RESEARCH ARTICLE

Key Points:
- Of the four nitrate sources, our model shows the manure source is the most distinctive
- Septic and fertilizer waste were more difficult to distinguish
- Model predictions broadly correlate to historical land use

Supporting Information:
- Supporting Information S1

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Bayesian nitrate source apportionment to individual groundwater wells in the Central Valley by use of elemental and isotopic tracers

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Abstract Groundwater quality is a concern in alluvial aquifers that underlie agricultural areas, such as in the San Joaquin Valley of California. Shallow domestic wells (less than 150 m deep) in agricultural areas are often contaminated by nitrate. Agricultural and rural nitrate sources include dairy manure, synthetic fertilizers, and septic waste. Knowledge of the relative proportion that each of these sources contributes to nitrate concentration in individual wells can aid future regulatory and land management decisions. We show that nitrogen and oxygen isotopes of nitrate, boron isotopes, and iodine concentrations are a useful, novel combination of groundwater tracers to differentiate between manure, fertilizers, septic waste, and natural sources of nitrate. Furthermore, in this work, we develop a new Bayesian mixing model in which these isotopic and elemental tracers were used to estimate the probability distribution of the fractional contributions of manure, fertilizers, septic waste, and natural sources to the nitrate concentration found in an individual well. The approach was applied to 56 nitrate-impacted private domestic wells located in the San Joaquin Valley. Model analysis found that some domestic wells were clearly dominated by the manure source and suggests evidence for majority contributions from either the septic or fertilizer source for other wells. But, predictions of fractional contributions for septic and fertilizer sources were often of similar magnitude, perhaps because modeled uncertainty about the fraction of each was large. For validation of the Bayesian model, fractional estimates were compared to surrounding land use and estimated source contributions were broadly consistent with nearby land use types.

1. Introduction

Nitrate contamination of shallow groundwater is a major problem in many agricultural areas of the United States [*Dubrovsky et al.*, 2010] and around the world [*Wongsanit et al.*, 2015; *Gu et al.*, 2013; *Ghiglieri et al.*, 2009; *Mattern et al.*, 2009]. Nitrate is a naturally occurring form of nitrogen and is necessary for plant growth, however, animal manure and synthetic fertilizers applied in excess to plant uptake can cause nitrate to leach to groundwater [*Canter*, 1997]. In addition, poorly maintained septic systems, high septic system density in rural and peri-urban areas, or leaky sewer piping in urban areas can be a significant source of nitrate leaching [*Viers et al.*, 2012; *Bremer and Harter*, 2012; *Wakida and Lerner*, 2005]. Two studies of domestic wells in the San Joaquin Valley, an intensively farmed region of California, have found between 40 and 50% of sampled wells exceeded the recommended drinking water standard for nitrate concentration (some wells as high as 5–6 times the standard) [*Lockhart et al.*, 2013; *CSWRCB*, 2013]. Drinking water with a nitrate concentration above the drinking water standard has been linked to negative health effects including miscarriage, low blood oxygen levels in infants, and cancer [*Ward et al.*, 2005; *ATSDR*, 2013].

The diffuse, nonpoint source loading of groundwater with nitrate across diverse and heterogeneous agricultural, peri-urban, and even urban landscapes [*Kourakos et al.*, 2012] pose a particular challenge to identifying the actual nitrate sources in impacted wells, whether for regulatory compliance or land use management. In this paper, we propose and evaluate the use of two traditional source tracers (nitrogen and oxygen isotopes

of nitrate) in combination with two novel source tracers (boron isotopes and iodine) as part of a new Bayesian mixing model approach not before employed in groundwater contamination studies, to quantify the potential contributing sources to contaminated well water composed of an unknown mixture of groundwater nitrate sources.

Many studies, typically qualitative in nature, have used nitrogen or a combination of nitrogen and oxygen isotopes of nitrate to determine the likely source(s) of nitrate in groundwater [*Kreitler*, 1979; *Amberger and Schmidt*, 1987; *Wassenaar*, 1995; *Panno et al.*, 2001; *Widory et al.*, 2004, 2005; *Pastén-Zapata et al.*, 2014]. The source signatures of nitrate derived from synthetic fertilizer, human or animal waste, uncultivated (natural) soils, and atmospheric deposition are generally distinct with the combination of both nitrogen and oxygen isotopes of nitrate, though overlap of the ranges does occur [*Kendall*, 1998; *Kendall et al.*, 2007]. Nitrogen isotopes of nitrate are subject to fractionation and obscuring of the original source isotopic composition due to denitrifcation and/or nitrification of organic nitrogen compounds [*Kendall*, 1998; *Panno et al.*, 2001].

Boron isotopes can potentially decrease uncertainty in nitrate source signatures as an additional comigrating source tracer of nitrate [*Xue et al.*, 2009]. The major benefit of boron isotopes in the context of nitrate source determination is that $\delta^{11}B$ values are mostly distinct for human and animal waste [*Widory et al.*, 2004]. The unique $\delta^{11}B$ values found in septic waste and wastewater of human origin is due to the use of sodium perborate ($NaBO_3$) in household cleaning products [*Raymond and Butterwick*, 1992] and this signature has been shown to remain intact through waste water treatment processes [*Vengosh et al.*, 1994]. Boron isotopes have been used to trace injected treated wastewater at a site in El Paso, Texas [*Bassett et al.*, 1995] and treated wastewater recharged through spreading basins in Israel [*Vengosh et al.*, 1994]. A combination of boron and nitrate isotopic signatures has been successfully used as groundwater nitrate tracers for multiple nitrate sources in two studies in France [*Widory et al.*, 2004, 2005] and one in Nevada, United States [*Seiler*, 2005]. Boron isotopes are not affected by denitrification, but other processes can affect boron isotope values: boron species can be absorbed to clays or certain minerals, released by dissolution within the aquifer matrix, or can be affected by mineral precipitation in extremely saline environments [*Bassett et al.*, 1995; *Widory et al.*, 2005].

Iodine is a potentially significant tracer to identify groundwater nitrate because it is used on dairies as a disinfectant, found in human urine, and absent any marine influences, background iodine levels in groundwater are expected to be low. Background levels of iodine in groundwater not influenced by marine sources are generally expected to be less than 10 μg/L [*Zhang et al.*, 2013]. Iodine has been measured in septic waste at concentrations above the background level (between 30 and 40 μg/L) [*Panno et al.*, 2005]. Iodine in dairy waste can have even greater concentrations: measurements of iodine in groundwater from a set of monitoring wells with dairy corral and lagoon source areas in the San Joaquin Valley, California were as high as 355 μg/L (T. Harter and K. M. Ransom, University of California Davis, unpublished dairy monitoring well data). Iodine as iodide ion (I^-) has been shown to have very little sorption to sediments and geologic materials in batch and column experiments [*Hu et al.*, 2012]. Iodine has been used in combination with other halides to qualitatively determine likely sodium and chloride sources to groundwater in Illinois, USA [*Panno et al.*, 2006], and likely sources of nitrate to groundwater in northeastern Mexico [*Pastén-Zapata et al.*, 2014].

Beyond geochemical characterization, isotopic and elemental tracers in water samples can be used in mathematical mixing models to quantify the fractional source contributions from multiple contamination sources. Mixing models rely on known or approximated concentrations of conservative tracers within each source as a source signature. These signatures are then compared with tracer concentrations in the sampled mixture by mass balance or graphical techniques. Variability is expected in the source signatures as well as in multiple measurements of the mixture sample. Overlap and variation of tracer compositions from different sources have been listed as major problems in the use of isotopes as tracers in mixing models [*Kendall et al.*, 2007].

Previous studies have used deterministic mass-balance mixing techniques in conjunction with isotopic tracers to infer the potential contribution of nitrate sources to surface water and/or groundwater [*Deutsch et al.*, 2006; *Voss et al.*, 2006; *Accoe et al.*, 2008], but it can be cumbersome to account for variability in the source signatures, especially for three or four-source models. A 2001 study derived formulas to estimate the variance of calculated source fractional contributions using the variance of the source isotopic ratios; however,

these estimates require the variance of the mixture sample (known or estimated) [*Phillips and Gregg*, 2001]. Bayesian methods, in contrast, allow for the incorporation of source signature variability in the model structure and do not require multiple measurements of the mixture sample.

Recently, Bayesian isotope mixing models based on mass-balance have been developed to estimate the contributions of multiple sources of nitrate contamination to drinking water springs in Paris, France [*El Gaouzi et al.*, 2013], to surface waters in Flanders, Belgium [*Xue et al.*, 2012], and to the Baltic Sea [*Korth et al.*, 2014]. These three studies use the statistical computing program R (R Core Team, 2015, R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, http://www.R-project.org/) and a special package called SIAR (Stable Isotope Analysis in R, Andrew Parnell and Andrew Jackson, 2013, https://CRAN.R-project.org/package=siar), originally developed for ecological food-web studies, which requires the source isotope values to be initially assigned a Gaussian distribution [*Parnell et al.*, 2010]. Elemental tracers have been used in conjunction with Bayesian methods to quantify the contribution of different sources to surface water contamination of Lake Tahoe [*Massoudieh and Kayhanian*, 2013]. *Massoudieh and Kayhanian* [2013] developed a unique and flexible model design in the computing language C++. Mixing models, Bayesian or deterministic, have not been developed to address the groundwater nitrate issue in the San Joaquin Valley, California.

In this work, a Bayesian mass-balance mixing model was developed with nitrogen and oxygen isotopes of nitrate, boron isotopes, and iodine concentration to determine the fractional contribution of manure, septic, fertilizer, and natural sources (as nitrate leached from uncultivated soils) to groundwater nitrate concentrations. The proposed approach was employed on water samples from nitrate-impaired domestic wells of the San Joaquin Valley, sampled as part of our previous research [*Lockhart et al.*, 2013]. This is the first joint application of nitrogen and oxygen isotopes of nitrate, boron isotopes, and iodine to identify sources of groundwater nitrate. We also developed a novel approach to the Bayesian mixing model. Our model was fitted using the program JAGS (Martyn Plummer, 2003, JAGS: A program for analysis of Bayesian graphical models using Gibbs sampling), a general-purpose computational Bayesian tool which can be accessed through the R statistical language. The model syntax employed in JAGS gives the user considerable flexibility in specifying the form of the mixing model as well as the priors for source tracer values and fractional contributions. This Bayesian approach provides useful information and constraints on potential nitrate sources in regions with highly diverse land use patterns where nitrate contamination is a major issue, but detailed information about well depth, water age, and well source areas may be lacking.

2. Methods

2.1. Project Area

The San Joaquin Valley (SJV), California, is a large topographic and structural basin bounded to the east by the Sierra Nevada mountains, to the west by the Coast Ranges, to the north by the Sacramento-San Joaquin Delta, and to the south by the Tehachapi Mountains. The SJV is the southern and larger half of the Central Valley, California. It is approximately 400 km long and 95 km wide at its widest section between Kettleman City and Porterville. Alluvium from the Sierra Nevada Mountains and the Coast Ranges fills the upper portion of the SJV basin. The main geomorphic features in the SJV are alluvial plains and fans, lake beds, river flood plains and channels, and foothills along the east and west edges [*Croft and Gordon*, 1968]. The northern part of the SJV, the San Joaquin Basin, is drained by the San Joaquin River (which flows southwestward from the Sierra Nevada mountains and then turns northwestward along the axis of the SJV) and its tributaries. In the southern portion of the SJV, the Kings, Kaweah, Kern, and Tule Rivers drain to the semiterminal Tulare Lake Basin [*Faunt*, 2009].

Water bearing units in the SJV are unconsolidated continental, lacustrine, and marsh deposits of Tertiary to recent age that reach a maximum depth of approximately 915 m below ground surface (bgs) at the valley trough. Below the unconsolidated deposits are consolidated Tertiary marine rocks that generally do not yield fresh water (sandstone, siltstone, and shale) and that overlie the pre-Tertiary metamorphic and igneous rocks of the basement complex [*Croft and Gordon*, 1968]. Spring 2011 depth to groundwater (dtw) in the northern portion of the SJV near the cities of Stockton and Merced ranges from approximately 30 to 60 m along the eastern edge of the valley to approximately 3 to 15 m along the western edge.

Regional groundwater flow in the northern SJV is therefore predominately to the northeast. In the southern portion of the SJV, near the cities of Fresno and Tulare, regional groundwater flow is predominately to the southwest, with Spring 2011 dtw ranging from 6 to 15 m along the eastern edge and increasing up to 67 m near the boundary between Fresno and Kings counties (California Department of Water Resources, Groundwater Information Center Interactive Map Application, Spring 2011 Depth to Water Color Ramp, https://gis.water.ca.gov/app/gicima/). Agricultural irrigation in the study area has increased vertical groundwater flow which affects local groundwater systems and may result in a recharge-to-well scenario where groundwater along a lateral flow path is pumped and reapplied to the surface [*Phillips et al.*, 2007].

