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California GAMA Special Study: Distinguishing septic system and agricultural nitrate sources with stable isotope compositions and trace organic compounds: An investigation of nitrate sources in Chico, CA

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Final Report for the California State Water Resources Control Board

GAMA Special Studies Task 5.1: *Field-based Studies of Water Quality Impacts of Septic Systems to Groundwater Basins*

Auspices Statement
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GAMA: AMBIENT GROUNDWATER MONITORING & ASSESSMENT PROGRAM SPECIAL STUDY

Water Boards

California GAMA Special Study:
Distinguishing septic system and agricultural nitrate sources with stable isotope compositions and trace organic compounds: An investigation of nitrate sources in Chico, CA

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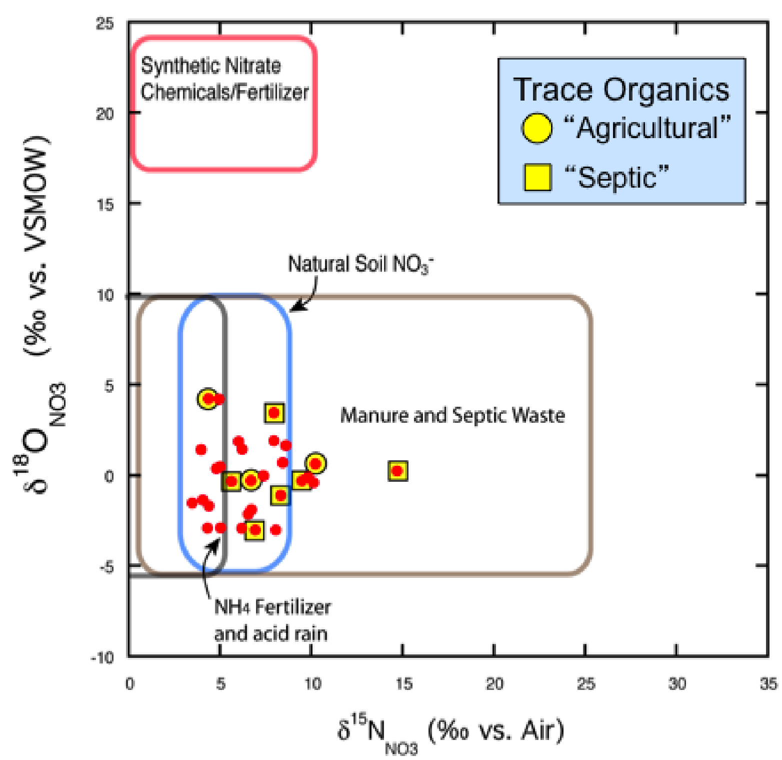

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California GAMA Special Study: Distinguishing septic system and agricultural nitrate sources with stable isotope compositions and trace organic compounds: An investigation of nitrate sources in Chico, CA (LLNL-TR-553871)

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Key Findings

- This study combines the detection of trace organic compounds including pesticides, pharmaceuticals, and personal care products with $^{3}H/^{3}He$ apparent ages and isotopic compositions of nitrogen and oxygen in nitrate in order to distinguish between potential nitrate sources.
- Septic system-derived nitrate is formed by nitrification, and often cannot be differentiated from agricultural or background sources based on nitrate N and O isotopic compositions alone. Samples that lie within the overlapping fields of natural nitrate and septic discharge can be sometimes be differentiated by the presence of trace organic compounds specific to septic discharge.
- The isotopic composition of N and O in nitrate and infrequent, trace-level detections of carbamazepine, nonyl-phenol, and caffeine suggest that transport of wastewater, likely from septic discharge, affects groundwater within the urban area of Chico, at individual shallow monitoring wells that sample recent recharge. The impact of agricultural activities on groundwater nitrate appears to be limited to the outskirts of Chico where orchards are currently in use rather than being legacy sources in formerly agricultural areas that have been converted to residential use.
- The samples for this study were collected in 2005, and pre-date the improvements in groundwater quality anticipated from the ongoing conversion from septic to sewer waste discharge in the urban Chico area.

Nitrate Sources in Chico, California

The community of Chico, CA relies on groundwater for its supply of drinking water. Beginning in the early 1980's many Chico wells were found to have nitrate concentrations in excess of the 45 mg/L MCL, making the water unsafe for drinking. Some domestic wells in Chico have had nitrate concentrations reported as high as 200 mg/L. Based on a study of nitrate sources using nitrogen isotope compositions of nitrate (Aqua Resources, 1985), the domestic wells are impacted by nitrate from septic system leachate as well as fertilizer used in agricultural operations. In 2005, when this study was carried out, Geotracker showed only two active public drinking water supply wells, which are typically much deeper than the domestic wells, have had nitrate concentrations that exceed the MCL. These high nitrate findings in drinking water wells represented only temporary spikes, and in general most public supply wells have nitrate concentrations well below the MCL. In order to ensure a safe drinking water supply, Butte County developed a Nitrate Action Plan in 1985 and the Chico Urban Nitrate Compliance Plan in 2000. These plans called for gradually connecting residential areas reliant on septic systems to the city's sewer system and extending the city's water distribution network.

The purpose of our study is to develop an improved understanding of nitrate fate and transport around septic systems. In order to identify nitrate from septic system discharge, we combine the detection of trace organic compounds that are specific to domestic waste with isotopic compositions of nitrogen and oxygen in nitrate. Under anaerobic conditions and in the presence of an electron donor such as organic carbon, microbially mediated denitrification may transform nitrate to harmless nitrogen gas. We use a membrane inlet mass spectrometer (MIMS) system to detect the occurrence of saturated zone denitrification by measuring excess dissolved nitrogen gas. Groundwater age dating using the $^3H/^3He$ method provides a means of tracking the history of nitrate inputs to groundwater. The samples analyzed for this study were collected in 2005, before most of the planned sewer conversions had taken place. We do not anticipate that this study will provide an assessment of the ongoing sewering project, since the groundwaters sampled for this study likely pre-date the potential benefits of this project.

