Using Nitrate and Water Isotopes to Evaluate Groundwater Quality Beneath Dairy Farms in California

Task Report 2

Project

"Long Term Risk of Groundwater and Drinking Water Degradation from Dairies and Other Nonpoint Sources in the San Joaquin Valley"

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Abstract

In this study, groundwater samples were collected from two dairies in the northern San Joaquin Valley, where the water table is fairly shallow, and from five dairies in the Tulare Lake Basin, where the water table is much deeper. In each dairy, nitrate isotopes, water isotopes, nutrient concentrations, and other chemical and physical parameters were measured in monitoring wells located within different land use areas of the dairies. Monitoring wells were classified by the dairy-related land uses of corrals, fields receiving manure, waste lagoons, and mixed land use (undetermined). Across all sampled dairy monitoring wells, $\delta^{15}N\text{-}NO_3$ ranged from +2.9 to +49.4‰, and $\delta^{18}O\text{-}NO_3$ ranged from -3.3 to +19.2‰. Mean nitrate concentrations, $\delta^{15}N\text{-}NO_3$, and $\delta^{18}O\text{-}NO_3$ were significantly higher in the northern (Stanislaus County) dairy wells in comparison to the southern (Kings and Tulare Counties) dairy wells. Upgradient wells had lower $\delta^{15}N\text{-}NO_3$ values in comparison to other wells within an individual dairy, but did not have lower $\delta^{18}O\text{-}NO_3$ values or NO_3 concentrations. The higher $\delta^{15}N\text{-}NO_3$ values in the dairy land use wells clearly show the influence of manure-derived NO_3 in comparison to the upgradient wells. No consistent differences in nitrate isotopic compositions were found between the different land management units within the dairies, and large spatial variability in both nitrate concentrations and nitrate isotopic composition was observed within most of the individual dairies. When data from all the dairies was combined, the lagoon wells showed the greatest variability in $\delta^{15}N\text{-}NO_3$ values compared to the other land use categories. Within most of the dairies, higher $\delta^{15}N\text{-}NO_3$ values were not strongly correlated with decreasing NO_3 concentrations or decreasing dissolved oxygen concentrations, suggesting that the higher $\delta^{15}N\text{-}NO_3$ values observed primarily reflect a manure-derived nitrate isotope signal, and not in-situ denitrification. However, the positive linear relationship between $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ for the entire dataset is consistent with the expected trend for denitrification, which suggests that partial denitrification is a contributing factor to the overall nitrate isotope and concentration patterns, and significant in-situ denitrification appears to have impacted a small number of individual monitoring wells. These results emphasize the challenges associated with monitoring groundwater beneath dairies due to high spatial heterogeneity in the aquifer and groundwater constituents.

The distribution of $\delta^{15}N\text{-}NO_3$ within the entire dataset, including upgradient wells, suggests that nitrate dominated by synthetic fertilizer sources in this study area falls toward the high end of the $\delta^{15}N\text{-}NO_3$ synthetic fertilizer range reported for studies in other regions. The lowest $\delta^{15}N\text{-}NO_3$ value measured in this study was +2.3‰, measured in one of the upgradient wells. Upgradient wells and wells in the Tulare dairy group in which geochemistry did not indicate manure impacts to the groundwater had $\delta^{15}N\text{-}NO_3$ ranges from +2.3 to +7.8‰. A typical range for $\delta^{15}N\text{-}NO_3$ values of synthetic fertilizers has been estimated as -4 to +4‰ (Kendall et al., 2007) and -6 to +6‰ (Xue et al., 2009). This suggests that caution must be used and other geochemical tracers measured when attempting to evaluate whether moderately elevated $\delta^{15}N\text{-}NO_3$ values in the Central Valley indicate the presence of manure-derived in wells.

At four of the seven dairies, $\delta^{18}O$ and $\delta^{2}H$ of the ground water in wells located immediately down-gradient of waste lagoons were distinct in comparison to water from other wells within the same dairy. However, the water isotope values were higher than the other wells for three of the dairies, and distinctly lower than the other wells for one of the dairies, again reflecting the high heterogeneity associated with dairy land uses. The relatively higher water isotope values detected in the lagoon wells most likely reflect evaporative effects within the flushing lanes and open waste lagoons, and water isotopes may be a useful tracer for detecting mixing of waste lagoon water with groundwater.

Further information (publications, related reports, multi-media materials) is available at http://groundwater.ucdavis.edu.

1. Introduction

In California's Central Valley, nitrate contamination of drinking water wells is a significant concern, and there are multiple potential sources of nitrate in this area including septic discharge, synthetic and manure fertilizers, and concentrated animal feeding operations (CAFOs). Dairies represent the majority of animal feeding operations in California, and have been shown to be potential sources of nitrate and salinity (Bacchus and Barile, 2005; Harter et al., 2002) dissolved organic carbon (DOC) (Chomycia et al., 2008), and pathogens (Demirer and Chen 2005, McLeod et al 2003) to groundwater. Within individual dairies, there are different land use areas including barns and freestalls, corral areas, liquid waste lagoons, and fields for forage crops (often fertilized with animal waste, synthetic fertilizer, or both), each of which may have different impacts on the groundwater.

In order to identify sources of contamination to both surface water and drinking water, it is important to determine whether recharge from different land uses or management units within a dairy result in distinct, management unit-specific isotopic and geochemical composition of the recharge water. Each of the land management units within a dairy may experience different conditions contributing to the potential for leaching of nitrate and other solutes to groundwater. In a typical Central Valley dairy, there are barns or freestalls with concrete-lined flush lanes (which empty into the waste lagoons), corral areas, liquid waste lagoons, and fields for forage crops, many – but not all – of which are treated with solid manure, liquid manure, or both. The fields used for forage crops may also be fertilized with synthetic fertilizer containing N in various forms.

Due to the complex mix of land uses across the study areas and within the dairies themselves, tracing the sources of nitrate to any given groundwater monitoring well and determining the processes controlling the nitrate concentration can be very difficult. Stable isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$) and water ($\delta^{18}O$ and $\delta^{2}H\text{-}H_2O$) have been used in many studies to successfully identify dominant sources of nitrate to surface and groundwater, understand mixing of different water sources, and to better understand the dominant processes impacting nitrate concentrations and distributions (reviewed in Kendall 1998, Kendall et al., 2007, and Xue et al., 2009).

The combined use of dual nitrate isotope measurement (^{15}N and $\delta^{18}O\text{-}NO_3$), NO_3 concentrations, and physio-chemical parameters, particularly dissolved oxygen, may be used to distinguish different major nitrate sources. $\delta^{15}N\text{-}NO_3$ can often be used to separate nitrate derived from synthetic fertilizer from nitrate derived primarily from animal (manure) and/or human waste (Wassenaar 1995, Fogg et al., 1998) because of the different processes which function to set the isotopic values of these sources prior to reaching groundwater. Nitrogen in synthetic fertilizers is derived from atmospheric N_2, which has a $\delta^{15}N\text{-}NO_3$ value of 0‰. This value can be altered by various processes during fertilizer manufacturing, and by reactions in the shallow soil, although the $\delta^{15}N\ \text{-}NO_3$ values will remain relatively low. In contrast, nitrogen in animal and human waste is excreted at relatively low isotopic values, but the $\delta^{15}N\ \text{-}NO_3$ in the waste rapidly increases due to ammonia volatilization, which is associated with very high isotopic fractionation factors. The lighter isotopes are preferentially lost in the form of ammonia gas (NH_3), causing the $\delta^{15}N$ -NO_3 of the remaining nitrogen pool to increase (Aravena et al 1993; Wassenaar 1995; Fogg et al., 1998; Sebilo et al., 2006). $\delta^{18}O$-NO_3 can be used to identify contributions of synthetic NO_3 fertilizer (in contrast to synthetic fertilizer with other forms of nitrogen) and atmospheric nitrate as either wet or dry deposition. Synthetic fertilizer in the form of nitrate has distinct elevated $\delta^{18}O$-NO_3 values (approximately +17 to +25‰) because the oxygen in the synthetic nitrate is derived from atmospheric O_2 with a $\delta^{18}O$ value of +23.5‰ (Amberger and Schmidt, 1987, Xue et al., 2009). $\delta^{18}O$-NO_3 values in atmospheric wet and dry deposition will be even higher due to chemical reactions in the atmosphere (Kendall 1998), and were found to range from +63 to +94‰ in a national precipitation study (Elliott et al., 2007).

The isotopic signature of nitrate in groundwater will be controlled by both the isotopic composition of the nitrate source and various physical and biogeochemical reactions including physical mixing between nitrate sources, ammonia volatilization, nitrification, and denitrification. The isotopic compositions of nitrate and water can be used to identify the occurrence of these various processes. Denitrification will preferentially remove the light isotopes of both N and O from the remaining NO_3 pool, resulting in a coupled increase in both the $\delta^{15}N$ and $\delta^{18}O$-NO_3, concurrent with a decrease in the NO_3 concentration (Kendall et al., 2007). A wide range of isotope enrichment factors for both $\delta^{15}N$ and $\delta^{18}O$ has been reported for denitrification, and a linear relationship between $\delta^{15}N$ and $\delta^{18}O$-NO_3 with a slope between 0.5 and 0.8 has been identified as an indicator of denitrification in aquatic systems (Aravena and Robertson, 1998; Xue et al., 2009). Nitrification, in which NH_4 is converted first to NO_2, then to NO_3, will initially result in new nitrate with a $\delta^{15}N$-NO_3 value significantly lighter than the original N source, and will become isotopically identical to the original N source if complete nitrification occurs (Kendall 1998, Xue et al, 2009). The oxygen in the newly formed nitrate is derived from both the water and the dissolved oxygen in the water (Anderson and Hooper, 1983), and therefore correlations between $\delta^{18}O$-NO_3 and $\delta^{18}O$-H_2O can be used to track the contribution of in-situ nitrification to the total nitrate in groundwater.

The isotopic composition of groundwater ($\delta^{18}O$ and $\delta^{2}H$) primarily reflects the original isotopic signature of the precipitation source. Irrigation water from different sources may have distinct water isotope values depending upon the original precipitation source of the water, and evaporation conditions during storage, transportation, and active irrigation. Evaporation will shift the $\delta^{18}O$ and $\delta^{2}H$ of the water towards higher values, and significant evaporation may occur from open waste lagoons on the dairies. Although evaporation rates will be very high in the corral areas of a dairy, the amount of water that can potentially infiltrate from corrals is small compared to lagoon water and other irrigation water, and therefore it is unlikely that evaporative losses from within the corrals could be traced into the groundwater using water isotopes. The relative change in water isotope values within the lagoon will depend on environmental conditions (temperature and humidity), recycling of lagoon water (such as repeat flushing through freestall areas), and the length of time the water remains in the waste lagoon. If the water isotope values of the waste lagoon water become sufficiently higher in comparison to the water used on the rest of the dairy, water isotopes can serve as a tracer of waste lagoon water impacts to shallow groundwater.