2.2. Field and Chemical Methods

This study is based on a subset of groundwater chemistry data collected from 200 private domestic wells in Stanislaus, Merced, Tulare, and Kings counties [*Lockhart et al.*, 2013]. All wells were located on the valley floor. The well water sample collection field procedure is described in *Lockhart et al.* [2013]. At the time of initial sample collection (2010–2011), well water samples were analyzed for many constituents including nitrate as nitrogen (NO_3-N), boron, iodine, and nitrogen and oxygen isotopes of nitrate. For the purposes of this study, water for boron isotope analysis was collected and stored for analysis at a later date (see below for further details).

Well water samples for nitrate, boron, and iodine concentration analysis were field filtered with a 0.45 micron filter and collected in a 250 mL clear plastic Nalgene bottle. Nitrate as NO_3-N and boron analysis were performed by UC Davis Analytical Laboratory using the Cadmium Reduction Flow Injection Method, Standard Method 4500-NO_3-N I [*Clesceri et al.*, 1998] and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) according to the United States Environmental Protection Agency Standard Method 200.7 for soluble elements in water samples [*U.S. EPA*, 2001], respectively. See *Lockhart et al.* [2013] for further description of the nitrate quality control procedures. Water used for boron analysis was acidified in the laboratory to pH < 2 with 1:1 HNO_3 (nitric acid) prior to analysis. Iodine concentrations were measured at the Interdisciplinary Center for Plasma Mass Spectrometry at the University of California at Davis (ICPMS.UCDavis.edu) using an Agilent 7500CE inductively coupled plasma mass spectrometer (ICP-MS, Agilent Technologies, Palo Alto, CA). An unacidified aliquot of each sample was analyzed directly for total dissolved iodine. The samples were introduced using a MicroMist Nebulizer (Glass Expansion 4 Barlows Landing Rd., Unit 2A Pocasset, MA 02559) into a temperature controlled spray chamber with He as the Collision Cell gas. For calibration purposes, instrument standard for iodine was diluted daily using 18.2 Mohm-cm water and Ricca Chemical Company 0.0100N Iodine (Ricca Chemical Company, Arlington, TX 76012) to 0.318, 0.625, 1.27, 12.7, 63.5, 127, and 254 ppb. A quality control standard consisting of Ricca Chemical Iodine was diluted to 127 ppb, and analyzed every 12th sample as a quality control measure.

Samples for nitrogen and oxygen isotopes of nitrate were filtered in the field with a 0.45 micron filter and collected in 60 mL wide mouth screw-cap HDPE bottles and stored frozen for later analysis. Nitrogen and oxygen isotopes of nitrate were analyzed at the Menlo Park U.S. Geological Survey Stable Isotope Laboratory using the denitrifier method [*Sigman et al.*, 2001; *Casciotti et al.*, 2002]. $\delta^{15}N$ and $\delta^{18}O$ values are calculated relative to the Air and VSMOW standards, respectively. Precision of this method based on repeat standard measurements is 0.3‰ for $\delta^{15}N$ and 0.8‰ for $\delta^{18}O$. All samples were prepared and analyzed in duplicate on the same day, and then analyzed a third time or more until the precisions of replicate analysis met laboratory QAQC criteria of 0.8‰ for $\delta^{15}N$ and 1.5‰ for $\delta^{18}O$. After completing reanalysis of any samples not meeting those criteria, the average standard deviation for replicate analyses of samples from this study was 0.2‰ for $\delta^{15}N$ and 0.8‰ for $\delta^{18}O$.

Well water samples for boron isotope analysis were collected at the time of initial well sampling (2010–2011) from 157 wells and stored for later analysis. Well water samples for boron isotopes were filtered in the field with a 0.45 micron filter and collected in 2 - 1 L clear plastic Nalgene bottles. Nonacidified well water samples were stored in a dark room at room temperature. Of the 157 wells with stored sample water, 56 wells had nitrate concentrations above the drinking water standard of 10 mg/L NO_3-N and boron concentrations above the reporting limit of 0.02 mg/L. These 56 samples were selected for boron isotope analysis and the study is based on this subset of wells.

In order to obtain accurate and precise boron isotopic composition data, boron must first be separated from the matrix elements of the groundwater samples prior to analysis. Boron chemical separation was

performed at Lawrence Livermore National Laboratory, Livermore, CA, using an ion-exchange technique and a boron-specific ion exchange resin, Amberlite IRA 743. [*Eppich et al.*, 2011]. This method is described in detail by *Eppich et al* [2011], and is adapted from previously developed methods [*Kiss*, 1988; *Leeman et al.*, 1991; *Lemarchand et al.*, 2002; *Guerrot et al.*, 2011]. Chemically separated boron was dissolved in approximately 3 mL of 2% HNO_3 and stored in polyethylene tubes prior to isotope analysis. In addition to the 56 well water samples, Italian groundwater boron standards IAEA-B-2 and IAEA-B-3 [*Gonfiantini et al.*, 2003] were also chemically separated in order to verify the boron chemical separation procedure.

Boron isotopic composition measurements were performed using a Thermo Neptune Plus inductively coupled plasma mass spectrometer (MC-ICPMS) in the Department of Earth and Planetary Sciences at the University of California-Davis. A standard-sample-standard bracketing routine, utilizing the boron isotopic standard NIST SRM 951 (at 100 ppb), was used to correct for instrumental mass bias [*Lemarchand et al.*, 2002; *Guerrot et al.*, 2011]. Samples were diluted, where needed, to match the [11]B signal intensity of the SRM 951 solution. See supporting information Text S1 for further explanation of boron isotope analytical and quality control procedures.

2.3. Landuse Analysis

In order to detect potential relationships between predicted nitrate source(s) for each well and relevant land use types, land use around each well was classified as percent of total area for 13 land use groups within a 2.4 km radius circular buffer. A circular buffer was chosen as an approximation of the well source area due to unknown local groundwater flow direction and other conditions that can affect the source area such as hydraulic conductivity, groundwater gradient, recharge rate, and well construction characteristics [*Horn and Harter*, 2009]. We further justify the use of a circular well buffer as approximate source area with the assumption that land use surrounding wells is autocorrelated and this has been shown for urban land use up to a distance of 8 km for other wells within our study region [*Johnson and Belitz*, 2009]. The buffer radius was calculated based on an assumed hydraulic conductivity of 30.5 m/d, hydraulic gradient of 0.001, and recharge rate of 0.3 m/yr [see *Lockhart et al.*, 2013, for details] and is assumed to be the reasonable maximum length of the source area.

Land use/land cover from approximately the 1990s was used based on the approximate age of domestic well water in the study area compared to the time of sample collection for the study wells (2010–2011). A different set of domestic wells sampled as a part of a dairy monitoring project in the same counties as the study wells was analyzed for tritium/helium age. Each well pumped at least some modern (since 1950) water indicating recharge after the commencement of atmospheric nuclear testing in the 1950s. The calculated mean groundwater age of the modern water component ranged from 19 to >60 years (with corresponding recharge years of 1989–1948) (B. K. Esser, Lawrence Livermore National Laboratory, unpublished data, 2013). Well nitrate levels in the study area therefore reflect cumulative land use impacts over the past two to six decades. In order to account for at least the youngest difference between groundwater age and time of sampling (approximately 20 years), the California Augmented Multisource Landcover (CAML) map for the year 1990 (A. D. Hollander, Information Center for the Environment, University of California, Davis) was used. The 1990 CAML map is a compilation of data from several sources ranging in date from 1988 to 1995 including the: California Department of Conservation Farmland Mapping and Monitoring Program (FMMP), the United States Geological Surveys (USGS) National Land Cover Data set (NLCD) (1992), California Department of Forestry and Fire Protection Fire and Resource Assessment Program Multisource Landcover Layers (MSLC), and the California Department of Water Resources (DWR) Land Use Survey. The 1990 CAML map is the most accurate and detailed historical land use data set available for the SJV at this time. For the purpose of this study, the land use categories from the CAML map were reclassified into 13 groups based on similarity in land use/crop type: natural (uncultivated land) and water, citrus and subtropical, tree fruit, nuts, cotton, field crops, forage crops, alfalfa and pasture, confined animal feeding operation (CAFO, here mostly dairies), vegetables and berries, grapes, urban, and peri-urban (see supporting information Table S3 for original crop and land use types included in grouped categories).

2.4. Statistical Methods

The statistical mixing model was based on mass balance equations from *Accoe et al.* [2008], where the isotope value for each well is assumed to be the sum of the fractional source contribution of the nitrate source

to the well multiplied by the isotope signature in that source, for each source of nitrate to the well. An equation for iodine of the same form is also included.

$$\delta^{15}N_{mixture} = \sum_{source=1}^{4} f_{source} * \delta^{15}N_{source} + \epsilon_N, \tag{1}$$

$$\delta^{18}O_{mixture} = \sum_{source=1}^{4} f_{source} * \delta^{18}O_{source} + \epsilon_O, \tag{2}$$

$$\delta^{11}B_{mixture} = \sum_{source=1}^{4} f_{source} * \delta^{11}B_{source} + \epsilon_B, \tag{3}$$

$$I_{mixture} = \sum_{source=1}^{4} f_{source} * I_{source} + \epsilon_I, \tag{4}$$

where ϵ is a Gaussian error term, unique to each well, reflecting stochastic variation in the tracer value. In the model, the mass balance equations were used together in matrix form in order to share information about source signatures across wells. The matrix equation for the mixing model comes from *Massoudieh and Kayhanian* [2013] and can be written:

$$C = YF + E \tag{5}$$

where C is a m x 56 matrix of m measured tracers in 56 wells, Y is a m x n matrix of m tracer signatures in n sources, F is a n x 56 matrix of fractional contributions to each well for each of the n sources, and E is a m x 56 matrix of errors for each tracer/well combination. In contrast to typical linear models, both F and Y in equation (5) are unknown and must be estimated. Statistical identification of F and Y is aided by the fact that the fractions in each column of F must add to one, and by use of informative prior distributions for the source tracer signatures in Y.

In contrast to deterministic models, Bayesian models assume that fractional contributions and tracer signatures vary probabilistically. Bayesian models incorporate previous knowledge about each of these parameters by the assignment of a "prior" probability distribution that reflects the current state of knowledge of the parameter. Prior distributions can be either "non-informative" (high-variance, wide, or flat distributions) or "informative" (lower variance, less wide, more specific structure) depending on the available information or model design. Bayesian models combine the prior probability distributions for each parameter, the observations, and an assumed error structure via Bayes' Theorem to estimate a "posterior" distribution for each parameter. Posterior distributions can be thought of as prior distributions updated by the observations [*Stauffer*, 2008; *Ryan*, 2009]. In the present case, the posteriors cannot be solved for directly and are estimated via Markov Chain Monte Carlo (MCMC) simulation.

For equation (5), a Dirichlet prior shared across the columns of F ensures that the fractional contributions sum to one for each well. Background nitrate concentrations are typically less than 2 mg/L [*Mueller and Helsel*, 1996]. Because nitrate concentrations in the samples (Table 1) are 5–20 times as large as this upper bound, it is clear that other land use types and sources contribute more significantly. The highly heterogeneous land use in the study area and the seasonal changes in local groundwater flow directions due to nearby large capacity irrigation or municipal well pumping further suggest that the prior distribution for fractional contributions should give equal weights to dairy, septic, and fertilizer sources at the expense of natural sources. Therefore, Dirichlet parameters (1, 1, 1, 1/3) were chosen. These yield prior mean fractional contributions of 0.3 and prior variances of 0.05 for dairy waste, septic waste, and fertilizer; for natural sources, the corresponding prior mean and variance are 0.1 and 0.02 (See supporting information Text S2 for details on Dirichlet mean and variance calculations). Ninety-five percent prior credibility intervals for each of the four sources were calculated and are shown in Figure 2 as a visual representation of the Dirichlet prior imposed on each well. Despite the low prior variance imposed by the choice of the Dirichlet parameters, the selected parameters lead to wide credibility intervals for the prior case, which allows for various degrees of mixing and the selection of a dominant source in the presence of strong evidence in the tracer values.