Thirty wells were sampled as part of this study: 22 shallow monitoring wells and 8 water supply wells. The analytes determined are listed in Table 1; sample data are tabulated in Table 2. Nitrate concentrations in these wells range from 0.9 mg/L to 92 mg/L. Total organic carbon ranges from <0.5 mg/L to 2.2 mg/L. The presence of total organic carbon may provide an electron donor source necessary for denitrification. Ammonium is below detection limits (<0.02 mg/L) in all but two samples (Table 2).

Most of the wells sampled for this study produce water derived from very recent recharge (Figure 1a). Of the 27 wells where age was determined, 18 wells contain water recharged in the last two years or less. Six public supply wells had ages ranging from recent water to 29 years. Most of the drinking water wells are near Big Chico Creek, and receive recharge from the creek. One private supply well contains relatively old water (>50 years).

Wells with NO_3^- concentrations higher than 20 mg/L were all recharged within the last 5 years (Figure 2a). All of these high nitrate samples were collected from first encounter monitoring wells. The young age and high nitrate concentrations indicate a nearby source of nitrate at these wells. This relationship is also consistent with a modern source of nitrate rather than a legacy source at formerly agricultural sites.

Dissolved gases in Chico groundwater primarily contain N_2 from equilibration with air and incorporation of excess air in the vadose zone. There is little evidence for extensive production of N_2 by saturated zone denitrification in the groundwater beneath Chico. Based on noble gas determinations of recharge temperature and excess air incorporation at each Chico well, the maximum expected N_2/Ar ratio ranges from 38.3 to 42.7. There are twenty wells with N_2/Ar ratios slightly above this threshold (Figure 2b), which may indicate minor amounts of excess nitrogen due to denitrification (equivalent to the reduction of 1 to 16 mg/L nitrate to N_2). The lack of any samples showing complete denitrification suggests that there is significant mixing of denitrified water with water that has not been affected by denitrification.

Nitrate concentrations are also lowered in some areas due to dilution by recharge from Big Chico Creek. Overdraft of the aquifer has created large cones of depression in the urbanized areas of Chico. Water from Big Chico Creek is drawn into the groundwater system, resulting in decreased nitrate concentrations, elevated recharge temperatures and lower $\delta^{18}O$ values near the creek (Figure 3a and 3b). This pattern is present in both the deep wells sampled previously and in shallow wells from this study.

Table 1: Analytes for Chico wells in the nitrate source study.

Trace Organics: (partial list of target compounds)	Carbamazepine , Nonylphenol, DEET, Triclosan, Tris (2-chloroethyl) phosphate, Tris (1,3-dichloroisopropyl) phosphate, Triphenyl phosphate, Coprostanol, Cholesterol, Stigmastanol, Atrazine, Norflurazon
Stable isotopes:	$\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3, $\delta^{18}O$-H_2O, $\delta^{2}H$-H_2O
Solutes:	Chloride, Nitrate, Ammonium
Carbon sources:	Total organic carbon
Dissolved gases:	Nitrogen, Oxygen, Argon, Helium, Krypton, Xenon, Neon
Groundwater age:	$^3H/^3He$

Table 2: Data for Chico wells in the nitrate source study.