Although it is well established that animal waste (manure) typically has significantly higher $\delta^{15}N-NO_3$ values in comparison to synthetic fertilizers, there are many factors which can complicate the prediction of the final nitrate isotope value produced when manure-derived nitrogen leaches into groundwater. Manure handling practices may result in changes in the initial isotopic values, with very fresh manure having lower $\delta^{15}N-NO_3$ values, and manure that has been extensively cycled (such as re-use of waste lagoon water) or allowed to sit for long periods of time will generally have higher $\delta^{15}N-NO_3$ values due to greater loss of NH_3. Processes within the unsaturated zone and groundwater, such as nitrification and denitrification, may also significantly alter both the nitrate isotope composition and the nitrate concentration. Even within a CAFO, it cannot be assumed that all the nitrogen that could potentially leach to groundwater will be derived from manure, since other types of fertilizer may be applied, and there may be existing nitrogen present from previous land uses.

The goals of this study were to 1) determine whether nitrate isotopes could be used to detect manure-derived nitrate within shallow groundwater near the top of the water table directly beneath dairies, 2) determine if various land management practices within dairies resulted in distinct nitrate and water isotope signatures in shallow groundwater, 3) better understand the processes (mixing, nitrification, denitrification) which may significantly alter the nitrate isotope values and nitrate concentrations beneath the dairies, 4) better understand how local conditions such as soil type, depth to groundwater, and length of use as a dairy affect first-encounter groundwater nitrate isotopic compositions and concentrations, and 5) use the information from the dairy monitoring well networks to better constrain the isotopic range of relatively pure manure-derived nitrate in the study region (San Joaquin Valley) for comparison to nitrate isotopic compositions measured within the domestic well survey.

2. Methods

2.1 Project Area, Wells, and Land Use

Seven dairies were chosen for this study, two of which are located in Stanislaus County in the Lower San Joaquin Valley (referred to as Stan dairies for this study), and five of which are located in Kings and Tulare Counties in the Tulare Lake Basin within the San Joaquin Valley (Kings and Tul dairies) (***Table 1***). Detailed descriptions of the geology and hydrology at the Stan dairy sites are given in Harter et al., 2002 and Watanabe et al., 2008, and in other chapters within this report. The Stan dairies are located in a hydrologically open basin underlain by an unconfined aquifer which receives recharge from precipitation and irrigation. Groundwater levels at the Stan sites are typically between 3 to 7 meters below surface, and therefore highly vulnerable to contamination from land use activities. Soils on the Stan dairies consist of loamy sand to sandy soils, originating from alluvial deposits of the Tuolumne, Stanislaus, and San Joaquin Rivers (Harter et al., 2002, Chomycia et al., 2008). The Kings and Tul dairies are located in the hydrologically closed eastern Tulare Lake Basin, and the top of the water table was between 14 and 44 m below surface, with strong seasonal fluctuations in the water table level (up to 10 m) during the course of this study. There are no direct groundwater discharges to surface waters in the area of the Kings and Tul dairies, but there is significant use of groundwater for various purposes including drinking water and irrigation.

Monitoring wells on all the dairies were screened to sample as close to the top of the groundwater table as possible. In the Stan dairies, monitoring wells were screened between 2 and 10 meters due to the shallow groundwater table. Harter et al. 2002 demonstrated that the source area for these shallow wells was typically between 150 m to several hundred meters long and relatively narrow, and therefore the water sampled from these wells is representative of land use immediately upgradient of the well. Due to large fluctuations in the groundwater table (driven primarily by pumping for irrigation water) around the Kings and Tul dairies, some wells were installed with multiple screen depths in order to consistently obtain shallow groundwater samples with seasonally changing groundwater levels, and to better understand water quality dynamics within the upper portion of the groundwater. Multi-level wells were installed on three dairies, two in Kings County, and one in Tulare County. In the Kings and Tul dairies, depths to the top of the well screens ranged from 11.6 to 51.8 meters.

All dairies in this study had similar land management units, although the dairies varied in size and length of time that the land had been used for dairy operations. The land management units on the dairies consisted of corrals and freestalls where the animals were housed, liquid manure storage ponds (waste lagoons), and forage crop fields which were irrigated and fertilized with dry manure and diluted liquid manure from the waste lagoons. Some of the dairies may also have supplemented manure applications to the fields with synthetic fertilizer applications.

Table 1. Summary of dairies and monitoring wells used in this study

Dairy & Location	Total Monitoring Wells (multi-depth?)	Waste Lagoon wells	Corral Wells	Field Wells	Mixed Land Use Wells	Upgradient wells
Stanislaus County						
Dairy 37-42	9	1	2	5	--	1
Dairy 37-39	8	1	5	1	--	1
Kings County						
Dairy 36-15	7 (15 w/ md)	1	1	3	2	--
Dairy 36-19	7 (15 w/ md)	1	3	2	1	--
Tulare County						
Dairy 36-04	3 (6 w/ md)	--	--	2	1	--
Dairy 36-11	4	1	1	1		1
Dairy 36-27	3	1	--	--	2	--
Total	**41 (60 w/ md)**	**6**	**12**	**14**	**6**	**3**

md = multi-depth wells

2.2 Sample Collection

Groundwater samples were collected from monitoring wells installed on two Stanislaus County dairies (Stan dairies), two Kings County dairies, and three Tulare Country dairies (Kings and Tul dairies) in January, April, and September 2008, and March 2009. Prior to sample collection, wells were purged with a stainless steel, variable speed submersible sampling pump (Grundfos) attached to Teflon tubing. While purging, the water was monitored for temperature, electrical conductivity, and dissolved oxygen. Samples were collected after a minimum of five well volumes were removed and field water quality parameters had stabilized. Once purging was complete, field water quality parameters (temperature, Eh, pH, EC, DO) were measured and recorded. Samples for nitrate isotope, nutrient, and chemical analysis were filtered at the time of sample collection by passing the water through a 0.45 micron filter connected to the pump outlet. Samples were kept on ice in coolers during transport, and either stored at 1°C or frozen upon return to the laboratory as appropriate for various analyses. Samples for water isotope analysis were not filtered, and were collected directly into 20mL scintillation vials with Teflon-cone screw caps. Water isotope samples were stored at room temperature prior to analysis. Samples for nitrate and water isotope analysis were delivered to the Menlo Park U.S. Geological Survey Stable Isotope Laboratory, and samples for nutrient and chemical analysis were delivered to the UC Davis Analytical Laboratory (DANR).

2.3 Analytical Methods

2.3.1. Nitrate Isotope Analysis

The Menlo Park U.S. Geological Survey Stable Isotope Laboratory uses the denitrifier method (Sigman et al., 2001, Casciotti et al., 2002) for simultaneous measurement of $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ in which the nitrate is converted quantitatively to N_2O, which is then measured for $\delta^{15}N$ and $\delta^{18}O$ of NO_3 in water samples. Briefly, splits of field-filtered sample water were thawed and aliquots were taken based upon measured nitrate concentrations. The aliquots were injected into sealed vials containing prepared colonies of *Pseudomonas aureofaciens* denitrifying bacteria and triptic soy broth media. The vials were allowed to sit overnight to allow the bacteria to convert all of the nitrate into N_2O gas. The gas in the vials was then introduced via an autosampler into an IsoPrime continuous flow mass spectrometer. The N_2O was analyzed simultaneously for both $\delta^{15}N$ and $\delta^{18}O$, and these values were used to calculate the $\delta^{15}N$ and $\delta^{18}O$ of the nitrate in the original sample. The raw data was corrected for instrument drift, size linearity, blank contribution, and fractionation effects by using repeated analyses of five different standards (international standards USGS-34, USGS-35, and IAEA-N3; internal standards 9707 and WEN-D, a standard containing nitrate with a heavy $\delta^{18}O\text{-}H_2O$ spike, and a blank vial with media but no added nitrate). All samples were prepared and analyzed in duplicate on the same day, and then analyzed a third or more times until the precisions met laboratory QAQC standards. The $\delta^{15}N$ and $\delta^{18}O$ values are reported in ‰ relative to the Air and VSMOW standards, respectively.

2.3.2. Water Isotope Analysis

Both $\delta^{18}O$ and $\delta^{2}H$ of water were measured using laser spectroscopy on a Los Gatos Research DLT-100 Liquid-Water Isotope Analyzer, using a modification of the method described in Lis et al. (2008). This instrument uses near infrared absorption spectroscopy to determine the isotopic composition of water samples. 2mL aliquots of sample were loaded into 2mL glass vials with split-cap septa and placed into the auto-sampler. For each sample, 4 to 6 sequential 1.2 µL aliquots of sample were injected into the instrument through the auto-sampler. Two internal water standards were measured after every 5th sample. The results for the first aliquot were discarded to eliminate any memory effect, the remaining aliquots were examined for additional outliers, and the acceptable aliquots were then averaged and corrected for permil scale linearity. Each sample was analyzed in duplicate, on different days, and if the repeats didn't match, the samples were reanalyzed again. Precision of this method based on repeated standard measurements is <0.2 ‰ for $\delta^{18}O$ and <1.0‰ for $\delta^{2}H$.

2.3.3. Nutrient and Chemical Analysis

Samples were analyzed for a large suite of nutrient and chemical concentrations at the UC Davis Analytical Laboratory (DANR). Complete analytical methods are provided on the DANR website (http://anlab.ucdavis.edu/), and a summary of the analytical methods and quality control methods is provided in Chapter 1 of this report.

2.3.4. Statistical Analysis

Descriptive statistical analyses were performed using the software package Tibco Spotfire S+ (Tibco, 2008). Since the data collected from a single well on different collection dates are not statistically independent, average values for each well were calculated from all available sampling dates for some evaluations. Results from each individual sampling event were used in the correlations analysis and comparison of group medians, because it was possible for the water source to any given monitoring well to change over time, and therefore averaging could have obscurde isotopic or geochemical relationships in wells with changing water sources. Due to changes in accessibility and fluctuating water tables, some wells could not be sampled on all four dates, and therefore data from some wells is either from a single sampling event, or an average of two or three sampling events. Relationships between isotope values and physical and geochemical parameters were examined using Spearman's Rank Correlation because of the relatively small size of the data set and non-normal distribution of many of the parameters. For wells with multiple screening depths, only data from the shallowest screen depth within the water table at the time of sampling was used in the statistical comparisons, in order to best represent first-encounter groundwater. For the correlation analyses, the Kings dairies were treated as a separate group from the Tul dairies because the larger number of individual monitoring wells on the Kings dairies in comparison to the Tul dairies and some strong geochemical differences between the two groups would cause the correlation patterns of the Kings dairies to dominate the combined dataset. For the land use analyses, data from the Kings and Tul dairies were combined due to their close geographic proximity and the limited number of total wells available to represent each land use.

