundwater subbasins in Tulare County, including the following:

- **Kings Subbasin**: The Kings Subbasin underlies northern Tulare County west of the Sierra foothills. The groundwater system consists of unconsolidated deposits of alluvium, lacustrine sediments, and flood plain deposits. Approximately 17% of the sampled wells were located in the Kings Subbasin.
- **Kaweah Subbasin**: The Kaweah Subbasin underlies central Tulare County west of the Sierra foothills. The major water-bearing units are made up of unconsolidated Pliocene, Pleistocene, and Holocene-age sediments. Continental lacustrine and marsh deposits are found in the western portion of the subbasin, closer to the Tulare Lake bed. Clay beds associated with lacustrine deposits form aquitards that influence the vertical and possibly horizontal movement of local groundwater. The most well-known clay bed is the Corcoran clay, which underlies the western half of the Kaweah Subbasin from 200 to 500 feet below ground surface (bgs). Paleosols or similar oxidized deposits outcrop in the eastern parts of the subbasin closer to the Sierra foothills. The county's population centers of Visalia and Tulare are located within the Kaweah Subbasin. Approximately 44% of the sampled wells were located in the Kaweah Subbasin.
- **Tule Subbasin**: The Tule Subbasin underlies southern Tulare County west of the Sierra foothills. Water bearing deposits in the Tule Subbasin are comprised of flood-basin deposits, alluvium, the Tulare Formation, and undifferentiated continental sediments deposited during the Pliocene to Holocene. The Tulare Formation contains the Corcoran Clay, which is the major confining unit in the subbasin. Approximately 20% of the sampled wells were located in the Tule Subbasin.
- **Foothills**: The Foothills area is not a DWR-defined basin. It is comprised of wells located east of the valley portion of Tulare County in the higher-elevation. The water bearing unit is generally fractured crystalline rock associated with uplift and emplacement of the Sierra Nevada Mountains. Approximately 19% of the sampled wells were located in the foothills.

In Tulare County, municipal and irrigation wells are typically completed to a total depth of 100 to 500 feet bgs, except for within the Tule Subbasin where well depths range between 200 to 1,400 feet bgs (DWR, 2004). Groundwater recharge in the county occurs through river and stream seepage, percolation of irrigation water, canal seepage, and intentional recharge. Land subsidence of up to 16 feet occurred due to deep compaction of fine-grained units. This subsidence is thought to be due to groundwater withdrawal.

Well Construction Data

The completed depths of wells sampled in Tulare County as part of the Domestic Well Project are shown in Table 1 (well construction data was available for 141 of the 181 sampled wells). The data suggest that the shallow aquifer system provides adequate water supply for domestic use. Over 50% of the wells sampled as part of the Domestic Well Project were completed at a depth less than 200 feet.

TABLE 1: DOMESTIC WELL DEPTHS GAMA DOMESTIC WELL PROJECT, TULARE COUNTY FOCUS AREA. NOTE THAT WELL DEPTH DATA IS NOT AVAILABLE FOR ALL WELLS.

Total Well Depth (feet bgs)	Number of Wells
0-24	1
25-49	1
50-74	8
75-99	19
100-124	9
125-149	18
150-174	14
175-199	13
200-224	5
225-249	8
250-274	7
275-299	9
300-324	11
325-349	0
350-374	1
375-400	4
400-900	12

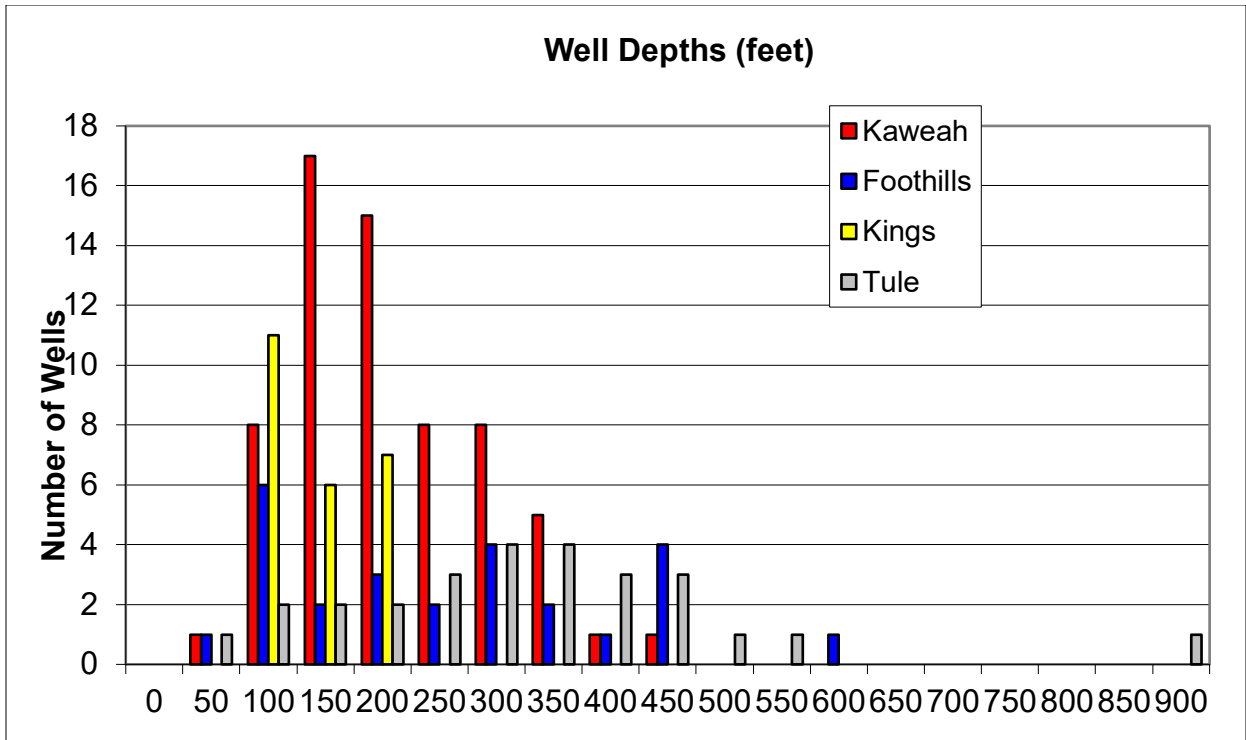


FIGURE 2. WELL DEPTH HISTOGRAM BY SUBBASIN

The depths of wells sampled as part of the Domestic Well Project were grouped by subbasin.

- Wells sampled in the Kaweah Subbasin are generally completed to depths between 100 and 250 feet bgs. However, a significant number of wells in the Kaweah Subbasin are completed at depths greater than 250 feet bgs.
- Wells sampled in the Kings Subbasin are generally completed at shallower depths – all sampled wells are less than 200 feet bgs.
- Wells sampled in the Tule Subbasin are in general deeper than wells drilled in other parts of the county. Approximately 68% of wells sampled in the Tule Subbasin are completed to depths greater than 250 feet bgs, suggesting that either depth to groundwater is greater or that domestic well owners are avoiding shallower groundwater in this subbasin.
- There is no discernable pattern observed in wells sampled in the Foothills area, where both very shallow and very deep wells are observed.

METHODS

Well Selection

Tulare County was selected by GAMA due to the large number of domestic wells within the county and the availability of electronic well owner data. Based on a 1999 survey by the State of California, Department of Finance census, over 20,000 private domestic wells are located in Tulare County. Tulare County is the eighth largest user of domestic well water in California, based upon volume of withdrawals (Figure 3).

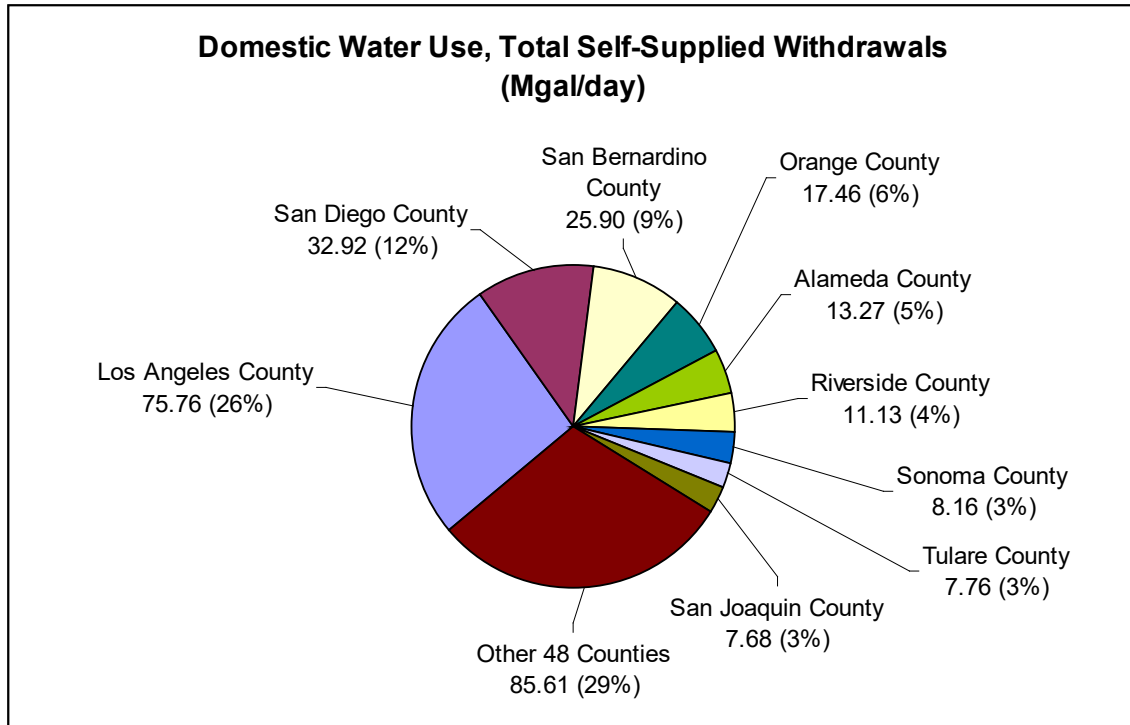


FIGURE 3. TOP 10 CALIFORNIA COUNTIES, VOLUMN OF DOMESTIC WATER USE

The Tulare County Department of Health and Human Services provided GAMA staff with an electronic database containing the names, mailing addresses, and parcel map book numbers of domestic well owners. Approximately 1,500 of these domestic well owners were mailed a brochure in Spanish and English containing information about the GAMA well testing program and inviting them to participate. A total of 181 domestic well owners volunteered to have their well tested.

Sample and Data Collection

Well construction information was obtained from either well owners or well completion reports (well logs). Observations at each well noted the location of nearby septic systems, large-scale agriculture, or livestock enclosures that could result in contamination of the well. Well locations were recorded using a Geographic Positioning Satellite (GPS) unit. Water temperature, pH, and specific electrical conductance were measured and documented in the field.

Groundwater samples were collected as close to the well head as possible. Most often the sample was collected from a faucet or spigot just before or after the pressure tank. New nitrile gloves were worn by field staff during sample collection to minimize contamination during sampling. Samples were collected in laboratory supplied pre-cleaned bottles, and were stored in an iced cooler until delivery to the lab within 24 hours.

Trip blank and duplicate samples were collected at approximately 10 percent of the well locations. These samples are collected and analyzed to help determine if cross contamination was introduced during sample collection, processing, storage, and/or transportation. All trip blank and duplicate data results were within acceptable range criteria.

Sample Analysis

Groundwater samples were analyzed by Delta Environmental Laboratories in Benicia, California for the following:

- Bacteria (total and fecal coliform)
- Inorganic parameters (metals, major anions and general minerals)
- Volatile organic compounds (VOCs)
- Non-routine analytes: radionuclides, pesticides, perchlorate

Selected groundwater samples were also analyzed by LLNL for the following:

- Stable isotopes of oxygen and hydrogen in water
- Stable isotopes of nitrogen and oxygen in nitrate

Stable isotope results are summarized in the report by LLNL, Appendix B.

RESULTS

Detections Above a Drinking Water Standard

There are no Federal or State water quality standards that regulate private domestic well water quality. The Domestic Well Project has compared the test results to the following public drinking water standards: CDPH primary maximum contaminant levels (MCLs), secondary MCLs (SMCLs), and notification levels (NLs). The MCL is the highest concentration of a contaminant allowed in public drinking water. Primary MCLs address health concerns, while secondary MCLs (SMCLs) address aesthetics, such as taste and odor. NLs are health-based advisory levels for chemicals in public drinking water that have no formal regulatory standards.

Analytes that were detected in one or more wells above a drinking water standard:

- Total and Fecal Coliform Bacteria
- Nitrate (NO_3^-)
- Nitrite
- 1,2-Dibromo-3-Chloropropane (DBCP)
- 1,2,3-Trichloropropane
- Gross alpha activity
- Radium 226+228
- Uranium
- Perchlorate
- Arsenic
- Beryllium
- Boron
- Chromium
- Thallium
- Nickel
- Iron

- Aluminum
- Manganese
- Vanadium
- Zinc
- Total Dissolved Solids (TDS)

A summary of all analytes detected above a drinking water standard is outlined in Table 2. Detailed results of the domestic well sampling are summarized below.

TABLE 2: SUMMARY OF DETECTIONS ABOVE A DRINKING WATER STANDARD. TOTAL NUMBER OF WELLS SAMPLED:181

Constituent Type	Chemical Constituent of Concern	Number of Wells Above Public Drinking Water Standard	Percentage of Wells Above Public Drinking Water Standard	Range of Detections Above Public Drinking Water Standards ¹	Public Drinking Water Standards - MCL ²	Public Drinking Water Standards - SMCL ³	Public Drinking Water Standards - NL ⁴
Bacteria Indicators	Total Coliform	60	33%	NA ⁵	Present		
Bacteria Indicators	Fecal Coliform	13	7%	NA	Present		
Metals	Aluminum	2	1%	275 - 450 µg/L		200 µg/L	
Metals	Arsenic	2	2%	10.4 - 14 µg/L	10 µg/L		
Metals	Beryllium	1	<1%	113 µg/L	4 µg/L		
Metals	Boron	1	<1%	48.4 mg/L			1 mg/L
Metals	Chromium	2	1%	76.7 - 91.9 µg/L	50 µg/L		
Metals	Iron	2	1%	608 - 650 µg/L		300 µg/L	

¹µg/L = micrograms per liter, or parts per billion (ppb); mg/L = milligrams per liter, or parts per million (ppm). A microgram is 1/1000th of a milligram.

² MCL = Division of Drinking Water (DDW-formerly the California Department of Public Health) Primary Maximum Contaminant Level

³ SMCL = DDW Secondary Maximum Contaminant Level

⁴ NL = DDW Notification Level

⁵ NA = Coliform are evaluated on a presence/absence criteria. No range can be determined.

Constituent Type	Chemical Constituent of Concern	Number of Wells Above Public Drinking Water Standard	Percentage of Wells Above Public Drinking Water Standard	Range of Detections Above Public Drinking Water Standards ¹	Public Drinking Water Standards - MCL ²	Public Drinking Water Standards - SMCL ³	Public Drinking Water Standards - NL ⁴
Metals	Manganese	2	1%	93.5 - 172 µg/L		50 µg/L	
Metals	Nickel	3	2%	121 - 213 µg/L	100 µg/L		
Metals	Thallium	6	3%	2.11 - 7.32 µg/L	2 µg/L		
Metals	Vanadium	14	8%	50.1 - 42.9 µg/L			50 µg/L
Metals	Zinc	1	<1%	17.3 mg/L		5 mg/L	
Major Ions & General Chemistry	Nitrate (as N)	72	40%	10.1 - 54 mg/L	10 mg/L		
Major Ions & General Chemistry	Nitrite (as N)	4	2%	1.52 - 4.08 mg/L	1 mg/L		
Major Ions & General Chemistry	Perchlorate	2 (of 30 tested)	6%	7.9 - 13 µg/L	6 µg/L		
Major Ions & General Chemistry	Total Dissolved Solids	4	2%	1,002 - 1,052 mg/L		1,000 mg/L	
Major Ions & General Chemistry	Specific Conductance	4	2%	1,820 - 2,060 µmhos/cm		1,600 µmhos/cm	

Constituent Type	Chemical Constituent of Concern	Number of Wells Above Public Drinking Water Standard	Percentage of Wells Above Public Drinking Water Standard	Range of Detections Above Public Drinking Water Standards ¹	Public Drinking Water Standards - MCL ²	Public Drinking Water Standards - SMCL ³	Public Drinking Water Standards - NL ⁴
Organic Compounds (Pesticides and VOCs ⁶)	1,2-Dibromo 3-chloropropane (DBCP)	8	4%	0.221 - 2.83 µg/L	0.2 µg/L		
Organic Compounds (Pesticides and VOCs)	1,2,3-Trichloropropane	1	<1%	0.8			0.005 µg/L
Radionuclides	Gross Alpha	3 (of 13 tested)	23%	15.1 - 602 pCi/L	15 pCi/L		
Radionuclides	Radium 226+228	1 (of 13 tested)	8%	5.1 pCi/L	5 pCi/L		
Radionuclides	Uranium	1 (of 13 tested)	8%	228 pCi/L	20 pCi/L		

¹µg/L = micrograms per liter, or parts per billion (ppb); mg/L = milligrams per liter, or parts per million (ppm). A microgram is 1/1000th of a milligram.

² MCL = Division of Drinking Water (DDW-formerly the California Department of Public Health) Primary Maximum Contaminant Level

³ SMCL = DDW Secondary Maximum Contaminant Level

⁴ NL = DDW Notification Level

⁵ NA = Coliform are evaluated on a presence/absence criteria. No range can be determined.

⁶ VOCs = volatile organic compounds

Coliform Bacteria

Total coliform bacteria were detected in 60 wells (33% of total samples). Thirteen of the wells with positive total coliform detections also tested positive for fecal coliform (7% of sampled wells). Figure 4 shows the distribution of total and fecal coliform bacteria detected in sampled domestic wells.

General Minerals

General minerals detected in domestic well samples are summarized in Table 3. General minerals include measures of alkalinity, hardness, and total dissolved solids (TDS). All of the general minerals listed in Table 3, with the exception of foaming agents (MBAS), naturally occur in groundwater. However, human activities can sometimes change the concentrations of these minerals in groundwater.

There are no established regulatory levels for many general mineral analytes; only foaming agents (MBAS), EC, and TDS have SMCLs. MBAS, which are typically associated with the presence of detergents, were not detected at a concentration above the MCL. TDS, which is an estimate of the total concentration of all non-settleable (dissolved) components in water, was detected at concentrations above the SMCL (1,000 mg/L) in four wells.