LLNL ID #	Well type	Latitude	Longitude	Sample Date	Cl^- (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	ORP (mV)	DO (mg/L)	TOC (mg/L)	$\delta^{18}O$ H_2O (‰ SMOW)	$\delta^{15}N$ NO_3^- (‰ Air)	$\delta^{18}O$ NO_3^- (‰ SMOW)	$^3H/^3He$ age (yr)	Noble gas recharge temperature (°C)	^3H (pCi/L)	Excess N_2 (as mg/L NO_3^-)	Trace organics detected
103023	MW	39.7454	-121.8560	10/25/2005	20.7	40.5	3.23	92	6.0	0.5	-9.4	6.7	-2.8			10.1 +/- 0.6	0	Carbamazepine
103022	MW	39.7354	-121.8776	10/25/2005	23.0	61.3	<0.01	56	8.9	1.0	-8.9	3.3	-1.4			11.5 +/- 0.7	2	
103021	MW	39.7266	-121.8230	10/13/2005	19.9	32.5	<0.04	207	4.4	0.5	-9.0	14.5	0.4	1 +/- 1	20 +/- 1	10.3 +/- 0.5	10	Tris (1,3-dichloroisopropyl) phosphate
103020	MW	39.7353	-121.8378	10/13/2005	13.9	3.6	<0.04	176	3.0	<0.5	-9.9	7.2	0.1	<1	19 +/- 1	15.5 +/- 0.7	ND	
103019	MW	39.7574	-121.8640	10/05/2005	45.4	30.9	<0.04	120	9.1	0.7	-8.5	4.6	0.5	1 +/- 1	19 +/- 1	9.4 +/- 0.5	10	
103018	MW	39.7613	-121.8602	10/05/2005	11.1	25.2	<0.04	95	8.8	<0.5	-8.7	7.8	3.6	2 +/- 2	20 +/- 1		ND	Carbamazepine
103017	MW	39.7614	-121.8650	10/05/2005	14.8	30.0	<0.04	33	8.7	<0.5	-8.8	7.9	-2.8	5 +/- 7	23 +/- 4		ND	
103014	MW	39.7572	-121.8558	10/05/2005	41.8	60.7	<0.04	252	9.5	1.0	-8.3	4.2	-1.5	0 +/- 2	19 +/- 1		3	
103013	MW	39.7516	-121.8565	10/05/2005	38.3	68.6	<0.04	309	9.3	1.4	-9.1	3.8	1.5	<1	19 +/- 1		ND	Caffeine
103012	PS	39.7588	-121.8523	08/18/2005	8.5	13.5	<0.04			<0.5	-9.7	4.1	-2.7	15 +/- 1	17 +/- 1	12.3 +/- 0.6	ND	
103011	PS	39.7648	-121.8489	08/18/2005	4.0	4.8	<0.04			<0.5	-8.7	5.8	2.0	<1	20 +/- 1		4	
103010	PS	39.7618	-121.8649	08/18/2005	5.0	6.7	<0.04			<0.5	-9.1	3.9	-1.2	7 +/- 1	19 +/- 1	7.5 +/- 0.4	2	
103009	PS	39.7450	-121.8773	08/18/2005	8.5	8.7	<0.04			<0.5	-10.1	6.0	-2.7	25 +/- 1	13 +/- 1	21.8 +/- 0.9	ND	
103008	PS	39.7308	-121.8808	08/18/2005	17.3	19.2	<0.04			<0.5	-10.2	7.8	2.0	25 +/- 1	16 +/- 1		2	
103007	PS	39.7308	-121.8690	08/18/2005	17.2	18.2	<0.04			0.5	-9.9	9.7	0.0	29 +/- 1	17 +/- 1		1	
103006	MW	39.7729	-121.8623	07/14/2005	17.2	16.6	<0.02		5.7	1.1	-8.4	10.0	0.8	<1	18 +/- 1	9.3 +/- 2.0	2	Desmethylnorflurazon
103005	MW	39.7599	-121.8752	07/13/2005	32.4	55.1	<0.02		5.2	2.2	-8.8	8.2	0.8	0 +/- 2			16	
103004	MW	39.7347	-121.8420	07/13/2005	15.8	7.3	<0.02		4.6	<0.5	-10.1	6.4	-2.0	12 +/- 1	19 +/- 1		5	
103003	MW	39.7347	-121.8420	07/13/2005	17.7	10.5	<0.02		3.4	<0.5	-9.9	6.0	1.6	9 +/- 1	19 +/- 1	8.7 +/- 0.5	6	
103002	MW	39.7347	-121.8420	07/13/2005	12.5	8.5	<0.02		3.0	0.6	-9.9	5.4	-0.2	1 +/- 1	17 +/- 1	13.2 +/- 0.6	5	Nonylphenol, DEET
103001	MW	39.7352	-121.8350	10/13/2005	12.6	3.1	<0.04	171	4.2	0.6	-10.0	4.8	-2.7	0 +/- 1	19 +/- 1	12.5 +/- 0.6	7	
103000	MW	39.7309	-121.8935	10/12/2005	28.6	92.1	<0.04	122	6.6	1.1	-9.1	4.8	4.3	0 +/- 1	16 +/- 1		4	Desisopropyl atrazine
102999	MW	39.7287	-121.8734	10/12/2005	40.4	24.5	<0.04	127	4.7	0.5	-9.6	9.3	-0.2	0 +/- 1	19 +/- 1		7	Carbamazepine
102998	MW	39.7191	-121.8491	10/12/2005	21.7	25.6	<0.04	109	4.2	<0.5	-9.2	8.4	1.8	1 +/- 1	20 +/- 1	10.7 +/- 0.6	7	
102997	MW	39.7079	-121.8430	10/12/2005	16.8	35.3	<0.04	96	6.6	0.9	-8.9	6.5	-0.1	1 +/- 1	20 +/- 1	9.6 +/- 0.5	2	Atrazine
102996	MW	39.7626	-121.8527	10/05/2005	10.5	23.9	<0.04	189	8.5	<0.5	-8.6	8.1	-0.9	1 +/- 2	19 +/- 1		ND	Carbamazepine
102995	MW	39.7538	-121.8538	10/05/2005	13.1	30.6	<0.04	34	8.1	0.7	-8.5	9.9	-0.3	1 +/- 1	19 +/- 1		ND	
102994	MW	39.7599	-121.8404	06/14/2005	20.0	21.0	<0.02		5.3	0.6	-8.5	6.5	-1.7	2 +/- 1	21 +/- 1	8.9 +/- 0.5	6	
102993	PS	39.7794	-121.8783	06/14/2005	20.0	0.9	2.68	-61	0.8		-10.0	4.2	4.3		19 +/- 1	2.3 +/- 0.2	2	Caffeine
102992	PS	39.7316	-121.8650	06/14/2005	39.5	8.1	<0.02			<0.5		4.8	0.6	>50		0.8 +/- 0.2	0	