Table 1. Measured Tracer Values for Each Study Well (Including Boron Concentration Which Was Not Used as a Tracer) and Normalized Central Tendencies of Source Fractional Contribution to Total Nitrate in Well Water Samples, for Each Source and Well.[a] Central Tendency Values Are Calculated as the Geometric Mean of All Realizations in Each Posterior Probability Distribution for the Fractional Contribution of Each Source in Each Well, That Are Then Normalized by Well

Well	$\delta^{15}N$	$\delta^{18}O$	$\delta^{11}B$	I (μg/L)	B (mg/L)	NO$_3$-N (mg/L)	Manure	Septic	Fertilizer	Natural
10-DOM	11.1	4.8	19.0	35.32	0.20	61.99	0.58	0.24	0.17	0.01
9-DOM	9.0	5.3	23.8	31.07	0.11	56.63	0.50	0.19	0.28	0.03
130-DOM	6.5	4.8	30.3	7.43	0.06	54.35	0.20	0.17	0.44	0.19
4-DOM	10.5	4.5	18.7	48.81	0.16	44.47	0.61	0.23	0.15	0.01
129-DOM	5.4	4.5	24.2	9.52	0.05	44.35	0.16	0.20	0.55	0.09
6-DOM	8.0	2.2	38.0	15.55	0.10	43.67	0.29	0.22	0.16	0.33
135-DOM	12.4	10.6	16.7	66.86	0.16	39.59	0.83	0.05	0.12	0.00
5-DOM	12.0	3.3	20.3	26.90	0.15	39.03	0.55	0.31	0.12	0.02
118-DOM	7.0	0.6	23.6	9.96	0.17	38.79	0.19	0.48	0.22	0.11
106-DOM	10.9	2.5	34.5	32.08	0.11	36.55	0.57	0.24	0.10	0.09
120-DOM	4.7	0.0	14.1	6.46	0.03	35.71	0.08	0.57	0.32	0.03
107-DOM	6.0	4.2	32.4	11.86	0.05	35.19	0.20	0.18	0.40	0.22
57-DOM	5.2	6.5	12.6	3.90	0.04	35.06	0.11	0.15	0.73	0.01
105-DOM	6.5	1.4	21.1	22.77	0.17	29.63	0.26	0.43	0.25	0.06
43-DOM	11.1	8.1	21.7	29.69	0.06	28.33	0.60	0.10	0.29	0.01
17-DAR	13.2	2.2	4.6	2.08	0.07	27.38	0.34	0.52	0.13	0.01
13-DOM	10.3	4.7	19.8	37.15	0.09	26.06	0.56	0.23	0.19	0.02
42-DOM	11.4	6.3	28.6	36.24	0.12	24.65	0.65	0.13	0.18	0.03
176-DOM	17.8	10.3	24.3	79.45	0.12	24.12	0.96	0.02	0.02	0.00
110-DOM	10.8	3.5	32.8	9.99	0.03	24.10	0.43	0.24	0.18	0.16
152-DOM	4.6	3.9	15.6	13.38	0.03	23.71	0.13	0.27	0.57	0.03
197-DOM	3.3	3.1	19.8	16.33	0.07	21.12	0.09	0.26	0.60	0.05
202-DOM	7.4	−0.2	33.4	15.69	0.07	18.49	0.23	0.37	0.14	0.27
122-DOM	5.9	1.2	15.8	7.76	0.04	17.89	0.13	0.50	0.33	0.03
174-DOM	7.7	0.0	19.7	21.89	0.04	17.40	0.29	0.50	0.17	0.04
75-DOM	4.3	3.7	33.1	8.74	0.04	16.42	0.09	0.17	0.45	0.29
19-CSD	5.2	4.6	28.9	16.51	0.12	16.41	0.21	0.17	0.50	0.12
124-DOM	5.0	−0.6	10.6	3.26	0.04	16.29	0.07	0.63	0.28	0.02
149-DOM	10.6	8.5	13.1	61.73	0.10	15.80	0.71	0.09	0.19	0.00
49-DAR	17.3	7.6	12.0	43.92	0.35	15.30	0.85	0.09	0.05	0.00
27-DOM	8.5	3.1	26.8	12.73	0.04	15.29	0.32	0.30	0.26	0.11
136-DOM	3.8	3.5	19.5	14.31	0.26	14.30	0.10	0.26	0.59	0.04
116-DOM	4.4	−7.7	16.7	5.51	0.03	14.29	0.03	0.88	0.06	0.02
138-DOM	5.2	3.0	10.3	33.60	0.50	14.20	0.26	0.35	0.37	0.01
18-CSD	8.8	−0.2	12.4	5.78	0.09	14.11	0.21	0.61	0.16	0.02
173-DOM	6.2	3.4	24.6	23.63	0.03	14.10	0.29	0.27	0.36	0.07
172-DOM	8.6	2.1	19.4	12.22	0.04	14.00	0.30	0.44	0.22	0.04
68-DOM	13.4	5.1	17.8	13.94	0.03	13.82	0.56	0.25	0.17	0.02
115-DOM	5.3	−3.0	10.9	4.02	0.02	13.79	0.06	0.77	0.15	0.02
198-DOM	5.0	2.9	13.9	12.39	0.03	13.79	0.14	0.35	0.49	0.02
113-DOM	5.4	1.8	18.0	8.69	0.04	13.69	0.13	0.42	0.40	0.05
133-DOM	8.0	2.6	23.6	18.62	0.06	13.50	0.33	0.36	0.26	0.06
195-DOM	7.5	2.5	39.4	12.69	0.68	12.49	0.23	0.18	0.17	0.41
50-DOM	8.6	1.1	10.3	9.73	0.16	12.40	0.25	0.53	0.21	0.02
24-CSD	7.3	6.4	33.6	8.37	0.06	12.39	0.28	0.12	0.42	0.18
125-DOM	5.8	0.1	12.7	11.96	0.02	12.29	0.14	0.58	0.25	0.02
199-DOM	5.1	2.0	18.9	18.98	0.03	12.29	0.17	0.38	0.41	0.04
14-DOM	6.6	2.9	30.5	19.98	0.06	12.21	0.27	0.25	0.31	0.18
54-DOM	7.4	5.6	18.5	15.83	0.06	11.90	0.31	0.18	0.49	0.02
53-DOM	7.2	5.5	19.3	13.89	0.06	11.40	0.29	0.19	0.50	0.03
44-DOM	7.2	6.4	22.8	6.66	0.03	11.30	0.25	0.14	0.57	0.04
1-DOM	4.3	5.5	7.0	3.90	0.07	11.22	0.08	0.19	0.72	0.01
83-DOM	7.5	2.7	24.2	8.30	0.04	10.82	0.23	0.35	0.31	0.11
20-CSD	5.9	5.4	16.4	5.47	0.08	10.81	0.16	0.19	0.63	0.03
21-CSD	5.9	4.9	18.0	5.29	0.08	10.61	0.15	0.21	0.60	0.04
137-DOM	4.6	3.2	16.3	12.44	0.28	10.10	0.12	0.32	0.52	0.03

[a]Wells are sorted by nitrate concentration in decreasing order.

Either a Gamma or Student t-distribution was chosen to represent the prior probability density for each tracer, for each source, based on values compiled from the literature or previous studies (Table 2, see supporting information Text S2 for Gamma and Student t-probability equations). Initial model runs revealed that posterior inferences were sensitive to choices of priors, and that uninformative priors yielded a poor fit

Table 2. Reference Articles and Data Sets Used to Characterize Tracers in Nitrate Sources[a]

Tracer in Nitrate Source	Reference Values for Prior Probability Densities	Type of Prior
δ^{15}N-NO$_3$ dairy manure	Groundwater monitoring well samples from wells on SJV dairies with corral or lagoon source areas [Young et al., 2013]	Gamma
δ^{15}N-NO$_3$ synthetic fertilizer	Literature values [Vitòria et al., 2004; Mariotti and Létolle, 1977; Shearer et al., 1974; Kreitler, 1979; Freyer and Aly, 1974; Heaton, 1986; Wassenaar, 1995; Fogg et al., 1998]	Student-t
δ^{15}N-NO$_3$ septic waste	Literature values [Aravena et al., 1993; Fogg et al., 1998]	Gamma
δ^{15}N-NO$_3$ natural sources (dissolved inorganic nitrogen as nitrate in natural soils)	Literature values (given as range only) [Kendall, 1998]	Student-t
δ^{18}O-NO$_3$ dairy manure	Groundwater monitoring well samples from wells on SJV dairies with corral or lagoon source areas [Young et al., 2013]	Student-t
δ^{18}O-NO$_3$ synthetic fertilizer	Literature Values [Vitòria et al., 2004; Amberger and Schmidt, 1987]	Student-t
δ^{18}O-NO$_3$ septic waste	Literature values [Aravena et al., 1993; Panno et al., 2005]	Student-t
δ^{18}O-NO$_3$ natural sources (dissolved inorganic nitrate in natural soils)	Literature values (given as range only) [Kendall et al., 2007]	Student-t
δ^{11}B dairy manure	Literature Values [Widory et al., 2004, 2005; Bassett et al., 1995; Komor, 1997]	Student-t
δ^{11}B synthetic fertilizer	Literature values [Komor, 1997; Vengosh et al., 1999; Accoe et al., 2008; Tirez et al., 2010; Widory et al., 2005; Chetelat and Gaillardet, 2005]	Student-t
δ^{11}B septic waste	Literature values [Widory et al., 2004, 2005; Bassett et al., 1995; Leenhouts et al., 1998; Vengosh et al., 1999; Seiler, 2005; Accoe et al., 2008; Barth, 1998; Chetelat and Gaillardet, 2005]	Student-t
δ^{11}B natural sources (boron in groundwater samples with nitrate below drinking water standard)	Literature values (given as range only)[b] [Eppich et al., 2012]	Student-t
Iodine dairy manure	Groundwater monitoring well samples from wells on SJV dairies with corral or lagoon source areas (T. Harter and K. M. Ransom, University of California Davis, unpublished dairy monitoring well data) and Literature values [Panno et al., 2005]	Gamma
Iodine synthetic fertilizer	Literature values [Panno et al., 2005]	Gamma
Iodine septic waste	Literature values [Panno et al., 2005; U.S. Department of Health and Human Services, 2004]	Gamma
Iodine natural sources	Literature values (given as range only) [Zhang et al., 2013]	Gamma

[a]The Gamma distribution was chosen as the prior probability density for tracers that are either highly unlikely to exhibit negative values in the source (δ^{15}N in manure and septic waste due to ammonia volatilization) or where negative values are impossible (iodine concentrations in all four sources).
[b]δ^{11}B measured in groundwater samples from San Diego County, with NO$_3$-N < 10 mg/L.

of the model to the observations. Therefore, it was necessary to constrain the prior densities around the bulk of the literature values. These informative priors caused any lack of fit to be shared equally across all four tracers (see supporting information Figure S3 for goodness of fit plot). Ten degrees of freedom (implying low prior variances) were used for all tracers modeled with t-distribution priors in order to give the model less latitude to shift posterior distributions away from the priors. For both distribution types, the mean was set at or near the empirical mean value (the median value when only a range was available). For the Gamma distribution, a rate was chosen based on the empirical mean and in order to ensure a reasonable prior variance. For the t-distribution, a scale was chosen based on the model's sensitivity to the prior, where priors with high sensitivity were given a scale of 1 in order to make them more restrictive. Priors modeled with a t-distribution that did not display high sensitivity were assigned a scale parameter that ensured coverage over the entire range of literature values. See Figures 6–9 for histograms of literature or previous study values and the corresponding prior probability distribution for each tracer in each source.

Bayesian models require the use of a "likelihood" function, typically in the form of a probability density function. The likelihood function here is based on a Gaussian distribution of errors around expected tracer values for each well. The Gaussian distribution permits the linear form of equations (1)–(4), derived from mass balances. Gaussian errors seem reasonable for all tracers except iodine, which has a heavy upper tail. We understand mass balances in the tracers' conventional units of measurement (as opposed to log-scale units) to be an essential feature of the model, and are therefore willing to accept a less-than-ideal error distribution for iodine.

MCMC methods were used to infer the marginal posterior distributions for each source fractional contribution, for each source and each well. MCMC is a simulation technique in which a long Markov chain is constructed in order to sample from the (unknown) posterior distribution. MCMC was performed using the Gibbs sampler JAGS (Martyn Plummer, 2003, JAGS: A program for analysis of Bayesian graphical models using Gibbs sampling). JAGS was run from within the statistical computing program, R (R Core Team, 2015, R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna,
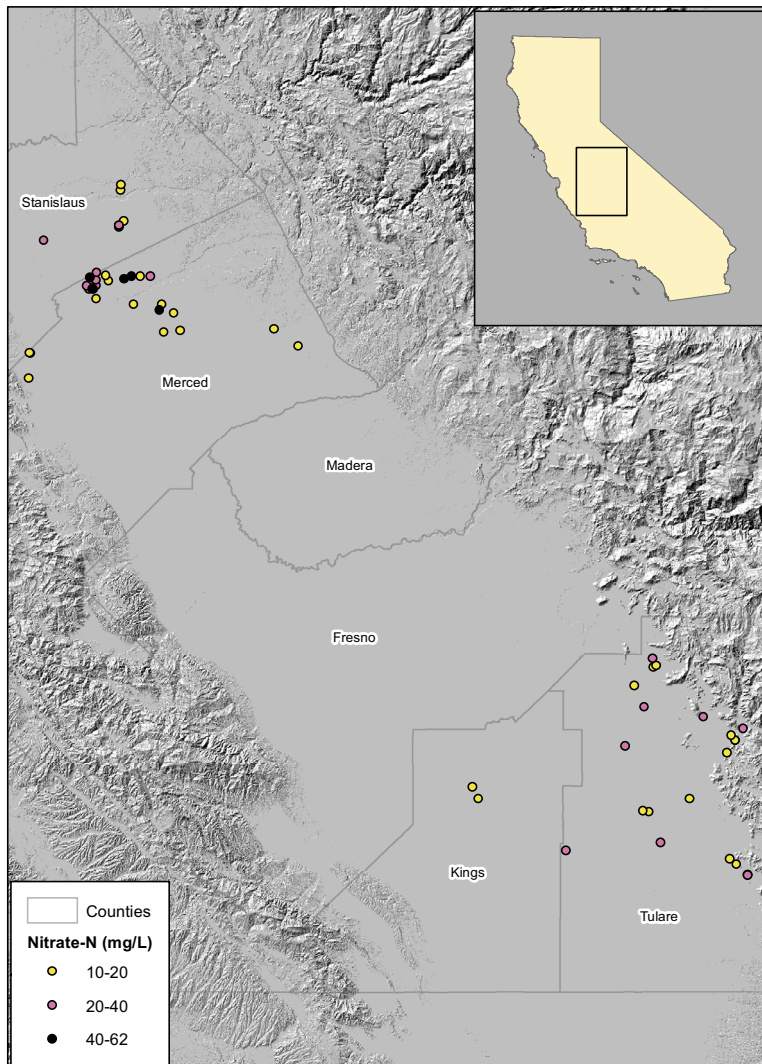
Figure 1. Study wells color coded by nitrate concentration.

