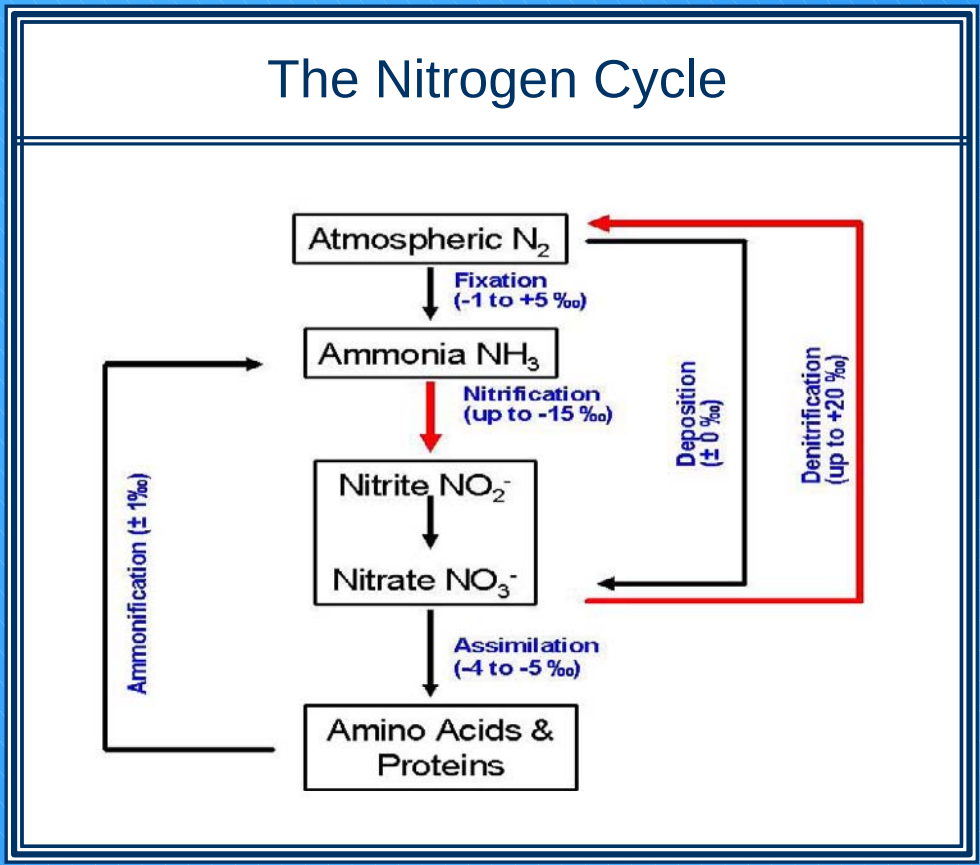
Using Isotopic Ratios and Major Minerals Data to Identify The Sources of Ground Water and Ground Water Nitrate In Relation to Pesticide Residues



CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
Environmental Monitoring Branch
California Department of Pesticide Regulation
1001 I Street Sacramento, California 95812

Final Report
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USING ISOTOPIC RATIOS AND MAJOR MINERALS DATA TO IDENTIFY THE SOURCES OF GROUND WATER AND GROUND WATER NITRATE IN RELATION TO PESTICIDE RESIDUES

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(Isotope Ratios of Nitrate in Ground Water)

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by

C. John Suen, Sc.D., P.G.

California Water Institute, California State University, Fresno

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EXECUTIVE SUMMARY

Sixty-nine groundwater samples were collected by the California Department of Pesticide Regulation in Fresno and Tulare Counties of eastern San Joaquin Valley as part of their groundwater monitoring program. To identify the main source of nitrate contamination, the samples were also analyzed for their $\delta^{15}N$ and $\delta^{18}O$ isotopic ratios in dissolved as well as their major mineral concentrations, in addition to analyses of herbicide residues and metabolites. To delineate groundwater components and mixing trends, major mineral analyses were also conducted by a commercial laboratory.

The nitrate isotope ratios and the anionic mixing trend are consistent with the interpretation that the main source of nitrate is from fertilizer application in the form of ammonium sulfate, and that nitrate from animal or human wastes may be secondary. Although nitrate concentrations do not correlate significantly with herbicide residues in the samples, they do exhibit a moderately significant positive trend with herbicide metabolites, such as ACET and DACT. Hence, the concentrations of groundwater nitrate and other agrichemicals may provide a reasonably significant proxy for determining travel pathways for the movement of herbicide residues and metabolites in the vadose zone, thus provide additional data for groundwater transport model development and calibration.

These preliminary results look promising. It is therefore recommended that this work should be followed by more detailed multivariate and spatial data analyses. Other related data such as land-use patterns and sampling depths will also be useful.

USING ISOTOPIC RATIOS AND MAJOR MINERALS DATA TO IDENTIFY THE SOURCES OF GROUND WATER AND GROUND WATER NITRATE IN RELATION TO PESTICIDE RESIDUES

1. INTRODUCTION

1.1 Background

The California Department of Pesticide Regulation (DPR) protects human health and the environment by regulating and registering the use of pesticides in the state. To evaluate the effectiveness of the regulations, DPR's Environmental Monitoring Branch analyzes pesticide residues and other agricultural contaminants in ground water and use computer models to estimate the transport pathways and degradation rates in the subsurface.

In addition to herbicide residues and degradates, dissolved nitrate in the ground water samples is also analyzed. Since the main source of nitrate can be attributed to the use of fertilizers on croplands, pesticide residues in groundwater are expected to have originated primarily from the same source areas as nitrate. Furthermore, the transport mechanism and pathway of nitrate through the vadose zone is expected to be similar to those of pesticides, and therefore, nitrate concentration trends may be used as a proxy for pesticide trends. Also, nitrate concentrations may be used to provide additional supporting data for the calibration of pesticide transport models.

However, nitrate in ground water may have originated from multiple sources including: (1) organic and inorganic fertilizer application from croplands, (2) animal waste from confined animal facilities, (3) septic systems and sewage treatment facilities, (4) other agricultural/industrial waste, and (5) soil and natural deposition (Collins, 1993; Canter, 1997; Kendall and Aravena, 2000). In the Central Valley, these different possible sources are often found within close proximity to one another, and therefore, the nitrate present in ground water may be the result of mixing components from different groundwater sources. Hence, it is necessary to validate the assumption that the main source for the groundwater nitrate is from fertilizer application and that both the herbicide residues and the nitrate in ground water originate from the same source areas (namely, croplands). This can be accomplished possibly by identifying the sources of groundwater nitrate based on the stable isotope ratios of nitrogen and oxygen ($\delta^{15}N$ and $\delta^{18}O$) of dissolved nitrate (Kendall, 1998; Kendall, et al, 1996).

1.2 Study Objectives

This project is to provide data survey on the potential sources of nitrate in the domestic well system as determined from measurements of the nitrogen and oxygen isotopic compositions of dissolved nitrate in the sampled well water. It is expected that pesticide concentrations originate from surface applications, and they are dissolved or mixed with percolating irrigation water. They follow similar pathways as the dissolved nitrate and reach ground water by advection. If the sole source of nitrate was determined to be from fertilizer applications, then this would indicate that surface water percolation would be a major component of recharge of groundwater aquifers. On the other hand, if the isotope data indicate for other sources of nitrate, such as from septic systems, that would imply that nitrate concentrations may not have a significant statistical correlation for herbicides residues and degradates, and therefore, they may not be used as a statistical proxy.

These data are important for validating models currently used to determine movement of herbicide residues in the subsurface. Up to date, DPR models assume that all water for recharge originates from surface additions. The presence of other significant recharge component would suggest the necessity to revisit this assumption used in or modeling procedure and most likely result in a revision of the procedure.

Accordingly, the objectives of this study are:

1. to identify the main source of nitrate present in the ground water,

2. to examine the relationship between the concentrations of herbicide residues and the concentrations of nitrate in ground water,

3. to delineate the components of ground water mixing so that the contribution to ground water from deep percolation of farm irrigation can be estimated by their major mineral compositions, and

4. to generate additional data to help understand the pathway for the movement of agricultural chemicals in the subsurface which is important in the interpretation of the herbicide concentrations in ground water.

1.3. Study Area and Locations

Since 1999, seventy domestic wells located in Fresno and Tulare counties for the presence of agricultural chemicals. The data from these wells are intended to be used to evaluate the effectiveness of pesticide regulations to

protect vulnerable areas, called ground water protection areas (GWPAs). The locations of the sampled wells are shown in Figure 1 based on GPS coordinates provided by DPR.

The average travel time for water flow through the vadose zone from the surface to the water table and eventually to wells in these GWPAs has been estimated at around 5-7 years. Therefore, there is a long-term commitment to sample these wells in order to provide the data necessary to determine water quality trends of well water over time.

Analysis for nitrate was also conducted in these wells. Elevated nitrate concentrations have been detected, with 50% of the wells containing concentrations that are above the health maximum contaminant level (MCL) of 45 ppm (N as nitrate). The apparent source of nitrate in ground water is from the application of fertilizers in agricultural operations. However, other possible sources may be due to leaching from septic systems and from dairy operations, both of which are common in the area.