ND = not detected; MW = monitoring well; PS = public supply well

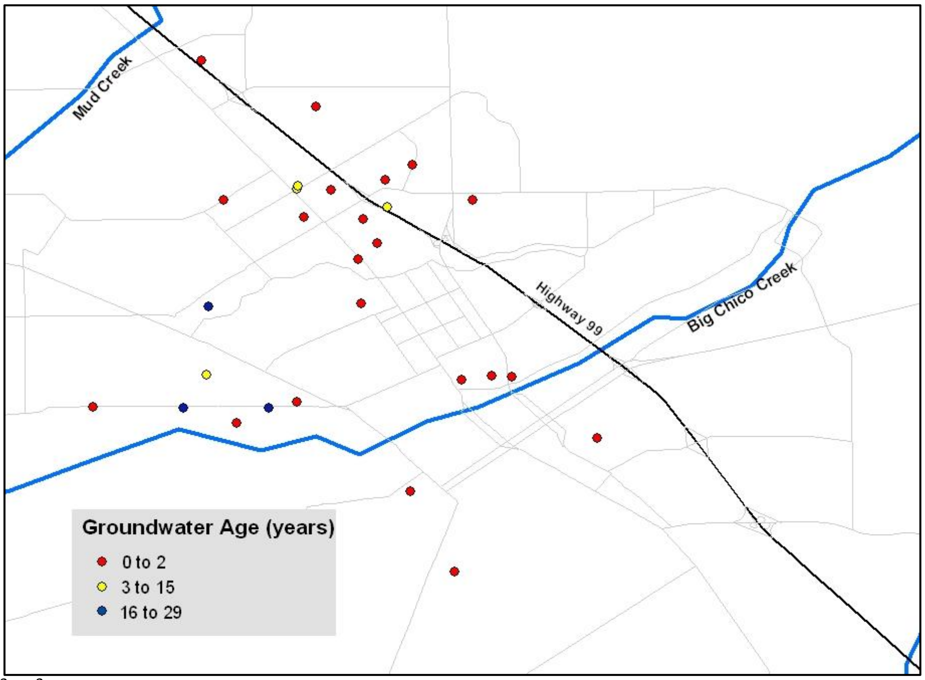

Figure 1a: $^3H/^3He$ apparent ages of groundwater at wells sampled for this study. The predominance of ages <2 years show that the monitoring wells in the Butte County nitrate monitoring network produce recently recharged groundwater.

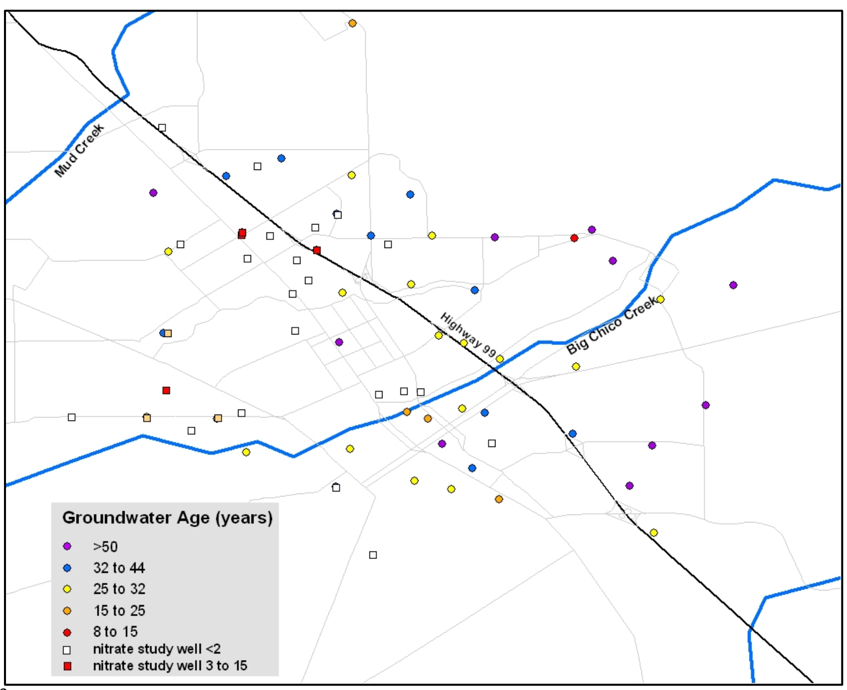

Figure 1b: $^3H/^3He$ apparent ages of groundwater at wells sampled for this study, along with groundwater ages determined in the previous GAMA-CAS study (Moran et al., 2005) that included Chico area drinking water wells. Recently recharged groundwater in monitoring wells contrasts sharply with old groundwater tapped by many of the drinking water wells from the CAS study.

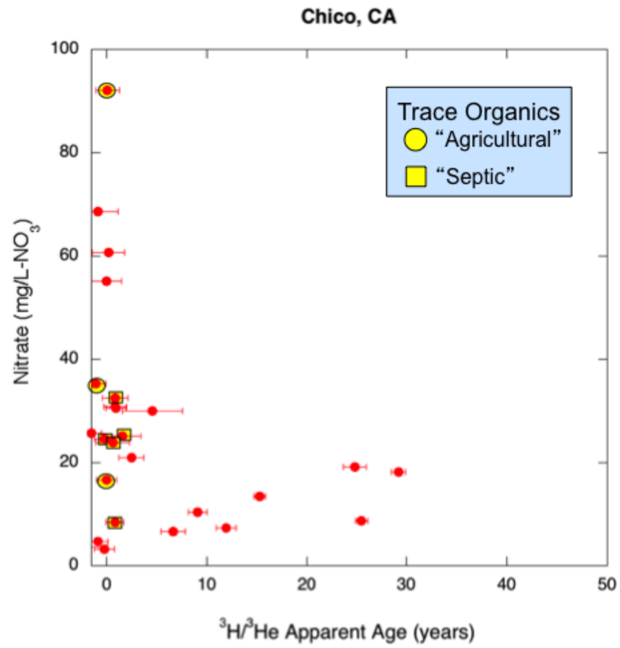

Figure 2a: Apparent age and nitrate concentrations in Chico groundwater.

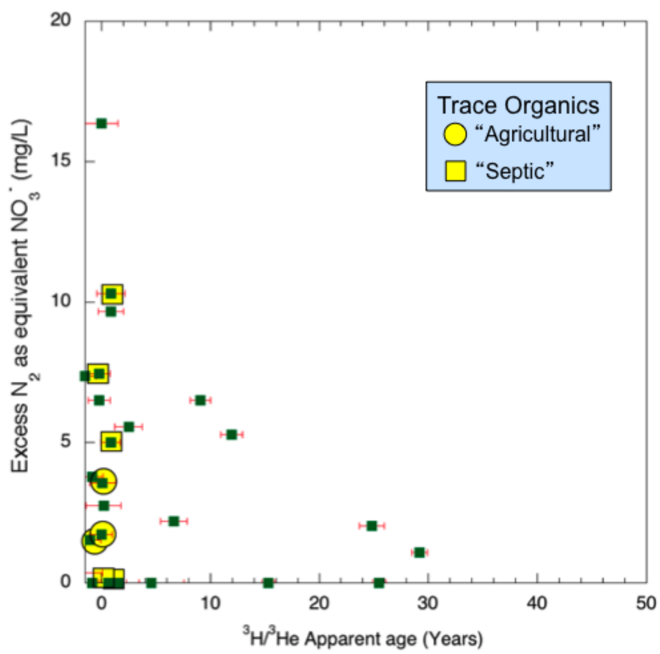

Figure 2b: Excess nitrogen and apparent groundwater age.

