Final Report:

Water Quality Assessment of the Beaumont Management Zone: Identifying Sources of Groundwater Contamination Using Chemical and Isotopic Tracers

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Introduction

Nitrate contamination from human activities adversely affects both surface and groundwater in the United States, however determining sources of nitrate is often difficult due to non-point pollution sources and complex groundwater systems within watersheds. A prior study (Wildermuth 2007) identified elevated nitrate levels in some groundwater wells within the Beaumont Management Zone (BMZ) in Riverside County. Subsequent action by the Riverside County Board of Supervisors placed a moratorium on new on-site waste disposal systems (i.e., private septic systems) unless they were designed to remove 50% of the nitrogen in the effluent stream. The Beaumont Board of Supervisors formed the Ground Water Quality Evaluation Committee (GWQEV) and directed them to review technical data on groundwater quality and express their concerns regarding groundwater regulation in the Beaumont Management Zone. The Committee disputed the findings of the Wildermuth 2007 report and has identified potential shortcomings in sampling design and project execution (GWQEC 2009). In the Committee's report to the Supervisors dated June 15, 2009, they make the following findings and recommendations:

"*1. Findings: The Wildermuth report titled: Water Quality Impacts from On-site Waste Disposal Systems in the Cherry Valley Community of Interest March 2007 Wildermuth Environmental Inc. had parameters that were too narrowly focused; used well water sources located in close proximity to on-site wastewater disposal systems and used exaggerated build out approximations.*

Recommendation:

• An independent third party study conducted by someone other than Wildermuth Environmental, who conducted the initial report, is needed to evaluate this perceived regional issue. The study should evaluate beyond those areas studied in the initial report, consider reasonable build-out projections and consider other possible sources of groundwater contamination such as septic systems in the Cherry Oaks Tract and beyond to the Hidden Meadows Tract area and the surrounding communities including the City of Beaumont."

This project was funded as a Supplemental Environmental Project by the State Water Resources Control Board, in response to the recommendation by the GWQEC and a desire for improved understanding of groundwater quality and risks in the BMZ. Using existing information on wells and surface water in the BMZ, scientists at the University of California, Riverside selected 40 wells and 11 surface water sites for sampling during 2011. All wells sampled were in active use and were operated by private homeowners, businesses, public agencies or water districts. The sites selected provided good spatial coverage of the BMZ and included regions where waste is handled by septic systems and consolidated sewers.

We utilized dual isotopic analysis of nitrate in rigorously collected groundwater samples to ascertain the source of nitrate and determine if denitrification is affecting nitrate isotope signatures in groundwater. We also measured a suite of pharmaceutical and personal care

products (PPCPs) to confirm the presence of human waste in surface and groundwater and to aid evaluation of nitrate concentration and isotope data. Major ion chemistry, nutrient chemistry, dissolved oxygen and landuse data were also measured and used to aid our interpretation of the isotope and PPCP data.

Using a variety of methods including mass balance modeling and multivariate statistical analysis we attempted to answer the following questions about groundwater water quality in the BMZ:

1. Can different groundwater regions within the BMZ be defined using isotope, PPCP and general chemical parameters?

1A. Do areas with septic systems have different chemistry than areas with sewers?

1B. Do areas where groundwater is recharged with water from the State Water Project or wastewater treatment plant effluent have different chemistry from other areas?

2. What sources contribute nitrate to groundwater of the BMZ?

2A. Do different regions within the BMZ have different sources of nitrate?

2B. Do regions of the BMZ with different types of human waste disposal (i.e., septic vs. sewer) have different sources of nitrate?

2C. What areas of the BMZ, if any, have nitrate that appears to come from animal or human waste?

3. How much nitrate from human waste is making its way into the groundwater of the BMZ?

3A. Can models based on isotopes and mass balances be used to estimate septic inputs?

3B. How much would nitrate concentrations decline if sewer service was extended to regions within the BMZ currently using septic tanks? How long would it take for reductions to occur?

Methods

Sampling Sites

Forty wells were chosen for sampling from the Key Well Water Quality Program (Wildermuth 2010; Table 1 and Figure 1). The 40 wells provide good spatial coverage of the BMZ and encompass a large variety of the land-use types found in exurban areas such as Beaumont: residential areas served by septic and sewer, chicken farms, horse ranches, fruit orchards, cemeteries, golf courses, and riparian river wells. Location information of all sampling sites was provided by Dr. Cindy Li of the SWRCB, Samantha Adams (Senior Scientist II, Wildermuth Environmental, Inc.) and the Beaumont Cherry Valley Water District (BCVWD).

An additional 11 surface water sampling sites including State Water Project (SWP) recharge basins, storm water storage basins, and major creeks and storm drains were sampled. SWP recharge water was re-sampled in July 2011 to investigate water quality when only Project water was being used for recharge. A set of samples was also collected near and below the discharge site for the City of Beaumont Wastewater Treatment Plant.

To aid data analysis, the BMZ was subdivided into four zones based on differences in landuse and methods used for processing and disposal of human waste (Figure 2). **Zone 1** is an area in the southern part of the BMZ which could be affected by wastewater treatment plant effluent discharged into Cooper's Creek and San Timoteo Creek by the City of Beaumont. **Zone 2** is located in the northern part of the BMZ and included production wells within the bed of Little San Gorgonio Creek. Groundwater recharge in this zone is thought to be dominated by percolation of mountain-front flow. A large percentage of Zone 2 is wildland terrain and the remaining area is low-density housing where human waste is handled by on-site waste disposal systems. **Zone 3** is more heavily urbanized and is located south of Zone 2. Most of the homes and businesses in Zone 3 use on-site waste disposal systems and a small percentage are served by sewer. Zone 3 is also the site for groundwater recharge using storm flows and water from the State Water Project (i.e., San Gorgonio Pond and BCVWD Pond). **Zone 4** is an urban area located between Zone 3 and Zone 1 and most of the homes and businesses are served by a consolidated sewer system.

Collection of Water Samples

Groundwater sampling began in March 2011 (wet season) and continued into July 2011 (dry season). Because the holding times for PPCPs and nutrients were short, we could not collect and process more than 5 to 10 samples per sampling trip, thus sampling had to be spread over several weeks.

Groundwater samples were collected from well-heads using a rigorous procedure designed to avoid contamination and yield samples representative of local groundwater. Wells used for municipal water supplies were allowed to run at least overnight prior to sampling and in most cases were in continuous operations for many days prior to sample collection. Most of the wells used for individual homes, ranches or businesses had pressure tanks. At sites with pressure tanks, water was drained from the pressure tank with the well pump turned off, then power was restored and the tank refilled. This procedure was repeated once more after which the well pump was turned on and run continuously for 15-20 minutes.

At municipal well heads and pre-flushed pressure tanks, measurements of water quality (pH, temperature, conductivity, and dissolved oxygen (DO)) were made at 10 minute intervals using a calibrated YSI meter to ensure water was representative of local groundwater. When three consecutive measurements produced variation less than the criteria listed in Table 2, the well water was directed into a 5 gallon bucket from which subsamples for individual chemical analyses were then collected. This HDPE bucket was rigorously cleaned in the laboratory by a 3-

day soaking in 18 megaohm deionized water followed by multiple rinses with more deionized water and 6 rinses with well water. Between sampling sites the bucket was rinsed three-times with deionized water and 3 times with well water. Field personnel wore powder-free nitrile gloves during sample collection.

Surface water samples were collected by dipping a clean HDPE bucket underwater with a gloved hand or a clean 1-liter HDPE bottle was dipped underwater using a telescoping pole. All sample bottles was rinsed 3-times with sample before filling. Two duplicate well water samples and one duplicate surface water sample were collected for this project to verify field collection methods were rigorous. At least one blank was taken during each sampling trip (8 blanks in total).

Samples for major anions, cations, nutrients and stable isotope measurements were subsampled out of the 5 gallon bucket or 1-liter bottle (Table 3). A Solinst peristaltic pump was used to withdraw water from the bucket/bottle and force it through a 0.45 μm, Whatmann Polycap GW capsule filter. The filters were pre-cleaned in the laboratory by flushing 4 liters of deionized water (18 megaohm) through the filter. In the field at least one-liter of sample water was passed through the Polycap filter prior to collection of water samples. Each capsule filter and length of peristaltic pump tubing was used for only a single sampling site to prevent cross-contamination. Major cation and anion samples were collected in new 125ml HDPE bottles that had been soaked in deionized water (18 megaohm) for several days and rinsed three times with filtered sample water; these samples were stored at 4°C. Samples for nutrient fractions were collected in new 60ml HDPE bottles that had been soaked in deionized water (18 megaohm) for several days and rinsed three times with filtered sample water; these samples were filled to the neck and stored frozen at -20°C. Filtered samples for DOC were collected in sample-rinsed 40 ml amber vials (pre-muffled at 450 °C) and preserved with 2 drops of trace metal grade HCl (pH~2). Immediately following collection, samples were kept on ice in a cooler until they were delivered to the UCR laboratory where they were either stored at -20°C or 5°C prior to analysis.

Samples for PPCP analyses were pumped out of the sample bucket using the peristaltic pump and into 1-liter, pre-cleaned glass sample bottles that were triple rinsed with sample. These bottles were cleaned with laboratory detergent, a brush, and hot tap water. After scrubbing, the glass bottles were rinsed three to four times with deionized water and rinsed consecutively with 5 ml MTBE, 5 ml HPLC grade methanol and 5 ml ultra-pure water. The bottles were then stored in a dedicated glassware cabinet to prevent external contamination of samples. At the lab, the PPCP samples were extracted within 48 hours of sampling. Every 10th PPCP well sample was collected in duplicate.

Bottle blanks were produced by filling a clean sample bottle in the laboratory with deionized water. Field blanks consisted of deionized water run through the peristaltic pump tubing and Polycap cartridges and into clean sample bottles in the field. Bottle and field blanks were collected before on each sampling date and analyzed as regular samples. For major ions, nutrients and isotopes of nitrate, and all other analytes with the exception of PPCP compounds,

all blanks produced analyte concentrations below the method detection limits and demonstrated that our sampling procedures were robust. Some of the PPCP field and laboratory blanks produced measureable analyte quantities and are discussed below. All analyses were conducted following the procedures outlined in the February 17, 2011 Quality Assurance Project Plan.

During collection, samples were labeled with individual site codes, sample date and time, and numbered consecutively. The result was a unique identification number for each sample collected. These identification labels were entered directly on the chain-of-custody (COC) form in the field. A COC form accompanied every sample brought into the UCR laboratory. Samples were stored in refrigerators and freezers in locked laboratories.

Major Ion, Nutrient and Isotope Analyses

The chemical species we determined were chosen to: (a) provide diagnostic indicators of the presence of human waste in groundwater (e.g., NO_3, TN, DOC, isotopes of NO_3, PPCP), (b) to help identify distinctive groundwater regions within the BMZ and provide information on potential pollutant sources (e.g., major cations and anions) and (c) provide general knowledge of groundwater conditions in the Beaumont region (e.g., pH, acid neutralizing capacity, specific conductance, Cl, phosphorus, boron and SO_4).

Specific conductance was measured with a laboratory conductivity meter equipped with a graphite conductivity electrode with a cell constant of K=1 cm^{-1}. Laboratory pH measurements were made with a high quality pH meter equipped with an Orion-Ross combination electrode. The pH meter and electrode were calibrated using pH buffer solutions (4, 7 and 10) and the calibration checked by measuring the pH of two weak-HCl solutions (10^{-4} N (pH: 4.0) and 10^{-5}N (pH: 5.0)). Acid neutralizing capacity (ANC) of samples was measured by Gran Titration using the calibrated laboratory pH meter and Ross electrode. Hydrochloric acid with a normality of 0.1 was used to titrate the sample past the equivalence point. At least four titrant-pH measurement pairs were made between pH 4.3 and 3.7 and used in the Gran computation. Bicarbonate concentration was calculated based on measured ANC and pH value (equation 1).

$$[HCO_3^-] = \frac{(2\times ANC)-10^{-14+pH}}{1+2K_2\times 10^{pH}} \qquad \text{(Equation 1)}$$

Where $K_2 = [H^+]\times[CO_3^{2-}]/[HCO_3^-] = 10^{-10.3}$.

Total dissolved solids (TDS) was calculated based on measured specific conductance and the following equation (2):

$$\text{TDS (ppm)} = \text{Specific Conductance} \times 0.67 \qquad \text{(Equation 2)}$$

Major anions (Cl, Br, NO_3, NO_2, PO_4 and SO_4) were measured using chemically suppressed ion chromatography on a Dionex ion chromatograph following EPA Method 300.1. Major cations were measured by inductively coupled plasma - atomic emission spectroscopy (EPA Method 200.7).

Total dissolved nitrogen (TDN) was determined in samples after NaOH-potassium persulfate digestion, with the nitrate produced by the digestion measured by EPA Method 353.2. Dissolved organic nitrogen was estimated as the difference between TDN and the sum of inorganic nitrogen (nitrate+nitrite). Ammonium was not measured for this project, but the well oxygenated condition of most samples indicates it would be present in very low concentrations. Dissolved organic carbon was measured on a Shimadzu TOC 5050 analyzer employing high-temperature Pt-catalyzed combustion (EPA 9060A).

Isotopes of nitrate were measured using the microbial denitrifier method (Révész and Casciotti 2007). In this method, bacteria (*Pseudomonas* aureofaciens) were used to convert NO_3 into N_2O gas which was then analyzed for isotope ratios ($\delta^{15}N$ vs. air and $\delta^{18}O$ vs. VSMOW) in a Delta V Plus isotope ratio mass spectrometer (Thermo Scientific) at the Facility for Isotope Ratio Mass Spectrometry at UC Riverside.

For the ICP-AES, ion chromatography and nutrient assays we employed NIST-traceable standards and constructed multi-point calibration curves that spanned the entire range of sample concentrations. For stable isotope analyses we used NIST or IAEA certified isotope standards in each analytical run and corrected isotopic values for non-linearity and sample size differences if needed.

Pharmaceutical and Personal Care Products

The analysis of pharmaceutical and personal care products (PPCP) in water was based on the methods developed by Vanderford and Snyder (2006). At UC Riverside, rigorous procedures were used to validate the recovery, precision, and determine the instrument limits of detection (ILOD). The compounds of interest are shown in Table 4. PPCP analyses were conducted on all well and creek samples and in State Water Project water at groundwater recharge facilities within the BMZ. The use of UPLC-MS/MS to detect PPCP in water included several steps. These steps were preparation of stock and working solutions of the target compounds and their labeled counterparts, sample preparation, sample solid phase extraction, instrument calibration and QA/QC evaluation.

***Solid Phase Extraction*:** Compounds of interest were extracted from water samples using Oasis HLB solid phase extraction (SPE) cartridges (Waters Corporation, Milford, MA). Prior to extraction, surrogate compounds were added to each sample. A pre-filtered water sample of 1 L was passed through a cartridge and the compounds of interest were retained while interferants passed through. The compounds of interest were then eluted and reconstituted to 1 mL prior to analysis.

Standard Preparation: PPCP compounds and their isotopically labeled counterparts were purchased from Sigma Aldrich (St. Louis, MO), Toronto Research Chemicals (North York, Ontario, Canada), United States Pharmacopea (Rockville, MD), and C/D/N Isotopes, Inc. (Poimte-Claire, Quebec, Canada). Individual stock solutions (100 $\mu g\ L^{-1}$ or 10 $\mu g\ L^{-1}$ for each compound) were prepared by weighing the exact amount of each compound and dissolving in

methanol. A multiple PPCP working solution (100 ng L^{-1} of each compound) was prepared by appropriate dilutions of the stock solutions in methanol.

UPLC-MS/MS Analysis: Analyses were conducted using an Aquity UPLC system coupled with a Trinity triple quadrupole mass spectrometer equipped with an electrospray ionization source (ESI) (Waters, Milford, MA). The column was a BEH C18 (100 mm X 2.1 mm i.d. with 1.7 μm particle size). Individual tune files were created by infusing the individual compounds to determine the optimum capillary and cone voltages, collision energies, product ions. The ILODs ranged from 0.1 to 10 ng/ml for individual analytes, for the listed PPCPs.

Quality Control: For PPCP samples, deuterated surrogates (10 ng ESI + and 25 ng ESI -) for each analyte of interest were added to samples prior to extraction to assess method performance as well as correct for matrix suppression, solid phase extraction variability, and instrument variability. Field replicates were to determine the reproducibility of the PPCP analysis. Losses of each analyte and its deuterated counterpart are known to decrease at the same percentage throughout the extraction, cleanup with SPE and analysis. Therefore, the recovery of surrogate compounds was used to correct for concentration losses of the non-deuterated compound.

PPCP field blanks were collected on each sampling date to assess potential sample contamination levels that could occur during field sampling and sample processing. Field blanks (DI water) were taken to the field, transferred to the appropriate container, preserved, and otherwise treated the same as a sample. With the exception of two batches of samples collected in May 2011, all the field blanks were not contaminated and the values were below the detection limit for each analyte. During the two May 2011 runs we measured trace to low levels of several PPCP compounds in both the field blanks and laboratory prepared blanks. Following this incident all glassware was rewashed and new reagents were prepared. The PPCP data from these two batches was discarded and was not used in any data analyses in this report. The wells from these two PPCP batches (BCVWD #1, 4, 5, 6, 10, 12, 14, 19, 20, 21, 23, and 26) were resampled in July 2011 and the field and laboratory blanks were below detection for all PPCP compounds.

Performance evaluation of the UPLC for analysis of PPCP was made by analyzing standards of the normal and deuterated target PPCPs. When the linearity of the standard curve or reproducibility of replicated samples exceeded limits of errors, instrument recalibration was conducted. Chromatographic instruments were typically calibrated by cleaning or changing the sample injection port, changing or reinstalling the column, cleaning the cone, changing the gas filters, or changing/fabricating the detectors.

Results

Quality Control

Precision: Precision is the reproducibility of an analytical method. Within each analytical run, measurements of precision was performed at a 10% frequency (i.e., one duplicate for every 10 samples) or at least once if the run contains less than 10 samples. Both certified reference material and natural samples were used in measurements of precision. The relative percent

difference for all duplicate measurements was lower than 10% for all the analytes we measured meeting the QAPP target.

Accuracy: Accuracy is a measure of how well a measured analyte value compares to the true value. In this study we estimate analytical accuracy using spike recoveries made in reference solutions and natural samples. For all analytes accuracy fell in the range of 85-115% meeting the QAPP target.

Field Duplicates: The field duplicate samples were collected in the same manner and as close in time as possible to the original sample. Two well water duplicates and one surface water duplicate were collected during this study. Percent relative standard deviation (%RSD) for the vast majority of analytes was a few percent or less. In cases where analyte levels were at or near the detection limit (for example Fe), %RSD values could be higher (Table 6).

Physical and Chemical Characteristics of Surface and Groundwater

Field Temperature: Field temperatures for groundwater ranged from 11.6°C to 21.9°C, with an average of 17.9 ± 0.4°C (n=52) (Table 5). The coldest groundwater was observed in Zone 2 and the warmest groundwater was observed in Zones 1 and 4 (Figure 3). Most (87%) groundwater temperatures were 15°C - 22°C and 23% of them were between 19-20°C (Figure 4A). Field temperature of surface water (8.5-24.2°C) was highly dependent on air temperature and the elevation where sampling occurred.

pH: Sample pH was measured both in the field and lab, and the difference between these two measurements was less than 10% for all samples. Only pH measurements from the lab were used in this report. The average groundwater water pH was 7.50±0.05 (n=55) with a range of 7.01-7.83 (Figure 4B), except for two wells near San Timoteo Creek with pH of 8.70 and 9.28 respectively (Table 5). No strong spatial patterns were evident for pH (Figure 5). Surface water pH was similar to groundwater pH and ranged from 6.86 – 7.85.

Field Dissolved Oxygen: Field dissolved oxygen (DO) was between 0.29 to 10.63 mg/L, with an average of 6.89±0.34 mg/L (n=55) (Table 5). In 15% of groundwater samples (6 wells), DO was lower than 4 mg/L (Figure 4C). Five of these six wells, with DO lower than 3 mg/L, were located along San Timoteo Creek. This may indicate higher possibilities of denitrification occurring in the groundwater of these sites (Figure 6). The other groundwater sample with low DO (3.63 mg/L) was observed at a horse ranch (site 1207012). Dissolved oxygen in all the other groundwater samples was higher than 5 mg/L (Figure 4C). DO concentrations in surface water were all higher than 4 mg/L (Table 5).

Specific Conductance: Specific conductance was measured both in the field and in lab, with less than 10% difference between these measurements. Specific conductance ranged between 333 – 708 µS/cm, with average 452±12 µS/cm, except two wells at horse ranch and chicken farm on San Timoteo Creek with specific conductivities of 965µS/cm and 1147µS/cm respectively (Table 5 and Figure 4D). Sixty eight percent of groundwater specific conductance values was

between 333-463 µS/cm (Figure 4D). S Except for Cooper's Creek and lower San Timoteo Creek, the specific conductance of surface water was lower than that in groundwater (p=0.001) (Figure 7).

Acid neutralizing capacity (ANC): Acid neutralizing capacity was between 2030-4114 µeq/l with an average of 3232.52±56.93 µeq/l, excluding the high values found at the horse ranch and chicken farm (5784 µeq/l and 5329 µeq/l respectively (Table 5)). 87% of groundwater samples had ANC between 2700-4000 µeq/l (Figure 4E). However, surface water had significantly lower ANC compared with groundwater with p value 0.001 (2471±387µeq/l), excepting lower San Timoteo Creek surface (Figure 8).

Total Dissolved Solid (TDS): Total dissolved solid was calculated based on specific conductance and Equation 2. Resulting spatial variability was identical to that observed for specific conductance (Figure 9).

Dissolved Organic Carbon (DOC): Dissolved organic carbon concentrations in groundwater were significantly lower than in surface water with $p<0.0001$ (Table 5). The average DOC concentrations in groundwater and surface water were 0.20±0.04 mg/L and 3.8±0.53 mg/L respectively. DOC distribution in the BMZ is shown in Figure 10. DOC concentrations in 79% groundwater samples were lower than 0.25 mg/L (Figure 4F). The highest groundwater DOC (1.7 mg/L C) was found at the horse ranch well (site 1207012).

Major Ions and Nutrients: Major ions were measured for each sample and the data is listed in Table 6. A Geostiff diagram was produced for each well and surface water site to describe the major ion chemistry. The Geostiff diagrams were then plotted in Figure 11. In general, bicarbonate was the dominant anion, followed by sulfate in Beaumont groundwater samples (Figure 11). The major cations were calcium and magnesium, followed by sodium (Figure 11). Geostiff diagrams show that surface water contains different major ion concentrations than groundwater. Triangle plots showing the percentages of major cations and anions are presented in Figure 12 and broken down by sample type and Zone.

Nitrate is a key indicator of groundwater quality (Hill, 1982; Pionke and Urban, 1984; Koh et al, 2009), long-term monitoring in the BMZ has shown increasing concentrations, especially in the period of 1960-1980 (Figure 13). During the 1960-1980s the rate of nitrate increase was on the order of 0.15 mg NO_3-N/L/year. Increases in groundwater nitrate-nitrogen after 1990 (where evident), range from 0.05 to 0.1 mg NO_3-N/L/year. For the wells shown in Figure 13 nitrate-nitrogen levels vary from 0.60 to 21 with an average of 3.5±0.54 mg/L during our survey period 2011 (Table 6). The distribution of nitrate-nitrogen in BMZ is shown in Figure 14. Thirty nine of 55 groundwater samples (71%) had NO_3-N concentration lower than 2.5 mg/L (Figure 15A). Forty four of 55 groundwater samples (80%) satisfied the drinking water standard < 5 mg/L requested by the Regional Water Quality Control Board. Alternatively, 11 of 55 groundwater samples (20%) exceeded the standard required by the Regional Water Quality Control Board. The highest nitrate-nitrogen groundwater was observed at the horse ranch well

(21 mg/L at site 1207012, Table 6), followed by groundwater near the City of Beaumont waste water treatment plant #1 (WWTP#1) and at site 1007022 (Figure 14). Surface water had significantly lower nitrate-nitrogen concentrations than groundwater ($p = 0.017$) with an average of 0.86±0.11 mg/L (range of 0.32-1.50 mg/L) (Figure 14).

Bicarbonate was the dominated anion in both Beaumont groundwater (~73%) and surface water (~59%) (Figure 12). The average bicarbonate concentration was 201±5.1 mg/L and 164±26.3 mg/L in groundwater and surface water respectively. Groundwater bicarbonate varied from 103 to 352 mg/L, and 90% of well water bicarbonate was between 150-250 mg/L (Figures 15B and 16).

Sulfate was the second most abundant major anion in Beaumont groundwater and surface water, and represented 12% and 20% of the total negative charges respectively (Figure 15C). Groundwater sulfate varied from 8.6-79 mg/L (Table 6), with an average of 27±2.3 mg/L. Most of the groundwater had sulfate lower than 30 mg/L (Figure 17). Surface water sulfate (mean 42±5.44 mg/L) was statistically higher than groundwater sulfate in the BMZ ($p=0.01$).

Chloride represented about 10% and 18% of the total negative charges in Beaumont groundwater and surface water respectively (Figure 12). The average groundwater chloride was 18±2.9 mg/L, and varied from 4.0 mg/L to 147 mg/L (Figure 18). Most (85%) groundwater samples had chloride concentrations lower than 30 mg/L (Figure 15D). Surface water had significantly higher ($p = 0.04$) negative charge percentage and higher absolute chloride concentration (25±6.1 mg/L) compared to groundwater. Higher chloride values were observed along San Timoteo Creek and sites close to the SWP recharge basins (Figure 18).

Fluoride accounted for less than 5% of total negative charges, and ranged from 0.3-3.0 mg/L with an average of 0.50±0.06 mg/L (Table 6). Seventy three percent of the groundwater fluoride values were between 0.25-0.50 mg/L (15E). The variation of surface water fluoride was from 0.04-0.64 mg/L, with no statistical difference between groundwater and surface water fluoride concentrations (Figure 19).

The average phosphate concentration in Beaumont groundwater was 0.06±0.01 mg/L (Table 6). All but two sites were below 0.15 mg/L phosphate, the cemetery site (1002958) at 0.61 mg/L and the chicken farm at 0.26 mg/L (1208432) (Figure 15F and Figure 20). Phosphate was not detected in 18 of the 55 well samples. Surface water had significantly higher ($p<0.001$) phosphate concentrations (0.47±0.18 mg/L) compared with groundwater.

Calcium was the dominant cation in Beaumont groundwater, and accounted for about 50% of positive charges (Figure 12). Groundwater calcium varied 1.8 mg/L to 90 mg/L (Figure 21A), with average of 45±1.9 mg/L. Most groundwater calcium concentrations (93%) fell between 28 and 66 mg/L (Figure 22). The highest calcium level in groundwater (90 mg/L) was found at the chicken farm located adjacent to Cooper's Creek. Calcium was also the dominant cation in surface water with an average of 35±4.8 mg/L.

Magnesium was the second most common cation, accounting for about 25% of the total positive charges in both groundwater and surface water (Figure 12). Average magnesium concentrations were 15±0.8 mg/L and 13±1.8 mg/L in groundwater and surface water respectively. Most (89%) magnesium concentrations in groundwater were between 8 to 22 mg/L (Figure 21B). No significant difference in magnesium concentrations was observed between groundwater and surface water (p=0.34). The highest magnesium concentrations were found at the horse ranch (site 1207012) and chicken ranch (site 1208432) with 35 mg/L and 32 mg/L respectively (Figure 23).

Sodium was the third most abundant cation, accounting for 25% of the total positive charges both in groundwater and surface water (Figure 12). Sodium in groundwater varied from 11 to 85 mg/L, with an average of 29±2.6 mg/L (Figure 24). However, 84% of groundwater had sodium lower than 40 mg/L (Figure 21C). Sodium in surface water was not significantly different than groundwater, with an average of 28±6.1 mg/L.

Potassium was least abundant base cation, with less than 2% of the total positive charges (Figure 12), with an average value of 1.6±0.08 mg/L. Eighty percent of groundwater samples had potassium concentrations between 1-2 mg/L (Figure 21D). However, surface water potassium (3.3±0.82 mg/L) was significantly higher ($p < 0.0001$) than groundwater (Figure 25).

All the other cations (aluminum, boron, and iron) accounted for less than 1% of total positive charges in groundwater. Aluminum and iron were only detected at a few sites (Table 6).

Isotopes of Nitrate: δ^{15}N-NO_3 and δ^{18}O-NO_3

The measurement of $\delta^{15}N\text{-}NO_3$ in groundwater is an established method of identifying sources of nitrate (Aravena et al., 1993; Aravena and Robertson, 1998; Kendall, 1998; Roadcap et al., 2002). In the BMZ, $\delta^{15}N\text{-}NO_3$ varied from 2.0‰ to 21‰ with an average of 5.3±0.6‰ (n=55) (Table 7). About 70% of the groundwater samples had $\delta^{15}N\text{-}NO_3$ lower than 5‰ (Figure 26A) Higher $\delta^{15}N\text{-}NO_3$ values were observed in groundwater and surface waters along San Timoteo Creek and Cooper's Creek, in groundwater recharge waters within Zone 3, and in several wells within Zone 3 (Figure 27). Moderate to high values of $\delta^{15}N\text{-}NO_3$ were observed in the BCVWD wells within Zone 2. The lowest groundwater $\delta^{15}N\text{-}NO_3$ values were found in Zone 4. The lowest surface water $\delta^{15}N\text{-}NO_3$ values were often found after rain events. In Nobel Creek and San Gorgonio Creek, $\delta^{15}N\text{-}NO_3$ values were -0.58‰ and 0.26‰ respectively. Water samples collected from SWP recharge ponds had significantly higher $\delta^{15}N\text{-}NO_3$ (8.9±0.2, n=4) values (Table 7, Figure 27) in comparison with groundwater $\delta^{15}N\text{-}NO_3$, however nitrate-nitrogen concentrations in SWP recharge water were only 0.3 mg/L.

The $\delta^{18}O$ of nitrate provides additional information to determine nitrate sources and understand microbial processing of nitrate within aquifers (Kendall 1998). The variation $\delta^{18}O\text{-}NO_3$ within the Beaumont Basin groundwater was -0.85‰ to 9.4‰, with an average of 2.2±0.3‰ (n=55). About 85% of groundwater $\delta^{18}O\text{-}NO_3$ values were lower than 4‰ (Figure 26B). The highest groundwater $\delta^{18}O\text{-}NO_3$ values were observed along San Timoteo Creek,

followed by groundwater in Edgar Canyon and Beaumont Cherry Valley (Table 7, Figure 28). The range of surface water $\delta^{18}O\text{-}NO_3$ was from -3.9‰ to 10.4‰ (Table 7). The SWP water had significantly lower $\delta^{18}O\text{-}NO_3$ values (-2.9±0.5‰, n=4) compared to other surface water sites (3.4±1.4‰) with p = 0.016 (Table 7).

The ratio of $\delta^{18}O\text{-}NO_3$ vs. $\delta^{15}N\text{-}NO_3$ could be an additional tool to distinguish sources of nitrate. Nitrate from human or animal waste may produce a ratio between about 1.0 and 4.0. Soil nitrate could produce a ratio of 0.2 to 2 while mineralization of reduce nitrogen fertilizer could produce a ratio of 0.6 to -1.3. Nitrate from precipitation will typically produce values of the ration < -0.5 or greater than 10. The ratio was mapped in Figure 29. Wells within Zone 4 typically had ratios between -0.4 and +0.3 which may nitrate derived from natural soil nitrogen or reduced nitrogen fertilizers. Wells in Zone 2 generally had ratios in the range of +0.4 to 1.0 which overlaps the ratios expected from natural soil nitrogen and fertilizer. Wells in Zone 3 generally had the highest ratios and in several cases the values overlapped the ratios expected from human or animal waste. The isotopes of nitrate in Zone 1 were strongly influenced by denitrification (see below) which tends to reduce the ratio therefore confounding its usefulness for tracing nitrate sources.

Pharmaceutical and Personal Care Products (PPCPs)

Samples were analyzed for 16 compounds, and 15 were identified above the detection limit in at least 1 of the 51 samples assayed (40 groundwater, 9 surface water and 2 recharge water). There were a total of 6 well water samples (12%) with no detections, and 7 (14%) samples with 1-3 detects of compounds with concentrations below the quantification limit (Table 8). PPCPs were identified above the detection limit in 34 of the 40 wells samples with an average detects per well of 2.3 compounds (range 0 to 7). PPCPs were detected in every surface water sample with an average detect of 4.2 compounds per site (range 1-13). However, some of these detects were below the limits of quantitation.

Diclofenac was not detected in any sample. Diuron (55%) and sulfamethoxazole (50%) were the most commonly detected compounds in groundwater samples, while diuron (89%), trimethoprim (78%) and gemfibrozil (67%) were most commonly found in surface waters. The two SWP recharge water site samples contained similar concentrations of the exact same compounds (meprobamate, diuron, carbamazepine and sulfamethoxazole). The most commonly detected compounds among all samples were diuron (63%) and sulfamethoxazole (49%).

The spatial distribution of PPCP detections within the BMZ was not homogenous. Generally, the highest concentrations and detections occurred in Zone 1 and the lowest concentrations and least detections occurred in Zone 4 (Figure 30).

To aid in statistical evaluation of PPCP data, we derived an equation based on PPCP concentrations and the number of detections. This equation provides an index, C, to judge the likelihood that water samples contain human waste.

$$C = Ln\left[(\sum J \times 100)\,\frac{L}{L_i}\right] \qquad \text{(Equation 3)}$$

Where C is the PPCP contamination index, $\sum J$ is the sum concentration (ng L^{-1}) of all the detected analytes, L is the number of compounds detected and L_i is the total number of analytes in the method. Sites with highest probability of containing human waste are those with multiple compound detections at relatively higher concentrations. Sites with less human waste are those with few or no detects at lower concentrations. The highest C values were measured in surface and groundwater within Zone 1 (Figure 31). Lowest C values were measured in Zone 4 and Zone 2. Levels in Zone 3 were higher than in Zones 2 and 4, but overall were less than those in Zone 1. While diuron was examined and is discussed with PPCPs throughout the text, it was not used to calculate the PPCP contamination index. Diuron is an herbicide, and while it may be found in septic and wastewater effluents, it is also applied regularly in the environment and therefore not strictly associated with septic or wastewater effluents.

Principal Components Analysis (PCA) of Environmental and Chemical Data

Principal components analysis (PCA) was used to determine the major gradients in the water chemistry dataset, and to identify clusters of sites exhibiting similar water chemistry. PCA is a common ordination technique for linear indirect gradient analysis (ter Braak 1988), which is especially useful for visualizing large and complex data sets in reduced dimensions that are more interpretable. PCA identifies patterns in data and expresses the data in a way that highlights similarities and differences among samples and sample attributes.

Principal components analysis (PCA) was chosen based on initial data exploration using DCA (detrended correspondence analysis), which identified short lengths of gradients (lower than 1.5) in our dataset. Therefore the PCA was used to assess the overall variability. Environmental data was log (log+1, for data containing zeros), square root, or Box –Cox (Box and Cox 1964) transformed prior to analysis, to achieve normality and remove negative values. Because our variables were measured in different units (e.g. pH, DO, Conductivity etc.) we used center and standardize settings to better interpret distance between groups of samples. All ordinations were performed using CANOCO version 4.5 (ter Braak and Smilauer. 1998).

Principal components analysis (PCA with all groundwater environmental variables included) revealed that PPCPs, isotopic composition ($\delta^{15}N$ and $\delta^{18}O$), major ions (Cl, SO_4) and major water chemistry parameters (Conductivity, pH, DO, TN, DON and DOC) were the most significant environmental variables in explaining the variance in the wells sampled in our survey of groundwater in the BMZ (Figure 32). A significant portion of the variance in our data was explained by both Axis 1 and 2 (37.1 %). For large datasets such as ours, even less than 10% explained variance is considered normal. The first axis, which accounted for 22.8% of the variance within the well data, was strongly related to parameters associated with the ionic strength and nitrogen concentrations of groundwater. The second PCA axis is more directly influenced by PPCPs and isotopic values of nitrate. In Figure 32, the length of the arrow denotes the importance of that variable in explaining variability among the wells. The direction that the

arrow points generally indicates a gradient of increasing values for each variable. For example, samples with high ionic strength (i.e., high specific conductance = COND) also tended to have high total nitrogen (TN). Similarly, samples with higher values of $\delta^{15}N\text{-}NO_3$ (.15N in figure) tend to be found in wells with higher PPCP concentrations (primidone, carbamazepine, meprobamate) and lower field dissolved oxygen (FDO).