3. Results and Discussion

3.1. Nitrate isotope distributions

Within this chapter "dairy monitoring wells" refers to all monitoring wells except for the upgradient wells (located on both Stan dairies and one Tul dairy). Results for the upgradient wells will be identified specifically as "upgradient" in this report and were not included in any of the statistical analyses.

In the dairy monitoring wells, $\delta^{15}N\text{-}NO_3$ ranged from +2.9 to +49.4 ‰ and $\delta^{18}O\text{-}NO_3$ ranged from -3.3 to +19.2 ‰ (***Table 2***). In the three upgradient wells, $\delta^{15}N\text{-}NO_3$ ranged from +2.7 to +11.6 ‰ and $\delta^{18}O\text{-}NO_3$ ranged from -3.8 to +7.8 ‰. Median $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ were highest for the Stan dairies and lowest in the Tul dairies (***Figure 1***). Both the Stan and Kings dairy monitoring wells showed wide ranges of both $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ (***Figure 2a&b***). $\delta^{15}N\text{-}NO_3$ values above +10‰ are generally considered to be clearly indicative of animal waste (in contrast to fertilizer or natural soil nitrate) unless significant denitrification is the cause of the higher $\delta^{15}N\text{-}NO_3$ values (Kendall et al., 2007). All of the measurements made in the Stan dairy wells showed $\delta^{15}N\text{-}NO_3$ values above +10‰, with a mean $\delta^{15}N\text{-}NO_3$ value for all the Stan dairy wells of +19.8‰. $\delta^{15}N\text{-}NO_3$ in the Stan dairy wells was not significantly correlated to either NO_3 concentration or dissolved oxygen saturation, suggesting that the high $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ values reflect a nitrate source dominated by manure, rather than in-situ denitrification.

Tul dairies 36-04 and 36-11 both had small, low ranges of $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ values, very similar to the ranges measured for the upgradient wells (***Figure 3***). The nitrate isotope patterns in the 36-04 and 36-11 wells suggest that the nitrate is predominantly derived from synthetic fertilizers, because natural soil nitrogen cannot account for the elevated concentrations of NO_3 in these wells (***Figure 4***). Tul Dairy 36-27 showed elevated $\delta^{15}N\text{-}NO_3$ values in comparison to the other Tul dairies, but did not show $\delta^{15}N$ and $\delta^{18}O\text{-}NO_3$ values extending as high as some of the measurements made in the Kings dairies. $\delta^{15}N\text{-}NO_3$ values in Tul dairy 36-27 wells were negatively correlated to NO_3 concentration (Spearman's rho = -0.82, $p \leq 0.01$, linear correlation $R^2 = 0.59$) which is consistent with the effects of denitrification. However, NO_3 concentration and dissolved oxygen saturation were not correlated within the 36-27 wells, suggesting that the $\delta^{15}N\text{-}NO_3$ distribution could be caused by a combination of denitrification and mixing between different nitrate sources. Dairy 36-27 has been in operation as a dairy for less than ten years, but has much shallower depths to first encounter groundwater than the rest of the Tulare and Kings County dairies (***Figure 5***), which could make it more vulnerable to faster downward leaching of any newly-applied nitrogen source, including manure.

Table 2. Means, standard deviations, medians (in parentheses), and ranges of nitrate isotope compositions for the dairy monitoring wells. In multi-depth wells, only the values from the uppermost screened interval containing groundwater were included in the analyses. All values reported as per mil (‰).

Group	$\delta^{15}N\text{-}NO_3$	Range $\delta^{15}N\text{-}NO_3$	$\delta^{18}O\text{-}NO_3$	Range $\delta^{18}O\text{-}NO_3$
All	+14.6±8.5 (+14.1)	+2.9 to +49.4	+4.9±5.0 (+4.8)	-3.3 to +19.2
Stan	+19.8 ±5.4 (+19.7)	+11.1 to +31.8	+8.2± 4.4 (+7.8)	-1.4 to +19.2
Kings	+14.0 ±9.7 (+12.9)	+4.1 to +49.4	+4.3± 4.8 (+3.8)	-2.4 to +18.5
Tul	+7.8 ±3.6 (+6.9)	+2.9 to +16.2	+1.0 ±2.6 (+0.8)	-3.3 to +5.3
Stan 37-42	+18.5 ±5.5 (+16.5)	+11.1 to +30.0	+5.8 ±3.6 (+6.6)	-1.4 to +12.9
Stan 37-39	+21.4 ±5.0 (+20.6)	+14.1 to +31.8	+11.2 ±3.3 (+11.5)	+5.9 to +19.2
Kings 36-15	+13.2 ±13.4 (+7.5)	+4.1 to +49.4	+3.7 ±6.1 (+1.3)	-2.4 to +18.5
Kings 36-19	+14.8 ±3.4 (+15.6)	+8.8 to +21.7	+5.0 ±3.0 (+5.5)	-1.8 to +10.3
Tul 36-04	+5.4 ±1.4 (+5.2)	+3.2 to +7.6	+0.0 ±1.5 (+0.5)	-3.1 to +2.4
Tul 36-11	+6.0 ±2.4 (+6.1)	+2.9 to +8.7	-1.1 ±2.2 (-1.3)	-3.3 to +4.3
Tul 36-27	+11.6 ±2.9 (+11.4)	+6.8 to +16.2	+3.7±1.2 (+4.0)	+1.3 to +5.3

The three upgradient monitoring wells sampled in this study showed consistently lower δ^{15}N-NO_3 values in comparison to all of the Stan dairy wells (***Figure 6a***), although the nitrate concentrations in the upgradient wells fell within the range measured for the Stan dairy wells (***Figure 6b***). This indicates that although manure-derived nitrate was the dominant source of nitrate in the dairy monitoring wells, synthetic fertilizer-derived nitrate is also present in the area and contributed significantly to local nitrate distribution in first-encounter groundwater in all of the upgradient wells.

3.2. Relationships between nitrate isotopes and other parameters

Within the full dairy monitoring well data set, δ^{15}N and δ^{18}O-NO_3 were strongly positively correlated (Spearman's rho = 0.81, $p < 0.001$), indicating coupled behavior of the two isotopes. This can be caused when nitrate concentrations are dominated by two sources with distinct δ^{15}N and δ^{18}O of NO_3 values, or by biogeochemical processes such as denitrification which caused coupled changes in both the δ^{15}N and δ^{18}O-NO_3 as NO_3 was removed. This observed relationship was consistent within each geographic group of wells (Stan, Kings, and Tul groups). Within the entire dataset, δ^{15}N-NO_3 was negatively correlated to dissolved oxygen, which is consistent with denitrification at low oxygen levels causing high δ^{15}N-NO_3 values. However, when the wells were divided by county groups, this relationship was only moderately positive and statistically significant (spearman's rho = -0.63, $p< 0.001$) for the Stanislaus dairies. Within the entire dataset, there was no correlation between δ^{15}N-NO_3 and δ^{18}O-NO_3 but there was a moderate negative correlation between these two parameters within the Stanislaus dairy group (Spearman's rho = -0.46, $p< 0.001$). These patterns suggest that denitrification plays a more important role in controlling nitrate concentrations and isotopic compositions beneath the Stanislaus dairies in comparison to the other dairies.

Across the entire dataset and within each county dairy group, δ^{15}N-NO_3 was weakly to moderately positively correlated to both TKN and DOC concentrations, which suggests that nitrate with high δ^{15}N-NO_3 values was associated with a source of organic carbon and nitrogen, consistent with leaching of manure.

Table 3. Summary of major parameters correlated with $\delta^{15}N\text{-}NO_3$, with Spearman's rho correlation coefficients. This analysis does not include trace metals run by ICPMS. All parameters with a reported coefficient are statistically significant at $p \leq 0.05$.

parameter	**All wells**	**Stan**	**Kings**	**Tul**	**Comments**
$\delta^{18}O\text{-}NO_3$	0.81	0.64	0.80	0.61	Consistent across well groups
NO_3	--	--	-0.46	--	
Dissolved O_2	-0.59	--	-0.63	-0.25	
Depth to water	-0.65	-0.44	--	-0.76	
EC (uS/cm)	--	--	-0.26	0.55	
$\delta^{18}O\text{-}H_2O$	0.39	--	-0.27	0.28	
$\delta^{2}H\text{-}H_2O$ offset	-0.39	--	--	-0.30	
TKN	0.63	0.57	0.28	0.43	Consistent across well groups
$NH_4\text{-}N$	0.31	0.46	--	--	
DOC	0.74	0.54	0.50	0.55	Consistent across well groups
Ca (mg/L)	--	0.35	-0.49	--	
Mg (mg/L)	0.46	0.25	--	0.46	
Na (mg/L)	--	--	--	0.62	
K	--	--	-0.26	--	
HCO_3 (meq/L)	0.52	0.28	--	0.25	
Cl (mg/L)	--	--	-0.51	0.75	
SO_4 (mg/L)	--	--	-0.35	0.72	

Boron (mg/L)	0.51	--	--	--	
P soluble (mg/L)	0.59	--	0.40	**	
Mn (μg/L)	0.77	0.77	0.63	--	
Fe (mg/L)	--	0.37	--	**	
Cu (μg/L)	0.63	0.31	0.41	--	
Se (μg/L)	--	--	-0.79	0.31	

-- no statistically significant correlation (Spearman's rho <0.25, or p >0.05)

** parameter was either entirely or mostly below detection limits so no correlation analysis could be performed

3.3 Nitrate isotopes and land uses within dairies

All of the dairy land uses (waste lagoons, corrals, manured fields) showed wide ranges of nitrate concentrations and isotope values. There were no consistent differences in nitrate isotope values between the corral and manured field wells (***Figure 7 & 8***). Monitoring wells downgradient from the waste lagoons showed the greatest variability in $\delta^{15}N\text{-}NO_3$ of any of the land use types, with $\delta^{15}N\text{-}NO_3$ values ranging from +3.2 to +49.4‰. Water isotopes in some of the waste lagoon wells were distinctive in comparison to the other wells within an individual dairy. The waste lagoon wells on dairies Stan 37-39 and Kings 36-15 had consistently heavier water isotope values in comparison to other wells on each dairy (***Figure 9***), which could reflect a different water source, or more likely, increased evaporation of the lagoon water in comparison to the other water used on the dairies. The lagoon well on Tul 36-11 also had heavier water isotope values in comparison to the other 36-11 wells, however, this lagoon well was only sampled once (the well was dry during the other sampling events), and therefore it is not known if this was a consistent trend. In Tul 36-27, the lagoon well had consistently lower water isotope compositions compared to the other 36-27 wells, indicating that the waste lagoon water was consistently distinct from the water infiltrating from the other land uses. Although the waste lagoon wells on Stan 37-42 and Kings 36-19 did not have distinct water isotope values in comparison to the other wells on each dairy, other geochemical parameters were distinct for these lagoon wells. This suggests that while water isotopes can be useful for identifying waste lagoon influences to shallow groundwater, lagoon water does not always carry an isotopically distinct signal.