In early experimental runs, we learned that the Markov chains mixed slowly: successive samples from the posterior distribution were correlated even at large lags, and therefore long chains were required for reliable estimation. For inference, two chains were run, both with an adaptive phase of 10 million iterations in which the sampler adjusted parameters in order to achieve efficient sampling (e.g., step size). Then, the first 10 million samples of both chains were discarded as the burn-in period (the period before the model converges and proper mixing of the chains can be assumed). After burn-in, each chain was sampled 10 million times with a thinning rate of 20,000 in order to produce 500 well-mixed realizations per chain. These realizations were then combined, for a total of 1000 posterior samples of each parameter. Posterior probability distributions, traceplots, and autocorrelation plots were inspected to verify proper mixing of chains and lack of autocorrelation. Final model run time was approximately 8 h on a Intel Core I-5 4670 processor with 16 GB of 1600 MHz DDR3 RAM.

The central tendency of the fractional contribution for each source to each well was calculated from the posterior realizations as the geometric mean of all the realizations for each fractional contribution and source combination, normalized by well [*Aitchison et al.*, 2003]. The central tendency gives a single estimate of the fractional contribution from each source to each well's total nitrate value. Central tendencies were
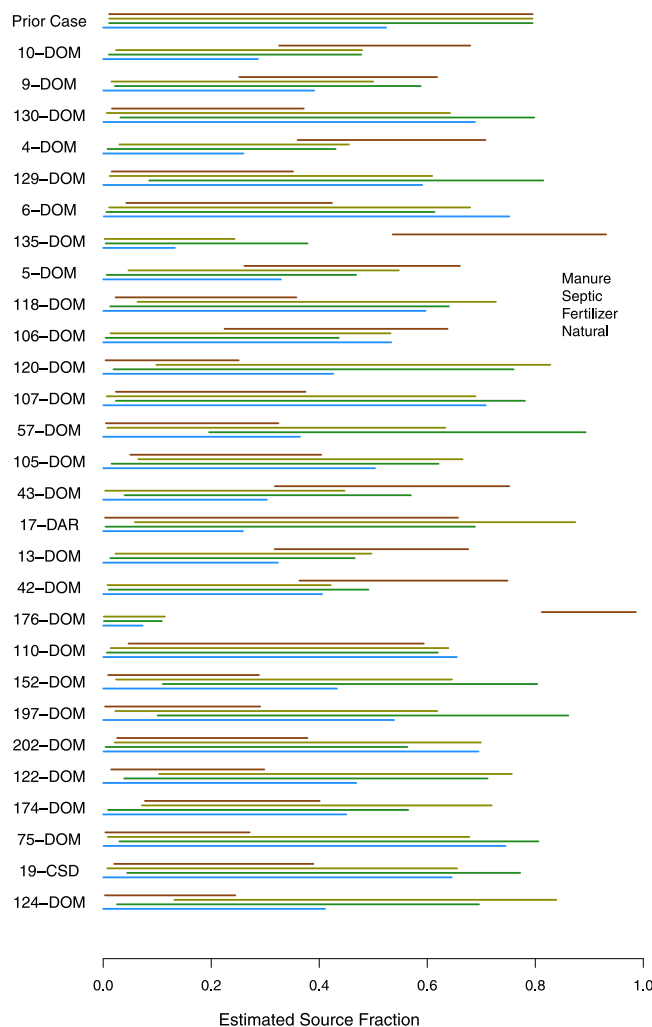
Figure 2. 95% credibility intervals for fractional source contributions by well and source. The first plot is the prior case example, shown to illustrate the prior credibility intervals imposed on each well. Below the prior case example, wells are sorted by measured nitrate concentration (as in Table 1), in descending order (first 28 wells are shown). The dot is the mean for each source.

mapped in order to examine potential regional trends and also compared graphically to land use surrounding each well. We emphasize that, in this work, the land use information near each well was not used as prior information, but instead as a validation tool.

3. Results

The 56 domestic wells used for this study are broadly distributed throughout the four counties investigated, with highest nitrate values found near dairies in Merced and Stanislaus counties (Figure 1). Table 1 lists the wells, their associated nitrate value, and the measured value of each tracer as well as the measured value for boron concentration, which was not used as a tracer. The model is based on these 56 wells. Previous analysis of δ^{15}N-NO$_3$ and δ^{18}O-NO$_3$ in the full suite of 200 domestic wells did not find significant evidence for denitrification in the wells as a whole and this is based on a combination of high δ^{15}N-NO$_3$ values also associated with high nitrate values and a scattered relationship between δ^{15}N-NO$_3$ and δ^{18}O-NO$_3$ [*Young et al.*, 2013]. In addition, estimated oxygen reduction rates for the Central Eastern SJV, which includes the northern portion of our study area are low (median rate of 0.12 mg L^{-1} yr^{-1}) [*Green et al.*, 2016] and dissolved oxygen content in our

study wells with a measurement was above 5 mg/L on average. We therefore do not expect significant denitrification within the shallow aquifer of our study region and consider the nitrate isotope data reliable indicators of original nitrate source.

Ninety-five percent posterior credibility intervals for fractional source contributions are shown in Figures 2 and 3. The credibility intervals for fractional source contributions are mostly wide, with some extending nearly the entire 0–1 range. Credibility intervals for different sources tend to overlap, especially for septic and fertilizer. Credibility intervals for the manure source are generally much narrower than for septic and fertilizer, and there are several wells for which the manure interval has little or no overlap with intervals for other sources (4-DOM, 135-DOM, 42-DOM, 176-DOM, 149-DOM, 49-DAR). Credibility intervals for the natural source are generally wider than the manure source, but more narrow than fertilizer and septic.

Calculated central tendency values for each well can be found in Table 1. Central tendency values and relevant land use fractions were plotted on scatterplots to check for relationships between estimated fractional contributions and land use (Figure 4). Wells surrounded by higher proportions of CAFO land use and forage crops (to which dairy manure may be applied) appear to also have greater central tendency values for manure, while wells surrounded by greater proportions of citrus and subtropical crops and nut

Figure 3. 95% credibility intervals for fractional source contributions by well and source. Wells are sorted by measured nitrate concentration (as in Table 1), in descending order (last 28 wells are shown). The dot is the mean for each source.
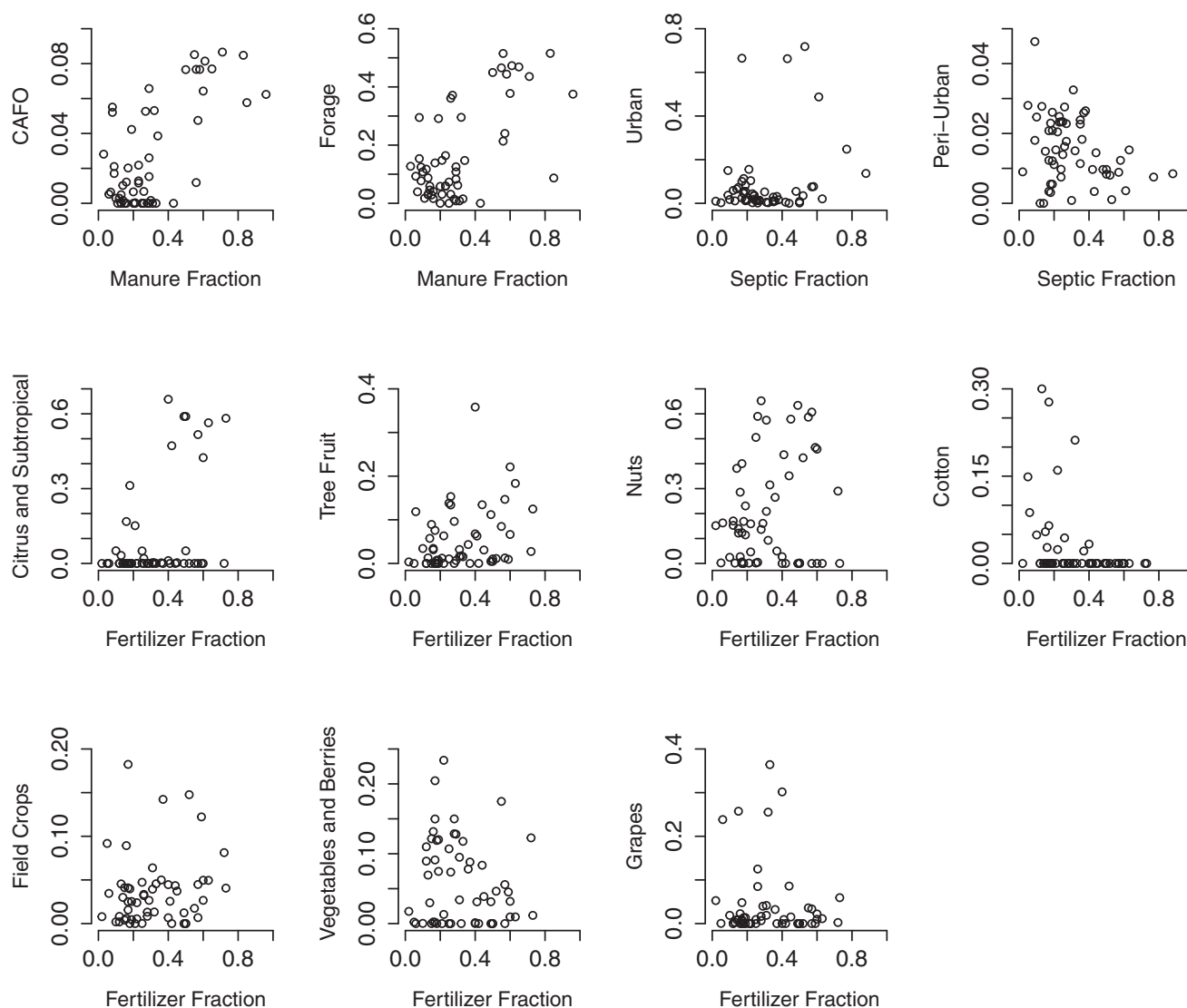
crops appear to have high central tendency values for fertilizer. Peri-urban land use surrounding wells appears to be negatively correlated with central tendency values for septic waste. Central tendency values were plotted as pie charts for each well on a map and examined for regional trends (Figure 5). Several potential trends stand out on the figure: a grouping of wells with larger predicted manure fractions between the cities of Patterson, Turlock, Newman, and Hilmar, corresponding to a region with a high density of dairies; wells with a dominant fertilizer fraction along the eastern edge of Tulare County near Orosi and Woodlake, corresponding to a region with long-standing citrus and tree-fruit cultivation; and several wells with high septic fractions near large urban centers such as well 120-DOM north of Visalia and wells 115-DOM and 116-DOM east of Tulare city.

Posterior probability densities of source tracer signatures are shown in Figures 6–9 superimposed over the prior probability densities and compiled tracer values used to define the prior densities. Posteriors are typically concentrated within the range of prior values, except for δ^{18}O in fertilizer, where the posterior shifts noticeably to lower values (Figure 7). The posterior for δ^{11}B in natural sources spans the approximate range of the prior; however, the posterior has a noteworthy increase in the median value (approximately 25‰ for the prior versus 45‰ for the posterior). Posteriors for δ^{15}N and δ^{18}O in manure as well as δ^{15}N in septic are noticeably more narrow than the respective priors. All posteriors were unimodal except for iodine in manure, which is bimodal with modes at approximately 55 and 80 μg/L. The Gaussian error model for iodine measurements does not appear to negatively affect inferences, as the posteriors for iodine are relatively well-behaved.

4. Discussion

We chose parameters of the Dirichlet prior that implied equal fractional contributions for manure, septic, and fertilizer, with lower expected contributions from natural sources. This implemented our hypothesis that the model should not favor one source over the others (except to down weight natural sources) prior to confronting actual tracer values. The Dirichlet parameters further implied low prior variances for the fractional contributions. We found that low prior variances led to better mixing of Markov Chains. This is likely because high Dirichlet variance gives the model the flexibility to interpret slight differences in tracer values as evidence for one dominant source, even though those values for a single tracer may be within the overlapping range for two different sources. Mixing of multiple nitrate sources seems to be inherent to the hydrogeological processes that generated the measured tracer values in these wells; in contradiction to

Figure 4. Calculated central tendency values and land use fractions, by well, for relevant source-land use comparisons. Central tendency values are calculated as the geometric mean of all realizations in each posterior probability distribution for the fractional contribution of each source in each well, that are then normalized by well. Within each plot, *x* and *y*-axis ranges may differ, in order to accommodate different scalings of land use fractions and estimated source contributions.

this, large Dirichlet variances appeared to disfavor mixing of multiple sources. The Dirichlet parameters we finally chose were flexible, in that prior credibility intervals for mixing fractions were wide enough to accommodate various amounts of mixing (see Figure 2, "Prior Case"), yet the prior parameters allowed one source to dominate if the empirical evidence was strong.