We performed Pearson Product Moment Correlation (PPMC) to quantify relationships among some of the most important parameters identified in the PCA analysis. The following parameters were most strongly correlated to PPCP index values in groundwater of the BMZ ($p<0.01$):

- $\delta^{18}O\text{-}NO_3$: r = +0.76
- $\delta^{15}N\text{-}NO_3$: r = +0.75
- Boron: r = +0.72
- Sodium: r = +0.68
- Chloride: r = +0.65
- Dissolved oxygen: r = -0.64
- Sulfate: r = +0.57
- Total dissolved solids or: specific conductance r = +0.53

The following parameters were most strongly correlated to $\delta^{15}N\text{-}NO_3$ values in groundwater of the BMZ ($p<0.01$):

- $\delta^{18}O\text{-}NO_3$: r = +0.88
- PPCP index: r = +0.75
- Dissolved oxygen: r = -0.75
- Boron: r = +0.72
- Sodium: r = +0.71
- Chloride: r = +0.59
- Total dissolved solids or: specific conductance r = +0.39

The following parameters were most strongly correlated to total nitrogen (TN) concentrations in groundwater of the BMZ ($p<0.05$) (the strong positive correlations between TN and nitrate-nitrogen and DON are not presented):

- Total Dissolved Solids or: Specific Conductance r = +0.69
- Sulfate: r = +0.56
- Chloride: r = +0.48
- ANC or HCO_3: r = +0.47
- Sodium r = +0.35
- Boron: r = +0.32
- pH r = -0.27

The correlation analysis demonstrates that a strong positive relationship exists between the two parameters we chose to identify contamination from human waste (PPCPs and isotopes of nitrate). Higher levels of PPCPs and enrichment of the nitrogen and oxygen isotopes of nitrate tended to occur in groundwater with lower dissolved oxygen and higher concentrations of salts which is consistent with expected water quality impacts from human waste. Higher total nitrogen concentrations were also associated with higher concentrations of salts which is consistent with influence from human waste. Total nitrogen was positively correlated with the PPCP index and δ^{15}N-NO_3, but the r- and p-values did not reach the thresholds for statistical significance (r-values of +0.18 and +0.13 and p-values of 0.2 and 0.36, respectively). We did note a statistically significant positive correlation between TN and δ^{18}O-NO_3 (r value of +0.38, p-value 0.004). We speculate that the lack of correlation among TN (or nitrate-nitrogen or DON) and the PPCP index and δ^{15}N-NO_3 results from the non-conservative nature of nitrate in the vadose zone and in low oxygen environments.

The clustering of individual groundwater samples in the PCA is presented in Figure 33. In the figure, wells from Zones 1 through 4 and surface water are colored to show their grouping. Zone 4 wells formed the tightest cluster (blue diamonds) and constitute a chemically distinct group of wells based on general water chemistry, isotopes of nitrate and PPCP levels. The position of Zone 4 wells in the PCA indicates that they generally have the lowest ionic strength, lowest total nitrogen and lowest PPCP levels of all the wells sampled in the BMZ. The second tightest grouping was Zone 2 wells (red diamonds) and these wells are further down along the axis related to ionic strength and total nitrogen. While not as tightly clustered, many of the wells within Zone 1 plot away from the main clusters of wells and further along the axis related to higher PPCP concentrations and higher nitrogen and oxygen isotope values. Zone 3 groundwater formed a looser, less distinct cluster of wells. Compared to Zones 2 and 4, Zone 3 wells were often further along the axis indicating higher ionic strength and total nitrogen and further along the axis indicating higher PPCP levels and higher isotope values. Surface waters did not form a single tight cluster. The samples from the SWP formed a cluster in the upper left of the PCA owing to their low ionic strength and low total nitrogen levels relative to groundwater in the BMZ. In contrast samples of Cooper's Creek and lower San Timoteo Creeks plot into the upper right of the PCA indicating relatively high levels of PPCP, heavier isotopes, higher ionic strength and higher total nitrogen.

Discussion

The potable water supply in the BMZ is mainly supported by groundwater. Due to increases in urban and agricultural water demand, the water table level has dropped as much as 100 feet since 1920s in some areas of the BMZ (USGS, 2006). The total groundwater extraction in the BMZ increased from 1,630 acre-feet in 1936 to over 8,000 acre feet in 2005 (USGS 2006). Areal recharge, mountain-front recharge and general head boundary are the major natural sources of recharging groundwater, which accounted for ~100% of total inflow in 1960s, but decreased to about 40% of total inflow in current years (USGS 2006, Report by Wildermuth Environmental

Inc. 2010). Even though there is a significant amount of natural water recharge, artificial recharge is necessary to slow the decline of groundwater storage in the BMZ. There are several sources of artificial recharge to the basin including return flow from irrigation of crops, golf courses, and landscaping. Septic tank seepage and imported water from the State Water Project (SWP) also contribute to groundwater recharge within the BMZ. Artificial return flow of applied SWP and storm-flow water accounted for less than 1% of the local groundwater recharge in 1960s, but has increased to about 20% in recent years. Percolation of surface water (including artificial return flow) is estimated to take about 50-100 years to reach the water table (USGS 2006). However, infiltration of septic waste water and SWP water appears to be faster, taking 5-10 years to reach the water table, depending on local geology and depth to the water table (personal communication, Samantha Adams, Wildermuth Environmental Inc.).

Nitrate is the most frequently observed nutrient contaminant detected in groundwater of the United States and its concentration is regulated by the US Environmental Protection Agency. Sources of groundwater nitrate in the BMZ include oxidized and reduced forms of nitrogen in precipitation, naturally occurring pools of nitrogen in soils, and fertilizers applied to agricultural lands, golf courses, and residential landscaping. Human waste may also contribute to groundwater nitrate through discharge of effluent from wastewater treatment plants, private septic tanks and during groundwater recharge with SWP water. Human waste contains nitrogen in three forms: nitrate, ammonium and dissolved organic nitrogen (DON). Under oxic conditions, ammonium can be converted into nitrate via the microbial nitrification reactions:

$$NH_4^+ + \tfrac{1}{2}O_2 + 2H_2O \rightarrow NO_3^- + 8H^+ \qquad \text{(Equation 4)}$$

DON can be converted in ammonium via microbial mineralization and then nitrified to produce nitrate.

When water containing nitrate enters a zone of zero oxygen or biological oxygen demand in infiltrating groundwater exhausts all dissolved oxygen, the process of microbial denitrification can convert nitrate into nitrous oxide or di-nitrogen gas. Two potential electron donors can catalyze the denitrification reaction, reduced iron or organic matter:

$$14NO_3^- + \mathbf{5FeS_2} + 4H^+ \rightarrow 7N_2(g) + 10SO_4 + 5Fe^{2+} + 2H_2O \qquad \text{(Equation 5)}$$

$$4NO_3^- + \mathbf{5CH_2O} \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$$

Because oxygen is usually plentiful in surface water and in soils within the vadose zone, most of the nitrogen that reaches the groundwater has undergone mineralization and nitrification. Denitrification occurs when groundwater migrates into a zone of zero oxygen which could occur in an aquifer, a septic tank or in a wastewater treatment plant. Successful application of nitrate isotopes for tracing sources requires an understanding of the effects of denitrification since it can obscure the original source signatures of nitrate (Figure 34). Denitrification leaves a geochemical fingerprint that can be interpreted as evidence for its occurrence and extent. The most obvious evidence for denitrification is the presence of a redox gradient that generates a series of

oxidation-reduction reactions, including the reduction of nitrate in the appropriate position in the sequence. Hence, in a closed system without oxygen, denitrification occurs between the disappearance of dissolved O_2 by aerobic respiration and the appearance of Mn^{2+} and Fe^{2+} (Mariotti et al., 1988). Importantly, during denitrification, the $\delta^{15}N\text{-}NO_3$ and $\delta^{15}O\text{-}NO_3$ values of the residual nitrate increase in proportion to the logarithm of the residual nitrate fraction if the aquifer or treatment plant or septic tank acts as a closed system (Kendall, 1998). Because the kinetic isotope effect of denitrification acts more strongly on the nitrogen isotope of nitrate, the magnitude of fractionation for nitrogen is about 2-times the fractionation experienced by oxygen. When $\delta^{15}N\text{-}NO_3$ and $\delta^{15}O\text{-}NO_3$ are plotted on an X:Y graph ($\delta^{18}O$ on the y-axis and $\delta^{15}N$ on the x-axis), one can identify the occurrence of denitrification when samples fall along a line with a slope of about 0.5 (Figure 34) (Roadcap et al., 2002).

In Figure 34 we show typical source signatures for nitrate and the potential effect of denitrification on nitrate isotope composition. Atmospheric nitrate and nitrate fertilizer produced from atmospheric N_2 typically have $\delta^{15}N$ values between -5 and + 5 per mil and $\delta^{18}O$ values greater than about 20 per mil (typical range +20 to +80 per mil). Nitrate produced from reduced nitrogen fertilizers has a $\delta^{15}N$ that hovers around zero per mil and a $\delta^{18}O$ between 0 and 5 per mil. Nitrate produced by microbial mineralization and nitrification has a $\delta^{15}N$ that can range between 0 to about +5 per mil $\delta^{15}N$ and 0 and 5 per mil $\delta^{18}O$. Nitrate from human or animal waste typically has the highest $\delta^{15}N$ values, +5 to >20 per mil. Note that denitrification of fertilizer or soil N could produce high $\delta^{15}N$ values, but $\delta^{18}O$ values would also increase.

To better understand the sources of groundwater nitrate, the BMZ was divided into four zones (Figure 35a) based primarily on how human waste is handled and secondly on landuse within the BMZ. Zone 3 was further divided into Zones 3-1 and 3-2 (Figure 35b) based on differences between the isotopes of nitrate in Zone 3 sub-regions (see below). The results from the PCA and cluster analysis provide validation for separating the well data into these zones (Figure 33). These four zones have real differences in water quality, including parameters that are diagnostic of groundwater contamination with human waste (PPCPs, salts and isotopes of nitrate).

In the following sections we will describe the water quality within each of these four zones and discuss the likelihood that zonal groundwater is affected by human waste. Where appropriate, we will also describe the changes in water quality that occur as the water moves laterally within each zone to gain better understanding of processes that could be impacting groundwater chemistry (for example mixing of groundwater basins or denitrification of nitrate).

Zone 1 – Region Influenced by Wastewater Treatment Plant Effluent: Zone 1 occupies the southernmost area of the BMZ and is defined as surface water and groundwater sampling sites nearby Cooper's Creek and San Timoteo Creek. Water quality in Zone 1 is influenced by effluent from the City of Beaumont wastewater treatment plant (WWTP #1 in Figure 35a). About 1.8 MGD (million gallons per day) of tertiary treated wastewater from the City of Beaumont is discharged to support riparian habitat in Cooper's Creek and San Timoteo Creek. This recycled

wastewater may take only a few years to reach the shallow water table in Zone 1 (USGS 2006). The groundwater in Zone 1 flows away from WWTP #1 in two directions (NW and SE), which is shown in Figure 35a. Several groundwater wells close to WWTP #1 had higher salt content, higher nitrate concentrations, and higher PPCP concentrations, compared with downstream sites and other sites in the BMZ (Figures 36 and 37). Based on ANOVA analysis, Zone 1 had significantly higher PPCP index values than zones 2 and 4 ($p < 0.001$), significantly higher nitrate concentrations than Zone 4 ($p<0.001$), significantly higher $\delta^{15}N$ and $\delta^{18}O$ of NO_3 than zones 2, and 4 ($p<0.001$) and significantly lower dissolved oxygen concentrations than zones 3 and 4 ($p < 0.001$).

Moving along a flowpath down-gradient from the WWTP, we observed marked changes in dissolved oxygen, nitrate and isotopes of nitrate (Figure 37). These changes are likely the result of microbial processes that consume oxygen and thereby generate conditions that favor denitrification. Alternatively, mixing of WWTP #1 with water in a deeper or adjacent aquifer could be driving the changes seen in Figure 37. Plots of nitrate isotope vs. nitrate concentration (Figure 38) were made for Zone 1 to distinguish between mixing ($\delta^{15}N$ vs. $1/[NO_3]$) or denitrification ($\delta^{15}N$ vs. $Ln[NO_3]$) and showed that both mixing and denitrification could be taking place and therefore did not say much regarding the relative importance of these two processes. However, a bi-plot of nitrate $\delta^{18}O$ vs. $\delta^{15}N$ provides strong evidence for denitrification within Zone 1 (Figure 39). The linear regression in Figure 39 produces an R^2 of >0.94 for all groundwater wells except 1208660 and the slope of this line, 0.43, is not significantly different from the slope of 0.5 expected from denitrification.

Extrapolation of the denitrification line in Figure 39 passes slightly above the position of the isotope values of Well 1208660 suggesting that Well 1208660 contains nitrate that is slightly different than that found in the other Zone 1 wells. Interestingly, one can draw a line through the two creek samples that passes through the isotope values for Well 1208660 which may indicate that nitrate in Well 1208660 is a mixture of more recently infiltrated nitrate from surface water and groundwater nitrate that has experienced substantial denitrification. At Well 1208660, six PPCP compounds were detected, including primidone (4.7 ng/L), meprobamate (3.0 ng/L), diuron (3.3 ng/L), carbamazepine (87.2 ng/L) and sulfamethoxazole (25.8 ng/L) (Table 8).

The water quality changes along the flowpath in Zone 1 tell a consistent story of nitrate inputs from a WWTP followed by microbial processes consuming oxygen, which produces conditions favorable for denitrification (Figure 37). During denitrification, nitrate is converted to N_2 gas which drives isotopic enrichment of the residual nitrate pool; this effect is clearly seen in the exponential reduction of nitrate concentrations and logarithmic increase in nitrate isotope values (Figure 37). Suitable conditions for denitrification, including depletion of DO (8.8 mg/L decreased to 0.3 mg/L) (Table 5 and Figure 37) and adequate supply of electron donors, such as iron and sodium (Table 6) were present along the water flowpath. Furthermore, Fe^{2+} was detected in the low DO groundwater of Zone 1 (Table 5) which indicates that redox conditions were suitable for denitrification.

The PPCP data provide additional evidence that much of the nitrate in Zone 1 comes from the WWTP effluent. Zone 1 had the highest frequency of PPCP detection, in both wells and surface water, of the BMZ (Figure 30). Five of the 10 wells located in Zone 1 contained 3 to 5 quantifiable concentrations of the target compounds. Two wells contained quantifiable concentrations of sulfamethoxazole and there were no compounds detected in the remaining three wells. The majority of the detections and highest concentrations were located along the NW flowpath of the WWTP 1 outfall. The concentration and detections of PPCPs in groundwater were lower along the SE flowpath.

The two surface water samples from the NW flowpath of the WWTP effluent contained 10-13 detectable PPCP compounds, which was more than any well sample. These two surface water samples also had PPCP index values 10.9 and 11.9, the highest measured in the BMZ (Table 7).. The concentrations of PPCP compounds decreased by 22 to 86% with increasing distance from the WWTP #1 outfall (when adjusted for evaporation using chloride as a conservative tracer). Carbamazepine (22%) and sulfamethoxazole (23%) were reduced the least, while trimethoprim (86%) and gemfibrozil (80%) concentrations were reduced the most. Diuron concentrations increased with distance from the WWTP #1. This compound is a commonly used herbicide, which would likely have sources other than effluent from the WWTP. Concentrations of PPCP in surface water of Zone 1 were greater in all instances than what was detected in the groundwater of Zone 1. This is likely due to sorption and degradation of PPCP compounds as they travel from the WWTP discharge and percolate into the ground. The PPCP index values in groundwater ranged from 9.1 to 1.1 and generally decreased along the NW flowpath of the WWTP effluent (Table 7). The only two wells in this zone that had index values of zero were wells 1006132 and 1220050, which were along the SE flowpath of groundwater. This is the opposite direction of where most of the WWTP discharge flows.

Zone 2 – Wildland and Low Density Septic Disposal Region: Zone 2 is defined as the area uphill of Edgar Canyon to the north of Cherry Valley (Figure 2). Groundwater in this mostly wildland area has lower temperatures than elsewhere in the BMZ (Figure 3) which may be a result of the temperature lapse rate with elevation or faster recharge of groundwater (Brink 2007). Zone 2 wells, overall, were oxic (Figure 6), and had low to moderate concentrations of TDS (Figure 9). In the wells at the top of Zone 2, nitrate-nitrogen concentrations ranged from about 1 to 2.5 mg/L while concentrations were slightly higher in wells at the lower elevations in Zone 2 (2 to 2.8 mg/L; Figure 35a). Moving along the flowpath, downhill, we noted changes in major ion chemistry (Figure 40) and a slight decrease in $\delta^{15}N\text{-}NO_3$ and increase in $\delta^{18}O\text{-}NO_3$ (Figure 41). The oxygen isotope of nitrate in Zone 2 wells may be reflecting the $\delta^{18}O$ value of water used in nitrification (Equation 4) which is lower at higher elevations (Fry 2006). Plots of $\delta^{15}N$ vs. $1/[NO_3]$) and $\delta^{15}N$ vs. $Ln[NO_3]$) could not distinguish between isotope mixing or denitrification (Figure 42). A bi-plot of $\delta^{15}N\text{-}NO_3$ vs. $\delta^{18}O\text{-}NO_3$ reveals no evidence for denitrification of nitrate within Zone 2 or along the downhill flowpath (Figure 43). Overall, the isotopic values of nitrate in Zone 2 suggest that most of the nitrate in groundwater is derived

from natural soil nitrogen and/or fertilizer nitrogen (Figure 34). Higher values of $\delta^{15}N\text{-}NO_3$ in the lower-elevation portions of Zone 2 may indicate a small, but increasing influence of inputs of nitrate from human or animal waste.

All of the wells sampled in Zone 2 contained PPCPs, however diuron was the only compound detected in two of the wells. While diuron may be associated with septic waste, it is also common in the environment due to its usage as an agricultural herbicide. Sulfamethoxazole was the most commonly detected pharmaceutical compound in Zone 2 (4 wells), with higher concentrations in the lower elevation groundwater samples. Carbamazepine was also detected in wells at lower elevations. Both sulfamethoxazole and carbamazepine are commonly detected in the environment and are relatively more persistent than other PPCPs. The presence of these two compounds as well as primidone, atorvastatin and fluoxetine indicate that some water emanating from septic systems is entering the groundwater in Zone 2, although concentrations of nitrate and isotopic values of nitrate observed in Zone 2 indicate lower levels of human/animal waste contamination relative to zones 1 and 3 (discussed below). Generally higher concentrations of sulfamethoxazole at lower elevation wells may indicate that groundwater receives greater amounts of human waste at lower elevations within Zone 2. The two wells with the highest PPCP index were BCVWD 4 and BCVWD 6 with values of 4.7 and 4.1 respectively. The two surface water samples from the top of the mountain were relatively clean, with only diuron and gemfibrozil being detected, but at concentrations less than the limits of quantitation, therefore their PPCP index values are zero.

Zone 4 – Urban Region With Consolidate Sewer System: Zone 4 encompasses the portion of Beaumont utilizing a municipal sewer system. All sewage from the City of Beaumont is transported to WWPT #1 for tertiary treatment (USGS 2006). As discussed above, water applied to the soil surface could take 50-100 years to reach water table due to localized geology and groundwater table depths. Therefore, it is possible that the groundwater in Zone 4 is currently receiving water applied to the land surface around the 1960s (USGS 2006). SWP water takes less time to reach groundwater through the recharge ponds (5-10 years), but has only been occurring at the BCVWD spreading basins since 2005. Zone 4 groundwater might not yet be receiving large amounts of SWP water due to the slow groundwater infiltration rates (USGS 2006).

Groundwater in Zone 4 is oxic, and has lower than BMZ-average specific conductance (Figure 7), lower than average nitrate concentration (Figure 14), and lower than average sulfate and chloride levels (Figures 17 and 18). ANOVA tests demonstrate that nitrate concentrations are significantly lower in Zone 4 compared to all other zones ($p < 0.001$) and that $\delta^{15}N\text{-}NO_3$ values are significantly lower in Zone 4 compared to zones 1 and 4 ($p < 0.001$). The $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ measured in Zone 4 groundwater cluster tightly around 2 to 3 per mil and 0 per mil, respectively (Table 7), which suggests the major sources are natural soil nitrate or oxidation of reduced nitrogen fertilizer (Figure 34). In 11 of the 14 wells sampled in Zone 4 there were no PPCP compounds detected or they were detected below the limits of quantitation (Figures 30 and 31). The PPCP concentrations detected were all less than 1 ng/L (except acetaminophen – 13.9

ng/L and diuron – 2.1 ng/L). ANOVA tests indicate that PPCP index values in Zone 4 are significantly lower than in Zone 1 ($p < 0.001$) and Zone 3 ($p < 0.1$). Based on the major ion, nutrient, PPCP and isotope data, we conclude that the probability of human waste contamination is much lower in Zone 4 than in either zones 1 and 3 and similar to the contamination probability in Zone 2.

Zone 3 – Urban Region With On-site Septic Disposal Systems: Human waste from homes and businesses in Zone 3 is predominantly disposed of in on-site waste disposal systems. The groundwater within Zone 3 was well-oxygenated with the exception of the western-most well which had DO between 2 and 4 mg/L (Figure 6). Several wells within Zone 3 had higher than average levels of specific conductance and TDS (Figures 7 and 9). It is noteworthy that groundwater in Zone 3 contained higher nitrate concentrations than surface water and SWP recharge water (Figure 35a). Five wells within Zone 3 had nitrate-nitrogen concentrations greater than 5 mg/L (Figure 14); sulfate and chloride levels in these wells were higher than average for the BMZ. Six wells in Zone 3 had $\delta^{15}N\text{-}NO_3$ greater than 5 per mil (Figure 27) and PPCP index values higher than any well outside of Zone 1 (Figure 31). The $\delta^{15}N\text{-}NO_3$ values of groundwater in Zone 3 were significantly ($p<0.001$) higher compared to nitrate in zones 2 and 4 (Figure 27).

Groundwater flowpaths in Zone 3 were more difficult to define, so we attempted to discern gradients in water quality moving away from groundwater recharge sites using SWP inputs (Figure 44). A clear gradient in anion percentage was observed in Zone 3 with a weaker trend detectable in major cations (Figure 44). SWP water was characterized by relatively high values for $\delta^{15}N\text{-}NO_3$ (> +8 per mil), which suggests a higher contribution of nitrate from human or animal waste. However, nitrate-nitrogen concentrations in the SWP were only 0.32 mg/L. In water samples taken at the San Gorgonio Pass Water Agency and Beaumont Cherry Valley Water District spreading basins, carbamazepine, sulfamethoxazole, meprobamate and diuron were detected. The first three compounds are associated with human waste, while diuron is a herbicide. The concentrations of each of the four compounds were nearly identical between the two sampling sites, indicating homogeneity of water from the SWP. The index values for PPCP contamination in the SWP were both 5.3. The source waters for the SWP contain wastewater effluent discharge points (Loraine and Pettigrove 2006), therefore, the SWP may be influenced by anthropogenic sources of nitrate. Additionally, PPCPs have also been detected in the source water for the SWP (Loraine and Pettigrove 2006).

Water from Well 1007022 contained dilantin, diuron, primidone and sulfamethoxazole and a PPCP index value of 6.7 (the sixth highest index value within the BMZ). A nearby well (1206853) also contained sulfamethoxazole and had an index value of 3.6. While these two wells are in the BMZ, they are actually in the Singleton groundwater storage unit. The Singleton storage unit is separated from the Beaumont Basin by the Cherry Valley Fault to the South and Southeast. This fault likely impedes groundwater movement from the Singleton storage unit into the adjacent storage units. This may be one reason that we see a several detects within well 1007022.

Three additional groundwater wells in Zone 3 contained sulfamethoxazole, albeit at lower concentrations than the two wells within the Singleton storage unit. Atorvastatin and diuron were also detected in two of the three wells, and the concentration of diuron in BCVWD Well 16 was 336 ng/L. These wells had index values for PPCP contamination from 1.9 to 3.5. Two wells had index values of zero. The surface water sample taken in San Gorgonio Creek, near San Gorgonio High School contained gemfibrozil (0.2 ng/L), trimethoprim (1.2 ng/L) and diuron (1061 ng/L) resulting in a PPCP index value of 2.9. The concentration of diuron in this sample was the highest of any compound in all of the samples examined. This sample was taken during a "first flush" rain event. Trimethoprim was also detected in the surface water sample taken from Noble Creek at Noble Avenue (C value of 1.2).

Zone 3 was further separated into two sub-regions to provide more information on groundwater quality within distinct parts of Cherry Valley that lie within Zone 3 (Figure 35b). Zone 3-1 represents wells sampled near the center of Cherry Valley and wells within Zone 3-2 generally lie around the periphery of Cherry Valley (see Table 1 for individual well classifications). Groundwater at the center of Cherry Valley in Zone 3-1 had significantly higher NO_3–N concentrations, higher $\delta^{15}N\text{-}NO_3$ values, higher PPCP index values and higher TDS than wells in Zone 3-2 and Zone 4 (Figure 45). The data in Figure 45 suggest that groundwater within Zone 3-1 has the highest probability of contamination by human waste in the BMZ outside of Zone 1. Furthermore, groundwater quality appears to improve markedly when moving in a direction southward out of Cherry Valley and into Zone 4 which is served by a sewage treatment plant.

Apportioning Sources of Nitrate in Zone 3 Using Isotope Mixing Analysis: Zone 3, due to its geographic position in the center of the BMZ, its varied landuse patterns and recharge program using SWP water, is perhaps the most complex zone within the BMZ to apportion groundwater nitrate inputs. A bi-plot of $\delta^{15}N\text{-}NO_3$ vs. $\delta^{18}O\text{-}NO_3$ reveals two clusters of points: Zone 3-1 plots further to the right and higher in the graph relative to Zone 3-2 (Figure 46). A linear regression fit to the Zone 3 data in Figure 46 produces an R^2 of 0.15 and slope of 0.31 indicating that the influence of denitrification on nitrate in Zone 3 is relatively low and that the isotope values faithfully record source signatures. In order to quantify the amount of nitrate contributed by various sources in Zone 3, we defined potential source endmembers and performed an isotope mixing analysis using the software program IsoSource.

Artificial recharge makes up about 20% of the annual groundwater recharge in the BMZ therefore it is a potential source for nitrate contamination in Zone 3 so it was considered in the isotope mixing analysis. We assigned nitrate in the SWP isotopic values of -2.74 per mil and +8.88 per mil for $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$, respectively (i.e. the average of the points labeled SWP in Figure 46). Because of the relatively high density of septic tanks in Zone 3, we included an endmember representative of nitrate from human waste. We set this endmember value to equal the isotopic composition of nitrate discharged at the City of Beaumont Wastewater Treatment Plant with $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ values of 5.36‰ and 11.8‰ respectively (i.e., the

average of the points labeled Septic Waste in Figure 46). Because of Zone 3's location downhill from Zone 2, we included an endmember with $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ of 3.01‰ and 3.02‰ respectively, which was the average isotopic composition of wells in the lower portions of Zone 2 (i.e., the average of the points labeled Zone 2 in Figure 46) Lastly, we included an endmember representative of uncontaminated natural groundwater and used the average isotopic composition of nitrate in Zone 4 to approximate its isotope values: $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ equal to -0.31‰ and 2.46‰ respectively (i.e., the average of the points labeled Native Groundwater in Figure 46).

IsoSource uses the isotope composition of nitrate of the endmembers to compute all possible mixtures of sources that can produce observed values of $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ in Zone 3 groundwater. We used the software to separately predict the source contributions to zones 3-1 and 3-2 using their mean isotopic values to guide the mixing computations. Note that IsoSource does not compute a single source contribution for each endmember but a range of possible contributions. If the isotope mixing model is not well constrained by the available data, then mixing contributions can span wide ranges and not provide much useful information. In many cases, IsoSource solutions allow one to estimate a minimum or maximum endmember contribution which can be very useful.

The results for central Cherry Valley groundwater (Zone 3-1) are graphed in Figure 47. Natural groundwater contributes from zero to 36% of the nitrate in central Cherry Valley groundwater, and SWP recharge could contribute from zero to 15%. Contributions from lateral movement of Zone 2 groundwater and septic systems are better constrained. Based on the IsoSource model, lateral transport of nitrate from Zone 2 is likely the single largest source of nitrate in Zone 3-1 with a contribution ranging from 33 to 69%. Contributions of nitrate from septic systems could potentially supply between 18 to 30% of the nitrate in groundwater of Zone 3-1, suggesting that human waste is an important source of nitrate in central Cherry Valley. Based on this model, extension of sewer service to central Cherry Valley could result in a 30% decrease in groundwater nitrate concentrations over time.

IsoSource mixtures for Zone 3-2 (Figure 48) indicate that natural groundwater is the single largest sources and could potentially supply between 51 to 81% of the groundwater in peripheral areas of Cherry Valley. Lateral movement of Zone 2 groundwater is the next largest source with possible contributions of between 12 to 39%. Both the SWP and septic systems contribute a maximum of about 9 to 10% of the nitrate in Zone 3-2 groundwater. Based on our IsoSource mixing analysis, extension of sewer service to peripheral areas of Cherry Valley could lead to a 9% reduction in groundwater nitrate concentrations given current population density.

Apportioning Sources of Nitrate in the BMZ Using Mass Balance Analysis: If one assumes that groundwater in the BMZ can be modeled as a mixed reactor, then it is possible to construct simple water and mass budgets based on annual fluxes of water and nitrate. If one can estimate the volume of groundwater in the BMZ and one can quantify recharge pathways and water withdrawals it is possible to assign nitrate concentrations to these pools and fluxes and construct a mass balance for nitrate in the BMZ. We utilized recent estimates of groundwater pools and

groundwater fluxes computed by Wildermuth Environmental and nitrate concentrations from our study and Wildermuth Environmental to compute an annual nitrate mass balance for the BMZ (Table 9).

In the mass balance, the nitrate concentration for total groundwater storage is the average of all wells sampled during our study, including duplicates. Nitrate concentrations for the State Water Project are the average of four measurements made at the BCVWD recharge basins during our study. The natural surface water nitrate value is the average nitrate concentration in all surface water samples collected during our study. Nitrate in mountain-front groundwater was computed as the average nitrate value for all Zone 2 wells. The nitrate concentration for well pumpage is the average of nitrate values measured in large volume wells operated by the BCVWD within the entire BMZ. Wastewater treatment plant effluent volume was estimated to be 1.8 million gallons per day which equals 2016 acre-feet per day. The nitrate concentration for WWTP effluent was set to 6 mg/L based on the information offered by California State Water Boards (Dr. Cindy Li, personal communication). Denitrification was estimated based on the relative reduction of nitrate (change from 16 to 14.5 mg/L = 90.6% nitrate reduction) observed along the flowpath in Zone 1 and the average concentration of nitrate in effluent from the City of Beaumont Wastewater Treatment Plant(Figure 37). Negative signs in the table indicate that BMZ aquifer is losing either water or nitrate-nitrogen.

Groundwater storage in the BMZ is estimated to be almost 190,000 acre feet (AF) and based on our study, it has a mean nitrate-nitrogen concentration of 3.49 mg/L which yields a total groundwater nitrate-nitrogen pool of about 815,000 kg (Table 9). The largest sources of nitrate to the BMZ are effluent from the City of Beaumont WWTP and septic waste, which add about 15,000 kg each year respectively. However, denitrification occurring along the flowpath in Zone 1 (see Figure 37) removes a large amount of the WWTP nitrate (Table 9). Pumpage of groundwater represents another large loss of nitrate from the aquifers within the BMZ and is on the order of -47,000 kg per year (we assumed that the nitrate in pumpage was completely assimilated by vegetation during landscape irrigation with the remainder accounted for in septic waste and WWTP effluent).

Mountain-front drainage, primarily from Zone 2, contributes about 10,000 kg of nitrate-nitrogen per year. Despite representing 8,000 AF of water, the SWP adds only about 3,200 kg of nitrate-nitrogen owing to its very low nitrate concentration. Lastly recharge by natural surface water adds about 5,200 kg of nitrate-nitrogen to the groundwater within the BMZ.

On an annual basis we estimate that the BMZ is near a steady state in terms of water storage, however without groundwater recharge with SWP water, there would be an overdraft of about 8,000 AF per year or about 4% of the groundwater pool. We estimate that there is currently net removal of nitrate from groundwater in the BMZ on the order of -12,500 kg per year. This decrease in nitrate-nitrogen storage would translate into a 0.05 mg/L/yr decline in groundwater nitrate concentrations. A complete phase-out of septic systems over time would increase the rate of nitrate-nitrogen decline to 0.12 mg/L/yr under current conditions.

The nitrate mass balance underscores an important point. Most of the nitrogen added to the BMZ is derived from human waste and its ultimate source lies in food imported into the region. Currently the human population within the BMZ produces 2,016 + 341 = 2,356 AF of sewage per year with a weighted nitrate-nitrogen concentration of 10.2 mg/L. This waste adds 29,642 kg of nitrogen per year to the groundwater within the BMZ which is equal to about 3.4% of the current mass of nitrate-nitrogen held in the BMZ aquifers. However, the large majority of nitrate discharged by the City of Beaumont WWTP is effectively removed from the basin through the process of denitrification in Zone 1. In contrast, current septic system designs do not produce large reductions in nitrate-nitrogen concentrations. We estimate that if sewer service was extended to all homes and businesses within the BMZ, nitrate-nitrogen loading to the groundwater would be reduced by 341 x (35-6) x 0.906 = 8,959 kg per year.

However, groundwater quality improvements from a phase-out of septic systems could be negated to some extent if the region increases the use of treated wastewater for irrigation of landscaping. Current projections estimate that 642 AF of recycled water per year could be applied within the BMZ with an expected average nitrate-nitrogen concentration of 10.79 mg/L (Wildermuth Environmental). This represents a diversion of 8,542 kg/yr of nitrate-nitrogen from the riparian zone in Zone 1 where there is efficient removal of nitrogen via denitrification. While some of the nitrate in the irrigation water will be utilized by plants, we speculate that the majority will infiltrate below the rooting zone and eventually add to the load of nitrate to the BMZ aquifers. It is possible that nitrogen additions from the use of recycled WWTP effluent could substantially offset nitrate decrease expected from a phase-out of septic systems within the BMZ.

Can We Answer the Questions Posed at the Beginning of This Report?

In the Introduction to this report we posed three main questions regarding groundwater quality within the Beaumont Management Zone. We will know attempt to answer them using the results of our 2011 water quality investigation.

1. Can different groundwater regions within the BMZ be defined using isotope, PPCP and general chemical parameters?

Based on the principal components and cluster analyses we were able to delineate four statistically distinct groundwater sub-zones within the BMZ. The first of these regions, Zone 1, was characterized by relatively high levels of PPCPs, isotopes of nitrate that were indicative of human waste contamination and major ion chemistry that supported the supposition that discharge from the City of Beaumont wastewater treatment plant is affecting wells along the Cooper's Creek and San Timoteo Creek drainages. Our data suggest that this region has the highest likelihood for nitrate contamination from human waste. Within Zone 1, nitrate behaves in a non-conservative manner likely owing to high biological oxygen and groundwater

conditions that favor denitrification. Thus, a substantial proportion of the nitrate exiting the WWTP is being converted to gaseous nitrogen forms.

In the northern part of the BMZ we identified a region of mainly wildlands with some low-density urban development served by septic systems. This region, Zone 2, had detectable levels of some PPCPs, but nitrate concentrations and isotopes suggest that septic inputs to the groundwater are relatively minor. Overall, the groundwater nitrate in Zone 2 appeared to originate from natural soil nitrogen and/or nitrate from oxidation of reduced nitrogen fertilizers. However, there was evidence for greater contributions from human waste in the lower-elevation areas of Zone 2 that bordered a higher density urban region.

In the central part of the BMZ we identified a region, Zone 3, with several wells showing clear signs of contamination by septic systems. The groundwater within the central part of Cherry Valley appeared to be more strongly affected by septic systems than groundwater on the periphery of Cherry Valley. Several wells within Zone 3 had relatively high concentrations of PPCPs and major anions and cations suggesting septic waste was entering the groundwater system. Nitrogen isotope values of nitrate in several Zone 3 wells fell in a range consistent with human or animal waste and, when combined with the PPCP data, led us to conclude that groundwater within Zone 3 has a moderate to high probability of contamination by human waste.