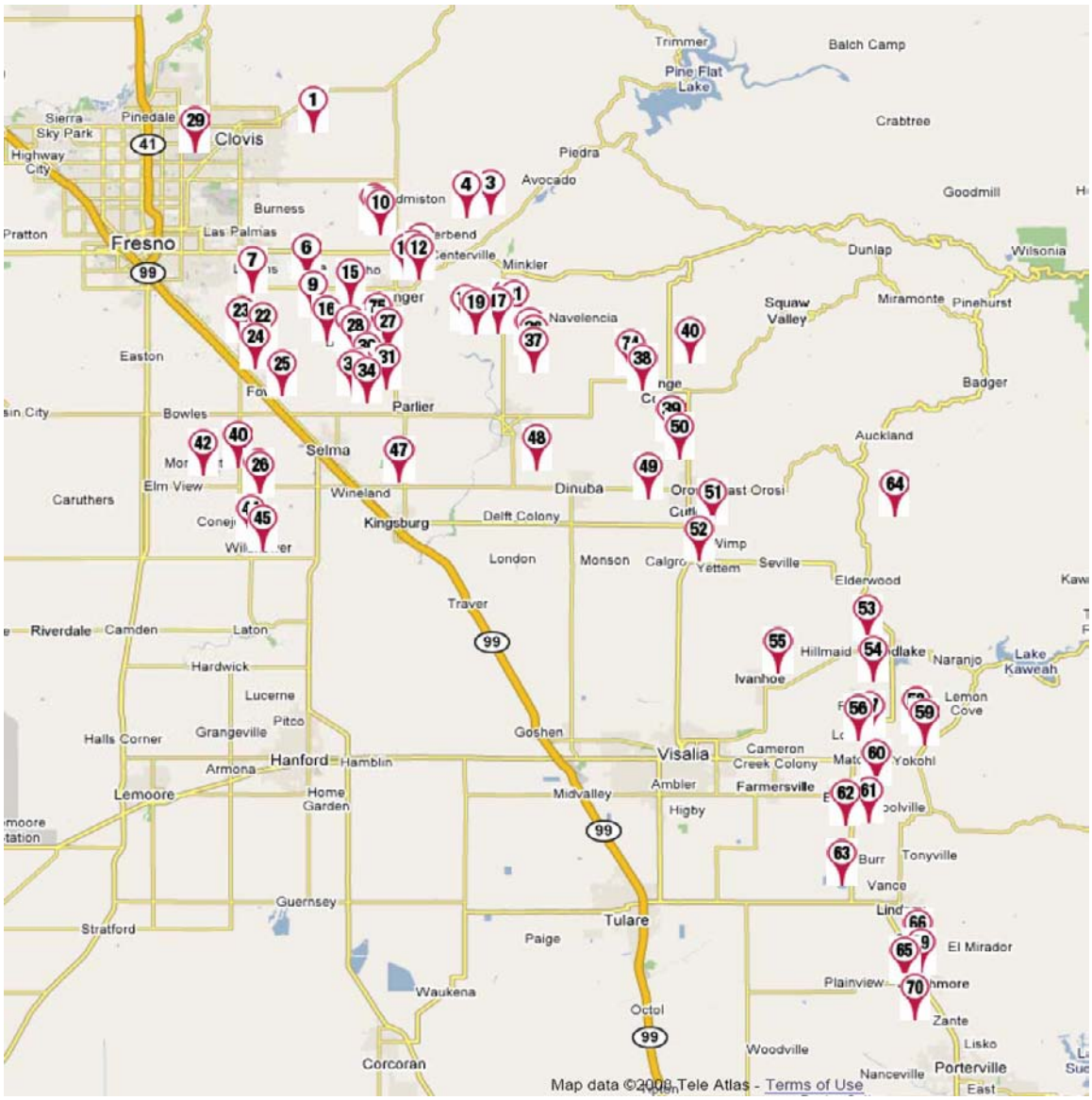

Figure 1: Well locations

2. METHODOLOGY

2.1 Stable Isotopes Technique

Recent research has indicated that analysis of the ratio of isotopes of nitrogen and oxygen ($\delta^{15}N$ and $\delta^{18}O$) in dissolved nitrate can provide a method to distinguish various sources of nitrate contamination. Researchers at the USGS and other research universities recently reported on the use of this method to determine potential sources of nitrate where higher and found that high $\delta^{15}N$ ratios were due to animal waste and/or sewage (for example, Wassenaar, 1995; Kendall, 1998; Kendall, et al, 1996; Steffy and Kilham, 2004). This study uses the same methodology and is based on the same isotope hydrological principle and earlier findings of similar studies (Kendall and Aravena, 2000; Suen, et al, 2005; Glowacki and Suen, 2004; Fogg, et al, 1998).

The latest developed mass spectrometry method was used for analyzing nitrogen and oxygen isotopic ratios in dissolved nitrates. This new and more efficient method is currently being adopted by isotope laboratories across the country, including Harvard, Woods Holes, UGGS, Menlo Park and USGS, Reston. It adds denitrifying bacteria strains (*Pseudomonas chlororaphis and Pseudomonas Aureofaciens*) to the samples in sealed vials and incubated overnight to convert all the nitrate into N_2O. The headspace of the vials are sampled by an automatically by an on-line sampler and the gas is purified on-line by cold traps, drying agents, and a GC column. (Sigman et al., 2001).

This method can be applied to measure both $\delta^{15}N$ and $\delta^{18}O$ ratios (Casciotti et al., 2002). However, $\delta^{18}O$ ratio does require comparison to a known nitrate standard to correct for possible fractionation of oxygen.

2.2 Isotope Analytical Procedure

Water samples (71) from wells were collected by DPR personnel. The samples were collected with one-liter desterilized High-density polyethylene (HDPE) bottles and the bottles were kept cool in the field by using an ice chest. They were transported to the laboratory on the same day and were kept at about 4°C. The water was filtered after collection with a 0.45 µm paper filter to remove any suspended sediments. The bottles were then frozen before they were transferred to the isotope analytical laboratory of the United State Geological Survey's Menlo Park campus.

The samples subsequently thawed completely before aliquots were taken in order to avoid isotope fractionation effect. Approximately, 20 ml. of the samples were used to measure $\delta^{15}N$ and $\delta^{18}O$ ratios of dissolved nitrate using the latest bacterial denitrifier method as described above in conjunction with a

GV Isoprime mass spectrometer in continuous flow mode. All samples were prepared according to the standard denitrifier procedure used by the USGS and analyzed by mass spectrometry. A brief description of the USGS procedure is given in Appendix A.

2.3 Nitrate and Major Mineral Concentrations

In order to set up the mass spectrometer gain, concentrations of nitrate for the sample were required. They were analyzed by a commercial laboratory (Dellavalle Laboratory, Fresno) and supplied by Ms. Cindy Garretson of DPR. In addition, major mineral concentrations were also obtained at the same time. They include the following: chloride, total alkalinity (as $CaCO_3$), Sulfate, calcium, magnesium, sodium, potassium, and iron. Electrical conductivity and pH were also recorded in the laboratory. These data provide additional information for data interpretation and analysis.

2.4 Herbicide Residues and Degradates

Concentrations of herbicides, such as simazine, diuron, bromacil, norflurazon, and propazine, as well as herbicide degradates, such as demethyl-norflurazon, ACET and DACT were analyzed with standard procedures and supplied by DPR.

3. RESULTS AND DISCUSSIONS

3.1 $\delta^{15}N$ and $\delta^{18}O$ in Dissolved Nitrate

The analytical results for $\delta^{15}N$ and $\delta^{18}O$ in dissolved nitrate of 69 samples are presented in Table 1. Based on the dual isotope ratios approach (Kendall, 1998; Kendall, et al, 1996), the $\delta^{18}O$ values are plotted against the $\delta^{15}N$ values in Figure 2a. (Appendix B describes the scientific convention for stable isotope ratio measurements). The $\delta^{18}O$ values range from -2 to +8‰ (per mil) and the $\delta^{15}N$ values from +2 to +8‰ (per mil), except two samples which have $\delta^{15}N$ values at about +10‰. When compared with the typical ranges of different nitrate sources compiled by Kendall (1998) as shown in Figure 2b, the isotope ratio values fall in the typical range of mineralized fertilizers (NH_4 in inorganic fertilizer) also overlapping the typical range of nitrogen in soil organic matter. These values also lie in the same range of ground water samples collected from eastern San Joaquin Valley in Fresno County in a previous study (Suen, et al, 2005; Marrero, 2008), which finds groundwater nitrate attributing to mainly fertilizer applications. Also similar to the previous study (Suen, et al, 2005; Marrero, 2008), there is no evidence for any significant contribution from animal or human waste components.