Table 4. Means, standard deviations, and medians (in parentheses) of nitrate isotope compositions for the dairy monitoring wells grouped by primary land use for the estimated well recharge area. In multi-depth wells, only the values from the uppermost screened interval containing groundwater were included in the analyses. Kings and Tul wells were grouped for analysis due to the small number of wells for each land use within the Tul dairies.

Group	**# of wells**	**$\delta^{15}N-NO_3$**	**$\delta^{18}O-NO_3$**	**$\delta^{18}O-H_2O$**	**$\delta^{2}H-H_2O$**
Management Unit-All Dairies					
Corral	16	14.3±5.6	5.6±4.3	-10.8±1.3	-82.0±8.1
		(+14.7)	(+5.5)	(-10.6)	(-80.2)
Field	15	12.6±7.0	3.0±4.8	-10.7±0.7	-80.8±4.1
		(+10.2)	(+1.4)	(-10.8)	(-81.9)
Lagoon	7	19.5±15.8	6.2±6.7	-10.6±1.9	-77.6±12.0
		(+15.5)	(+4.4)	(-10.6)	(-80.7)
Upgradient	3	5.8±2.6	3.3±4.3	-10.5±1.0	-79.3±6.4
		(+4.6)	(+5.0)	(-10.4)	(-78.8)
Management Unit-Stan only					
Corral	7	17.5±4.5	8.9±3.5	-9.8±0.5	-75.9±3.0
		(+15.6)	(+8.6)	(-9.9)	(-76.1)
Field	6	19.8±5.3	6.0±5.7	-9.9±0.4	-76.4±2.3
		(+20.0)	(+6.9)	(-9.9)	(-76.7)
Lagoon	2**	28.8±1.2	11.9±0.7	-7.9±2.3	-64.0±14.3
		(+28.8)	(+11.9)	(-7.8)	(-64.3)
Upgradient	2	6.5±3.0	5.7±2.7	-9.9±0.6	-75.5±3.7
		(+5.8)	(+6.9)	(-9.9)	(-75.3)
Management Unit-Kings & Tulare only					
Corral	9	12.2±5.4	3.4±3.3	-11.3±1.2	-85.9±7.9

		(+13.3)	(+3.8)	(-11.6)	(-86.2)
Field	9	8.0±2.8	1.0±2.8	-11.2±0.4	-83.8±1.8
		(+7.3)	(+0.48)	(-11.2)	(-83.9)
Lagoon	5	18.2±16.5	5.4±6.7	-10.8±1.0	-82.3±6.3
		(+14.0)	(+4.3)	(-10.9)	(-81.6)
Upgradient	1	4.3±0.2	-1.7±1.6	-11.7±0.4	-87.0±0.6
		(+4.3)	(-1.2)	(-11.7)	(-87.0)

**Both 37-42 and 37-39 have lagoon wells, but only the lagoon well on 37-39 contained enough nitrate for isotope analysis. Water isotope analysis was completed for both wells.

3.4 Isotopes show rapid response to major land use changes

On Dairy 36-04, manure applications began on one field during the course of this study, and both the nitrate isotopes and nitrate concentrations showed a rapid response (***Figure 10a & b***). Manure applications on the field where nested MW6 was located started sometime in the spring of 2008. Prior to the start of the manure applications, well MW6 already had elevated NO$_3$-N concentrations, but the δ^{15}N-NO$_3$ values were between +4.5 and +5.5‰, lower than those measured in MW5, and consistent with nitrate dominated by synthetic fertilizers. The higher NO$_3$-N concentrations could result from differences in soil types within the unsaturated zone, since higher sand contents can lead to more rapid infiltration and therefore faster nitrate movement with less natural attenuation (such as unsaturated zone denitrification). Between the synoptic sampling dates of April 2008 and September 2008, a distinct increase in δ^{15}N-NO$_3$ was observed, and NO$_3$-N concentrations increased as well. δ^{15}N-NO$_3$ in all depths of MW6 increased to between +6.8 and +7.6‰, which does not indicate that manure-derived nitrate was the primary nitrate source to the water, but most likely reflects mixing between synthetic fertilizer-derived nitrate and manure-derived nitrate in the shallow groundwater. The clear and rapid response in both NO$_3$-N concentrations and δ^{15}N-NO$_3$ demonstrates that nitrate isotopes can be a powerful tool for monitoring changes in nitrate sources to individual wells over time.

3.5 Comparison to surface water isotope compositions

Due to the mix of irrigation sources used both seasonally and inter-annually by the dairies, it is very difficult to determine whether or not surface water measurements might be representative of the irrigation water composition. We were not able to obtain stable isotope and nutrient data for surface water in the region of the Kings and Tulare County dairies (primarily Kings River water). The Kings and Tul dairies use a combination of surface and groundwater for irrigation, and it would therefore require a dedicated nutrient, isotope, and geochemical study to fully characterize the composition of irrigation water to these dairies.

In order to provide a basic comparison between the isotope composition of the shallow groundwater sampled in the dairy monitoring wells and some regional surface water, we used data collected from the San Joaquin River and many tributaries as part of the CALFED DO TMDL & PIN700 project (Kendall et al., 2008). In the CALFED DO TMDL & PIN700 projects, samples were collected approximately monthly between 2005 and 2007 and analyzed for a wide range of physio-chemical, nutrient, stable isotope, and geochemical parameters. ***Figure 11*** shows the nitrate isotope composition of the dairy monitoring wells (averages for each well) in comparison to the nitrate isotope composition of surface waters collected from the Stanislaus, Merced, and Tuolumne Rivers. The Stan and Kings dairy wells showed elevated δ^{15}N and δ^{18}O-NO_3 values in comparison to the surface water values, while the Tul dairy wells had lower median δ^{15}N and δ^{18}O-NO_3 values (***Figure 12***). Average NO_3-N (mg/L) concentrations in the Stanislaus, Merced, and Tuolumne Rivers were 0.23± 0.13, 1.47 ±1.37, and 1.09± 0.75, respectively during the 2005 to 2007 study period, much lower than the mean and median NO_3-N concentrations for the Stan, Kings, or Tul dairy monitoring well groups.

3.6 Changes in nitrate and water isotope compositions with depth

For most of the multi-level wells, changes with depth in δ^{15}N and δ^{18}O-NO_3 were fairly small, while changes in both nitrate isotopes between sampling events for a single well were much larger. Multi-level wells on dairy 36-15 showed very little change in δ^{15}N-NO_3 with depth, except for the lagoon well (MW2), which showed a 7.8‰ decrease between the well screened at 29.3 m and the deeper well screened at 35.1 m. Samples collected from the upper screen depth during the different sampling events were within 1.6‰ of each other. Water isotope measurements indicate that there was no change in water source to the upper screen between sampling events, but that the water sampled at the deeper screen is isotopically distinct. On dairy 36-15, the δ^{15}N-NO_3 values measured in each well changed very little between the different sampling events. In MW4 on dairy 36-15, a field well, NO_3-N concentrations showed fairly large changes with depth, but there was very little change with depth in δ^{15}N-NO_3, and fairly small changes in δ^{18}O-NO_3. This suggests that the primary nitrate source was not changing significantly with depth, but that the total amount of nitrate from that source was changing. The δ^{15}N-NO_3 values for MW4 ranged between +5.5‰ and +8.9‰, suggesting a primarily synthetic-fertilizer derived nitrate source, or possibly a mixed synthetic fertilizer and manure source. On dairy 36-19, large changes with depth in δ^{15}N and δ^{18}O-NO_3 were observed in MW2 and MW7 during different events, and there were large differences in δ^{15}N-NO_3 in the same depths between different sampling events for monitoring wells 1, 2, 3, 6, and 7 (MW 5 and MW9 showed very little change between sampling events). In dairy 36-04, δ^{15}N-NO_3 showed very little change with depth for the three sampling events where multi-level well samples were collected for isotope analysis. Dairy 36-05 MW5 was sampled at two depths during the April 2008 sampling, and showed a 0.4‰ decrease with depth, which is within analytical error for field duplicate samples. MW6 was sampled at two depths in January 08, and at three depths in Sept 08, and both these events showed δ^{15}N-NO_3 variation less than field duplicate analytical error. However, there were distinct overall shifts in the $\delta^{15}N\text{-}NO_3$ (up to 2.9‰ for MW5) between the different sampling events.

4. Summary of Findings and Conclusions

Median $\delta^{15}N$ and $\delta^{18}O$-NO_3 were highest for the Stan dairies and lowest in the Tul dairies. Both the Stan and Kings dairy monitoring wells showed wide ranges of both $\delta^{15}N$ and $\delta^{18}O$-NO_3, and all of the measurements made in the Stanislaus dairy wells showed $\delta^{15}N$-NO_3 values above +10‰, with a mean $\delta^{15}N$-NO_3 value for all the Stanislaus dairy wells of +19.8‰. $\delta^{15}N$-NO_3 in the Stanislaus dairy wells was not significantly correlated to either NO_3 concentration or dissolved oxygen saturation, suggesting that the high $\delta^{15}N$ and $\delta^{18}O$-NO_3 values reflect a nitrate source dominated by manure, rather than in-situ denitrification.

Tul dairies 36-04 and 36-11 both had small, low ranges of $\delta^{15}N$ and $\delta^{18}O$-NO_3 values, very similar to the ranges measured for the upgradient wells. The nitrate isotope patterns in the 36-04 and 36-11 wells suggest that the nitrate is predominantly derived from synthetic fertilizers. Changes in both the $\delta^{15}N$-NO_3 and NO_3-N concentrations during the course of the study in one well (MW-6) on Tul dairy 36-04 appeared to show increasing inputs of manure-derived nitrate between April 2008 and Sept 2008 sampling events.

Tul Dairy 36-27 showed elevated $\delta^{15}N$-NO_3 values in comparison to the other Tul dairies, but did not show $\delta^{15}N$ and $\delta^{18}O$-NO_3 values extending as high as some of the measurements made in the Kings dairies. $\delta^{15}N$-NO_3 values in Tul dairy 36-27 wells were negatively correlated to NO_3 which is consistent with the effects of denitrification. However, NO_3 concentration and dissolved oxygen saturation were not correlated within the 36-27 wells, suggesting that the $\delta^{15}N$-NO_3 distribution could be caused by a combination of denitrification and mixing between different nitrate sources.