TABLE 3: GENERAL MINERAL RESULTS FOR THE GAMA DOMESTIC WELL PROJECT TULARE COUNTY FOCUS AREA

Analytes	Range of Detected Values (mg/L)	Public Drinking Water Standard (mg/L)	Number of Wells Above Standard
Total Alkalinity (as CaCO ₃)	34 - 660	NA	0
Bicarbonate	41 - 805	NA	0
Carbonate	122	NA	0
Calcium	7.92 - 169	NA	0
Magnesium	0.42 - 93.3	NA	0
Potassium	0.35 - 14.1	NA	0
Sodium	230 - 296	NA	0
Foaming Agents (MBAS)	0.06 - 0.07	0.5 (SMCL)	0
Hardness (Total) as CaCO ₃	19.8 - 608	NA	0
pH, Laboratory	5.48 - 8.39	NA	0
Total Dissolved Solids (TDS)	5.52 – 1,052	1,000 (SMCL)	4

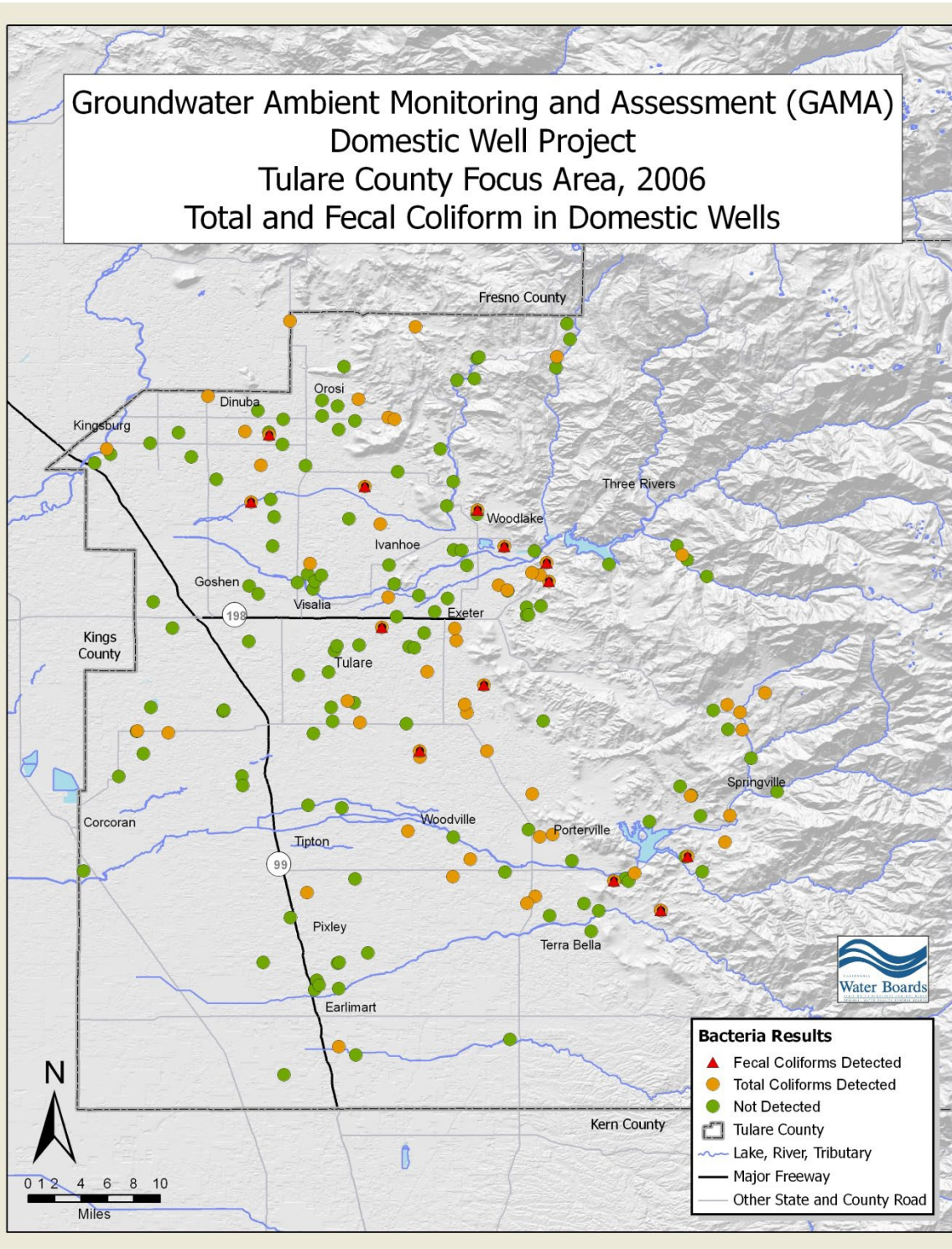


FIGURE 4. TOTAL AND FECAL COLIFORM RESULTS

Major Anions

Major anions detected in domestic well samples are summarized in Table 4.

Nitrate (NO₃⁻), nitrite (NO₂⁻), and perchlorate were detected at concentrations above a drinking water standard. Nitrate was measured as mg/L as N. Nitrate was detected in 173 wells at concentrations ranging from 0.11 to 54 mg/L (as N). Nitrate was detected above the MCL (10 mg/L as N) in 72 wells. The distribution of nitrate in domestic wells is shown on Figure 5. Nitrite was detected in 68 wells, and was detected at concentrations above the MCL (1.0 mg/L) in four wells. Perchlorate was sampled in a smaller subset of wells (30 wells), and was detected above the MCL (0.006 mg/L) in two wells.

TABLE 4: MAJOR ANION RESULTS FOR THE GAMA DOMESTIC WELL PROJECT TULARE COUNTY FOCUS AREA

Analytes	Range of Detected Values (mg/L)	Public Drinking Water Standard (mg/L)	Number of Wells Above Standard
Chloride	1.1 - 341	500 SMCL	0
Fluoride	0.1- 0.7	2 MCL	0
Nitrate (as N)	0.11 - 54	10 MCL	72
Nitrite (as N)	0.1 - 4.1	1 MCL	4
Perchlorate	0.6 - 13	0.006 MCL	2
Sulfate	2.4 - 220	500 SMCL	0

Notes: MCL = Maximum Contaminant Level, SMCL = Secondary Maximum Contaminant Level. mg/L = milligrams per liter

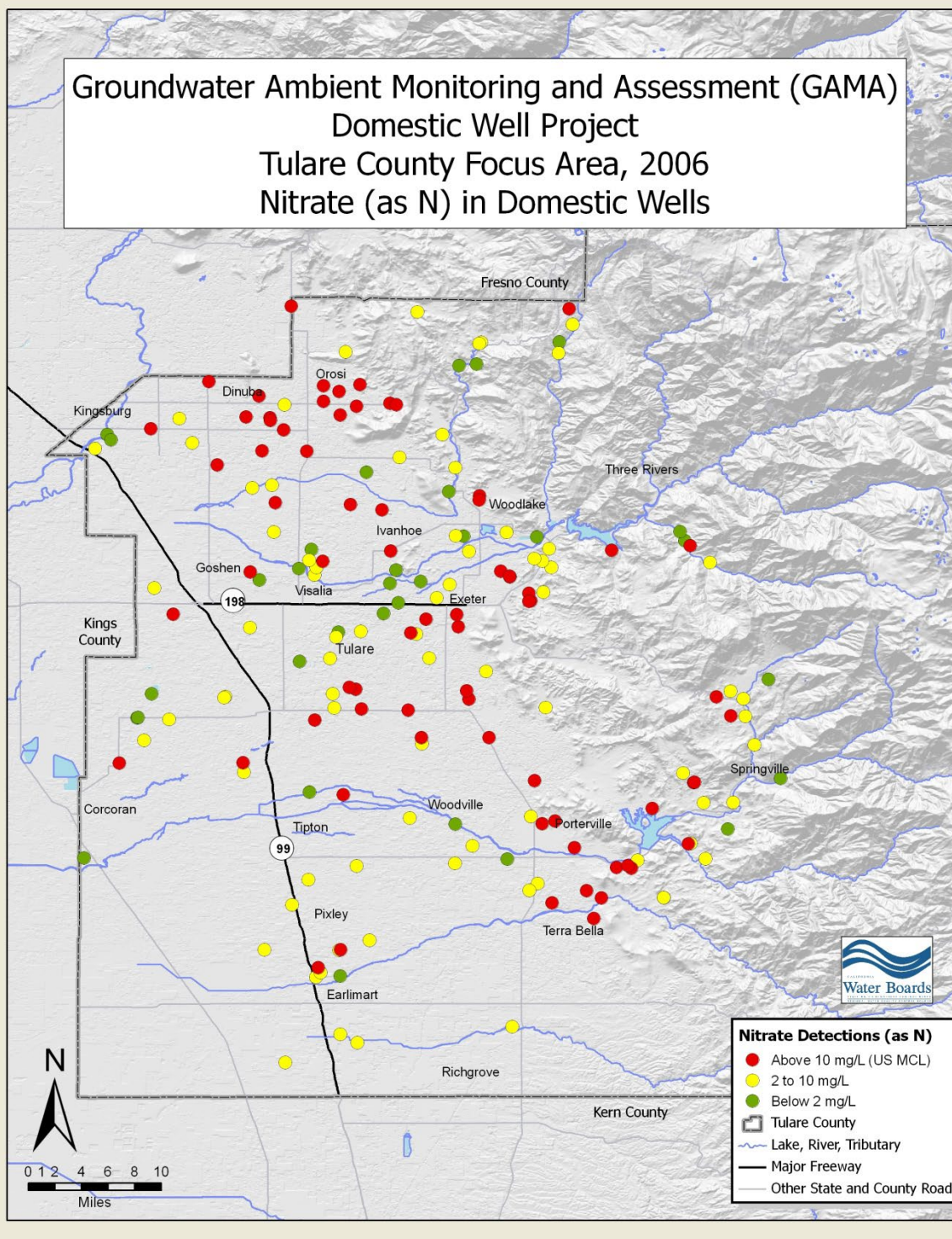


FIGURE 5. NITRATE (AS N) RESULTS

Metals

Metals detected in domestic well samples are shown in Table 5. Eleven metals (aluminum, arsenic, beryllium, boron, chromium, iron, manganese, nickel, thallium, vanadium, and zinc) were detected at concentrations above a public drinking water standard. A summary of metals detected above a drinking water standard is provided below. The locations of wells with detections of vanadium are shown in Figure 6. The locations of thallium and nickel above a drinking water standard are shown in Figure 7.

- Aluminum was detected in 120 wells at concentrations ranging from 5.85 to 450 µg/L. Aluminum was detected above the SMCL (200 µg/L) in two wells.
- Arsenic was detected in 126 wells at concentrations ranging from 0.1 to 14 µg/L. Arsenic was detected above the MCL (10 µg/L) in two wells.
- Beryllium was detected in one sample at 113 µg/L. This concentration is above the MCL of 4 µg/L.
- Boron was detected in 161 wells at concentrations ranging from 7.8 to 48,400 µg/L. Boron was detected above the NL (1,000 µg/L) in one well.
- Total chromium was detected in 42 wells at concentrations ranging from 2.36 to 91.9 µg/L. Chromium was detected above the MCL (50 µg/L) in two wells.
- Manganese was detected in 149 wells at concentrations ranging from 0.11 to 172 µg/L. Manganese was detected above the SMCL (50 µg/L) in two wells.
- Iron was detected in 44 wells at concentrations ranging from 20.1 to 650 µg/L. Iron was detected above the SMCL (300 µg/L) in two wells.
- Nickel was detected in 55 wells at concentrations ranging from 2.16 to 213 µg/L. Nickel was detected above the MCL (100 µg/L) in three wells.
- Thallium was detected in 25 wells at concentrations ranging from 0.2 to 7.32 µg/L. Thallium was detected above the MCL (2 µg/L) in six wells.
- Vanadium was detected in 165 wells at concentrations ranging from 3.77 to 92.9 µg/L. Vanadium was detected above the NL (50 µg/L) in 14 wells.
- Zinc was detected in 171 wells at concentrations ranging from 1.37 to 17,300 µg/L. Zinc was detected above the SMCL (5 mg/L) in one sample.

TABLE 5: METALS RESULTS FROM THE GAMA DOMESTIC WELL PROJECT TULARE COUNTY FOCUS AREA

Analytes	Range of Detected Values (µg/L)	Public Drinking Water Standard (µg/L)	Number of Wells Above Standard
Aluminum	5.85 - 450	200 SMCL	2
Arsenic	0.1 - 14	10 MCL	2
Barium	1.54 - 495	1,000 MCL	0
Beryllium	113	4 MCL	1
Boron	7.8 – 48,400	1,000 NL	1
Cadmium	1.16	5 MCL	0
Chromium (Total)	0 - 91.9	50 MCL	2
Copper	1.1 - 60.6	1,000 SMCL	0
Iron	20.1 - 650	300 SMCL	2

Lead	0.11 - 6.48	15 NL	0
Manganese	0.11 - 172	50 SMCL	2
Nickel	3.16 - 213	100 MCL	3
Selenium	0.11 - 1.55	50 MCL	0
Silver	33.6	100 SMCL	0
Thallium	0.2 - 7.32	2 MCL	6
Vanadium	0.2 - 92.9	50 NL	14
Zinc	1.37 - 17,300	5,000 SMCL	1

MCL = Maximum Contaminant Level, SMCL = Secondary Maximum Contaminant Level, NL = Notification level. $\mu\text{g/L}$ = micrograms per liter

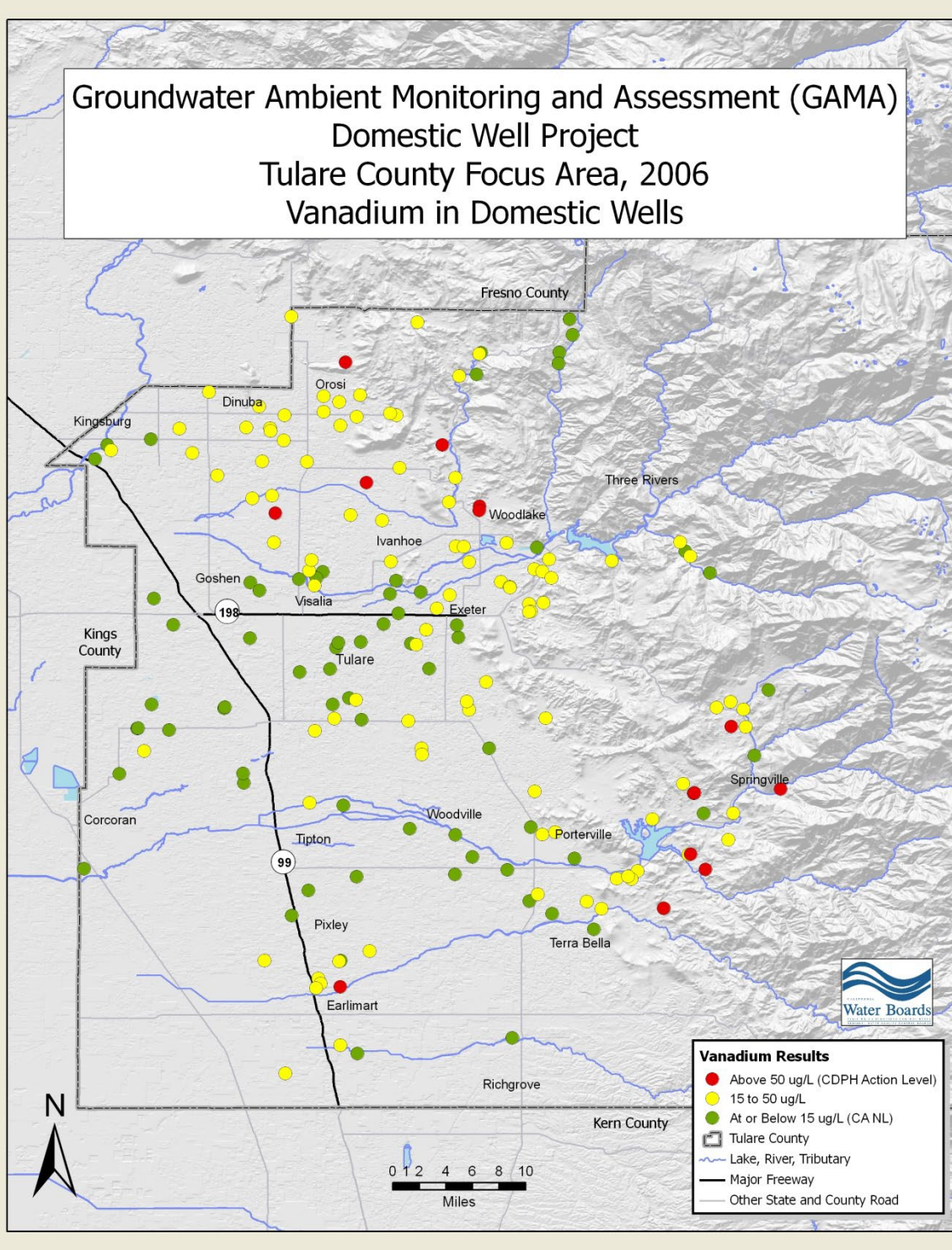


FIGURE 6. VANADIUM RESULTS

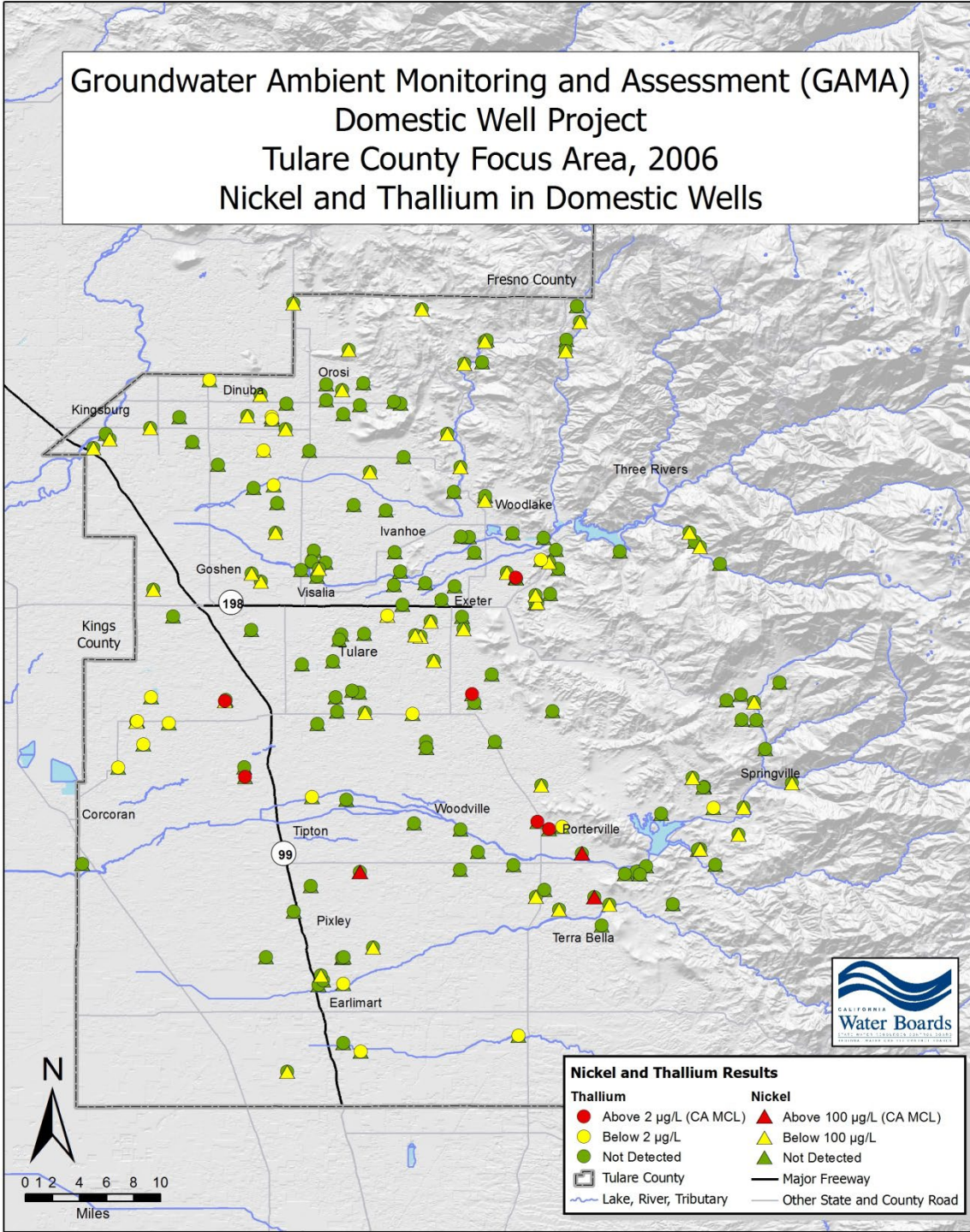


FIGURE 7. THALLIUM AND NICKEL RESULTS

Radionuclides

Thirteen domestic wells were selected for radionuclide analyses. Test results are shown in Table 6. Radionuclide analyses included gross alpha particle activity, gross beta particle activity, combined radium (the activity of radium-226 and radium-228), tritium, and uranium. Drinking water standards for radionuclides are in picocuries per liter (pCi/L) or millirems per year (millirem/yr). A curie is the radioactivity associated with one gram of radium – a picocurie is one trillionth of a curie. The gross beta activity drinking water standard is in terms of millirems per year. A ‘rem’ is a unit of measure describing how a specific type of radiation damages biologic tissue. A millirem is one thousandth of a rem. There is no simple conversion between a curie and a rem. Gross beta activity previously had an MCL of 50 pCi/L, which was replaced by the 4 millirem/yr standard. Gross beta activity of 50 pCi/L is still used as a trigger for additional testing by CDPH. A summary of radionuclide test results is included below. The locations of wells sampled for uranium, gross alpha activity, and radium (226+228) is shown in Figure 8.