This finding is further supported by a significant positive correlation shown in Figure 3 between sulfate concentrations and nitrate concentrations. This observation can be attributed to the common application of sulfate fertilizers and soil amendments in the form of ammonium sulfate ($(NH_4)_2SO_4$) in areas with alkaline soils in eastern San Joaquin Valley. The sulfate ion (SO_4^{2-}) helps lower the pH of the soil and the ammonia provides nitrogen for plant growth.

To further examine the molal proportions of sulfate among the anions, a Piper diagram is constructed using the major mineral compositions (Figure 4). (major mineral data are included in Appendix C). The pristine ground water in eastern San Joaquin, which originates mostly from recharge from the Sierra mountains, is expected to have a carbonate-type water composition plotted close to the (HCO_3 + CO_3) low-left corner of the triangular anionic components plot. It can be seen that most ground water samples are plotted on a linear trend close to the (HCO_3^-+ CO_3^{2-}) – SO_4^{2-} (carbonate-sulfate) side of the triangle with only few samples whose points are displaced towards the chloride (Cl^-) corner. These data suggest that the original ground water is contaminated with an addition of a sulfate component more than with a chloride component, which is typically associated with wastewater.

Table 1: Oxygen and Nitrogen Isotopic Compositions of Dissolved Nitrate

Lab ID	Field ID	Well #	NO_3 µMols/L	Avg of $\delta^{15}N$	StDev of $\delta^{15}N$	# runs	Avg of $\delta^{18}O$	StDev of $\delta^{18}O$
11125	552	1	458	6.45	0.99	6.00	1.82	1.53
11128	568	2	398.6	2.75	0.02	2.00	3.28	0.34
11129	318	3	394	6.32	0.84	4.00	0.36	1.23
11106	474	4	1964	4.27	0.18	2.00	6.19	0.59
11107	478	5	952	6.45	0.06	2.00	4.36	0.70
11097	322	6	1794	3.30	0.82	3.00	1.56	0.58
11109	328	7	862	5.98	0.17	2.00	0.82	0.50
11131	462	8	392	5.98	0.77	4.00	-1.77	0.99
11111	470	11	802	5.11	0.47	2.00	5.07	0.54
11136	564	12	288.6	5.05	0.09	2.00	4.41	0.35
11121	454	13	616	5.48	0.16	2.00	7.95	0.30
11124	466	15	512	5.55	0.27	2.00	3.03	1.22
11099	342	16	1906	5.31	0.93	2.00	1.94	0.07
11101	390	18	944	5.10	0.50	3.00	0.39	0.98
11104	450	19	948	5.41	0.11	2.00	5.52	1.19
11113	482	20	752	3.73	0.27	2.00	3.07	1.03
11103	414	21	3220	4.35	0.24	3.00	2.23	0.26
11095	310	22	2100	2.84	0.04	2.00	4.08	0.81
11096	314	23	1314	5.88	0.37	2.00	4.15	0.64
11134	374	24	326	5.56	0.69	4.00	0.21	1.31
11120	434	25	622	3.88	0.20	3.00	0.17	0.86
11115	442	26	716	4.75	0.15	2.00	0.92	0.77
11123	438	27	578	4.49	0.13	2.00	2.21	0.05
11100	383	29	1566	4.97	1.20*	3.00	-0.11	0.36
11117	378	30	668	4.35	0.47	2.00	2.14	0.40
11130	350	32	394	3.89	0.67	3.00	-0.42	0.93
11137	374	34	240	3.52	0.12	2.00	3.25	0.62
11127	366	35	439.2	4.34	0.27	2.00	2.92	0.25
11133	370	36	354	5.12	0.44	4.00	-1.14	0.94
11119	362	37	632	4.79	0.32	3.00	2.22	0.67
11139	346	43	214	5.23	0.04	2.00	0.39	0.54
11126	302	44	454	4.59	0.04	2.00	2.40	1.32
11091	290	47	1554	6.58	0.64	4.00	5.75	1.04
11092	294	48	2160	6.49	0.88	3.00	3.54	0.78
11102	398	49	5700	6.78	0.51	3.00	4.06	0.64
11145	282	50	25.2	2.57	0.00	2.00	-2.18	0.86
11144	338	51	35.8	6.74	0.33	2.00	3.29	0.62
11114	358	52	729.8	5.65	0.07	2.00	-0.49	0.69
11093	298	53	1080	3.77	0.71	2.00	-1.70	0.07
11090	278	54	1236	1.87	0.51	2.00	-1.02	0.50
11098	334	56	2180	3.66	0.42	3.00	-0.24	0.59
11112	222	57	762	4.25	0.54	2.00	1.63	1.15
11142	286	58	120	9.95	0.90	2.00	7.96	1.26
11086	262	59	1112	5.82	0.59	3.00	3.99	0.44
11089	274	61	1852	6.92	0.09	3.00	2.30	0.53

Lab ID	Field ID	Well #	NO_3 µMols/L	Avg of $\delta^{15}N$	StDev of $\delta^{15}N$	# runs	Avg of $\delta^{18}O$	StDev of $\delta^{18}O$
11088	270	63	1086	4.97	0.62	2.00	4.92	1.44
11132	556	65	368	6.51	0.47	4.00	0.44	1.28
11143	238	68	70	6.70	0.33	2.00	5.11	2.89*
11087	266	69	1254	6.40	0.66	3.00	5.97	1.14
11081	230	71	1156	4.97	0.00	2.00	4.76	0.12
11080	226	72	1558	5.00	0.27	2.00	6.60	0.04
11108	254	73	904	6.23	0.16	4.00	3.34	0.22
11082	234	74	1456	6.89	0.62	2.00	5.43	0.54
11083	246	75	1270	5.44	0.64	2.00	4.75	1.13
11135	218	79	310	10.47	0.75	3.00	6.35	1.59
11079	206	80	2620	6.93	0.81	2.00	5.20	0.52
11084	250	84	1698	7.80	0.40	3.00	3.33	0.87
11085	258	85	1478	5.30	0.44	4.00	6.13	1.28
11078	202	86	1842	6.53	0.42	2.00	4.70	1.15
11141	210	88	152	6.95	0.01	2.00	-2.12	0.45
11138	410	89	216	4.41	0.05	2.00	0.67	0.79
11122	386	90	606	5.11	0.23	2.00	2.07	0.18
11116	330	92	688	7.25	0.32	2.00	3.53	1.18
11094	306	94	1606	6.05	0.52	2.00	6.32	0.56
11140	394	95	192	4.21	0.28	2.00	1.36	0.01
11105	458	101	1144	5.61	0.19	3.00	0.75	0.30
11118	446	102	648	4.39	0.21	4.00	1.73	0.36
11147	103	103	93.9	6.54	0.22	2.00	1.28	0.39
11110	426	105	860	2.58	0.34	2.00	-0.96	0.35

* Higher than normal

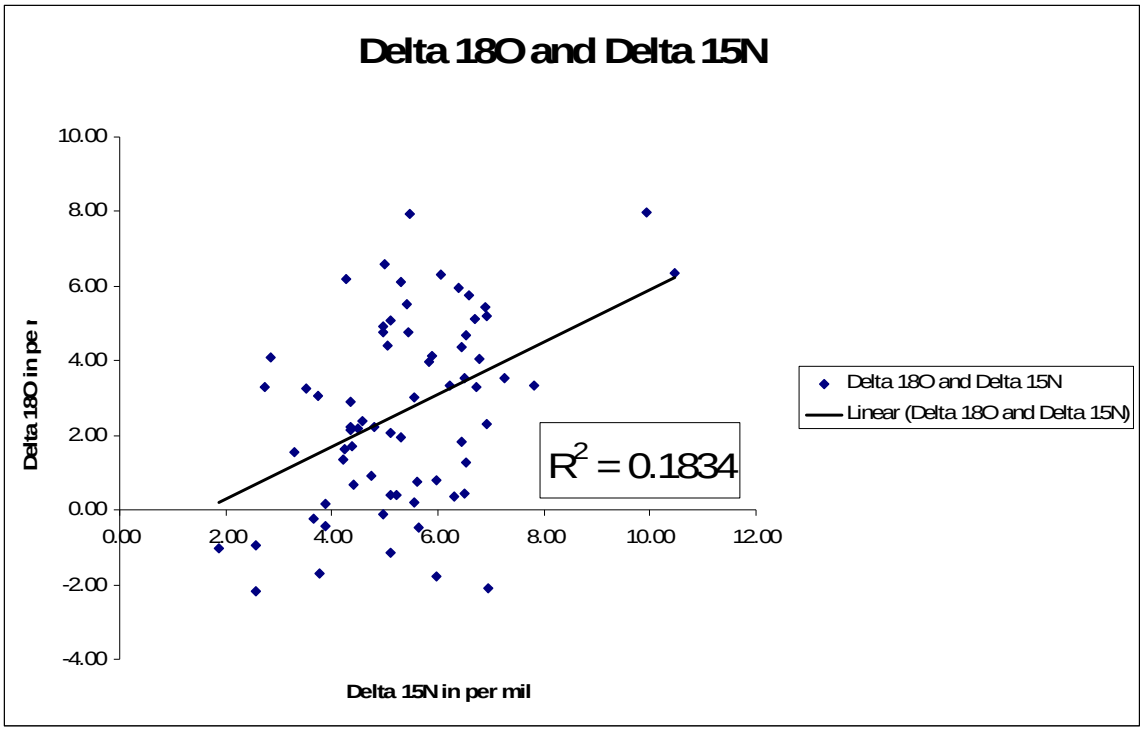

Figure 2a: Dual isotope plot of $\delta^{18}O$ versus $\delta^{15}N$.

