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California GAMA Special Study: Stable Isotopic Composition of Boron in Groundwater – San Diego County Domestic Well Data

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GAMA Special Studies Task 11.5 and 12.5:
Specialized Analyses in Support of the GAMA program

Auspices Statement

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GAMA: GROUNDWATER AMBIENT MONITORING & ASSESSMENT PROGRAM SPECIAL STUDY

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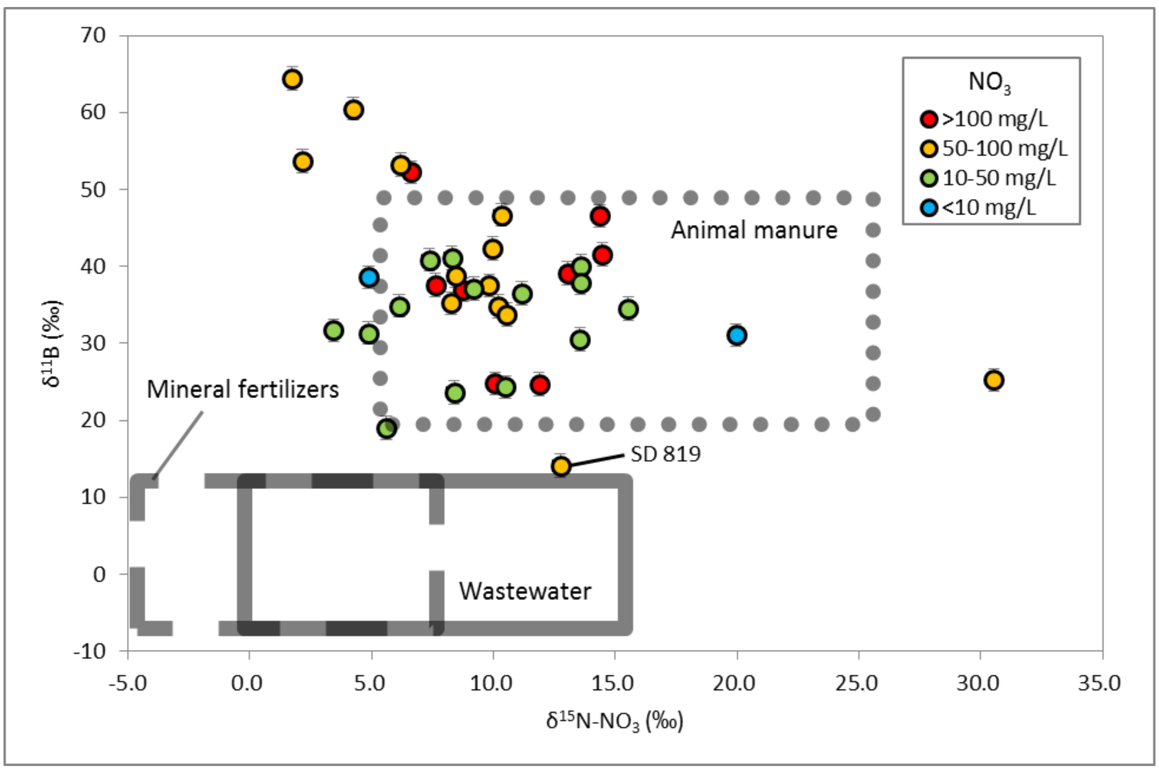

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Executive Summary

The Groundwater Ambient Monitoring and Assessment (GAMA) Program is a comprehensive groundwater quality monitoring program for the state of California. Managed by the California State Water Resources Control Board (SWRCB), the goals of the Program are to improve statewide groundwater monitoring, and to increase the availability of groundwater quality information to the public. The GAMA Domestic Well Project sampled 137 wells in San Diego County in an effort to assess the quality of these untested or infrequently tested domestic use water sources (SWRCB, 2010). Lawrence Livermore National Laboratory (LLNL) performed boron isotopic analyses on 56 of these domestic well water samples and provided initial interpretation of the data under GAMA Special Studies Tasks 11.5 ("Specialized Analyses for the GAMA Domestic Well Project") and 12.5 ("GAMA Specialized Analyses").

The boron isotopic composition data, in conjunction with water and nitrate isotopic composition data (Singleton et al., 2010), are useful for determining the sources of nitrate in potentially-contaminated San Diego County groundwater reservoirs. The isotopic composition of dissolved boron ($\delta^{11}B$) in groundwater sampled from San Diego County domestic wells varies from -0.8 to +64.4 ‰. Most sampled groundwaters (44 of 56) have $\delta^{11}B$ values between +20 and +50 ‰, within the isotopic composition range characteristic of animal manure. These samples tend to have high nitrate concentrations (>50 mg/L as NO_3). These results are consistent with isotopic composition of nitrogen in nitrate ($\delta^{15}N$) data from Singleton et al. (2010), indicating that animal manure is a primary source of nitrate in most groundwaters measured in this study. Seven samples have $\delta^{11}B$ values less than +20 ‰, outside of the animal manure $\delta^{11}B$ range. These groundwaters tend to have low nitrate concentrations (<10 mg/L as NO_3). No samples measured in this study have boron or nitrate isotopic compositions consistent with a mineral fertilizer nitrate source. Five sampled groundwaters have $\delta^{11}B$ values greater than +50 ‰, significantly higher than any known anthropogenic boron source. More work is needed to assess the source of nitrate and boron in the groundwaters with $\delta^{11}B$ greater than +50 ‰.

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SAMPLES AND METHODS

The analytical methods used in this study are described in detail in Eppich et al. (2011). In short, groundwater samples were collected unfiltered from wells in clean 50 mL polyethylene centrifuge tubes, following the methods of Singleton et al. (2010). Boron concentrations, NO_3 concentrations, and other water chemistry data used in this study were measured by laboratories subcontracted by the SWRCB. These data were obtained from the State of California Water Board's Geotracker GAMA Database (SWRCB, 2011), accessed in March 2011

For isotopic analysis, boron was chemically separated from samples using an ion-exchange technique (using the boron-specific ion-exchange resin Amberlite IRA-743) adapted from Lemarchand et al. (2002) and Guerrot et al. (2011). Isotopic composition measurements were performed using a standard-sample-standard bracketing routine on a Thermo Neptune MC-ICP-MS at University of California – Davis (Appendix B, Eppich et al., 2011). The boron isotopic standard NIST SRM 951 was measured before and after each sample measurement; these data were used to correct for instrumental mass bias. Due to the tendency of boron to sorb to front-end components of the mass spectrometer (the "memory effect"), background corrections are typically non-negligible for boron isotopic measurements by ICP-MS (Al-Ammar et al., 2000 11957). Blank solutions were measured before each sample and standard measurement. Mass 11 blank signal intensity was typically less than 5 % of mass 11 sample and standard intensity; mass 10 blank signal intensity was typically <1 mV on a Faraday detector. To assess whether isotopic fractionation occurred due to chemical purification (Lemarchand et al., 2002), boron isotopic standards NIST SRM 951, IAEA-B-2, and IAEA-B-3 were chemically purified and analyzed with each sample batch.