Upgradient wells had lower $\delta^{15}N$-NO_3 values in comparison to other wells within an individual dairy, but did not have lower $\delta^{18}O$-NO_3 values or nitrate concentrations. The upgradient wells showed a fairly wide range of $\delta^{15}N$-NO_3 values, and it is unclear if this reflects partial denitrification or other biological processing of an entirely synthetic-fertilizer dominated nitrate isotope signal, or if there is a small contribution of manure-derived nitrate (either from dairy operation or the application of organic fertilizers to other agricultural land use) present even in the upgradient groundwater.

All of the dairy land uses (waste lagoons, corrals, manured fields) showed wide ranges of nitrate concentrations and isotope values. There were no consistent differences in nitrate isotope values between the corral and manured field wells. Monitoring wells downgradient from the waste lagoons showed the greatest variability in $\delta^{15}N$-NO_3 of any of the land use types, with $\delta^{15}N$-NO_3 values ranging from +3.2 to +49.4‰.

Evaporative signature of water isotopes occurred in wells where other geochemical tracers indicated lagoon water, but in two of the lagoon wells where no evaporative signal was observed, other geochemical constituents indicated the presence of lagoon water. Therefore, an evaporative water isotope signal in comparison to other wells within a single dairy appeared to be strongly indicative of lagoon water, but the lack of an evaporative signal did not preclude the presence of lagoon waste impacts to groundwater.

5. Figures

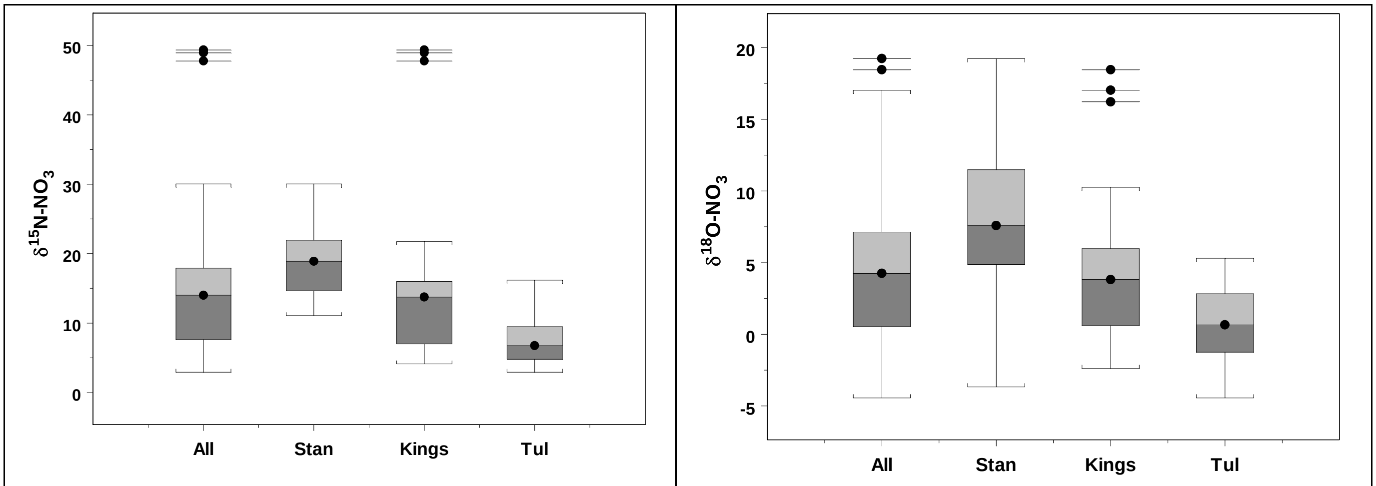

Figure 1a. Distributions of δ^{15}N and δ^{18}O-NO$_3$ for all monitoring wells, and for the different county groups based on all sampling events. One well on Kings dairy 36-15 immediately downgradient of a waste lagoon consistently had extremely high δ^{15}N and δ^{18}O-NO$_3$ values, very low NO$_3$ concentrations, and low dissolved oxygen levels, all consistent with significant denitrification.

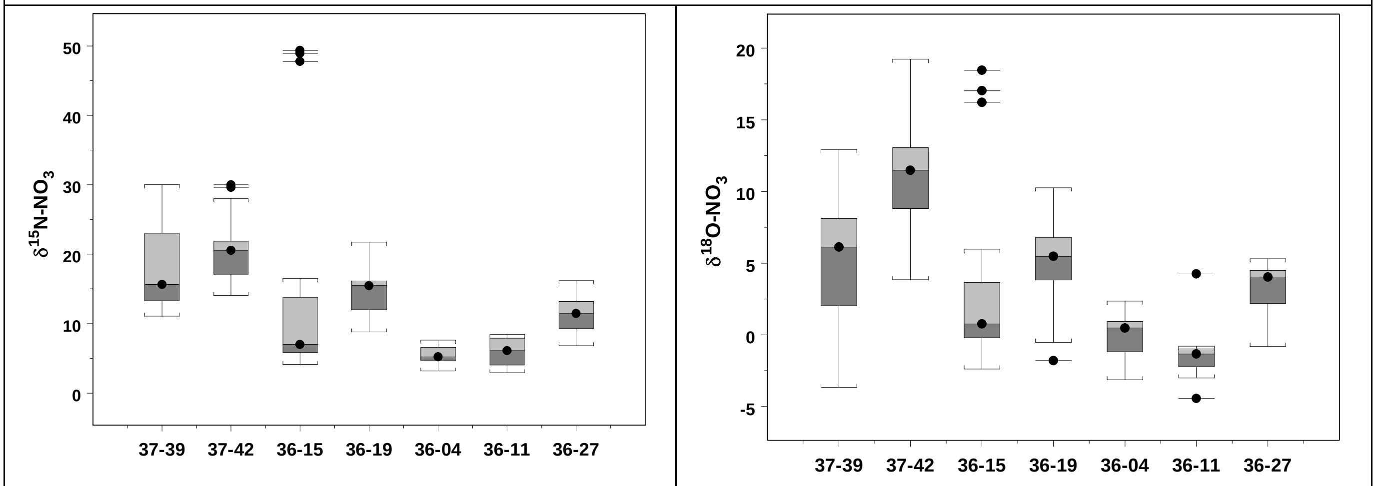

Figure 1b. Distributions of δ^{15}N and δ^{18}O-NO$_3$ for all monitoring wells within the individual dairies. Dairy 36-27 has a wider δ^{15}N and δ^{18}O-NO$_3$ range in comparison to the other Tulare Country dairies, and a higher median δ^{15}N -NO$_3$. This may be due to the shallower water table at Dairy 36-27 in comparison to Dairies 36-04 and 36-11.

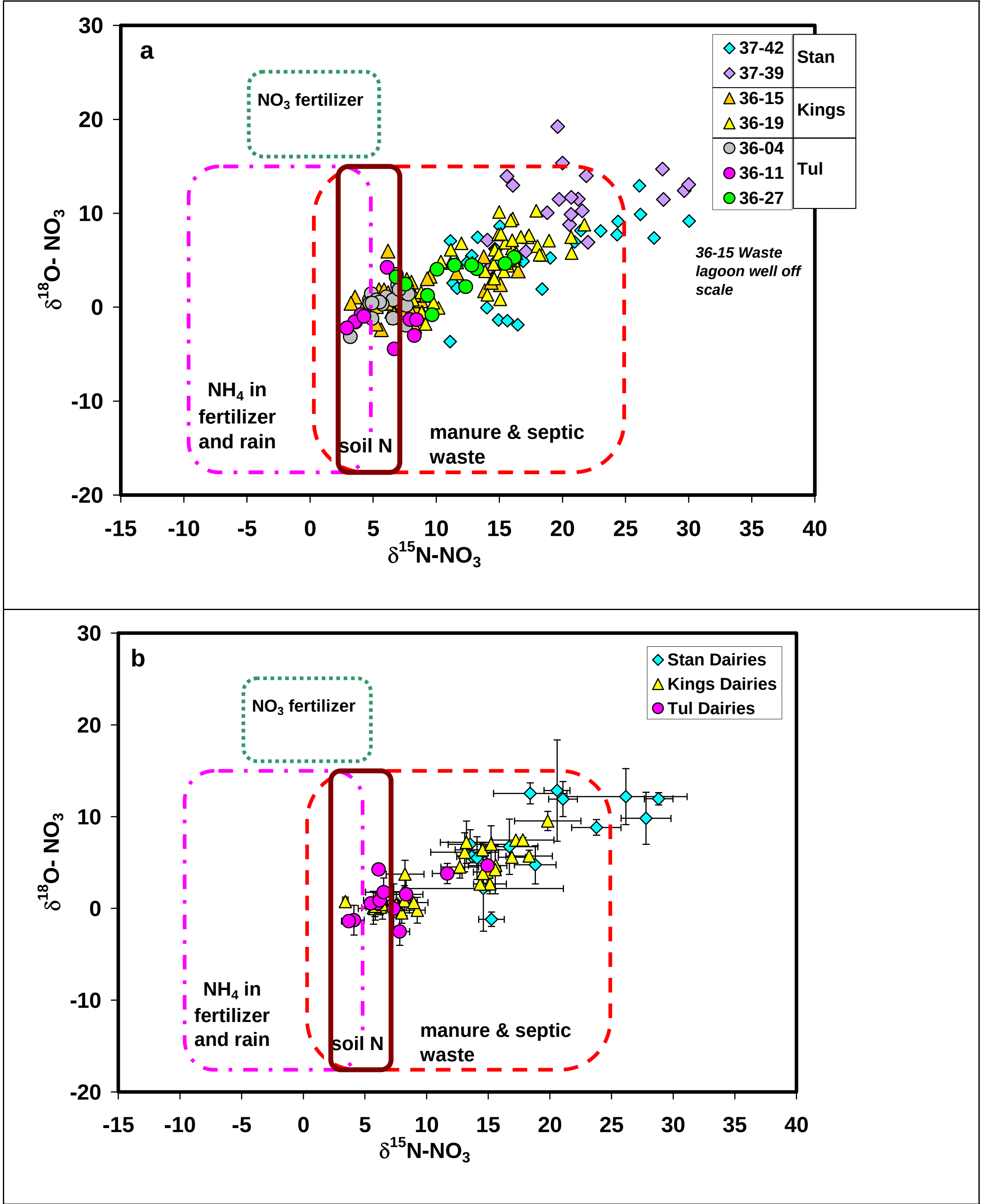

Figure 2. a) δ^{15}N and δ^{18}O-NO$_3$ values for all samples collected from the monitoring wells on the seven dairies. b) δ^{15}N and δ^{18}O-NO$_3$ averages for each well within the different country groups. Error bars represent standard deviations of the synoptic samples collected from the individual well. All Stanislaus dairy wells had fairly high δ^{15}N and δ^{18}O-NO$_3$ values consistent with manure-derived nitrate. Most of

the Tul dairy well samples fell within a much lower range, suggesting much higher contributions of fertilizer-derived nitrate.