- Gross alpha activity was detected in all thirteen sampled wells at activities ranging from 2.8 to 602 pCi/L. Gross alpha activity was above the MCL (15 pCi/L) in three wells.
- Gross beta activity was detected in twelve of the thirteen sampled wells, with activities ranging from 2.8 to 7.15 pCi/L. None of the gross beta activities were above the NL of 50 pCi/L.
- Combined radium (radium 226+228) activity was detected in nine of thirteen wells at activities ranging from 0.71 to 5.2 pCi/L. Radium activity was above the MCL (5 pCi/L) in one well.
- Tritium activity was detected in ten of thirteen sampled wells at activities ranging from 181 to 1,264 pCi/L. None of the wells were above the MCL (20,000 pCi/L).
- Uranium activity was detected in all thirteen sampled wells at activities ranging from 2.15 to 228 pCi/L. Uranium activity was above the MCL (20 pCi/L) in one well.

TABLE 6: RADIONUCLIDES RESULTS FOR THE GAMA DOMESTIC WELL PROJECT TULARE COUNTY FOCUS AREA

Analytes	Range of Detected Values (pCi/L)	Public Drinking Water Standard (pCi/L)	Number of Wells Above Standard
Gross alpha	2.8 - 602	15 MCL	3
Gross beta	2.8 - 7.15	50 NL 4 milirem/yr MCL	0
Radium 226+228	0.71 - 5.2	5 MCL	1
Tritium	181 – 1,264	20,000 MCL	0
Uranium	2.15 - 228	20 MCL	1

Notes: MCL = Maximum Contaminant Level. pCi/L = picocurie per liter. milirem/yr = millirems per year

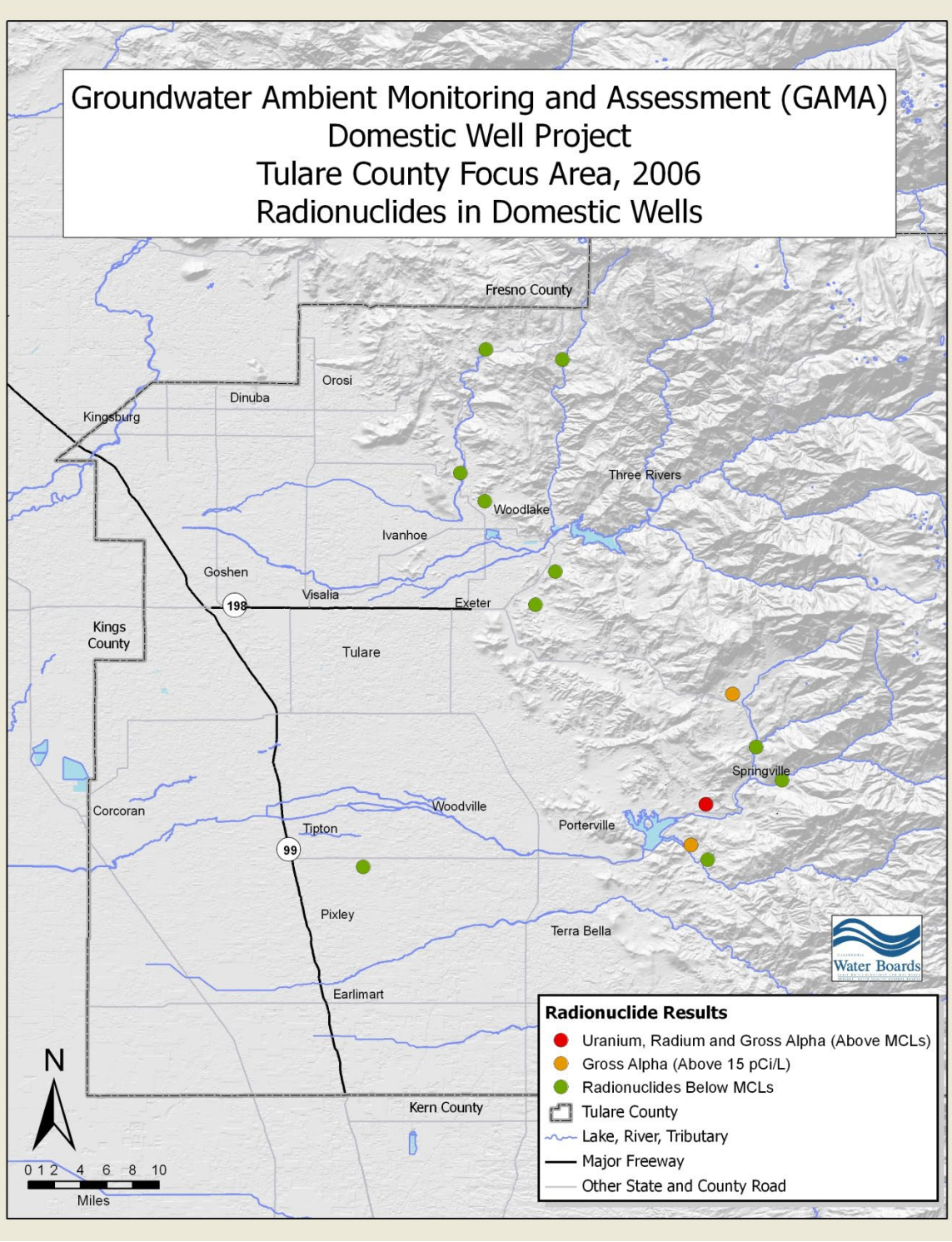


FIGURE 8. RADIONUCLIDES (GROSS ALPHA, RADIUM 226+228, AND URANIUM)

Pesticides

Pesticides have been used on crops for decades to maintain high production and prevent loss.

Historically, 1,2-dibromo-3-chloropropane (DBCP) has been detected in groundwater in the San Joaquin Valley at concentrations greater than the MCL. All 181 samples were analyzed for DBCP, EDB and 1,2,3-TCP using EPA method E504.1. Only DBCP was detected using this method; the locations of wells with detections of DBCP are shown in Figure 9.

Eighteen selected domestic well samples were also tested by LLNL for additional pesticides and pesticide degradates using California Department of Food and Agriculture (CDFA) method EMON-SM-62.9. Results are displayed on Figure 10 and detailed in the table shown in Appendix A. Prometon, metribuzin, and prometryn were not detected in any of the wells selected for pesticide testing. All pesticides, with the exception of DBCP, were detected at concentrations less than established drinking water standards. Pesticide compounds were detected as follows:

Analyzed in all 181 wells:

- DBCP was detected in 27 wells at concentrations ranging from 0.01 to 1.63 µg/L. Concentrations of DBCP were above the MCL of 0.2 µg/L in eight wells.

Analyzed in 18 selected wells by LLNL (CDFA Method):

- Hexazinone was detected in one sample at a concentration of 0.027 µg/L.
- Metolachlor was detected in one sample at a concentration of 0.077 µg/L.
- Cyanazine was detected in two samples, both at concentrations of 0.012 µg/L.
- Atrazine was detected in three wells at concentrations ranging from 0.012 to 0.037 µg/L.
- Deisopropyl-atrazine (DIA) was detected in eleven wells at concentrations ranging from 0.016 to 0.732 µg/L.
- Diaminochlorotriazine (DACT) was detected in five wells at concentrations ranging from 0.031 to 0.099 µg/L.
- Deethyl-atrazine (DEA) was detected in six wells at concentrations ranging from 0.012 to 0.050 µg/L.
- Diuron was detected in nine wells at concentrations ranging from 0.011 to 0.750 µg/L.
- Simazine was detected in ten wells with concentrations ranging from 0.011 to 0.158 µg/L.
- Bromacil was detected in eight wells at concentrations ranging from 0.016 to 1.021 µg/L.
- Norflurazon was detected in five wells at concentrations ranging from 0.022 to 1.390 µg/L.
- Desmethyl Norflurazon (a degradate of norflurazon) was detected in four wells at concentrations ranging from 0.093 to 0.323 µg/L.

In addition to pesticides, LLNL detected primidone at concentration of 0.067µg/L. This was confirmed in a duplicate sample at 0.070µg/L. Primidone is a pharmaceutical (anticonvulsant), and may indicate a connection between septic leachate and groundwater.

TABLE 7: PESTICIDES RESULTS FOR THE GAMA DOMESTIC WELL PROJECT, TULARE COUNTY FOCUS AREA

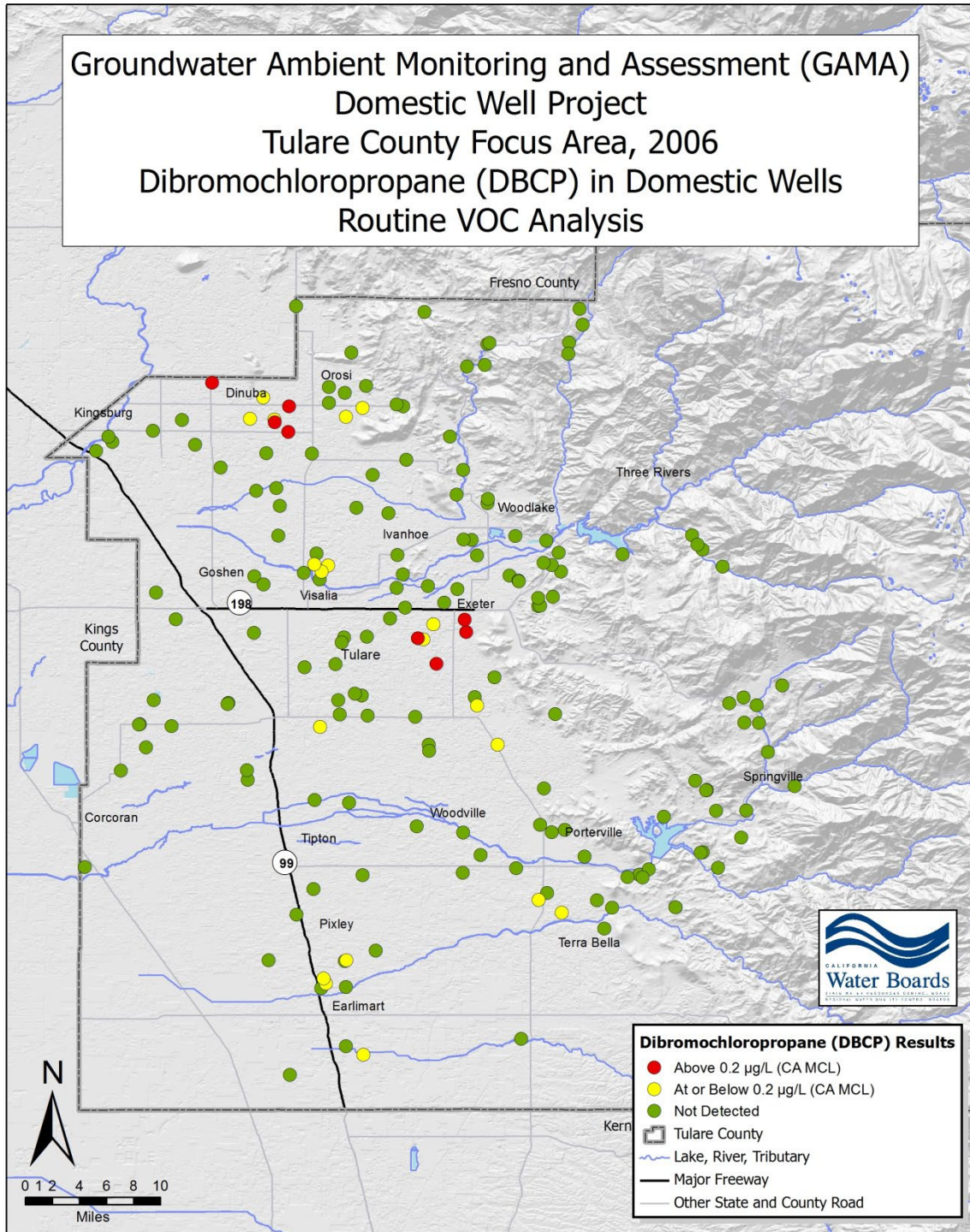
Analyte	Range of Detected Values (µg/L)	Public Drinking Water Standard (µg/L)	Number of Wells Above Standard	Wells Sampled/Detection
---------	---------------------------------	---------------------------------------	--------------------------------	-------------------------

DBCP	0.01 - 1.63	0.2 MCL	8	181/28
Diuron	0.011 - 0.750	NA	0	18/9
DACT	0.031 - 0.099	NA	0	18/5
DIA	0.016 - 0.732	NA	0	18/12
DEA	0.012 - 0.050	NA	0	18/7
Prometon	Not Detected	NA	0	18/0
Simazine	0.011 - 0.158	4 MCL	0	18/11
Atrazine	0.012 - 0.037	1 MCL	0	18/4
Metribuzin	Not Detected	NA	0	18/0
Prometryn	Not Detected	NA	0	18/0
Bromacil	0.016 - 1.021	NA	0	18/8
Cyanazine	0.012	NA	0	18/2
Hexazinone	0.027	NA	0	18/1
Primidone*	0.070	NA	0	18/1
Metolachlor	0.077	NA	0	18/1
Norflurazon	0.022 - 1.390	NA	0	18/5
Desmethyl Norflurazon	0.093 - 0.323	NA	0	18/4

NOTES: NA = NOT AVAILABLE PUBLIC DRINKING WATER STANDARDS ARE NOT AVAILABLE FOR ALL CHEMICALS, MCL = MAXIMUM CONTAMINANT LEVEL, $\mu\text{G/L}$ = MICROGRAMS PER LITER,

*= Primidone is a pharmaceutical

FIGURE 9. DBCP RESULTS



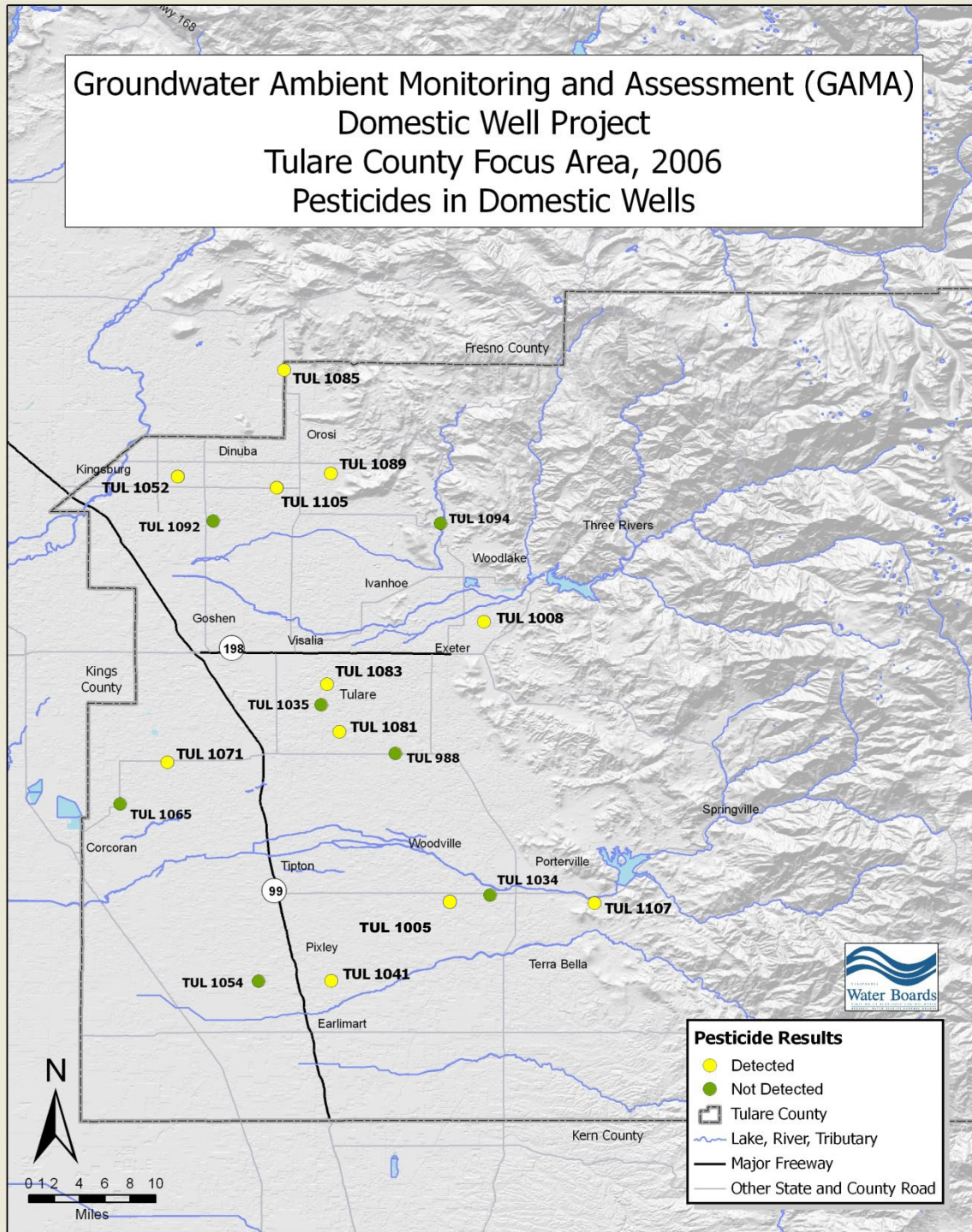


FIGURE 10. PESTICIDE RESULTS (LLNL ANALYSIS)

VOLATILE ORGANIC COMPOUNDS

Volatile Organic Compounds (VOCs) detected in domestic wells are summarized in Table 8. Dozens of VOCs were tested including benzene, toluene, ethylbenzene and xylenes. For a full list of analytes see table 8. A single VOC, 1,2,3-Trichloropropane was detected above a public drinking water standard (NL) in wells sampled as part of the Domestic Well Project. Low-level concentrations, below public drinking water standards, of six additional VOCs were detected.