As with the prior credibility intervals, the posterior credibility intervals for fractional contributions of different sources are also wide, with considerable overlap in many cases, indicating potentially similar contributions from each of septic, fertilizer, and/or manure. Posterior credibility intervals characterize our degree of uncertainty about estimated source fractions, with wider intervals indicating more uncertainty about the true value. In particular, as made apparent from the wide and often overlapping credibility intervals for septic and fertilizer, our ability to distinguish these two sources is limited, using the current set of tracers (see below for further discussion). To a limited degree, the significant overlap may also indicate that somewhat similar proportions of synthetic fertilizer and septic waste may contribute to the pumped groundwater in domestic wells. We believe the overlapping credibility intervals faithfully represent uncertainty that is inherent in the use of this set of tracers.
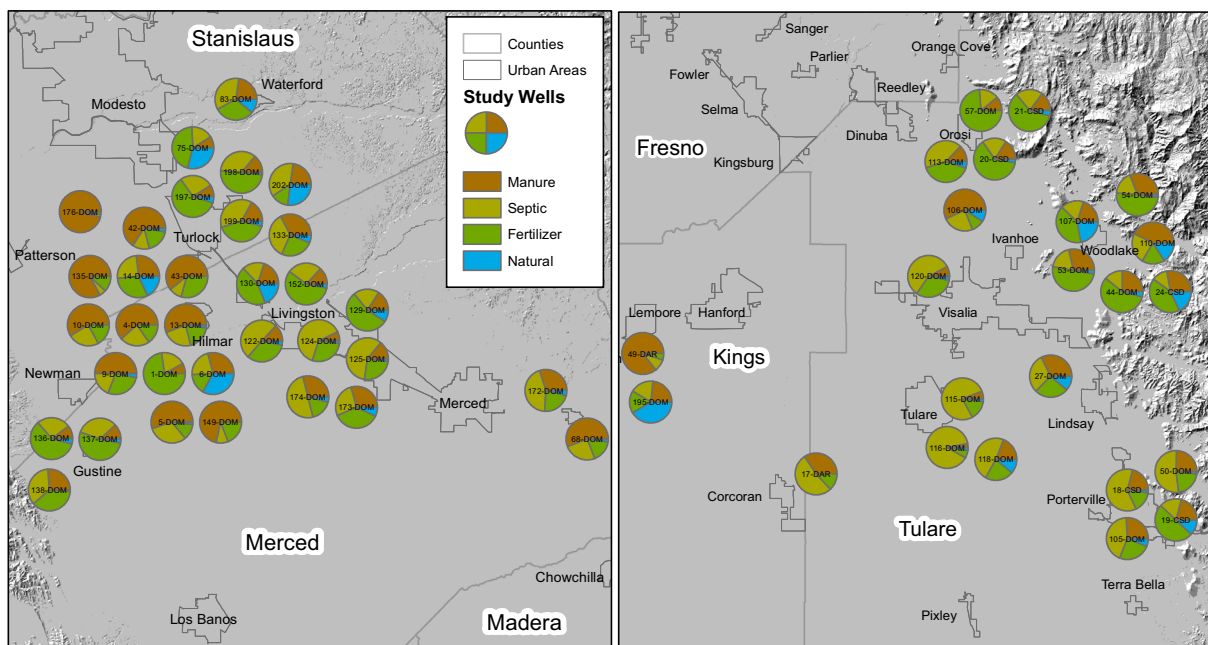
Figure 5. Calculated central tendency values of each source for each well. Central tendency values are calculated as the geometric mean of all realizations in each posterior probability distribution for the fractional contribution of each source in each well, that are then normalized by well. Wells with overlapping pie charts were offset to prevent overlap.

The evidence embedded in the water quality data was sufficiently strong in some cases to clearly identify one source as the majority contributor, mainly the manure source. This is the case for wells 4-DOM, 135-DOM, 42-DOM, 176-DOM, 149-DOM, and 49-DAR which all have $\delta^{15}N$ values above 10‰, have iodine concentrations among the highest 6 values for all wells in this study, and tend to have $\delta^{11}B$ values above or near 20‰ (all of these tracer values are within or specific to the signature profiles for manure, see Table 1). In the current model, the manure contribution of these wells can be described with relative certainty.

Normalized central tendency values were plotted on a map of the study area and two regional trends are apparent (Figure 5). The first and most apparent trend is the grouping of wells with a larger central tendency value for manure in the Stanislaus and Merced County region near the city of Hilmar and Turlock (west of Livingston and east of Newman). These include five of the six wells listed in the previous paragraph (4-DOM, 135-DOM, 42-DOM, 176-DOM, and 149-DOM) and five additional wells (43-DOM, 10-DOM, 13-DOM, 9-DOM, and 5-DOM). Each well listed has a normalized manure central tendency value above 0.5 and very strong evidence in the tracer values for a manure nitrate source. In terms of land use, these 10 wells are located in a region with very dense CAFO farming and each of these wells has dairy corrals and manure storage lagoons located within 2.4 km in all directions of the well. Wells with a greater amount of CAFO land use and/or forage crops (forage crops grown for dairy feed are typically irrigated with liquid manure from dairy lagoons) nearby appear to have greater predicted contributions from manure nitrate (Figure 4). It is therefore very likely that the well source area for each of these wells is affected by a dairy corral, manure storage lagoon, or liquid manure applied to forage crops on dairy lands.

Another notable regional trend is the larger central tendencies for fertilizer in three wells in the northern portion of Tulare County near Orosi (57-DOM, 21-CSD, and 20-CSD, with normalized central tendency values for fertilizer of 0.73, 0.60, and 0.63, respectively) and five wells in the eastern portion of the SJV in Tulare County near Woodlake (wells 107-DOM, 54-DOM, 53-DOM, 44-DOM, and 24-CSD, with normalized central tendency values for fertilizer of 0.40, 0.49, 0.50, 0.57, and 0.42, respectively). These nine wells are surrounded by mostly citrus and subtropical crops (with over 40 percent of well buffers for each well as citrus and subtropical). Wells surrounded by predominantly citrus and subtropical crops tend to have large estimated fertilizer contributions (Figure 4). Therefore, it is likely that wells in this region are affected by excess nitrogen fertilizers applied to these crops. The wells in this region with a predicted high nitrate contribution from fertilizer generally had iodine concentrations less than 16 μg/L, $\delta^{15}N$ values less than 10‰, $\delta^{18}O$ values greater
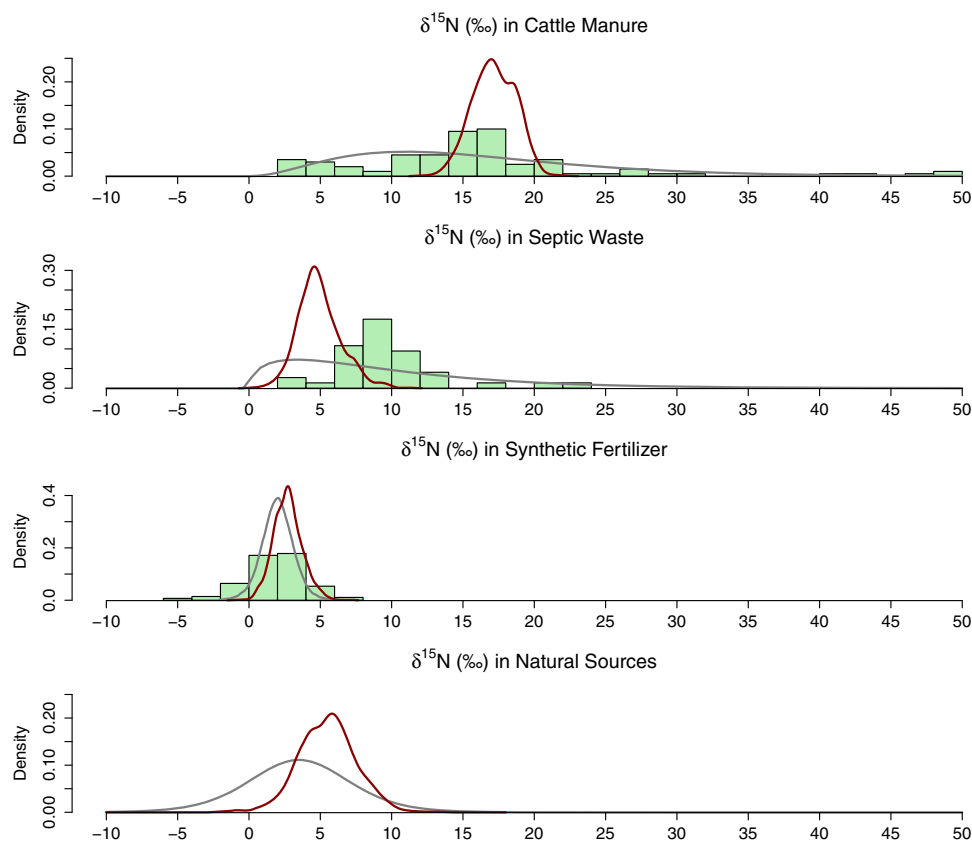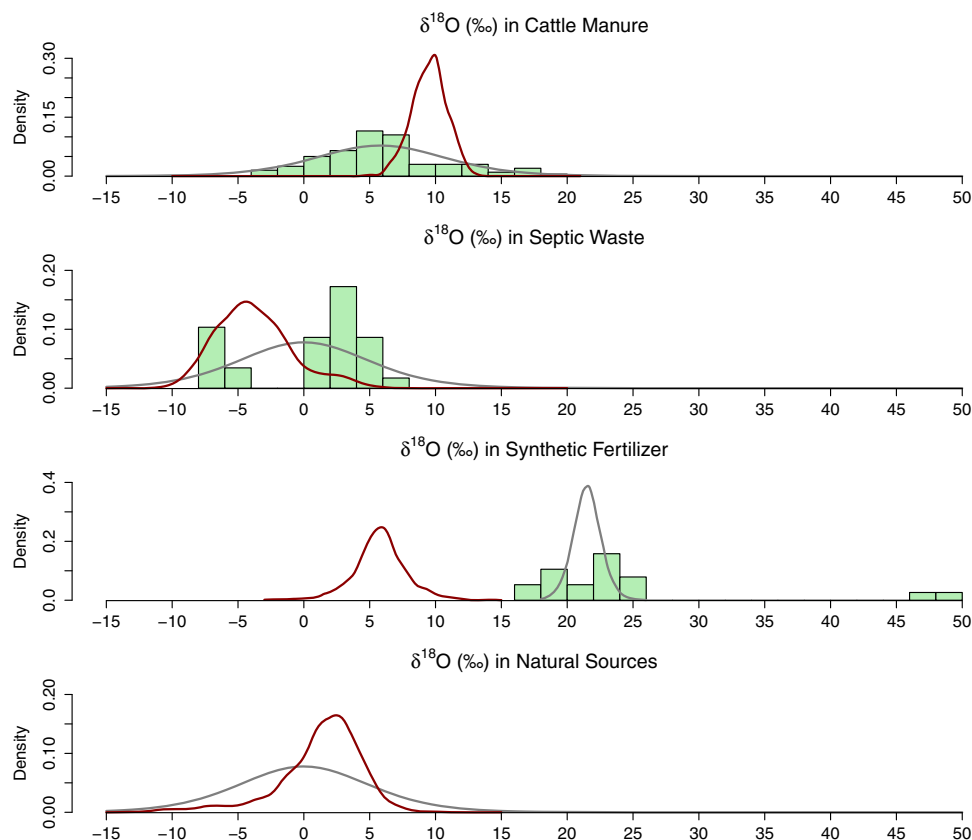
Figure 6. δ^{15}N-NO$_3$ measured in dairy manure, septic waste, synthetic fertilizers, and natural sources (dissolved inorganic nitrogen as nitrate in natural soils) as compiled from literature sources (green bars), prior probability density used in analysis (grey line), and posterior probability density predicted by the model (red line). If no green bars are shown, values were given as a range only (Table 2).

than 5‰, and δ^{11}B values less than 20‰ though this is not always the case. As an example, wells 107-DOM and 24-CSD have δ^{11}B values greater than 30‰ and the flexibility allowed here highlights the usefulness of the Bayesian aspect of the source tracers model.