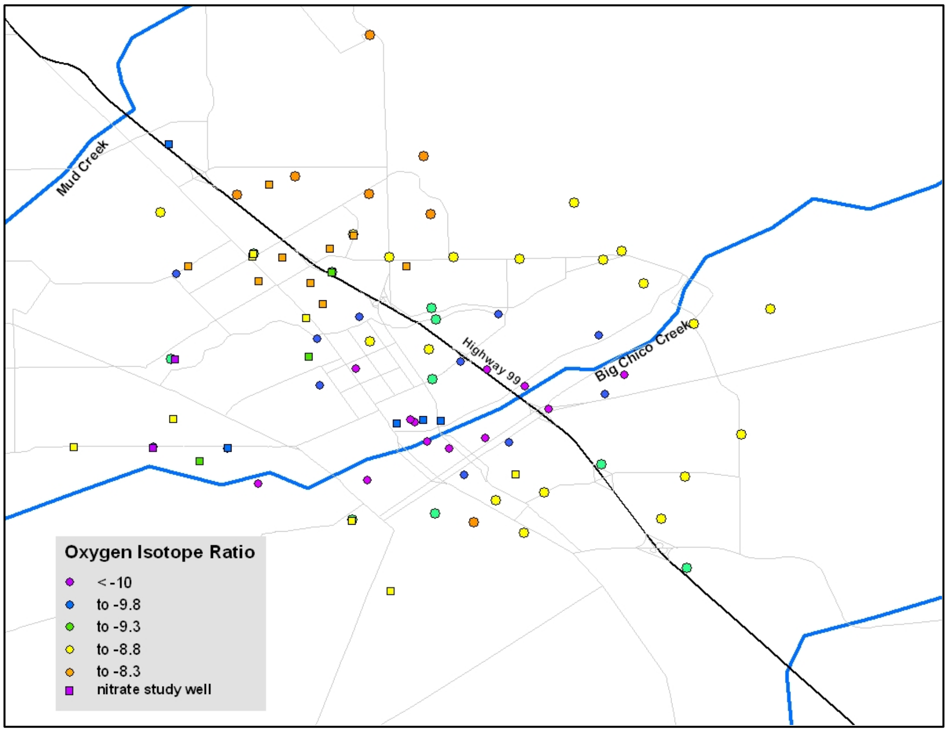

Figure 3a: Oxygen isotope ratios in nitrate study wells (square symbols) and in GAMA-CAS study area drinking water wells (circles), showing recharge is dominated by water from Big Chico Creek in wells adjacent to the creek.

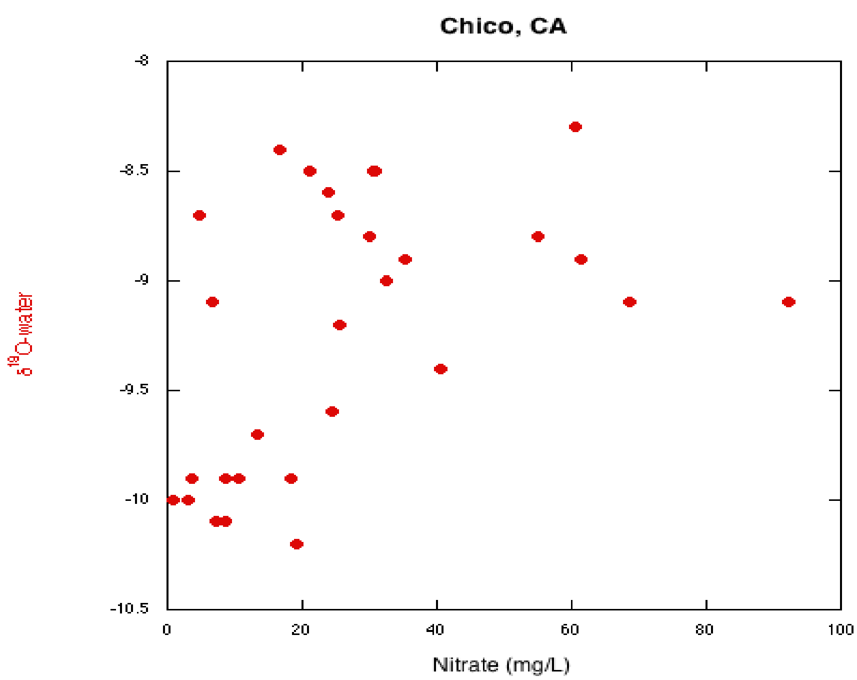

Figure 3b: Oxygen isotopic compositions and nitrate concentrations of Chico groundwaters.