- 1,1-Dichloroethane at a concentration of 0.6 µg/L in one well
- 1,2,3-Trichloropropane at a concentration of 0.8 µg/L in one well. This concentration is above the NL (0.005 µg/L).
- Chloroform at concentrations ranging from 0.7 to 15.8 µg/L in five wells
- Chloromethane at a concentration of 1 µg/L in one well
- N-butylbenzene at a concentration of 0.2 µg/L in one well
- Tetrachloroethene (PCE) at a concentration of 2.33 µg/L in one well
- Toluene at a concentration of 22 µg/L in one well

TABLE 8: VOCs GAMA DOMESTIC WELL PROJECT, TULARE COUNTY FOCUS AREA

Analytes	Range of Detected Values (µg/L)	Public Drinking Water Standard (µg/L)	Number of Wells Above Standard
1,1-Dichloroethane	0.6	5 MCL	0
1,2,3-Trichloropropane	0.8	0.005 NL	1
Chloroform	0.7 - 15.8	80 MCL	0
Chloromethane	1.0	NA	0
n-butylbenzene	0.2	260 NL	0
Tetrachloroethene (PCE)	2.33	5 MCL	0
Toluene	22	150 L	0

MCL = Maximum Contaminant Level , NL = Notification Level, µg/L = micrograms per liter, NA = Public drinking water standards are not available for this constituent

Isotopic Data Results

LLNL's data of stable isotope compositions of oxygen (O) and hydrogen in water show that private domestic wells in the Sierra foothills above an elevation of 400 feet mean sea level receive groundwater recharge derived from local precipitation that has experienced some evaporation. In contrast, Central Valley private domestic wells below an elevation of 400 feet mean sea level draw on groundwater heavily affected by irrigation from Kings and Kaweah River source water, as indicated by water isotopic composition.

Measured nitrate isotopic composition in the wells sampled varies with land use (dairies, agricultural/residential, and natural settings). Dairy nitrate-N (nitrogen) isotopic compositions are consistent with a manure source. Nitrate-O isotopic compositions are consistent with local nitrification of ammonium from manure, septic effluent, and/or synthetic ammonium fertilizer. In similar hydrogeologic settings, private domestic wells located close to dairies frequently have a different nitrate isotopic composition than wells distant from dairies. The isotopic compositions measured in wells distant from dairies are consistent with suspected sources of nitrate such as soil, fertilizer, manure, septic and/or community wastewater. Regardless of land-use, high concentrations of nitrate were detected in wells located in every land use category that has been developed.

Detailed description of data and methodology are described in the LLNL report, Appendix B.

POSSIBLE SOURCES OF CHEMICALS IN GROUNDWATER

Twenty one constituents were detected above water quality standards in the Tulare County Focus Area. Five of these constituents were observed in more than five percent of the sampled wells. Potential sources for these constituents, summarized from groundwater collected across the country, are discussed below. The focus of this sampling was not to pinpoint a source of chemicals found in groundwater, and the source descriptions do not imply that a chemical observed in a domestic well comes from any single, specific source. The summaries are provided as information for well owners. Additional information for domestic well owners is available on the GAMA website at:

http://www.waterboards.ca.gov/gama/wq_privatewells.shtml

Nitrate

Nitrate is commonly found in groundwater. Low levels of nitrate may be natural in origin; however, high concentrations of nitrate are generally related to fertilizer production and application, septic systems, agricultural and animal waste ponds, leaking sewer lines, sludge or manure application, and the production of explosives. The most significant health threat associated with nitrate is associated with methemoglobinemia ("blue baby" syndrome). Toxic effects occur when bacteria in an infant's stomach convert nitrate to more toxic nitrite, interfering with the body's ability to carry oxygen. High nitrate levels are also a health risk for pregnant women. Some studies suggest an association between high nitrate in drinking water and certain types of cancers (Weyer et al., 2001).

Coliform Bacteria

Total coliform bacteria are naturally present in the environment, and in general are harmless to people. However, some coliforms may cause illness in humans, and the presence of coliforms is an indication that other micro-organisms may be present. Fecal coliforms are found in human and animal wastes and, when present, indicate contamination. Drinking water that contains coliform bacteria increases the risk of becoming ill. Well owners should not drink water with fecal coliform in it.

Vanadium

Vanadium enters the environment from natural sources and from the burning of fossil fuels. It is generally considered a naturally-occurring element in groundwater although some industrial activities, such as mining, may result in increased groundwater concentrations. The health effects of ingesting high doses of vanadium are relatively unknown. Some animals that have ingested vanadium over a long time have developed minor kidney and liver damage, while ingestion of high levels of vanadium by pregnant animals has resulted in minor birth defects.

Radionuclides

Radionuclides are a natural component of groundwater, and are naturally present, typically at very low levels. Most radiation detected in groundwater is the result of interactions with natural geologic materials that contain trace levels of radioactive elements. Different radionuclides will interact and damage biologic activity differently – as a result, some constituents have greater or lower MCLs than others. Drinking water with concentrations of radionuclides above a public drinking water standard increases the risk of certain types of cancers.

DBCP

DBCP was used as a soil fumigant to control nematodes. Prior to 1979, DBCP was widely applied to over 40 types of crops. In California, DBCP was primarily used on grapes and tomatoes. DBCP was banned in the continental United States in 1979. However, DBCP travels easily in groundwater and may persist in groundwater for long periods of time. In sunlight, DBCP is rapidly degraded. Data collected on workers involved in manufacturing DBCP has shown that DBCP can cause sterility or other reproductive effects at very low levels of exposure. There is some evidence that DBCP may have the potential to cause cancer with lifetime exposure at levels above the MCL.

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Appendix A: LLNL Pesticide and Pharmaceutical Results (Part 1 of 2)

Well ID	Diuron	DACT	DIA	DEA	Prometon	Simazine	Atrazine	Metribuzin	Prometryn	Bromacil	Cyanazine	Norflourazon	Hexazinone
MDL($\mu\text{g/L}$)	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
TUL1005	0.045	ND	0.016	ND	ND	0.011	ND	ND	ND	ND	ND	1.390	ND
TUL1008	0,750	0.099	0.732	0.022	ND	0.065	ND	ND	ND	1.021	ND	0.053	ND
TUL1034	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TUL1035	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TUL1041	0.226	0.031	0.400	0.014	ND	0.100	ND	ND	ND	0.590	ND	ND	ND
TUL1043	ND	ND	0.025	0.031	ND	0.011	0.022	ND	ND	ND	ND	ND	ND
TUL1052*	ND	ND	0.055	0.050	ND	0.023	0.037	ND	ND	0.016	0.012	ND	ND
TUL1054	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TUL1065	0.498	ND	0.174	0.020	ND	0.062	0.017	ND	ND	0.060	ND	ND	0.027
TUL1071	0.011	0.049	0.620	ND	ND	ND	ND	ND	ND	0.053	ND	ND	ND
TUL1081	ND	ND	0.113	ND	ND	0.054	ND	ND	ND	ND	ND	0.019	ND
TUL1083	0.548	ND	0.130	ND	ND	0.155	ND	ND	ND	ND	ND	ND	ND
TUL1085	0.041	0.054	0.499	ND	ND	0.094	ND	ND	ND	0.054	ND	ND	ND
TUL1089	0.464	0.065	0.650	0.012	ND	0.048	ND	ND	ND	0.757	ND	0.155	ND
TUL1092	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TUL1094	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TUL1105	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TUL1107	0.050	ND	0.419	0.027	ND	0.158	0.012	ND	ND	0.772	0.012	0.022	ND
TUL988	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Notes:

All results reported in micrograms per liter ($\mu\text{g/L}$, parts per billion)

MDL = Method Detection Limit

ND = Non-Detect, reported as below MDL

*Duplicate of TUL1043

APPENDIX A: LLNL PESTICIDE AND PHARMACEUTICAL RESULTS (PART 2 OF 2)

Well ID	Desmethyl Norflurazone	DBCP	Metolachlor	Primidone**
MDL (µg/L)	0.010	0.010	0.010	0.040
TUL1005	ND	ND	ND	ND
TUL1008	0.202	ND	0.077	ND
TUL1034	0.093	ND	ND	ND
TUL1035	ND	ND	ND	ND
TUL1041	ND	ND	ND	ND
TUL1043	ND	ND	ND	0.067
TUL1052*	ND	ND	ND	0.070
TUL1054	ND	ND	ND	ND
TUL1065	ND	ND	ND	ND
TUL1071	ND	ND	ND	ND
TUL1081	0.210	ND	ND	ND
TUL1083	ND	ND	ND	ND
TUL1085	ND	ND	ND	ND
TUL1089	0.323	ND	ND	ND
TUL1092	ND	ND	ND	ND
TUL1094	ND	ND	ND	ND
TUL1105	ND	0.221	ND	ND
TUL1107	ND	ND	ND	ND
TUL988	ND	ND	ND	ND

Notes:

All results reported in micrograms per liter (µg/L, parts per billion)

MDL = Method Detection Limit

ND = Non-Detect, reported as below MDL

*Duplicate of TUL1043

**Primidone is a pharmaceutical (anticonvulsant), indicating a possible septic system impact

Appendix B: Nitrate and Water Isotopic Data for Tulare County
(LLNL report, August 2013)



LAWRENCE
LIVERMORE
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LABORATORY

LLNL-TR-450497

California GAMA Domestic Wells: Nitrate and Water Isotopic Data for Tulare County

*Michael J. Singleton, Sarah K. Roberts, Jean E.
Moran and Bradley K. Esser*

Lawrence Livermore National Laboratory

January 2011

August 2013 revised

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

GAMA Special Studies Task 7.2:
Specialized Analyses for GAMA Domestic Wells

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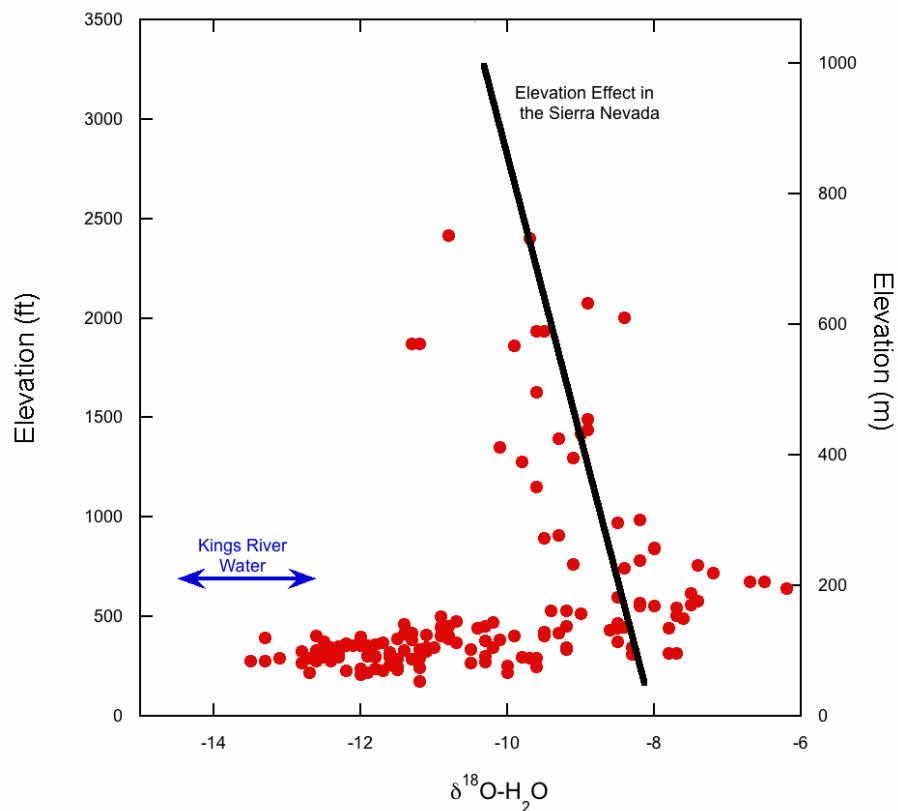
**GAMA: AMBIENT GROUNDWATER
MONITORING & ASSESSMENT PROGRAM
SPECIAL STUDY**



**California GAMA Domestic Wells: Nitrate and Water Isotopic Data for
Tulare County**

By Michael J. Singleton, Sarah K. Roberts, Jean E. Moran and Bradley K. Esser

Lawrence Livermore National Laboratory



Final Report for GAMA Special Studies Task 7.2
Specialized Analyses for GAMA Domestic Wells

LLNL-TR-450497

Prepared in cooperation with the California
State Water Resource Control Board

January 2011

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CALIFORNIA GAMA DOMESTIC WELLS: NITRATE AND WATER ISOTOPIC DATA FOR TULARE COUNTY

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Prepared in cooperation with the California State Water Resource Control Board

Introduction and 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). The goals of the GAMA Domestic Well Project are to provide specific information on water quality to domestic well owners, to provide a public outreach component to aid the public in understanding water quality issues affecting domestic water wells, and to help assess California groundwater quality and identify issues that may impact private domestic well water. The State Water Board works with local county agencies and Regional Water Boards to arrange sampling, which is voluntary and at no cost to the well owner. Results are shared with the well owners and used by GAMA to evaluate the quality of groundwater used by private well owners, which is largely unknown in the State of California. Lawrence Livermore National Laboratory performs specialized analyses of domestic well groundwater for the SWRCB.

In 2006, the Domestic Well Project sampled wells in Tulare County. LLNL analyzed 151 of the 181 domestic well water samples collected by the SWRCB for stable isotopes of oxygen and hydrogen in water; and analyzed 29 samples for stable isotopes of nitrogen and oxygen in dissolved nitrate. These isotopic data constrain the source of water recharging the groundwater produced by the domestic wells in this survey, and help to constrain the source of nitrate in these groundwaters.

For the purpose of discussion, wells with ground surface elevations below 400 feet are referred to as “valley” wells, and wells with ground surface elevations above 400 feet are referred to as “foothill” wells. The water isotopic evidence shows that domestic wells in the foothills (with elevations above 400 feet) receive recharge derived from local precipitation that has experienced some evaporation. In contrast, valley domestic wells below 400 feet surface elevation draw on groundwater heavily impacted by irrigation with Kings and Kaweah River water, as indicated by water isotopic composition. This finding is consistent with both the long and heavy usage of Kings River water for irrigation in this area, and with the assumed shallow depth of these domestic wells. Nitrate associated with these waters is presumably associated with the same source (chemical or organic fertilizer in irrigation water) or is mobilized by irrigation (septic effluent or soil nitrogen compounds).

Foothill and valley domestic wells in Tulare County differ in dissolved nitrate concentration (SWRCB, 2010). In general, foothill wells have low nitrate concentrations, while valley wells have moderate to high nitrate concentrations. Nitrate concentrations in the most polluted wells are sufficiently high to preclude a significant contribution from soil or atmospheric sources. Such sources cannot be precluded in wells with nitrate concentrations below the regulatory drinking water limit, however the data set does not include enough samples near typical background concentration levels to assess the isotopic characteristics of natural nitrate sources in this area.

Nitrate isotopic compositions indicate a dairy manure or septic effluent source for the majority of the most heavily impacted wells, with the exception of one well with high nitrate concentration and an isotopic composition indicative of a synthetic fertilizer source. For less heavily impacted wells, the sparse nitrate isotopic data alone

does not definitively constrain the nitrate source. The observed pattern could be produced by a single source (natural soil N) or by mixing between multiple sources (fertilizer, manure, septic). An analysis of land use and the distribution of potential nitrate sources would be extremely useful.

A preliminary investigation of the correlation between land use and nitrate isotopic composition was conducted (see Appendix "GAMA Domestic Well Project - Tulare County. Nitrate Source Attribution: The Isotopic Evidence"). The sparse nitrate isotopic data set, and the cursory approach to assigning land use limit conclusions, but patterns observed are suggestive of multiple anthropogenic sources, including dairy wastewater, septic effluent and synthetic fertilizer.

Significant findings of the study are listed below:

- Nitrate isotopic composition appears to vary with land use
 - Dairy, agricultural/residential, and wild-land sites are isotopically distinct
 - Dairy site nitrate-N isotopic data are isotopically consistent with a manure source
 - Nitrate-O isotopic data are isotopically consistent with local nitrification of ammonium (from manure, septic effluent, or synthetic ammonium fertilizer)
- The isotopic evidence is consistent with more than one nitrate source
 - Domestic wells located close to dairies frequently have a different nitrate isotopic composition than wells not close to dairies in similar hydrogeologic settings.
 - The isotopic compositions measured are consistent with the suspected sources of nitrate to these wells (soil, fertilizer, manure, septic or community wastewater).
 - High concentrations of nitrate occur in all developed land use categories.

Sampling Protocols and Analytical Methods

Sample Handling

Sampling and handling requirements, including hold times, are listed in Table 1. Groundwater samples for the project were collected by State Water Resources Control Board. Samples for specialized analyses were collected following guidance provided by LLNL. When possible, wells were purged by pumping at least three (3) well casing volumes were pumped prior to collecting the water sample. Samples collected for determination of nitrate and water stable isotope composition do not require filtering.

Stable isotopes of water: A 30-mL glass bottle (clear, French-square type) with Qorpak™ polyseal-lined cap is triple rinsed with water directly from the sampling port, then filled just below the threads on the bottle. Filtering, preservatives and/or refrigeration are not required, but the cap should be tightly closed. Samples may be shipped at room temperature or in a cooler with ice, and are stored at room temperature.

Stable isotopes of nitrate: Either a 50-mL polyethylene centrifuge tube or a small (60-mL or 125-mL) HDPE bottle is triple rinsed with water directly from the sampling port, then filled with approximately 40-mL of sample water leaving sufficient head space to accommodate freezing.

Shipping and preservation: During field sampling, samples were shipped to LLNL by next-day service within three days of collection. Upon arrival at LLNL, samples were logged with both the supplied GAMA Domestic Wells Project ID and with a unique LLNL ID and preserved appropriately. Water Board staff also supplied LLNL with nitrate concentration data for collected samples to allow appropriate aliquoting for nitrate isotopic composition analysis. For samples collected for nitrate isotopic composition determination, a small aliquot was taken for confirmation of nitrate concentration by ion chromatography as necessary and the remainder of the sample was frozen. Samples collected for determination of water isotopic composition were stored at room temperature with a tightly sealed cap.

Table 1: Sampling and Handling Requirements for Stable Isotope Analysis

Determination	Container	Min. sample size (mL)	Preservation	Recommended Hold	Regulatory hold
Nitrate $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$	Plastic	30 mL	Refrigerate at 6°C or freeze	6 months after thawing	Not applicable
Water $\delta^{18}\text{O}$ and $\delta^2\text{H}$	Glass	30 mL	None	1 year	Not applicable

Stable Isotope Terminology and Reporting

Isotopic composition is determined by measuring the atom ratio of a minor abundance isotope to a major abundance isotope. For oxygen, the ratio measured is $^{18}\text{O}/^{16}\text{O}$, i.e. the atom ratio of Oxygen-18 to Oxygen-16. Oxygen-18 is a minor isotope of oxygen (approximately 0.2% of oxygen isotopes are ^{18}O), while Oxygen-16 is the major isotope of oxygen (approximately 99.76% of oxygen isotopes are ^{16}O).

For hydrogen, the ratio measured is $^2\text{H}/^1\text{H}$, i.e. the atom ratio of hydrogen-2 (~0.015%, abundant) to hydrogen-1 (~99.985% abundant). Hydrogen-2 is also referred to as deuterium (D). For nitrogen, the ratio measured is $^{15}\text{N}/^{14}\text{N}$, i.e. the atom ratio of nitrogen-15 (~0.37% abundant) to nitrogen-14 (~99.63% abundant).

Isotope ratios are reported in the standard delta (δ) notation as parts per thousand (per mil or ‰) variations relative to a reference material of known composition and defined by the following equation:

$$\delta_x = 1000 \frac{R_x - R_{ref}}{R_{ref}}$$

where R_x is the ratio of the sample and R_{ref} is the ratio of the reference material. For oxygen and for hydrogen in water, we use Vienna Standard Mean Ocean Water (VSMOW; Craig, 1961). We also use VSMOW for oxygen in nitrate. For nitrogen in nitrate, we use air as a reference material.