Wells with high septic central tendency values appear to be located on the outskirts of urban centers. Several examples of this pattern are: three wells in Porterville (18-CSD, 50-DOM, and 105-DOM), two wells in Tulare (115-DOM and 116-DOM), one well immediately north of Visalia (120-DOM), and three wells on the south side of Livingston (125-DOM, 124-DOM, and 122-DOM) (Figure 5). All wells in this study were located at homes or dairies that were not connected to a central sewage disposal system and therefore each have a potential for contamination by septic waste due to preferential flow paths along the well gravel pack [*Horn and Harter*, 2009]. Though, the likelihood that septic system waste affects a well depends on several variables including condition of the septic system, setback distance, and septic system density. Poorly maintained systems, too low a setback distance between the well and the septic system or high density of systems increases the probability that septic waste will contaminate a well [*Bremer and Harter*, 2012]. In addition, leaky sewer systems can be an important source of nitrate in urbanized or incorporated areas [*Viers et al.*, 2012]. The specific wells listed above are likely affected by a wastewater source as septic system density tends to be high in the rural and unincorporated areas where these wells are located and due to the proximity of potentially leaky sewer lines within the incorporated zones.

Results of the land use analysis show the percentage of peri-urban land use in well buffers appears to be negatively correlated with septic central tendency values; however, no apparent correlation exists between urban land use and septic values (Figure 4). The counterintuitive negative correlation between peri-urban and septic is likely the result of a significant amount of manure or synthetic fertilizer applied to crop lands immediately adjacent to farmstead residences. Peri-urban land use in this study is mostly the Department

Figure 7. $\delta^{18}O$-NO_3 measured in dairy manure, septic waste, synthetic fertilizers, and natural sources (dissolved inorganic nitrate in natural soils) as compiled from literature sources (green bars), prior probability density used in analysis (grey line), and posterior probability density predicted by the model (red line). If no green bars are shown, values were given as a range only (Table 2).

of Water Resources "farmstead residence" land use category (see supporting information), which appears to only include the residence and surrounding landscape area and not the crop land typically associated with such residences. Therefore, our model predicts a greater septic nitrate contribution for wells with fewer farmstead residences nearby as areas with many farmstead residences are likely to have high manure and fertilizer nitrate contributions. Alternatively, farmstead residences are more likely to occur further from urban centers and wells with less farmstead residences nearby are more likely to have a greater amount of urban land use near the well, which appears to include rural unincorporated areas with high septic system density.

Two wells in areas of dense CAFO land use within Tulare County (17-DAR, located on a dairy, and 118-DOM) had greater normalized central tendency values for septic (0.52 and 0.88, respectively) and lower central tendency values for manure (0.34 and 0.03, respectively). The septic source contribution predicted for these wells is likely greater because both of these wells had iodine concentrations less than 10 μg/L and the posterior probability density for iodine in manure excludes the possibility of low iodine concentration dairy waste (less than 20 μg/L). The posterior density for iodine in dairy waste was noticeably shifted away from lower concentrations incorporated in the prior, an effect known as "Bayesian learning," in which empirical evidence overwhelms the prior, concentrating posterior probability in a different range. The shift to higher posterior iodine concentrations for dairy sources suggests that wells with higher iodine concentrations also tended to have measured values for the other three tracers that were consistent with a manure signature. Well 17-DAR, more likely affected by septic sources, had the lowest $\delta^{11}B$ value measured in the sample (4.6‰), making manure sources unlikely. Well 118-DOM had a $\delta^{11}B$ value (23.6‰) that may indicate some manure contributions or may be due to septic waste from a household not using soaps containing sodium perborate. While the model indicates that septic waste is likely to be a dominant source of nitrate to this well, it does not exclude the possibility that 118-DOM is impacted by manure from nearby dairies that may not use iodine disinfection products.
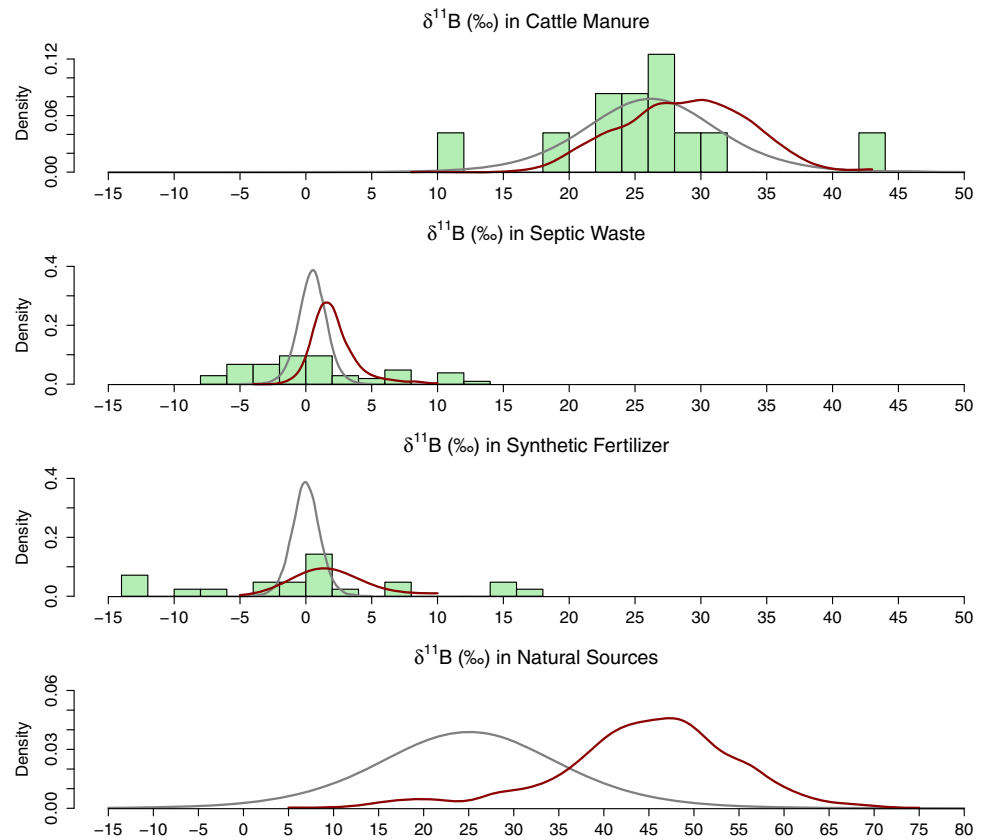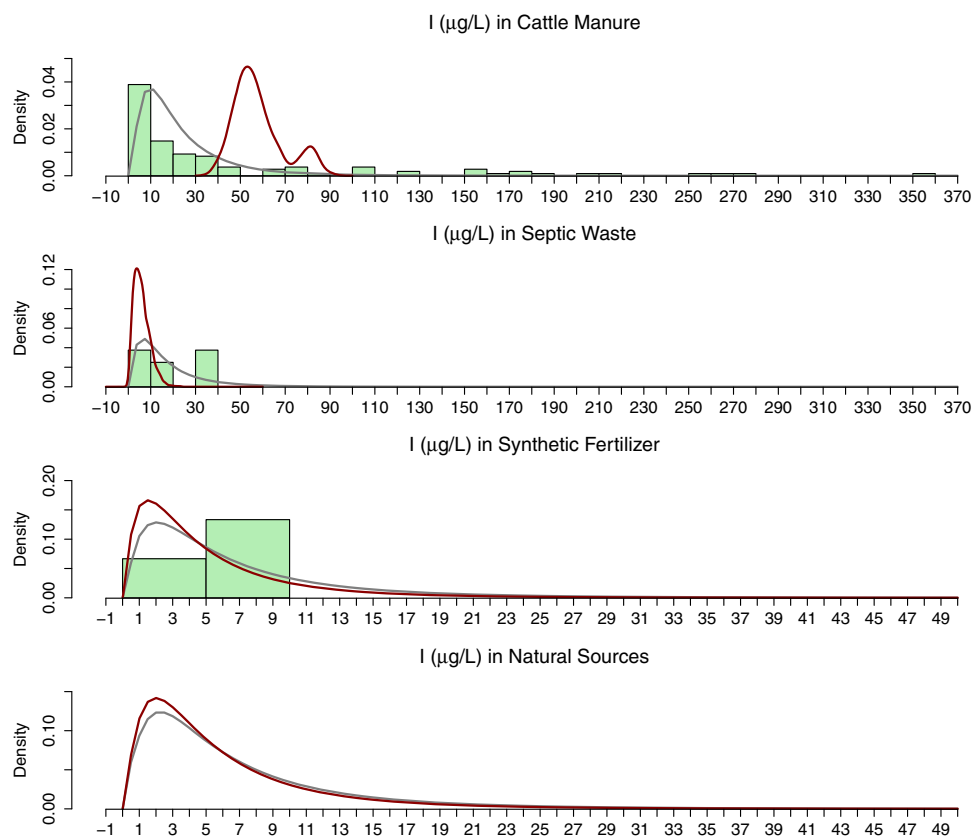
Figure 8. $\delta^{11}B$ measured in dairy manure, septic waste, synthetic fertilizers, and natural sources as compiled from literature sources (green bars), prior probability density used in analysis (grey line), and posterior probability density predicted by the model (red line). If no green bars are shown, values were given as a range only (Table 2).

Several wells do not have normalized central tendency values for the three main nitrate sources that appear significantly different from the prior mean value (0.3). This is caused by a lack of evidence in the measured tracer values for a dominant source, and may indicate even contributions from manure, septic, and fertilizer sources. In other words, the chemical signature detected provides no strong evidence that the contributions of various nitrate sources are different from the naively assumed contributions, based on a general notion of the potential available sources.

It is important to keep in mind that the central tendencies (Figure 5) are useful to understand spatial trends, but do not reflect the statistical range predicted by the model. We further point out that the contribution from several types of nitrogen sources, particularly the contribution of natural sources to the nitrogen signature in a well, may be due to the presence of spatially adjacent, multiple sources within the source area (recharge area) of a well; but it may also be due to changes in land use over time, as the water samples represent a mixed age of travel time. Within the study area, groundwater age tends to increase with depth, with older water typically entering in the lower portion of the well screen and younger water the upper portion of the well screen [*Burow et al.*, 2007]. Partial contribution from natural sources may reflect older water ages in the sample, from low nitrate recharge prior to intensive use of fertilizer as studies have shown that the primary driver controlling groundwater nitrate concentrations over time within the Central Valley is agricultural nitrogen loading [*Landon et al.*, 2011; *Viers et al.*, 2012]. Similarly, partial contributions from manure sources may reflect younger fractions of the water sample associated with the large increase in animal herd density and manure disposal at California dairies between the 1960s and the 2000s [*Viers et al.*, 2012].

Posterior probability densities for values of the tracers in the sources can be considered secondary results of the model. Most tracers show evidence of Bayesian learning, the posteriors having noticeably shifted or concentrated mass, in comparison to the priors. The posterior for $\delta^{18}O$ values in fertilizer is something of an extreme example: here the measured tracer values in wells seem almost incompatible with the prior

Figure 9. Iodine (μg/L) measured in dairy manure, septic waste, synthetic fertilizers, and natural sources as compiled from literature sources (green bars), prior probability density used in analysis (grey line), and posterior probability density predicted by the model (red line). If no green bars are shown, values were given as a range only (Table 2).

distribution based on data from the literature (Table 1 and Figure 7). This disagreement between the measured well water values and the prior values for $\delta^{18}O$ could be due to the $\delta^{18}O$ values typically found in the types of fertilizer used to define the priors versus the values in the types of fertilizer actually applied. The prior for $\delta^{18}O$ in fertilizer nitrate was based on nitrate as nitrate fertilizer values and did not include values for nitrate nitrified from ammonium fertilizers, which are much lower (between approximately -15 to $15‰$) [*Kendall et al.*, 2007]. Nitrate as nitrate fertilizer generally has high $\delta^{18}O$ values (between about 15 and 25‰) due to the incorporation of atmospheric oxygen (23‰) in the fertilizer manufacturing process [*Kendall et al.*, 2007]. On the other hand, nitrate derived from subsurface nitrification of ammonium fertilizers within the unsaturated zone has a lower $\delta^{18}O$ value due to the theoretical incorporation of one oxygen atom from air and two from the surrounding soil water [*Kendall et al.*, 2007].

Reported fertilizer sales for the year 1991 within the four counties in which the study wells are located report a greater amount of sales of nitrate fertilizers (by weight); however, ammonium fertilizers account for approximately forty percent, by weight, of total nitrogen products sold (California Department of Food and Agriculture, Fertilizing Materials Tonnage Report, January through December, 1991, http://www.cdfa.ca.gov/is/ffldrs/Fertilizer_Tonnage.html). In order to calculate the total sales of each type of nitrogen fertilizer, we split the reported weights for ammonium nitrate products evenly between the ammonium and nitrate categories and ignore the blood meal category and the category classified as other. Fertilizers purchased within these counties may not necessarily be applied within the county. However, it is reasonable to assume that the wells are affected by ammonium fertilizers or a mixture of nitrate and ammonium fertilizers. These results are consistent with the findings in *Young et al.* [2013].

