



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-427960

California GAMA Domestic Wells Data Report: Water and Nitrate Isotopic Data for San Diego County

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

Lawrence Livermore National Laboratory

Final: April, 2010
Revised: January, 2012

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

GAMA Special Studies Task 9.4 :
Specialized Analyses for GAMA Domestic Wells

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Auspices Statement

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

California GAMA Domestic Wells Data Report: Water and Nitrate Isotopic Data for San Diego County

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

Lawrence Livermore National Laboratory

Prepared in cooperation with the California State Water Resource Control Board

Final report for the California State Water Resources Control Board
GAMA Special Studies Task 9.4: Specialized Analyses for GAMA Domestic Wells

April 2010 (Final report)

January 2012 (Revised final report)

Suggested citation:

Singleton M.J., Roberts, S.R., and Esser B.K. (2010) California GAMA Domestic Wells Data Report: Isotopic Data for San Diego County, LLNL-TR-427960 revised.

Introduction

The Groundwater Ambient Monitoring and Assessment (GAMA) Program is a comprehensive groundwater quality monitoring program managed by the California State Water Resources Control Board (SWRCB). The GAMA Domestic Well Project samples domestic wells for commonly detected chemicals. Results are shared with the well owners and used by GAMA to evaluate the quality of groundwater used by private well owners. The Domestic Well Project has sampled wells in San Diego County in 2008 and 2009, and collected samples for determination of water and nitrate isotopic composition.

Lawrence Livermore National Laboratory performed specialized analyses of domestic well groundwater for the SWRCB. For the San Diego County focus area, LLNL analyzed domestic well water samples collected by the SWRCB for stable isotopes of oxygen and hydrogen in the water molecule; and for stable isotopes of nitrogen and oxygen in dissolved nitrate.

Revision: In Table 3 of the originally submitted report, an inadvertent mismatch between SWRCB ID and LLNL ID resulted in the misreporting of eight samples (SD 942, SD 943, SD 945, SD 946, SD 947, SD 948, SD 949, and SD 950). This error only affected Table 3 of this document. IDs for all data uploaded to the GAMA Geotracker database were properly matched.

Sample Handling

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

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

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

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

Table 1: Sampling and Handling Requirements for Stable Isotope Analysis

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

Analytical Methods

Short descriptions for the analytical methods, terminology and reporting conventions are given in the text below.

STABLE ISOTOPE TERMINOLOGY AND REPORTING

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

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

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

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

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

ANALYTICAL METHODS—STABLE ISOTOPES OF WATER

Oxygen isotope analyses are conducted using the carbon dioxide equilibration method for $^{18}\text{O}/^{16}\text{O}$ and analyzed with an automated water equilibration unit. Isotope ratio measurements are performed on a VG PRISM isotope ratio mass spectrometer housed in the Chemical Sciences Division at Lawrence Livermore National Laboratory. The LLNL standard operating procedure for determination of the stable isotopic composition of water in groundwater samples is SOP-UGTA-128, and is available upon request.

Analyses in the Stable Isotope Laboratory are calibrated to internal standards referenced against National Institute of Standards and Technology (NIST) standard reference materials. Internal standards consist of (1) Pacific Ocean water sample $\delta^{18}\text{O} = +0.35\text{‰}$, (2) two isotopically distinct California meteoric water samples $\delta^{18}\text{O} = -9.78$ and -14.62‰ , and (3) Alaskan Tap Water (-21.02‰). The composition and isotopic values of these internal standards span the range of natural waters typically observed in potable groundwater of California. For each 24 $\delta^{18}\text{O}$ analyses, 2 each of 3 internal standards are also analyzed and used for calibration. The internal

standards are periodically compared to the three NIST reference standards (NIST RM 8535; NIST RM 8536; NIST RM 8537): SMOW, Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP).

The analytical precision for these $\delta^{18}\text{O}$ measurements, from one run to the next, is $\pm 0.10\%$, which is defined in terms of the difference of the internal standard from the precisely known NIST standards. One duplicate is analyzed for every eighteen samples. These duplicates are not “blind” however, but are typically samples from the previous run. If this duplicate varies by more than $\pm 0.10\%$, the sample is run for a third time. If this duplicate is not within the 0.10% precision, the entire set of eighteen samples is re-analyzed.

Water $\delta^2\text{H}$ is determined on unfiltered samples, usually the same bottle collected for water- $\delta^{18}\text{O}$. Samples are usually analyzed by the high-temperature chromium reduction technique. A small volume of water ($\sim 0.4\mu\text{L}$) is injected by an autosampler into an elemental analyzer containing chromium metal. The sample oxygen bonds with the chromium and the resulting H_2 gas is carried in a stream of helium to a Micromass IsoPrime continuous flow IRMS.