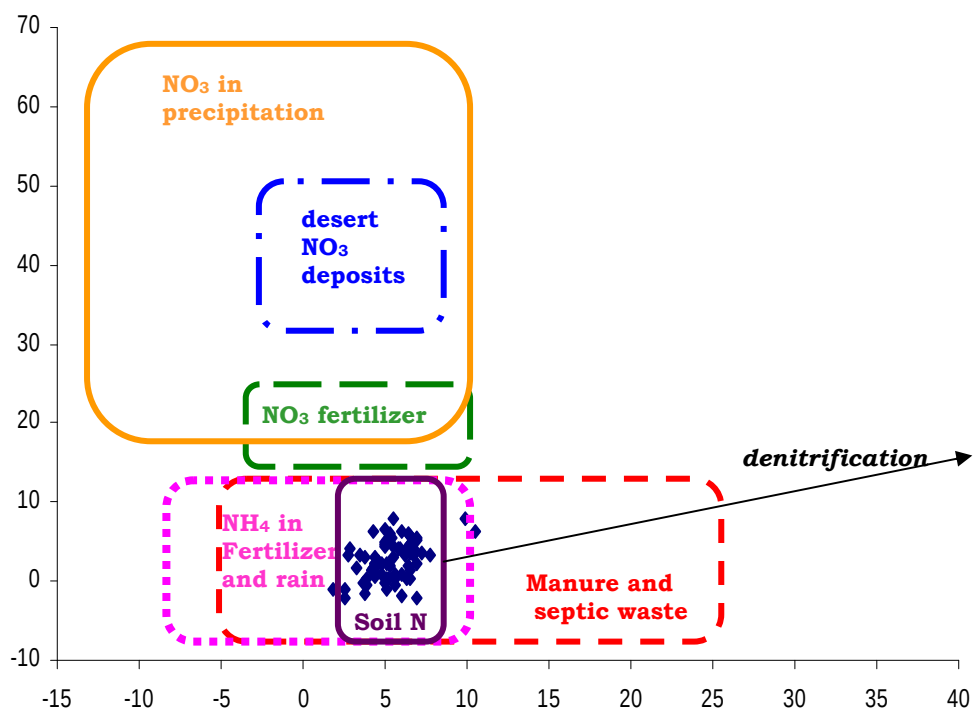

Figure 2b: Sample data in relation to the typical ranges of nitrate sources (Kendall, 1998). The denitrification trend is shown by the arrow.

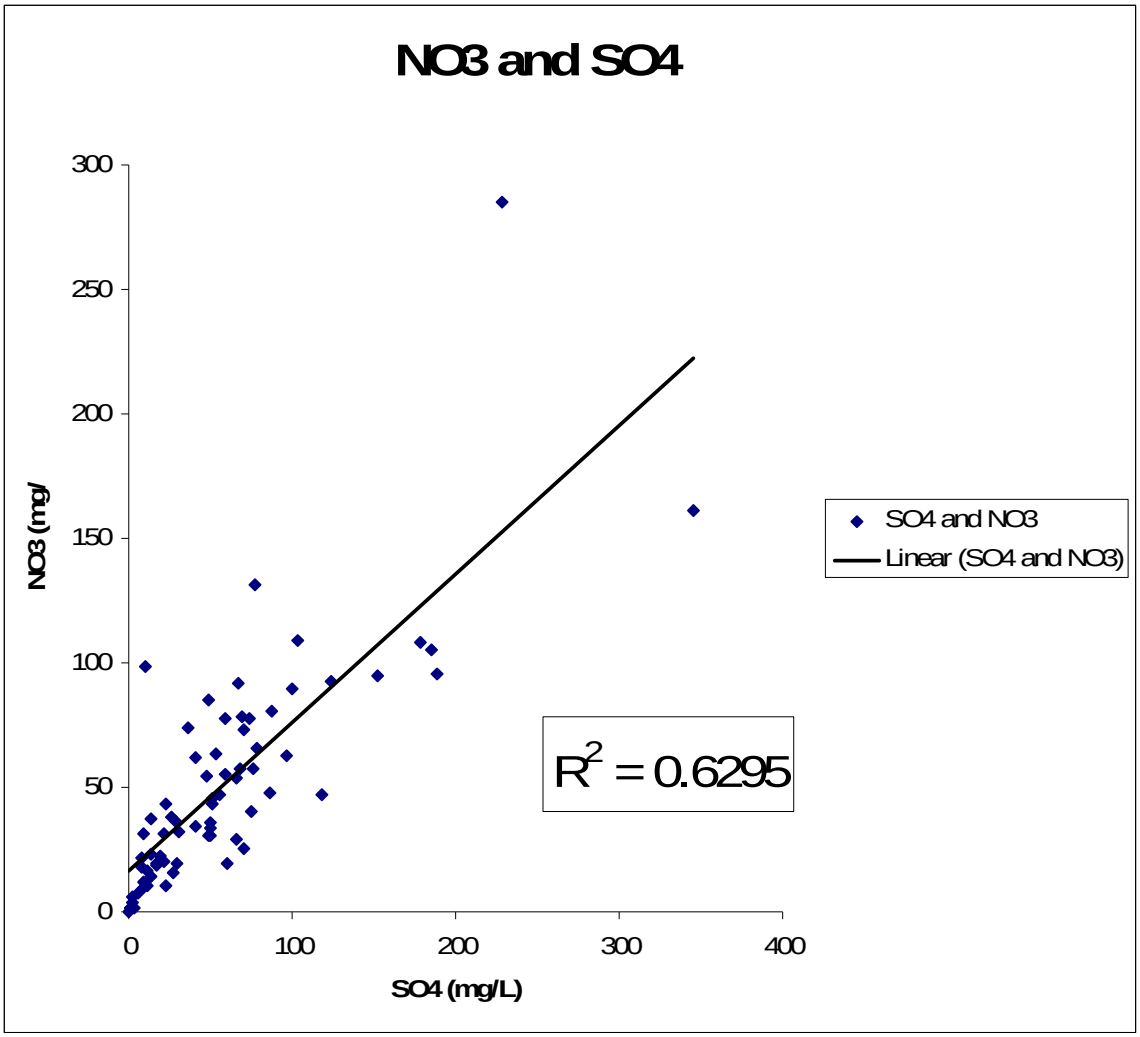

Figure 3: Plot of nitrate concentrations versus sulfate concentrations. A significant correlation is shown by the linear regression line.