Boron isotope ratios were calculated relative to NIST SRM 951 using Eq. 1,

Equation 1:

$$\delta^{11}\mathrm{B}_{\mathrm{sample}}(‰) = \left[\frac{\mathrm{R}_{\mathrm{sample}}}{\left(\mathrm{R}_{\mathrm{SRM\ 951\ (1)}} + \mathrm{R}_{\mathrm{SRM\ 951\ (2)}}\right) \div 2} - 1\right] \times 1000$$

where R_{sample} is the sample $^{11}B/^{10}B$ ratio and $R_{SRM\ 951\ (1)}$ and $R_{SRM\ 951\ (2)}$ are $^{11}B/^{10}B$ ratios of NIST SRM 951 measured before and after R_{sample}. All ratios are corrected for blank. Isotopic composition is reported using delta notation ($\delta^{11}B$) in per mil (‰) relative to NIST SRM 951.

We selected a subset of 56 samples to analyze for $\delta^{11}B$ (Table 1). Samples were chosen to represent a wide geographic distribution throughout San Diego County. Furthermore, we chose samples for $\delta^{11}B$ analysis that had been previously measured for nitrate isotopic composition by Singleton et al. (2010). These samples have high nitrate concentrations (>10 mg/L) relative to samples not chosen for analysis. Therefore, $\delta^{11}B$ results reported here reflect sampling bias towards high-NO_3 samples.

Quality Assurance/Quality Control (QA/QC) criteria, established for $\delta^{11}B$ analyses by Eppich et al. (2011), were met for all sample batches processed through boron purification chemistry (Tables 2-4). Accuracy was assessed by measurement of reference standards with known isotopic composition. Measurements of purified NIST SRM 951 were within 0.75 ‰ of the certified value ($\delta^{11}B$ = 0 ‰, by definition) (Table 2). Measurements of groundwater boron isotopic standards (IAEA-B-2 and IAEA-B-3) purified in the same manner as the samples were typically within 1.5 ‰ of recommended values (Gonfiantini et al., 2003 11955) (Table 2). In one case, the measured isotopic composition of IAEA-B-2 was 2.6 ‰ lower than the recommended value (Batch 6). However, measurements of NIST SRM 951 and IAEA-B-3 were within specifications for this batch, suggesting that this measurement is an outlier.

Analytical precision and reproducibility was assessed both from statistics of individual analyses and from analysis of submitted field duplicates (collected during the same sampling event into two bottles) and by analyzing procedural duplicates (performed by taking two aliquots of water from the same bottle). Analytical precision for individual analyses was typically better than 0.25‰. Field duplicates of domestic well groundwater sample SD 831 were analyzed for boron isotopic composition (Table 3), and were reproducible to better than 1.5 ‰. Procedural duplicates were performed for a minimum of one sample in each batch (eight duplicates total; Table 4), and were typically reproducible to better than 1.5 ‰. In two cases (SD 843 and SD 946), the difference between the two measurements was 2.34 and 2.27 ‰, respectively. The sample dataset is too limited to assess sample heterogeneity (possibly related to the fraction of colloidal material aliquoted in each replicate) as a source of slight deviations in boron isotopic composition in replicate analyses. These deviations are not significant enough to affect the conclusions of this report. We conservatively report uncertainty for $\delta^{11}B$ as ±1.5 ‰, based on replicate analysis of samples and reference standards.

Table 1. Boron concentration and isotopic composition of groundwater samples.

Sample	Collection Date	Location	B (µg/L)	δ^{11}B (‰)	Nitrate (µg/L)	Nitrate δ^{15}N (‰)	Nitrate δ^{18}O (‰)	Water δ^{18}O (‰)	Water δD (‰)
SD 801	04/29/2008	Ramona	77	46.6	249	14.3	4.6	-6.8	-48.7
SD 811	05/06/2008	Ramona	42	25.3	57	30.5	18	-6.4	-43.4
SD 814	05/07/2008	Ramona	83	52.2	111	6.6	5.2	-6.3	-42.6
SD 816	05/08/2008	Ramona	133	24.7	113	11.9	4.6	-7.1	-46.2
SD 819	05/13/2008	Ramona	190	14.1	67	12.7	5.4	-6.7	-43.6
SD 820	05/13/2008	Ramona	78	41.6	140	14.5	6.2	-6.6	-42.1
SD 823	05/14/2008	Ramona	116	39.1	162	13	5.6	-7.6	-45.9
SD 831	05/20/2008	Ramona	83	42.3	51	10	4.5	-6.8	-48.2
SD 838	05/27/2008	El Cajon	274	33.8	57	10.5	8.1	-7.4	-58.4
SD 842	05/28/2008	Fallbrook	53	53.7	55	2.2	7.8	-5.5	-34.7
SD 843	05/28/2008	Fallbrook	56	64.4	89	1.7	6.9	-6.2	-40.6
SD 844	05/28/2008	Fallbrook	67	53.2	73	6.2	7.4	-6.8	-50.2
SD 845	05/29/2008	El Cajon	255	37.8	32	13.6	6.2	-6.6	-41.9
SD 848	05/28/2008	Fallbrook	123	37.2	29	9.2	7.3	-6.8	-49.3
SD 850	05/06/2008	Ramona	106	36.5	47	11.2	7.3	-6.6	-44.8
SD 851	05/28/2008	Fallbrook	29	35.9	2.9	na	na	-5.9	-35.1
SD 852	05/28/2008	Valley Center	145	24.3	nd	na	na	-6.7	-46.2
SD 857	06/04/2008	Fallbrook	215	42.7	7.7	na	na	-7.4	-51.8
SD 858	06/05/2008	El Cajon	412	34.8	65	10.2	4.1	-7.5	-52.7
SD 860	06/05/2008	Lakeside	176	43.7	nd	na	na	-5.9	-36
SD 861	06/10/2008	Lakeside	170	40.1	45	13.6	8.5	-6.4	-37.6
SD 862	06/10/2008	Lakeside	186	28.0	6.0	na	na	-6.8	-40.9
SD 863	06/10/2008	Lakeside	62	28.5	6.3	na	na	-6.8	-39.3
SD 864	06/10/2008	Lakeside	100	46.7	87	10.3	2.7	-6.7	-38.4
SD 865	06/10/2008	Lakeside	130	37.5	73	9.8	9.4	-6.4	-36.1
SD 870	06/11/2008	El Cajon	134	42.9	17	na	na	-7.3	-55.8
SD 872	06/12/2008	Alpine	136	35.2	51	8.3	3.3	-7.5	-51.3
SD 873	06/12/2008	El Cajon	193	25.7	27	na	na	-7.5	-51.8
SD 874	06/12/2008	Alpine	61	31.7	15	3.4	5	-7.3	-44.6
SD 877	06/17/2008	Alpine	326	24.8	106	10.1	6.2	-8	-51.7
SD 880	06/17/2008	Descanso	108	29.0	nd	na	na	-7.7	-46.9
SD 886	06/18/2008	Descanso	104	30.6	43	13.5	8.3	-7.9	-47.3
SD 889	06/18/2008	Boulevard	97	31.4	18	4.9	3.4	-8.3	-54.5
SD 890	06/19/2008	Boulevard	94	37.5	117	7.6	4.3	-8.1	-53.6
SD 895	06/19/2008	Campo	161	15.8	5.8	na	na	-7.4	-46.9
SD 896	06/19/2008	Campo	187	14.1	7.4	na	na	-7.7	-49.6
SD 897	05/29/2008	Pala	78	40.5	5.8	na	na	-6.5	-40.3
SD 901	12/02/2008	Jamul	170	19.0	16	5.6	6.4	-6.9	-44.3
SD 902	12/02/2008	Campo	44	34.9	44	6.1	1.9	-7.7	-50.2
SD 907	12/03/2008	Alpine	56	38.8	82	8.4	1.8	-6.8	-42.4