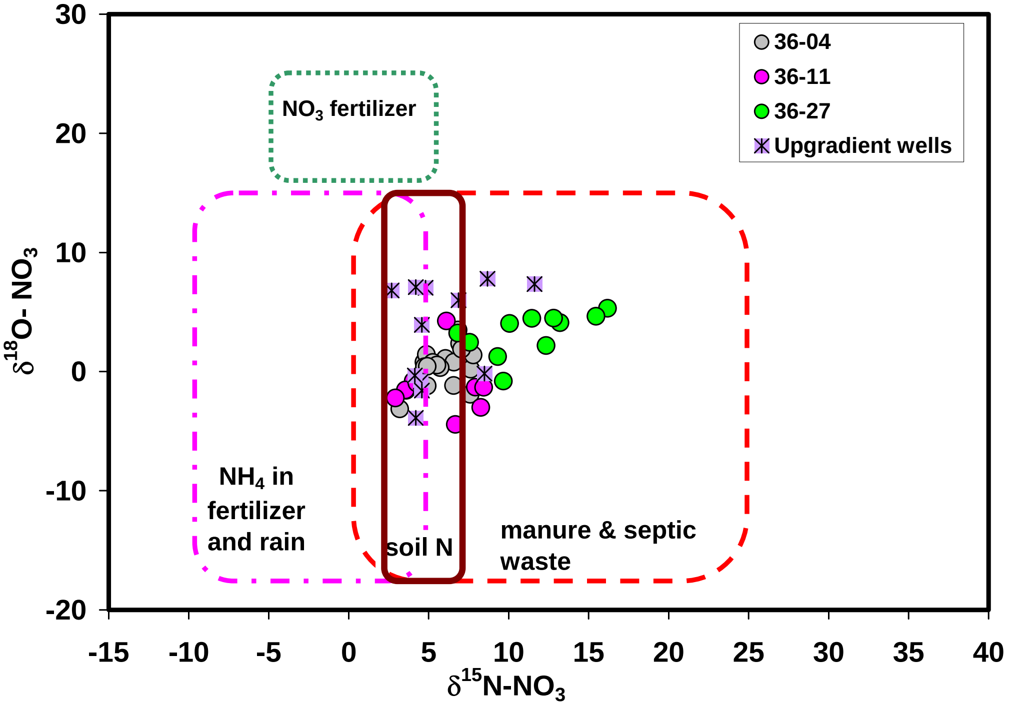

Figure 3. δ^{15}N and δ^{18}O-NO_3 values measured for all sampling events in the Tul dairy well and the three upgradient wells. The upgradient wells were located on each of the Stan dairies and one of the Tul dairies. Wells on dairy 36-27 have a wider range and higher δ^{15}N-NO_3 values in comparison to the other Tul dairies.

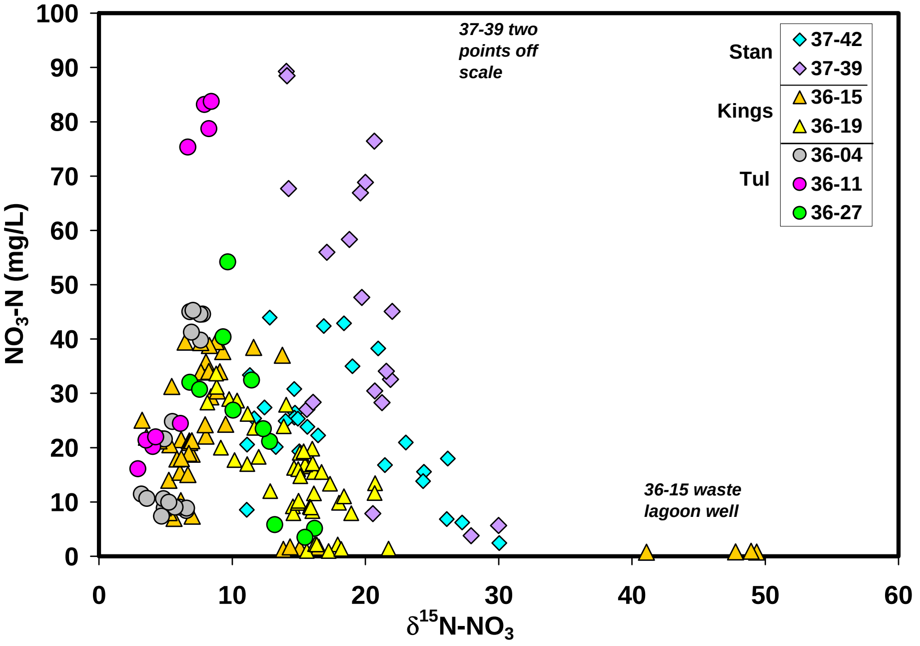

Figure 4. δ^{15}N-NO_3 values and NO_3 concentrations for all sampling events.

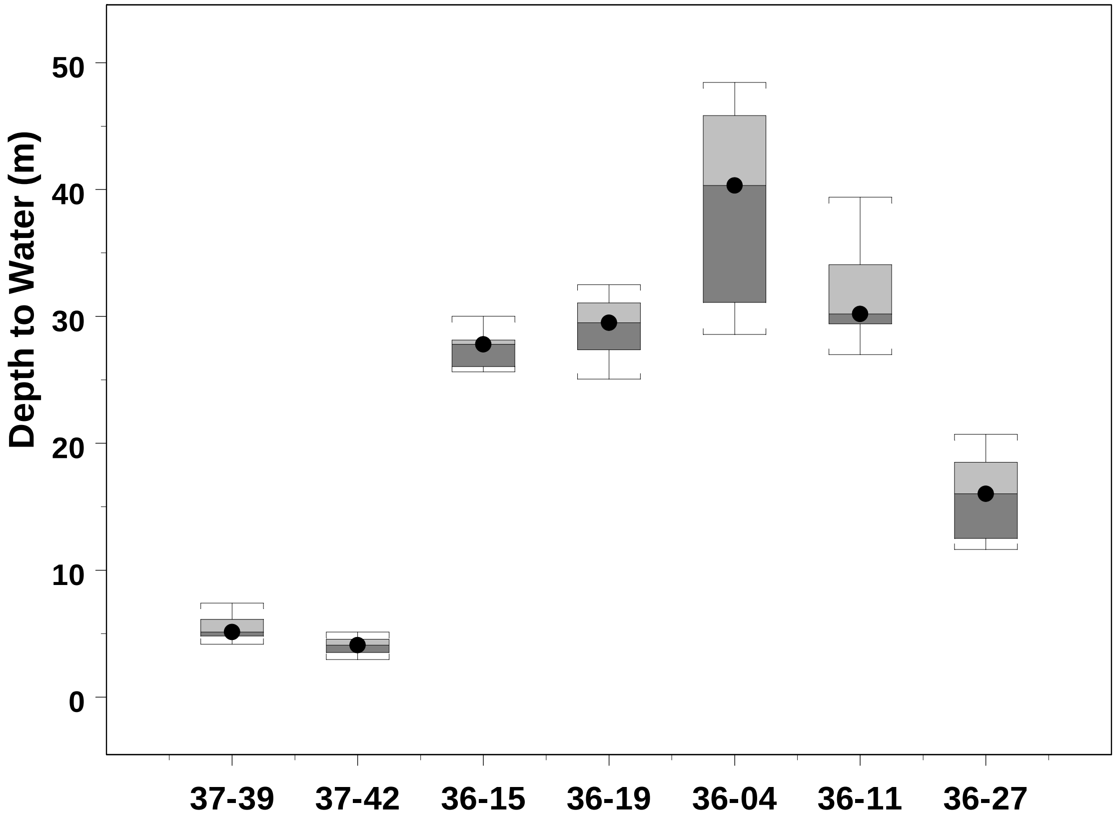

Figure 5. Depth to water in monitoring wells (upper screened interval only for multi-depth wells) in all the dairies. Although Dairy 36-27 is a very young dairy, the much shallower depths to water in comparison to the other Kings and Tulare County dairies may increase the vulnerability to manure-derived nitrate impacts.

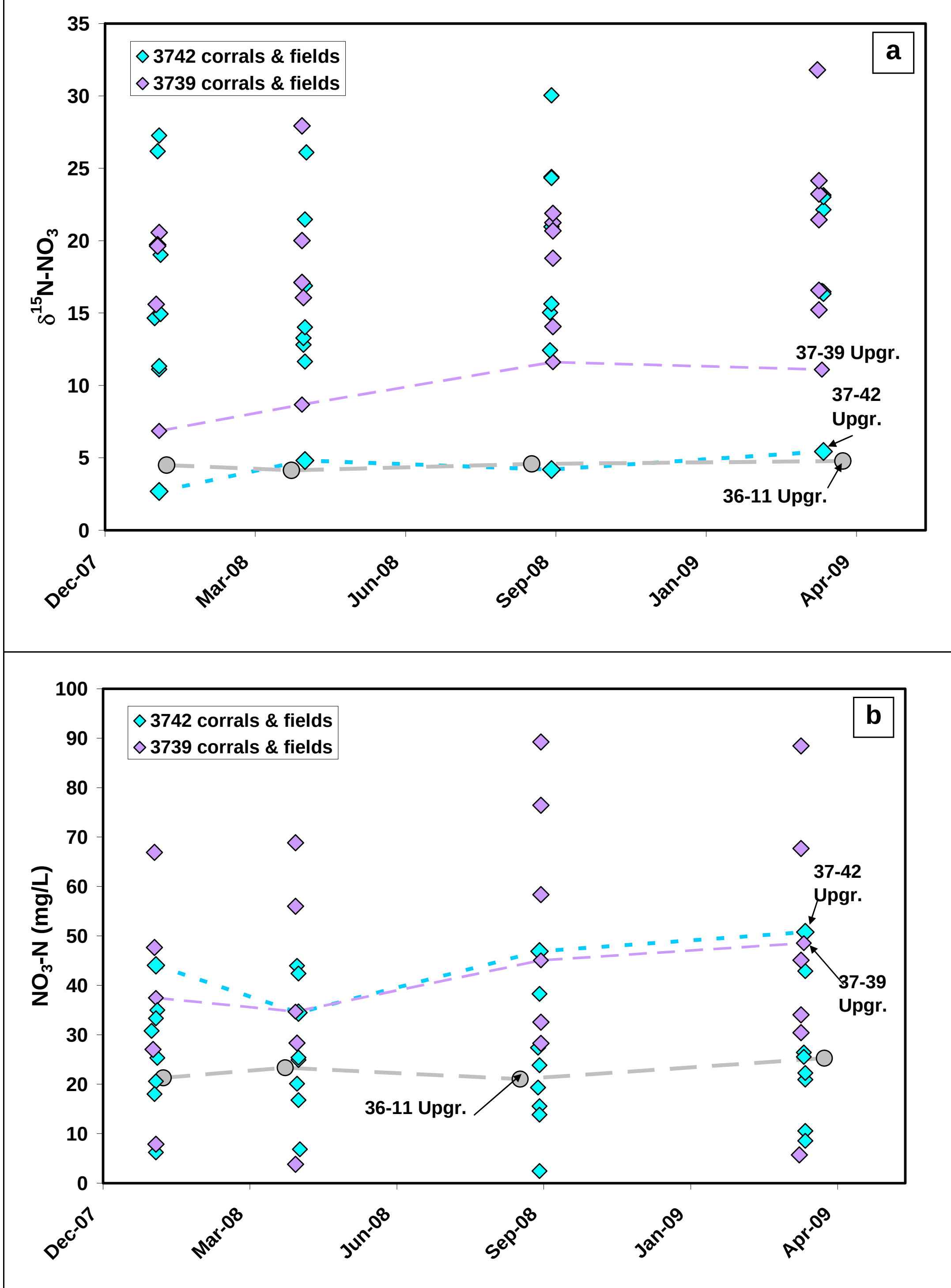

Figure 6. a) Distribution of δ15N-NO3 values in the Stan dairy wells in comparison to the three upgradient monitoring wells over time. b) Distribution of NO3-N concentrations in the dairy monitoring wells and upgradient wells over time. The δ15N-NO3 values clearly show that the

upgradient wells have a different dominant source of nitrate in comparison to the Stan dairy wells which also contributes high concentrations of nitrate to first encounter groundwater.