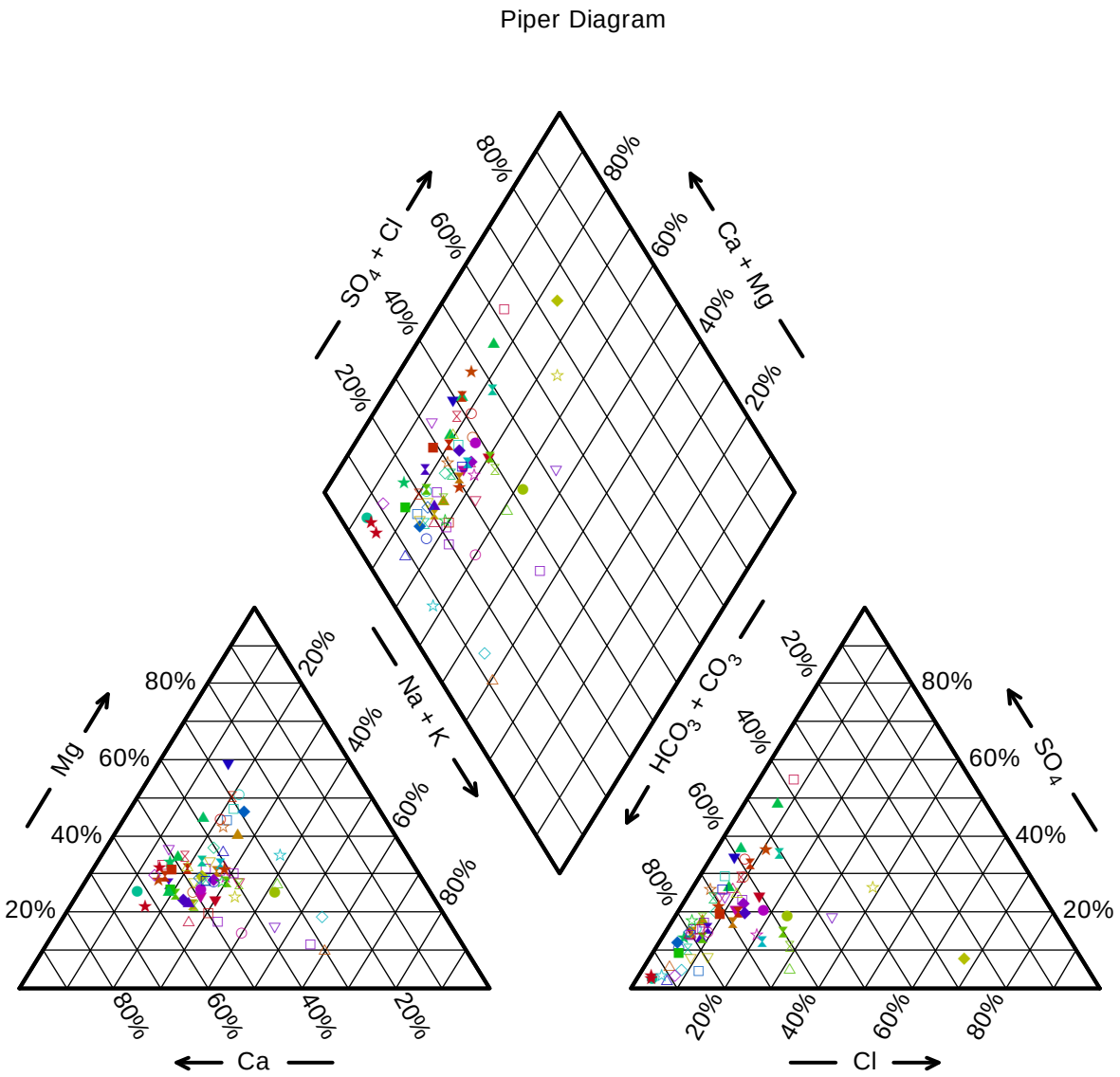

Figure 4: Piper diagram showing molal proportions of major cations and anions.

In addition, the $\delta^{15}N$ values have not been significantly affected by the denitrification process in the soil with the possible exception of two high-end $\delta^{15}N$ values (Well No. 58 and No. 79). The typical denitrification trend is also shown in Figure 2. If the original $\delta^{15}N$ values have been widely affected by the process, a correlation between $\delta^{15}N$ values and nitrate concentrations is expected. However, Figure 5 shows no significant correlation between $\delta^{15}N$ values and nitrate concentrations, and therefore, the ground water samples have retained the nitrogen isotope signature without subsequent modification by denitrification in the soil.

3.2 Relationship Between Nitrate and Herbicide Concentrations

Figures 6 and 7 show the relations between nitrate concentrations and the concentrations of simazine and diuron in the ground water samples. No significant correlations are observed.

However, the herbicides most likely have undergone considerable degradation during movement through the vadose zone where they are subjected to chemical decomposition and biological degradation processes, such as hydrolysis, aerobic, or anaerobic bacterial degradation. To examine the relation of herbicide and fertilizer applications, the concentration of herbicide degradates, DACT (diamino chlorotriazine) and ACET (2-amino-4-chloro-6-ethylamino-s-triazine) are plotted against nitrate concentrations in Figures 8 and 9. Moderate correlations are observed. Although the correlations are moderately significant, they do show positive trends indicating a general relationship between the herbicide and fertilizer applications. Therefore, the movement of herbicide residues and degradations most probably follows similar subsurface pathways as other widely used agrichemicals such as inorganic fertilizers, and they are found in ground water in the same general areas.

Hence, for the purpose of model calibration and for indentifying the vulnerability in ground water protection areas, a survey of nitrate concentrations and nitrate isotope ratios in ground water may be used as statistical proxy. However, it is important to point out that this study only represents a preliminary analysis with limited data and data controls. Therefore, more detailed analyses of the available data and expanded spatial coverage and sampling control are desirable and recommended. Other useful data may also include sampling depths, land use (crop patterns), subsurface geology and soil types, water-table depths, amounts of fertilizer and herbicide usage, and estimates of nitrate loading.

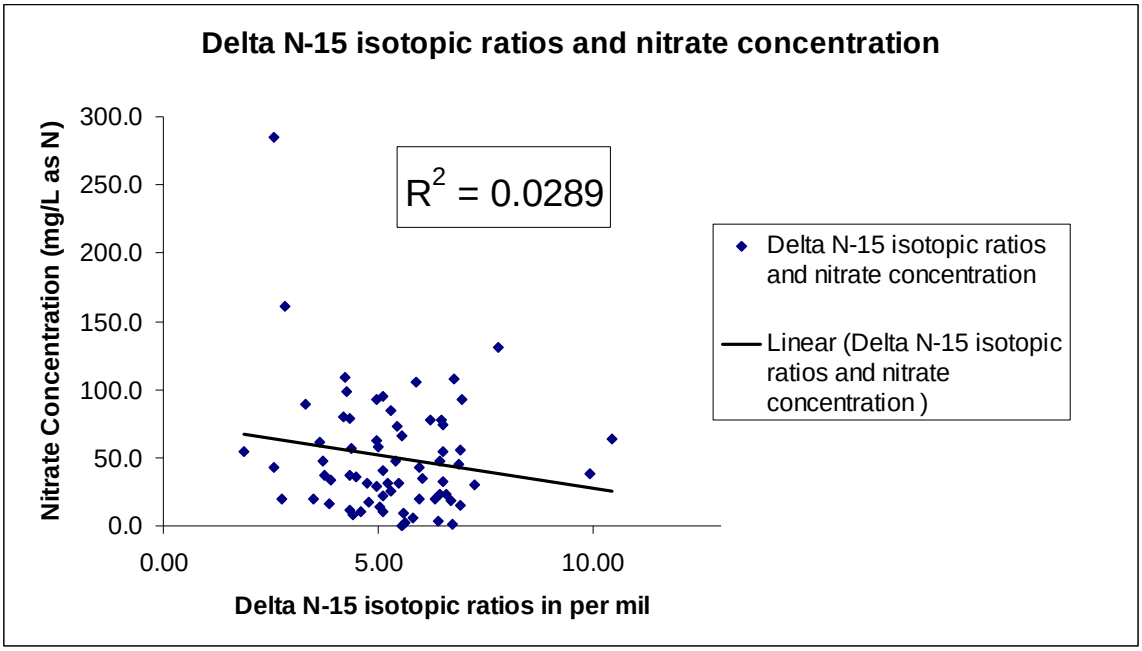

Figure 5: Plot of nitrate concentrations versus the values of $\delta^{15}N$. No significant correlation is observed. $\delta^{15}N$ of residual nitrate increases with denitrification. A negative correlation would indicate that the samples have undergone significant denitrification process.

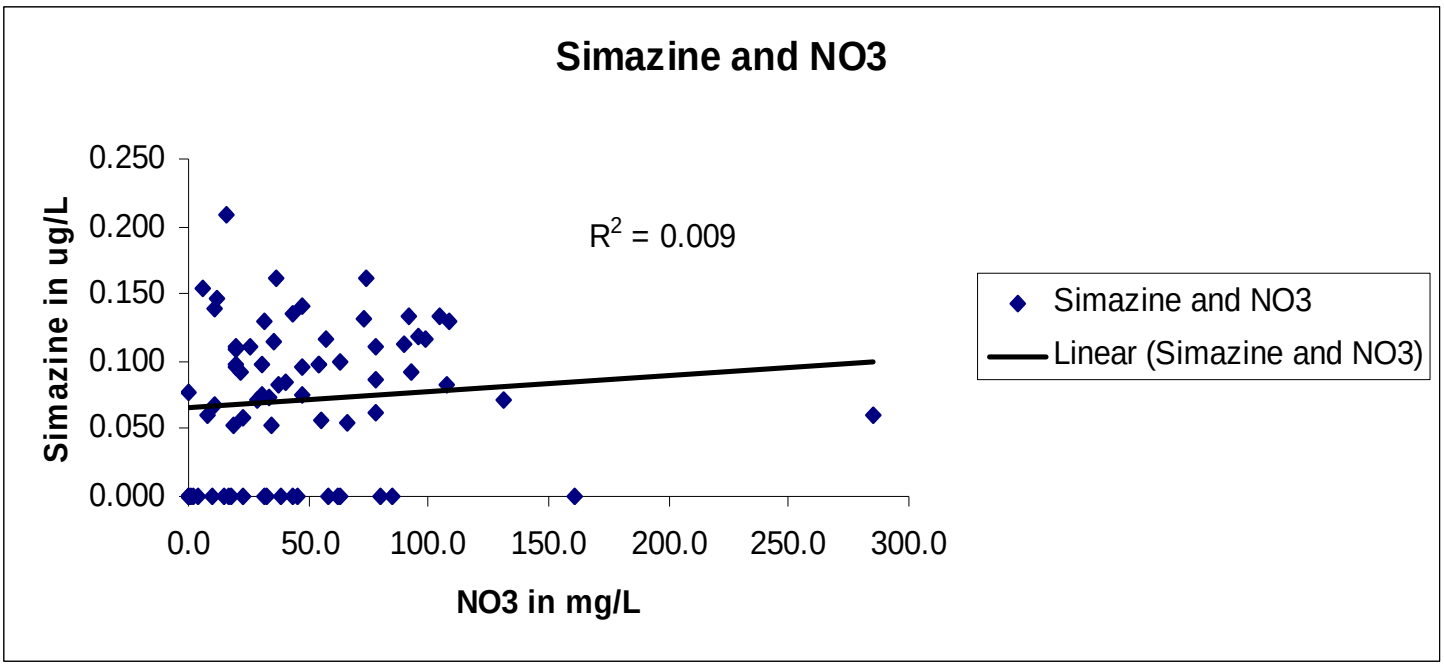

Figure 6: Plot of simazine residue concentrations versus nitrate concentrations. No significant correlation is observed.