Between zones 3 and 1 we identified a region, Zone 4, with groundwater showing the fewest signs of contamination by human waste. Most homes and businesses in Zone 4 are serviced by a consolidated sewer system that discharges treated wastewater into Zone 1. In Zone 4 we observed the fewest detections of PPCPs, relatively low concentrations of nitrate and the isotopic composition of nitrate suggested that the major inputs were natural soil nitrate and/or nitrate produced from nitrification of reduced nitrogen fertilizer.

1A. Do areas with septic systems have different chemistry than areas with sewers?

Our data suggest there are statistically significant differences between groundwater in areas with septic systems and groundwater in areas where sewer service is available. ANOVA tests revealed that Zone 4, with sewer service, had significantly lower nitrate concentrations and significantly lower $\delta^{15}N\text{-}NO_3$ values than groundwater in Zone 3 (septic systems). To underscore these differences, we performed t-tests on wells from zones 2, 3 and 4 wherein we classified each well as to whether it was in a region serviced by septic systems or sewer; we excluded wells from Zone 1 which are influenced by treated wastewater from the City of Beaumont Plant. We observed the following significant differences ($p < 0.05$) between the chemistry of wells in regions using septic tanks vs. wells in regions using sewers:

PPCP concentrations were significantly higher in areas with septic systems than in areas with sewer service (mean 2.3 ng/L vs. 0.46 ng/L)

TDS was significantly higher in areas with septic systems than in areas with sewer service (mean 308 mg/L vs. 243 mg/L)

Nitrate-nitrogen was significantly higher in areas with septic systems than in areas with sewer service (mean 10.4 mg/L vs. 6.1 mg/L)

The sum of base cations (Ca, Ng, Na, K) was significantly higher in areas with septic systems than in areas with sewer service (mean 82.3 mg/L vs. 67.4 mg/L)

Boron was significantly higher in areas with septic systems than in areas with sewer service (mean 9.7 µg/L vs. 8.6µg/L)

$\delta^{18}O\text{-}NO_3$ was significantly higher in areas with septic systems than is areas with sewer service (mean 1.96 per mil vs. -0.21 per mil)

$\delta^{58}N\text{-}NO_3$ was significantly higher in areas with septic systems than is areas with sewer (mean 3.78 per mil vs. 2.48 per mil)

1B. Do areas where groundwater is recharged with water from the State Water Project or wastewater treatment plant effluent have different chemistry from other areas?

The SWP recharge basins tended to produce more dilute groundwater in their immediate vicinity. Nitrate concentrations in the SWP water were much lower than groundwater in the BMZ. However, detections of PPCPs and the isotopic composition of nitrate in the SWP suggested that the SWP is contaminated with human waste prior to entering the BMZ. Zone 1 is a region where riparian ecosystems are supported by treated wastewater. We detected strong evidence for nitrate deriving from human waste in Zone 1 as well as strong biological attenuation of nitrate transported in groundwater.

2. What sources contribute nitrate to groundwater of the BMZ?

2A. Do different regions within the BMZ have different sources of nitrate?

2B. Do regions of the BMZ with different types of human waste disposal (i.e., septic vs. sewer) have different sources of nitrate?

2C. What areas of the BMZ, if any, have nitrate that appears to come from animal or human waste?

In Figure 49 we have created bi-plots of the oxygen and nitrogen isotopic composition of groundwater nitrate in each of the four groundwater zones within the BMZ. In zones 2 and 4, the isotopic composition of nitrate overlaps the expected values for soil nitrate and nitrate produced from nitrification of ammonia fertilizers (Figure 34). It is noteworthy that no wells sampled within zones 2 and 4 had a $\delta^{15}N\text{-}NO_3$ value greater

than 5 per mil, hence we can constrain the range of $\delta^{15}N$ values for soil nitrate shown in Figure 34 to a range of between 0 and +5 per mil in the BMZ. In Zone 1, we observed several sites where the $\delta^{15}N$ and $\delta^{18}O$ values of nitrate overlap those expected for human or animal waste; in all Zone 1 samples, $\delta^{15}N$-NO_3 values were greater than 5 per mil. In several wells within Zone 3, the $\delta^{15}N$ values of nitrate were greater than 5 per mil and suggest a high probability of inputs of nitrate from human or animal waste. The presence of PPCPs in most of these samples demonstrates the possibility that septic systems are contaminating groundwater within the central part of Cherry Valley.

3. How much nitrate from human waste is making its way into the groundwater of the BMZ?

3A. Can models based on isotopes and mass balances be used to estimate septic inputs?

3B. How much would nitrate concentrations decline if sewer service was extended to regions within the BMZ currently using septic tanks?

This is a challenging question to answer but we have data to make an approximate answer. Isotope mixing analysis for groundwater in Zone 3 shows that we cannot produce a mixture of nitrate sources to match the $\delta^{15}N$ and $\delta^{18}O$ of nitrate in central Cherry Valley groundwater without the additions of isotopically heavy nitrate from human waste. The mixing model suggests that between 18 to 30% of the nitrate in central Cherry Valley groundwater is derived from septic systems. These results suggest that if septic systems were completely phased out, nitrate concentrations in central Cherry Valley groundwater could decline by 30% once a steady state condition is achieved. It is difficult to estimate how long nitrate concentrations will take decline once septic systems are phased out, however, we would note that the residence time of groundwater in Zone 3 may be shorter than in other portions of the BMZ owing to relatively high rates of recharge from the SWP which has very low concentrations of nitrate.

At a larger scale, our t-test analysis demonstrated that wells in regions with septic systems had an average nitrate-nitrogen concentration of 10.4 mg/L while wells in areas serviced by sewers had a mean nitrate-nitrogen concentration of 6.1. If a phase out of septic systems were to reduce nitrate levels in septic-influenced wells to that measured in wells in sewered areas, groundwater nitrate levels could decline by (10.4-6.1)/10.4 = 41.3% (similar to the results from the isotope mixing analysis).

Our mass balance computations show that nitrate-nitrogen inputs from septic tanks is one of the largest input of nitrogen to groundwater in the BMZ. If this waste were diverted to the City of Beaumont WWTP, about 90.6% of the nitrate would be consumed by denitrification in the riparian areas of Zone 1, effectively removing about 30% of the current input of nitrate to ground water from human waste.

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Table 1.Sampling sites for groundwater (40) and surface water (11) in the Beaumont Management Zone. All sites were sampled during the period between February-May 2011 (wet season), and locations marked withan * were re-sampled in July 2011 (dry season). Samples marked with an $^{\Delta}$ were collected in duplicate.

Surfacewater				Groundwater			
	UTM		Zone #		UMT		Zone #
	Easting	Northing			Easting	Northing	
Noble Cr@ Noble Ave$^{\Delta}$	502986	3759467	3	1002958	498094	3757277	4
				1003072	495356	3759175	4
Drainage @Sundance	504880	3755558	4	1004370	501475	3753148	1
				1006132	501832	3753006	1
San Gorgonio Cr@HS	502089	3758005	3	1007022	500029	3758878	3-1
				1007025	500681	3756648	4
Riley Farm	505305	3765760	2	1201450	500978	3759867	3-2
Noble Cr below Powerline	502089	3756679	4	1201486	498494	3757277	4
				1201561	495985	3758865	4
San Timoteo Creek	492120	3759436	1	1206853	500095	3758396	3-1
Coopers Creek	500092	3753745	1	1206892	501810	3752753	1
Little San Gorgonio Creek	502089	3758005	3	1206995	497356	3756555	4
				1206996	498779	3756714	4
Stormwater recharge basin	504688	3765191	2	1207012	498146	3759288	3-1
				1207769	500337	3756840	4
BCVWD pond*	502388	3758655	SWP	1208432	499544	3753783	1
San Gorgonio Pond*	502460	3759568	SWP	1208660*$^{\Delta}$	496948	3754946	1
				1220050	503381	3753003	1
				1221612	500417	3754357	1
				1222079	494276	3757317	1
				1222080	494276	3757317	1
				BCVWD Well#1*	502724	3755313	4
				BCVWD Well#3	502908	3755205	4
				BCVWD Well#4*	503225	3760400	2
				BCVWD Well#5*	503554	3760837	2
				BCVWD Well#6*	503431	3763011	2
				BCVWD Well#10*	504647	3765018	2
				BCVWD Well#11	504860	3765116	2
				BCVWD Well#12*	504997	3765249	2
				BCVWD Well#14*	504254	3764826	2
				BCVWD Well#16$^{\Delta}$	502913	3759077	3-1
				BCVWD Well#19*	504717	3764974	2
				BCVWD Well#20*	504666	3764986	2
				BCVWD Well#21*	503293	3757563	3-1
				BCVWD Well#23*	502490	3757737	3-2
				BCVWD Well#24	500221	3757665	3-2
				BCVWD Well#25	504151	3756122	4
				BCVWD Well#26*	503441	3755078	4
				BCVWD Well#28	502885	3756095	4
				BCVWD Well#29	498512	3758423	3-2

Table 2. Water quality criteria used during collection of well samples.

Field Measurement	Stability Criteria[^]
pH	± 0.3 standard units
Temperature (T)	± 0.4°C (Thermistor thermometer)
Conductivity (μS cm^{-1} at 25°C)	± 1.0% for SC ≤ 100 μS cm^{-1}
	± 0.5% for SC > 100 μS cm^{-1}
Dissolved Oxygen (mg L^{-1})	± 0.5 mg L^{-1}

[^]*Allowable variation between 3 or more sequential field measurement values*

Table 3. Summary of general water quality and isotopic constituents measured in water samples collected in the Beaumont Management Zone.

Analyte	Well Samples	Creek Samples	SWP	Analytical Method
pH, Acid Neutralizing Capacity.	X	X	X	pH Electrode and Meter
Specific Conductance	X	X	X	Meter and K=1 cm^{-1} cell
Major Anions (Cl, PO4, NO_2, NO_3, SO_4,)	X	X	X	EPA Method 300.1
Major Cations (Ca, Mg, Na, K, B, Al, Fe)	X	X	X	EPA Method 200.7
Nutrients (NO_3, total dissolved N, organic N, total dissolved phosphate),	X	X	X	NaOH-Persulfate digestion, EPA 353.2
Dissolved Organic Carbon	X	X	X	EPA Method 9060A
$\delta^{15}N$ and $\delta^{18}O$ of Nitrate	X	X	X	USGS Method (RSIL Lab Code 2900)

Table 4. Pharmaceutical and personal care products used as septic waste indicators in groundwater and surface water samples in the Beaumont Management Zone.

Compound	Use	Compound	Use
Acetaminophen	Analgesic	Meprobamate	Human Tranquilizer
Atenolol	Beta Blocker	Naproxen	Non-steroidal Anti-inflammatory
Atorvastatin	Statin	Primidone	Anticonvulsant
Carbamazepine	Anti-epileptic	Sulfamethoxazole	Antibiotic
Diazepam	Barbiturate	Trimethoprim	Antibiotic
Diclofenac	Non-steroidal Anti-inflammatory		
Dilantin	Anti-epileptic		
^Diuron	Herbicide		
Fluoxetine	Anti-depressant		
Gemfibrozil	Fibrate		
Ibuprofen	Non-steroidal Anti-inflammatory		

^ *Diuron was measured, but was not used in computation of the PPCP contamination index*

Table 5. Field measurements of physical and chemical characteristics of surface water and groundwater in the Beaumont Management Zone. ANC = acid neutralizing capacity; TDS = total dissolved solids and DOC = dissolved organic carbon. Samples marked with an * were re-sampled in July 2011 and the samples marked with an Δ had duplicate samples collected. NA – not available.

		Sampling Date	Field Temp.	pH	Field Dissolved Oxygen	Specific Cond.	A.N.C.	Total Dissolved Solid	DOC
			°C		mg/L	µS/cm	µeq/l	ppm	mg/l
SurfaceWater	Noble Cr@Noble Ave	02/19/11	11.7	7.31	9.90	496	4041.66	332.32	4.97
	Noble Cr@Noble Ave$^{\Delta}$	02/19/11	11.7	7.45	9.90	492	4021.08	329.64	4.93
	Drainage@Sundance	02/19/11	15.0	7.49	9.30	368	2431.24	246.56	7.25
	San Gorgonio Cr@HS	02/19/11	12.8	7.82	9.40	530	4211.93	355.10	8.31
	Riley Farm	02/19/11	10.5	7.21	10.00	407	3497.59	272.69	2.25
	Noble Cr below Powerline	02/19/11	9.6	6.91	9.10	227	1622.98	152.36	4.41
	San Timoteo Creek	03/03/11	17.0	8.18	8.59	912	5941.82	611.04	3.15
	Coopers Creek	03/03/11	16.6	7.84	7.33	725	4070.26	485.75	3.91
	Little San Gorgonio Creek	03/03/11	13.2	7.31	4.20	366	1181.92	245.22	2.31
	Stormwater recharge basin	03/03/11	8.5	7.85	10.22	382	3172.66	255.94	1.62
	BCVWD pond	05/11/11	17.4	6.89	9.26	250	1008.92	167.57	3.09
	BCVWD pond*	07/19/11	24.2	7.17	7.45	241	924.90	161.47	3.07
	San Gorgonio Pond	05/11/11	17.9	6.86	7.77	253	1029.97	169.71	2.13
	San Gorgonio Pond*	07/19/11	24.2	7.22	6.80	238	909.90	159.53	2.16
Ground water	1002958	03/02/11	18.8	7.45	7.54	396	3321.29	265.32	0.07
	1003072	03/01/11	19.4	7.23	6.92	420	3248.26	281.40	0.07
	1004370	03/01/11	19.2	7.15	6.80	433	2500.72	290.11	0.22
	1006132	03/17/11	20.7	7.50	6.48	560	2924.85	375.20	0.20
	1007022	03/02/11	19.4	7.32	9.13	624	3444.29	418.08	0.33

		Sampling Date	Field Temp.	pH	Field Dissolved Oxygen	Specific Cond.	A.N.C.	Total Dissolved Solid	DOC
			°C		mg/L	µS/cm	µeq/l	ppm	mg/l
Groundwater	1007025	03/02/11	21.3	7.55	6.35	348	2936.56	233.16	0.08
	1201450	03/17/11	20.8	7.57	8.27	490	3528.61	328.30	0.16
	1201486	03/02/11	18.6	7.62	8.00	385	3213.34	257.95	0.07
	1201561	03/17/11	20.2	7.62	7.43	397	3296.29	265.99	0.07
	1206853	03/02/11	19.0	7.41	7.54	485	2873.70	324.95	0.14
	1206892	03/17/11	19.2	7.68	8.83	435	3036.81	291.45	0.13
	1206995	03/31/11	NA	7.83	10.63	335	2461.57	224.45	0.04
	1206996	03/31/11	19.5	7.43	7.98	362	2857.72	242.54	0.06
	1207012	03/17/11	20.1	7.03	3.63	965	5784.13	646.55	1.73
	1207769	03/02/11	21.1	7.56	6.60	333	2705.68	223.11	0.04
	1208432	03/03/11	19.1	7.40	1.41	1147	5329.29	768.49	0.82
	1208660	03/17/11	19.2	7.59	0.71	708	4114.09	474.36	0.32
	1208660*	07/18/11	20.8	7.80	1.75	567	3261.02	379.89	0.19
	1208660*$^{\Delta}$	07/18/11	20.8	7.80	1.75	567	3261.02	379.89	0.19
	1220050	03/01/11	19.5	7.24	6.52	517	3764.77	346.39	0.19
	1221612	03/03/11	21.9	7.78	2.14	578	3706.83	387.26	0.20
	1222079	07/18/11	21.1	8.70	0.35	382	2181.28	255.94	0.09
	1222080	07/18/11	21.9	9.28	0.29	355	2030.25	237.85	0.08
	BCVWD Well# 1	05/10/11	17.9	7.43	7.64	383	3214.27	256.61	0.06
	BCVWD Well#1*	07/19/11	20.6	7.60	10.17	352	3072.78	235.84	0.03
	BCVWD Well # 3	05/10/11	18.3	7.50	7.08	361	2994.36	241.87	0.04
	BCVWD Well # 4	05/10/11	15.2	7.33	5.92	579	3695.32	387.93	0.21
	BCVWD Well#4*	07/19/11	19.3	7.36	6.00	590	3756.86	395.30	0.20
	BCVWD Well # 5	05/10/11	15.1	7.35	7.50	463	3165.51	310.21	0.22
	BCVWD Well#5*	07/19/11	18.1	7.45	8.32	460	3126.97	308.20	0.15

		Sampling Date	Field Temp.	pH	Field Dissolved Oxygen	Specific Cond.	A.N.C.	Total Dissolved Solid	DOC
			°C		mg/L	µS/cm	µeq/l	ppm	mg/l
Groundwater	BCVWD Well # 6	05/10/11	14.0	7.30	7.63	456	3464.62	305.52	0.17
	BCVWD Well#6*	07/19/11	16.4	7.36	8.44	447	3412.56	299.49	0.14
	BCVWD Well#10	05/10/11	13.1	7.14	7.20	424	3395.67	284.08	0.21
	BCVWD Well#10*	07/19/11	15.7	7.25	6.26	424	3298.76	284.08	0.20
	BCVWD Well#11	05/11/11	13.5	7.28	8.22	454	3579.01	304.18	0.34
	BCVWD Well#12	05/11/11	13.7	7.08	6.78	416	3193.09	278.72	0.39
	BCVWD Well#12*	07/19/11	14.3	7.11	7.31	408	3125.63	273.36	0.30
	BCVWD Well#14	05/11/11	15.3	7.58	7.72	478	3782.09	320.26	0.25
	BCVWD Well#14*	07/19/11	16.6	7.59	8.20	477	3811.73	319.59	0.21
	BCVWD Well#16	05/26/11	16.8	7.47	8.74	620	3578.01	415.40	NA
	BCVWD Well#16$^{\Delta}$	05/26/11	16.8	7.52	8.74	612	3484.38	410.04	NA
	BCVWD Well#19	05/10/11	11.6	7.01	6.00	462	3687.87	309.54	0.51
	BCVWD Well#19*	07/19/11	17.5	7.22	6.82	439	3541.88	294.13	0.35
	BCVWD Well#20	05/10/11	12.8	7.07	6.72	451	3608.32	302.17	0.28
	BCVWD Well#20*	07/19/11	15.7	7.25	8.25	440	3454.11	294.80	0.19
	BCVWD Well#21	05/11/11	18.1	7.36	9.13	475	2692.43	318.25	0.13
	BCVWD Well#21*	07/19/11	NA	7.61	9.02	480	3139.85	321.60	0.07
	BCVWD Well#23	05/11/11	16.5	7.51	8.86	458	3526.00	306.86	0.20
	BCVWD Well#23*	07/19/11	19.2	7.74	8.96	429	3449.38	287.43	0.05
	BCVWD Well#24	05/11/11	17.0	7.49	8.53	365	2971.99	244.55	0.09
	BCVWD Well#25	05/11/11	17.3	7.55	8.40	402	3254.46	269.34	0.04
	BCVWD Well#26	05/10/11	19.6	7.54	7.08	348	2813.89	233.16	0.06
	BCVWD Well#26*	07/19/11	NA	7.78	8.06	346	2810.48	231.82	0.06
	BCVWD Well#28	05/11/11	16.5	7.47	9.40	408	3421.64	273.36	0.04
	BCVWD Well#29	05/11/11	17.3	7.58	8.80	396	3130.64	265.32	0.08

Table 6. Major and trace ion concentrations for surface water and groundwater in the Beaumont Management Zone Samples marked with an * were re-sampled in July 2011 and the samples marked with an Δ had duplicate samples collected. Charge balance error = (Σ positive charge – Σ negative charge) / Σ positive charge * 100%

		NO_3-N	HCO_3	SO_4	Cl	F	PO_4	NO_3	Ca	Mg	Na	K	Al	B	Fe	P	Charge Balance Error
		mg/L							mg/L								%
SurfaceWater	Noble Cr@Noble Ave	0.70	246.0	47.50	13.43	0.64	0.09	3.11	49.19	22.90	21.77	1.89	0.000	0.012	0.001	0.05	-1.3
	Noble Cr@Noble Ave$^{\Delta}$	0.70	244.6	47.50	13.41	0.64	0.08	3.11	49.22	22.82	21.32	1.86	0.000	0.012	0.001	0.04	-1.3
	Drainage@Sundance	1.23	147.8	48.01	15.45	0.26	0.95	5.47	36.23	11.03	20.38	3.77	0.000	0.024	0.013	0.35	-3.0
	San Gorgonio Cr@HS	1.06	255.2	57.38	15.40	0.62	0.31	4.68	53.11	23.13	26.85	3.82	0.000	0.020	0.000	0.09	-0.7
	Riley Farm	1.31	213.0	37.25	4.48	0.59	0.02	5.80	46.55	16.84	10.42	2.83	0.000	0.009	0.000	0.01	-3.2
	Noble Cr below Powerline	1.03	98.9	19.84	6.99	0.10	0.68	4.57	25.31	6.36	9.29	2.46	0.000	0.018	0.002	0.24	-0.8
	San Timoteo Creek	1.08	357.0	88.64	80.44	0.49	1.16	4.77	69.16	19.52	87.94	6.24	0.004	0.172	0.000	0.42	-4.9
	Coopers Creek	0.92	246.6	65.99	64.63	0.38	2.50	4.05	43.17	13.24	70.74	13.10	0.004	0.182	0.007	0.93	-3.9
	Little San Gorgonio Creek	1.26	71.9	47.16	47.34	0.04	0.26	5.59	18.91	8.49	33.51	2.55	0.000	0.098	0.002	0.10	-5.7
	Stormwater recharge basin	1.50	192.1	38.89	4.06	0.47	0.02	6.65	42.80	15.09	9.77	2.06	0.000	0.008	0.000	0.02	-4.3
	BCVWD pond	0.32	61.5	24.26	23.32	0.08	0.17	1.44	14.24	6.32	19.45	1.83	0.001	0.104	0.000	0.07	-0.9
	BCVWD pond*	0.32	56.3	18.47	21.77	0.07	0.15	1.42	14.14	5.88	21.76	1.54	0.006	0.092	0.006	0.08	6.3
	San Gorgonio Pond	0.32	62.8	24.05	23.15	0.07	0.19	1.43	14.14	6.28	21.55	1.82	0.006	0.104	0.004	0.07	0.7
	San Gorgonio Pond*	0.32	55.4	18.25	21.50	0.07	0.00	1.42	14.31	5.91	21.81	1.60	0.008	0.090	0.008	0.08	7.4
Groundwater	1002958	1.31	202.0	23.16	6.75	0.45	0.61	5.80	39.93	14.66	18.01	1.96	0.000	0.007	0.000	0.23	-0.6
	1003072	2.05	197.8	24.48	13.24	0.36	0.03	9.07	44.89	15.15	17.81	1.43	0.000	0.006	0.000	0.02	0.2
	1004370	11.10	152.3	22.28	16.51	0.38	0.11	49.15	48.44	8.46	23.50	1.50	0.000	0.010	0.000	0.05	-0.7
	1006132	15.86	177.8	24.66	30.86	0.68	0.03	70.23	51.16	16.27	31.18	3.31	0.000	0.012	0.003	0.01	-1.2
	1007022	11.52	209.7	70.67	32.28	0.54	0.29	51.02	51.00	25.77	32.13	0.92	0.000	0.028	0.000	0.10	-4.4
	1007025	1.38	178.5	16.53	7.82	0.31	0.04	6.13	32.36	8.79	24.25	1.53	0.000	0.010	0.000	0.03	-2.4
	1201450	2.17	214.4	52.92	20.86	0.57	0.13	9.61	45.43	17.39	28.10	1.24	0.000	0.018	0.000	0.04	-4.1
	1201486	1.69	195.2	21.34	7.36	0.36	0.00	7.48	35.71	14.89	20.46	1.46	0.000	0.006	0.000	0.03	-0.6
	1201561	1.71	200.2	25.30	8.88	0.25	0.04	7.59	43.90	11.77	21.34	1.76	0.000	0.007	0.000	0.01	-0.7
	1206853	8.71	174.8	34.09	23.16	0.67	0.06	38.59	42.90	16.54	26.07	1.38	0.000	0.013	0.000	0.04	-2.1
	1206892	3.99	184.4	9.26	25.25	0.62	0.07	17.65	37.78	10.80	33.11	1.88	0.000	0.015	0.000	0.02	0.3
	1206995	1.44	149.1	12.96	15.09	0.66	0.06	6.37	13.57	4.56	47.90	1.19	0.006	0.020	0.000	0.02	-1.6
	1206996	1.87	173.8	17.41	10.27	0.53	0.10	8.29	28.31	12.57	25.18	1.34	0.000	0.010	0.000	0.03	-1.1
	1207012	21.31	352.4	61.48	51.37	0.35	0.03	94.37	65.77	35.32	74.44	0.55	0.000	0.071	0.000	0.01	-3.0
	1207769	1.46	164.4	11.74	9.54	0.42	0.06	6.48	31.06	8.52	23.28	1.61	0.000	0.010	0.000	0.03	-0.3
	1208432	10.79	324.3	73.14	146.71	0.42	0.26	47.80	89.59	31.97	84.69	3.73	0.000	0.189	0.000	0.11	-3.6
	1208660	2.43	250.0	78.67	57.63	0.42	0.01	10.77	59.92	16.13	60.35	1.78	0.000	0.113	0.008	0.01	-3.7
	1208660*	1.61	197.7	25.79	47.59	0.42	0.00	7.12	35.78	9.57	68.43	1.53	0.000	0.088	0.000	0.00	3.2
	1208660*$^{\Delta}$	1.59	197.7	25.42	47.06	0.42	0.00	7.04	35.91	9.75	67.86	1.46	0.001	0.089	0.003	0.00	3.4
	1220050	5.20	229.2	20.74	22.51	0.42	0.04	23.01	58.79	13.97	24.44	2.16	0.000	0.016	0.000	0.02	-0.1
	1221612	6.09	224.7	42.05	30.35	0.42	0.01	26.95	34.17	14.88	60.94	3.82	0.000	0.029	0.000	0.01	-1.6
	1222079	1.03	126.6	17.81	22.42	0.42	0.00	4.55	5.35	0.48	77.74	0.77	0.050	0.061	0.034	0.02	6.0
	1222080	0.99	103.4	17.26	18.83	0.42	0.00	4.38	1.81	0.09	76.31	0.70	0.039	0.040	0.009	0.01	11.2
	BCVWD Well# 1	1.11	195.5	9.49	9.78	0.42	0.06	4.93	39.10	12.92	19.76	1.49	0.000	0.007	0.000	0.03	1.9
	BCVWD Well#1*	0.60	186.7	10.44	6.23	0.42	0.00	2.66	36.81	10.95	22.42	1.53	0.000	0.009	0.001	0.00	3.4
	BCVWD Well # 3	1.04	182.1	11.37	9.16	0.42	0.07	4.59	36.39	8.96	24.42	1.57	0.000	0.009	0.000	0.02	1.3

		NO_3-N	HCO_3	SO_4	Cl	F	PO_4	NO_3	Ca	Mg	Na	K	Al	B	Fe	P	Charge Balance Error
										mg/L							%
Groundwater	BCVWD Well # 4	2.10	224.9	49.12	26.20	0.47	0.04	9.29	61.93	20.24	22.99	1.58	0.000	0.010	0.000	0.01	-6.8
	BCVWD Well#4*	2.06	228.6	46.19	24.29	0.37	0.00	9.13	64.82	21.30	21.81	1.79	0.000	0.011	0.001	0.00	3.7
	BCVWD Well # 5	2.86	192.7	33.75	13.37	0.47	0.03	12.66	51.09	15.81	18.13	1.49	0.000	0.009	0.000	0.01	2.4
	BCVWD Well#5*	2.46	190.2	29.52	12.09	0.39	0.00	10.91	50.40	15.94	19.36	1.71	0.000	0.011	0.000	0.00	13.0
	BCVWD Well # 6	2.81	210.9	24.55	8.13	0.36	0.03	12.44	49.89	16.18	16.67	1.15	0.000	0.008	0.000	0.01	1.8
	BCVWD Well#6*	2.41	207.7	22.54	6.45	0.30	0.00	10.66	49.37	16.38	18.77	1.47	0.000	0.009	0.000	0.00	5.0
	BCVWD Well#10	1.59	206.8	24.41	5.48	0.33	0.02	7.03	47.58	15.41	12.35	1.64	0.000	0.008	0.001	0.00	0.5
	BCVWD Well#10*	2.07	200.9	19.79	4.94	0.32	0.00	9.16	48.64	16.12	13.89	1.74	0.000	0.010	0.001	0.00	4.9
	BCVWD Well#11	2.43	217.9	25.22	5.65	0.41	0.04	10.76	51.02	17.01	12.05	2.06	0.000	0.008	0.000	0.00	0.9
	BCVWD Well#12	2.48	194.5	25.16	5.06	0.41	0.07	11.00	46.50	15.20	11.62	1.73	0.000	0.007	0.000	0.01	0.9
	BCVWD Well#12*	1.67	190.4	22.97	3.95	0.34	0.00	7.41	46.05	15.42	12.92	1.93	0.000	0.008	0.001	0.00	4.4
	BCVWD Well#14	1.71	229.8	30.28	5.25	0.34	0.00	7.59	55.37	16.55	16.76	1.09	0.000	0.008	0.000	0.00	2.1
	BCVWD Well#14*	1.56	231.6	26.79	4.25	0.27	0.00	6.90	55.89	17.23	18.53	1.38	0.000	0.010	0.001	0.00	4.7
	BCVWD Well#16	5.71	217.6	60.03	21.10	0.76	0.08	25.30	54.78	20.25	35.92	1.32	0.000	0.023	0.000	0.04	1.3
	BCVWD Well#16$^{\Delta}$	5.70	211.8	60.09	21.02	0.76	0.10	25.24	54.59	20.31	35.29	1.29	0.000	0.023	0.000	0.04	1.8
	BCVWD Well#19	2.35	224.7	27.96	5.66	0.43	0.04	10.41	52.63	17.92	11.59	2.03	0.000	0.008	0.000	0.01	0.5
	BCVWD Well#19*	1.15	215.7	22.00	4.15	0.37	0.00	5.08	50.70	17.59	11.74	2.43	0.000	0.010	0.000	0.00	3.9
	BCVWD Well#20	2.21	219.8	25.61	5.51	0.39	0.03	9.79	52.50	17.36	11.40	1.77	0.000	0.009	0.000	0.00	1.4
	BCVWD Well#20*	1.82	210.3	23.03	4.62	0.32	0.00	8.07	51.69	17.67	12.74	1.93	0.000	0.010	0.005	0.00	4.9
	BCVWD Well#21	8.65	163.9	30.97	16.38	0.72	0.07	38.32	44.54	15.03	24.58	1.43	0.000	0.016	0.000	0.02	1.4
	BCVWD Well#21*	4.46	190.7	28.04	13.60	0.47	0.00	19.77	47.30	17.27	25.63	1.70	0.005	0.019	0.007	0.01	5.5
	BCVWD Well#23	1.12	214.4	11.08	9.89	0.38	0.14	4.97	39.51	16.77	17.44	1.28	0.000	0.006	0.000	0.03	0.3
	BCVWD Well#23*	1.68	209.2	15.99	8.02	0.31	0.00	7.46	45.17	14.27	23.32	1.73	0.000	0.011	0.000	0.01	4.3
	BCVWD Well#24	2.64	180.7	20.28	12.43	0.41	0.14	11.68	48.56	17.09	18.85	1.41	0.000	0.009	0.000	0.03	8.6
	BCVWD Well#25	1.48	197.8	11.32	6.58	0.42	0.08	6.55	38.17	12.28	17.97	1.39	0.000	0.007	0.000	0.03	-0.7
	BCVWD Well#26	1.01	171.0	12.71	9.17	0.26	0.09	4.49	42.20	13.11	21.35	1.54	0.000	0.009	0.000	0.03	9.9
	BCVWD Well#26*	0.90	170.4	8.56	7.79	0.28	0.00	4.00	32.43	9.27	26.09	1.74	0.000	0.009	0.000	0.01	4.4
	BCVWD Well#28	1.09	208.1	9.87	9.05	0.31	0.07	4.82	32.77	9.38	24.68	1.51	0.000	0.010	0.000	0.03	-5.9
	BCVWD Well#29	1.80	190.2	11.68	12.86	0.34	0.08	7.98	41.20	14.21	16.84	1.56	0.000	0.008	0.000	0.03	1.7

Table 7. Oxygen and nitrogen isotopes of nitrate (units are per mil: ‰), their ratio and PPCP indexof surface water and groundwater in Beaumont Management Zone. Samples marked with an * were re-sampled in July 2011 and the samples marked with an Δ had duplicate samples collected.

Surfacewater				
	$\delta^{18}O\text{-}NO_3$	$\delta^{15}N\text{-}NO_3$	$\delta^{18}O/\delta^{15}N$	PPCP Index
	‰			
Noble Cr @Noble Ave	1.90	-0.46	-4.17	1.3
Noble Cr @Noble Ave$^{\Delta}$	1.75	-0.70	-2.52	1.2
Drainage @Sundance	10.41	6.92	1.50	4.6
San Gorgonio Cr@HS	9.62	-0.26	-37.63	2.9
Riley Farm	1.22	5.76	0.21	0.0
Noble Cr below Powerline	2.50	6.03	0.41	1.1
San Timoteo Creek	4.34	15.60	0.28	10.9
Coopers Creek	-3.88	5.38	-0.72	11.9
Little San Gorgonio Creek	-3.30	9.36	-0.35	0.0
Stormwater recharge basin	2.30	6.31	0.36	0.0
BCVWD pond	0.21	0.15	1.36	-
BCVWD pond*	-1.49	8.39	-0.18	-
San Gorgonio Pond	-3.00	8.96	-0.33	5.3
San Gorgonio Pond*	-3.18	8.81	-0.36	5.3

Groundwater				
	$\delta^{18}O\text{-}NO_3$	$\delta^{15}N\text{-}NO_3$	$\delta^{18}O/\delta^{15}N$	PPCP Index
	‰			
1002958	-0.21	2.45	-0.09	0.0
1003072	0.52	3.36	0.15	0.0
1004370	3.89	9.87	0.39	1.1
1006132	5.05	8.72	0.58	0.0
1007022	3.58	5.86	0.61	6.7
1007025	-0.12	2.31	-0.05	0.0
1201450	1.33	3.85	0.35	2.1
1201486	-0.60	2.02	-0.30	0.0
1201561	0.17	2.27	0.08	0.0
1206853	1.26	7.17	0.18	3.6
1206892	2.32	5.16	0.45	3.0
1206995	1.79	3.31	0.54	-0.1
1206996	-0.56	2.68	-0.21	2.4
1207012	3.05	2.44	1.25	0.0
1207769	-0.05	2.56	-0.02	0.0
1208432	5.36	11.84	0.45	9.1
1208660	9.43	21.08	0.45	9.1
1208660*	8.27	20.19	0.41	8.1
1208660*$^{\Delta}$	8.76	20.49	0.43	8.1
1220050	3.35	7.39	0.45	0.0
1221612	4.44	9.52	0.47	7.5
1222079	5.77	10.43	0.55	4.5
1222080	5.67	13.39	0.42	4.8
BCVWD Well# 1	-0.48	2.61	-0.19	-
BCVWD Well#1*	-0.60	2.14	-0.28	0.0
BCVWD Well # 3	-0.37	3.28	-0.11	0.0
BCVWD Well # 4	3.42	2.90	1.18	-
BCVWD Well#4*	3.21	3.39	0.95	4.7
BCVWD Well # 5	2.84	3.40	0.84	-
BCVWD Well#5*	2.74	3.03	0.91	0.0
BCVWD Well # 6	2.70	2.79	0.97	-
BCVWD Well#6*	3.16	2.59	1.22	4.1
BCVWD Well#10	1.58	4.48	0.35	-
BCVWD Well#10*	2.56	3.08	0.83	0.0
BCVWD Well#11	1.88	4.29	0.44	0.0
BCVWD Well#12	2.23	3.12	0.71	-
BCVWD Well#12*	2.04	3.78	0.54	1.7
BCVWD Well#14	1.75	2.98	0.59	-
BCVWD Well#14*	1.61	3.26	0.49	-0.4
BCVWD Well#16	3.42	5.20	0.66	3.4
BCVWD Well#16$^{\Delta}$	3.16	5.12	0.62	3.3
BCVWD Well#19	1.91	4.16	0.46	-
BCVWD Well#19*	2.20	4.21	0.52	0.2
BCVWD Well#20	1.34	3.78	0.35	-
BCVWD Well#20*	1.62	3.79	0.43	0.8
BCVWD Well#21	1.78	6.84	0.26	-
BCVWD Well#21*	1.77	5.79	0.31	3.5
BCVWD Well#23	-0.85	2.29	-0.37	-
BCVWD Well#23*	0.84	3.57	0.24	1.9
BCVWD Well#24	1.04	3.97	0.26	0.0
BCVWD Well#25	-0.05	2.31	-0.02	0.0
BCVWD Well#26	-0.20	2.48	-0.08	-
BCVWD Well#26*	-0.49	2.34	-0.21	4.5
BCVWD Well#28	-0.53	2.50	-0.21	0.0
BCVWD Well#29	0.86	3.08	0.28	0.0

Table 8. PPCP detections in groundwater, surface water and SWP recharge water, including concentration range, average quantifiable concentration and percentage of total detected compounds. LOQ – limit of quantitation.