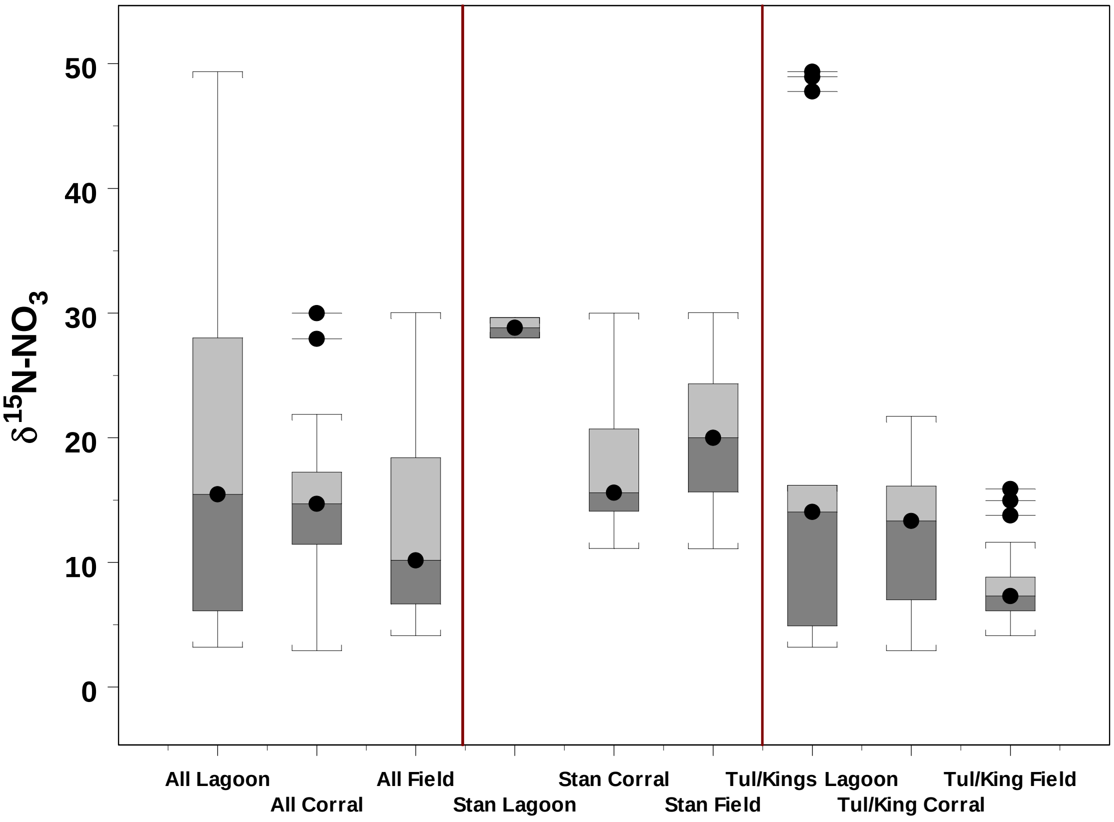

Figure 7. Box plot of $\delta^{15}N\text{-}NO_3$ values for the major dairy land use categories used in this study. Distribution of $\delta^{15}N\text{-}NO_3$ for the entire dataset is shown in the left panel, followed by the distributions for the Stan dairies and Tul/Kings dairies. Data for the Tul & Kings dairies was combined for the land use analysis because the Tul dairies alone did not have enough wells representing the different land use categories to examine general trends. One of the two lagoon wells in the Stan dairy group could not be analyzed for nitrate isotopes due to non-detectable NO_3-N concentrations.

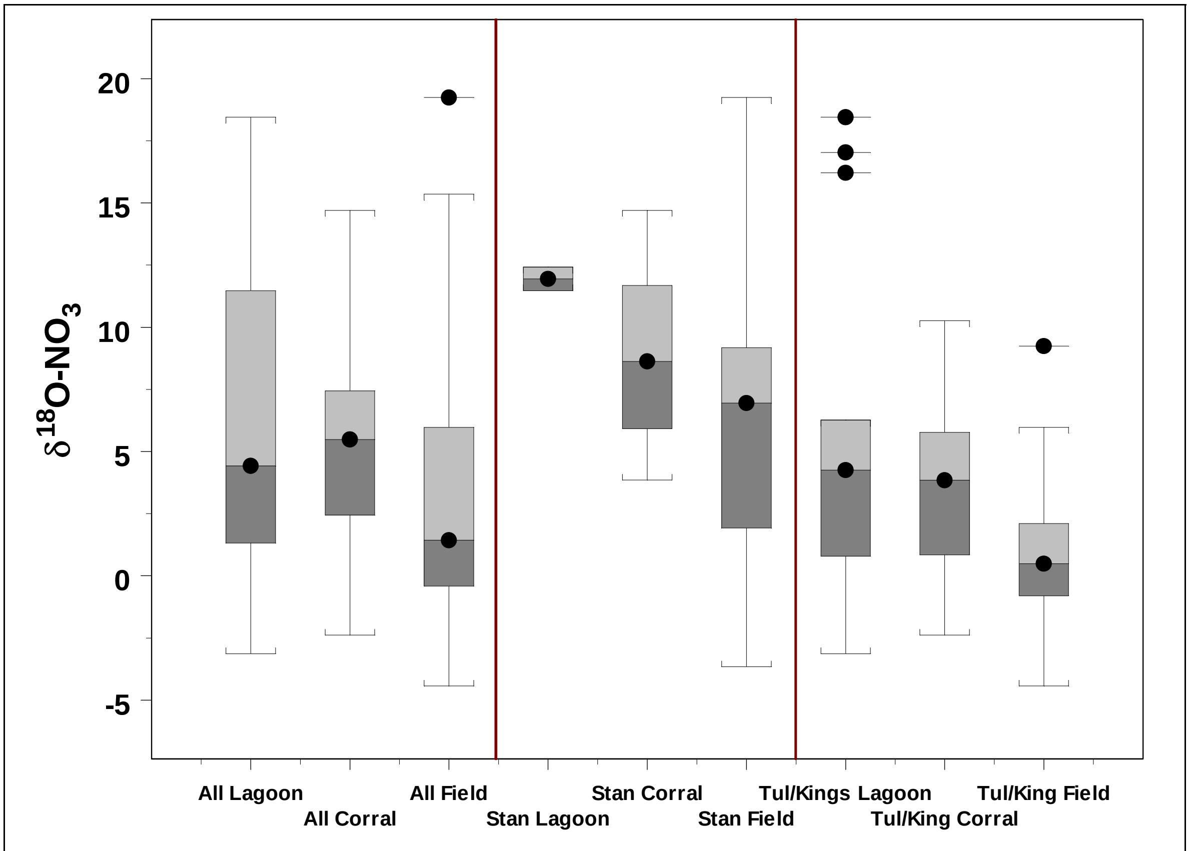

Figure 8. Box plot of δ18O-NO3 values for the major dairy land use categories used in this study.