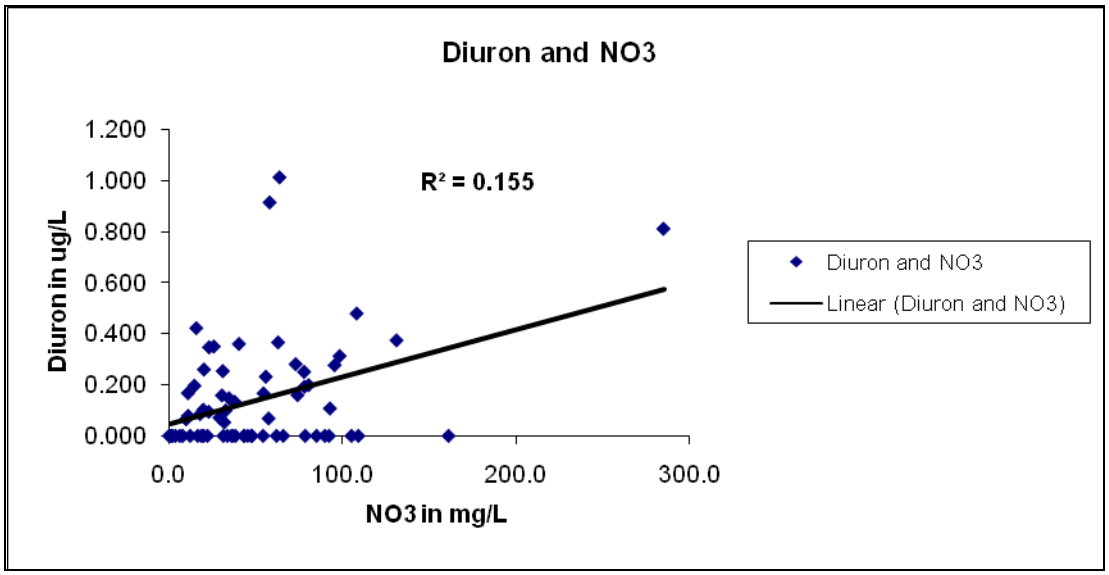

Figure 7: Plot of diuron residue concentrations versus nitrate concentrations. No significant correlation is observed.

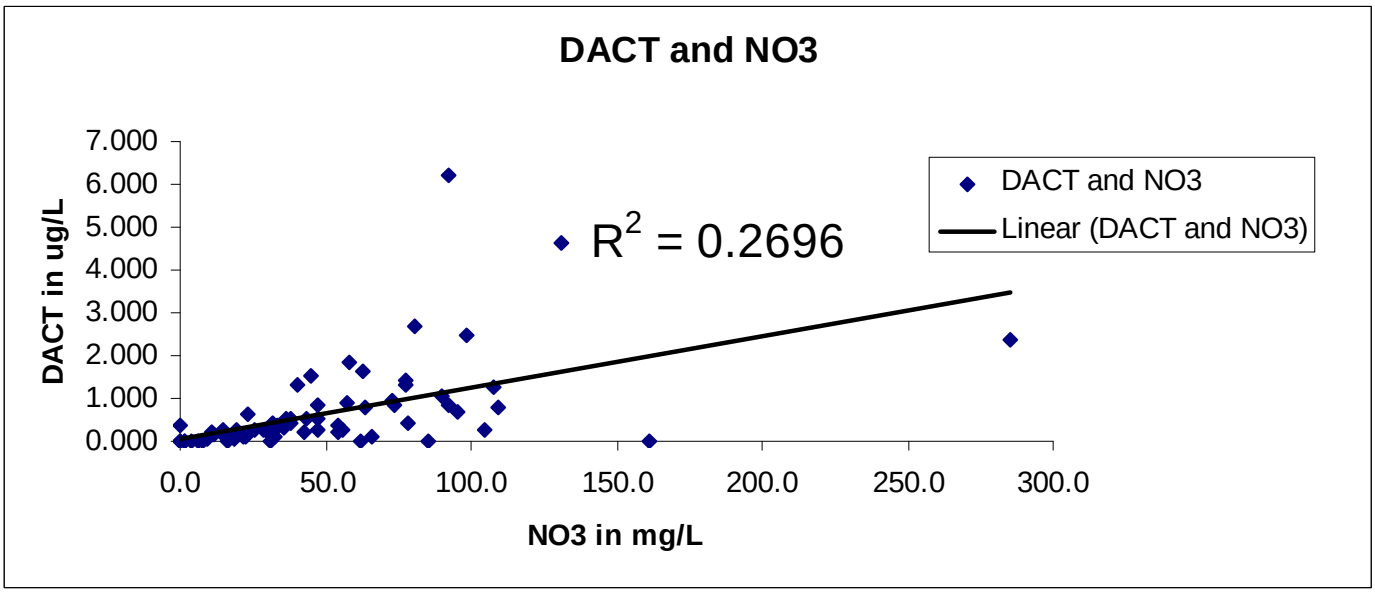

Figure 8: Plot of DACT (diamino chlorotriazine) concentrations versus nitrate concentrations. They are moderately correlated as shown by the linear regression line.

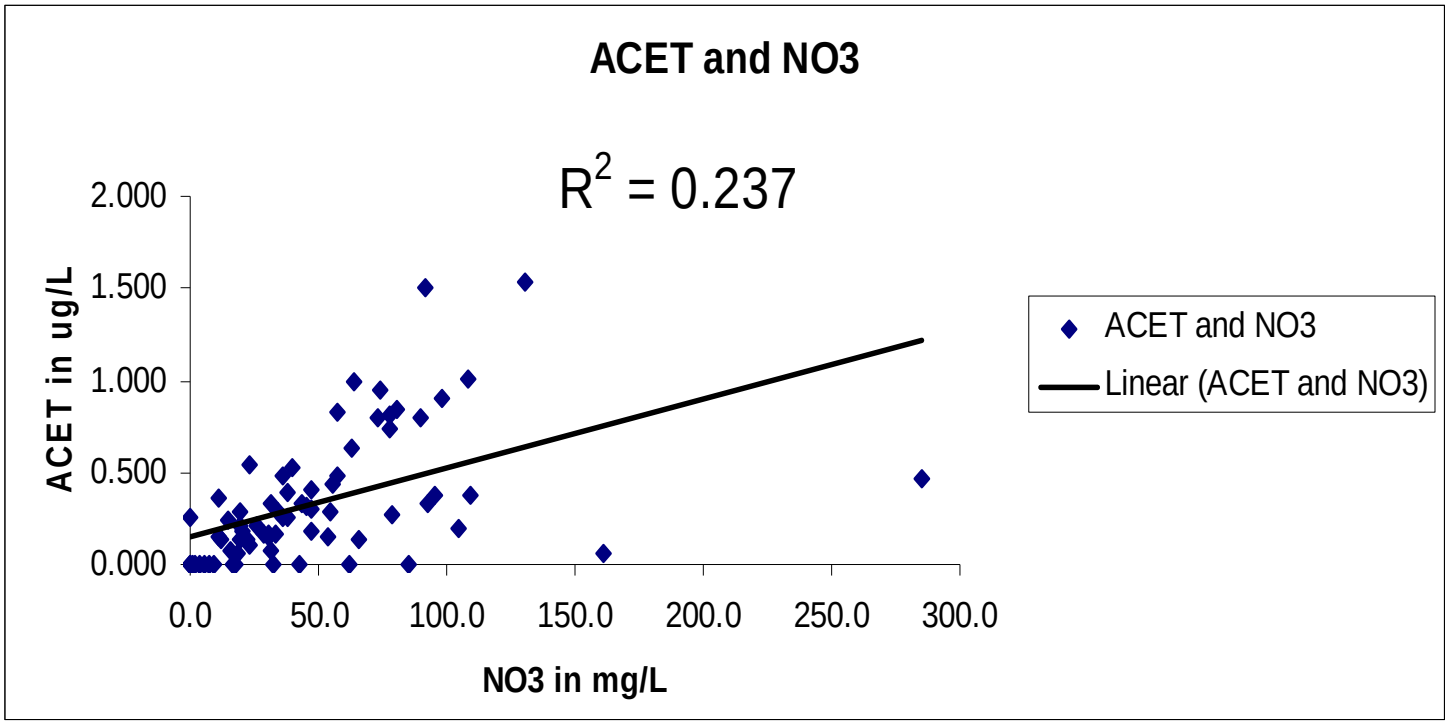

Figure 9: Plot of ACET (2-amino-4-chloro-6-ethylamino-s-triazine) concentrations versus nitrate concentration. They are moderately correlated as shown by the linear regression line.