Sample	Collection Date	Location	B (µg/L)	$\delta^{11}B$ (‰)	Nitrate (µg/L)	Nitrate $\delta^{15}N$ (‰)	Nitrate $\delta^{18}O$ (‰)	Water $\delta^{18}O$ (‰)	Water δD (‰)
SD 908	12/03/2008	Jamul	41	24.1	nd	na	na	-6.7	-41.2
SD 909	12/03/2008	Boulevard	74	34.5	22	15.5	8.6	-8	-52.7
SD 912	12/04/2008	Dulzura	70	31.1	2.5	20	13.2	-6.4	-40.1
SD 917	12/09/2008	Rancho Santa Fe	150	22.7	nd	na	na	-5.9	-53.8
SD 918	12/09/2008	Escondido	306	40.9	50	7.4	6.7	-8.8	-64.4
SD 919	12/09/2008	Escondido	211	60.5	85	4.2	4.3	-6.6	-44.4
SD 920	12/10/2008	Escondido	209	36.9	203	8.8	17.8	-8	-57.1
SD 921	12/10/2008	Escondido	141	49.7	nd	na	na	-6	-39.8
SD 923	12/11/2008	Valley Center	106	24.3	22	10.5	1.7	-7.2	-50.4
SD 927	12/17/2008	Ramona	194	9.1	nd	na	na	-6.9	-42.4
SD 931	12/17/2008	Vista	283	41.1	31	8.3	1.2	-8.6	-65.4
SD 933	01/06/2009	Santa Ysabel	162	23.7	15	8.4	4.6	-6	-40.8
SD 937	12/18/2008	Warner Springs	607	5.1	nd	na	na	-9.7	-69.2
SD 942	12/18/2008	Santa Ysabel	295	-0.8	nd	na	na	-7.1	-46.8
SD 945	01/06/2009	Campo	57	38.6	3.0	4.9	5.5	-8	-51.4
SD 946	01/08/2009	Borrego Springs	1110	6.5	nd	na	na	-9.4	-72.7

Boron isotopic compositions from this study.
Nitrate and water isotopic compositions from Singleton et al. (2010).
Nitrate and boron concentration data from Geotracker GAMA Database.

Boron ^{11}B compositions are with respect to NIST SRM 951.
Nitrate ^{15}N compositions are with respect to air; Nitrate ^{18}O compositions are with respect to SMOW.
Water ^{18}O and D compositions are with respect to SMOW.

“nd” = not detected; “na” = not analyzed.

Table 2. $\delta^{11}B$ measurements of standard reference materials.

Measured values and the difference between measured and certified or recommended values are shown. SRM 951 has a NIST certified value of 0.00‰. Recommended values for IAEA-B-2 (+14.65‰) and IAEA-B-3 (-21.37‰) are from Gonfiantini et al. (2003).

Batch	SRM 951		IAEA-B-2		IAEA-B-3	
#	meas	*diff*	meas	*diff*	meas	*diff*
1	-0.01	*0.01*	15.29	*0.64*	-20.50	*0.87*
2	0.49	*0.49*	15.65	*1.00*	-19.85	*1.52*
3	-0.02	*0.02*	15.70	*1.05*	-20.46	*0.91*
4	0.71	*0.71*	15.78	*1.13*	-19.62	*1.75*
5	-0.20	*0.20*	14.96	*0.31*	-21.13	*0.24*
6	0.07	*0.07*	12.05	*2.60*	-21.55	*0.18*

Table 3. $\delta^{11}B$ measurements of field duplicates of groundwater samples.

Sample ID	Collection Date	$\delta^{11}B$ (‰)
SD 831	05/20/2008	42.30
SD 1831	05/20/2008	41.13
difference		*1.17*

Table 4. $\delta^{11}B$ measurements of total procedural duplicates of groundwater samples.

Sample ID	Run 1 $\delta^{11}B$ (‰)	Run 2 $\delta^{11}B$ (‰)	*Difference $\delta^{11}B$ (‰)*
SD 816	24.66	24.63	*0.03*
SD 920	36.93	37.05	*0.12*
SD 923	24.31	24.99	*0.68*
SD 890	37.54	37.75	*0.21*
SD 945	38.60	38.28	*0.32*
SD 946	6.55	4.28	*2.27*
SD 843	64.38	62.04	*2.34*
SD 919	60.50	59.29	*1.21*

RESULTS

Boron: Boron isotopic composition results for San Diego County groundwater samples are summarized in Table 1 and Figure 1. Boron isotopic composition in sampled San Diego County groundwaters varies from -0.8 to +64.4 ‰, a much larger spread than reported in similar studies of different regions (Widory et al., 2004; Widory et al., 2005). Most sampled groundwaters (44 of 56) fall within the range +20 to +50‰, although five have $\delta^{11}B$ values greater than +50‰ and seven have $\delta^{11}B$ values less than +20‰. The relationship between $\delta^{11}B$ and B concentration is complex. Samples with $\delta^{11}B$ less than +20‰ tend to have the highest B concentration (>200 µg/L), although some samples with enriched $\delta^{11}B$ also have high B concentration. Samples with the lowest B (<50 µg/L) tend to have $\delta^{11}B$ values between +20 and +40‰. Boron concentration and isotopic composition of the low-B concentration samples most closely resembles atmospheric precipitation, which can be highly variable in $\delta^{11}B$, but typically has low B concentrations. Most samples from this study with high NO_3 (>50 mg/L) have $\delta^{11}B$ values greater than +20‰.