In this study, manure sources appeared to be well distinguished from septic and fertilizer sources, but the latter sources were not readily distinguishable from one another. Prior values of boron isotopes in septic and fertilizer largely overlap likely due to the use of the same boron containing minerals in fertilizers and

household products [*Vengosh et al.*, 1999]. In addition, boron as Borax (aka sodium borate) was reported as being sold for agricultural use in California in 1992 (California Department of Food and Agriculture, Fertilizing Materials Tonnage Report, January through June 1992, https://www.cdfa.ca.gov/is/ffldrs/pdfs/1992_Tonnage.pdf). However, prior information for the values of the four selected tracers in septic waste and fertilizer sources show a unique signature for both septic waste and fertilizer with septic waste having potentially elevated δ^{15}N values and iodine concentration, while nitrate fertilizer is expected to have a highly elevated δ^{18}O value. The posterior distributions for δ^{15}N and iodine in septic waste are more focused on the lower values covered by the priors. Also, the posterior distribution for δ^{18}O in fertilizer shows a significant shift toward lower values, making the posterior signatures of septic waste and fertilizer sources fairly similar. This shift is likely due, as discussed above, to the application of a combination of ammonium and nitrate fertilizers, resulting in nitrate with a lower δ^{18}O value than that of pure nitrate fertilizers. Therefore, the fertilizer source in the current model can be thought of as a mixed source in itself.

Given the current set of tracers, it is possible to tell the difference between septic waste and nitrate fertilizers, but not septic waste and ammonium fertilizers. However, if ammonium and nitrate fertilizers are approximately evenly mixed, a unique signature for each of septic and fertilizer could still exist, with fertilizer having slightly elevated δ^{18}O values as shown by our model output (Figure 7). Where the credibility intervals for septic waste and fertilizer are wide and mostly overlap: either no single source dominates in its contribution to the well water (septic and fertilizer sources are well mixed); or one source is in fact dominating in its contribution, but the analysis cannot identify that source with statistical significance. Mixing of fertilizer and septic waste may be common in the rural unincorporated areas where the well water samples were collected and our results indicate that, in general, we cannot currently differentiate fractional contributions from the two sources with a high degree of certainty.

This model design requires at least an equal number of tracers for the number of selected sources. Additional tracers such as sodium, chloride, pesticides expected to comigrate in the subsurface with fertilizer leachate, or substances specific to septic waste such as personal care by-products or pharmaceuticals may be added in order to improve model predictions. Specifically, an additional tracer with a unique signature between ammonium fertilizer and septic waste could improve our ability to differentiate between these two sources.

The majority of source tracer signatures were approximated based on literature values and this is considered the best possible approximation of end member tracer signatures, given the available resources, and especially considering the degree of variability (both geographically and historically) in land use and agricultural practices across the large study region. At the time of this study, there was no information on the δ^{15}N, δ^{18}O, and δ^{11}B values, or iodine concentrations in septic waste, synthetic fertilizers, and natural sources specific to the SJV. There are also no δ^{11}B values in manure available that are specific to the SJV. Characterizing study-area specific source tracer values in a region as diverse as the SJV would require a large-scale study, but could potentially improve model predictions. In addition, information on type of nitrogen fertilizer applied to crops and use of iodine containing disinfection products on dairies could improve the reliability of the model's prior source signatures.

This study does not account for nitrate in atmospheric deposition, a potentially important source of nitrate to groundwater in some areas, though contributions are expected to be much lower than those of manure, fertilizer, or septic waste [*Viers et al.*, 2012]. Nitrate from atmospheric deposition was not selected over natural sources because atmospheric deposition is not a significant source of boron or iodine. The addition of at least one more tracer would allow the incorporation of the atmospheric deposition source. Depending on the selected tracer source signatures, the addition of a fifth nitrate source could improve or further obscure the model fractional contribution predictions.

5. Conclusions

The Bayesian mixing model is a principled, data-driven way to provide objective insight about the probability distribution of the fractional contribution of various nitrate sources to nitrate in an individual well. The model makes explicit use of variability in end-member tracer measurements, allows for overlap between source signatures, accounts for the uncertainty within those signatures in the model results, and includes

the opportunity for updating our current knowledge about source tracer signatures via "Bayesian learning," all distinct advantages of the Bayesian model approach over the deterministic approach.

Our model output shows the manure source to have the most distinctive signature in terms of the four selected tracers, and we find manure is clearly the dominant source of overall nitrate to several study wells in areas where dairy corrals and lagoons as well as manure-receiving forage fields play a prominent role in the landscape. Septic and fertilizer waste were more difficult to distinguish though several wells seem dominated by one or the other and the results were consistent with nearby land use types. Septic and fertilizer waste may mix more often, or our ability to distinguish between the two could be affected by the application of ammonium fertilizers which have tracer signatures similar to septic waste. Tracer values in distinct types of the same general source (such as ammonium versus nitrate fertilizers) should be considered in future studies. Fractionation of isotope signatures in the subsurface such as from denitrification or absorption of dissolved boron to the aquifer matrix can also further hamper our ability to distinguish sources.

In contrast to deterministic mixing models, the Bayesian analysis proposed here clearly identifies the degree of uncertainty that remains in apportioning contributions from different nitrate sources to well nitrate, even with the unique signatures from the four tracers selected here. For some wells, our analysis predicts near equal mixing proportions for each of septic, fertilizer, and manure sources, with a high degree of uncertainty. This could reflect true mixing, or a lack of information in the tracer values as sources were initially assigned equal mixing proportions for each source (with the exception of natural, which was given a lower initial mixing proportion). Equal mixing proportions for the three major sources of nitrate were initially assigned to each well due to a lack of detailed site-specific information in each case.

Predictions could be improved by either better defining source tracer signatures for each source by analyzing sources local to the study area, or by narrowing down potential source contributions to each well based on site-specific investigations. Useful information could include well depth and detailed hydrogeologic information to identify the actual well source area as opposed to relying on an approximated circular well buffer, historical information on nearby fertilizer application types and rates (and specifically whether or not those fertilizers contained boron), historical information on nearby manure applications (including solid manure exported off dairies and applied to crops greater than 16 km from a dairy), use of iodine on nearby dairies, amount of iodine in nearby septic waste, and historical and current information on use of sodium perborate containing products in surrounding households. Future studies could improve upon our current findings with further investigation into the sources of uncertainty listed here.

References

Accoe, F., M. Berglund, S. Duta, C. Hennessy, P. Taylor, K. Van Hoof, and S. De Smedt (2008), Source apportionment of nitrate pollution in surface water using stable isotopes of N and O in nitrate and B: A case study in Flanders (Belgium), technical report, JRC Scientific and Tech. Rep. EUR 23425 EN, Office for Official Publications of the European Communities, Luxembourg.

Aitchison, J., G. Mateu-Figueras, and K. W. Ng (2003), Characterization of distributional forms for compositional data and associated distributional tests, Math. Geol., 35(6), 667–680.

Amberger, A., and H.-L. Schmidt (1987), Natrliche isotopengehalte von nitrat als indikatoren fr dessen herkunft, Geochim. Cosmochim. Acta, 51(10), 2699–2705, doi:10.1016/0016-7037(87)90150-5.

Aravena, R., M. L. Evans, and J. A. Cherry (1993), Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems, Ground Water, 31(2), 180–186, doi:10.1111/j.1745-6584.1993.tb01809.x.

ATSDR (2013), ATSDR case studies in environmental medicine nitrate/nitrite toxicity, Tech. Rep. WB2342, U.S. Dep. of Health and Human Serv., Atlanta, Ga.

Barth, S. (1998), Application of boron isotopes for tracing sources of anthropogenic contamination in groundwater, Water Res., 32(3), 685–690, doi:10.1016/S0043-1354(97)00251-0.

Bassett, R. L., P. M. Buszka, G. R. Davidson, and D. Chong-Diaz (1995), Identification of groundwater solute sources using boron isotopic composition, Environ. Sci. Technol., 29(12), 2915–2922, doi:10.1021/es00012a005.

Bremer, J., and T. Harter (2012), Domestic wells have a high probability of pumping septic tank leachate, Hydrol. Earth Syst. Sci., 16, 2453–2467.

Burow, K. R., N. M. Dubrovsky, and J. L. Shelton (2007), Temporal trends in concentrations of DBCP and nitrate in groundwater in the eastern San Joaquin Valley, California, USA, Hydrogeol. J., 15(5), 991–1007, doi:10.1007/s10040-006-0148-7.

Canter, L. W. (1997), Nitrates in Groundwater, 263 pp., CRC Press, LLC, Boca Raton, Fla.

Casciotti, K. L., D. M. Sigman, M. G. Hastings, J. K. Böhlke, and A. Hilkert (2002), Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, Anal. Chem., 74(19), 4905–4912, doi:10.1021/ac020113w.

Chetelat, B., and J. Gaillardet (2005), Boron isotopes in the Seine River, France: A probe of anthropogenic contamination, Environ. Sci. Technol., 39(8), 2486–2493, doi:10.1021/es048387j.

Clesceri, L., A. E. Greenberg, and A. D. Eaton (1998), Standard Methods for the Examination of Water and Wastewater, 20th ed., Am. Publ. Health Assoc., Washington, D. C.

Croft, M., and G. Gordon (1968), Geology, hydrology, and quality of water in the Hanford-Visalia area, San Joaquin Valley, California, *U.S. Geol. Surv. Open File Rep. 68-67*, 63 pp.

CSWRCB (2013), Groundwater ambient monitoring and assessment (GAMA) domestic well project groundwater quality report, Tulare County focus area, technical report, Calif. State Water Resour. Control Board, Groundwater Prot. Sect., Sacramento, Calif.

Deutsch, B., M. Mewes, I. Liskow, and M. Voss (2006), Quantification of diffuse nitrate inputs into a small river system using stable isotopes of oxygen and nitrogen in nitrate, *Org. Geochem.*, *37*(10), 1333–1342, doi:10.1016/j.orggeochem.2006.04.012

Dubrovsky, N., et al. (2010), Nutrients in the Nations streams and groundwater, 1992-2004, *U.S. Geol. Surv. Circ.*, *1350*, 174 pp.

El Gaouzi, F.-Z. J., M. Sebilo, P. Ribstein, V. Plagnes, P. Boeckx, D. Xue, S. Derenne, and M. Zakeossian (2013), Using $\delta^{15} - N$ and $\delta^{18} - O$ values to identify sources of nitrate in karstic springs in the Paris basin (France), *Appl. Geochem.*, *35*, 230–243.

Eppich, G. R., J. B. Wimpenny, Q. Yin, and B. K. Esser (2011), California GAMA special study: Stable isotopic composition of boron in groundwater analytical method development, *Tech. Rep. LLNL-TR-498360*, Lawrence Livermore Natl. Lab. and Univ. of Calif., Davis.

Eppich, G. R., M. J. Singleton, J. B. Wimpenny, Q. Yin, and B. K. Esser (2012), California GAMA special study: Stable isotopic composition of boron in groundwater San Diego county domestic well data, *GAMA Special Studies Task 10.4: Development of New Wastewater Indicator Methods, Tech. Rep. LLNL-TR-533174*, Lawrence Livermore Natl. Lab., Livermore, Calif.

Faunt, C. C. (Ed.) (2009), Groundwater availability of the Central Valley aquifer, California, *U.S. Geol. Surv. Prof. Pap.*, *1766*, 225 pp.

Fogg, G. E., D. Rolston, D. Decker, D. Louie, and M. Grismer (1998), Spatial variation in nitrogen isotope values beneath nitrate contamination sources, *Ground Water*, *36*(3), 418–426, doi:10.1111/j.1745-6584.1998.tb02812.X.

Freyer, H., and A. Aly (1974), Nitrogen-15 variations in fertilizer nitrogen, *J. Environ. Qual.*, *3*(4), 405–406.

Ghiglieri, G., G. Barbieri, A. Vernier, A. Carletti, N. Demurtas, R. Pinna, and D. Pittalis (2009), Potential risks of nitrate pollution in aquifers from agricultural practices in the Nurra region, northwestern Sardinia, Italy, *J. Hydrol.*, *379*(3–4), 339–350, doi:10.1016/j.jhydrol.2009.10.020.

Gonfiantini, R., et al. (2003), Intercomparison of boron isotope and concentration measurements. part ii: Evaluation of results, *Geostand. Newsl.*, *27*(1), 41–57, doi:10.1111/j.1751-908X.2003.tb00711.x.

Green, C. T., B. C. Jurgens, Y. Zhang, J. J. Starn, M. J. Singleton, and B. K. Esser (2016), Regional oxygen reduction and denitrification rates in groundwater from multi-model residence time distributions, San Joaquin Valley, USA, *J. Hydrol.*, in press.

Gu, B., Y. Ge, S. X. Chang, W. Luo, and J. Chang (2013), Nitrate in groundwater of China: Sources and driving forces, *Global Environ. Change*, *23*(5), 1112–1121, doi:10.1016/j.gloenvcha.2013.05.004.

Guerrot, C., R. Millot, M. Robert, and P. Négrel (2011), Accurate and high-precision determination of boron isotopic ratios at low concentration by MC-ICP-MS (Neptune), *Geostand. Geoanal. Res.*, *35*(2), 275–284, doi:10.1111/j.1751-908X.2010.00073.x.

Heaton, T. (1986), Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review, *Chem. Geol.*, *59*, 87–102, doi:1016/0168-9622(86)90059-X.

Horn, J. E., and T. Harter (2009), Domestic well capture zone and influence of the gravel pack length, *Ground Water*, *47*(2), 277–286, doi:10.1111/j.1745-6584.2008.00521.x.