4. CONCLUSIONS AND RECOMMENDATIONS

Based on this preliminary data survey, the following are the initial conclusions and recommendations for further studies:

1. Stable isotope ratios ($\delta^{15}N$ and $\delta^{18}O$) of dissolved nitrate in ground water samples from eastern San Joaquin valley lies within the typical range of isotopic values from mineralized fertilizers. The range of values from this study is similar to those from a previous ground water study in the same region. These values are consistent with the assumption that the main source of nitrate in the ground water is from the application of fertilizers and soil amendments.

2. The predominant fertilizer and soil amendment component is ammonium sulfate which is a commonly applied in the region.

3. Although nitrate contributions from animal or human waste are possible, the results indicate that they are probably not the predominant source of nitrate in the ground water samples.

4. There is no evidence of significant denitrification. Thus, the isotope ratios provide a reasonably reliable signature with regard to nitrogen sources.

5. The concentrations of nitrate do not show a strong correlation with the concentrations of the herbicide residues. However, nitrate concentrations do exhibit moderately significant positive trends with the concentrations of herbicide degradates (DACT and ACET). They probably follow similar pathways and are controlled by the same advective transport process through the vadose zone. Therefore, ground water nitrate and other agrichemicals could provide a statistical proxy for herbicide movement in the subsurface environment.

6. More detailed multivariate, spatial data analyses, for example, multiple regression and principal components analysis using major minerals and other related data are highly recommended. In additional, other data sets, such as land-use data, sampling depths, and fertilizer and herbicide application, should also be included so that a more thorough understanding of their interrelationships could be obtained.

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APPENDIX A

Procedure for Isotope Ratio Analyses
(United States Geological Survey laboratory, Menlo Park)

Collection

Pre-Field Preparation

50 mL Nalgene bottles are rinsed and allowed to dry for nitrate collection.

Collection

During collection, a 60 mL syringe is triple rinsed with sample water then filled with sample and a 0.2 or 0.45 um syringe filter is attached. Sample bottles are filled approximately 80% full and stored chilled in the field and frozen in the lab. Samples may be stored frozen for 6 months. Samples are logged into the nitrate database (referred to as the N Database) and receive a unique lab ID which is affixed to each sample bottle.

Analysis

Laboratory Preparation

Nitrate concentration will be determined by the collaborating project or by arrangement with a USGS lab. Procedures for the preparation of the bacterial cultures are described in detail in Sigman et al. (2001) and Casciotti et al. (2002). 80 vials are inoculated with a sample volume to yield 60nmoles NO_3-N. Solutions of working standard #9707 and international standards IAEA N3, USGS 34, and USGS 35 are added between every 10 samples. The sample sequence is recorded on the nitrate sample sequence form. After lysing the cells (Sigman et al., 2001 and Casciotti et al. 2002) samples are loaded into the nitrate auto analyzer.

Analysis

Following analysis and before corrections are applied, a preliminary inspection of sample size, standard values, blanks and duplicates is conducted to confirm proper instrument function during the run. Raw data are stored (1) in hard copy in the IsoPrime file cabinet, (2) in electronic file format on indexed zip disks, and (3) electronically copied to the data correction lab for final correction. δ^{15}N and δ^{18}O data are corrected for bacterial isotopic fractionation, exchange, and linearity, and entered in the nitrate database.

APPENDIX B

Scientific Convention for Stable Isotope Ratios

Isotopes are different kinds of atoms of the same element. They have different masses because they have different numbers of neutrons in their atomic nuclei. However, isotopes of the same element have the same number of protons and electrons, and therefore, have similar chemical properties and exhibit same behaviors in chemical reactions. Nevertheless, due to their slight difference in atomic masses and bonding energies, isotopes are fractionated by natural biogeochemical processes. Hence, some elements from different sources and reservoirs in the natural environment exhibit different "isotopic signatures".

Nitrogen

In nature, nitrogen has two common stable isotopes: ^{14}N and ^{15}N. ^{14}N is most abundant in the atmosphere. The percent abundance of ^{14}N in air is 99.63%, and for ^{15}N, it is only 0.37 %. The ratio of ^{15}N /^{14}N helps to differentiate among different nitrogen sources, such as mineral fertilizers, human waste, and animal waste. By convention, the ^{15}N /^{14}N ratio is compared to a standard and reported by using the delta value as defined in the equation below (expressed in "per mil" with the symbol "‰"). Air is used as the standard for nitrogen stable isotope ratios.

$$\delta^{15}N\,(‰) = \frac{(^{15}N/^{14}N)_{Sample} - (^{15}N/^{14}N)_{Standard}}{(^{15}N/^{14}N)_{Standard}} \times 1000$$

If the delta ratio is positive the sample was enriched in ^{15}N with respect to air.

Oxygen

The two most abundant isotopes are ^{18}O and ^{16}O. The atmospheric abundance for ^{16}O is 99.763 % and for ^{18}O, it is 0.1995 %. The standard ratio for oxygen is VSMOW, Vienna Standard Mean Ocean Water. The delta value expressed in ‰ is given by the equation:

$$\delta^{18}O\,(‰) = \frac{(^{18}O/^{16}O)_{Sample} - (^{18}O/^{16}O)_{Standard}}{(^{18}O/^{16}O)_{Standard}} \times 1000$$

About the δ value

The δ value is a measurement compared to a standard and it can be positive or negative. If a sample ratio is higher than the standard's, then the δ value is positive; if lower than the standard's, than δ is negative.

For example,

The ratio of ^{15}N /^{14}N in air is approximately 1/250 (i.e. 0.004).

If a sample has 1% more ^{15}N than Air, its ratio would be:

$1.01 \times (1/250) = 0.00404$.

This 1% relative enrichment corresponds to (positive) +10‰ *(the ‰ symbol means per mil).*

If a sample has 1% less ^{15}N than Air, then:

$0.99 \times (1/250) = 0.00396$

This 1% relative depletion corresponds to (negative) −10‰.

APPENDIX C: Major Mineral Compositions

		unit	µmhos/cm	----------					----mg/L----	----------			
		pH	EC	Total	Cl	Ca	Mg	Na	Fe	Total	NO_3	K	SO_4
				Alkalinity						Hardness			
Well No.				as $CACO_3$						as $CACO_3$			
	MCL		900		250				0.3		45		250
	MDL				0.03	0.1	0.1	0.2	0.004	0.7	0.04	0.3	0.03
	RL	1.0 +/-	10	10	0.1	0.1	0.1	1	0.01	0.7	0.45	0.5	0.2
	SM	4500H-B	2510B	2320B	4500CL C	3120B	3120B	3120B	3120B	2340B	4500NO3E	3120B	
	EPA				300.0	200.7	200.7	200.7	200.7		300.0	200.7	300.0
1		8.1	603	265	28.4	42.9	34.1	31.3	<0.01	247	22.85	2.4	13.9
2		7.9	298	109	6.2	16.1	17.9	13.5	<0.01	114	19.93	1.5	21.3
3		7.0	388	107	10	27.6	21.3	17.9	<0.01	156	19.67	1.7	59.9
4		8.0	581	190	13.3	29.1	12.7	70	<0.01	125	98.19	1.6	10.1
5		7.7	959	383	24.5	70	51.3	61.6	<0.01	386	47.56	4.2	85.9
6		7.7	1052	374	30.9	94.3	53	59.6	<0.01	454	89.71	4.9	100
7		7.6	682	264	14.1	57.3	26.5	48.8	<0.01	252	43.06	4.0	50.6
8		8.0	288	87	6.4	21.4	9.3	19.6	<0.01	91.8	19.59	2.0	29.4
11		7.9	500	138	8.6	25.9	35.9	15.9	<0.01	212	40.11	2.7	75.2
12		7.5	223	82	4.3	13.3	13.8	9.7	<0.01	89.8	14.43	1.4	14.1
13		7.7	398	115	7.0	23.3	21.6	18.3	<0.01	147	30.79	1.9	49.9
14		7.6	60	27	1.5	4.3	2.4	2.9	<0.01	20.8	<0.45	0.6	0.5
15		7.7	570	200	9.0	40.2	29.6	27.5	<0.01	222	25.58	3.1	70.9
16		7.2	1080	313	21	91.7	65.3	43.7	<0.01	498	95.26	4.8	189
18		8.0	1050	339	46.1	67.8	15	133	<0.01	231	47.21	4.6	118
19		7.7	434	103	11.8	44.7	14.7	14.3	<0.01	172	47.36	2.4	55.6
20		7.4	258	73.5	3.8	25	6.4	13.7	<0.01	88.8	37.59	1.3	13.3