Analytical Methods—Stable Isotopes of Water

Water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are determined on unfiltered samples. Water $\delta^2\text{H}$ is also referred to as δD . Water $\delta^2\text{H}$ is determined on unfiltered samples, usually the same bottle collected for water- $\delta^{18}\text{O}$. Oxygen isotope analyses are conducted using the carbon dioxide equilibration method for $^{18}\text{O}/^{16}\text{O}$ and analyzed with an automated water equilibration unit. Hydrogen isotope compositions of water were analyzed using the Pt- H_2 equilibration method. Isotope ratio measurements are performed on a VG PRISM III isotope ratio mass spectrometer housed in the Chemical Sciences Division at Lawrence Livermore National Laboratory. The LLNL standard operating procedure for determination of the stable isotopic composition of water in groundwater samples is SOP-UGTA-128, and is available upon request.

Analyses in the Stable Isotope Laboratory are calibrated to internal standards referenced against National Institute of Standards and Technology (NIST) standard reference materials. The waters chosen as in-house standards consist of three isotopically distinct water samples ($\delta^{18}\text{O} = -3.1, -9.9$ and -15.5‰). The composition and isotopic values of these internal standards span the range of natural waters typically observed in potable groundwater of California. For each set of $\delta^{18}\text{O}$ analyses, 2 each of 3 internal standards are also analyzed and used for calibration. The internal standards are periodically compared to the three NIST reference standards (NIST RM 8535; NIST RM 8536; NIST RM 8537): SMOW, Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP). The analytical precision for these $\delta^{18}\text{O}$ measurements, from one run to the next, is $\pm 0.10\text{‰}$, and the analytical precision for $\delta^2\text{H}$ values is $\pm 2\text{‰}$.

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

Epstein, S., and Mayeda, T.K. 1953. Variation of O-18 content of waters from natural sources. *Geochimica Cosmochimica Acta*, **4**, 213-224.

Coplen, T.B., Wildman, J.D., and Chen, J. 1991. Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope-ratio analysis. *Analytical Chemistry*, **63**, p. 910-912.

Analytical Method—Stable Isotopes of Nitrate

The isotopic composition of dissolved nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) is determined on water samples filtered through 0.2 μm syringe filters (0.45 μm filters may be used for pre-filtering sediment-laden water). The samples are stored frozen in pre-cleaned, HDPE bottles. Samples are analyzed using an automated version of a new microbial denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). In this method, a strain of denitrifying bacteria is used to reduce dissolved nitrate in water samples to N_2O gas that can be analyzed for N and O isotopic composition on the MicroMass IsoPrime IRMS. Dr. Mike Singleton, the Stable Isotope Mass Spectrometry Laboratory Manager, has implemented this method at the Center for Isotope Geochemistry at Lawrence Berkeley National Laboratory (LBNL) and in the Chemical Sciences Division at LLNL. He has safely carried out hundreds of successful analyses over a period of four years. The original method has been adapted to decrease the time required for culture preparation and sample processing.

Casciotti, K.L., Sigman, D.M., Hastings, M.G., Bohlke, J.K., Hilkert, A. 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Analytical Chemistry*, **74**, p. 4905-4912.

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., Bohlke, J. K. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical Chemistry*, **73**, p. 4145-4153.

Singleton, M.J., Woods, K.N., Conrad, M.E., DePaolo, D.J., and Dresel, P.E. 2005. Tracking sources of unsaturated zone and groundwater nitrate contamination using nitrogen and oxygen stable isotopes at the Hanford Site, Washington. *Environmental Science & Technology*, **39(10)**, p. 3563-3570.

Data Quality Objectives and Quality Control

Data Objectives: Minimum acceptable measurement quality objectives (MQOs) for analytical techniques used in this project are summarized in Table 2. The MQOs for isotopic analyses reflect “accepted methods” for publication in high-quality scientific journals. Whenever possible, the methods with greater sensitivity and lowest detection limit will be employed as the primary method. Methods with lesser sensitivity and higher detection limits will be used for samples known to contain high concentrations of analytes, field confirmations, or as back-up methods in the case that the primary methods are not available or functioning properly for a particular sampling event. Analyses that do not meet minimum acceptable data quality objectives will be re-run when sample is available. When sample is not available, such data will not be reported or will be reported and flagged.

Precision and Accuracy: Precision (e.g., the reproducibility among replicate samples) will be determined by analysis of duplicate samples, laboratory control standards and matrix spikes as appropriate for each method. Precision is determined as the standard deviation of measurements divided by the mean and multiplied by 100. Precision measurements will be determined on both field and laboratory replicates).

Accuracy (e.g., how close the measurement is to the true value) will be measured on one or more quality control check standards (QCCS) prepared exactly as the calibration standards. The QCCS is analyzed after the calibration standards. The QCCS should be within 10% of the actual concentration or problems will be resolved and samples re-analyzed. For some methods, accuracy cannot be rigorously determined because there are no absolute external standards available.

Quality Control: Quality control samples will be analyzed to ensure valid data are collected. Field duplicates are collected and analyzed for at least every 20th sample. The precision of duplicates and splits are used to help identify sampling handling and preparation problems. All samples that fall outside the expected range for the sample type, location, and collection time are assessed for proper size and instrument function. The expected ranges are dependent on many factors and cannot easily be defined. Expected ranges are therefore determined on a case by case basis, initially by the analyst and finally by the PI in charge of data interpretation. Samples are re-analyzed as necessary to achieve the desired precision.

Instrument behavior is assessed by analysis of working standards as described in the individual SOPs for the various analysis types. Instruments are regularly tested for stability and linearity as described in Section 15 below. LLNL laboratories routinely participate in international calibration exercises to ensure the precision and accuracy of data reported. All instruments are regularly calibrated using NIST or IAEA standard reference materials with internationally-agreed-upon values. When in-run reference standards do not meet precision or accuracy criteria, samples from the same run will be re-analyzed. Records of instrument performance will be maintained indefinitely. All laboratories use Good Laboratory Practices (GLP), and routine analyses follow SOPs.

Table 2: Data Quality Objectives and Reporting for Stable Isotope Analysis.

Parameter	Method/ Range	Units	Reference	External Precision ¹	Instrumental precision ²
Nitrate $\delta^{18}\text{O}$ Nitrate $\delta^{15}\text{N}$	Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{15}\text{N}$: Air $\delta^{18}\text{O}$: VSMOW	$\delta^{15}\text{N} \pm 0.3 \text{ ‰}$ $\delta^{18}\text{O} \pm 0.8 \text{ ‰}$	$\delta^{15}\text{N} \pm 0.2 \text{ ‰}$ $\delta^{18}\text{O} \pm 0.5 \text{ ‰}$
Water $\delta^{18}\text{O}$ Water $\delta^2\text{H}$	Dual Inlet and/or Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{18}\text{O}$: VSMOW $\delta^2\text{H}$: VSMOW	$\delta^{18}\text{O} \pm 0.3 \text{ ‰}$ $\delta^2\text{H} \pm 2 \text{ ‰}$	$\pm 0.15 \text{ ‰}$ $\pm 1 \text{ ‰}$

¹. External (1 sigma) precision objectives apply to replicate analyses of a single sample.

2. Instrumental precision (1 sigma) applies to calibration check samples, laboratory control samples and other measurements of samples of known concentration and isotopic composition where the known value is compared to the measured value.
3. VSMOW = Vienna Standard Mean Ocean Water.

Data: Tulare County Domestic Wells

Sample isotopic data

This data report represents specialized analyses performed by LLNL on domestic well groundwater samples collected in Tulare County by State Water Resources Control Board staff for the GAMA Domestic Wells Project. Samples were collected between April, May and June of 2006. In total, LLNL analyzed 151 samples for water isotopic composition of both oxygen and hydrogen, and 29 samples for nitrate isotopic composition of both nitrogen and oxygen. Analyzed samples included 15 field duplicates for water isotopic composition; and two field duplicates for nitrate isotopic composition. Data are tabulated in Table 3. Sample names are of the form "TUL nnnn". Samples with nnnn less than 1000 are labeled to as either "TUL nnn" or "TUL 0nnn" or "TULnnnn". These three forms are equivalent, e.g. TUL 979, TUL 0979, and TUL0979 all refer to the same sample.

**Table 3: Water and Nitrate Isotopic Composition in Tulare County
Domestic Well Water Samples**

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, VSMOW)	Water- $\delta^2\text{H}$ (‰, VSMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, VSMOW)
TUL 901	103893	04/18/2006	-12.4	-89		
TUL 902	103894	04/18/2006	-12.8	-93		
TUL 903	103895	04/18/2006	-12.5	-89		
TUL 904	103896	04/18/2006	-10.2	-74		
TUL 905	103897	04/18/2006	-12.2	-87		
TUL 906	103898	04/18/2006	-12.2	-87		
TUL 907	103899	04/18/2006	-10.8	-81		
TUL 908	103900	04/18/2006	-12.5	-89		
TUL 909	103904	04/19/2006	-12.0	-84		
TUL 910	103905	04/19/2006	-10.8	-79		
TUL 911	103906	04/19/2006	-11.3	-81		
TUL 912	103907	04/19/2006	-10.9	-82		
TUL 913	103908	04/19/2006	-11.4	-81	0.0	3.7
TUL 914	103909	04/19/2006	-10.9	-80		
TUL 915	103910	04/19/2006	-8.0	-59		
TUL 916	103911	04/19/2006	-7.7	-58		
TUL 917	103912	04/19/2006	-10.8	-80	7.7	-1.7
TUL 918	103915	04/20/2006	-9.6	-67		
TUL 919	103913	04/19/2006	-7.5	-58		
TUL 920	103916	04/20/2006	-8.9	-65	1.5	2.8
TUL 921	103917	04/20/2006	-8.2	-58		
TUL 922	103918	04/20/2006	-9.9	-74		
TUL 923	103919	04/20/2006	-9.2	-63		
TUL 924	103920	04/20/2006	-9.4	-71	5.6	1.8
TUL 925	103921	04/20/2006	-11.3	-83		
TUL 926	103922	04/20/2006	-12.4	-87		
TUL 927	103923	04/20/2006	-11.2	-79		
TUL 928	103924	04/20/2006	-8.3	-64	6.2	11.0
TUL 929	103901	04/18/2006	-11.9	-86		
TUL 930	103954	04/25/2006	-11.3	-82		
TUL 932	103956	04/25/2006	-10.1	-76	3.5	-4.3
TUL 933	103957	04/25/2006	-10.7	-80		
TUL 934	103958	04/25/2006	-7.7	-64		
TUL 935	103976	04/27/2006	-9.2	-71	6.6	3.8
TUL 936	103966	04/26/2006	-11.8	-86		
TUL 937	103967	04/26/2006	-12.7	-91		
TUL 938	103968	04/26/2006			4.8	-3.2
TUL 939	103969	04/26/2006	-12.8	-92		
TUL 941	103960	04/25/2006	-12.4	-86	8.2	-0.3
TUL 943	103962	04/25/2006	-11.2	-79		
TUL 944	103980	04/27/2006	-10.4	-74	8.6	1.3

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, VSMOW)	Water- $\delta^2\text{H}$ (‰, VSMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, VSMOW)
TUL 945	103977	04/27/2006	-7.8	-63		
TUL 946	103978	04/27/2006	-11.1	-77		
TUL 947	103963	04/25/2006	-12.0	-84		
TUL 948	103970	04/27/2006				
TUL 949	103971	04/26/2006				
TUL 950	103972	04/26/2006			8.0	1.8
TUL 951	103973	04/26/2006				
TUL 952	103974	04/26/2006				
TUL 954	103964	04/26/2006	-12.4	-88	8.1	-0.8
TUL 955	103965	04/26/2006	-7.8	-63		
TUL 956	103975	04/25/2006				
TUL 957	103979	05/09/2006	-7.8	-63		
TUL 978	104106	06/06/2006	-8.5	-62	6.4	3.1
TUL 979	104107	06/06/2006	-7.8	-60	6.1	8.2
TUL 980	104108	06/06/2006	-9.1	-63	3.3	3.8
TUL 981	104025	05/16/2006	-6.5	-55		
TUL 981-1	104027	05/16/2006	-6.7	-55		
TUL 982	104026	05/16/2006	-8.5	-62		
TUL 983	104028	05/17/2006	-11.5	-85	7.2	3.8
TUL 984	104029	05/17/2006	-9.3	-66		
TUL 985	104030	05/16/2006	-9.6	-66		
TUL 986	104031	05/18/2006	-10.3	-72		
TUL 987	104032	05/18/2006	-9.6	-66		
TUL 988	104109	06/06/2006	-8.3	-62	7.2	1.8
TUL 989	104116	06/07/2006	-10.1	-74		
TUL 990	104033	05/16/2006	-7.4	-59		
TUL 991	104034	05/16/2006	-9.2	-71		
TUL 992	104035	05/18/2006	-11.5	-81		
TUL 993	104036	05/17/2006	-13.3	-98		
TUL 994	104037	05/17/2006	-9.5	-70		
TUL 995	104038	05/17/2006	-7.4	-54		
TUL 996	104039	05/16/2006	-11.8	-83		
TUL 997	104040	05/17/2006	-9.3	-71	7.0	3.3
TUL 998	104041	05/17/2006	-7.2	-60		
TUL 999	104042	05/18/2006	-11.2	-79		
TUL 1000	104043	05/18/2006	-12.0	-87		
TUL 1001	104044	05/16/2006	-10.8	-74		
TUL 1002	104045	05/16/2006	-8.9	-65		
TUL 1003	104046	05/18/2006	-12.3	-88		
TUL 1004	104047	05/18/2006	-11.5	-82		
TUL 1005	104110	06/06/2006	-10.7	-76	2.9	-0.3
TUL 1006	104117	06/08/2006	-10.3	-74	5.1	0.3
TUL 1007	104118	06/07/2006	-12.7	-94	5.3	-0.2

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, VSMOW)	Water- $\delta^2\text{H}$ (‰, VSMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, VSMOW)
TUL 1008	104119	06/08/2006	-9.5	-73		
TUL 1009	104120	06/07/2006	-8.0	-59		
TUL 1010	104066	05/24/2006	-13.3	-97		
TUL 1011	104067	05/24/2006	-10.0	-70		
TUL 1012	104068	05/24/2006	-10.3	-72		
TUL 1013	104069	05/24/2006	-11.6	-84	8.6	-2.6
TUL 1014	104070	05/25/2006	-13.1	-96		
TUL 1015	104071	05/23/2006	-10.2	-75		
TUL 1016	104072	05/23/2006	-8.5	-66		
TUL 1017	104073	05/24/2006	-11.5	-84		
TUL 1019	104074	05/23/2006	-9.3	-66		
TUL 1020	104075	05/25/2006	-11.6	-84		
TUL 1021	104076	05/23/2006	-9.2	-68		
TUL 1022	104077	05/24/2006	-11.2	-83		
TUL 1024	104078	05/25/2006	-8.2	-61		
TUL 1025	104079	05/23/2006	-11.9	-88		
TUL 1026	104080	05/23/2006	-8.5	-63		
TUL 1027	104081	05/23/2006	-12.4	-86		
TUL 1028	104082	05/23/2006	-12.3	-89		
TUL 1029	104083	05/25/2006	-11.9	-83		
TUL 1031	104084	05/24/2006	-13.5	-98		
TUL 1032	104085	05/25/2006	-10.5	-77		
TUL 1033	104086	05/25/2006	-11.5	-85		
TUL 1034	104121	06/08/2006	-11.3	-76		
TUL 1035	104111	06/06/2006	-12.5	-89	4.1	-1.0
TUL 1036	104112	06/06/2006	-12.5	-89	4.6	-2.4
TUL 1038	104087	05/23/2006	-12.0	-90		
TUL 1039	104088	05/24/2006	-11.2	-83		
TUL 1040	104089	05/25/2006	-11.5	-81		
TUL 1041	104122	05/24/2006	-10.5	-75		
TUL 1042	104123	06/07/2006	-11.8	-80		
TUL 1043	104124	06/08/2006	-8.5	-67		
TUL 1044	104125	06/08/2006	-12.6	-89		
TUL 1050	104113	06/06/2006	-12.4	-89	4.3	-3.2
TUL 1051	104126	06/07/2006	-11.8	-80		
TUL 1052	104127	06/08/2006	-8.5	-67		
TUL 1053	104128	06/07/2006	-8.0	-58		
TUL 1054	104134	06/13/2006	-10.0	-67		
TUL 1055	104135	06/13/2006	-11.9	-87		
TUL 1056	104136	06/13/2006	-12.5	-88		
TUL 1057	104149	06/14/2006	-11.4	-84		
TUL 1058	104150	06/14/2006	-8.5	-64	6.3	4.9
TUL 1059	104151	06/14/2006	-8.4	-65		

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, VSMOW)	Water- $\delta^2\text{H}$ (‰, VSMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, VSMOW)
TUL 1060	104152	06/15/2006	-11.0	-81		
TUL 1061	104153	06/14/2006	-8.5	-65		
TUL 1062	104154	06/15/2006	-8.6	-65		
TUL 1063	104155	06/14/2006	-9.1	-67		
TUL 1064	104137	06/13/2006	-12.8	-93		
TUL 1065	104138	06/13/2006	-12.0	-87		
TUL 1066	104139	06/13/2006	-12.2	-86		
TUL 1070	104156	06/14/2006	-11.6	-85		
TUL 1071	104140	06/13/2006	-11.7	-85		
TUL 1072	104157	06/14/2006	-9.6	-69		
TUL 1073	104158	06/14/2006	-11.9	-88		
TUL 1074	104159	06/14/2006	-11.2	-80		
TUL 1075	104160	06/15/2006	-11.7	-84		
TUL 1076	104161	06/15/2006	-11.1	-81		
TUL 1077	104141	06/13/2006	-12.5	-87	5.4	-0.2
TUL 1078	104162	06/14/2006	-9.7	-69		
TUL 1079	104163	06/15/2006	-12.5	-91		
TUL 1080	104164	06/15/2006	-12.3	-84		
TUL 1081	104165	06/15/2006	-11.9	-84	11.2	-1.9
TUL 1082	104166	06/15/2006	-12.6	-89		
TUL 1083	104167	06/15/2006	-12.6	-89		
TUL 1084	104169	06/20/2006	-12.6	-93		
TUL 1085	104170	06/20/2006	-10.9	-79		
TUL 1086	104171	06/20/2006	-9.7	-67		
TUL 1087	104172	06/20/2006	-8.9	-65		
TUL 1088	104173	06/20/2006	-8.2	-61		
TUL 1089	104174	06/20/2006	-10.3	-77		
TUL 1090	104180	06/21/2006	-7.5	-59		
TUL 1091	104181	06/21/2006	-7.6	-60		
TUL 1092	104182	06/21/2006	-11.2	-84		
TUL 1093	104183	06/21/2006	-9.8	-72		
TUL 1094	104184	06/21/2006	-9.0	-62		
TUL 1095	104185	06/21/2006	-9.8	-70		
TUL 1096	104190	06/22/2006	-8.4	-61		
TUL 1097	104191	06/22/2006	-9.9	-71		
TUL 1098	104186	06/21/2006	-11.8	-85		
TUL 1099	104192	06/22/2006	-8.4	-63		
TUL 1100	104175	06/20/2006	-9.0	-62		
TUL 1101	104193	06/22/2006	-6.2	-52		
TUL 1103	104176	06/20/2006	-12.5	-89		
TUL 1104	104194	06/22/2006	-9.5	-67		
TUL 1105	104177	06/20/2006	-11.1	-81	8.2	1.4
TUL 1106	104195	06/22/2006	-12.3	-87		

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, VSMOW)	Water- $\delta^2\text{H}$ (‰, VSMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, VSMOW)
TUL 1107	104196	06/22/2006	-8.2			
TUL 1108	104178	06/20/2006	-10.9	-80		
TUL 1109	104187	06/21/2006	-9.0	-62		
TUL 1110	104197	06/22/2006	-9.5	-66		
TUL 1111	104198	06/22/2006	-9.5	-72	7.2	3.1
TUL 1201	103902	04/18/2006	-12.1	-87		
TUL 1202	103925	04/20/2006	-11.3	-79		
TUL 1205	103914	04/19/2006	-11.4	-82		
TUL 1505	104090	06/08/2006	-10.0	-70	3.7	4.2

Sample QA/QC Data

Field duplicate data are tabulated in Table 4. For the two nitrate field duplicates, nitrate- $\delta^{15}\text{N}$ analyses agreed to better than 0.3‰, and nitrate- $\delta^{18}\text{O}$ analyses agreed to better than 0.8‰. For the 15 water field duplicates, water- $\delta^{18}\text{O}$ analyses agreed to within 0.1‰. Water- $\delta^2\text{H}$ analyses agreed to 2‰ or better with the exception of three samples which agreed to within 4‰. The agreement between the original and duplicate water isotopic composition determinations is shown in Figure 1.