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

Epstein, S.; Mayeda, T. K., Variation of O-18 content of waters from natural sources. *Geochim. Cosmochim. Acta* **1953**, 4, 213-224.

Morrison, J.; Brockwell, T.; Merren, T.; Fourel F., and Phillips, A.M., On-Line High-Precision Stable Hydrogen Isotopic Analyses on Nanoliter Water Samples, *Analytical Chemistry* **2001**, 73, 3570-3575.

ANALYTICAL METHOD—STABLE ISOTOPES OF NITRATE

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

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

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

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

Data Quality Objectives and Quality Control

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

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

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

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

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

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

Parameter	Method/ Range	Units	Reference	External Precision ¹	Instrumental precision ²
Nitrate $\delta^{18}\text{O}$ Nitrate $\delta^{15}\text{N}$	Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{15}\text{N}$: Air $\delta^{18}\text{O}$: SMOW	$\delta^{15}\text{N} \pm 0.3 \text{ ‰}$ $\delta^{18}\text{O} \pm 0.8 \text{ ‰}$	$\delta^{15}\text{N} \pm 0.2 \text{ ‰}$ $\delta^{18}\text{O} \pm 0.5 \text{ ‰}$
Water $\delta^{18}\text{O}$ Water $\delta^2\text{H}$	Dual Inlet and/or Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{18}\text{O}$: SMOW $\delta^2\text{H}$: SMOW	$\delta^{18}\text{O} \pm 0.3 \text{ ‰}$ $\delta^2\text{H} \pm 1.0 \text{ ‰}$	$\pm 0.15 \text{ ‰}$ $\pm 0.6 \text{ ‰}$

1. External (1 sigma) precision objectives apply to replicate analyses of a single sample.
2. Instrumental precision (1 sigma) applies to calibration check samples, laboratory control samples and other measurements of samples of known concentration and isotopic composition where the known value is compared to the measured value.
3. SMOW = Standard Mean Ocean Water

San Diego County Domestic Well Isotopic Data

This data report represents specialized analyses performed by LLNL on domestic well groundwater samples collected in San Diego County by State Water Resources Control Board staff for the GAMA Domestic Wells Project. Phase I samples were collected between March and June of 2008; Phase II samples were collected in December 2008 and January 2009. In total, LLNL analyzed 137 samples for water isotopic composition of both oxygen and hydrogen, and 47 samples for nitrate isotopic composition of both nitrogen and oxygen. Analyzed samples included one field duplicate for water isotopic composition and three field duplicates for nitrate isotopic composition. Data are tabulated in Table 3.

Three field duplicate samples were processed for nitrate isotopic composition. Duplicate comparisons were acceptable. These data are shown in Table 4. Nitrate- $\delta^{15}\text{N}$ field duplicate

analyses agreed to better than 0.1‰ for two of the field duplicate pairs and to within 1‰ for the third field duplicate pair. Nitrate- $\delta^{18}\text{O}$ field duplicate analyses agreed to within 0.5‰.

Table 3: Water and Nitrate Isotopic Composition in San Diego County Domestic Well Water Samples (Revised, January 2012)

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, SMOW)	Water- $\delta^2\text{H}$ (‰, SMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, SMOW)
SD 801	106492	04/29/2008	-6.8	-48.7	14.3	4.6
SD 802	106493	04/29/2008	-6.7	-41.8		
SD 803	106494	04/29/2008	-6.7	-45.4		
SD 804	106495	04/30/2008	-6.5	-45.8		
SD 805	106496	04/30/2008	-7.1	-45.2		
SD 806	106498	05/01/2008	-6.7	-44.0		
SD 807	106499	05/01/2008	-6.7	-40.5		
SD 808	106500	05/01/2008	-6.6	-42.2	8.0	5.1
SD 809	106501	05/01/2008	-6.5	-40.6		
SD 811	106502	05/06/2008	-6.4	-43.4	30.5	18.0
SD 813	106505	05/07/2008	-6.6	-41.1		
SD 814	106506	05/07/2008	-6.3	-42.6	6.6	5.2
SD 815	106507	05/07/2008	-6.7	-42.6		
SD 816	106530	05/08/2008	-7.1	-46.2	11.9	4.6
SD 817	106531	05/08/2008	-6.7	-41.5		
SD 818	106532	05/08/2008	-6.7	-44.1		
SD 819	106533	05/13/2008	-6.7	-43.6	12.7	5.4
SD 820	106534	05/13/2008	-6.6	-42.1	14.5	6.2
SD 821	106535	05/13/2008	-7.5	-46.1		
SD 822	106562	05/14/2008	-7.2	-42.4		
SD 823	106563	05/14/2008	-7.6	-45.9	13.0	5.6
SD 824	106564	05/14/2008	-5.4	-37.7		
SD 825	106565	05/15/2008	-6.6	-43.9		
SD 826	106566	05/15/2008	-7.0	-43.9		
SD 827	106567	05/15/2008	-6.1	-41.7		
SD 828	106571	05/20/2008	-6.2	-39.4		
SD 829	106572	05/20/2008	-6.6	-39.5		
SD 830	106573	05/20/2008	-7.0	-43.9		
SD 831	106568	05/20/2008	-6.8	-48.2	10.0	4.5
SD 832	106574	05/22/2008	-6.9	-44.6		
SD 833	106575	05/22/2008	-6.3	-40.2		
SD 834	106570	05/20/2008	-6.9	-44.6		
SD 836	106576	05/22/2008	-6.4	-40.1		
SD 837	106592	05/29/2008	-7.1	-42.3		
SD 838	106577	05/27/2008	-7.4	-58.4	10.5	8.1
SD 839	106578	05/27/2008	-7.5	-58.4		
SD 840	106579	05/27/2008	-5.9	-38.1		
SD 841	106580	05/27/2008	-5.9	-36.1		