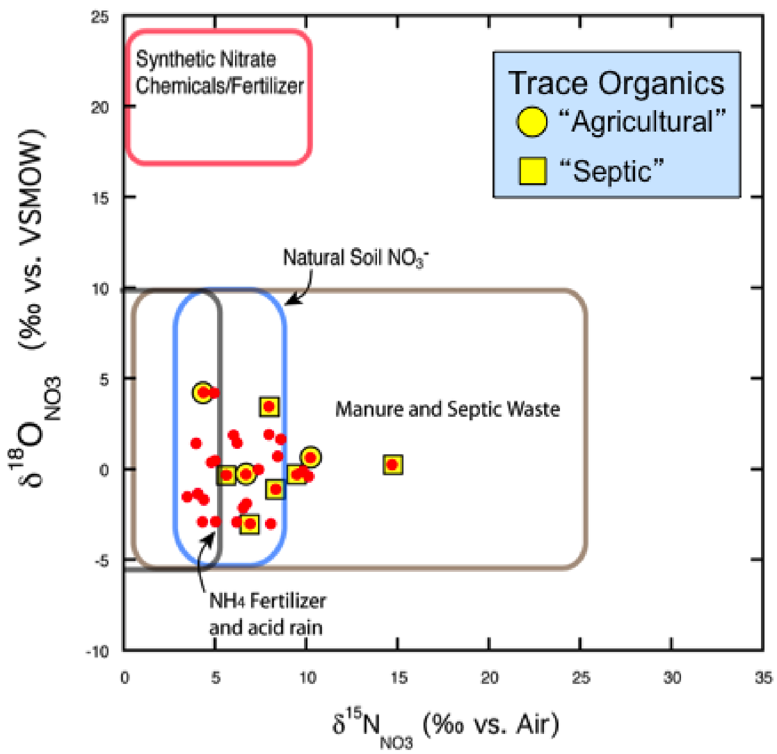

Figure 4: Oxygen and nitrogen isotopic compositions in nitrate from Chico groundwater samples. Ranges for expected isotopic compositions of nitrate after (Kendall 1998). Open squares designate samples where trace organic compounds indicative of septic waste were detected. Open circles designate detections of trace organics related to agriculture.

Thirty groundwater samples were analyzed for the oxygen and nitrogen isotopic compositions of nitrate (Figure 4). Nitrate $\delta^{15}N$ values range from 3.3 to 14.5 ‰, and $\delta^{18}O$ values range from -2.8 to 4.3 ‰. The isotopic compositions measured from nitrate around Chico are consistent with nitrate from septic system leachate and natural background nitrate. There is no strong evidence for the presence of chemical nitrate fertilizers, which lead to nitrate with high $\delta^{18}O$ values (10 to 24 ‰). The range of $\delta^{15}N$ values for natural nitrate is typically 4 to 8 ‰, which is overlapped by the range of $\delta^{15}N$ values common to septic system discharge (0 to 25 ‰). Both natural and septic system nitrate are formed by nitrification, which uses oxygen from local water and molecular oxygen in the atmosphere, so these sources cannot be differentiated based on nitrate $\delta^{18}O$ values.

Five samples from the Chico study have $\delta^{15}N$ values that are consistent only with septic system or manure derived nitrate. Many more samples that lie within the overlapping fields of natural nitrate and septic discharge are most likely from septic discharge due to the high concentrations of nitrate observed and the presence of trace organic compounds specific to septic discharge. The use of trace organic compounds to detect septic and agricultural sources of nitrate is discussed below.

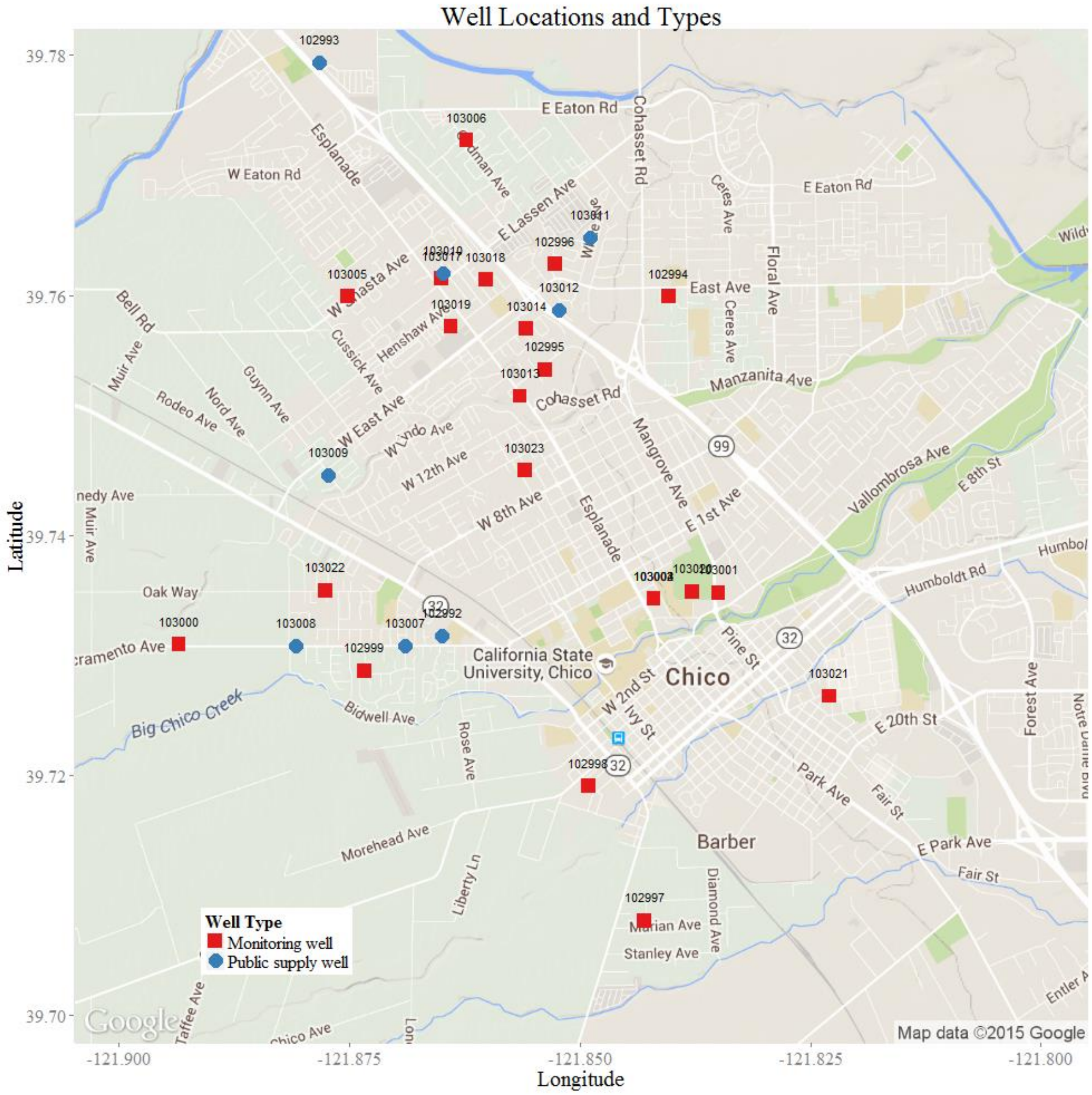

Figure 5a: Map showing locations of monitoring and public wells sampled for wastewater indicator compounds in vicinity of Chico, California for his study. Type of well (monitoring or public supply) is shown by color and shape of symbol. Above each is location is the six digit LLNL ID number for cross reference to Table 1.