	Concentration Range (ng/L)			Avg.Quantifiable Concentration (ng/L)			Groundwater	Surface Water	Recharge Water	Total Detects
	Groundwater	Surface Water	Recharge Water	Groundwater	Surface Water	Recharge Water	n = 40	n = 9	n = 2	n = 51
Acetaminophen	13.9	ND	ND	ND	ND	ND	3%	ND	ND	2%
Primidone	<LOQ - 8.5	5.5 - 9.4	ND	2.3 (n=7)	7.5 (n=2)	ND	20%	22%	ND	20%
Meprobamate	<LOQ -10.3	72.4 - 213.7	2.6 - 2.8	6.8 (n=2)	143.0 (n=2)	2.7 (n=2)	8%	22%	100%	14%
Diuron	<LOQ -359.3	<LOQ - 1061.3	50.7 - 52.3	23.5 (n=18)	354.2 (n=6)	51.5 (n=2)	55%	89%	100%	63%
Carbamazepine	<LOQ -304.0	<LOQ -545.5	1.8	81.6 (n=6)	445.1 (n=2)	1.8 (n=2)	23%	33%	100%	27%
Dilantin	<LOQ - 1.3	4.7 - 12.4	ND	0.7 (n=4)	8.5 (n=2)	ND	18%	22%	ND	18%
Sulfamethoxazole	<LOQ - 40.5	<LOQ - 495.9	5.4 - 5.6	7.8 (n=17)	401.2 (n=2)	5.5 (n=2)	50%	33%	100%	49%
Atenolol	ND	26.4 - 69.6	ND	ND	48.0 (n=2)	ND	ND	22%	ND	4%
Diazepam	<LOQ	<LOQ - 1.1	ND	ND	ND	ND	8%	22%	ND	10%
Trimethoprim	ND	0.5 - 93.7	ND	ND	15.4 (n=7)	ND	ND	78%	ND	14%
Fluoxetine	<LOQ - 0.1	<LOQ	ND	ND	ND	ND	5%	11%	ND	6%
Atorvastatin	<LOQ - 0.8	3.3	ND	0.3 (n=4)	ND	ND	23%	11%	ND	20%
Ibuprofen	<LOQ	ND	ND	ND	ND	ND	3%	ND	ND	2%
Naproxen	ND	<LOQ	ND	ND	ND	ND	ND	11%	ND	2%
Diclofenac	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Gemfibrozil	<LOQ - 0.1	<LOQ - 924.8	ND	ND	269.3 (n=4)	ND	18%	67%	ND	25%

Table 9. Annual mass balance of nitrate – nitrogen for groundwater in the Beaumont Management Zone. The groundwater storage and recharge volumes are from Wildermuth Environmental. Nitrate-nitrogen concentrations used in the computations are based on our current study except for the nitrate value for septic waste which is from Wildermuth Environmental and the nitrate value for wastewater treatment plant effluent which is from the State Water Resources Control Board. The nitrate concentration for total groundwater storage is the average of all wells sampled during our study, including duplicates. Nitrate concentrations for the State Water Project are the average of four measurements made at the BCVWD recharge basins during our study. The natural surface nitrate value is the average nitrate concentration in all surface water samples collected during our study. The nitrate concentration for mountain-front groundwater was computed as the average nitrate value for all Zone 2 wells. The nitrate concentration for well pumpage is the average of nitrate values measured in large-volume wells operated by the BCVWD throughout the entire BMZ. Denitrification was estimated based on the relative reduction of nitrate (90.6%) observed along the flowpath in Zone 1 and the average concentration of nitrate in effluent from the City of Beaumont Wastewater Treatment Plant (6 mg/L; Dr. Cindy Li personal communication). Negative signs indicate that BMZ aquifer is losing either water or nitrate-nitrogen.

	Beaumont MZ		
	Volume AF	**NO_3-N mg/L**	**N Pool or Flux kg**
Total Groundwater Storage	189,482	3.49	815,704
Mountain-front Groundwater	4,023	2.10	10,421
State Water Project	8,000	0.32	3,158
Septic Waste	341	35	14,722
Natural Surface Water	3,900	1.08	5,196
Wastewater Treatment Plant Effluent	2,016	6.00	14,920
Pumpage	-18,219	2.11	-47,418
Denitrification			-13,518
Gain or Loss	61	-0.05	-12,520

Sampling locations, Beaumont Management Zone

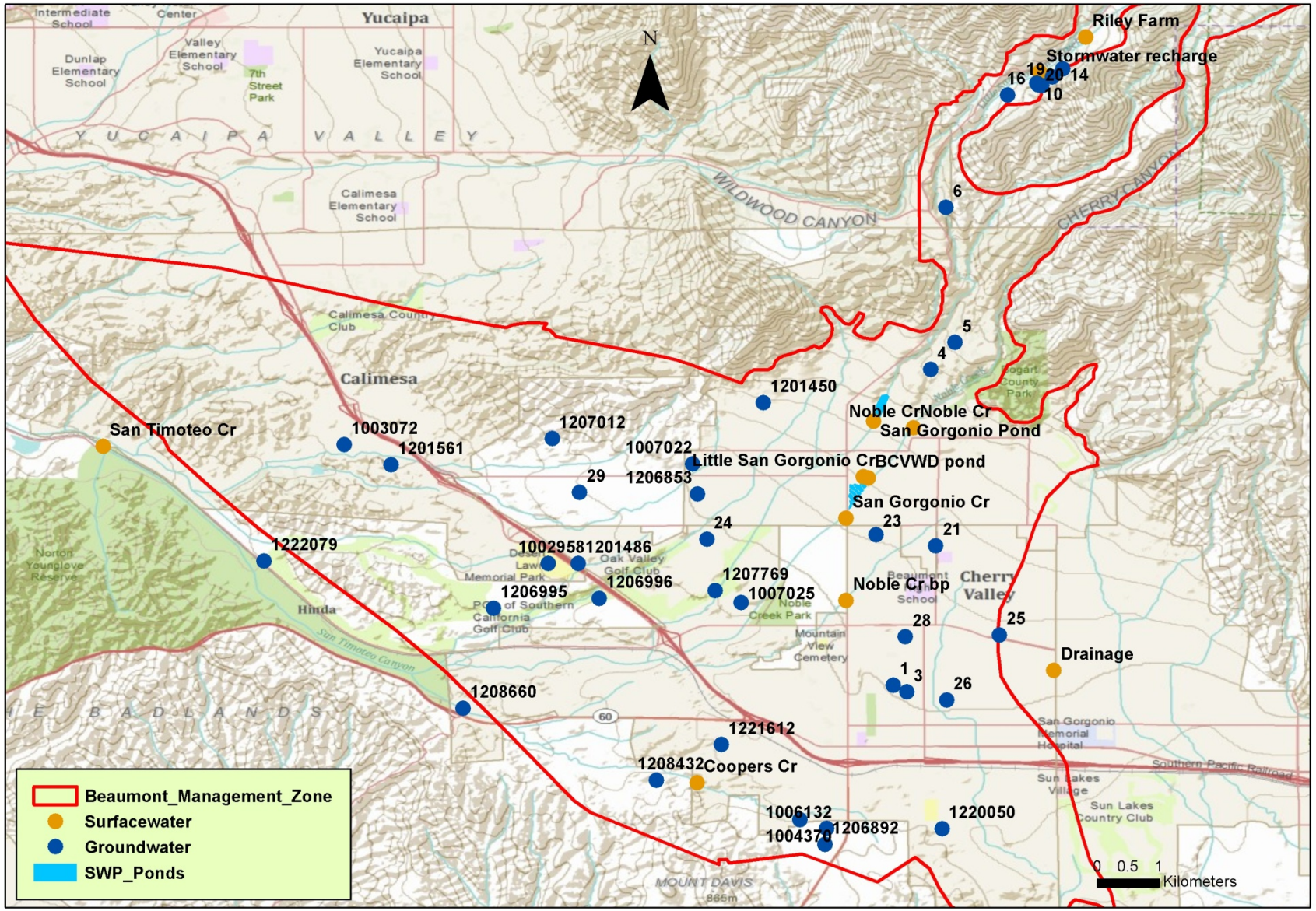

Figure 1. Sampling locations within and adjacent to the Beaumont Management Zone, with sample ID labeled. Surface water – yellow; groundwater – blue.

Groundwater Zones, Beaumont Management Zone

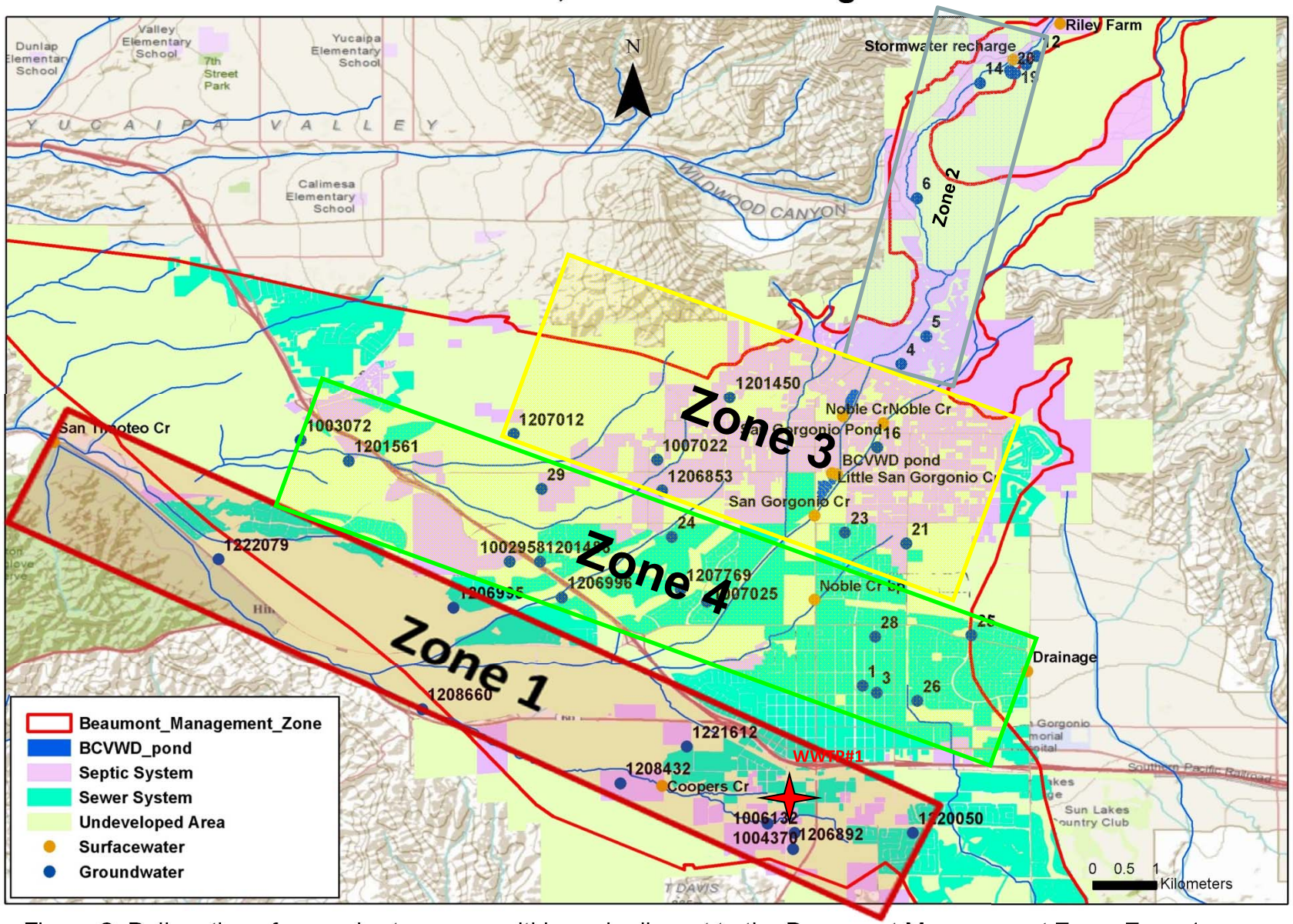

Figure 2. Delineation of groundwater zones within and adjacent to the Beaumont Management Zone. Zone 1 – Area affected by infiltration of wastewater treatment plant effluent; Zone 2 – Percolation of mountain-front flow; Zone 3 – Area with high concentration of on-site waste disposal systems; Zone 4 – Area with sewer service. WWTP #1 – City of Beaumont waste water treatment plant #1.

Water Temperature, Beaumont Management Zone

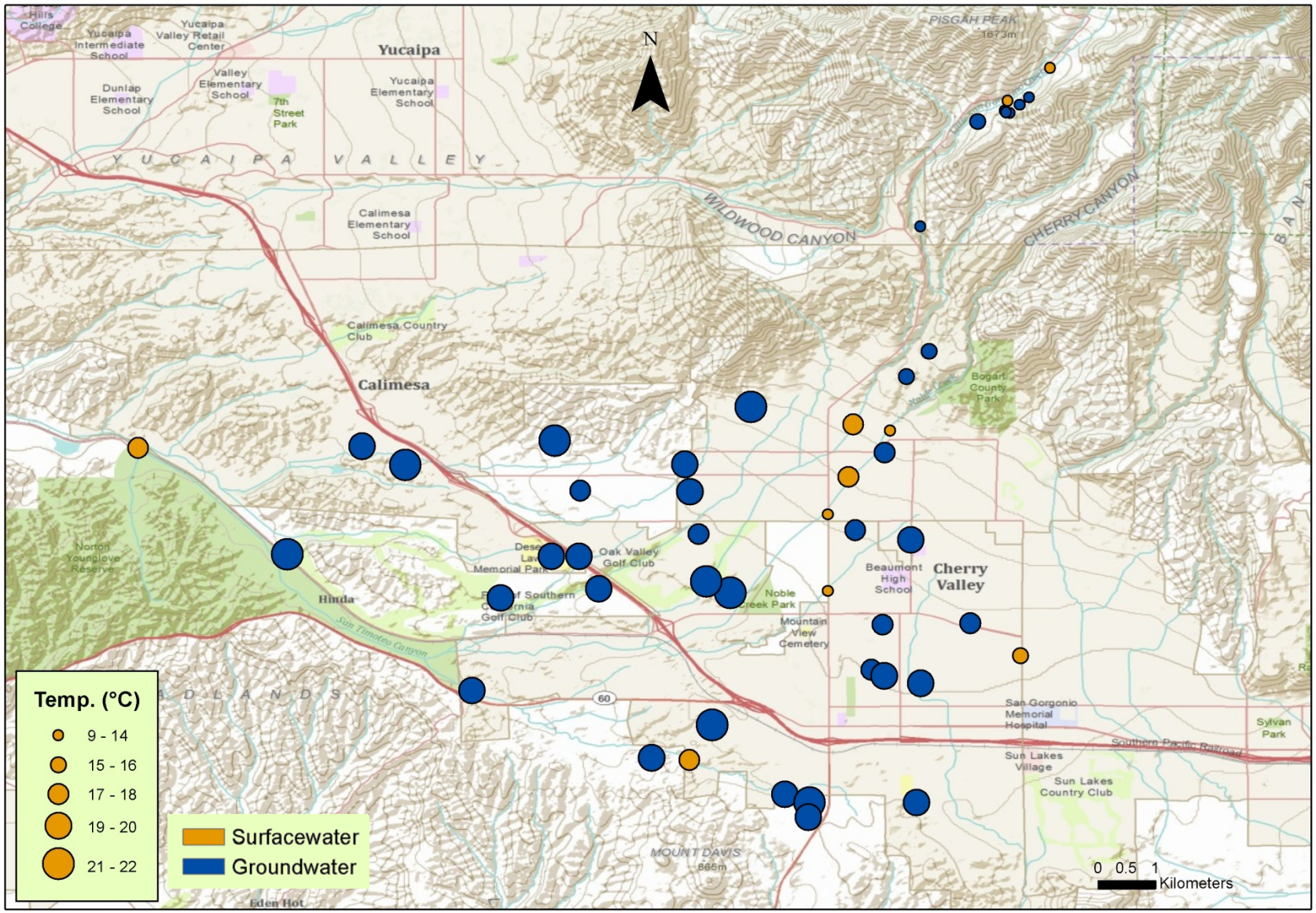

Figure 3. Water temperature in surface water and groundwater within and adjacent to the Beaumont Management Zone.

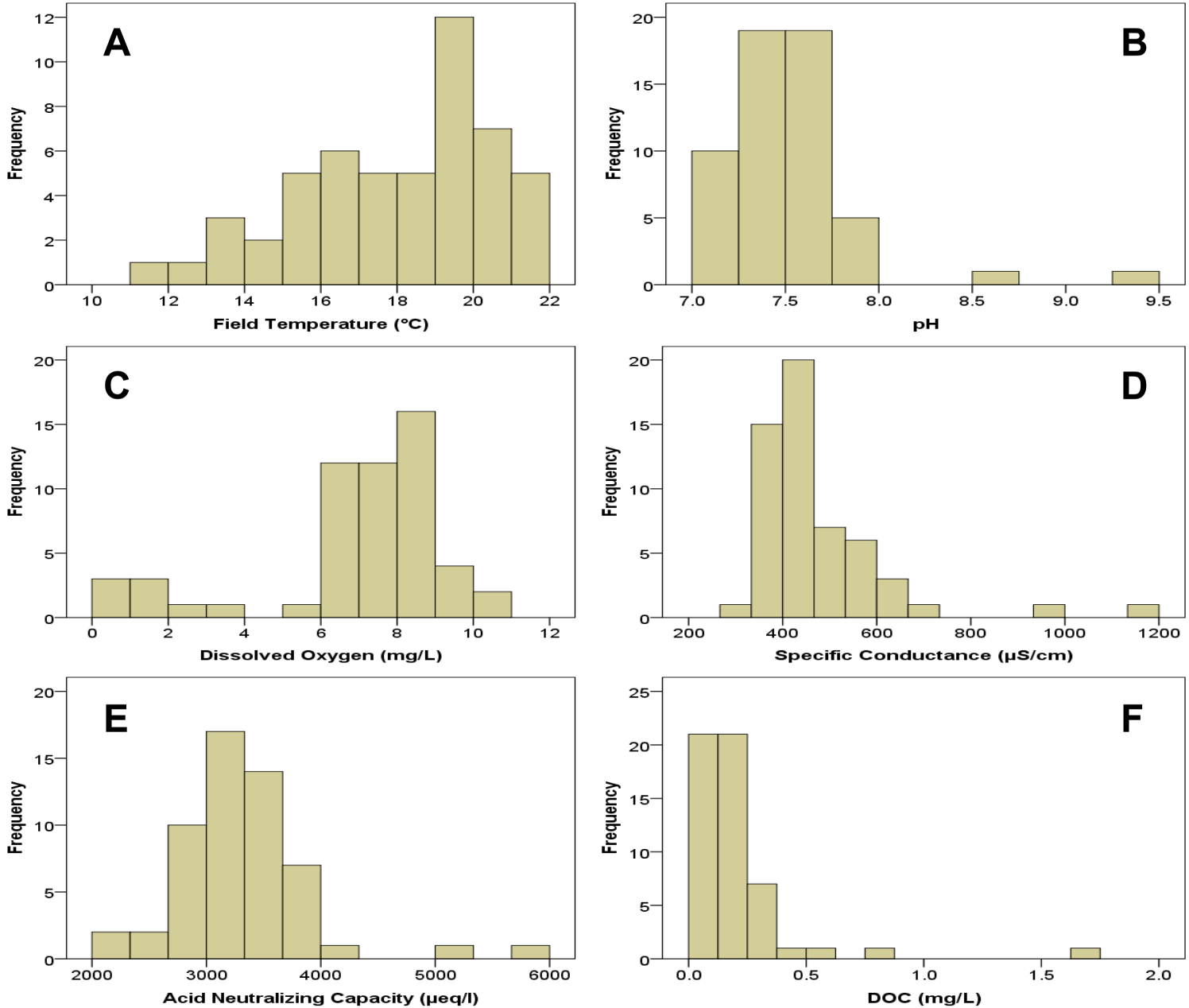

Figure 4. Histograms of physical and chemical characteristics of groundwater for A: field temperature; B: pH; C: dissolved oxygen; D: specific conductance; E: acid neutralizing capacity; F: dissolved organic carbon (F).

pH, Beaumont Management Zone

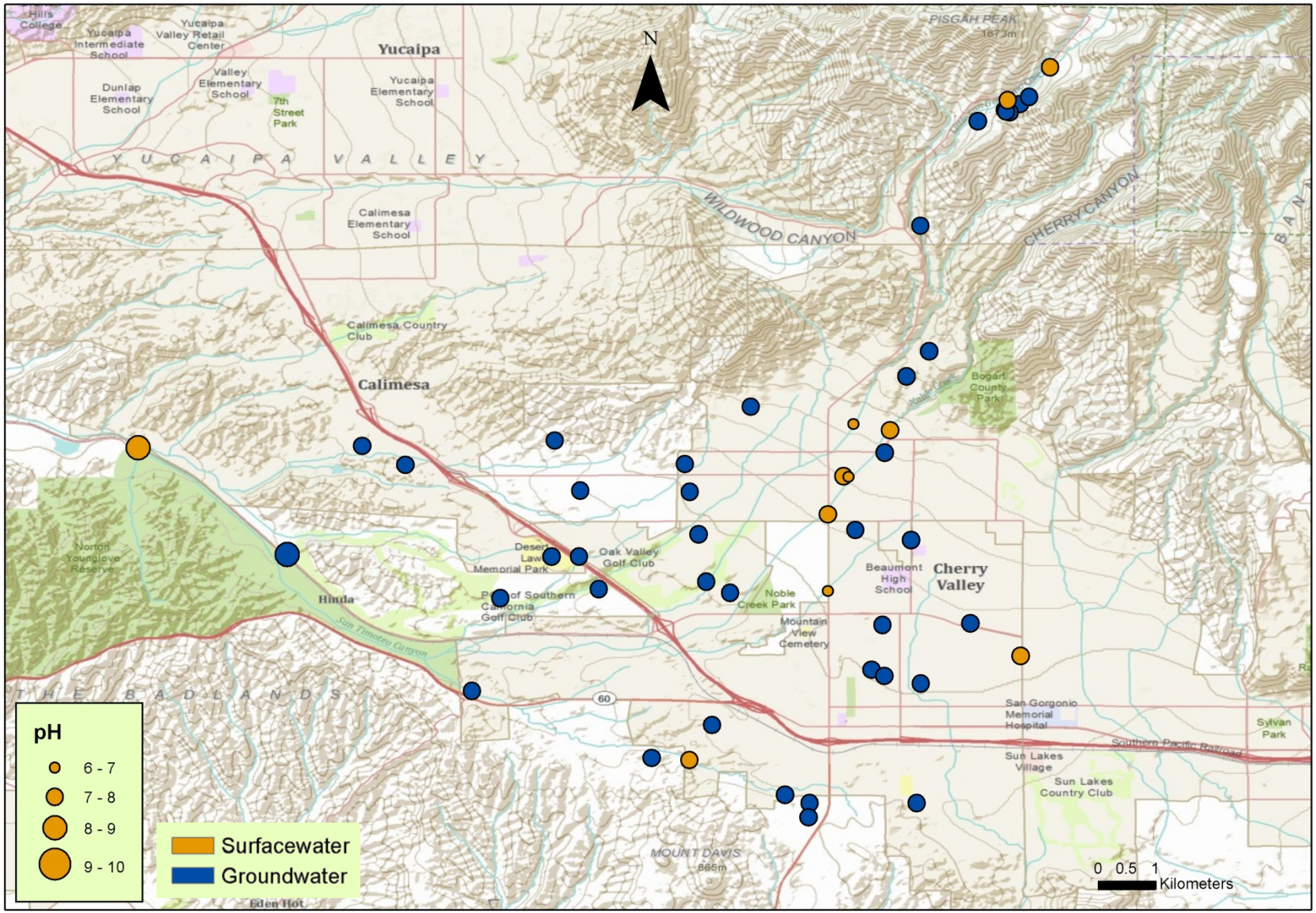

Figure 5. pH distribution in both surface water and groundwater within and adjacent to the Beaumont Management Zone.

Dissolved Oxygen, Beaumont Management Zone

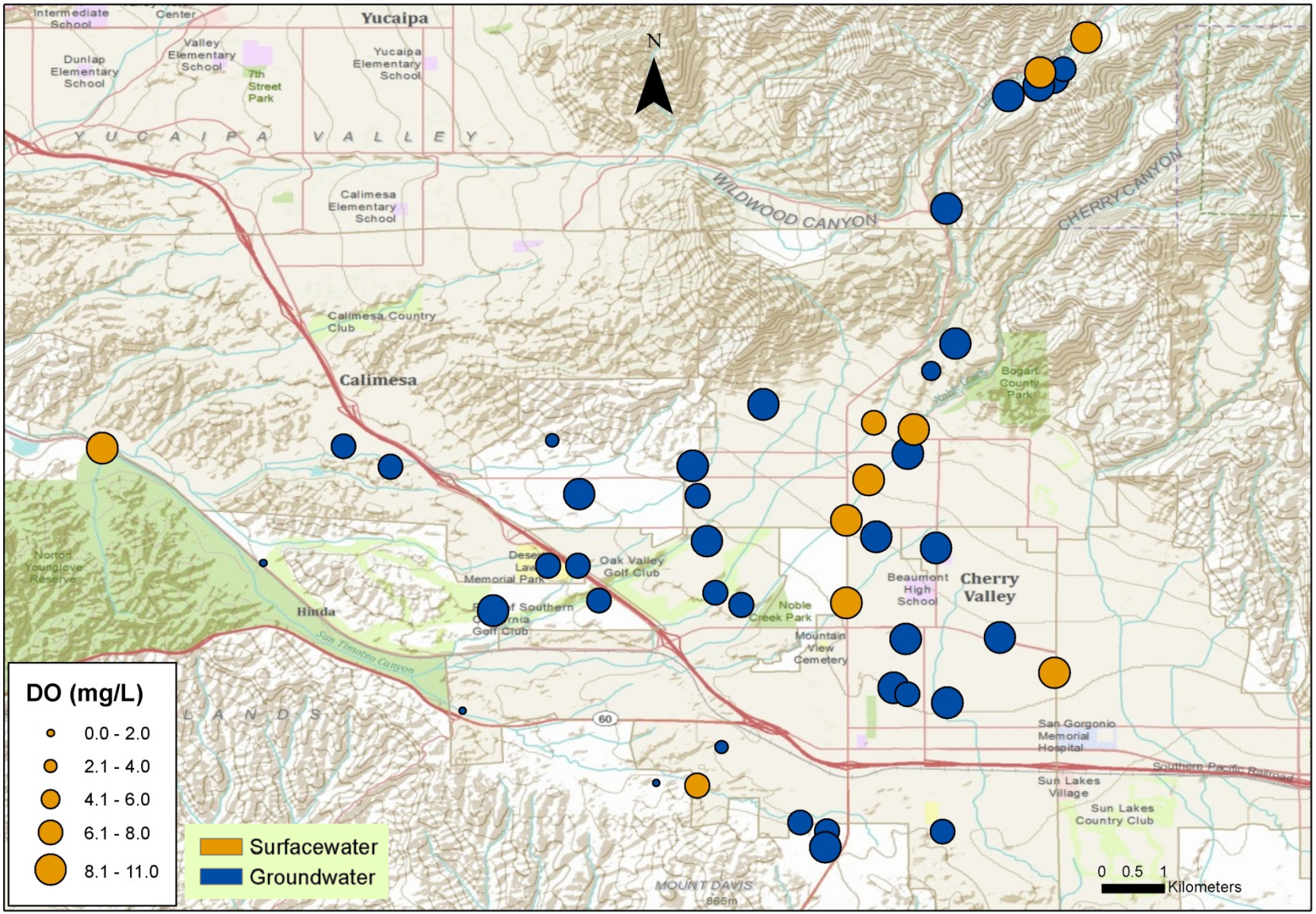

Figure 6. Dissolved oxygen (DO) of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Specific Conductance, Beaumont Management Zone

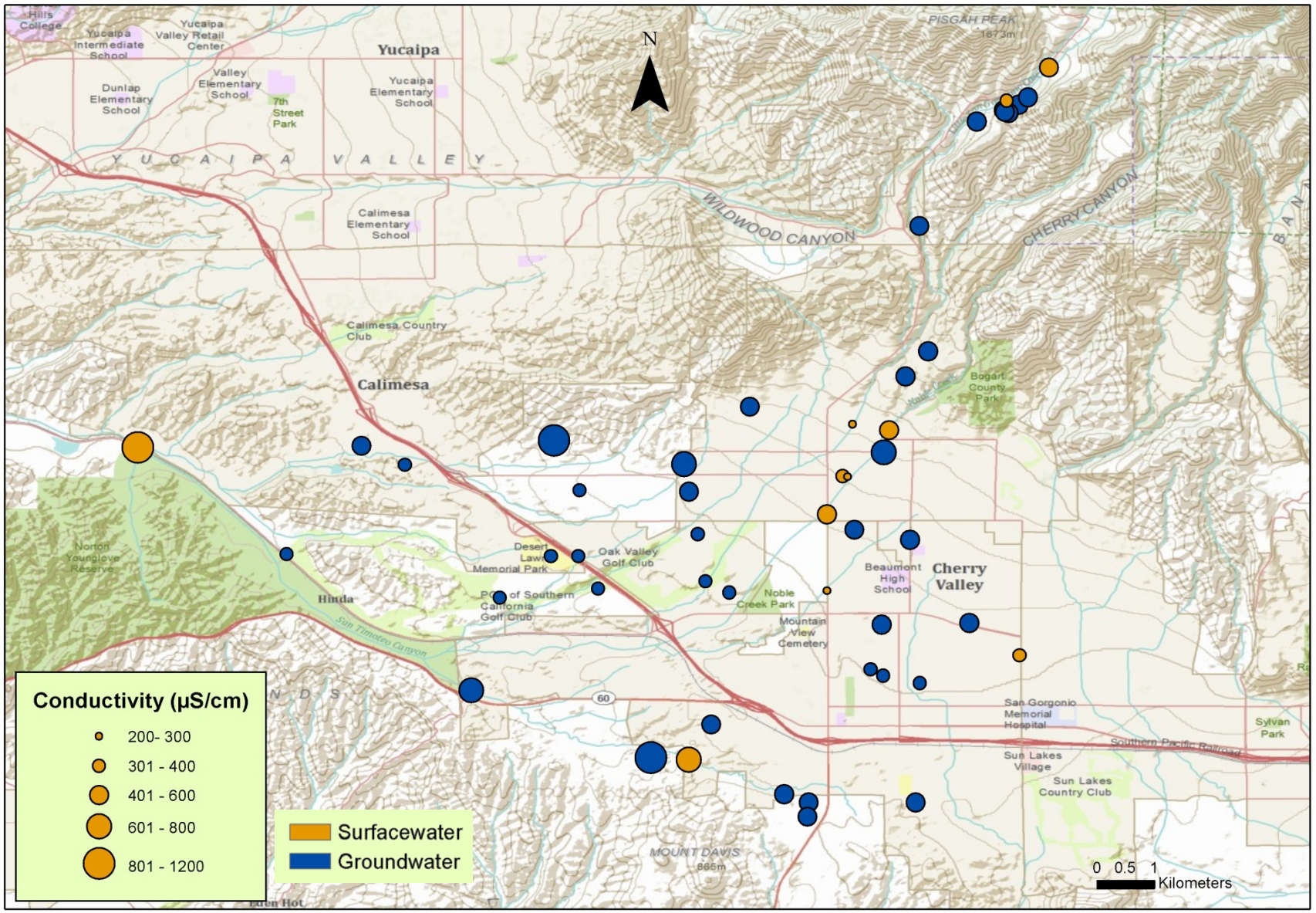

Figure 7. Specific conductance of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Acid Neutralizing Capacity, Beaumont Management Zone

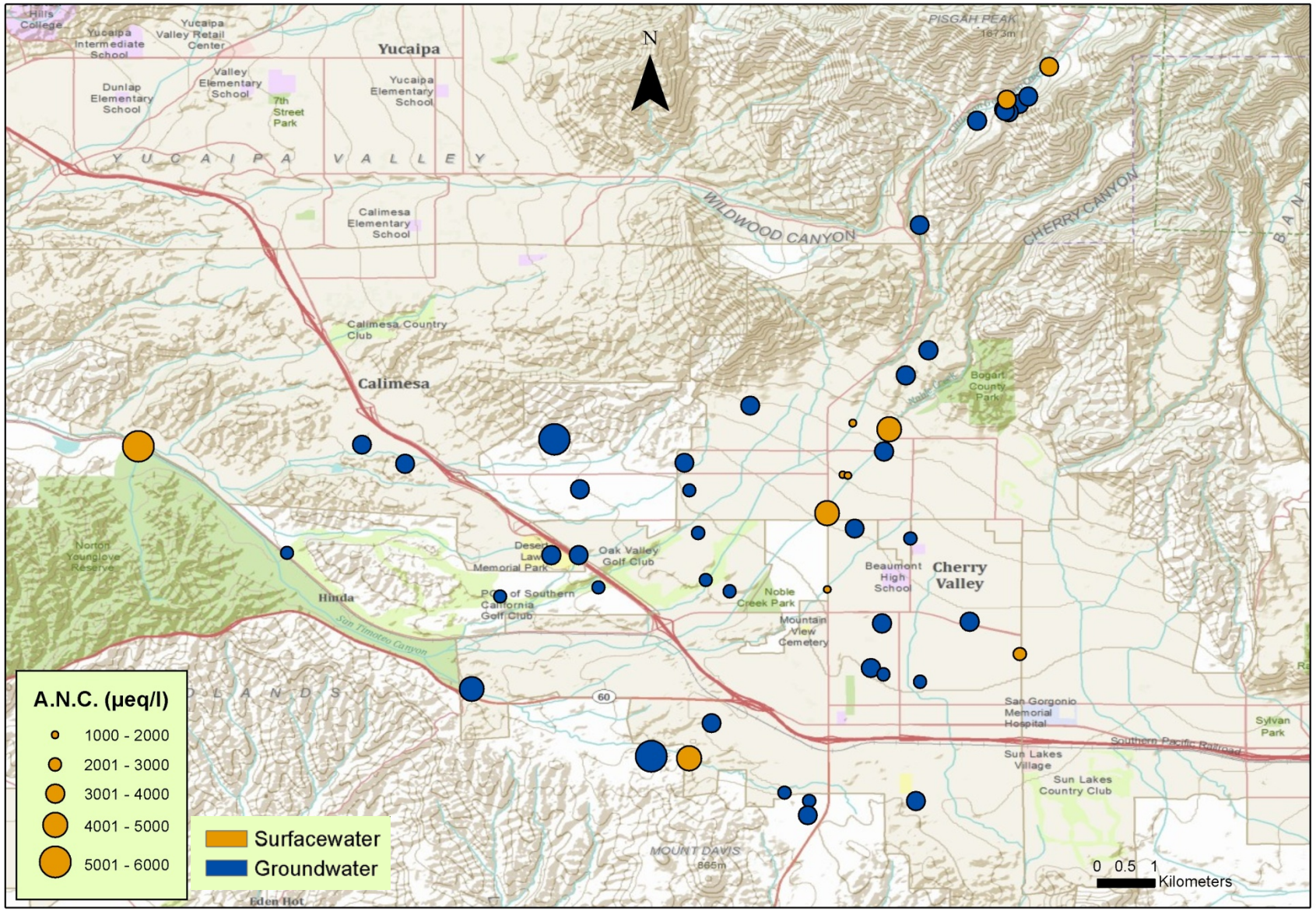

Figure 8. Acid neutralizing capacity (A.N.C.) of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Total Dissolved Solids, Beaumont Management Zone