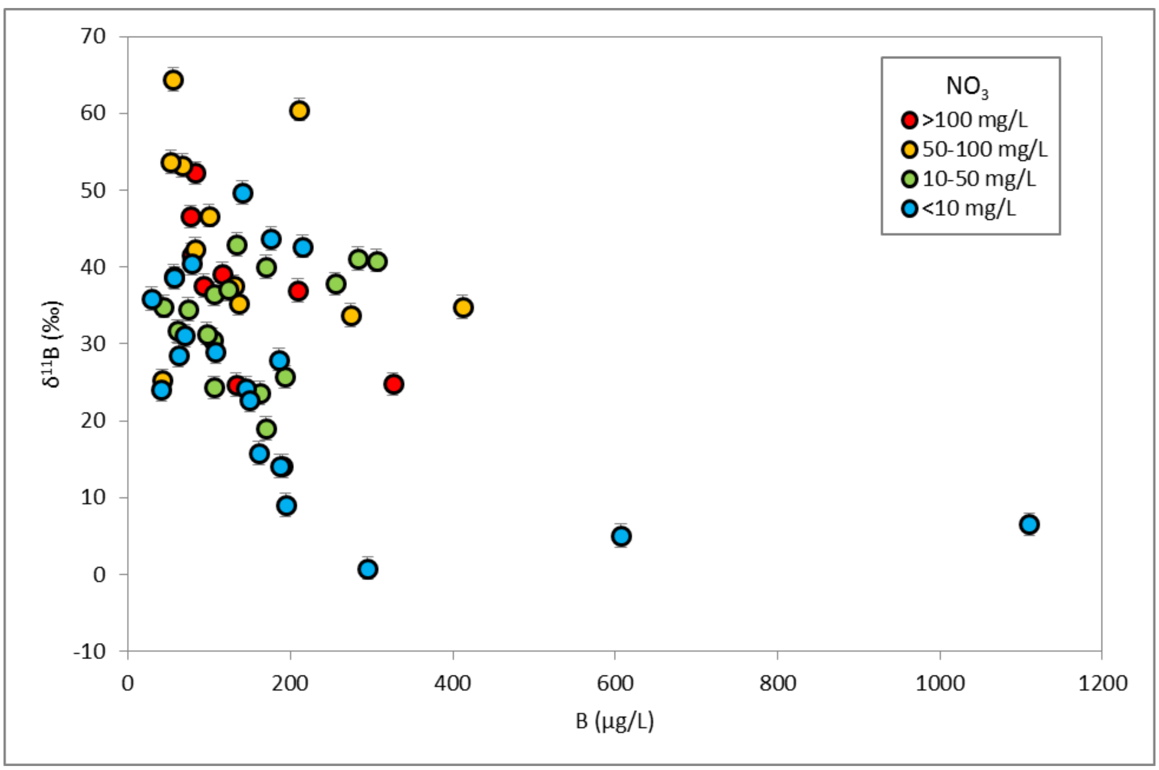

Figure 1. Boron concentration and isotopic composition of San Diego County groundwater samples. Symbol color refers to NO_3 concentration (see legend). $\delta^{11}B$ is reported relative to NIST SRM 951. Boron and nitrate concentration data are from the Geotracker GAMA Database.

Boron isotopic composition data are most useful for constraining nitrate sources when considered alongside other isotopic data, particularly δD and $\delta^{18}O$ in H_2O, and $\delta^{15}N$ and $\delta^{18}O$ in NO_3 (Widory et al., 2004; Widory et al., 2005). Singleton et al. (2010) reported water and nitrate isotopic results for the same San Diego County groundwater samples measured in this study; we present plots of those data here (Fig. 2 and 3). Water isotopic data (Figure 2) generally plot along the Global Mean Water Line (Craig, 1961), indicating that these groundwaters have a meteoric origin, and were not strongly affected by evaporation prior to recharge.

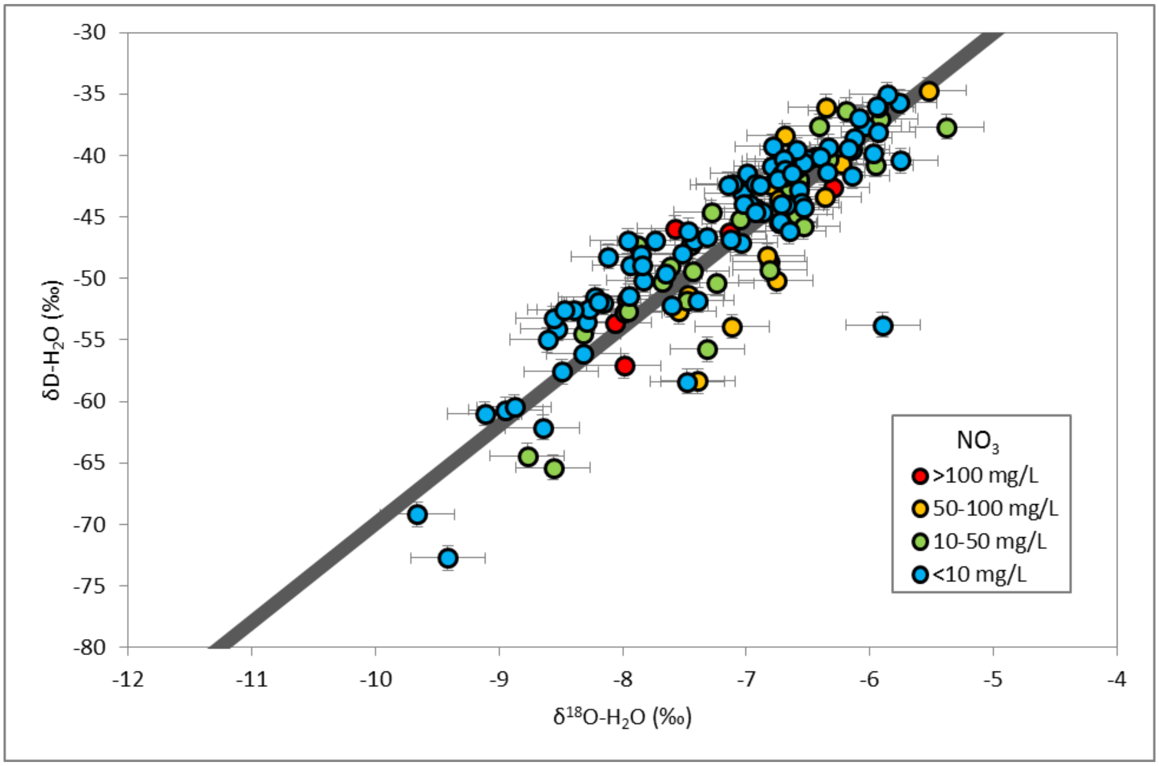

Figure 2. Water isotopic composition (δD, $\delta^{18}O$) of groundwater samples. Symbol color refers to NO_3 concentration (see legend). δD and $\delta^{18}O$ are reported relative to V-SMOW. Gray line is the Global Mean Water Line (Craig, 1961). Isotopic data are from Singleton et al. (2010). Nitrate concentration data are from the Geotracker GAMA Database.