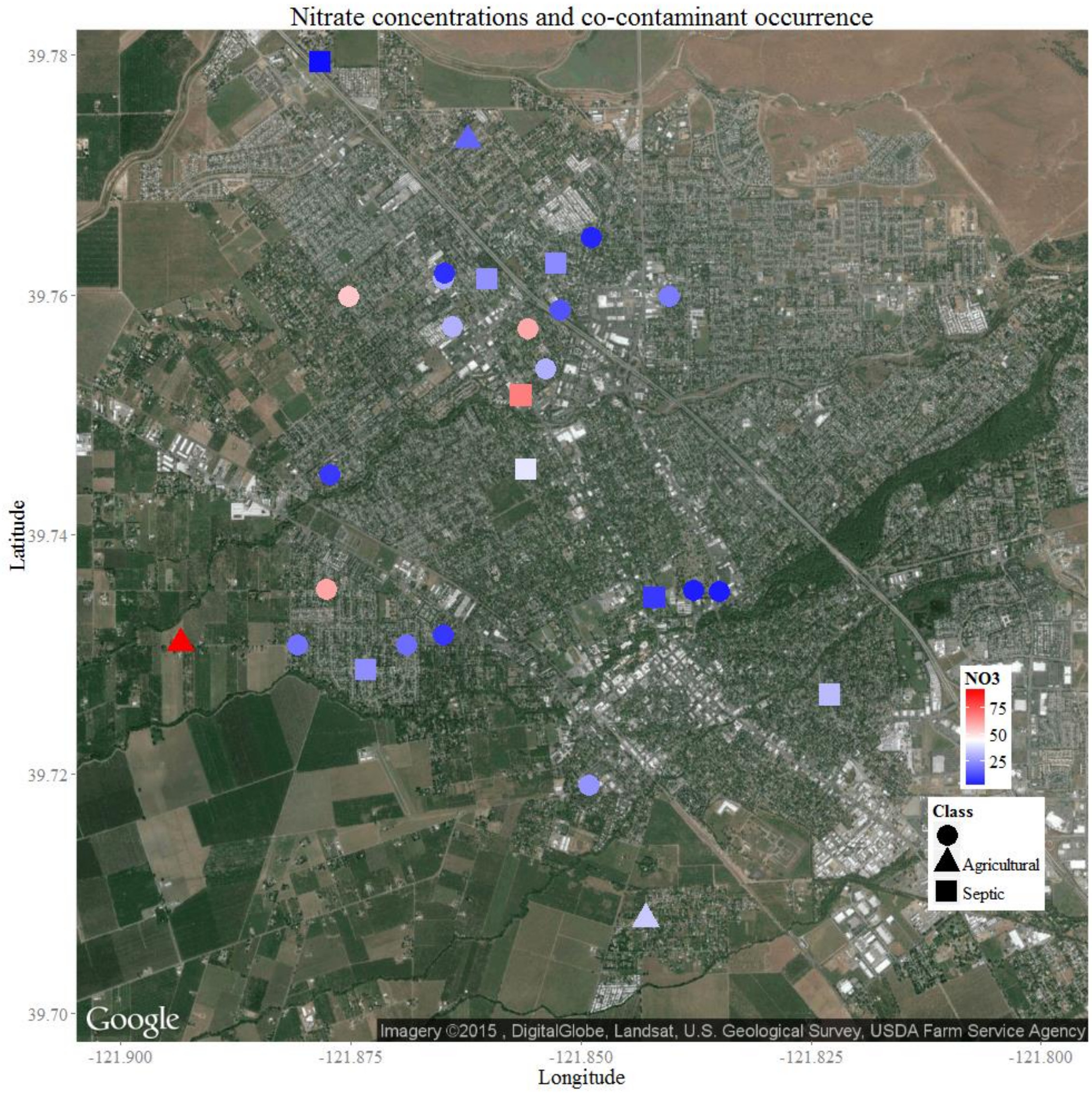

Figure 5b: Map showing nitrate concentrations and detection of organic co-contaminants in sampled wells. Groundwater nitrate concentrations are color-coded, with concentrations above the MCL in shades or red and concentrations below the MCL in shades of blue, and concentrations at the MCL in white. Wells in which groundwater contained detectable co-contaminants are shown are also shown. Groundwaters in which "agricultural" trace organic compounds (desmethylnorflurazon, desisopropyl atrazine, and atrazine) were detected are indicated by a triangular shape. Groundwaters in which "septic" trace organic compounds (tris (1,3-dichloroisopropyl) phosphate, carbamazepine, caffeine, and DEET) were detected are indicated by a square shape.

Twenty-two shallow monitoring wells and eight longer-screened drinking water wells in the Chico area were sampled for trace organics (Figure 5). Some target compounds are much more likely to come from septic system discharge than from agricultural irrigation return flow (caffeine, surfactants like APECs and LAS, ibuprofen and other pharmaceuticals and estrogenic compounds), others are more likely to be present in agricultural irrigation return (herbicides and their breakdown products). Wastewater indicator compounds could thus potentially serve as a way to distinguish nitrate sources.