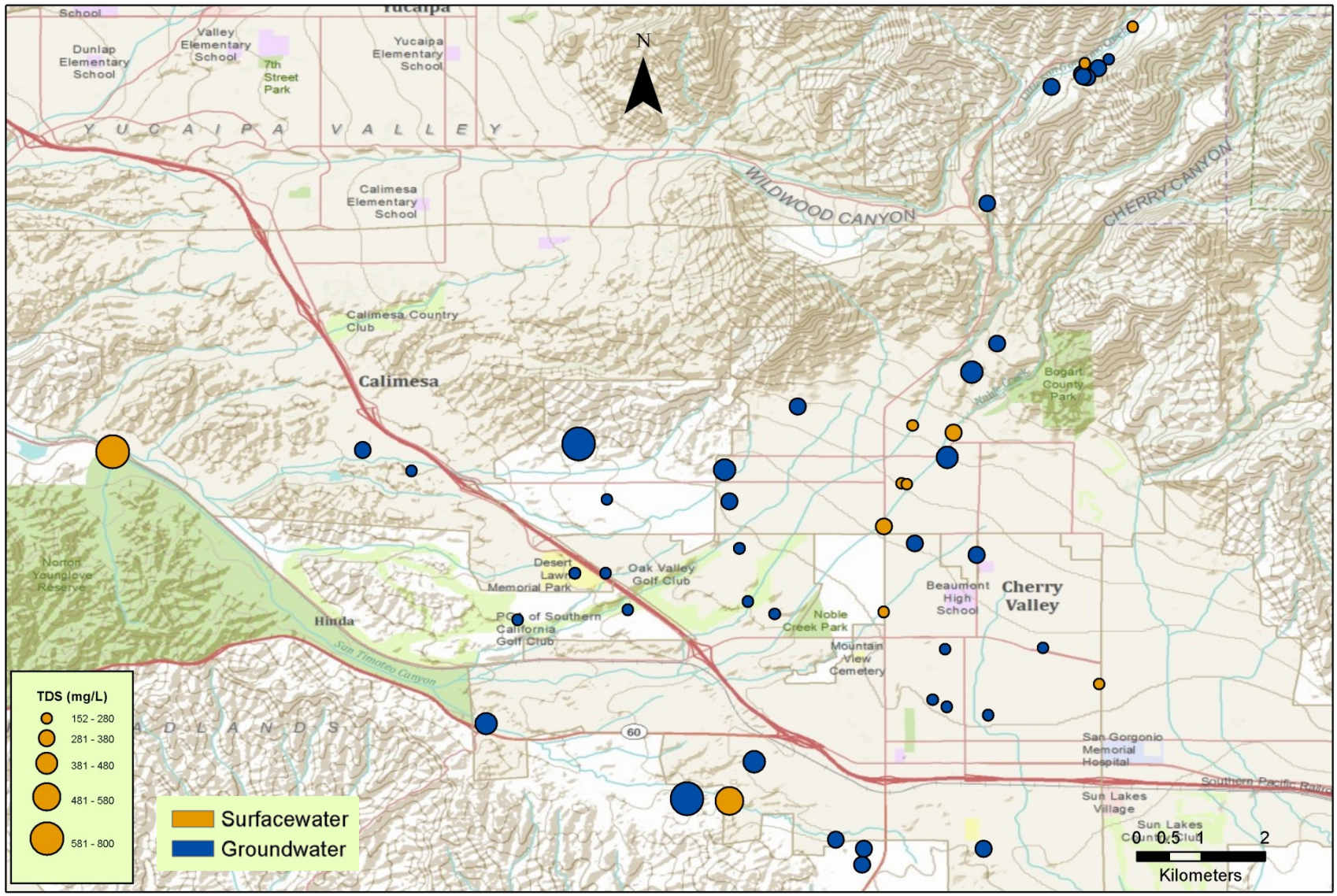

Figure 9. Total Dissolved Solids (TDS) of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Dissolved Organic Carbon, Beaumont Management Zone

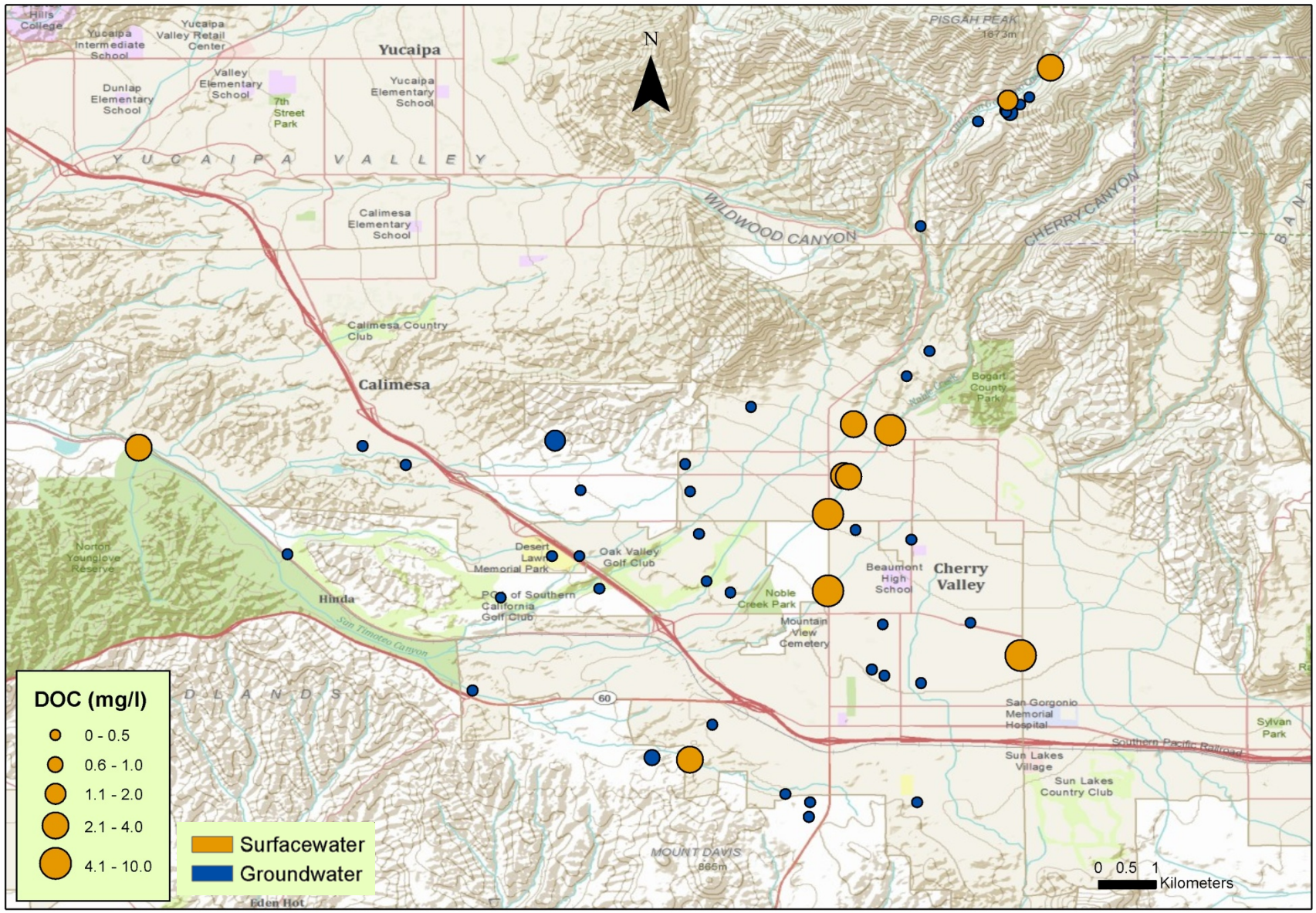

Figure 10. Dissolved organic carbon (DOC) of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Water Chemistry, Beaumont Management Zone

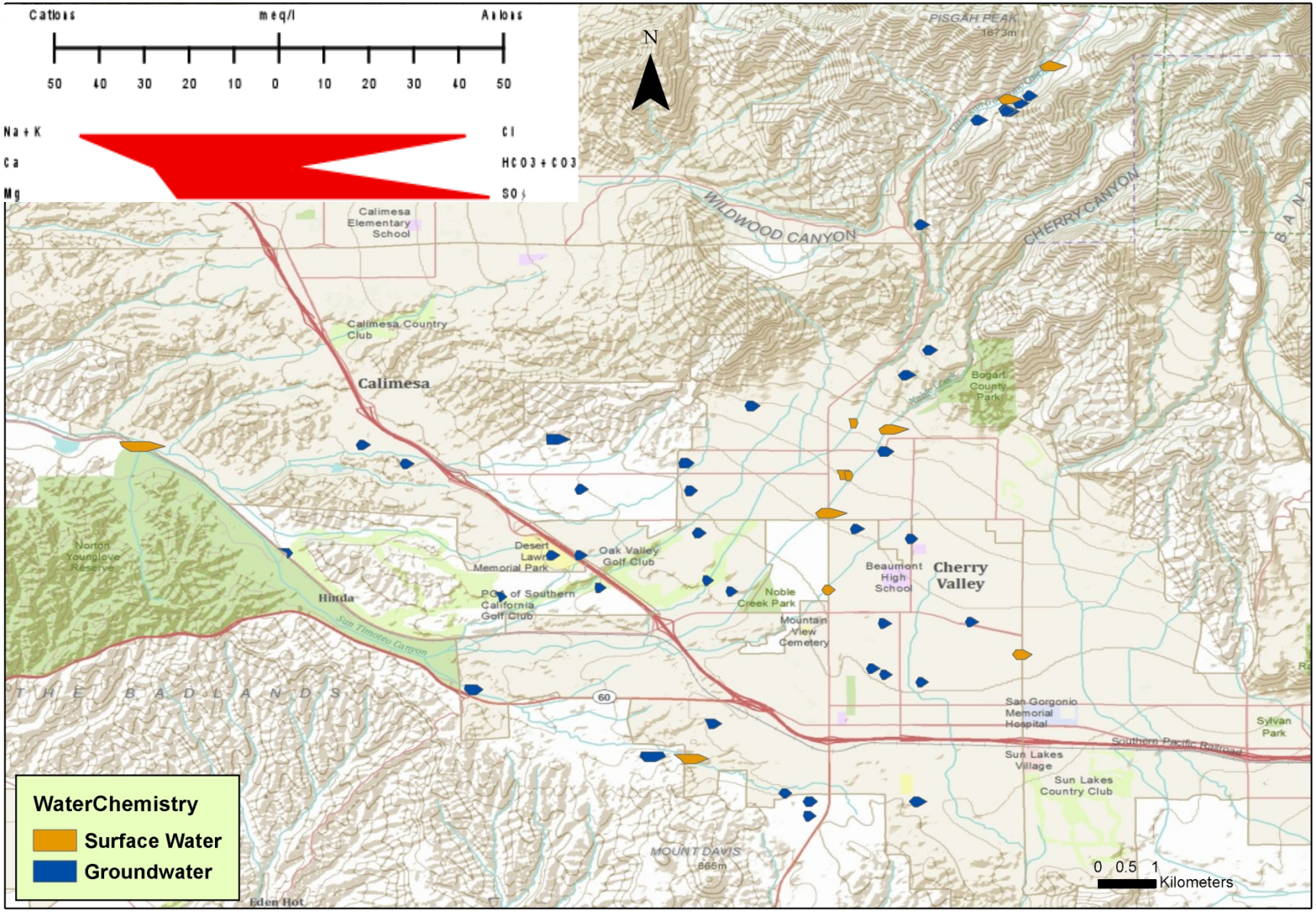

Figure 11. Geostiff diagram for major cations and anions of surface water and groundwater within and adjacent to the Beaumont Management Zone.

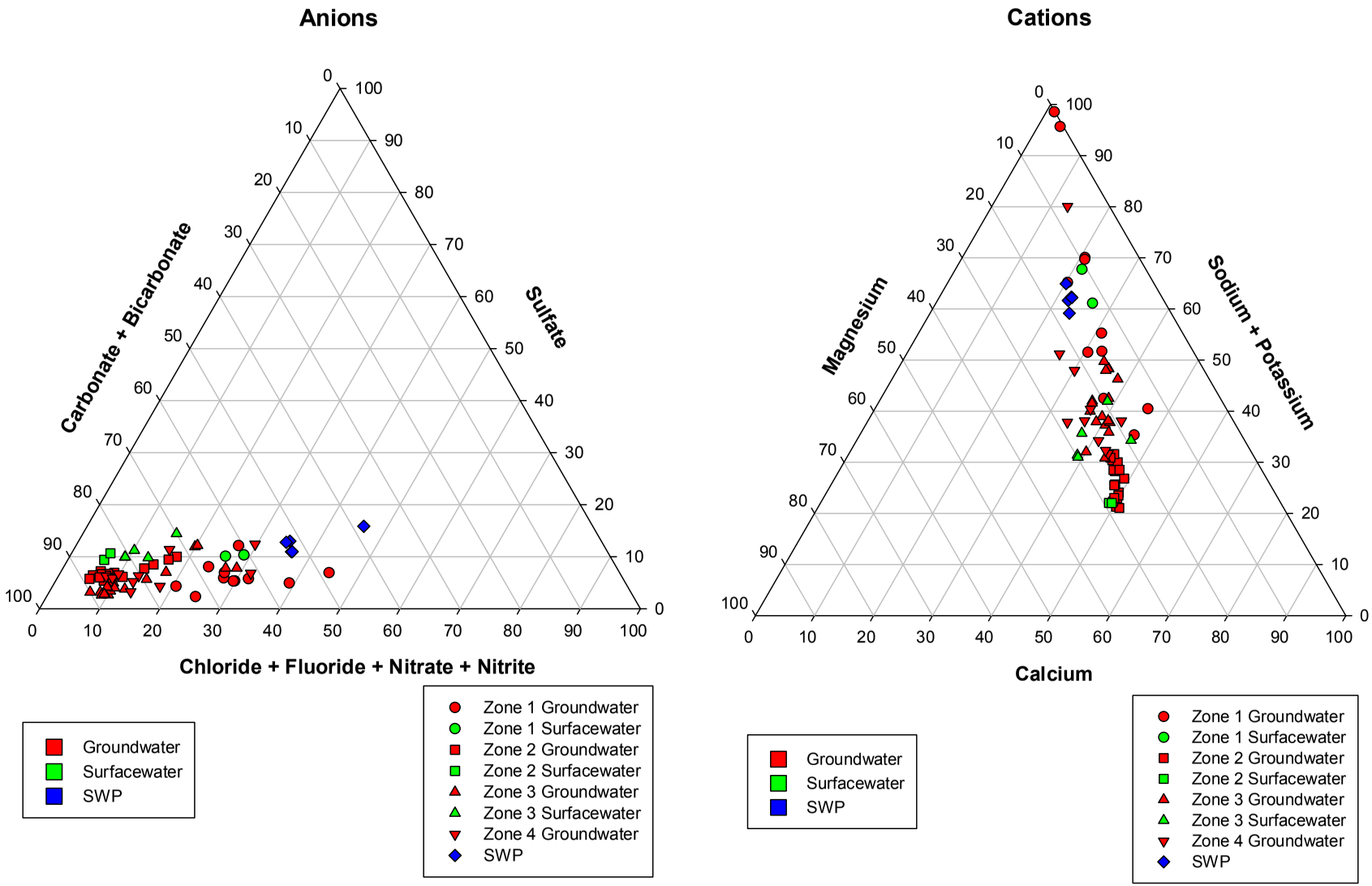

Figure 12. Percentages of major cations and anions in both surface water and groundwater. Red – groundwater; Green – surface water; Blue – state water project water; Circle – Zone 1; Square – Zone 2; Triangle – Zone 3; Inverted triangle – Zone 4. Zone delineation is described in Figure 2.

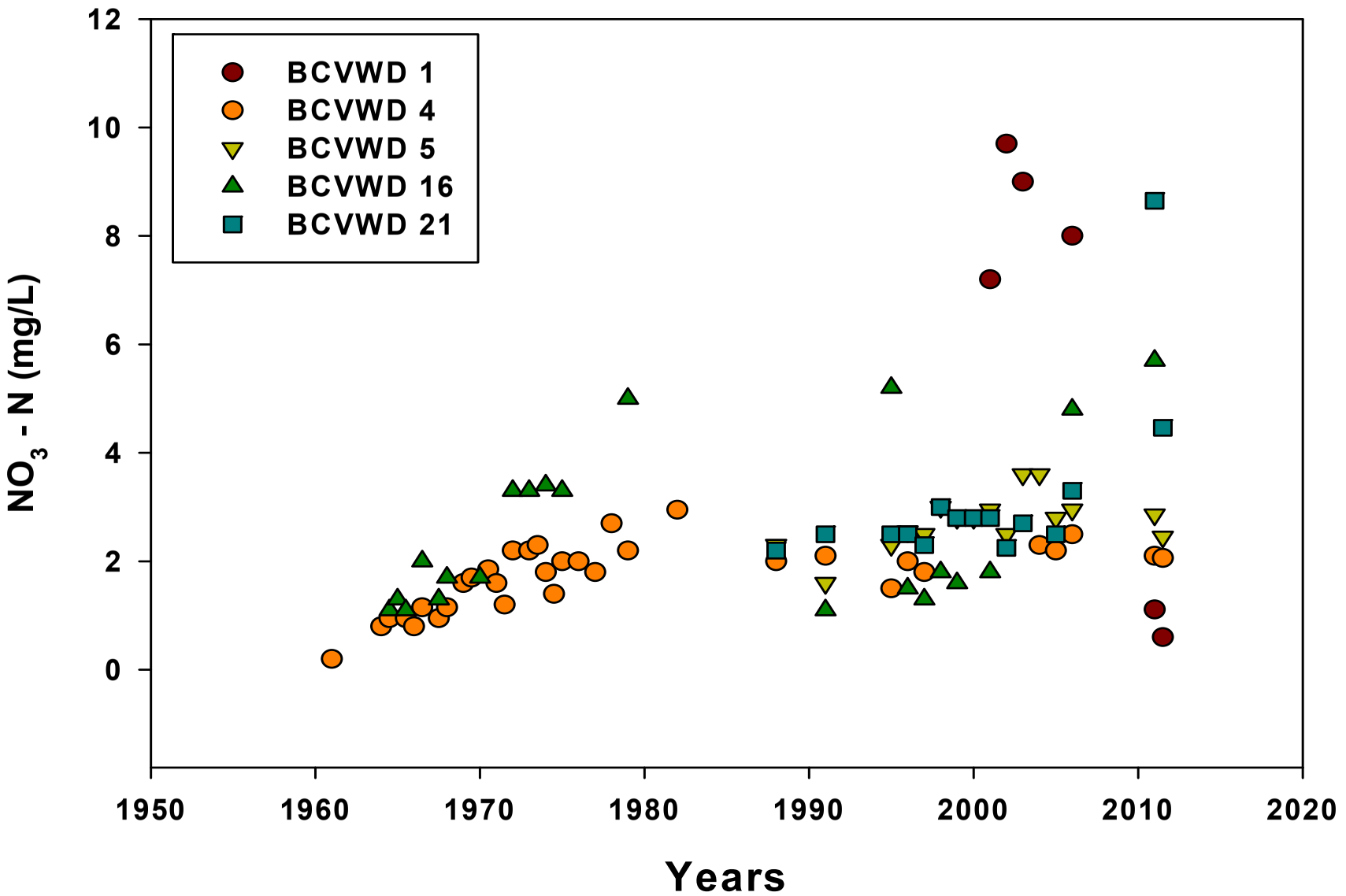

Figure 13. Historical changes in nitrate-nitrogen of wells operated by the Beaumont Cherry Valley Water District (BCVWD) Data are from EPA and the present study.

Nitrate-Nitrogen Concentration, Beaumont Management Zone

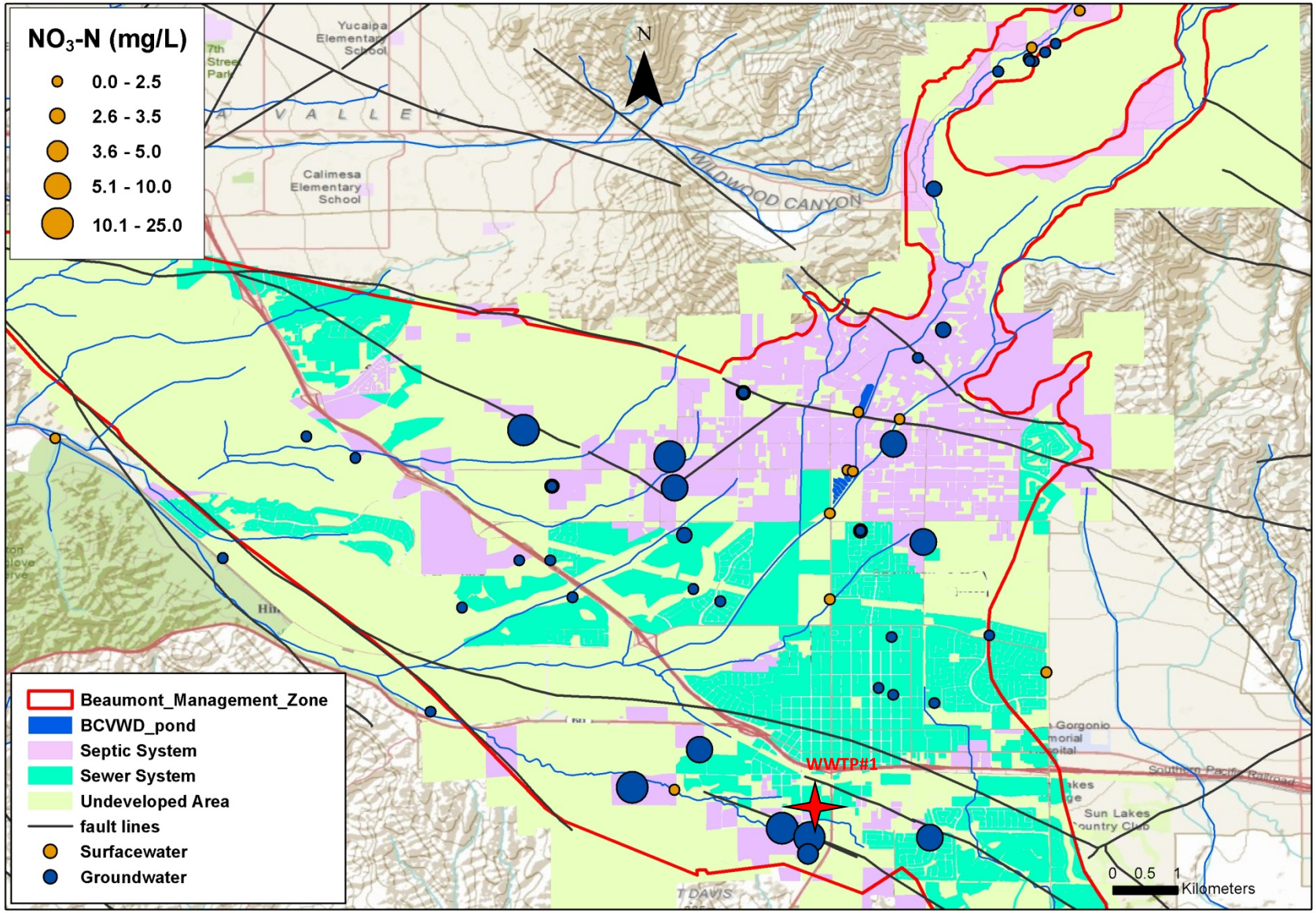

Figure 14. Nitrate-nitrogen concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone. The overlaid blue lines are stream courses, brown lines are roads and the black lines are geologic faults.

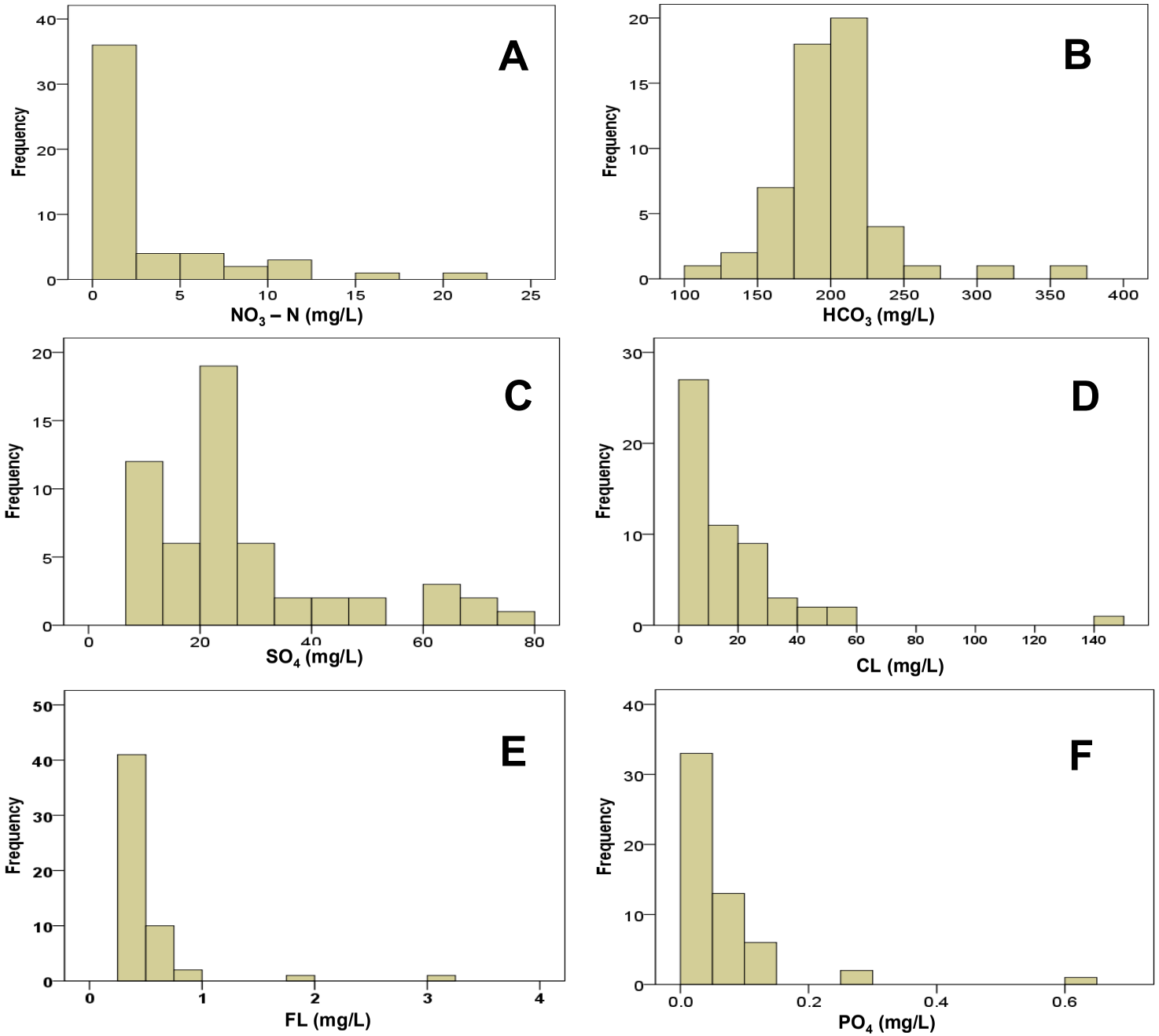

Figure 15. Histograms of major anions in groundwater within and adjacent to the Beaumont Management Zone. A: nitrate; B: bicarbonate; C: sulfate; D: chloride; E: fluoride; F:phosphate.

Bicarbonate, Beaumont Management Zone

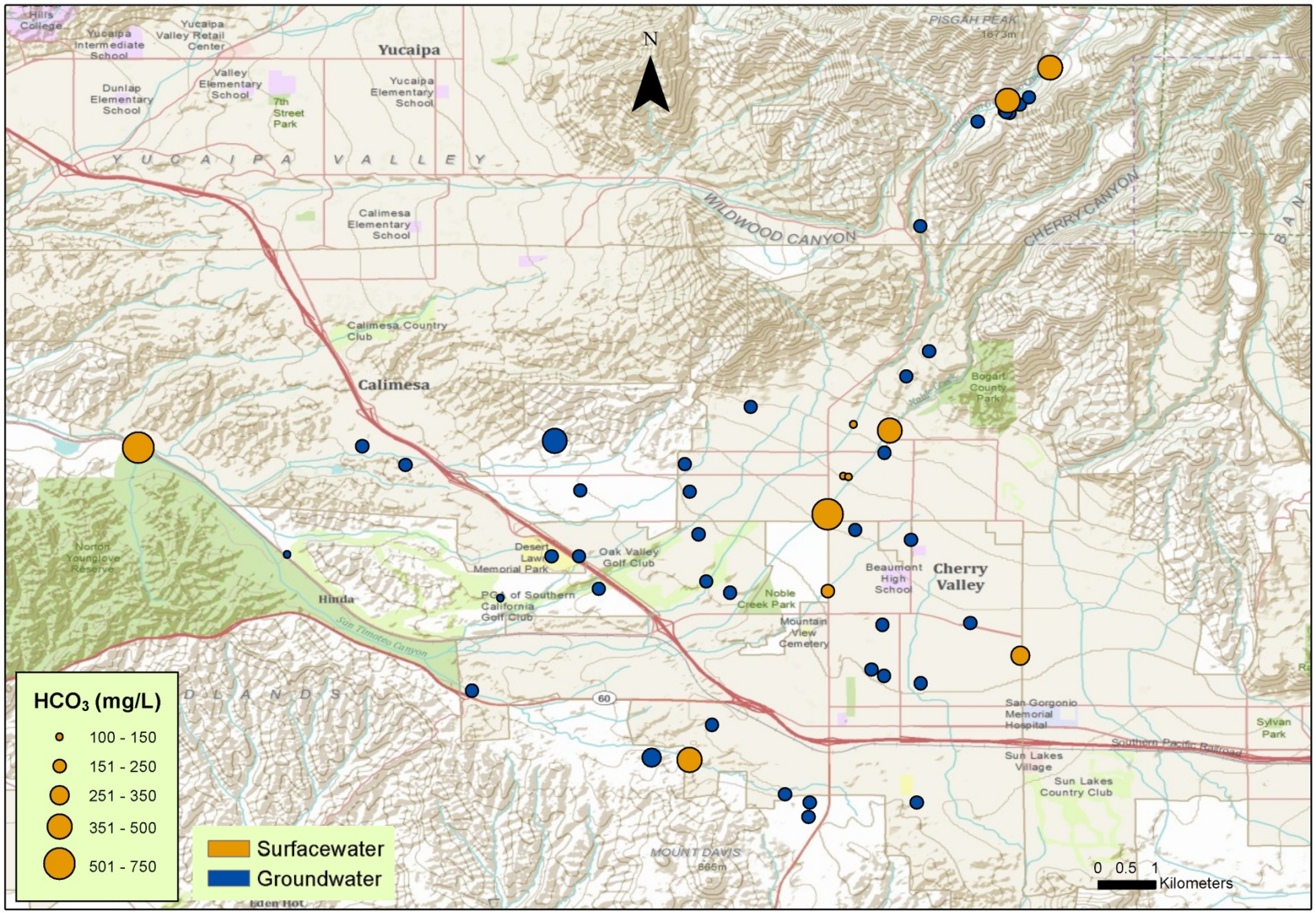

Figure 16. Bicarbonate ion concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Sulfate, Beaumont Management Zone

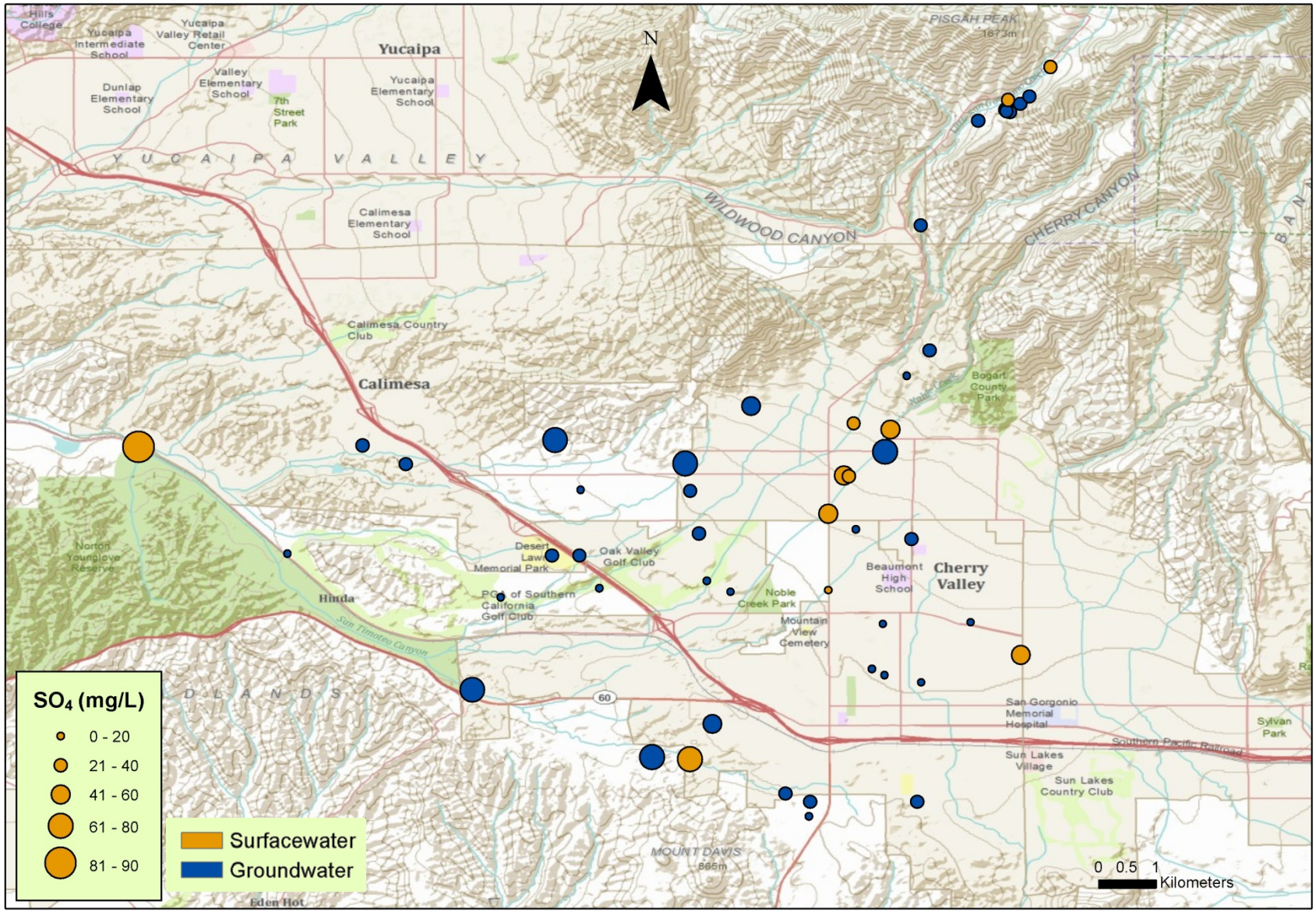

Figure 17. Sulfate concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Chloride, Beaumont Management Zone