Nitrate: Figure 3 shows the isotopic composition of potential nitrate sources based on literature data (Kendall, 1998; Xue et al., 2009) and the range of $\delta^{18}O$-H_2O in local waters. For oxygen, the isotopic composition of nitrate ($\delta^{18}O$-NO_3) produced by nitrification is correlated with local water isotopic composition ($\delta^{18}O$-H_2O), and source fields for nitrate resulting from nitrification should take into account the local range in water isotopic composition. Nitrification of ammonium derives oxygen from local water and air, typically in a 2:1 ratio. Atmospheric oxygen has a nearly constant $\delta^{18}O$ value of 23.5‰, but the isotopic composition of water is variable. For this reason, it is necessary to use measured local water $\delta^{18}O$ values ($\delta^{18}O$-H_2O) to calculate the expected range of nitrate $\delta^{18}O$ values ($\delta^{18}O$-NO_3) for sources where local nitrification of ammonium is an important process in the production of nitrate. These sources may include nitrate produced in the soil zone, nitrate from nitrification of applied ammonium fertilizers, and nitrate from ammonium wastes such as septic systems or manure. The range of $\delta^{18}O\text{-}NO_3$ for nitrified sources for the San Diego study area is predicted to fall between 0.1 and 5.3‰ (Figure 3), based on the measured groundwater $\delta^{18}O\text{-}H_2O$ values (over a range defined by the minimum value measured minus two standard deviations of all values measured to the maximum value measured plus two standard deviations of all values measured) and assuming that a 2:1 ratio of local water and atmospheric oxygen is imparted to the nitrate during nitrification. Nitrate from nitrification may have higher $\delta^{18}O\text{-}NO_3$ values if formed in the presence of water with higher $\delta^{18}O\text{-}H_2O$ values than those measured in this study, such as evaporated soil waters or summer precipitation. The source for nitrate may also be obscured due to denitrification, which leads to higher $\delta^{15}N$ and $\delta^{18}O$ values in the residual nitrate.

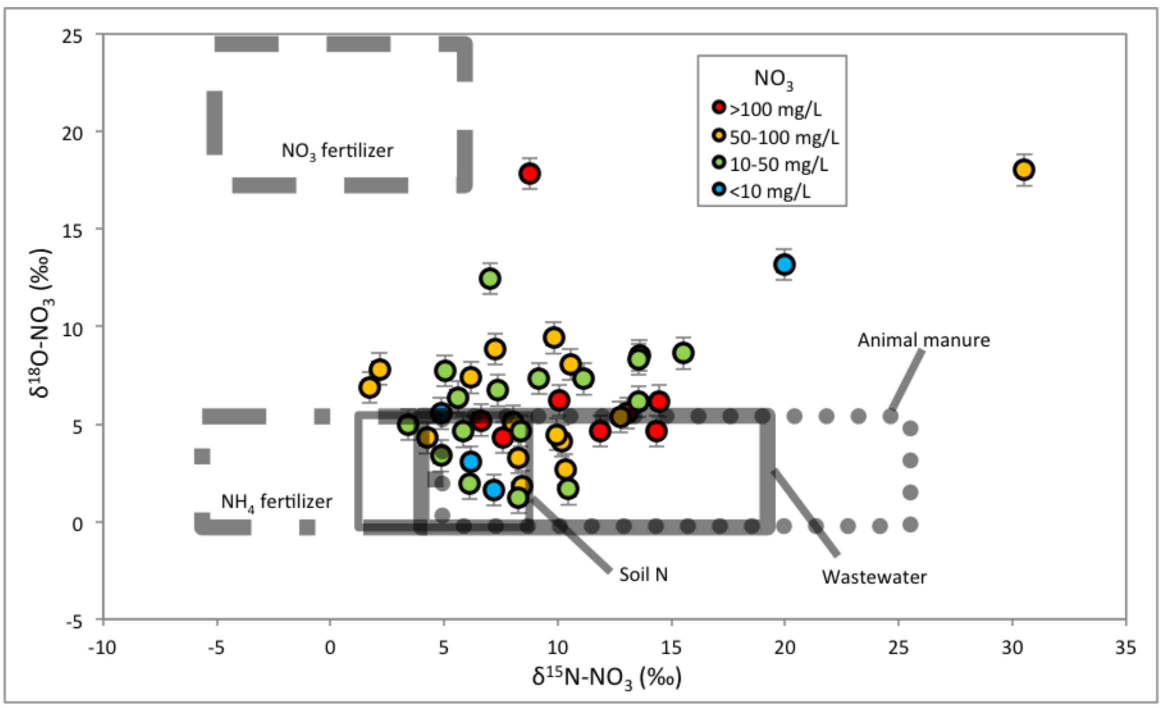

Figure 3. Nitrate isotopic composition ($\delta^{18}O$, $\delta^{15}N$) of groundwater samples. Symbol color refers to NO_3 concentration (see legend). $\delta^{15}N$ is reported relative to air; $\delta^{18}O$ is reported relative to V-SMOW. Gray boxes represent the isotopic composition of different nitrate sources (Kendall, 1998; Xue et al., 2009). The oxygen isotope ranges of nitrate from nitrified sources are calculated based on the observed oxygen isotope compositions of water measured in the study area. Horizontal error bars are smaller than the symbols. Isotopic data are from Singleton et al. (2010). Nitrate concentration data are from Geotracker GAMA Database.

The isotopic composition of nitrate in sample San Diego domestic wells waters is typically between 0 to +15‰ for $\delta^{15}N$ and 0 to +10‰ for $\delta^{18}O$. Although most of the sampled groundwaters have $\delta^{15}N$ compositions within the source fields for soil nitrate, wastewater, and animal manure, and many fall outside of the range of these sources, with higher $\delta^{18}O$ values than expected (Fig. 3). A few outliers have higher $\delta^{15}N$ and $\delta^{18}O$ values, possibly due to denitrification (Fig. 4). Due to the large overlap in $\delta^{15}N$ and $\delta^{18}O$ values for these three nitrate source fields, using nitrate isotopic data alone is inconclusive. Many of the nitrate $\delta^{18}O$ values fall slightly above the range predicted based on the local groundwater $\delta^{18}O$ values. The higher $\delta^{18}O$ values may reflect interaction with evaporated soil water, where nitrification likely took place, which would have a higher $\delta^{18}O$ values than the groundwater.

The groundwater nitrate isotopic compositions, however, are generally not consistent with synthetic nitrate or ammonium fertilizer being a significant or dominant source of nitrate in these groundwaters. Synthetic nitrate fertilizer has low $\delta^{15}N$ and high $\delta^{18}O$ values ($\delta^{15}N$ = -5 to +5‰, $\delta^{18}O$ = +17 to +25‰; Xue et al., 2009). None of the sampled groundwaters fall in this range, and all but two do not have compositions consistent with mixing between outside of the range for the sampled groundwaters (although two samples have nitrate isotopic compositions consistent with some mixing of nitrate fertilizer with a manure or sewage source). Nitrification of ammonia or ammonium fertilizer is also unlikely to be a sole source since only six samples from this study, and none of the highest NO_3 concentration (>100 mg/L) samples, have the low $\delta^{15}N$ isotopic compositions ($\delta^{15}N$ = -5 to +5‰, $\delta^{18}O$ = +0.1 to +5.3‰) characteristic of ammonium fertilizer.