		unit	µmhos/cm	----------					----mg/L----	----------			
		pH	EC	Total	Cl	Ca	Mg	Na	Fe	Total	NO_3	K	SO_4
				Alkalinity						Hardness			
Well No.				as $CACO_3$						as $CACO_3$			
	MCL		900		250				0.3		45		250
	MDL				0.03	0.1	0.1	0.2	0.004	0.7	0.04	0.3	0.03
	RL	1.0 +/-	10	10	0.1	0.1	0.1	1	0.01	0.7	0.45	0.5	0.2
	SM	4500H-B	2510B	2320B	4500CL C	3120B	3120B	3120B	3120B	2340B	4500NO3E	3120B	
	EPA				300.0	200.7	200.7	200.7	200.7		300.0	200.7	300.0
21		7.4	1355	246	35.6	160	59.2	47	<0.01	643	161	5.1	346
22		7.4	891	176	21.1	93.2	39.6	33.2	<0.01	396	105	5.4	185
23		8.0	729	242	14.4	71.7	26	40.3	<0.01	286	65.67	4.2	78
24		7.8	168	50.5	3.4	14.4	6.2	8.0	<0.01	61.7	16.29	1.6	11
25		7.9	196	57	2.5	18.3	7.2	5.4	<0.01	75.4	31.14	1.8	8.9
26		7.8	406	108	12.3	38.5	11.7	19.8	<0.01	144	35.75	2.8	49.9
27		7.9	688	229	36.2	72.8	19.4	33.8	<0.01	262	28.91	4.5	66
29		7.6	540	104	20.8	46.2	21	24.6	<0.01	202	78.31	3.8	69.8
30		7.4	446	132	13	35.8	17.2	26.1	<0.01	160	33.44	2.6	50.5
32		8.0	234	74.5	4.4	23.5	6.0	12	<0.01	83.3	19.72	2.9	17.6
34		7.4	148	47	3.9	14.7	4.5	5.0	<0.01	55.2	12.03	1.2	9.6
35		7.9	175	51	4.1	17.5	4.5	8.2	<0.01	62.2	21.96	2.4	8.1
36		7.9	161	47	3.9	16.6	4.6	6.5	<0.01	60.3	17.72	1.6	7.7
37		8.0	331	110	7.5	33.9	8.2	22.1	<0.01	119	31.61	2.8	21.1
43		7.9	434	186	11.6	39.7	14.9	24.2	<0.01	161	10.26	2.2	22.5
44		8.0	399	162	7.0	37.5	14.3	25.4	<0.01	152	22.66	2.3	19.8
47		7.5	741	191	34.9	68.8	21	48.6	<0.01	258	77.66	4.9	73.6
48		7.6	1089	270	40.2	137	42.4	41.4	<0.01	517	108	3.3	178
49		7.2	2284	311	243	174	60.3	160	<0.01	682	285	4.1	228

		unit	µmhos/cm	----------					----mg/L----	----------			
		pH	EC	Total	Cl	Ca	Mg	Na	Fe	Total	NO_3	K	SO_4
				Alkalinity						Hardness			
Well No.				as $CACO_3$						as $CACO_3$			
	MCL		900		250				0.3		45		250
	MDL				0.03	0.1	0.1	0.2	0.004	0.7	0.04	0.3	0.03
	RL	1.0 +/-	10	10	0.1	0.1	0.1	1	0.01	0.7	0.45	0.5	0.2
	SM	4500H-B	2510B	2320B	4500CL C	3120B	3120B	3120B	3120B	2340B	4500NO3E	3120B	
	EPA				300.0	200.7	200.7	200.7	200.7		300.0	200.7	300.0
50		7.8	132	61.5	1.7	15.2	3.8	3.0	<0.01	53.8	1.26	0.9	1.5
51		8.0	140	68	1.7	17.4	3.6	4.8	<0.01	58.3	1.79	0.7	1.7
52		8.0	458	171	8.8	52.1	9.7	28.5	<0.01	170	36.49	2.1	28.3
53		7.9	924	352	31.1	87.2	17	86.3	<0.01	288	54	3.9	65.7
54		7.8	675	245	13.1	64	14.0	48.8	<0.01	218	61.83	2.7	40.7
56		7.7	1096	349	45.6	114	34.3	68.3	<0.01	427	109	4.6	103
57		7.6	586	247	12.5	67.4	19.4	25	<0.01	248	38.09	3.4	25.7
58		7.7	192	87	2.1	19.3	6.9	4.9	<0.01	76.5	6.02	1.4	2.7
59		7.9	670	225	21.8	68.6	24.9	24.4	<0.01	274	55.57	2.7	59
61		7.9	952	272	28.8	90.2	40.0	37.2	<0.01	390	92.6	3.7	124
63		8.0	496	142	12.8	45.5	20.2	13.5	<0.01	197	54.34	1.4	48
65		7.7	441	167	18.9	44	15.2	24.1	<0.01	173	18.4	<0.5	17.2
68		7.9	185	83	5.4	19.8	6.4	5.1	<0.01	75.7	3.5	1.0	2.8
69		7.8	991	333	45.9	95.1	37.8	44.1	<0.01	393	62.72	2.8	96.3
71		7.7	846	285	39.4	74.1	32.4	51.9	<0.01	319	57.8	3.2	68.2
72		7.6	709	185	39.5	63.5	20.5	36.2	<0.01	243	77.89	4.4	59.2
73		7.6	784	249	54	62.5	26.8	48.4	<0.01	266	45.18	4.7	50.8
74		7.8	729	213	31.1	61.3	23.8	41.9	<0.01	251	72.8	2.5	70.3
75		7.8	938	296	71.1	72.8	35.4	52.6	<0.01	327	63.48	3.3	53.9

		unit	µmhos/cm	----------					----mg/L----	----------			
		pH	EC	Total	Cl	Ca	Mg	Na	Fe	Total	NO_3	K	SO_4
				Alkalinity						Hardness			
Well No.				as $CACO_3$						as $CACO_3$			
	MCL		900		250				0.3		45		250
	MDL				0.03	0.1	0.1	0.2	0.004	0.7	0.04	0.3	0.03
	RL	1.0 +/-	10	10	0.1	0.1	0.1	1	0.01	0.7	0.45	0.5	0.2
	SM	4500H-B	2510B	2320B	4500CL C	3120B	3120B	3120B	3120B	2340B	4500NO3E	3120B	
	EPA				300.0	200.7	200.7	200.7	200.7		300.0	200.7	300.0
79		7.7	1428	369	131	84.9	44.2	125.7	<0.01	394	15.53	3.7	26.9
80		7.8	1202	322	95.9	99.2	39.8	79	<0.01	412	131	6.0	77.1
84		8.0	663	152	45.6	39.1	18.3	54.7	<0.01	173	84.85	4.3	48.5
85		8.0	791	205	68.5	55.9	23.6	51.5	<0.01	237	73.91	4.0	35.8
86		7.6	2024	231	441	175	67.4	101.9	<0.01	714	92.08	6.4	67.3
88		8.0	353	172	7.2	19.5	15.4	30.8	<0.01	112	7.61	1.7	5.6
89		8.0	211	82	2.9	12	11.7	11.8	<0.01	77.3	10.8	<0.5	11.2
90		8.0	501	166	13.7	40.9	19.1	30.7	<0.01	181	30.25	3.5	48.6
92		8.0	375	106	9.2	38.7	10.7	13.8	<0.01	141	34.43	2.8	41.1
94		7.8	818	243	27.9	83.8	33.6	37.7	<0.01	347	80.3	3.5	87.8
95		7.6	155	53	2.6	13.8	5.1	7.2	<0.01	55.5	9.59	1.5	9.4
101		7.4	673	208	15.2	62.1	23.1	38.3	<0.01	250	57.16	2.9	76.5
102		8.1	394	141	5.6	31.9	12.6	23.8	<0.01	131	32.37	2.3	30.8
103		7.9	1775	400	201	136	35.6	188	<0.01	487	94.48	7.1	152
104		8.0	131	57	2.6	7.7	1.5	17	<0.01	25.5	1.68	1.4	3.4
105		8.0	603	238	18.1	54	25.7	34.9	<0.01	241	43	<0.5	22.3
	MCL=	Maximum Contaminant Level according to the California Domestic Water Quality and Monitoring Regulations (Title 22)											
	MDL=	Method Detection Limit											

		unit	µmhos/cm	----------					----mg/L----	----------			
		pH	EC	Total	Cl	Ca	Mg	Na	Fe	Total	NO_3	K	SO_4
				Alkalinity						Hardness			
Well No.				as $CACO_3$						as $CACO_3$			
	MCL		900		250				0.3		45		250
	MDL				0.03	0.1	0.1	0.2	0.004	0.7	0.04	0.3	0.03
	RL	1.0 +/-	10	10	0.1	0.1	0.1	1	0.01	0.7	0.45	0.5	0.2
	SM	4500H-B	2510B	2320B	4500CL C	3120B	3120B	3120B	3120B	2340B	4500NO3E	3120B	
	EPA				300.0	200.7	200.7	200.7	200.7		300.0	200.7	300.0
	RL=	Reporting Limit											
	SM=	Standard Methods for the Examination of Water and Wastewater, 19th ed., 1995											
	EPA=	Environmental Protection Agency methods unless otherwise indicated.											