Table 4: Isotopic Composition Analyses of Field Duplicates

SWRCB ID	LLNL ID	Collection	Water- $\delta^{18}\text{O}$	Water- $\delta^2\text{H}$	Nitrate- $\delta^{15}\text{N}$	Nitrate- $\delta^{18}\text{O}$
TUL0945	103977	4/27/06	-7.8	-63		
TUL0957	103979	4/27/06	-7.8	-63		
TUL0992	104035	5/18/06	-11.5	-81		
TUL1004	104047	5/18/06	-11.5	-82		
TUL0941	103960	4/25/06	-12.4	-86	8.2	-0.3
TUL0954	103964	4/25/06	-12.4	-88	8.1	-0.8
TUL1104	104194	6/22/06	-9.5	-67		
TUL1110	104197	6/22/06	-9.5	-66		
TUL1036	104112	6/6/06	-12.5	-89	4.6	-2.4
TUL1050	104113	6/6/06	-12.4	-89	4.3	-3.2
TUL1079	104163	6/15/06	-12.5	-91		
TUL1083	104167	6/15/06	-12.6	-89		
TUL0906	103898	4/18/06	-12.2	-87		
TUL1201	103902	4/18/06	-12.1	-87		
TUL1056	104136	6/13/06	-12.5	-88		
TUL1077	104141	6/13/06	-12.5	-88		

SWRCB ID	LLNL ID	Collection	Water- $\delta^{18}\text{O}$	Water- $\delta^2\text{H}$	Nitrate- $\delta^{15}\text{N}$	Nitrate- $\delta^{18}\text{O}$
TUL1033	104086	5/25/06	-11.5	-85		
TUL1040	104089	5/25/06	-11.5	-81		
TUL1042	104123	6/7/06	-11.8	-80		
TUL1051	104126	6/7/06	-11.8	-80		
TUL0927	103923	4/20/06	-11.3	-79		
TUL1202	103925	4/20/06	-11.3	-79		
TUL0911	103906	4/19/06	-11.4	-81		
TUL1205	103914	4/19/06	-11.4	-82		
TUL1094	104184	6/21/06	-9.0	-62		
TUL1109	104187	6/21/06	-9.0	-62		
TUL1025	104079	5/23/06	-11.9	-88		
TUL1038	104087	5/23/06	-12.0	-91		
TUL1085	104170	6/20/06	-10.9	-79		
TUL1108	104178	6/20/06	-10.9	-80		

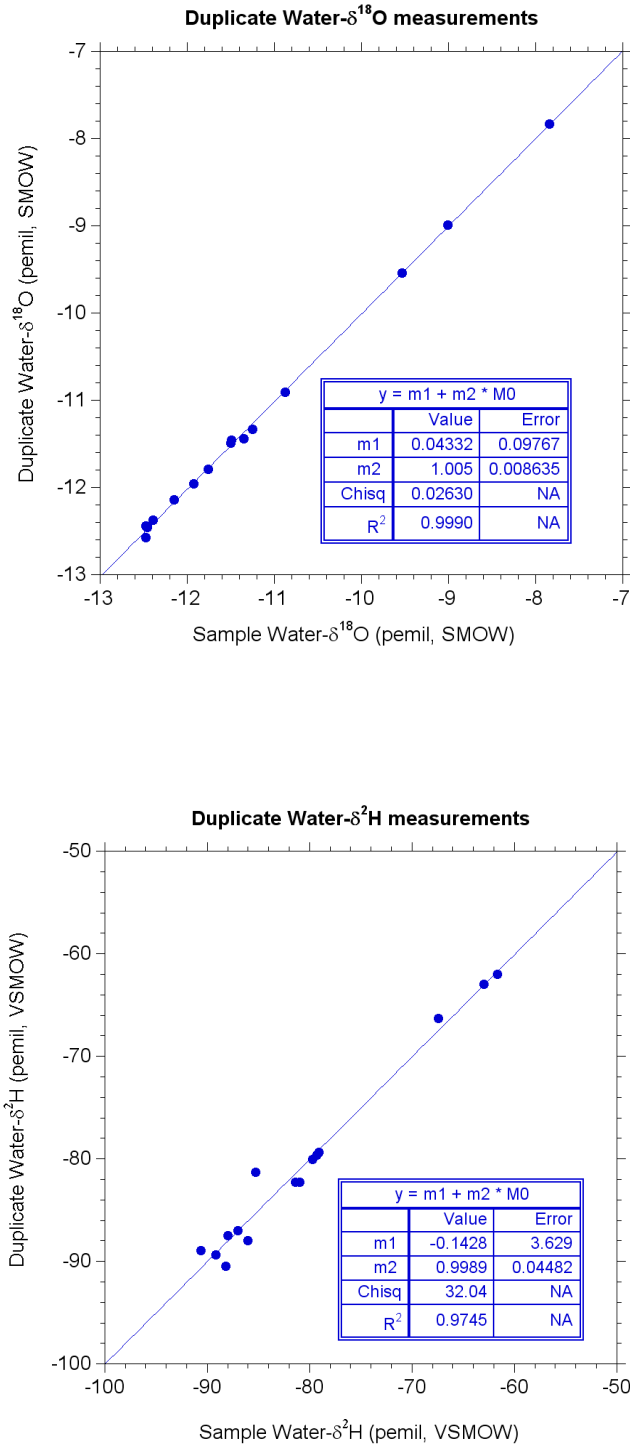


Figure 1. Plot of field duplicate water isotopic composition measurement against sample water isotopic composition measurements.

Discussion and Interpretation

Analyses

The spatial distribution of sampling for nitrate concentration, isotopic composition of water and isotopic composition of nitrate is shown in Figure 2.

Approximately 204 samples (including duplicates) were collected from domestic wells in Tulare County for the State Water Board GAMA Domestic Wells Project. These wells had NO_3 concentrations ranging from 0.8 to 240 mg/L as NO_3 . The highest nitrate concentrations were observed from wells located in the valley and along the margin of the foothills. Above 1000 ft elevation, only two samples had nitrate concentrations above the MCL.

A majority (151) of the samples from the Tulare County Private Domestic Well study area were analyzed for O and H isotope compositions of water. A small number (29) of samples were analyzed for the isotopic composition of N and O isotopic compositions of nitrate. The small number of nitrate isotopic samples analyzed were biased toward waters containing high concentrations of nitrate (median and mean of 23 and 49 mg/L as nitrate versus 12 and 26 mg/L for the entire sample set). The isotopic composition of water for samples analyzed for nitrate isotopic composition was not significantly different than for the entire data set (mean $\delta^{18}\text{O}\text{-H}_2\text{O}$ of -10.8‰ versus -10.4‰ for the entire data set).

Isotopic composition of water

A total of 151 samples were analyzed for O and H isotope compositions of water from the Tulare County Private Domestic Well study area. A large range in both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is observed, from a very light $\delta^{18}\text{O}$ value of -13.5‰ to a rather heavy $\delta^{18}\text{O}$ of -6.2‰ (Figure 3).

Typically for stable isotopes of water, there is a correlated decrease in the isotopic composition of precipitation with increasing elevation. In the Sierra, this correlation has been observed to be approximately -2.3‰ in $\delta^{18}\text{O}\text{-H}_2\text{O}$ per kilometer of elevation (Figure 4; Rose et al., 1996). This general pattern is observed in GAMA Private Domestic Well study results from El Dorado County, where lighter signatures (more negative $\delta^{18}\text{O}$ values) were observed with increasing elevation and heavier signatures (less negative $\delta^{18}\text{O}$ values) were observed in the valley floor, indicating the predominance of locally-derived water in the domestic wells sampled. The Tulare County pattern is distinctly different (Figure 5a). Many of the samples collected from lower elevations have *lower* $\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta\text{D}\text{-H}_2\text{O}$ values than would be predicted for precipitation at those elevations (Figure 4).

This apparent discrepancy is caused by extensive use of imported water from the Kings and Kaweah Rivers, which are fed from the upper Sierra. This water is used for irrigation, and recharges the shallow aquifer. Coplen and Kendall (2000) report $\delta^{18}\text{O}\text{-H}_2\text{O}$ values in the Kings River at Trimmer (elev. 942 ft RMSL) that range from -14.6 to -12.5 ‰, with an average value of -13.3 ‰. The low $\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta\text{D}\text{-H}_2\text{O}$ values in samples collected from domestic wells on the valley floor (Figures 4 and 5) indicate that these wells tap groundwater that is a mix of irrigation return water and locally derived precipitation. The extent of King's river water present in parts of the Tulare County valley groundwater system may be up to 100 percent.

The excess irrigation water has not experienced significant evaporation, despite the fact that it is applied mainly during summer months. Infiltration must take place relatively quickly after application. Evidence for lack of evaporative effects on these isotopically light samples comes from a plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ (Figure 3). Samples with isotope pairs that fall below the global meteoric water line (GMWL) have experienced significant evaporation, but for Tulare samples, only samples with $\delta^{18}\text{O}$ values greater than -9‰ show an evaporation effect. Samples with water $\delta^{18}\text{O}$ values greater than -9‰ are found on the eastern side of the study area, primarily in the foothills (Figures 4 and 5). These areas are not surrounded by irrigated agricultural fields, and irrigation return flow is not a likely source of significant recharge. Rather, $\delta^{18}\text{O}$ results from wells in the eastern portion of the study area suggest that local precipitation is the main source of recharge and that evaporation prior to recharge affects some wells. The $\delta^{18}\text{O}$ value for precipitation in the Tulare County valley area is predicted to be approximately -7.5‰ to -8‰. A pattern of decreasing $\delta^{18}\text{O}$ with increasing elevation within the foothill samples is evident in Figure 3. This is further evidence that recharge to wells in the foothill area is mainly from locally derived precipitation.

Isotopic composition of nitrate

The nitrate N and O isotope data set consists of 29 distinct samples (plus two duplicates), and is small relative to the total set of samples collected ($n=203$ including 22 duplicates). Of the samples analyzed for N and O isotope compositions, only two samples are from wells above 800 ft elevation (Figure 6). Most samples are collected from the valley and the margins of the foothills (Figures 7 and 8). We have delineated the sample set into two groups based on elevation (Figures 6): the valley wells (<400 ft. MSL) and the foothills and margins of the foothills (>400 ft. MSL). In general, these two areas are distinct in both hydrogeology and land use. The valley wells are located in the thick alluvial fan deposits, while the margin/foothills wells are more likely to overly a thinner sequence of alluvium and bedrock. Dairy operations, orchards and row crops are densely distributed at the valley elevations, while the margins and upper foothills are commonly planted with orchards. Most of Tulare County's population (which can be used as a proxy for septic effluent sources of nitrate) is located below 400 feet.

Seven samples that were analyzed for nitrate N and O isotopic composition had nitrate concentrations over the MCL. These seven samples with high NO_3 concentration have $\delta^{15}\text{N}\text{-NO}_3$ values that range from 3.7 to 11.2 ‰, with an average of 6.9 ‰. Nitrate $\delta^{15}\text{N}\text{-NO}_3$ values in this range are typically consistent with nitrification of ammonium from human waste or animal waste, i.e. septic effluent or dairy manure (see Figure 9).

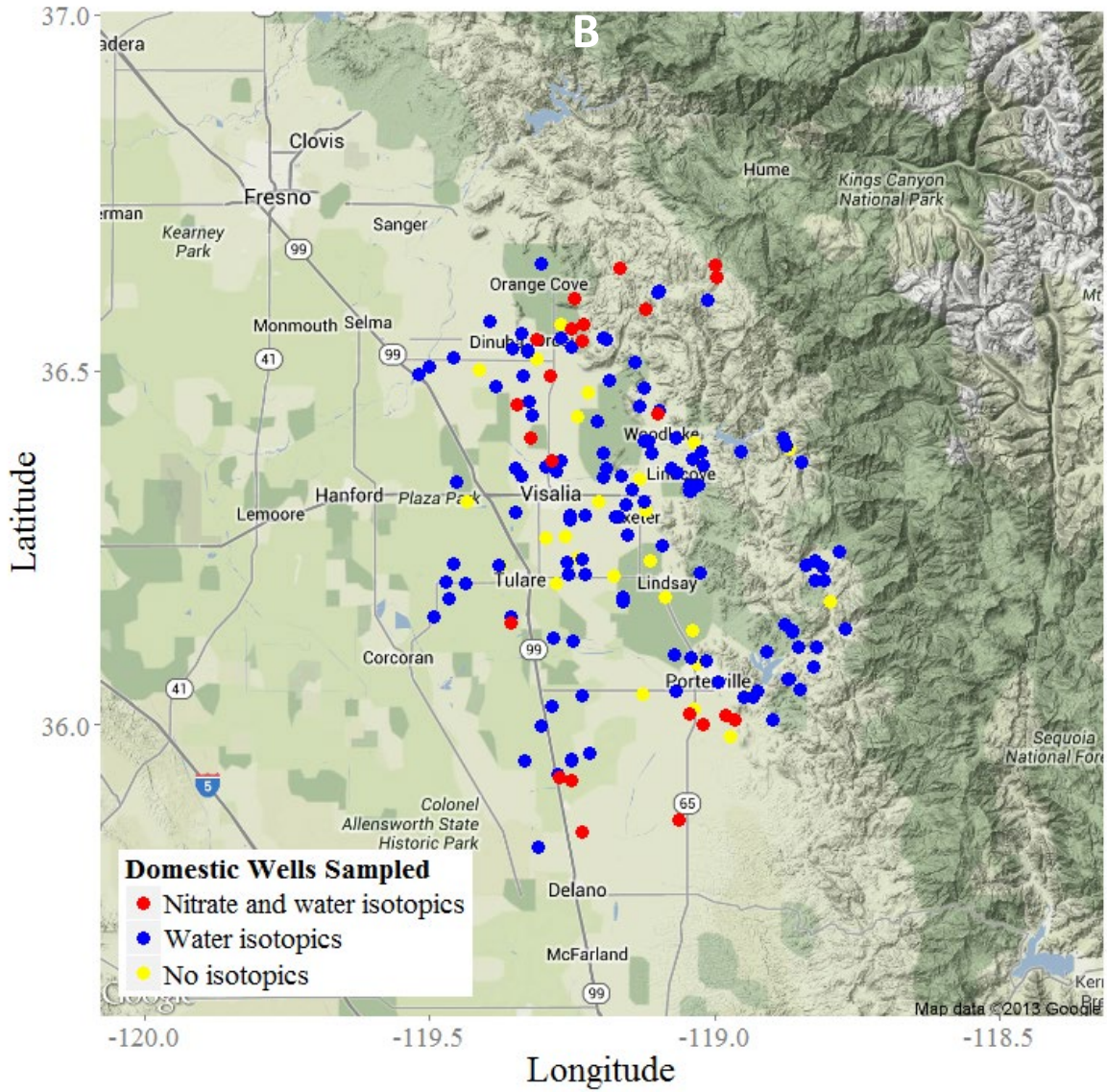


Figure 2. Tulare County domestic wells sampled for analysis of water and/or nitrate isotopic composition for the State Water Board GAMA Domestic Well Project.

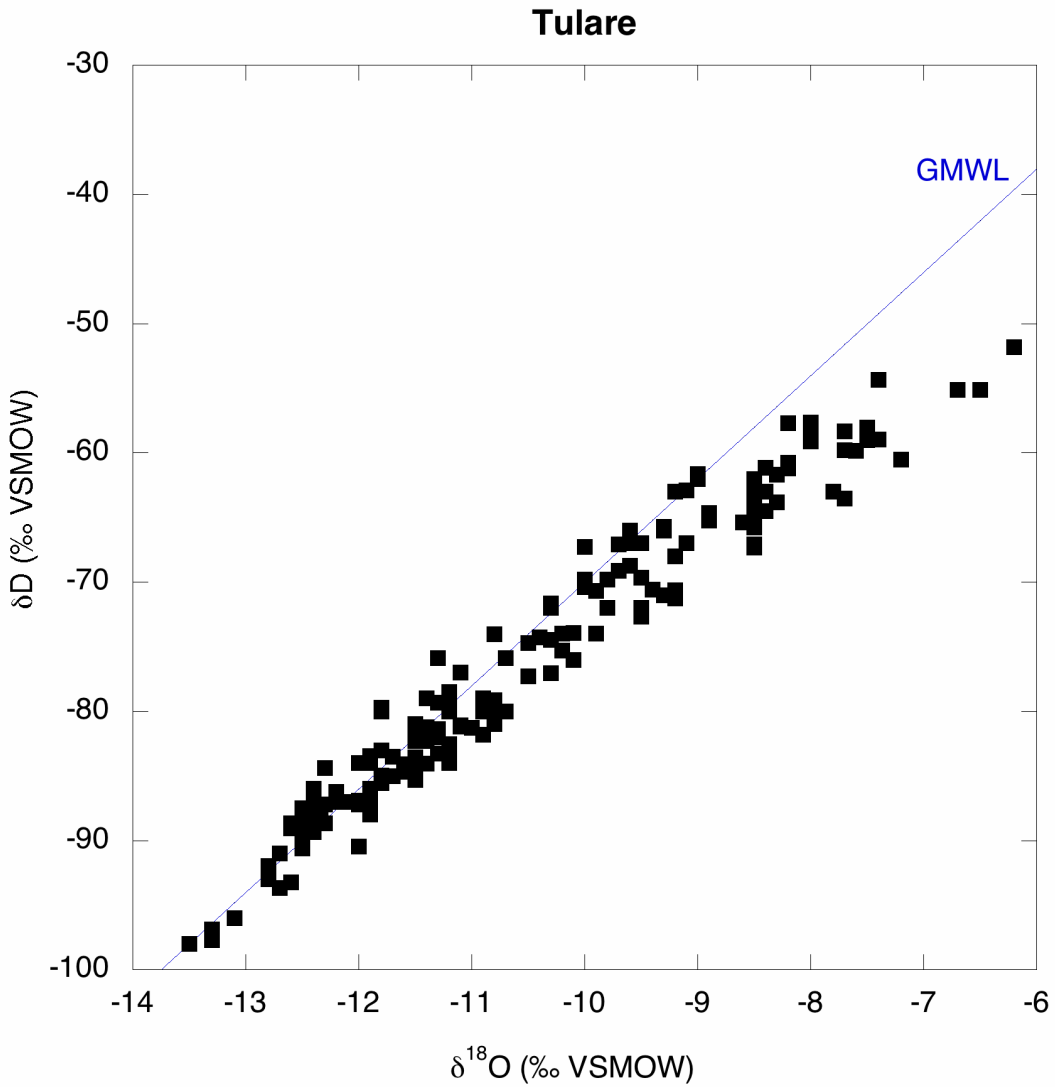


Figure 3. Stable isotope plot for samples from Tulare County Private Domestic wells. The most depleted (most negative) ratios observed are typical for Sierran River runoff sourced at high elevation. Enriched ratios (less negative) show evidence for evaporation, plotting below the meteoric water line.