Discussion

Wastewater and animal manure have distinct boron isotopic signatures. Wastewater contains high boron concentration primarily due to the use of detergents. Boron in detergents is derived from borax deposits (often containing other boron-bearing minerals such as kernite and ulexite) with typical $\delta^{11}B$ values of -20 to +10‰ (Finley et al., 1962; Mcmullen et al., 1961; Oi et al., 1989; Swihart et al., 1986), and wastewater $\delta^{11}B$ has been shown to be largely within this range (-8 to + 13 ‰; Accoe et al., 2008; Bassett et al., 1995; Eisenhut and Heumann, 1997; Seiler, 2005; Tirez et al., 2010; Vengosh et al., 1994; Widory et al., 2004). In contrast, measurements of $\delta^{11}B$ in animal manure are typically between +15 to +50‰ (Accoe et al., 2008; Komor, 1997; Tirez et al., 2010; Widory et al., 2004). Although Widory et al. (2004; 2005) subdivide the animal manure signature into cattle, hog, and poultry signatures, these end-member $\delta^{11}B$ signatures overlap considerably, are based on only a few measurements, and seem biased towards their highest measured values (which may be outliers). Therefore, we use $\delta^{11}B$ values of +20 to +50‰ for the animal manure range, and do not distinguish livestock species.

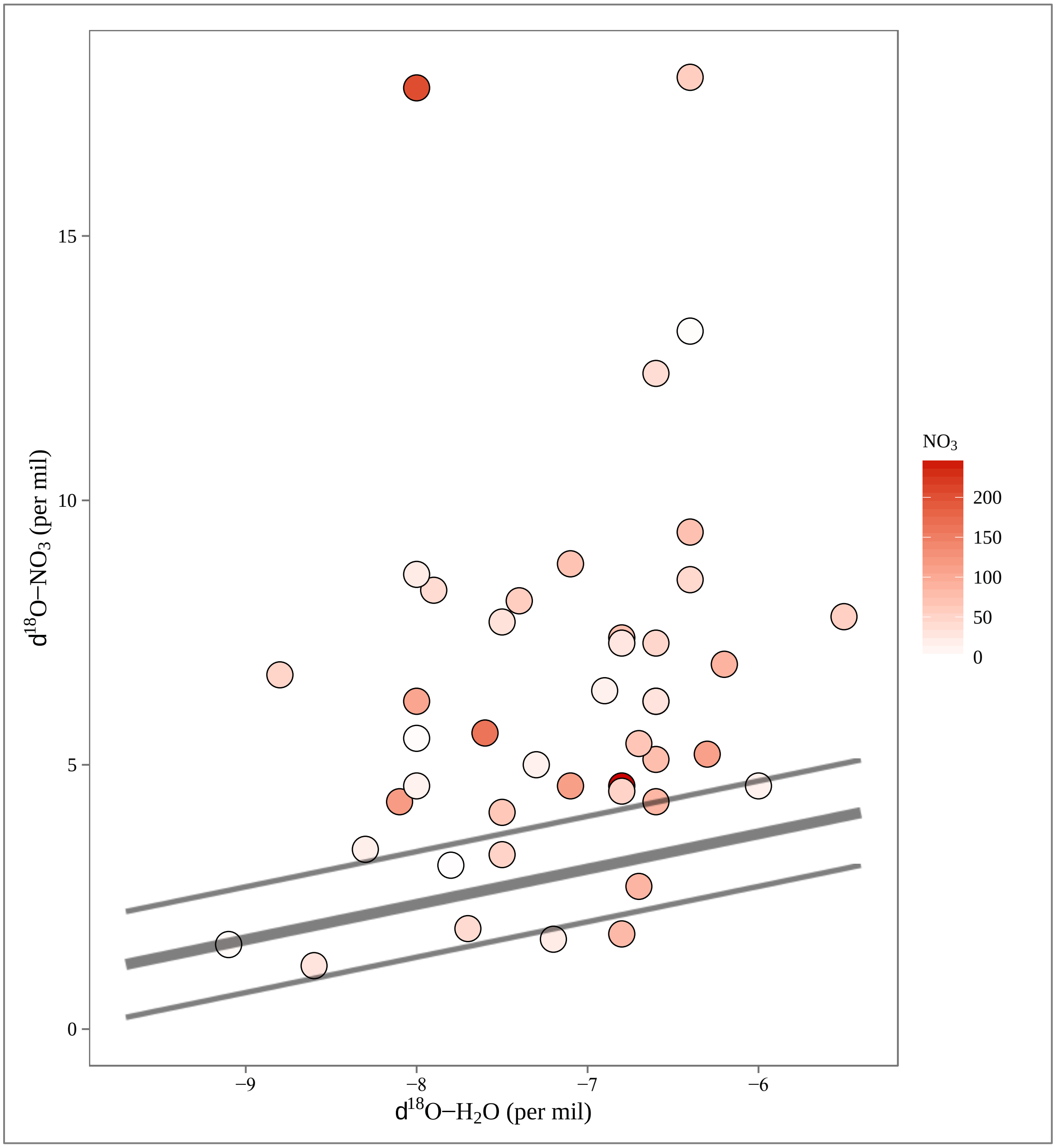

Figure 4. Oxygen isotopic composition of water and nitrate. Symbol color refers to NO_3 concentration. The thick gray line represents a denitrification trend, following the expression

$$\delta^{18}O_{NO_3} = \left(\frac{2}{3}\right) \times \ \delta^{18}O_{H_2O} + \left(\frac{1}{3}\right) \times \ 23$$

and bounded by thin gray lines of $\delta^{18}O_{NO_3}$ ± 1 ‰. Nitrate concentration data are from the Geotracker GAMA database.

Groundwaters measured in this study contain relatively high concentrations of both nitrate and boron (NO_3 > 50 mg/L, B > 10 ug/L) relative to typical natural levels. However, not all potential nitrate sources contain high concentrations of boron. Many previous studies have shown that wastewater has high concentrations of both nitrate and boron (approximately 1-5 mg/L of boron; Eisenhut and Heumann, 1997; Vengosh et al., 1994). Animal manure has also been shown to have variable but high boron concentrations (up to 8 mg/L; Komor, 1997). In contrast, most mineral fertilizers typically have low boron concentrations, excepting rare fertilizers that include boron as a major component (Chetelat and Gaillardet, 2005; Komor, 1997; Tirez et al., 2010). The relationship between boron and nitrate in sampled groundwaters can be seen in Figure 5. There is no straightforward relationship between boron and nitrate in these samples. Although there is a broad positive correlation between boron and nitrate concentrations, some samples have high nitrate concentrations and relatively low boron concentrations (albeit higher than typical background boron concentrations of <10 µg/L). Conversely, some samples have greatly elevated boron concentrations (>200 µg/L), and nitrate concentrations approaching background levels. The high-boron low-nitrate samples have low $\delta^{11}B$ values relative to samples with higher nitrate concentrations; this may imply the presence of a second, probably non-anthropogenic boron source.