Hu, Q., J. Moran, and J. Gan (2012), Sorption, degradation, and transport of methyl iodide and other iodine species in geologic media, *Appl. Geochem.*, *27*(3), 774–781, doi:10.1016/j.apgeochem.2011.12.022.

Johnson, T. D., and K. Belitz (2009), Assigning land use to supply wells for the statistical characterization of regional groundwater quality: Correlating urban land use and VOC occurrence, *J. Hydrol.*, *370*, 100–108.

Kendall, C. (1998), Tracing nitrogen sources and cycling in catchments, in *Isotope Tracers in Catchment Hydrology*, edited by C. Kendall and J. J. McDonnell, chap. 16, pp. 519–576, Elsevier, Amsterdam, Netherlands, doi:10.1016/B978-0-444-81546-0.50023-9.

Kendall, C., E. Elliott, and S. Wankel (2007), Tracing anthropogenic inputs of nitrogen to ecosystems, in *Stable Isotopes in Ecology and Environmental Science*, 2nd ed., edited by R. Michener and K. Lajtha, chap. 12, pp. 375–449, Blackwell, Malden, Mass.

Kiss, E. (1988), Ion-exchange separation and spectrophotometric determination of boron in geological materials, *Anal. Chim. Acta*, *211*, 243–256, doi:10.1016/S0003-2670(00)83684-3.

Komor, S. C. (1997), Boron contents and isotopic compositions of hog manure, selected fertilizers, and water in Minnesota, *J. Environ. Qual.*, *26*(5), 1212–1222.

Korth, F., B. Deutsch, C. Frey, C. Moros, and M. Voss (2014), Nitrate source identification in the Baltic Sea using its isotopic ratios in combination with a Bayesian isotope mixing model, *Biogeosciences*, *11*, 4913–4924.

Kourakos, G., F. Klein, A. Cortis, and T. Harter (2012), A groundwater nonpoint source pollution modeling framework to evaluate long-term dynamics of pollutant exceedance probabilities in wells and other discharge locations, *Water Resour. Res.*, *48*, W00L13, doi:10.1029/2011WR010813.

Kreitler, C. W. (1979), Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas, *J. Hydrol.*, *42*(12), 147–170, doi:10.1016/0022-1694(79)90011-8.

Landon, M. K., C. T. Green, K. Belitz, M. J. Singleton, and B. K. Esser (2011), Relations of hydrogeologic factors, groundwater reduction-oxidation conditions, and temporal and spatial distributions of nitrate, Central-Eastside San Joaquin Valley, California, USA, *Hydrogeol. J.*, *19*(6), 1203–1224, doi:10.1007/s10040-011-0750-1.

Leeman, W. P., R. D. Vocke, Jr., E. Beary, and P. Paulsen (1991), Precise boron isotopic analysis of aqueous samples: Ion exchange extraction and mass spectrometry, *Geochim. Cosmochim. Acta*, *55*(12), 3901–3907, doi:10.1016/0016-7037(91)90085-J.

Leenhouts, J. M., R. Basset, and T. Maddock, III (1998), Utilization of intrinsic boron isotopes as co-migrating tracers for identifying potential nitrate contamination sources, *Ground Water*, *36*(2), 240–250, doi:10.1111/j.1745-6584.1998.tb01089.x.

Lemarchand, D., J. Gaillardet, C. Göpel, and G. Manhès (2002), An optimized procedure for boron separation and mass spectrometry analysis for river samples, *Chem. Geol.*, *182*(2-4), 323–334, doi:10.1016/S0009-2541(01)00329-1.

Lockhart, K. M., A. M. King, and T. Harter (2013), Identifying sources of groundwater nitrate contamination in a large alluvial groundwater basin with highly diversified intensive agricultural production, *J. Contam. Hydrol.*, *151*, 140–154.

Mariotti, A., and R. Létolle (1977), Application de l'étude isotopique de l'azote en hydrologie et en hydrogéologie analyse des résultats obtenus sur un exemple précis: le Bassin de Mélarchez (Seine-et-Marne, France), *J. Hydrol.*, *33*(12), 157–172, doi:10.1016/0022-1694(77)90105-6.

Massoudieh, A., and M. Kayhanian (2013), Bayesian chemical mass balance method for surface water contaminant source apportionment, *J. Environ. Eng.*, *139*(1), 250–260.

Mattern, S., D. Fasbender, and M. Vanclooster (2009), Discriminating sources of nitrate pollution in an unconfined sandy aquifer, *J. Hydrol.*, *376*(1-2), 275–284, doi:10.1016/j.jhydrol.2009.07.039.

Mueller, D., and D. Helsel (1996), Nutrients in the Nation's waters - too much of a good thing?, *U.S. Geol. Surv. Circ.*, *1136*, 24 pp.

Panno, S., K. Hackley, H. Hwang, and W. Kelly (2001), Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators, *Chem. Geol.*, *179*(1–4), 113–128, doi:10.1016/S0009-2541(01)00318-7.

Panno, S., K. Hackley, H. Hwang, S. Greenberg, I. Krapac, S. Landsberger, and D. O'Kelly (2005), Database for the characterization and identi-fication of the sources of sodium and chloride in natural waters of Illinois, *Tech. Rep. Open File Ser. 2005-1*, Dep. of Nat. Resour. and Illi-nois State Geol. Surv., Champaign, Ill.

Panno, S., K. Hackley, H. Hwang, S. Greenberg, I. Krapac, S. Landsberger, and D. O'Kelly (2006), Characterization and identification of NaCl sources in groundwater, *Ground Water*, *44*(2), 176–187.

Parnell, A. C., R. Inger, S. Bearhop, and A. L. Jackson (2010), Source partitioning using stable isotopes: Coping with too much variation, *PLoS ONE*, *5*(3), e9672, doi:10.1371/journal.pone.

Pastén-Zapata, E., R. Ledesma-Ruiz, T. Harter, A. I. Ramírez, and J. Mahlknecht (2014), Assessment of sources and fate of nitrate in shallow groundwater of an agricultural area by using a multi-tracer approach, *Sci. Total Environ.*, *470–471*, 855–864.

Phillips, D. L., and J. W. Gregg (2001), Uncertainty in source partitioning using stable isotopes, *Oecologia*, *127*(2), 171–179, doi:10.1007/s004420000578.

Phillips, S., C. Green, K. Burow, J. Shelton, and D. Rewis (2007), Simulation of multiscale ground-water flow in part of the northeastern San Joaquin Valley, California, *U.S. Geol. Surv. Sci. Invest. Rep. 2007-5009*, 43 pp.

Raymond, K., and L. Butterwick (1992), Perborate, in *The Handbook of Environmental Chemistry, vol. 3 Part F, Anthropogenic Compounds, Detergents*, edited by N. de Oude and O. Hutzinger, Springer, Berlin.

Ryan, T. P. (2009), *Modern Regression Models*, 2nd ed., John Wiley and Sons, Inc. Hoboken, N. J.

Seiler, R. L. (2005), Combined use of ^{15}N and ^{18}O of nitrate and ^{11}B to evaluate nitrate contamination in groundwater, *Appl. Geochem.*, *20*(9), 1626–1636, doi:10.1016/j.apgeochem.2005.04.007.

Shearer, G., D. Kohl, and B. Commoner (1974), The precision of determinations of the natural abundance of nitrogen-15 in soils, fertilizers, and shelf chemicals, *Soil Sci.*, *118*(5), 308–316.

Sigman, D. M., K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J. K. Böhlke (2001), A bacterial method for the nitrogen isotopic anal-ysis of nitrate in seawater and freshwater, *Anal. Chem.*, *73*(17), 4145–4153, doi:10.1021/ac010088e.

Stauffer, H. B. (2008), *Contemporary Bayesian and Frequentist Statistical Research Methods for Natural Resource Scientists*, John Wiley and Sons, Inc. Hoboken, N. J.

Tirez, K., W. Brusten, D. Widory, E. Petelet, A. Bregnot, D. Xue, P. Boeckx, and J. Bronders (2010), Boron isotope ratio ($\delta^{11}b$) measurements in water framework directive monitoring programs: Comparison between double focusing sector field ICP and thermal ionization mass spectrometry, *J. Anal. At. Spectrom.*, *25*, 964–974, doi:10.1039/C001840F.

U.S. Department of Health and Human Services (2004), Toxicological profile for iodine, technical report, U.S. Dep. of Health and Human Serv. Publ. Health Serv. Agency for Toxic Substances and Disease Regist., Atlanta, Ga.

U.S. EPA (2001), Method 200.7: Trace elements in water, solids, and biosolids by inductively coupled plasma-atomic emission spectrometry, *Tech. Rep. EPA-821-R-01-010*, 68 pp., U.S. Environ. Prot. Agency, Washington, D. C.

Vengosh, A., K. G. Heumann, S. Juraske, and R. Kasher (1994), Boron isotope application for tracing sources of contamination in groundwa-ter, *Environ. Sci. Technol.*, *28*(11), 1968–1974, doi:10.1021/es00060a030.

Vengosh, A., S. Barth, K. G. Heumann, and S. Eisenhut (1999), Boron isotopic composition of freshwater lakes from Central Europe and pos-sible contamination sources, *Acta Hydrochim. Hydrobiol.*, *27*(6), 416–421, doi:10.1002/(SICI)1521-401X(199912)27:6 < 416:: AID-AHEH416 > 3.0.CO;2-2.

Viers, J., et al. (2012), Addressing nitrate in California's drinking water with a focus on Tulare Lake Basin and Salinas Valley groundwater. Report for the State Water Resources Control Board report to the Legislature, *Tech. Rep. 2*, Cent. for Watershed Sci., Univ. of Calif., Davis, Calif.

Vitòria, L., N. Otero, A. Soler, and Àngels Canals (2004), Fertilizer characterization: Isotopic data (N, S, O, C, and Sr), *Environ. Sci. Technol.*, *38*(12), 3254–3262, doi:10.1021/es0348187.

Voss, M., B. Deutsch, R. Elmgren, C. Humborg, P. Kuuppo, M. Pastuszak, C. Rolff, and U. Schulte (2006), Source identification of nitrate by means of isotopic tracers in the Baltic Sea catchments, *Biogeosciences*, *3*, 663–676.

Wakida, F. T., and D. N. Lerner (2005), Non-agricultural sources of groundwater nitrate: A review and case study, *Water Res.*, *39*(1), 3–16, doi:10.1016/j.watres.2004.07. 026.

Ward, M. H., T. M. deKok, P. Levallois, J. Brender, G. Gulis, B. T. Nolan, and J. VanDerslice (2005), Workgroup report: Drinking-water nitrate and healthrecent findings and research needs, *Environ. Health Perspect.*, *113*(11), 1607–1614.

Wassenaar, L. I. (1995), Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of ^{15}N and ^{18}O in NO_3, *Appl. Geochem.*, *10*(4), 391–405, doi:10.1016/0883-2927(95)00013-A.

Widory, D., W. Kloppmann, L. Chery, J. Bonnin, H. Rochdi, and J.-L. Guinamant (2004), Nitrate in groundwater: An isotopic multi-tracer approach, *J. Contam. Hydrol.*, *72*(1–4), 165–188, doi:10.1016/j.jconhyd.2003.10.010.

Widory, D., E. Petelet-Giraud, P. Négrel, and B. Ladouche (2005), Tracking the sources of nitrate in groundwater using coupled nitrogen and boron isotopes: A synthesis, *Environ. Sci. Technol.*, *39*(2), 539–548, doi:10.1021/es0493897.

Wongsanit, J., P. Teartisup, P. Kerdsueb, P. Tharnpoophasiam, and S. Worakhunpiset (2015), Contamination of nitrate in groundwater and its potential human health: A case study of lower Mae Klong river basin, Thailand, *Environ. Sci. Pollut. Res.*, *22*(15), 11,504–11,512, doi:10.1007/s11356-015-4347-4.

Xue, D., J. Botte, B. De Baets, F. Accoe, A. Nestler, P. Taylor, O. Van Cleemput, M. Berglund, and P. Boeckx (2009), Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater, *Water Res.*, *43*(5), 1159–1170, doi:10.1016/j.watres.2008.12.048.

Xue, D., B. De Baets, O. Van Cleemput, C. Hennessy, M. Berglund, and P. Boeckx (2012), Use of a Bayesian isotope mixing model to estimate proportional contributions of multiple nitrate sources in surface water, *Environ. Pollut.*, *161*, 43–49, doi:10.1016/j.envpol.2011.09.033.

Young, M., C. Kendall, K. Lockhart, and T. Harter (2013), Stable isotopes as tracers of sources and processes related to nitrate distributions in domestic supply wells in the San Joaquin Valley, California, *Tech. Rep. 4*, U.S. Geol. Surv. and Univ. of Calif., Davis, Calif.

Zhang, E., Y. Wang, Y. Qian, T. Ma, D. Zhang, H. Zhan, Z. Zhang, Y. Fei, and S. Wang (2013), Iodine in groundwater of the North China Plain: Spatial patterns and hydrogeochemical processes of enrichment, *J. Geochem. Explor.*, *135*, 40–53, doi:10.1016/j.gexplo.2012.11.016.