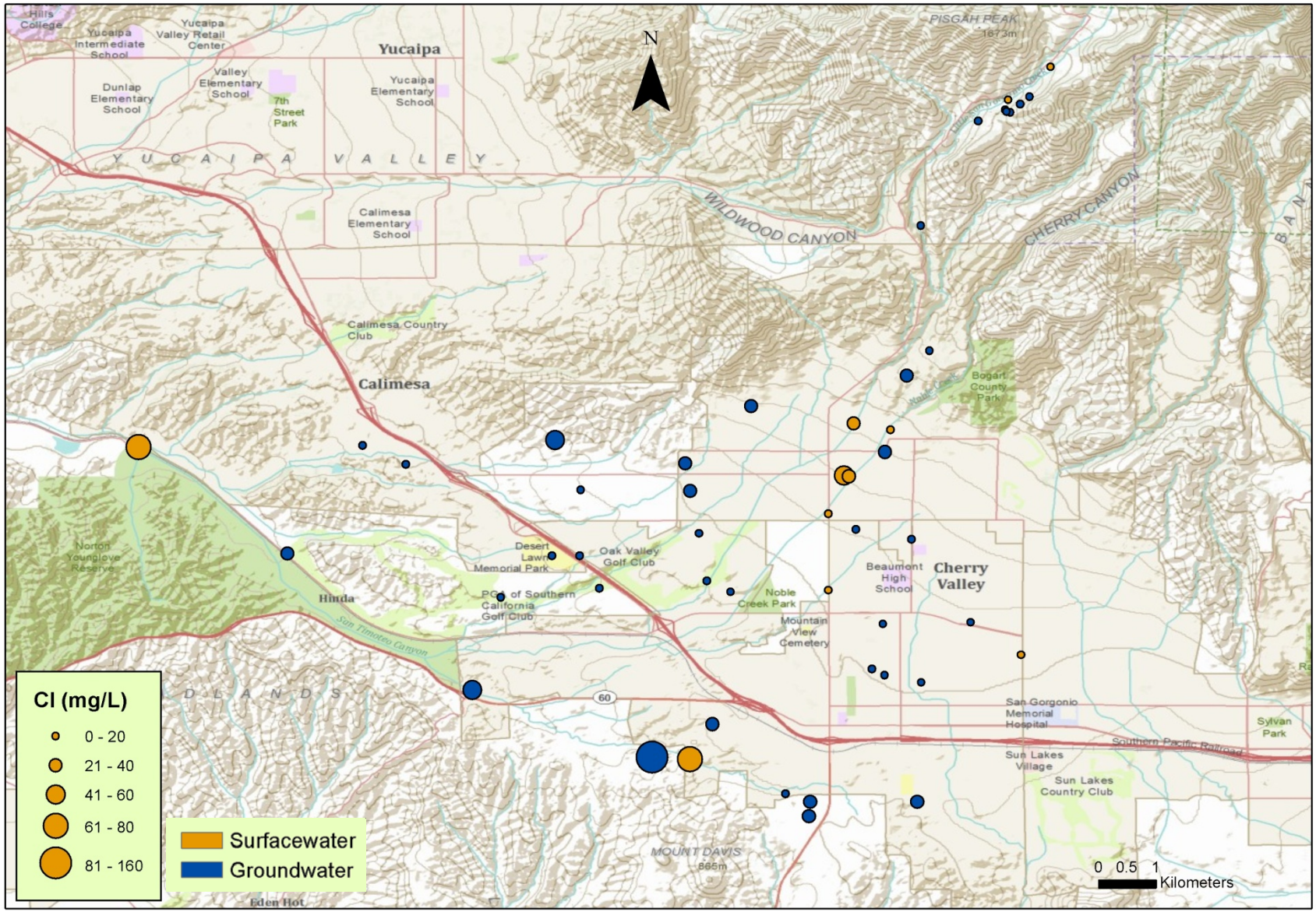

Figure 18. Chloride concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Fluoride, Beaumont Management Zone

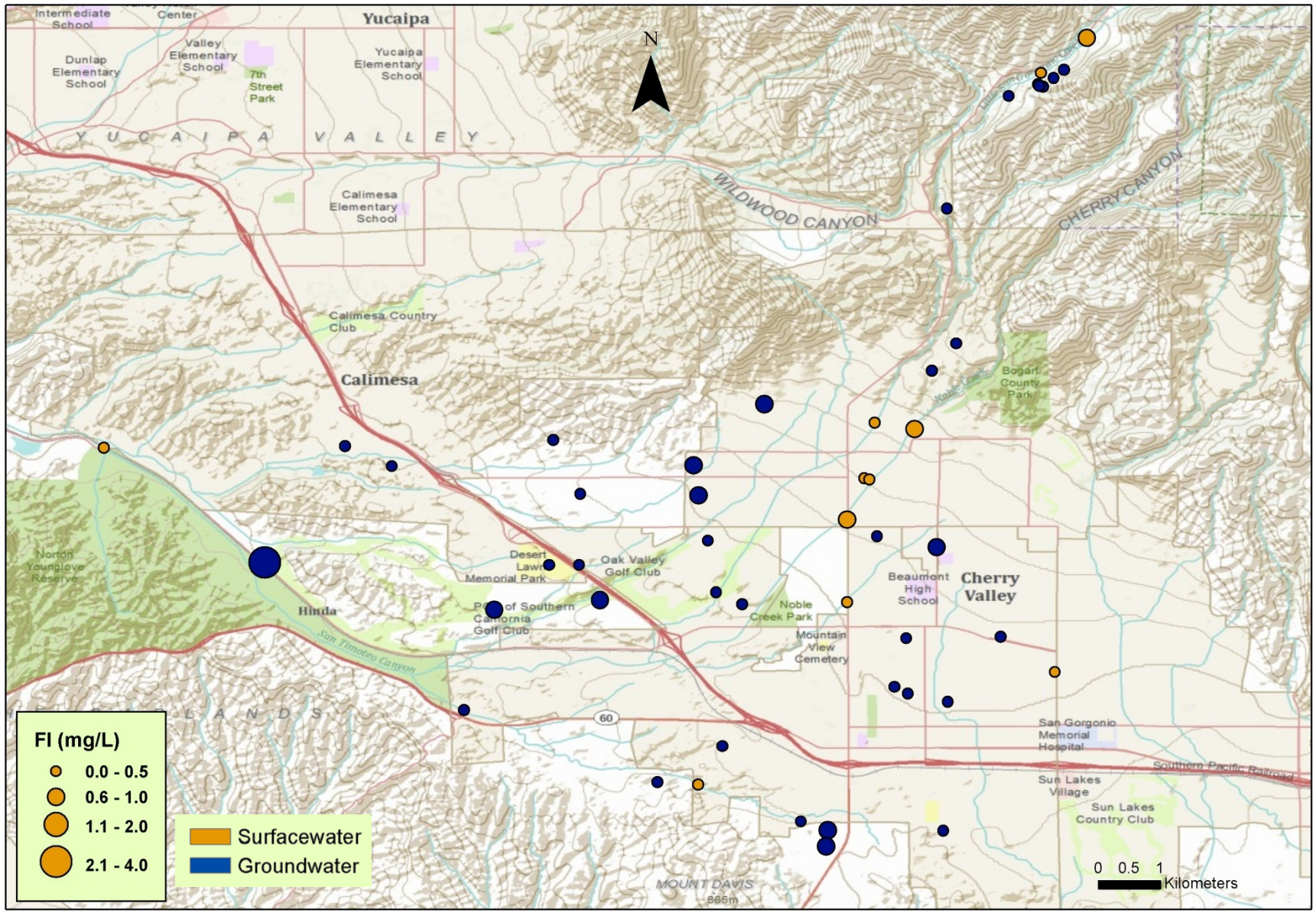

Figure 19. Fluoride concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Phosphate, Beaumont Management Zone

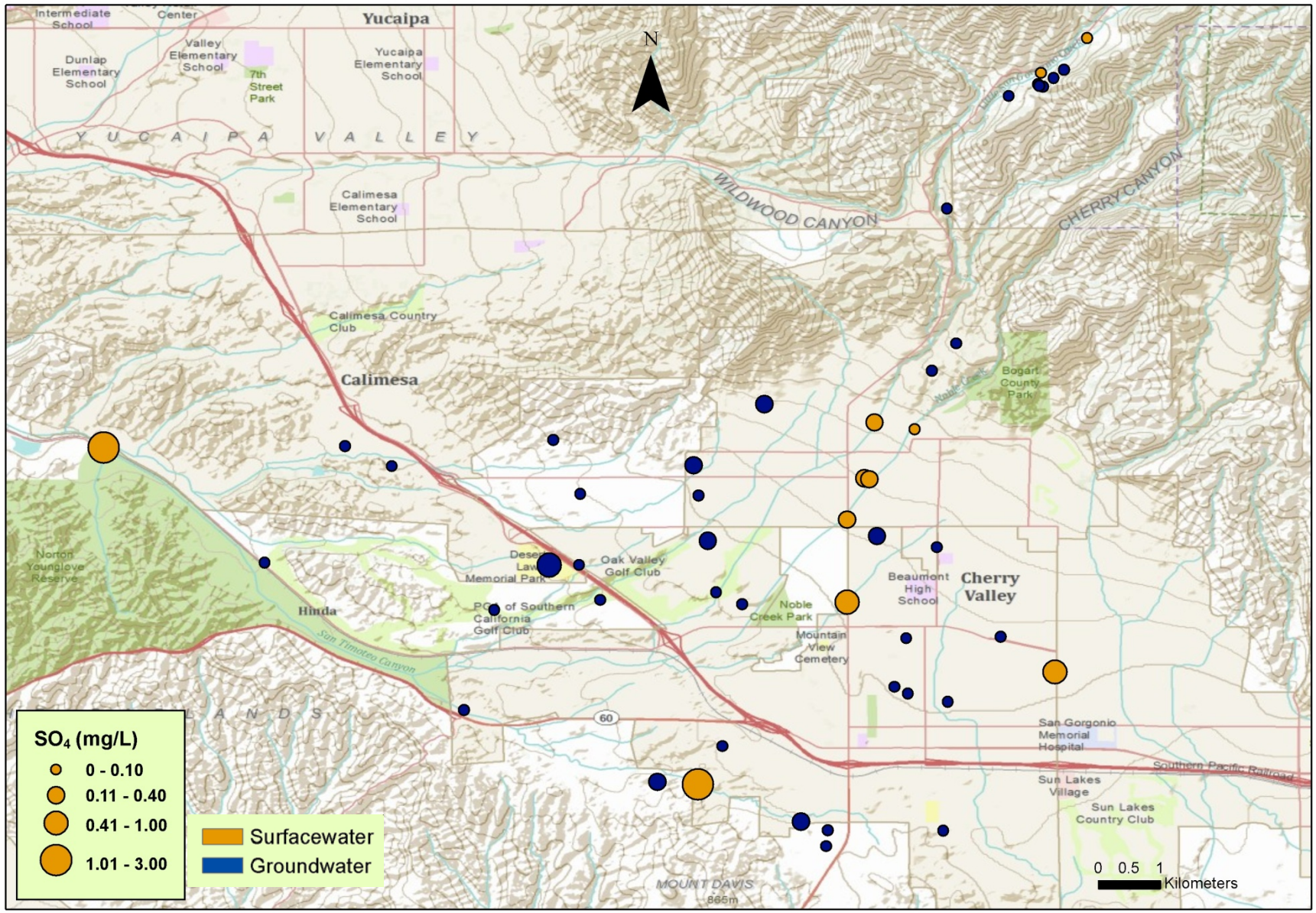

Figure 20. Phosphate concentrations of surface water and groundwater within and adjacent to the Beaumont Management Zone.

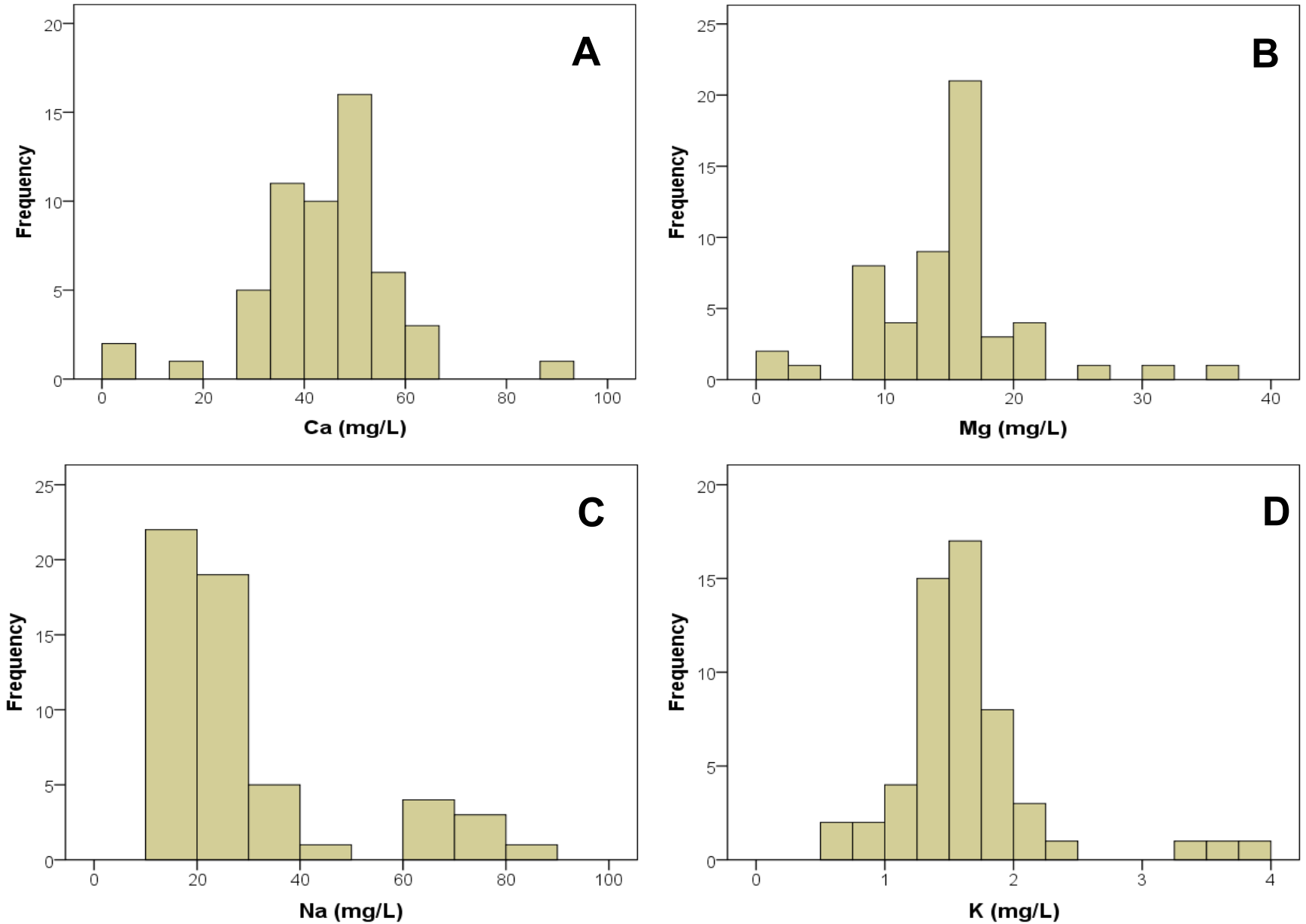

Figure 21. Histograms of major cations in groundwater within and adjacent to the Beaumont Management Zone. A: calcium; B: magnesium; C: sodium; D: potassium.

Calcium Concentration, Beaumont Management Zone

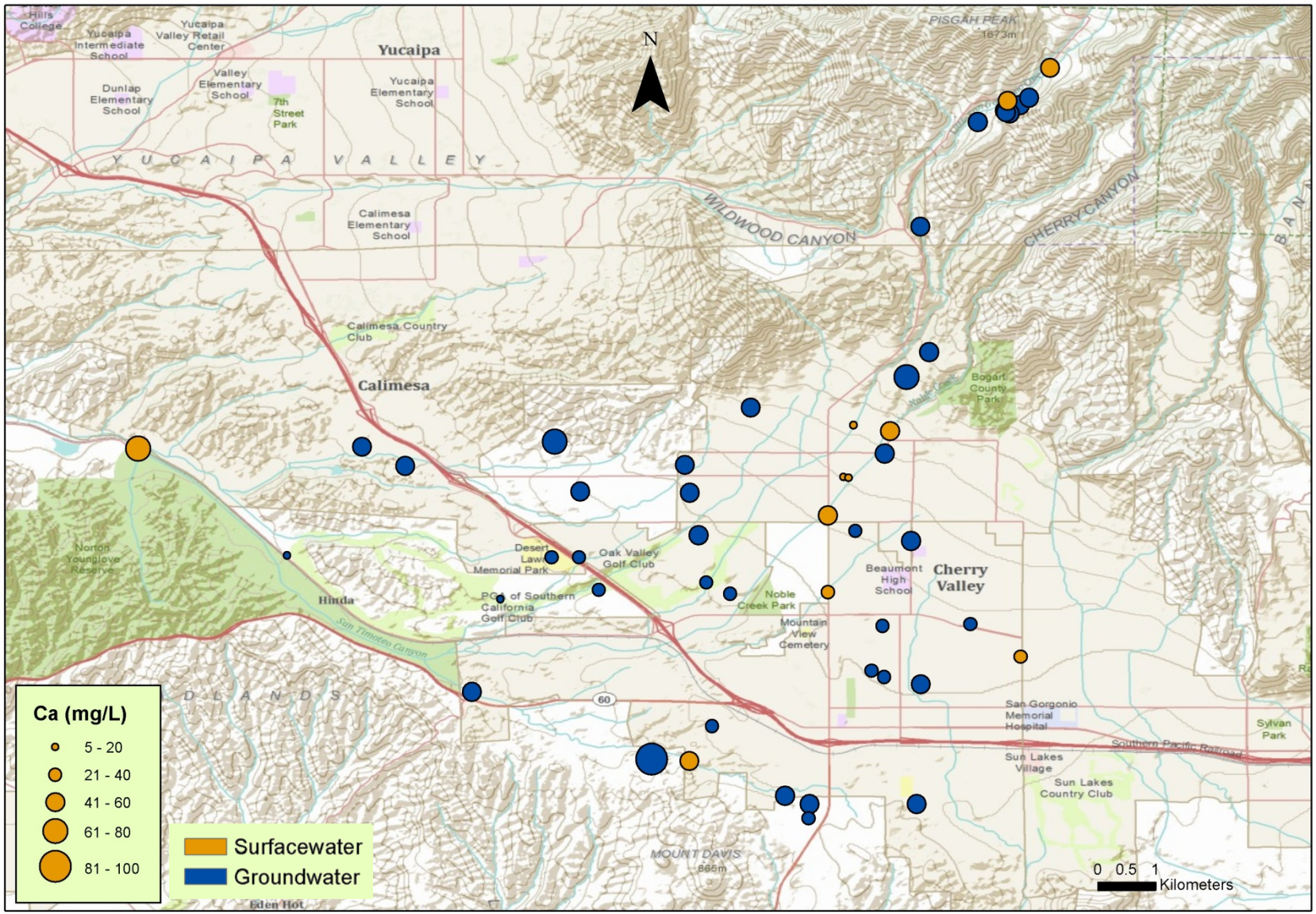

Figure 22. Calcium concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Magnesium Concentration, Beaumont Management Zone

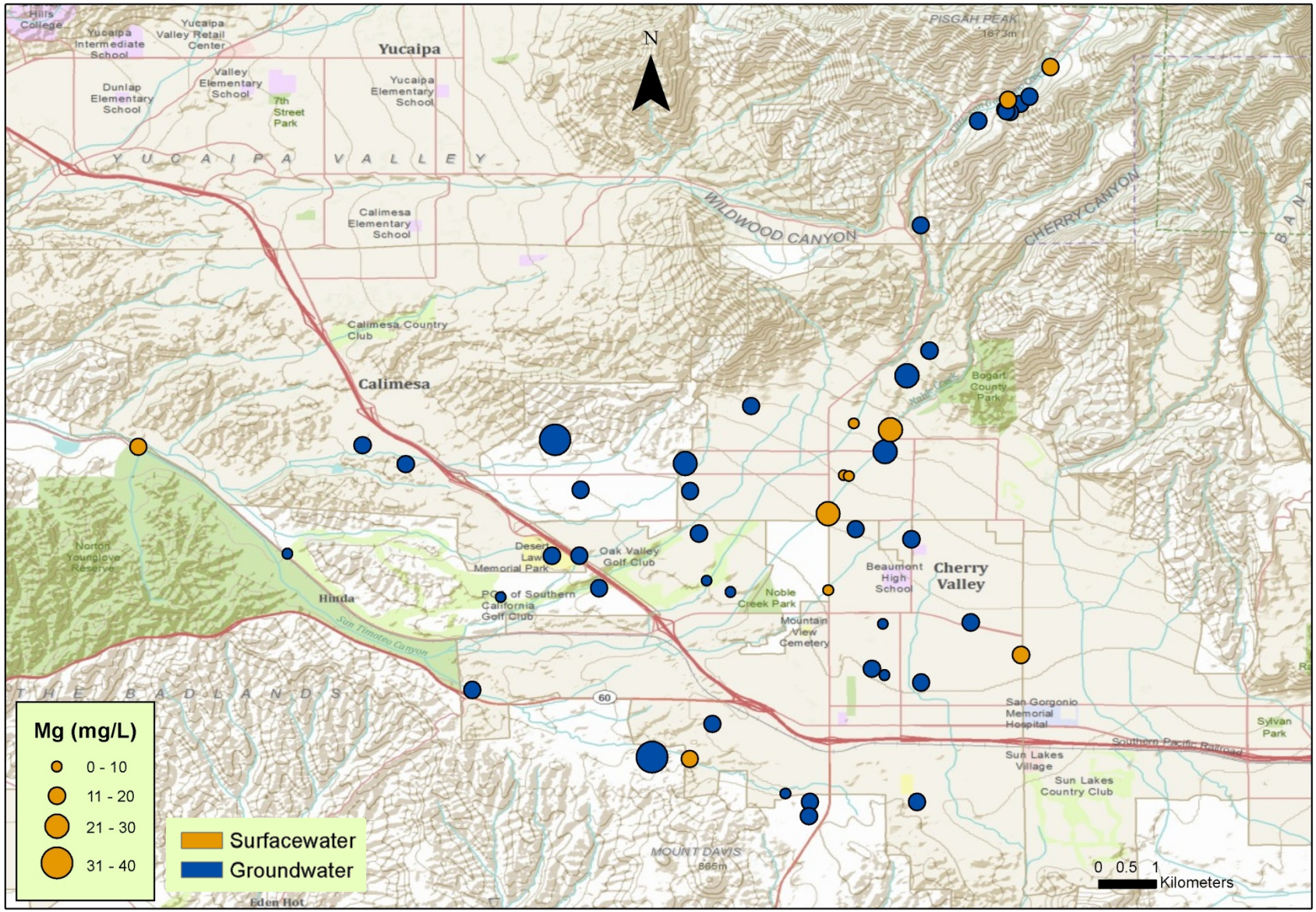

Figure 23. Magnesium concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Sodium Concentration, Beaumont Management Zone

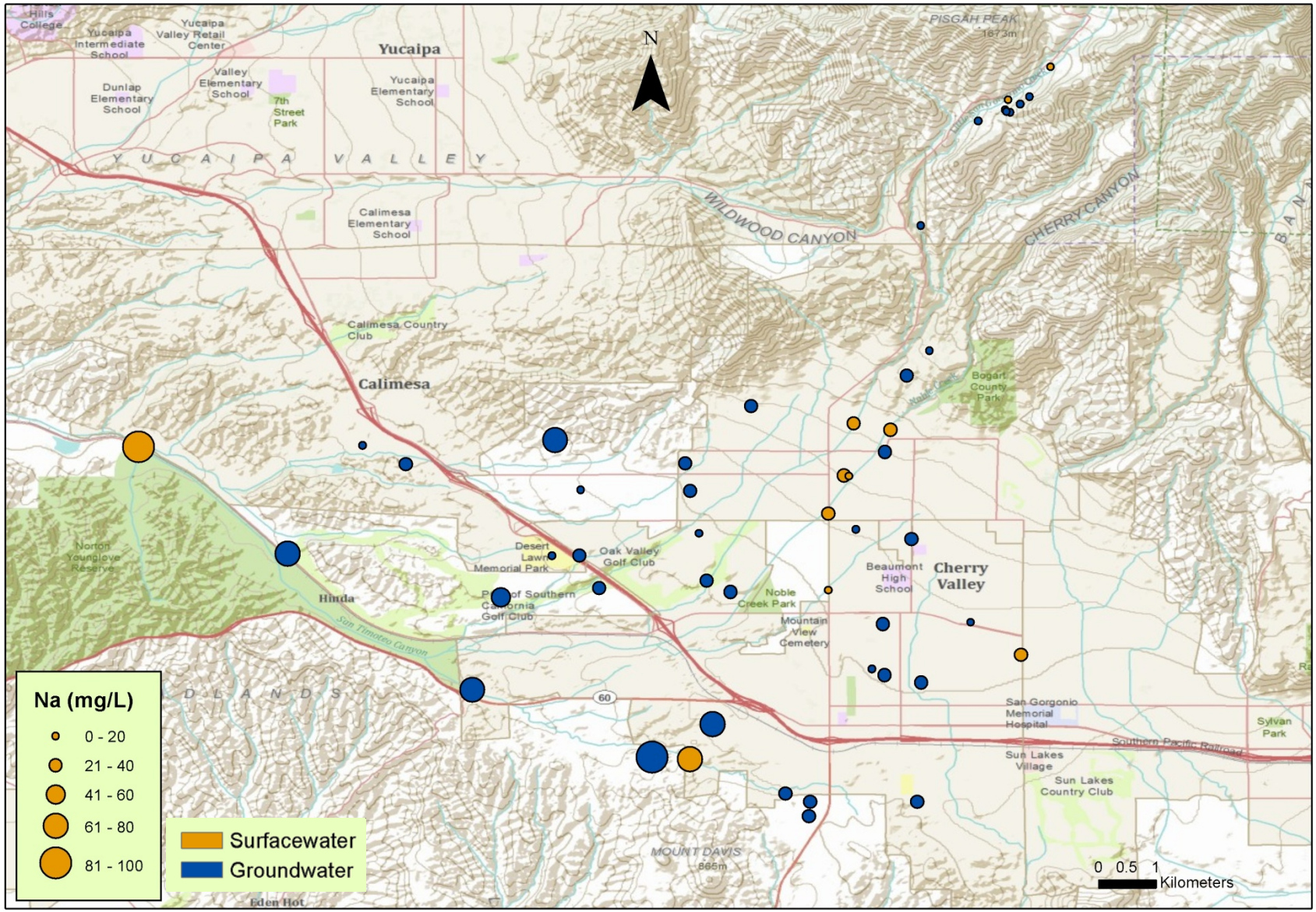

Figure 24. Sodium concentration of surface water and groundwater within and adjacent to the Beaumont Management Zone.

Potassium Concentration, Beaumont Management Zone

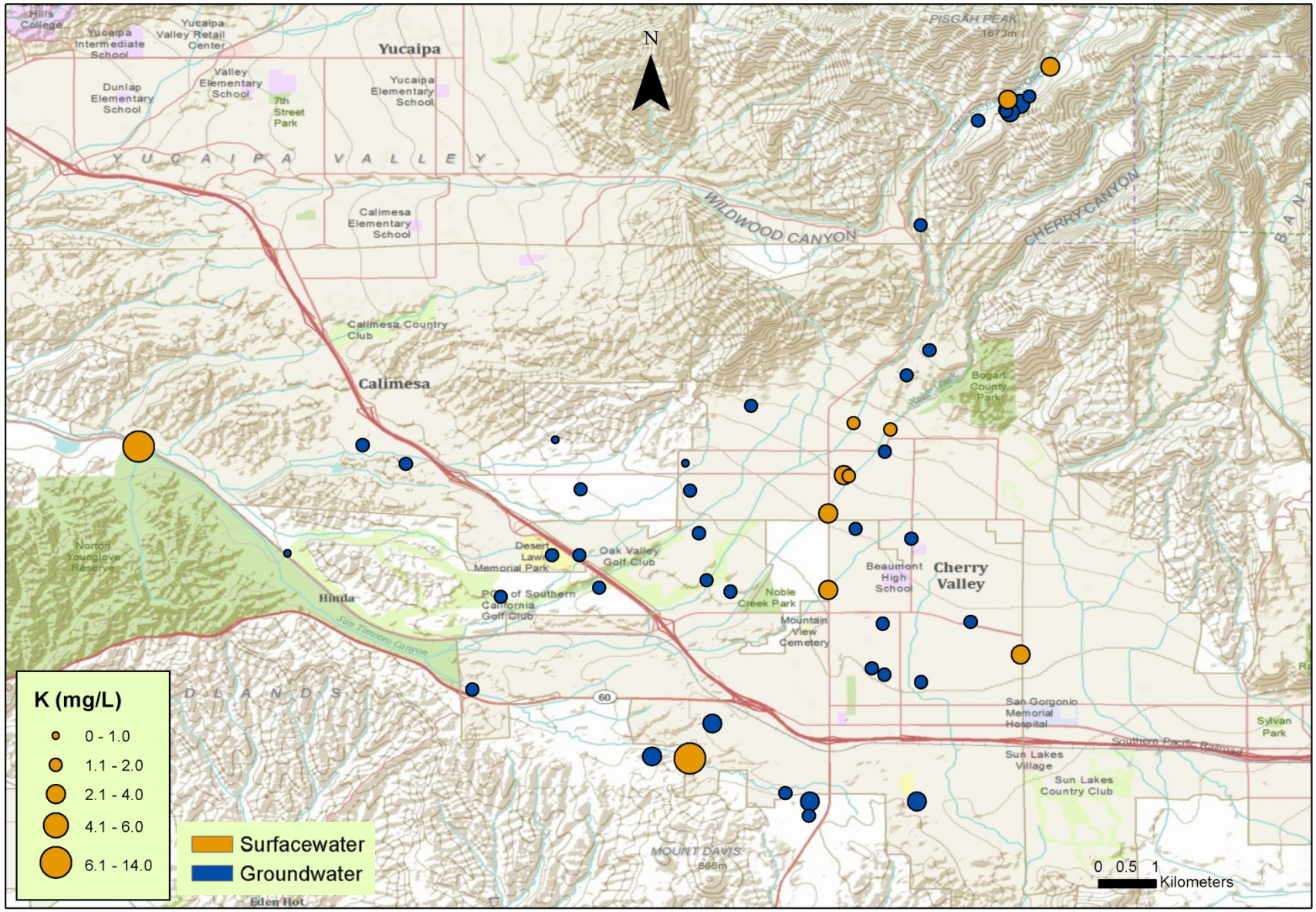

Figure 25. Potassium concentration of surface water and groundwater in Beaumont management zone.

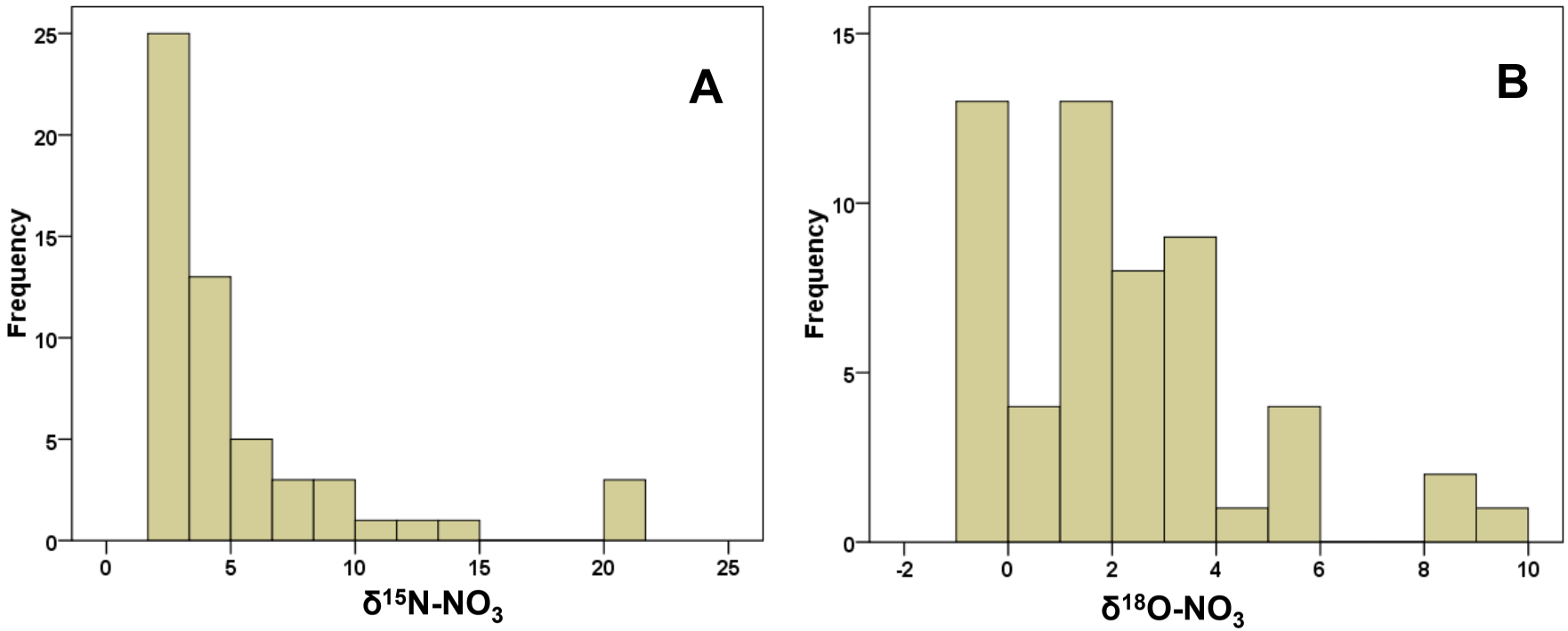

Figure 26. Histograms of isotopes of nitrate of groundwater within and adjacent to the Beaumont Management Zone. A: nitrogen isotope of nitrate; B: oxygen isotope of nitrate. Units are per mil.

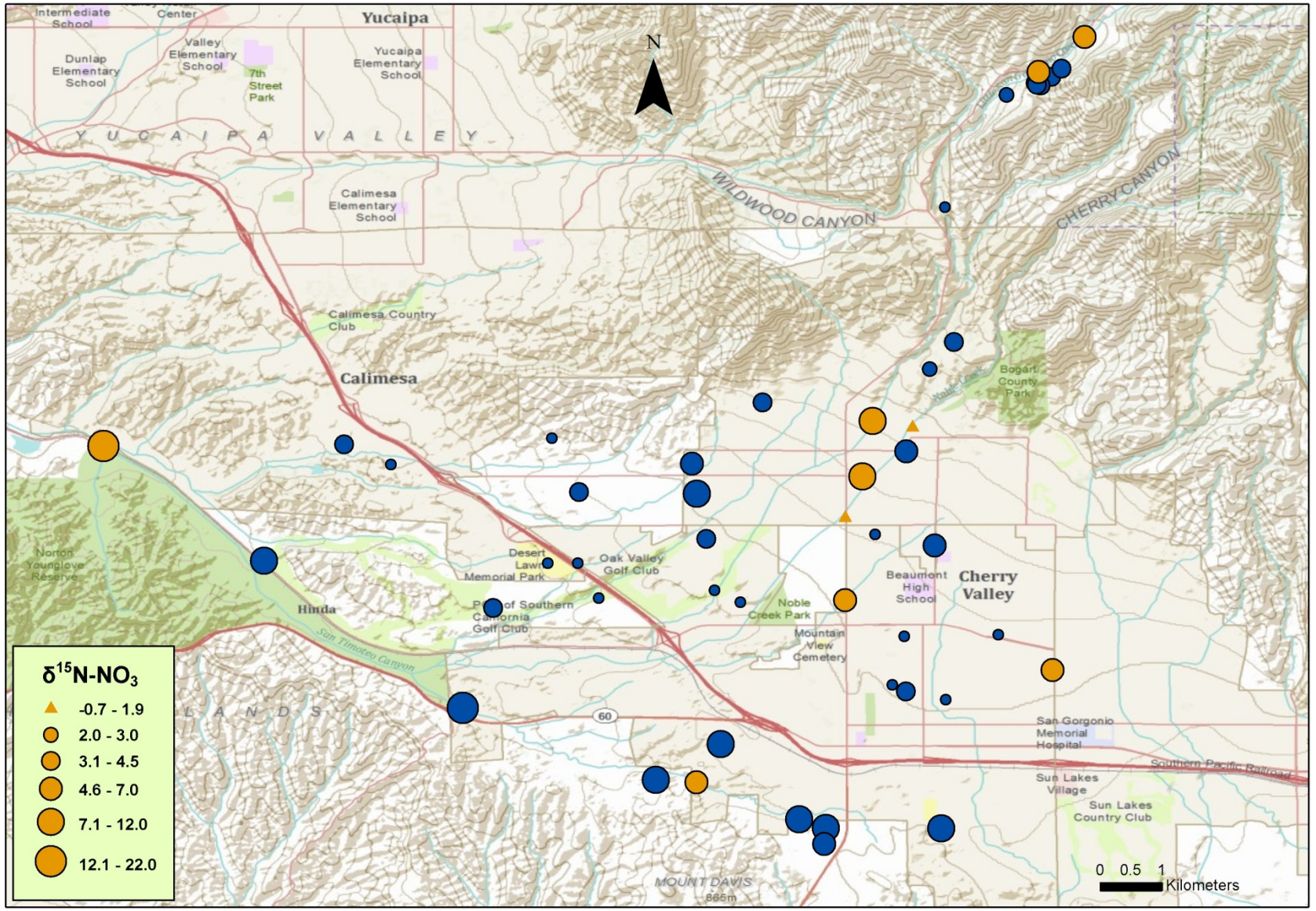

Figure 27. Nitrogen isotope composition of nitrate of surface water and groundwater within and adjacent to the Beaumont Management Zone. Units are per mil. Blue circles are groundwater, yellow circles are surface water.