GAMA Domestic Wells: San Diego County Isotopic Data

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, SMOW)	Water- $\delta^2\text{H}$ (‰, SMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, SMOW)
SD 842	106581	05/28/2008	-5.5	-34.7	2.2	7.8
SD 843	106582	05/28/2008	-6.2	-40.6	1.7	6.9
SD 844	106583	05/28/2008	-6.8	-50.2	6.2	7.4
SD 845	106591	05/29/2008	-6.6	-41.9	13.6	6.2
SD 846	106590	05/29/2008	-6.0	-37.6		
SD 847	106589	05/29/2008	-6.7	-45.5		
SD 848	106584	05/28/2008	-6.8	-49.3	9.2	7.3
SD 849	106594	05/29/2008	-6.2	-36.3		
SD 850	106504	05/06/2008	-6.6	-44.8	11.2	7.3
SD 851	106586	05/28/2008	-5.9	-35.1		
SD 852	106587	05/28/2008	-6.7	-46.2		
SD 853	106595	06/03/2008	-6.1	-36.9		
SD 854	106596	06/03/2008	-7.1	-53.9	7.2	8.8
SD 855	106597	06/04/2008	-7.6	-52.1		
SD 856	106598	06/04/2008	-7.4	-49.4		
SD 857	106599	06/04/2008	-7.4	-51.8		
SD 858	106604	06/05/2008	-7.5	-52.7	10.2	4.1
SD 859	106605	06/05/2008	-6.7	-40.3		
SD 860	106606	06/05/2008	-5.9	-36.0		
SD 861	106607	06/10/2008	-6.4	-37.6	13.6	8.5
SD 862	106608	06/10/2008	-6.8	-40.9		
SD 863	106609	06/10/2008	-6.8	-39.3		
SD 864	106610	06/10/2008	-6.7	-38.4	10.3	2.7
SD 865	106611	06/10/2008	-6.4	-36.1	9.8	9.4
SD 866	106613	06/11/2008	-6.1	-38.6		
SD 867	106615	06/11/2008	-5.9	-37.0		
SD 868	106616	06/11/2008	-6.6	-40.5		
SD 869	106617	06/11/2008	-6.3	-41.4		
SD 870	106618	06/11/2008	-7.3	-55.8		
SD 871	106641	06/12/2008	-6.3	-39.3		
SD 872	106643	06/12/2008	-7.5	-51.3	8.3	3.3
SD 873	106642	06/12/2008	-7.5	-51.8		
SD 874	106647	06/12/2008	-7.3	-44.6	3.4	5.0
SD 875	106646	06/12/2008	-6.1	-39.6		
SD 876	106648	06/17/2008	-7.0	-43.1		
SD 877	106649	06/17/2008	-8.0	-51.7	10.1	6.2
SD 878	106650	06/17/2008	-8.1	-48.2		
SD 879	106652	06/17/2008	-7.9	-49.0		
SD 880	106653	06/17/2008	-7.7	-46.9		
SD 881	106664	06/18/2008	-5.8	-40.4		
SD 884	106645	06/12/2008	-6.6	-42.8		
SD 885	106651	06/17/2008	-8.6	-53.2		
SD 886	106667	06/18/2008	-7.9	-47.3	13.5	8.3
SD 887	106666	06/18/2008	-7.6	-49.0		
SD 888	106668	06/18/2008	-8.5	-57.6		