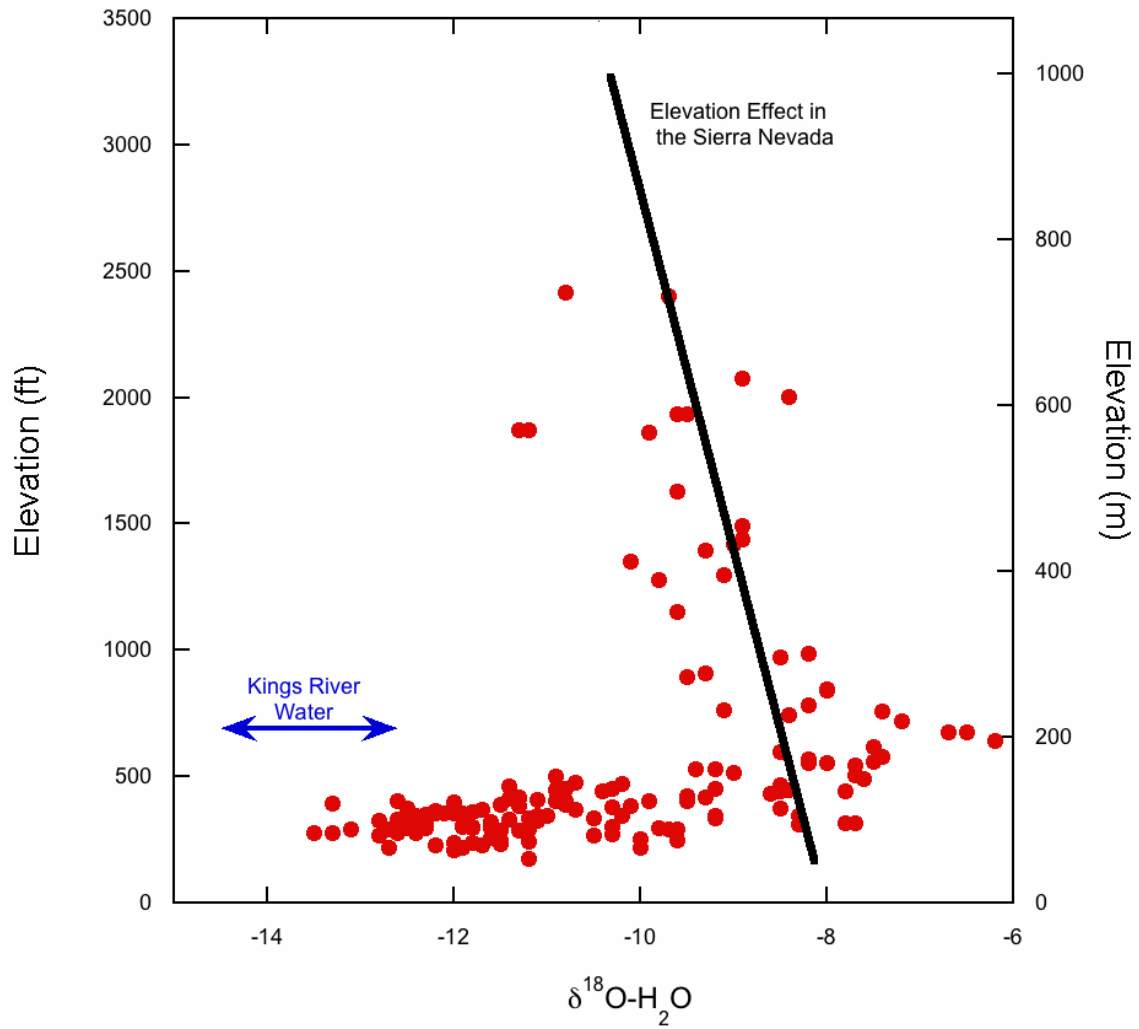


Figure 4. The elevation and oxygen isotope composition of waters collected from Tulare County domestic wells. The solid line shows the observed relation between elevation and $\delta^{18}\text{O-H}_2\text{O}$ in the Sierra (Rose et al., 1996). The observed range of Kings River water is shown based on data from Coplen and Kendall (2000).

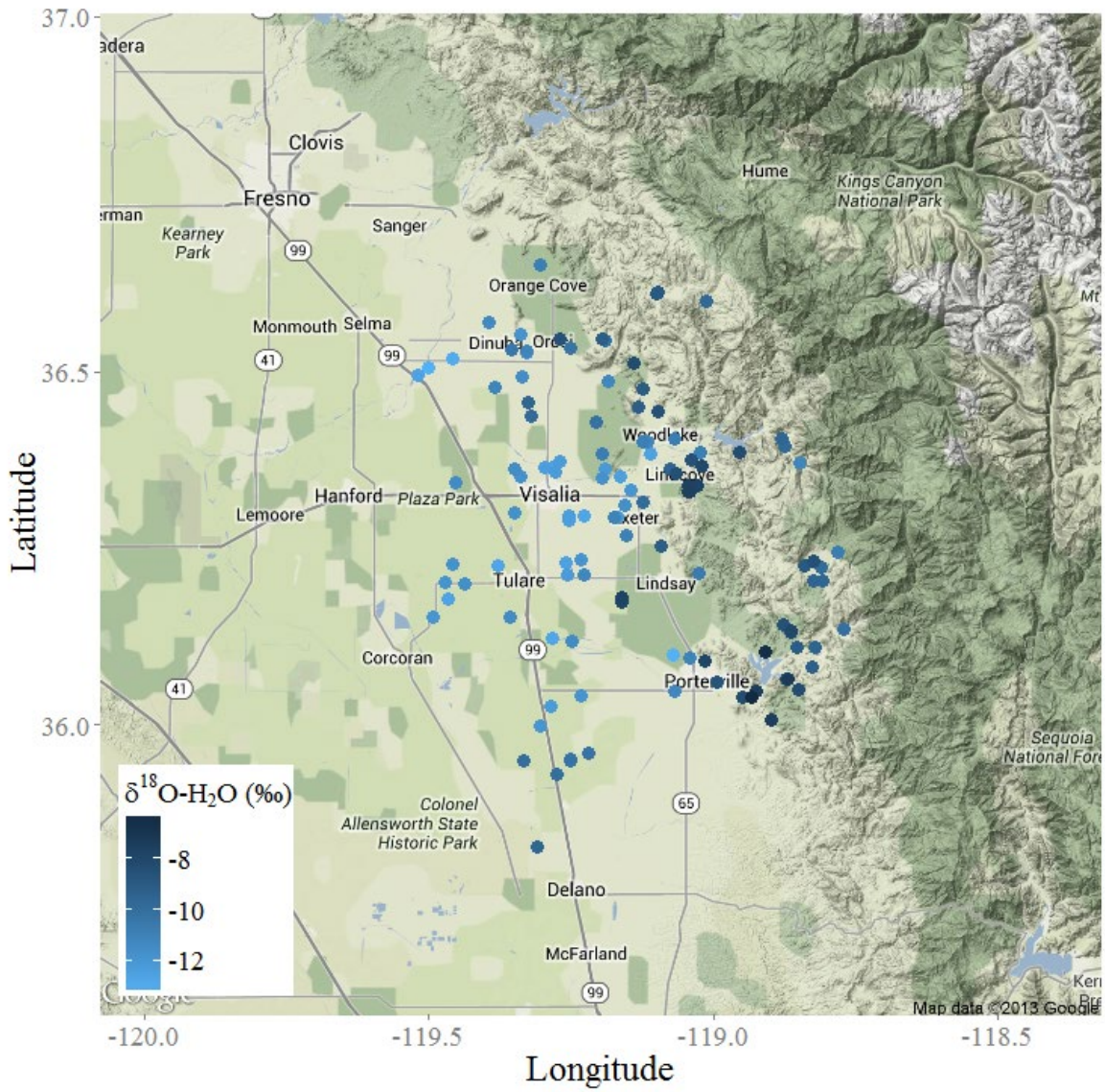


Figure 5a. Spatial distribution of water isotopic composition in Tulare County domestic wells.

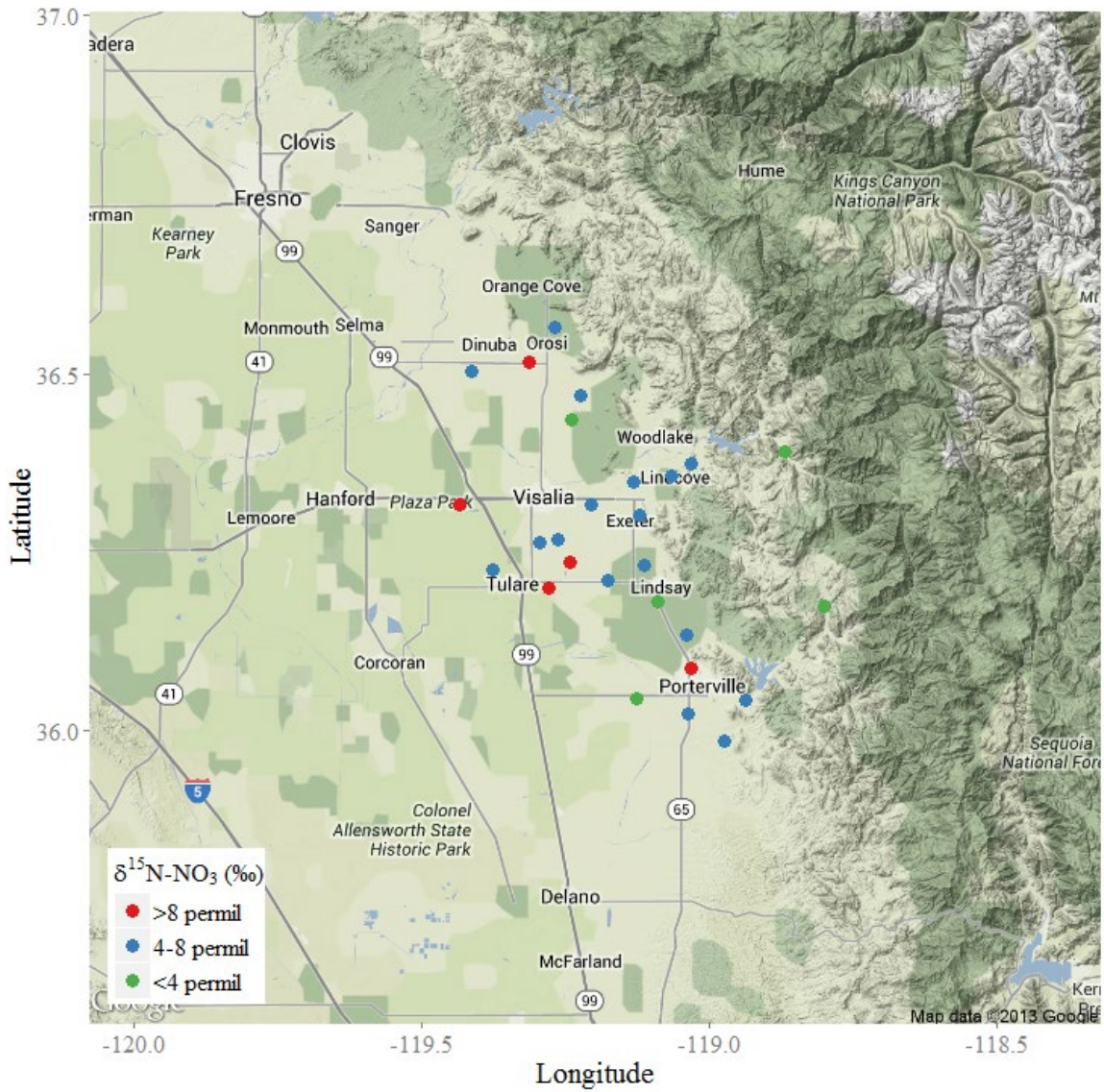


Figure 5b. Spatial distribution of nitrate isotopic composition in Tulare County domestic wells

The highest concentration sample, TUL 0979, was 240 mg/L-NO₃ and had a δ¹⁵N-NO₃ value of 6.1‰ and a δ¹⁸O-NO₃ value of 8.2‰ (Figure 6 and 7). The isotopic composition of nitrate in TUL 0979 is generally consistent with containing a component of nitrate or mixed nitrate/ammonium synthetic fertilizer (Figure 9). Nitrate in TUL 0928 also has an isotopic composition consistent with synthetic nitrate, but its nitrate concentration is low (1.6 mg/L-NO₃).

In general, the oxygen isotope composition of nitrate (δ¹⁸O-NO₃) produced by nitrification of ammonium is correlated with the oxygen isotope composition of local water (δ¹⁸O-H₂O). This correlation is due to incorporation of local water and atmospheric oxygen, typically in a 2:1 ratio, during production of nitrate from ammonium from either synthetic ammonium fertilizer or animal/human waste. The relation of oxygen isotope compositions in nitrate and water for Tulare County domestic wells is shown in Figure 10. Lines showing the predicted nitrate and water δ¹⁸O values produced from nitrification of ammonium are also plotted, with a range reflecting uncertainty in the local pore water δ¹⁸O values in the unsaturated zone where nitrification is most likely to occur. Most samples have nitrate and water δ¹⁸O values that are consistent with nitrification of ammonium in the presence of local water. Samples from the valley fall lower on the plot and reflect nitrification of ammonium in the presence of the irrigation return water with low δ¹⁸O-H₂O. Mixing with synthetic NO₃ fertilizer would cause samples to fall above the predicted lines.

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Geological Survey's NASQAN and Benchmark Surface-water Networks. USGS Open-File Report 00-160.

Kendall, C. 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C. and McDonnell, J. J. Eds.),

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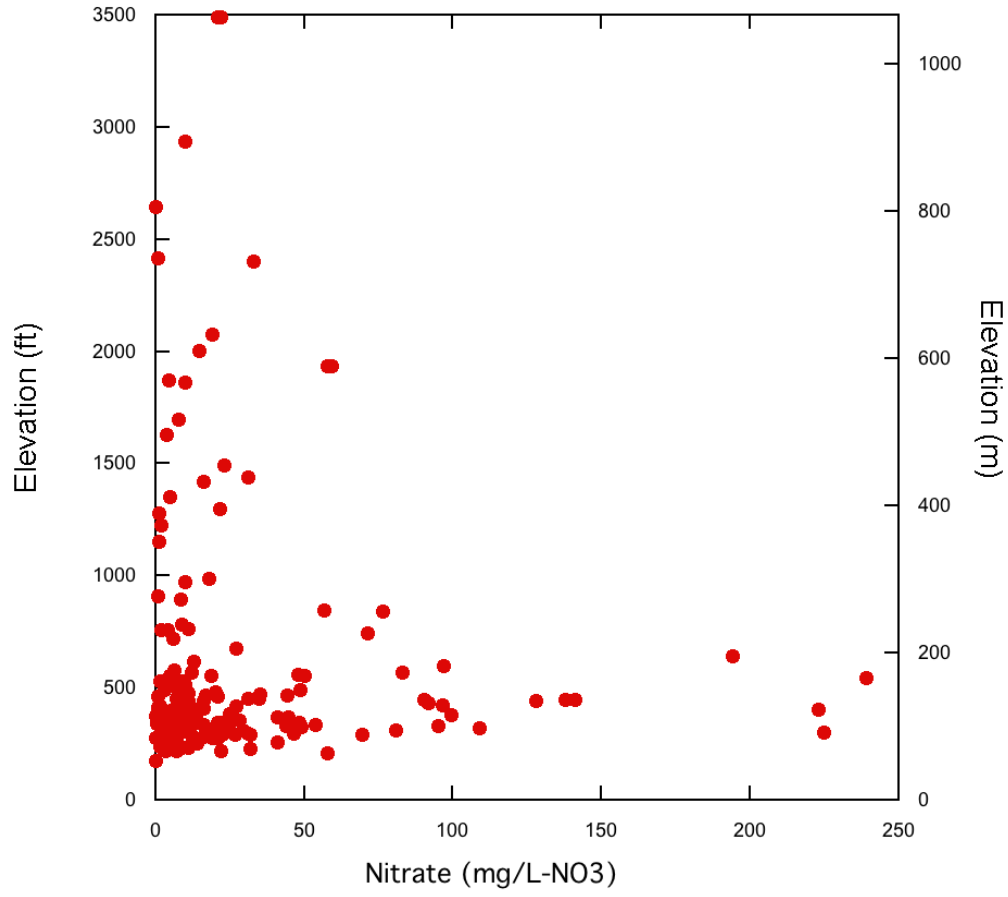


Figure 6. Well elevation versus dissolved nitrate concentrations in Tulare County domestic well samples.

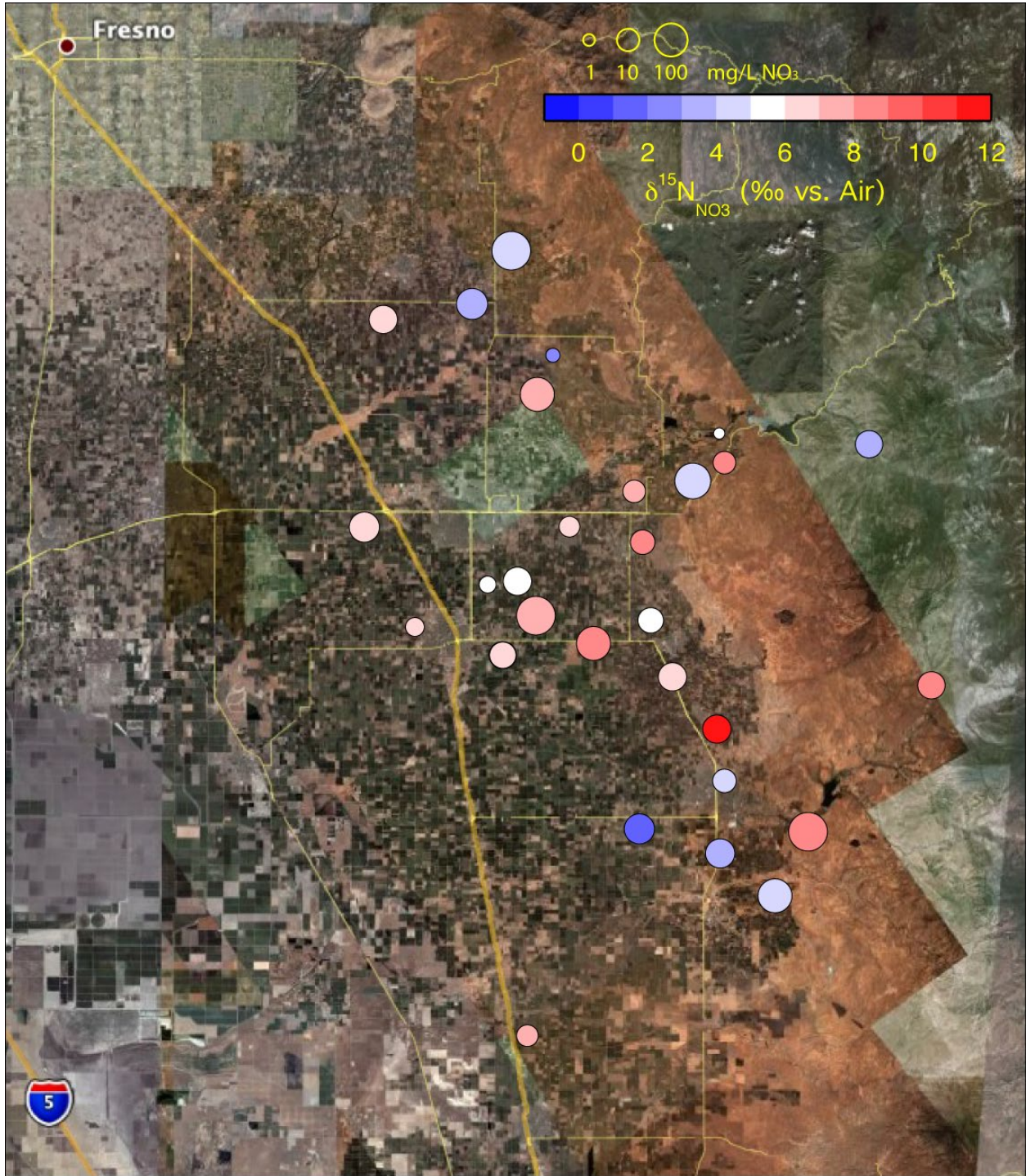


Figure 7. Wells analyzed for N isotope compositions in nitrate are shown on a Google Earth satellite image. The isotopic composition of nitrate-N ($\delta^{15}\text{N-NO}_3$) is represented by the color of the dot. The nitrate concentration of each well is represented by the size of the dot.