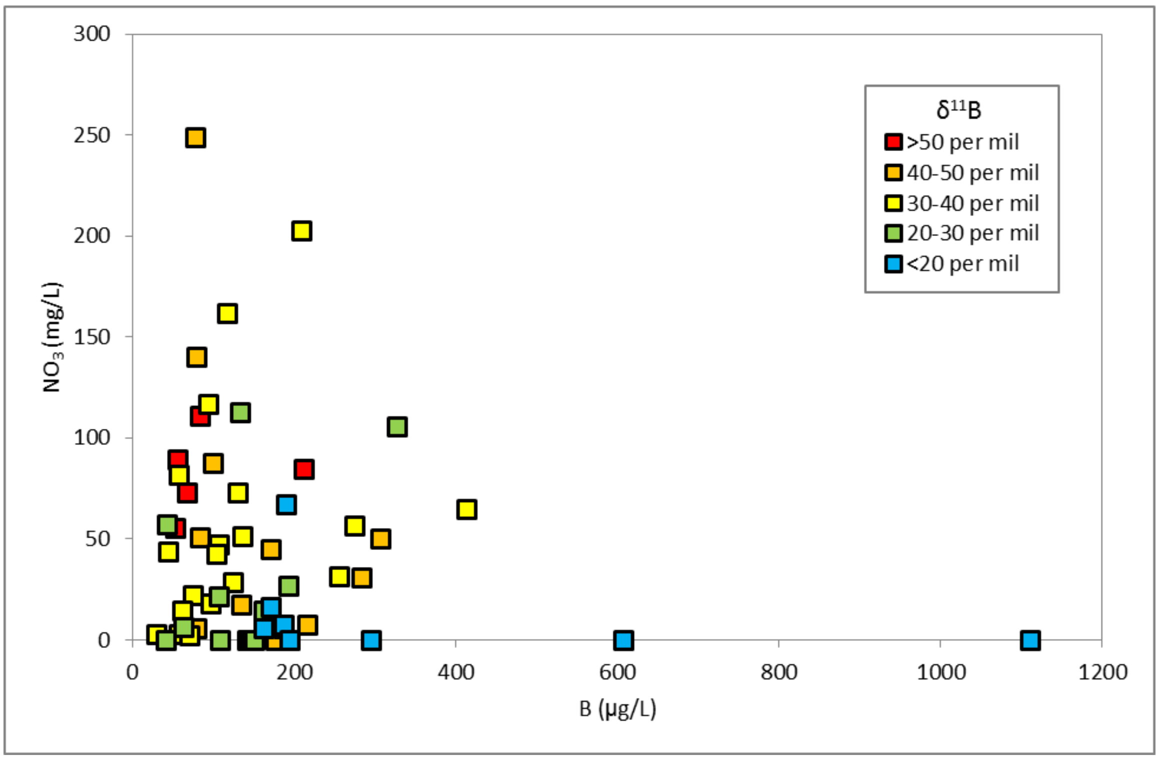

Figure 5. Boron and nitrate concentration of groundwater samples. Symbol color refers to boron isotopic composition (see legend). $\delta^{11}B$ is reported relative to NIST SRM 951. Boron and nitrate concentration data are from the Geotracker GAMA Database.

By combining groundwater $\delta^{15}N$ and $\delta^{11}B$ data on a single plot, it is possible in some cases to resolve the distinct isotopic signatures of animal manure, wastewater, and mineral fertilizer nitrate sources. To make this determination for San Diego County groundwaters, we use the $\delta^{15}N$ data from Singleton et al. (2010) and the $\delta^{11}B$ data from this study. Most sampled groundwaters fall within the $\delta^{15}N$ and $\delta^{11}B$ range of animal manure (Fig. 6), indicating that animal manure is the primary source of nitrate in these groundwaters. Of the samples that plot outside of the animal manure field, only one (SD 819) is within uncertainty of wastewater $\delta^{11}B$ and $\delta^{15}N$ ranges. No sampled groundwaters fall within the mineral fertilizers $\delta^{11}B$ and $\delta^{15}N$ ranges. However, it should be noted that when groundwater contains a mix of nitrate sources, source identification will be biased toward those with the highest concentration of boron.

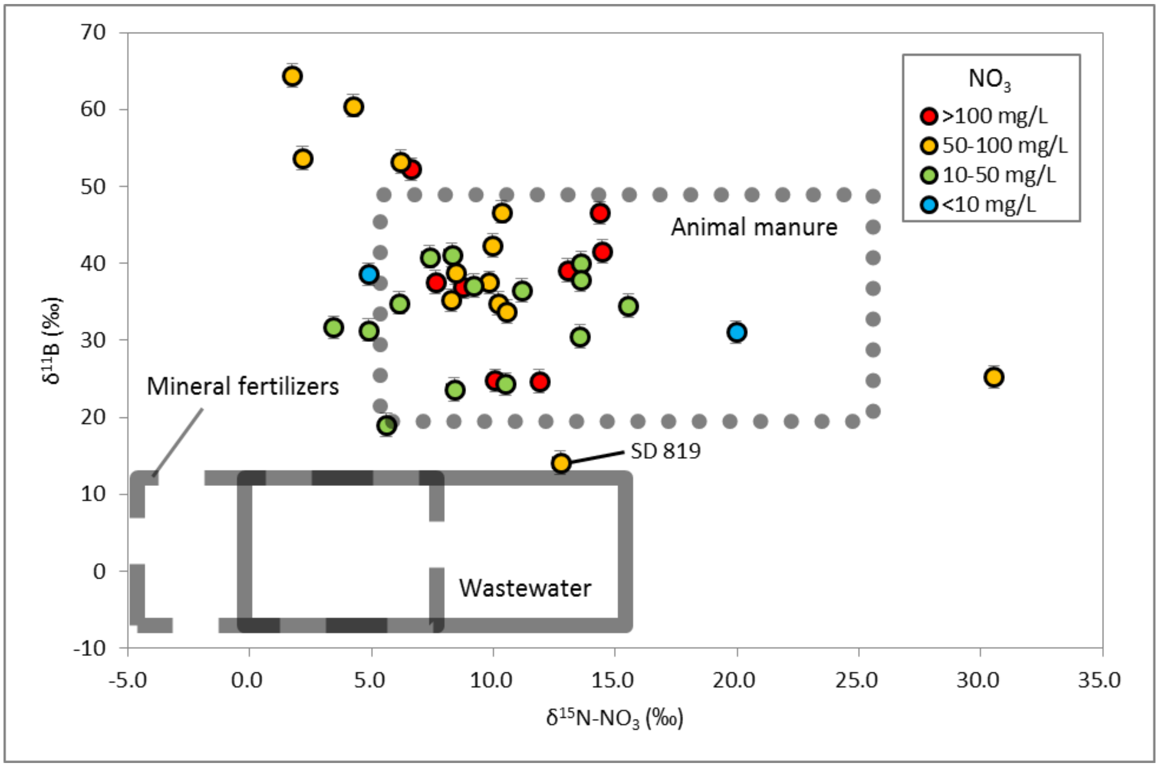

Figure 6. Boron and nitrate isotopic composition of groundwater samples. Symbol color refers to nitrate concentration (see legend). Nitrate isotope data is reported relative to air; boron isotope data are reported relative to NIST SRM 951. Horizontal error bars are smaller than the symbols. Gray boxes represent fields of isotopic composition; nitrate isotope fields are from Kendall, 1998 and Xue et al., 2009. Fields for boron isotopic composition compiled from measurements of wastewater, animal manure, and mineral fertilizers (Accoe et al., 2008; Bassett et al., 1995; Chetelat and Gaillardet, 2005; Eisenhut and Heumann, 1997; Komor, 1997; Leenhouts et al., 1998; Seiler, 2005; Vengosh et al., 1994; Widory et al., 2004). Nitrogen isotopic data from Singleton et al., (2010). Nitrate concentration data are from Geotracker GAMA Database.