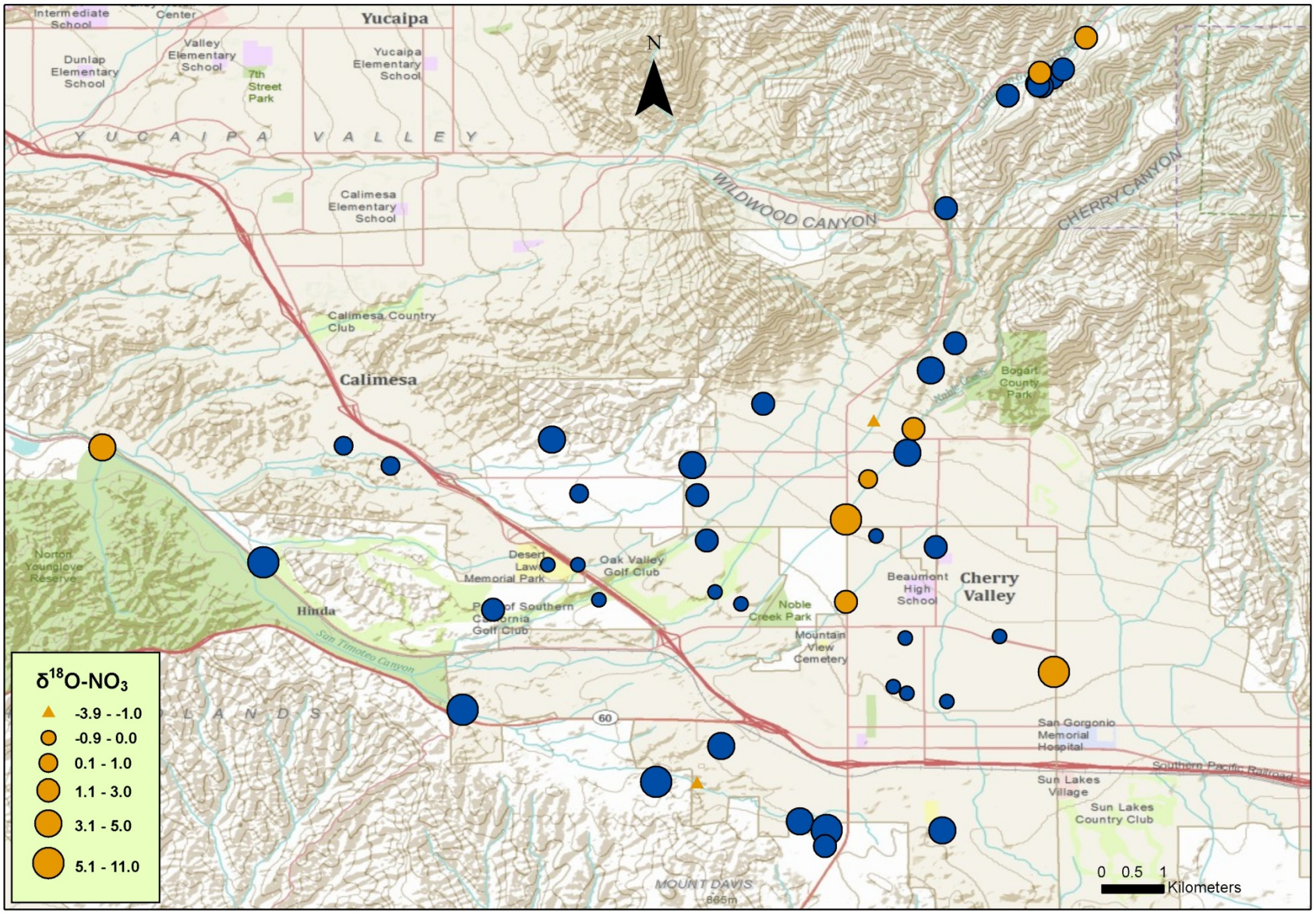

Figure 28. Oxygen isotope composition of nitrate of surface water and groundwater within and adjacent to the Beaumont Management Zone. Units are per mil. Blue circles are groundwater, yellow circles are surface water.

Ratio of $\delta^{18}O$: $\delta^{15}N$ of nitrate, Beaumont Management Zone

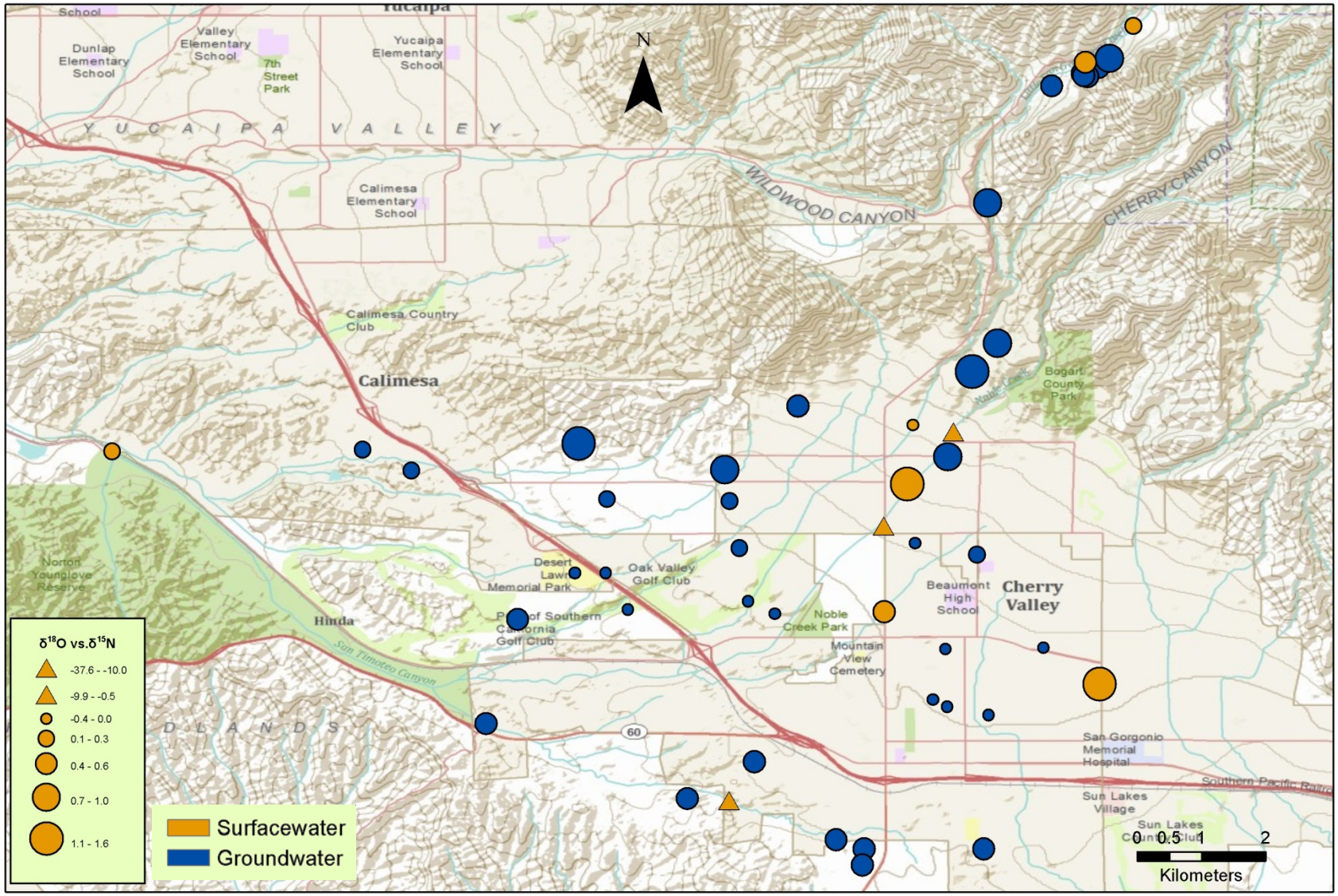

Figure 29. Ratio of $\delta^{18}O$: $\delta^{15}N$ of nitrate of surface water and groundwater within and adjacent to the Beaumont Management Zone. Units are dimensionless.

Groundwater PPCP, Beaumont Management Zone

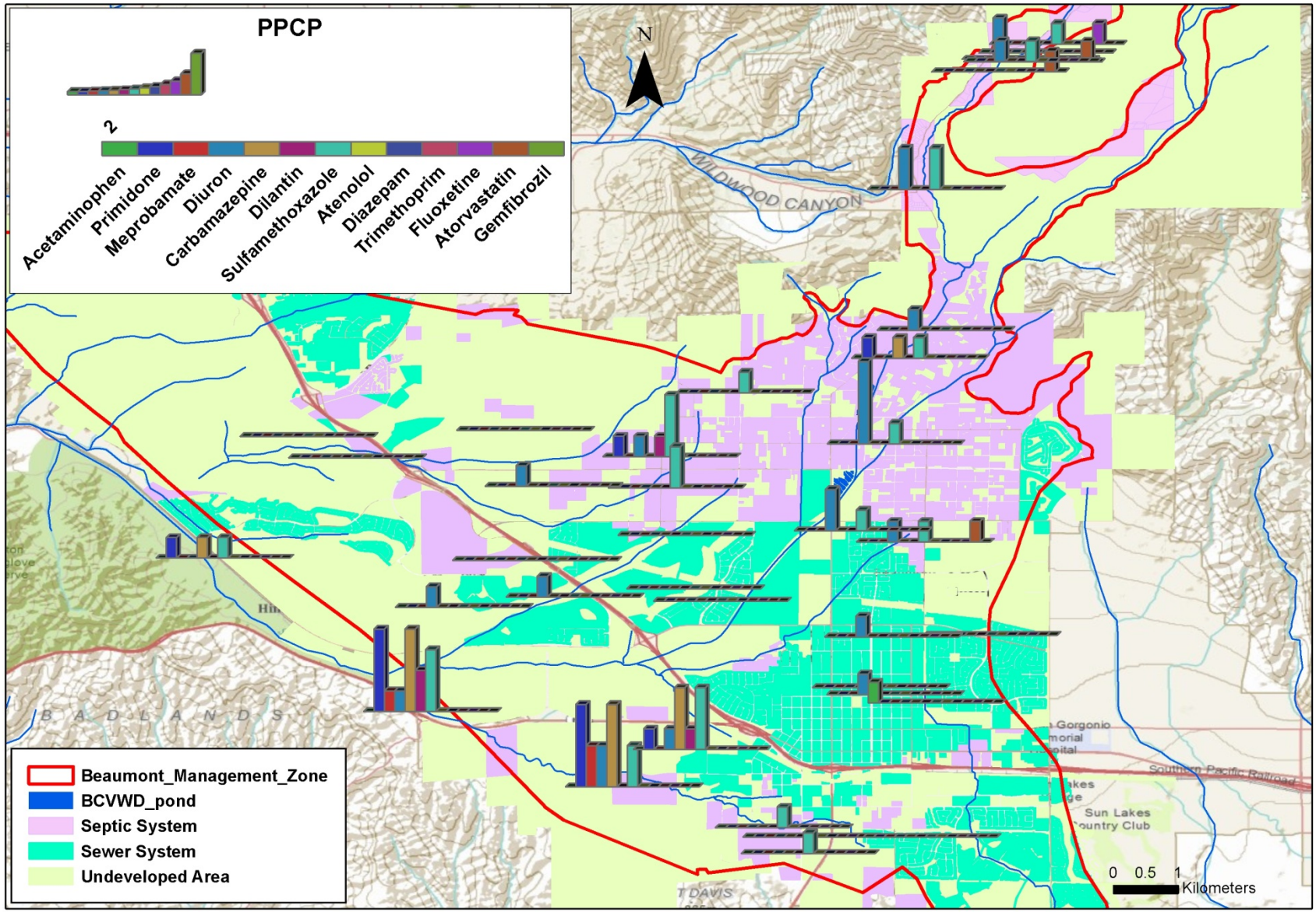

Figure 30. Concentrations of pharmaceutical and personal care products (PPCPs) of groundwater within and adjacent to the Beaumont Management Zone. Different colors indicate different PPCP compounds and the bar scale indicates the rank of PPCP concentration (0-4).

PPCP Index, Beaumont Management Zone

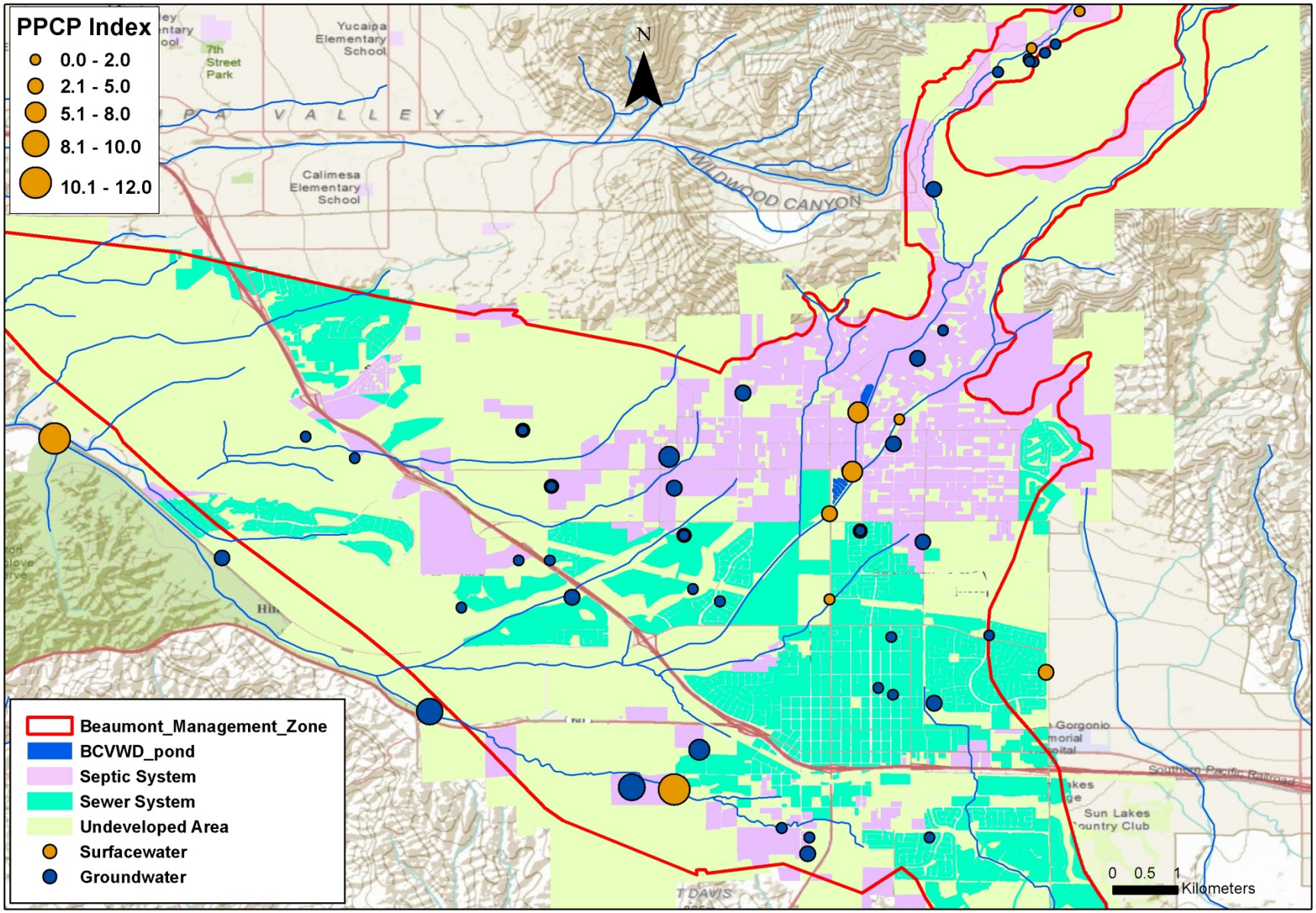

Figure 31. Index of pharmaceutical and personal care products (PPCPs) of groundwater within and adjacent to the Beaumont Management Zone. The higher the index value the higher the probability of groundwater contamination by human waste. Blue symbols denote groundwater and gold symbols are surface water.

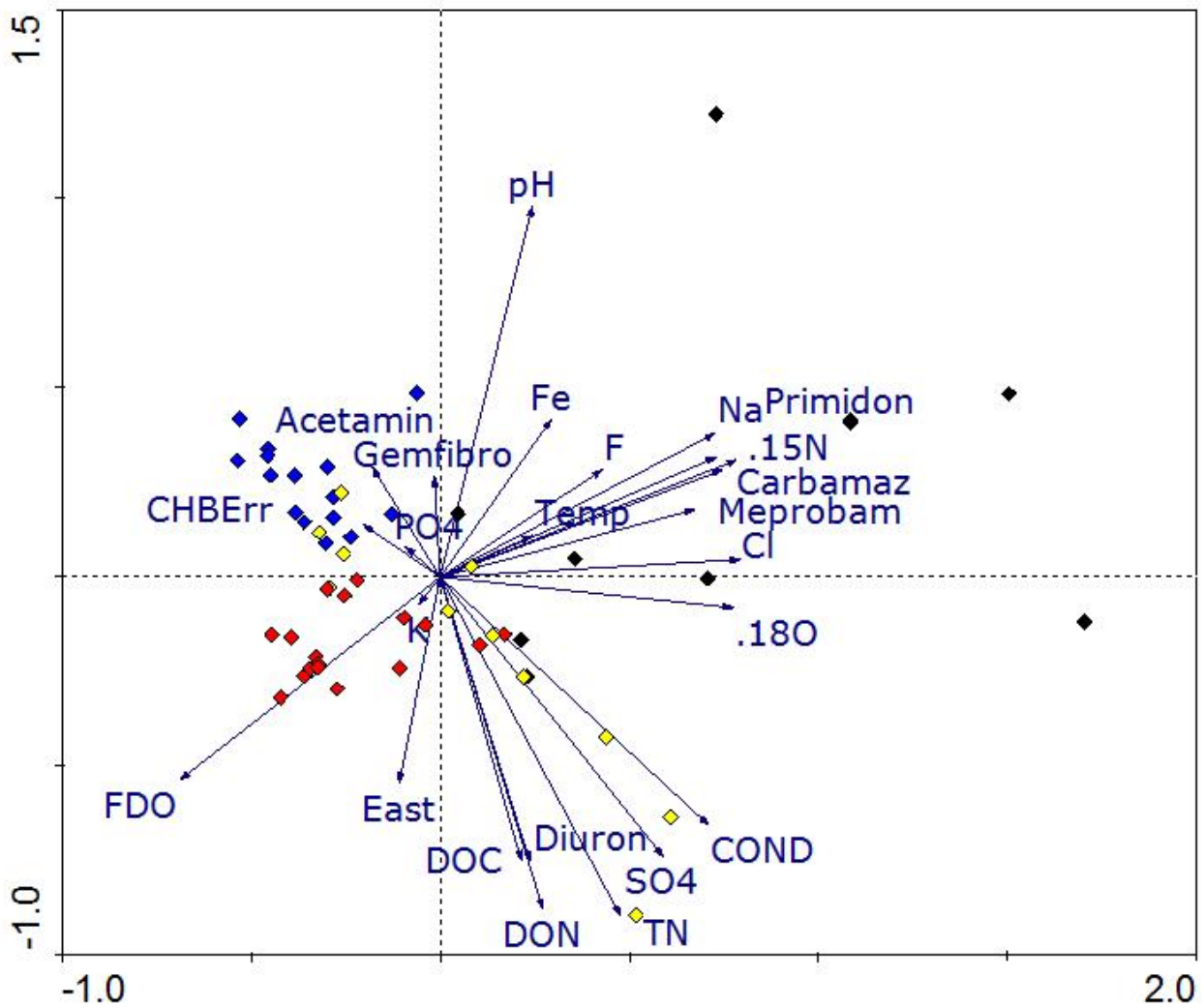

Figure 32. Principal component analysis (PCA) analysis of groundwater within and adjacent to the Beaumont Management Zone. This PCA represents measured environmental variables (arrows) in our dataset after removal of autocorrelated variables. Each arrow points in the direction of increasing values for the corresponding variable. The length of arrow is a measure of that variable's importance in explaining chemical variation among the sampling sites. Black diamond – Zone 1; Red diamond – Zone 2; Yellow diamond – Zone 3; Blue diamond – Zone 4.

env var code	description
E or East	Easting
N or North	Northing
T or Temp	Field Temp
FDO	Field Dissolved Oxygen
pH	pH
SC	Specific Cond.
A.N.C.	A.N.C.
TDS	TDS (total dissolved solid)
DOC	DOC
HCO_3	HCO_3
F	F
Cl	Cl
NO_2	NO_2
NO_3	NO_3
PO_4	PO_4
SO_4	SO_4
NO_3-N	NO_3-N
TN	TN
DON	DON
Ca	Ca
Mg	Mg
Na	Na
K	K
Al	Al
B	B
Fe	Fe
P	P
CHBErr	Charge balance error
$\delta^{18}O$	$\delta^{18}O$
$\delta^{15}N$	$\delta^{15}N$
$\delta^{18}O/\delta^{15}N$	$\delta^{18}O/\delta^{15}N$
Acetamino	Acetaminophen
Primidone	Primidone
Meprobam	Meprobamate
Diuron	Diuron
Carbamaze	Carbamazepine
Dilantin	Dilantin
Sulfametho	Sulfamethoxazole
Atenolol	Atenolol
Diazepam	Diazepam
Trimethopri	Trimethoprim
Fluoxetine	Fluoxetine
Atorvastatin	Atorvastatin
Ibuprofen	Ibuprofen
Naproxen	Naproxen
Diclofenac	Diclofenac
Gemfibrozil	Gemfibrozil

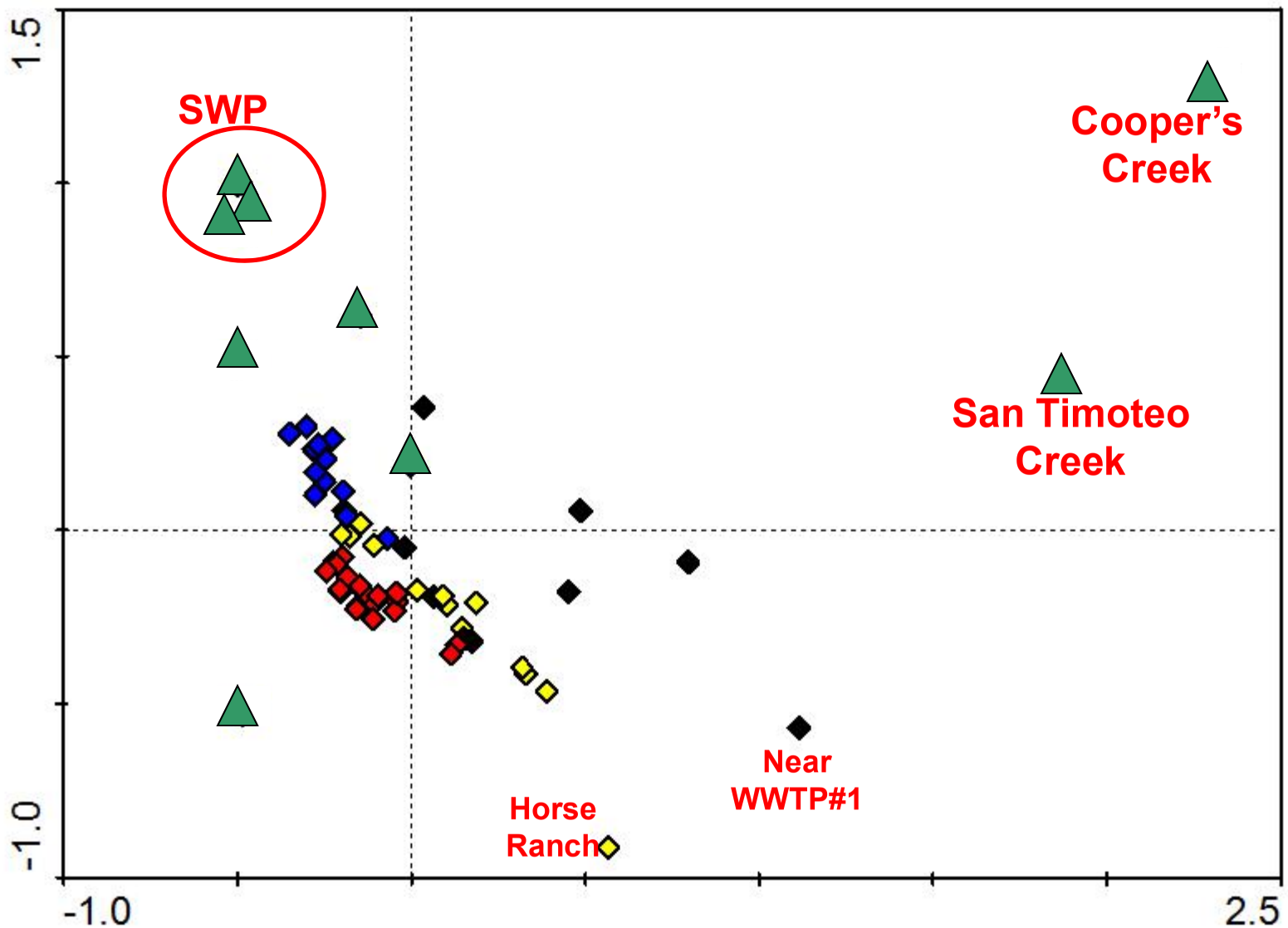

Figure 33. Cluster analysis of groundwater and surface water in Beaumont management zone. Black diamonds – Zone 1 groundwater; Red diamonds – Zone 2 groundwater; Yellow diamonds – Zone 3 groundwater; Blue diamonds – Zone 4 groundwater; Green triangles – Surface water.

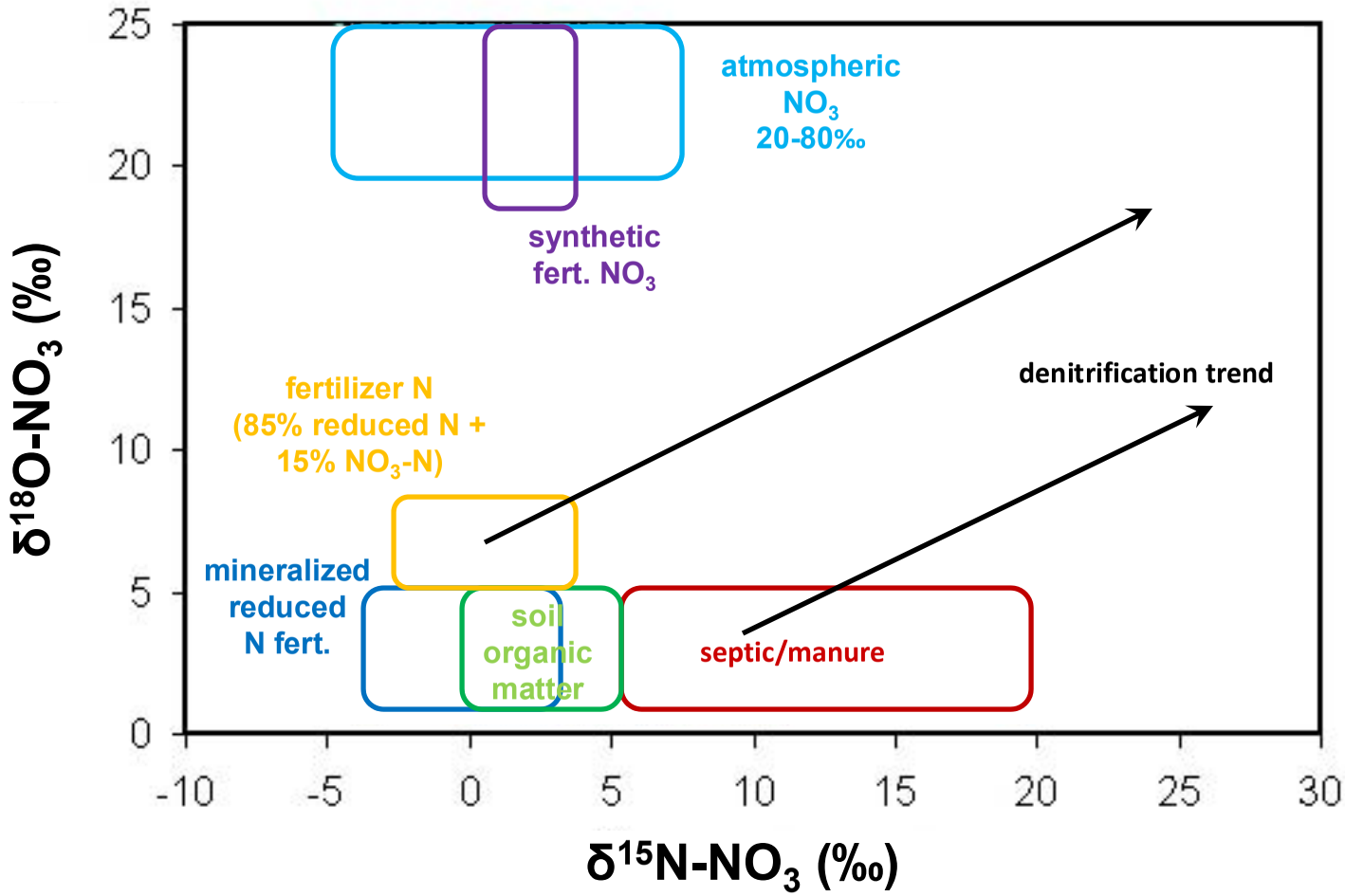

Figure 34. Crossplot of typical $\delta^{18}O\text{-}NO_3$ and $\delta^{15}N\text{-}NO_3$ values for different nitrate sources and the trend of isotopic compositions caused by denitrification (estimated based on Roadcap et al. 2002, Kendall and McDonnell 1998 and data in this study)

Nitrate-Nitrogen Concentration, Beaumont Management Zone

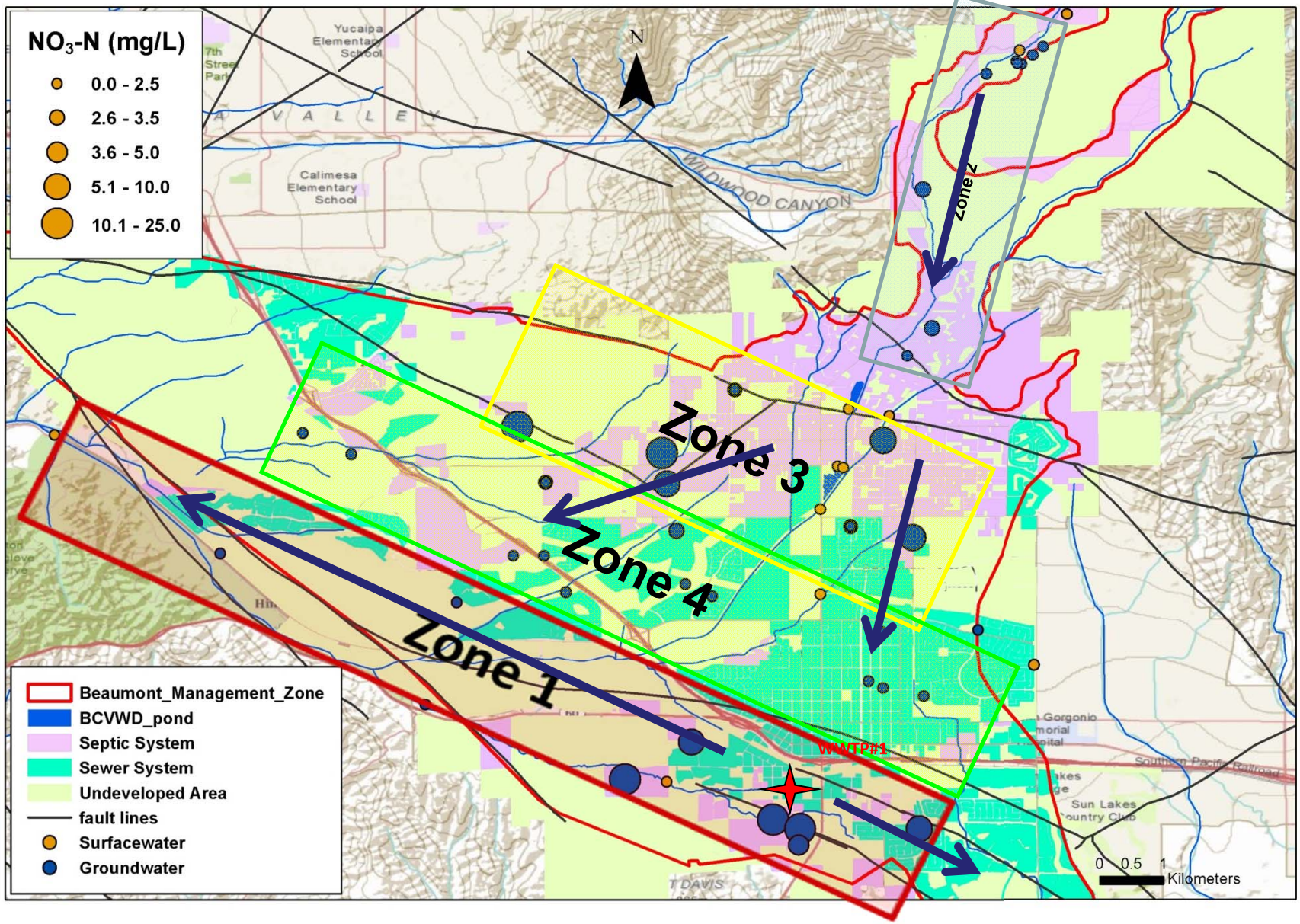

Figure 35a. Nitrate-nitrogen concentration corresponding with different zones in Beaumont Basin. The blue arrows indicate general horizontal flow paths for groundwater.