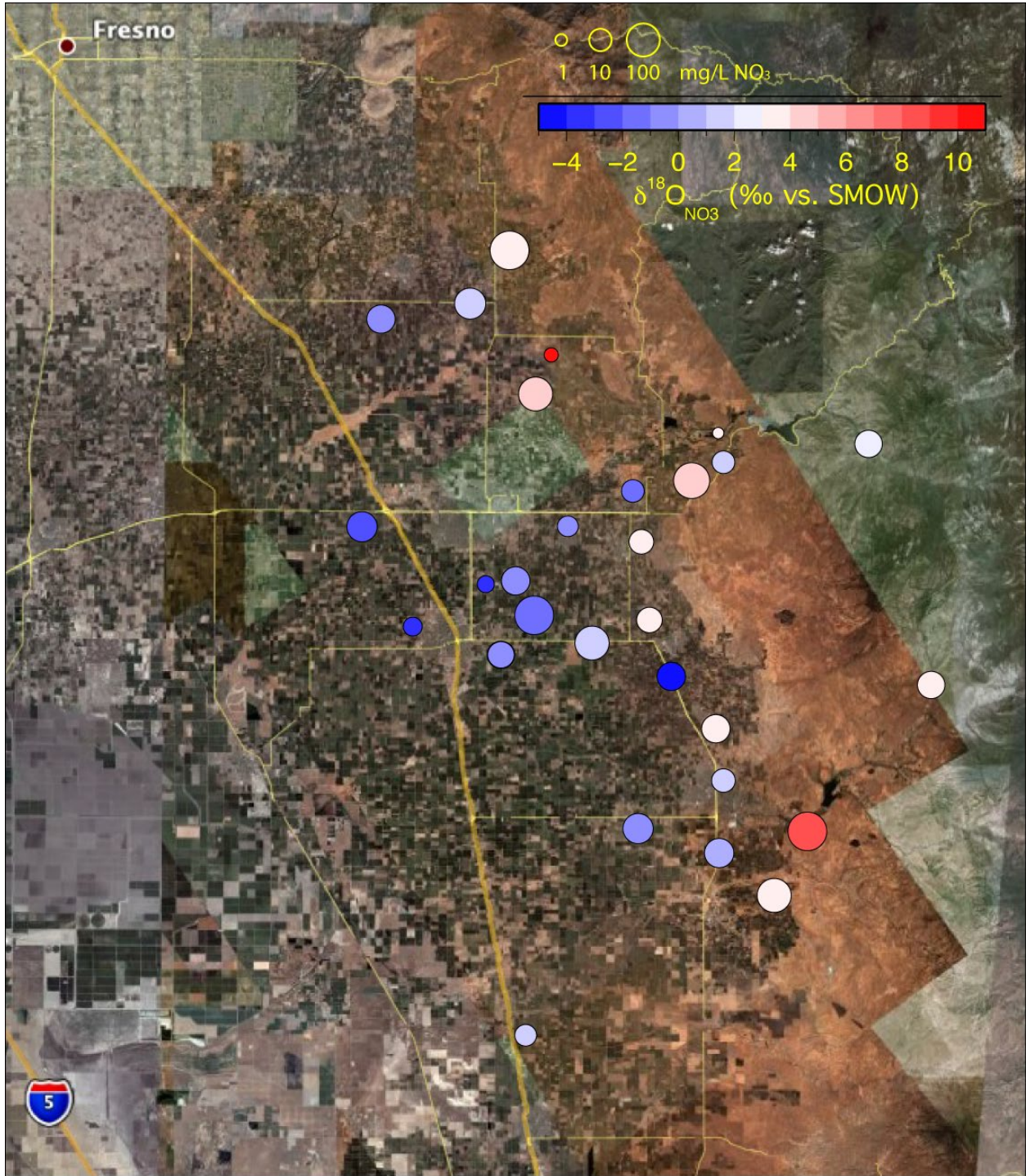


Figure 8. Wells analyzed for O isotope compositions in nitrate are shown on a Google Earth satellite image. The isotopic composition of nitrate-O ($\delta^{18}\text{O-NO}_3$) is represented by the color of the dot. The nitrate concentration of each well is represented by the size of the dot.

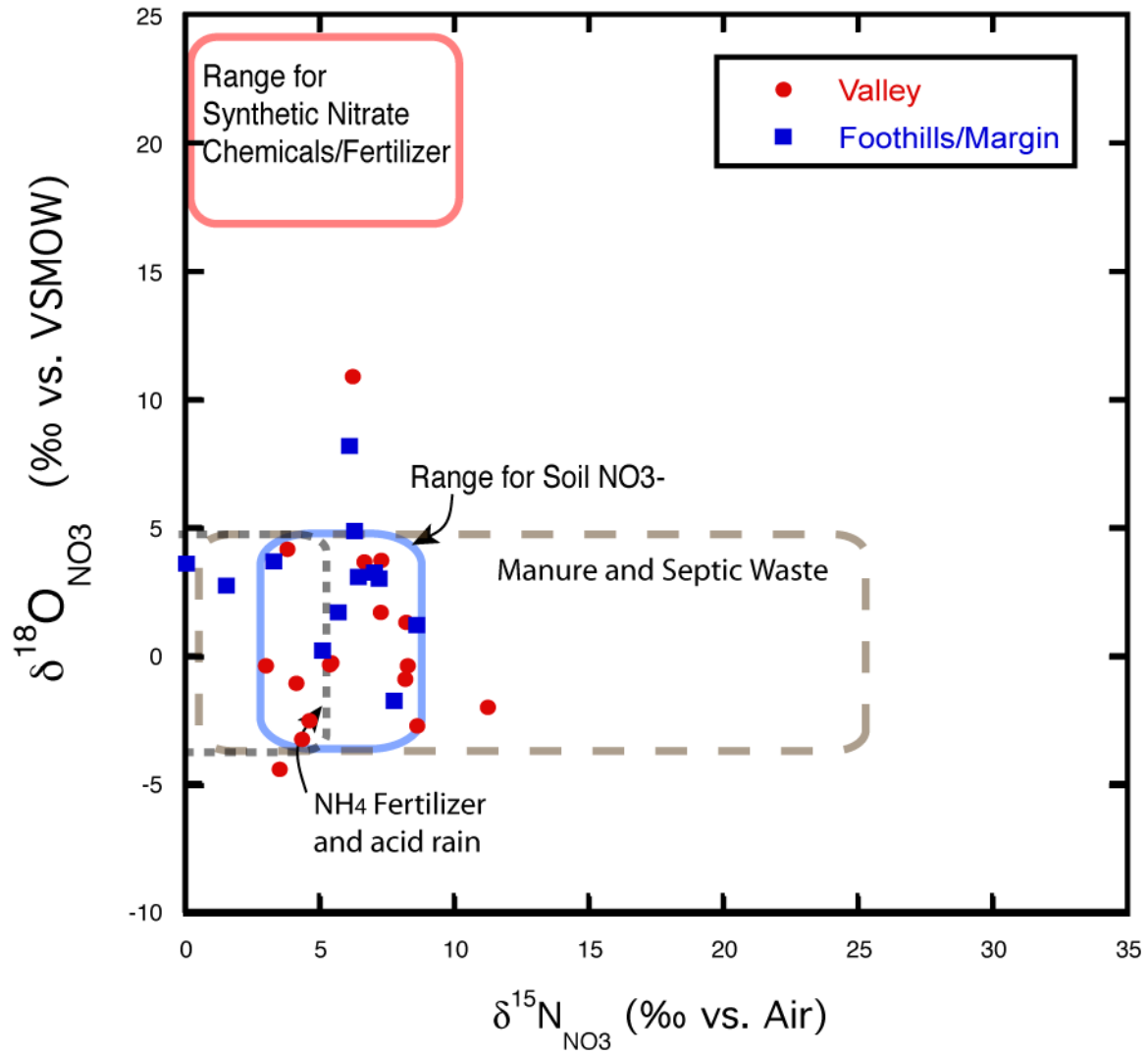


Figure 9. Nitrogen and oxygen isotope compositions of dissolved nitrate in Tulare County wells. Observed ranges from nitrate sources are modified from Kendall (1998) based on the observed oxygen isotope composition of water from this study.

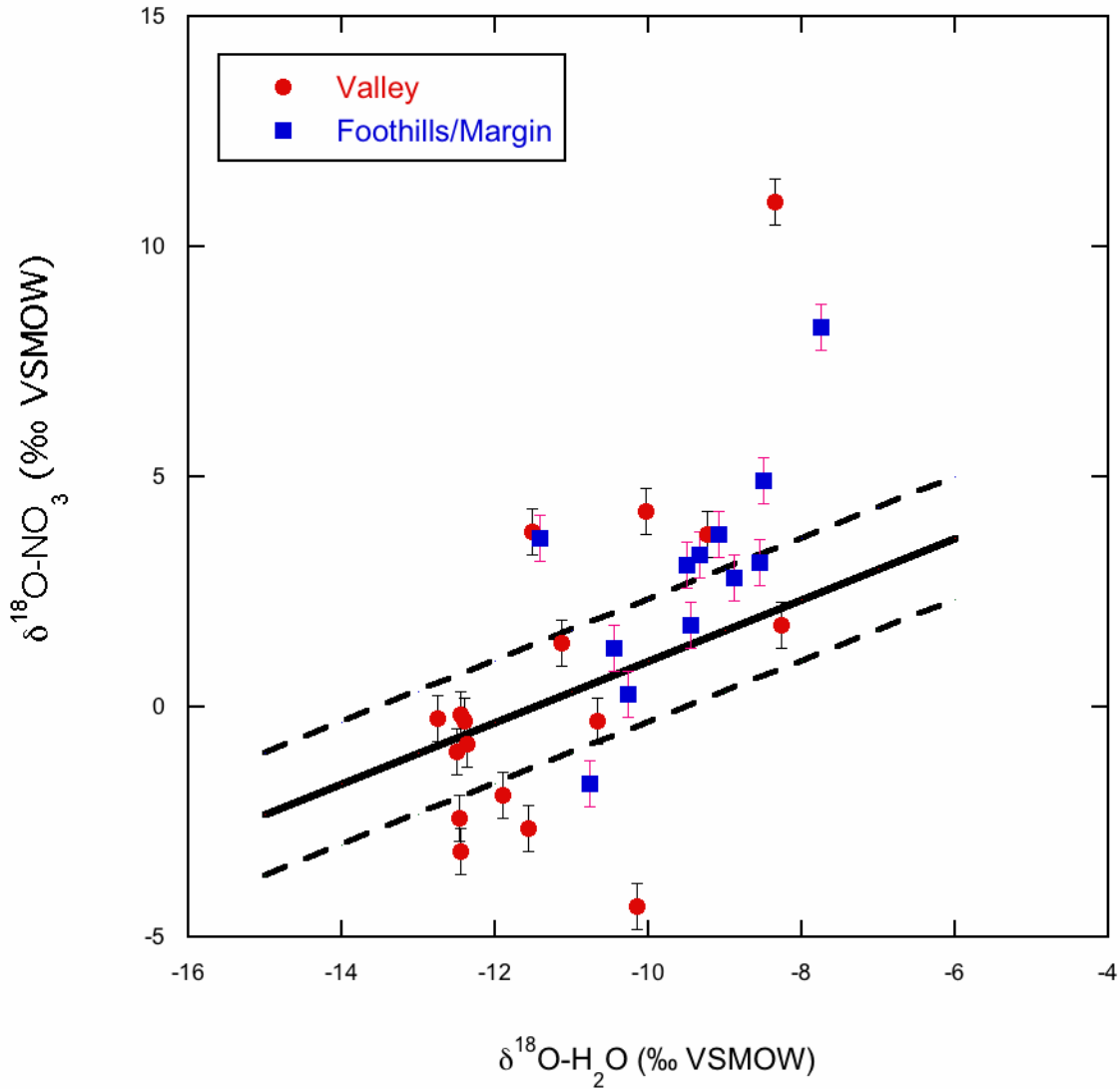


Figure 10. Oxygen isotope compositions in water and nitrate from Tulare County domestic wells. The predicted relation between oxygen isotope compositions in water and nitrate produced by nitrification of ammonium are shown (solid line) with additional lines to account for a range of $\delta^{18}\text{O-H}_2\text{O}$ values that may occur in unsaturated zone pore waters where nitrification is likely to occur (dashed lines).

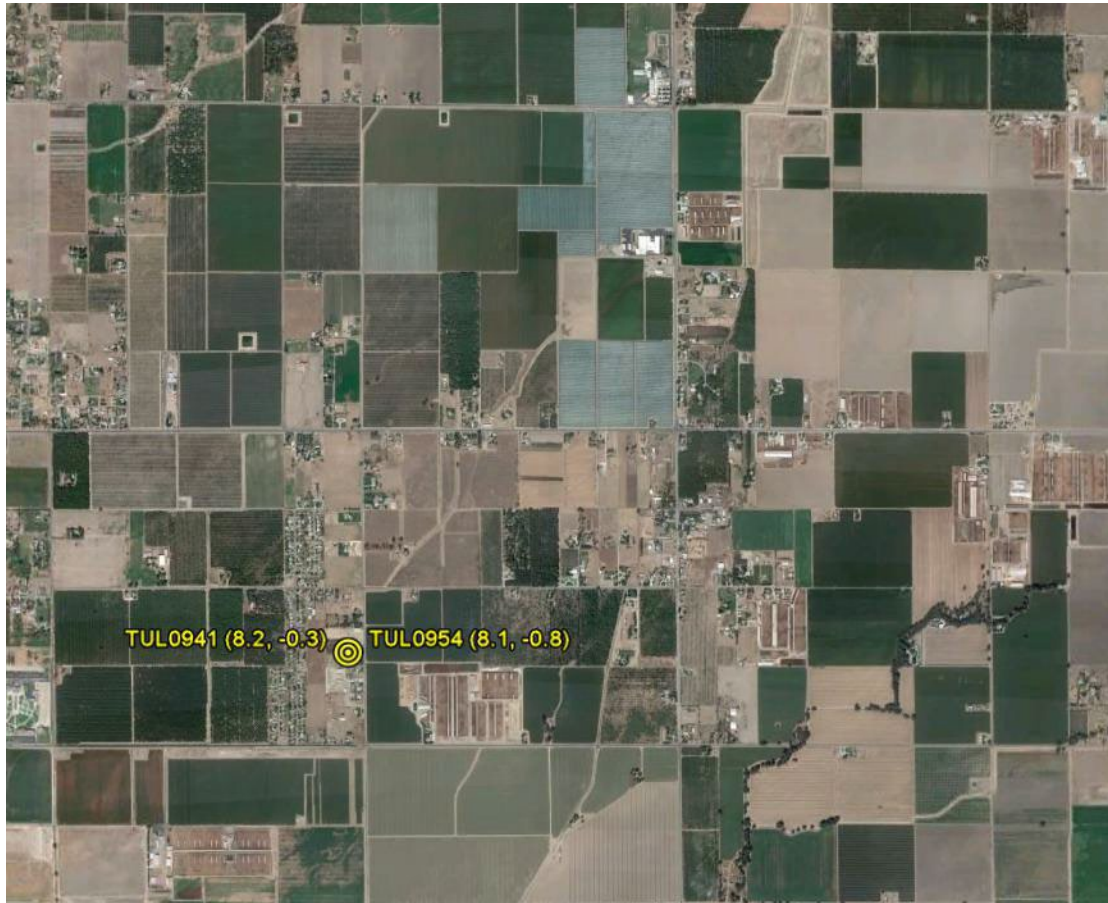


Figure 11. Location of duplicate samples TUL 0941 and TUL 0954 on a Google Earth 2010 satellite image. Both isotopic composition and concentration for these samples reproduced well: 19 vs. 21 mg/L nitrate; 8.2 vs. 8.1 ‰ $\delta^{15}\text{N-NO}_3$, -0.3 vs. -0.8 ‰ $\delta^{18}\text{O-NO}_3$ (TUL 0941 vs TUL 0954). This valley well (elevation 279 feet) is close to two dairy operations, and the groundwaters have nitrate isotopic compositions within the range of nitrate associated with a dairy manure source.



Figure 12. Location of well TUL979 on a Google Earth 2010 satellite image. This foothill well (elevation 546 feet) is in a sparsely populated area surrounded by orchards and has high nitrate concentration (240 mg/L nitrate). The nitrate isotopic composition ($\delta^{15}\text{N-NO}_3 = 6.1$, $\delta^{18}\text{O-NO}_3 = 8.2$), in particular the high $\delta^{18}\text{O-NO}_3$, is indicative of a synthetic fertilizer source.

Significant Findings

- In general, higher domestic well water nitrate concentrations are found in valley wells below 400 feet surface elevation.
- Domestic wells below 400 feet surface elevation draw on groundwater heavily impacted by irrigation with Kings and Kaweah River water, as indicated by water isotopic composition. This finding is consistent with both the long and heavy usage of Kings River water for irrigation in this area, and with the assumed shallow depth of these domestic wells. Nitrate associated with these waters is presumably associated with the same source (chemical or organic fertilizer in irrigation water) or is mobilized by irrigation (septic effluent or soil nitrogen).
- Domestic wells in the foothills (with elevations above 400 feet) receive recharge derived from local precipitation that has experienced some evaporation.
- Nitrate concentrations in the most polluted wells are sufficiently high to preclude a significant contribution from soil or atmospheric sources. Such sources cannot be precluded in wells with nitrate concentrations below the regulatory drinking water limit, however the data set does not include enough samples near typical background concentration levels to assess the isotopic characteristics of natural nitrate sources in this area.
- Nitrate isotopic compositions indicate a dairy manure or septic effluent source for the majority of the most heavily impacted wells, with the exception of one well with high nitrate concentration and an isotopic composition indicative of a synthetic fertilizer source. An analysis of land use and the distribution of potential nitrate sources would be extremely useful.

A preliminary investigation of the correlation between land use and nitrate isotopic composition was conducted (see Appendix “GAMA Domestic Well Project - Tulare County. Nitrate Source Attribution: The Isotopic Evidence”). The sparse nitrate isotopic data set is under-represented by domestic wells with no potential anthropogenic sources within 500 m of the well, and the method used to assign land use is cursory. Patterns observed, however, are consistent with multiple anthropogenic sources, including dairy wastewater, septic effluent and synthetic fertilizer.

- Nitrate isotopic composition does appear to vary with land use
 - Dairy, agricultural/residential, and wild-land sites are isotopically distinct
 - Dairy site nitrate-N isotopic data are isotopically consistent with a manure source
 - Nitrate-O isotopic data are isotopically consistent with local nitrification of ammonium (from manure, septic effluent, or synthetic ammonium fertilizer)
- The isotopic evidence is consistent with more than one nitrate source
 - Domestic wells located close to dairies do have a different nitrate isotopic composition than wells not close to dairies in similar hydrogeologic settings.
 - The isotopic compositions measured are consistent with the suspected sources of nitrate to these wells (soil, fertilizer, manure, septic or community wastewater).
 - High concentrations of nitrate occur in all developed land use categories.