Nitrate, boron, and $\delta^{11}B$ systematics of sampled groundwaters are summarized in Figure 7. Groundwaters with low nitrate concentrations are characterized by low NO_3/B ratios and $\delta^{11}B$ values between +0 and +50‰, while manure-contaminated groundwaters have high NO_3/B ratios and $\delta^{11}B$ values between +20 and +50‰. Variability in the uncontaminated end-member groundwater can be partially explained by the natural variability of precipitation $\delta^{11}B$ (Rose-Koga et al., 2006). Boron in atmospheric precipitation is ultimately derived from seawater ($\delta^{11}B$ = 39.6 ‰; Foster et al., 2010), but can vary considerably in isotopic composition due to isotopic fractionation associated with evaporation and condensation (Rose-Koga et al., 2006). In most settings, the isotopic composition of boron in atmospheric precipitation varies from +20 to +45‰, and is dependent upon local weather and climate, as well as atmospheric contamination (e.g., Chetelat et al., 2005; Fogg and Duce, 1985; Millot et al., 2010; Rose-Koga et al., 2006; Rose et al., 2000). Bedrock/soil dissolution is another process resulting in the introduction of boron to groundwater. Crystalline bedrock contains boron in concentrations of several µg/g, and with $\delta^{11}B$ values of -5 to +5‰ (Palmer and Swihart, 1996 and references therein). Non-marine evaporites ($\delta^{11}B$ = -20 to +10‰) are common in some sedimentary settings, and may contribute greatly to the groundwater boron budget. Dissolution of either rock type will load groundwater with boron, resulting in a lowering of groundwater $\delta^{11}B$ from precipitation values towards these lower values (Negrel et al., 2012; Palmer and Swihart, 1996). Some boron-rich rock types, such as evaporates, are expected to dominate the boron budget of local groundwater (Negrel et al., 2012) which may obscure the signature of anthropogenic boron.

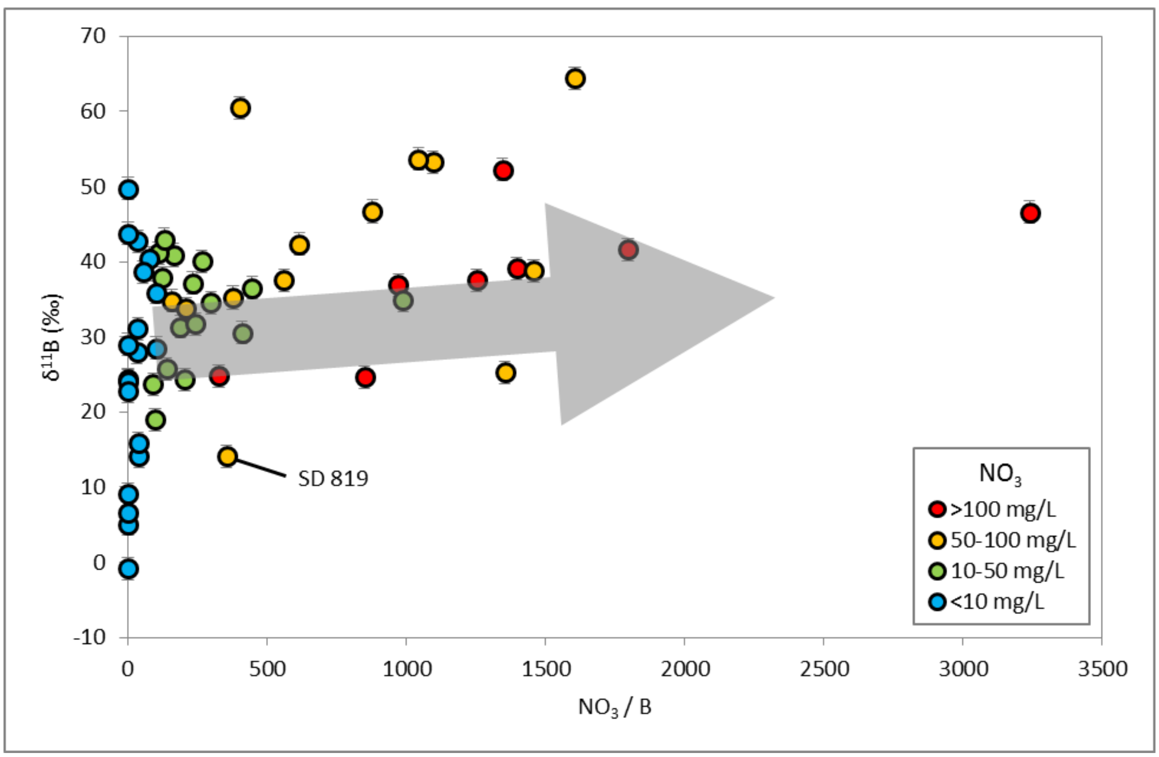

Figure 7. Boron isotopic composition and nitrate/boron ratio of groundwater samples. Symbol color refers to nitrate concentration (see legend). Solid gray arrow represents trend of increasing anthropogenic contamination. Boron and nitrate concentration data are from Geotracker GAMA Database.

Five samples have anomalously enriched $\delta^{11}B$ values (greater than +50‰, Fig. 6), among the highest ever measured in natural waters. Natural sources with such anomalous $\delta^{11}B$ signatures, such as marine brines and hot springs (Palmer and Swihart, 1996; Vengosh et al., 1991) are unlikely sources of boron in this environment. All five of these samples have NO_3 greater than 50 mg/L. There is no currently known anthropogenic source for boron with such high $\delta^{11}B$. The upper range of the animal manure $\delta^{11}B$ is poorly-known and may extend to values greater than +50‰. More work must be performed to constrain the source(s) of boron and nitrate in these anomalous groundwaters.

CONCLUSIONS

San Diego County groundwater samples measured in this study vary in boron isotopic composition ($\delta^{11}B$) from -0.8 to +64.4‰. Most sampled groundwaters have $\delta^{11}B$ between +20 and +50‰. There is no simple relationship between $\delta^{11}B$ and boron concentration, although the high-NO_3 samples tend to have $\delta^{11}B$ values greater than +20‰. Nitrogen and oxygen isotopic compositions of nitrate from Singleton et al. (2010) indicate that the primary sources of nitrate are either animal manure or sewage. By combining this data with boron isotope measurements from this study, we determined that animal manure is the most likely primary source of nitrate in most groundwaters. One groundwater (SD 819) may also have a significant wastewater nitrate source. No sampled groundwaters have boron and nitrate isotopic compositions consistent with a mineral fertilizer nitrate source. Five sampled groundwaters have anomalously high $\delta^{11}B$ values (>50‰), significantly higher than the known isotopic range of anthropogenic boron. More work must be performed to understand the source of boron and nitrates in these anomalous groundwaters.

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