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, SMOW)	Water- $\delta^2\text{H}$ (‰, SMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, SMOW)
SD 889	106669	06/18/2008	-8.3	-54.5	4.9	3.4
SD 890	106635	06/19/2008	-8.1	-53.6	7.6	4.3
SD 891	106636	06/19/2008	-8.6	-55.0		
SD 892	106637	06/19/2008	-8.5	-54.1		
SD 894	106638	06/19/2008	-5.8	-35.7		
SD 895	106639	06/19/2008	-7.4	-46.9		
SD 896	106640	06/19/2008	-7.7	-49.6		
SD 897	106588	05/29/2008	-6.5	-40.3		
SD 898	106612	06/10/2008	-7.0	-41.4		
SD 900	106670	06/19/2008	-7.9	-48.9		
SD 901	107166	12/02/2008	-6.9	-44.3	5.6	6.4
SD 902	107167	12/02/2008	-7.7	-50.2	6.1	1.9
SD 903	107168	12/02/2008	-7.9	-48.1		
SD 904	107169	12/02/2008	-6.5	-44.2		
SD 905	107170	12/02/2008	-8.0	-46.9		
SD 906	107172	12/03/2008	-7.5	-47.9		
SD 907	107173	12/03/2008	-6.8	-42.4	8.4	1.8
SD 908	107174	12/03/2008	-6.7	-41.2		
SD 909	107175	12/03/2008	-8.0	-52.7	15.5	8.6
SD 910	107176	12/03/2008	-8.0	-52.6	5.9	4.6
SD 911	107177	12/04/2008	-6.8	-41.9		
SD 912	107179	12/04/2008	-6.4	-40.1	20.0	13.2
SD 913	107180	12/04/2008	-6.6	-42.6	7.0	12.4
SD 914	107181	12/04/2008	-8.3	-53.5		
SD 915	107182	12/04/2008	-8.2	-51.6		
SD 916	107183	12/04/2008	-8.2	-52.0		
SD 917	107184	12/09/2008	-5.9	-53.8		
SD 918	107185	12/09/2008	-8.8	-64.4	7.4	6.7
SD 919	107186	12/09/2008	-6.6	-44.4	4.2	4.3
SD 920	107187	12/10/2008	-8.0	-57.1	8.8	17.8
SD 921	107188	12/10/2008	-6.0	-39.8		
SD 922	107190	12/11/2008	-7.3	-46.6		
SD 923	107191	12/11/2008	-7.2	-50.4	10.5	1.7
SD 925	107240	01/21/2009	-7.0	-47.1		
SD 926	107192	12/16/2008	-8.3	-52.4		
SD 927	107194	12/17/2008	-6.9	-42.4		
SD 928	107241	01/21/2009	-6.9	-42.3		
SD 929	107204	12/18/2008	-8.2	-51.9		
SD 930	107200	12/18/2008	-9.1	-61.0	7.2	1.6
SD 931	107196	12/17/2008	-8.6	-65.4	8.3	1.2
SD 932	107197	12/18/2008	-7.5	-47.3	5.0	7.7
SD 933	107233	01/06/2009	-6.0	-40.8	8.4	4.6
SD 934	107201	12/18/2008	-7.8	-48.9		
SD 935	107193	12/16/2008	-8.4	-52.5		
SD 936	107235	01/07/2009	-8.3	-56.1		

SWRCB ID	LLNL ID	Collection Date	Water- $\delta^{18}\text{O}$ (‰, SMOW)	Water- $\delta^2\text{H}$ (‰, SMOW)	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, SMOW)
SD 937	107203	12/18/2008	-9.7	-69.2		
SD 940	107242	01/21/2009	-8.5	-52.5		
SD 942	107198	12/18/2008	-7.1	-46.8		
SD 943	107202	12/18/2008	-7.8	-50.1	6.1	3.1
SD 945	107234	01/06/2009	-8.0	-51.4	4.9	5.5
SD 946	107236	01/08/2009	-9.4	-72.7		
SD 947	107237	01/20/2009	-8.9	-60.5		
SD 948	107238	01/20/2009	-8.9	-60.7		
SD 949	107239	01/20/2009	-8.6	-62.1		
SD 950	107244	01/22/2009	-6.6	-41.4		

Table 4: Nitrate Isotopic Composition Analyses of Field Duplicates

SWRCB ID	LLNL ID	Collection Date	Nitrate- $\delta^{15}\text{N}$ (‰, Air)	Nitrate- $\delta^{18}\text{O}$ (‰, SMOW)
SD 811	106502	05/06/2008	30.53	18.0
SD 1811	106503	05/06/2008	31.71	18.4
			1.19	0.4
SD 831	106568	05/20/2008	9.96	4.5
SD 1831	106569	05/20/2008	10.00	4.3
			0.04	-0.2
SD 930	107200	12/18/2008	7.19	1.6
SD 1930	107199	12/18/2008	7.15	2.1
			-0.04	0.51