In all, 8 different target compounds were detected at 11 monitoring wells. Carbamazepine was detected at 4 wells, polycyclic musk compounds and flame retardants were detected at one well, caffeine was detected at 2 wells, DEET and nonylphenol were detected at one well, and herbicides and their breakdown products were detected at 3 wells. Each of the detections is discussed below. The eight drinking water wells sampled in Chico had no detections of any of the target analytes. The lack of detections of trace organic compounds in many of the shallow monitoring wells, and in drinking water wells, suggests that transport of wastewater indicator compounds is not widespread.

Three samples from the Chico study area contained low levels of herbicides or herbicide breakdown products. Two water samples contained triazine herbicides. The sample with the highest nitrate concentration of wells analyzed for this study (Figure 6), contained desisopropyl atrazine (25 ng/L) and a trace amount of simazine (6 ng/L). Another sample contained atrazine (33 ng/L) and desethylatrazine (12 ng/L). Except for the parent triazine herbicides and the breakdown products, the GC/MS total ion chromatogram was clean and no additional compounds were found. Desmethylnorflurazon was present in one sample at a concentration of 140 ng/L but the parent herbicide norflurazon was not detected. These three samples did not have detections of any of the wastewater indicator compounds, and are all located on the outer fringe of the study area, where irrigation return flow from agriculture is most likely to affect shallow groundwater.

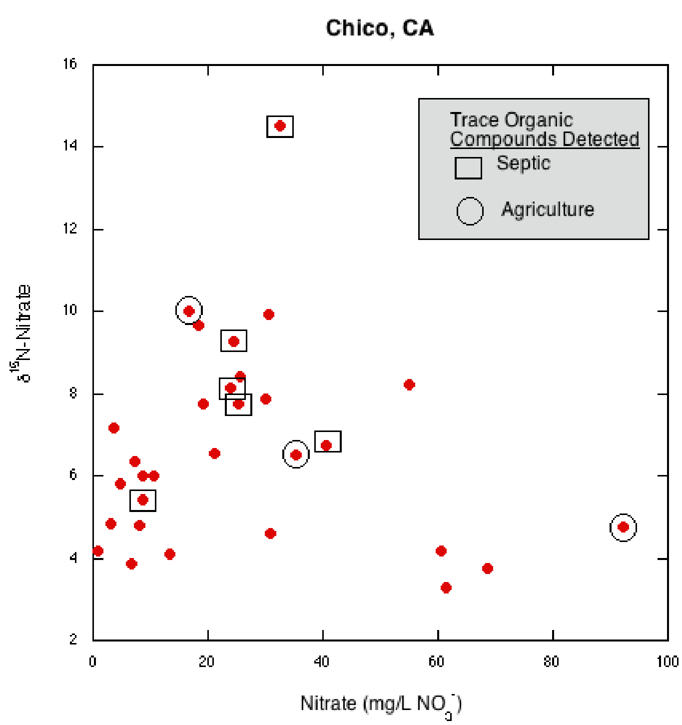

Figure 6: Nitrogen isotopic composition and concentration of nitrate in Chico groundwater. Detections of trace organic compounds associated with septic systems (squares) and agricultural activity (circles) are noted.

Four samples contained a detectable quantity of the pharmaceutical carbamazepine. Carbamazepine is an anticonvulsant that has been used as a tracer of municipal wastewater effluent in both surface and ground waters (Clara et al., 2004). Recent studies suggest that it is one of the most refractory of the high-use pharmaceuticals, and is likely to persist in groundwater (e.g., Drewes et al., 2002, Fenz et al., 2005). It was also detected at lower levels in the GC/MS SIM runs of two other samples, but clean mass spectra in the full scan runs were not obtained. The presence of carbamazepine in these samples suggests that the shallow groundwater in the central part of the study area has a component of wastewater, perhaps from septic discharge, although a direct connection between septic systems and the wells with occurrences cannot be made with the data at hand. Both NP (110 ng/L) and DEET (16 ng/L) were detected in one sample. One of the GC/MS target compounds, tris (1,3-dichloroisopropyl) phosphate, was detected in a sample at a concentration of 27 ng/L. This compound is a commonly used flame retardant chemical and typically found in effluent from wastewater treatment plants.

The six wells where trace organic compounds related to septic system waste were detected also had nitrate nitrogen and oxygen isotopic compositions that are consistent with a septic system source of nitrate (Figure 4). The nitrate in four of these wells could arguably be attributed either to natural soil nitrate or septic system/manure derived nitrate. The detection of trace organic compounds related to septic discharge removes this uncertainty.

Trace organic compounds related to agricultural application of herbicides were detected in three wells from this study. Two of these detections correspond to nitrate N and O compositions consistent with soil nitrate, while one sample contained the breakdown product of the herbicide norflurazon with nitrate that had a $\delta^{15}N$ value of 10.0 ‰ and a $\delta^{18}O$ value of 0.8 ‰. The isotopic composition of nitrate in this well is consistent with either a manure or septic system source of nitrate. Given the well location is on the outskirts of town in an agricultural area it does not seem likely that nitrate is derived from a septic system. It is not known whether manure is used as a fertilizer in this area.

In summary, taken on their own, the use of trace organic analyses or nitrate isotopic compositions is in some cases inconclusive as to the source of nitrate at a particular well. However, combining these analytical techniques in a number of affected wells allows for more conclusive attribution of nitrate sources in the Chico area. The isotopic composition of N and O in nitrate and infrequent detections of carbamazepine, nonyl-phenol, and caffeine suggest that transport of wastewater, likely from septic discharge, affects groundwater locally, at individual wells that sample recent recharge. The impact of agricultural activities on groundwater quality appears to be limited to the outskirts of Chico where orchards are currently in use rather than being legacy sources in formerly agricultural areas that have been converted to suburban use.

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