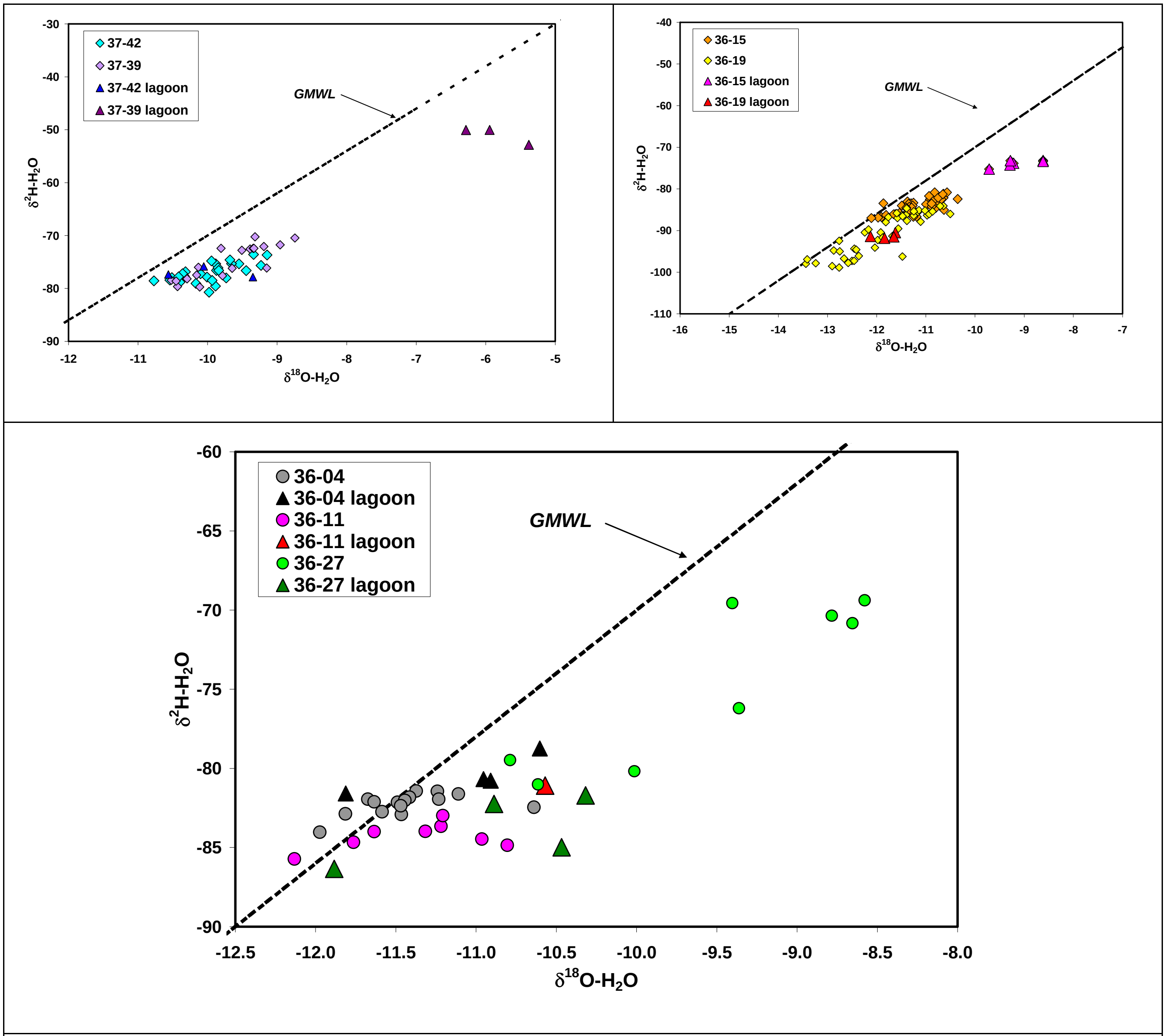

Figure 9. Water isotope compositions for all sampling events on the individual dairies, showing the results for the lagoon wells in comparison to the other wells (corral, field, mixed land use) on each dairy. The water isotope compositions for the lagoon wells on dairies 37-39, 36-15, and 36-27 were distinct from the other wells within those dairies. GMWL is the global meteoric water line.

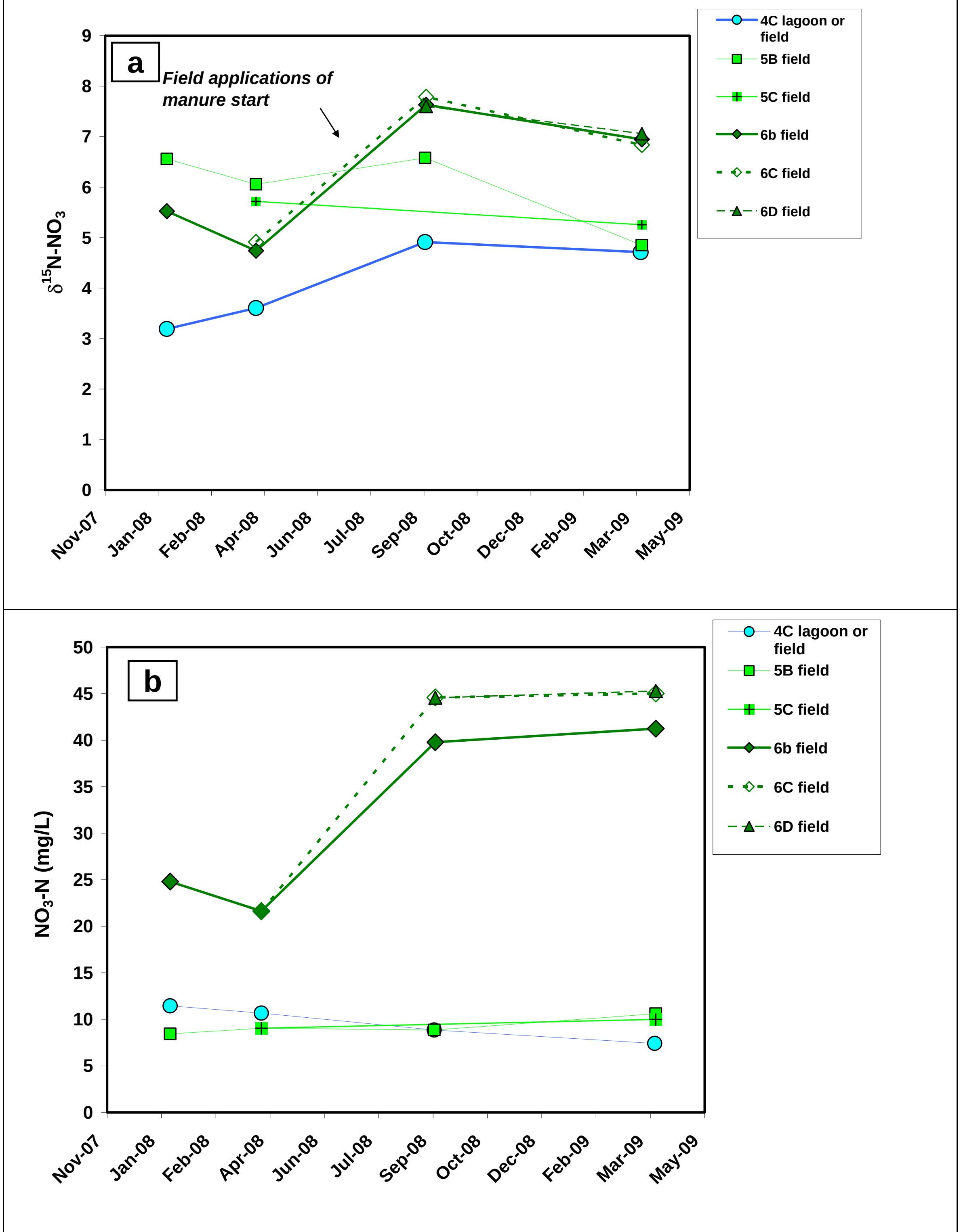

Figure 10. a) Changes in $\delta^{15}N-NO_3$ over time in the monitoring wells on Tul Dairy 36-04. Sometime between the synoptic sampling events of April 2008 and September 2008, there was a distinct shift towards heavier $\delta^{15}N-NO_3$ values only in MW-6, most likely reflecting mixing with new inputs of manure-derived nitrate. b) This same pattern can be seen in the NO_3-N concentrations in all depths of

MW-6.

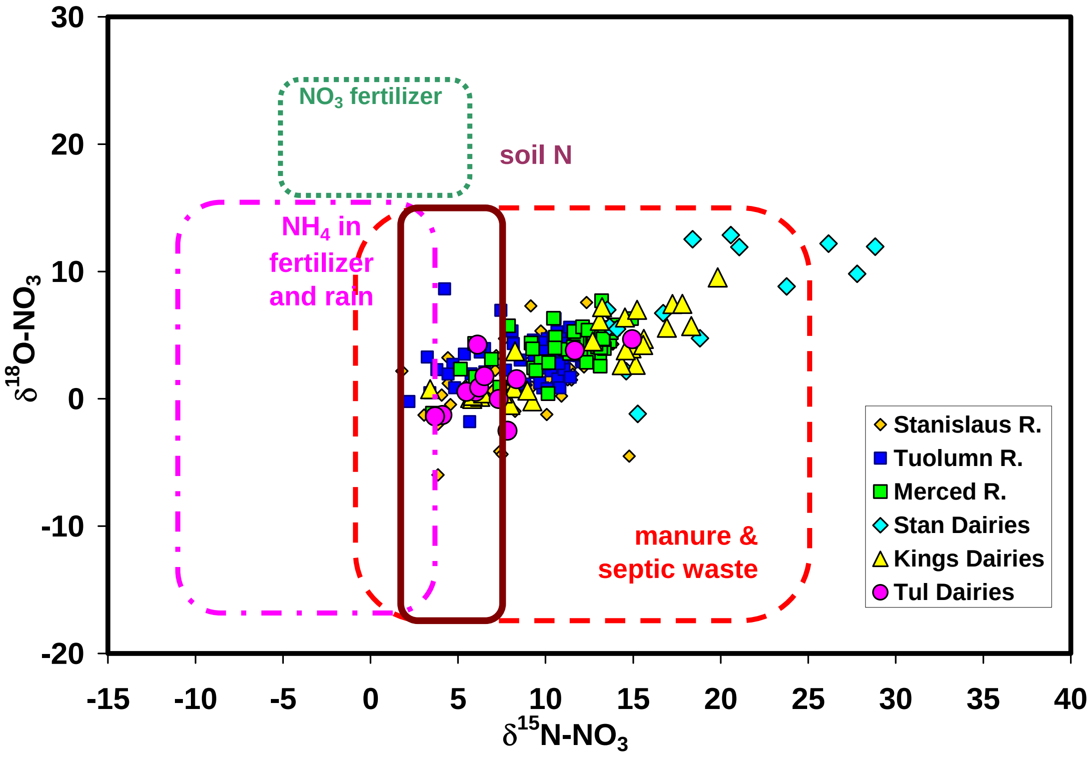

Figure 11. Nitrate isotope compositions in dairy monitoring wells (average of each well) and surface water. In the Stan dairies, almost all wells show elevated nitrate isotope values in comparison to surface water values, while the Kings & Tul dairies show some relatively elevated values and many values within the range of surface water.

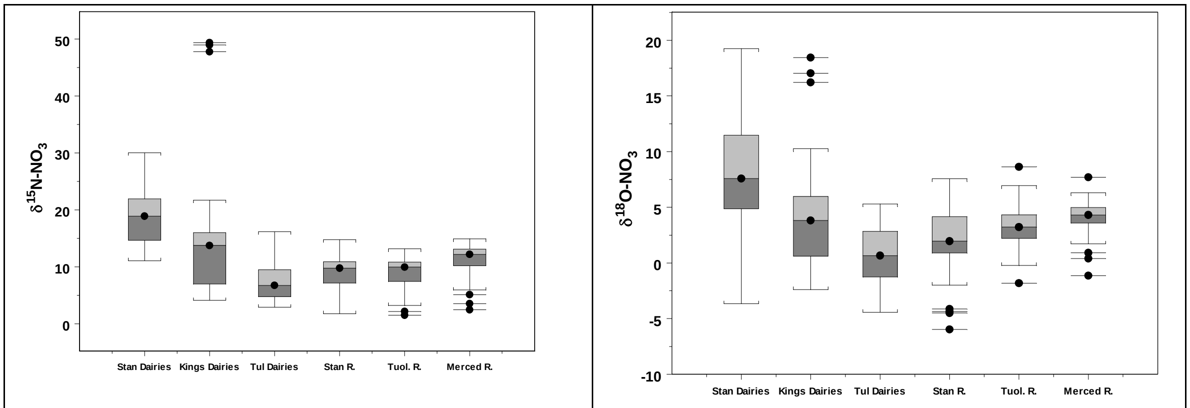

Figure 12. Box plots of nitrate isotope distributions in dairy wells and surface waters. Median $\delta^{15}N\text{-}NO_3$ values are higher in the Stan and Kings dairies in comparison to the northern surface water measurements, while the Tul dairies have lower $\delta^{15}N\text{-}NO_3$ values.

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