Nitrate-Nitrogen Concentration, Beaumont Management Zone 3

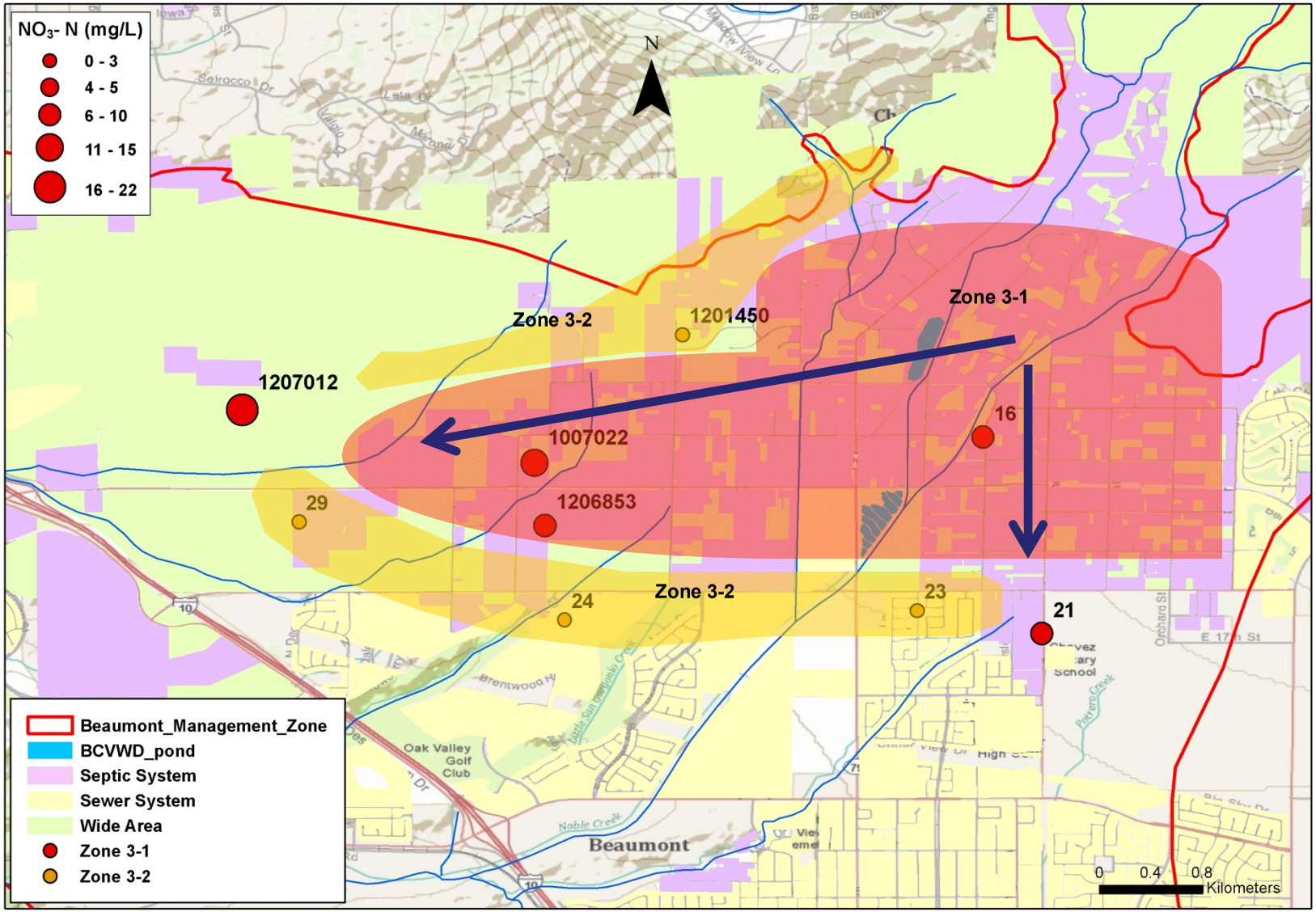

Figure 35b. Nitrate-nitrogen concentration of Zone 3 in Beaumont Basin. The blue arrows indicate general horizontal flow paths for groundwater.

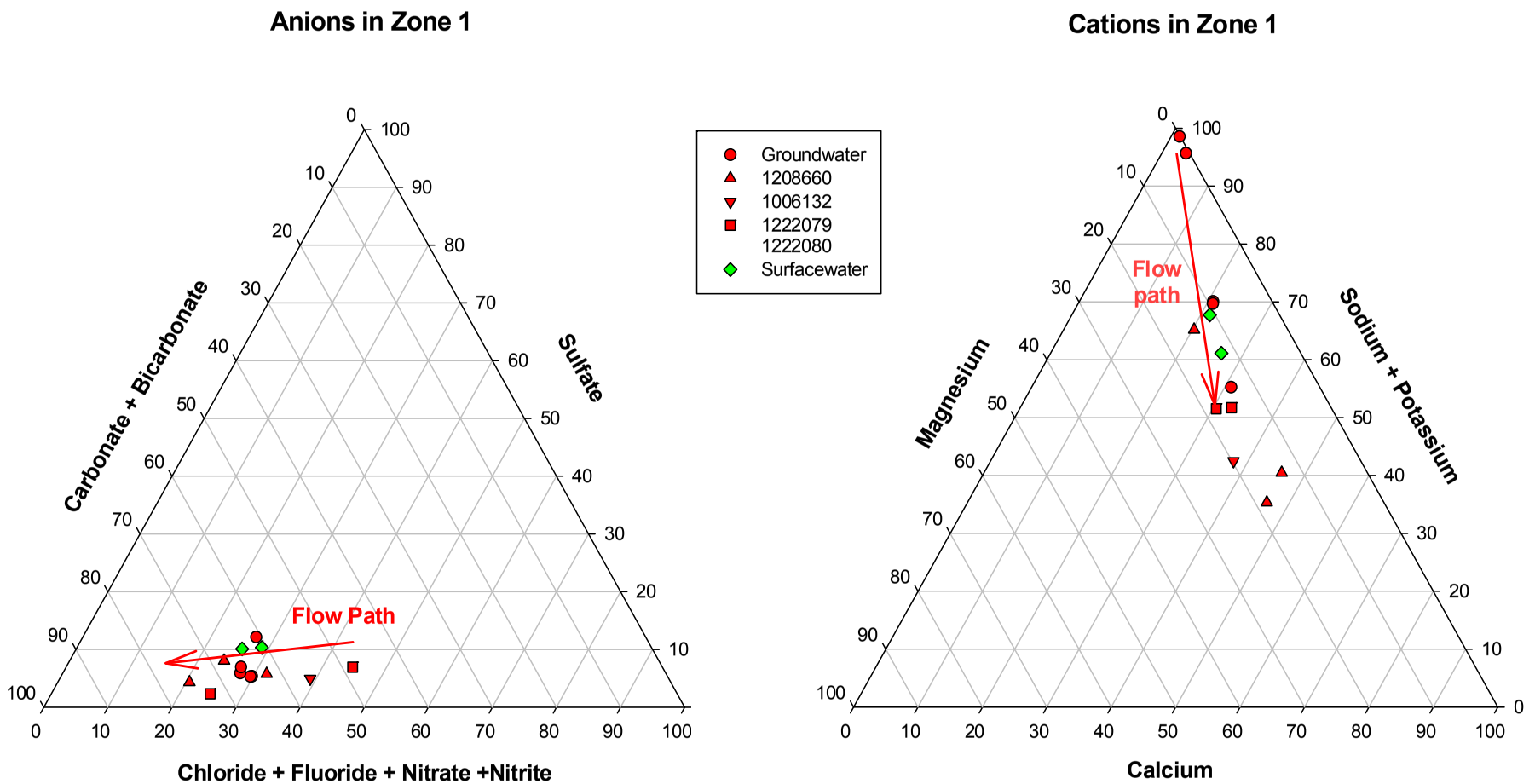

Figure 36. Variation of major ions along the general flow path in Zone 1.

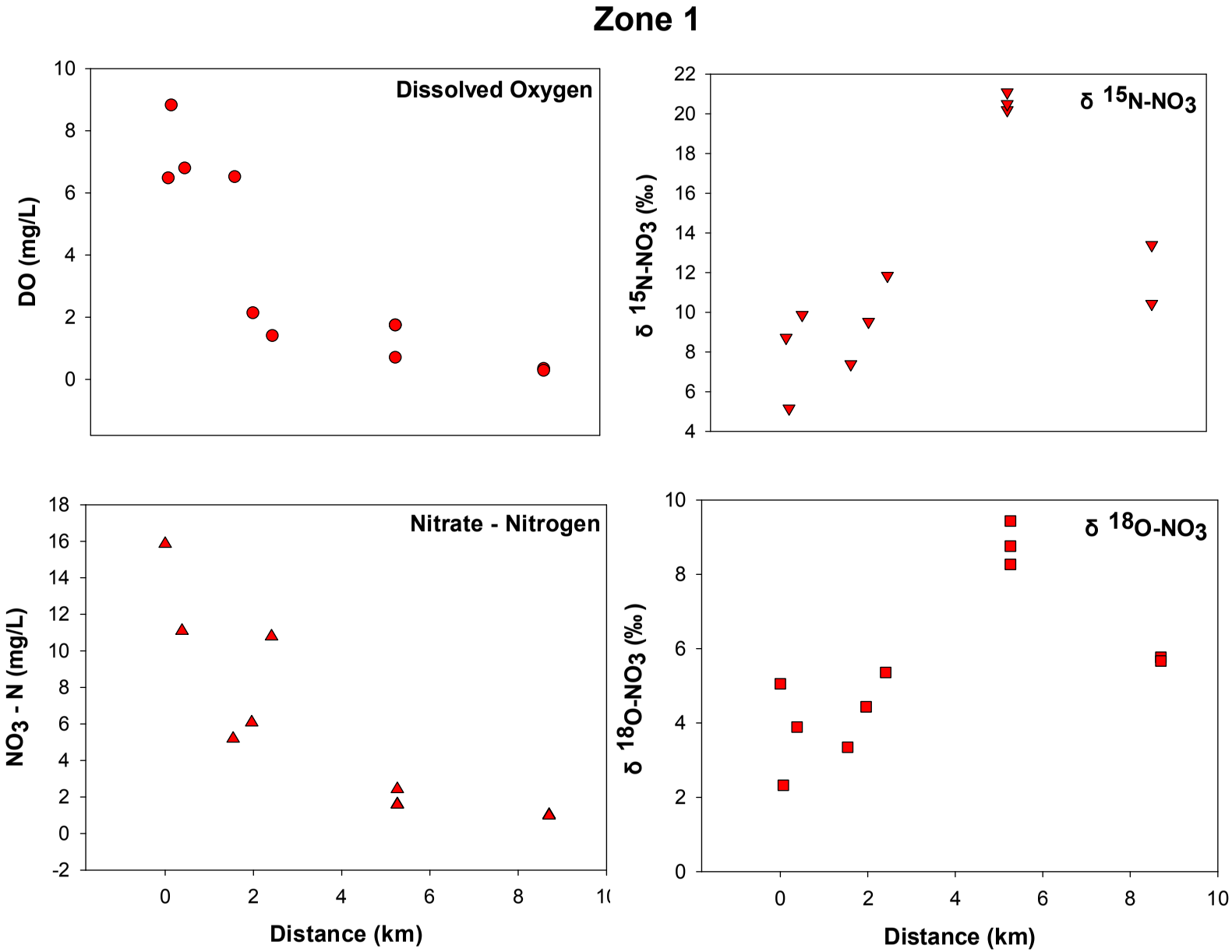

Figure 37. Variation of dissolved oxygen, nitrate concentration and isotopes along the general flow path in Zone 1

Zone 1

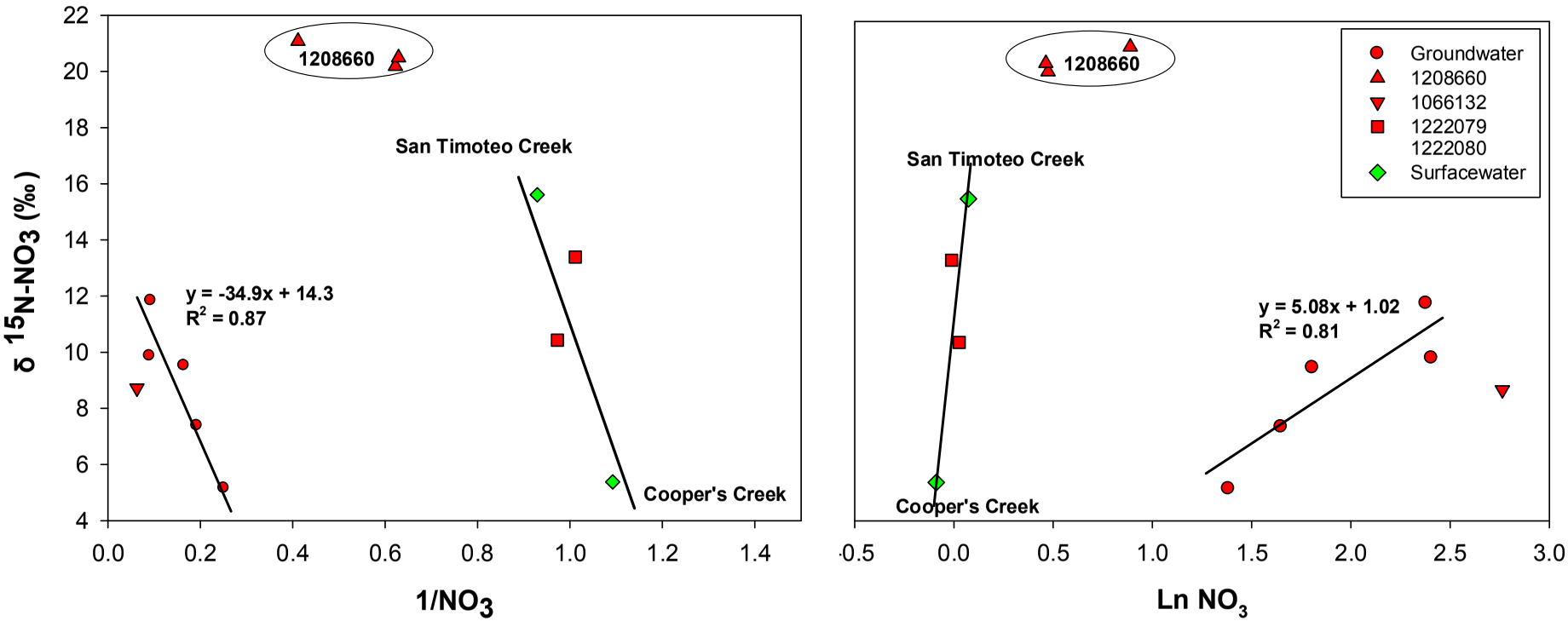

Figure 38. Relationships between $\delta^{15}N$ of nitrate and nitrate concentrations in Zone 1.

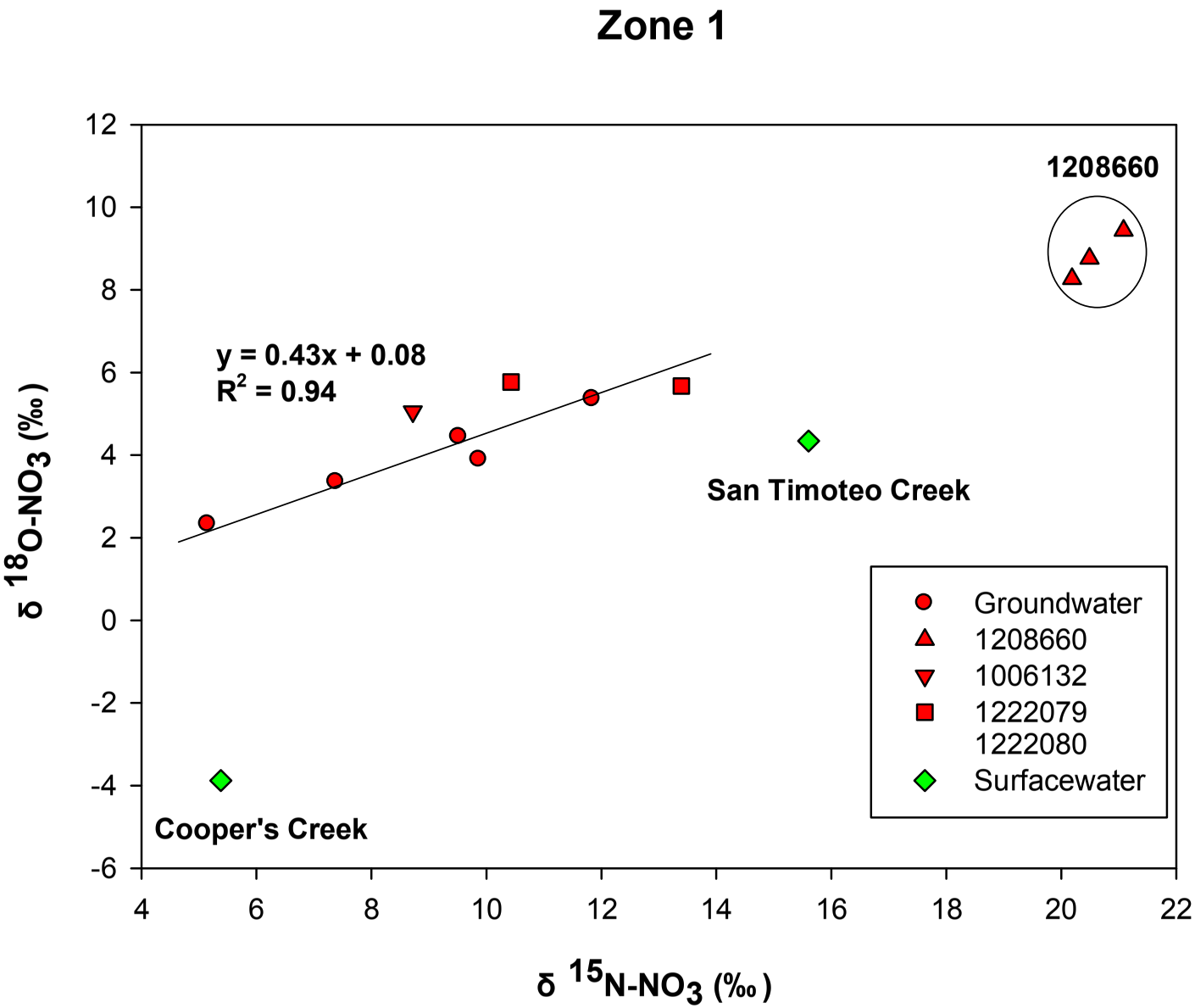

Figure 39. Relationship between $\delta^{15}N$ and $\delta^{18}O$ of nitrate in Zone 1.

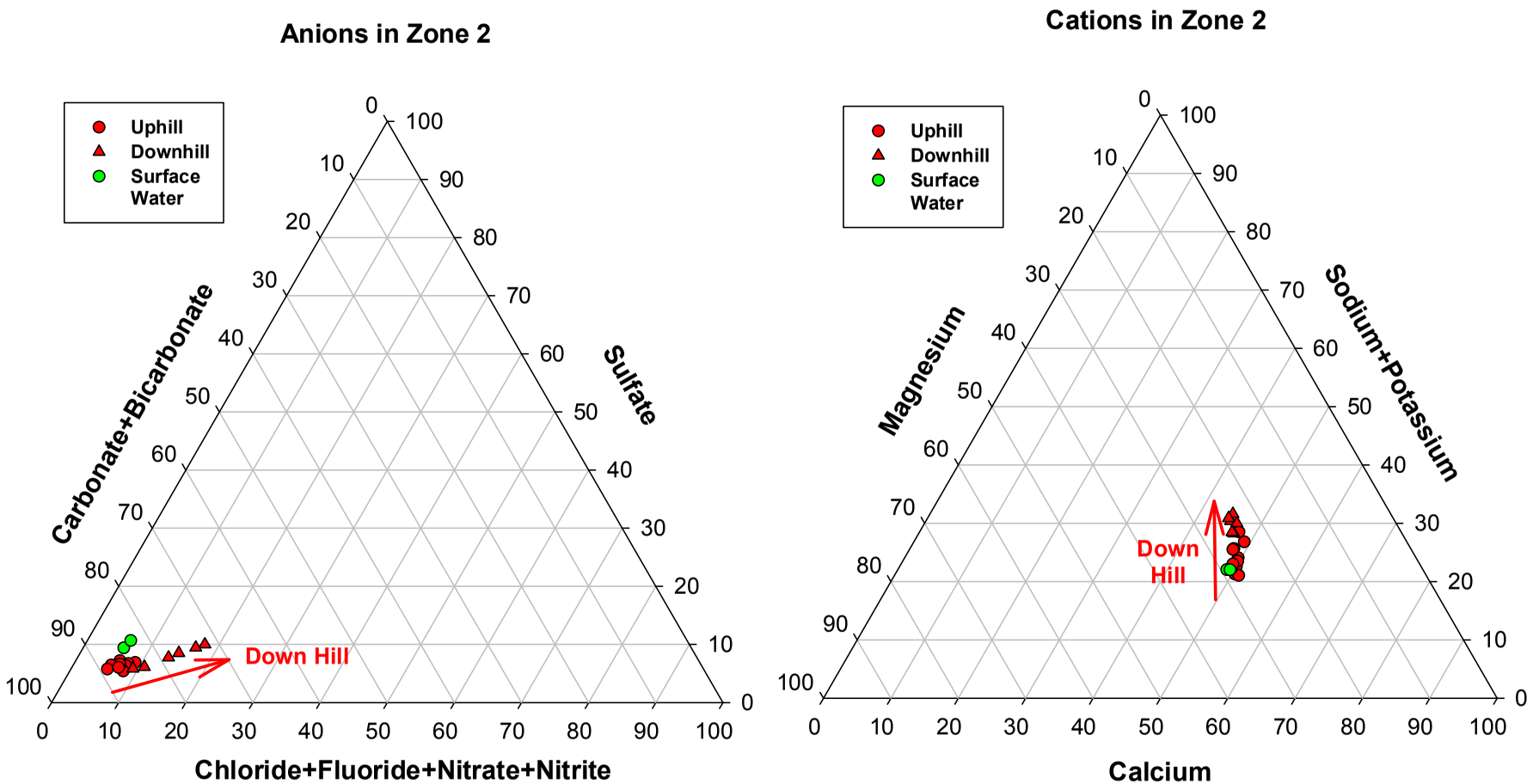

Figure 40. Variation of major ions moving along the general flow path in Zone 2.

Zone 2

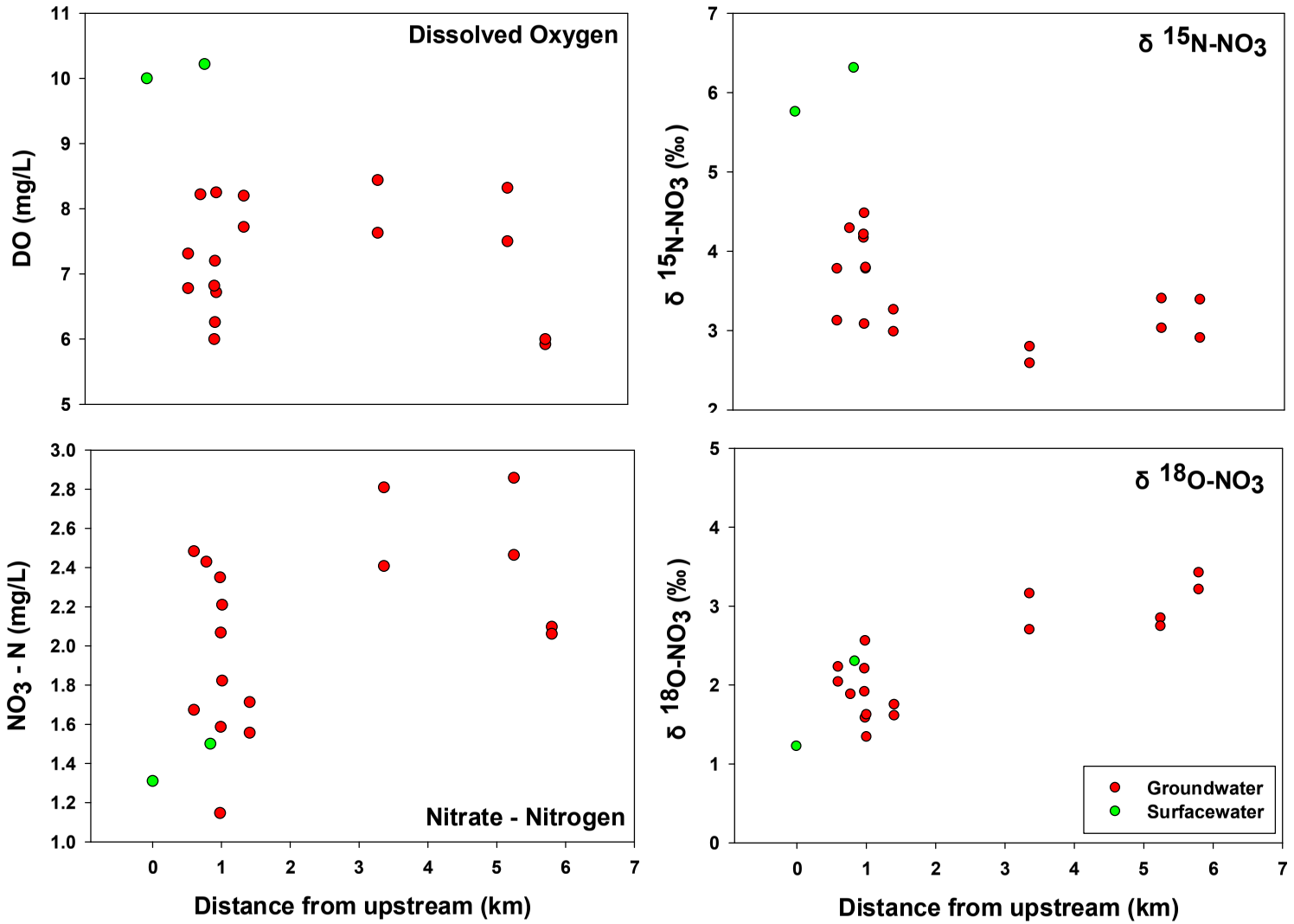

Figure 41. Variation of dissolved oxygen, nitrate concentration and isotopes moving along the general flow path in Zone 2.

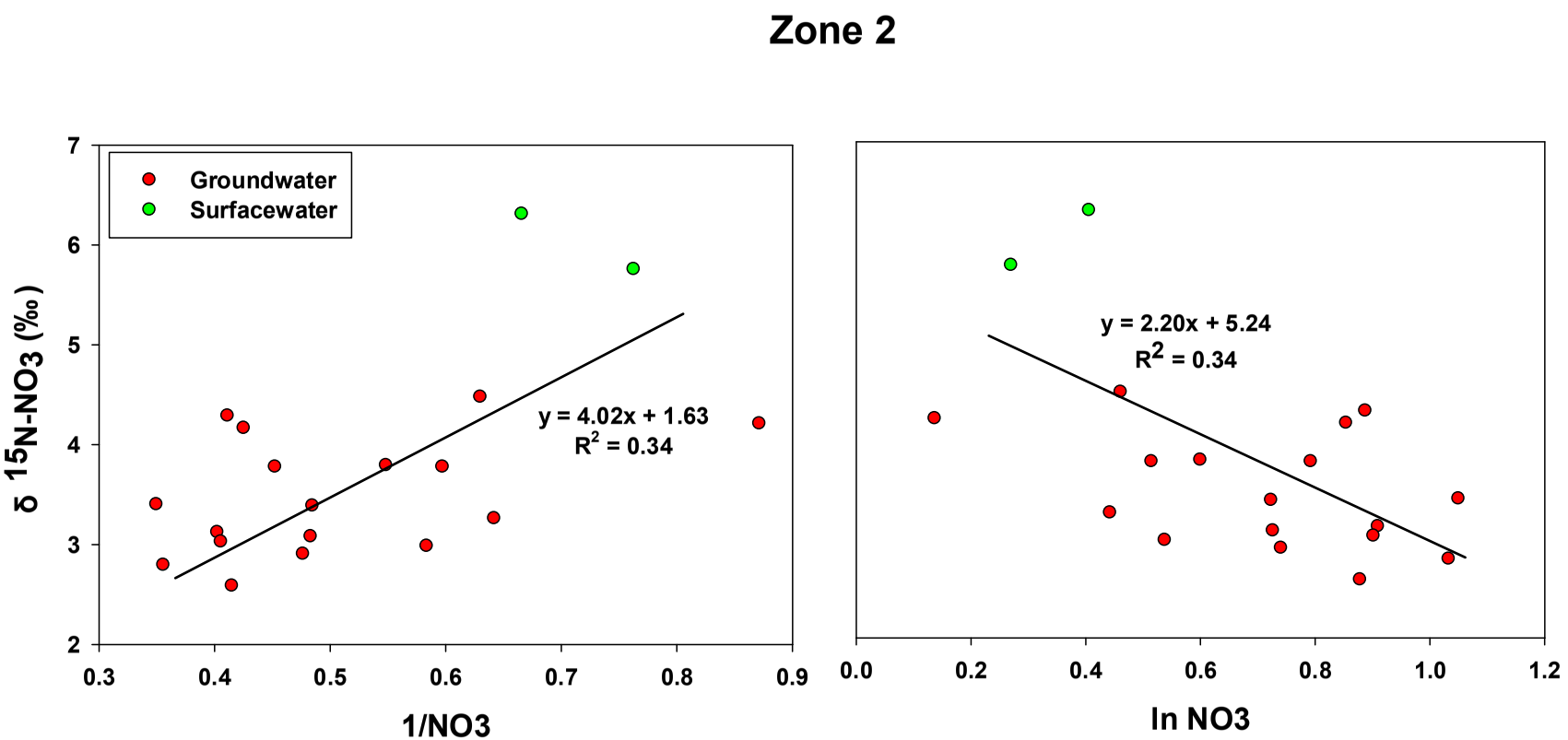

Figure 42. Relationships between $\delta^{15}N$ of nitrate and nitrate concentrations in Zone 2.

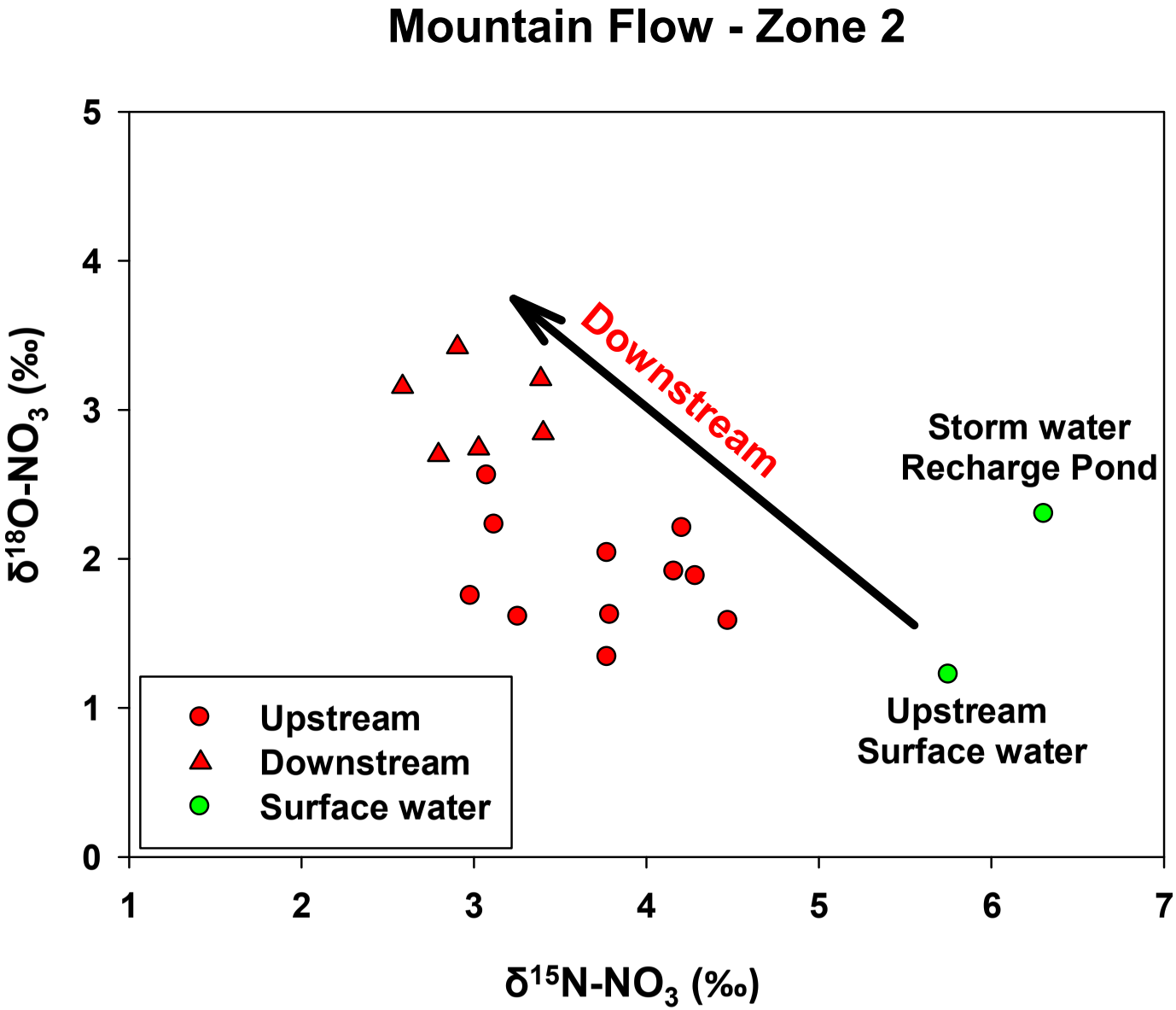

Figure 43. Relationship between $\delta^{15}N$ and $\delta^{18}O$ of nitrate in Zone 2.

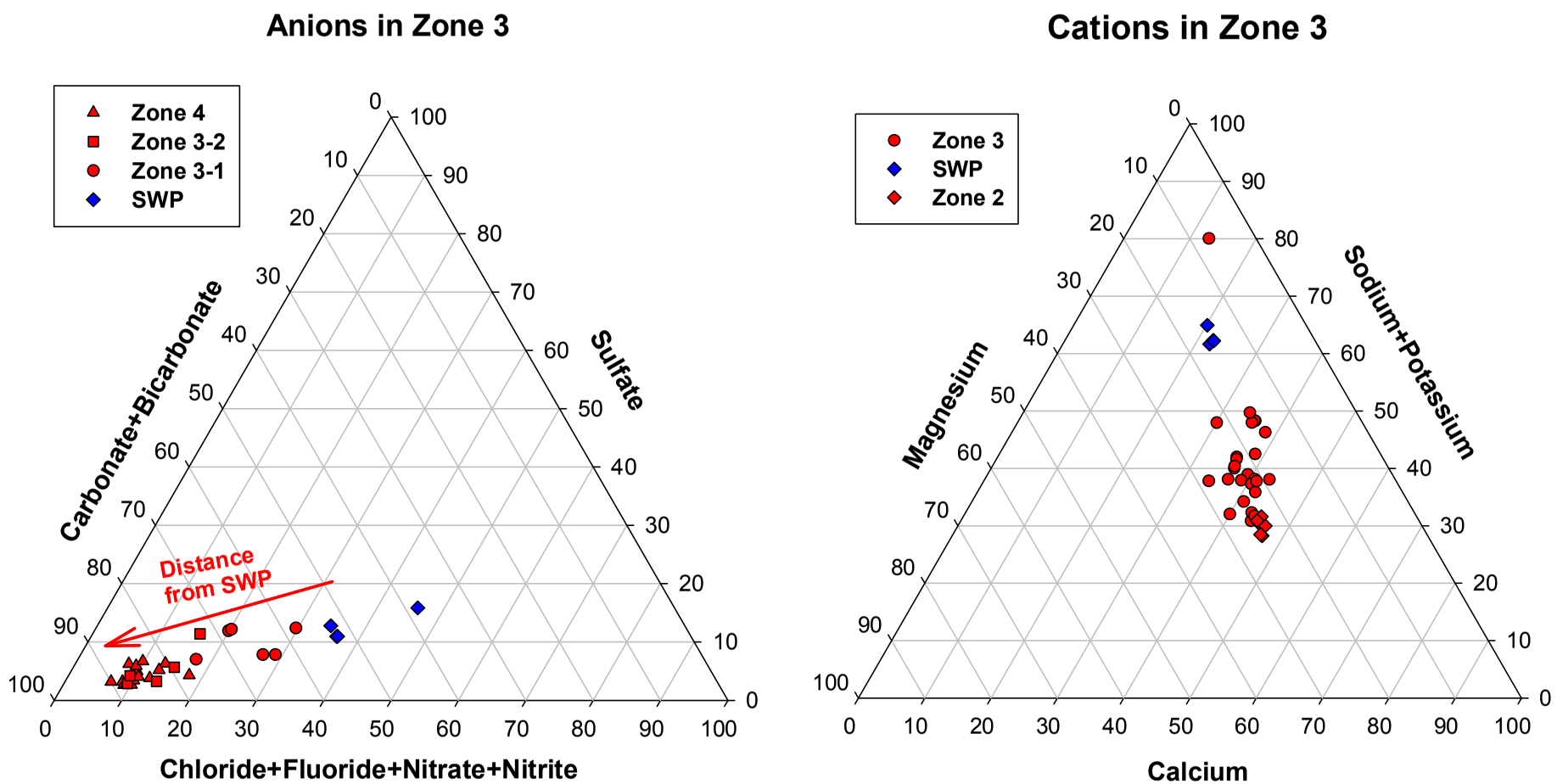

Figure 44. Variation of major ions moving away from groundwater recharge sites in Zone 3.

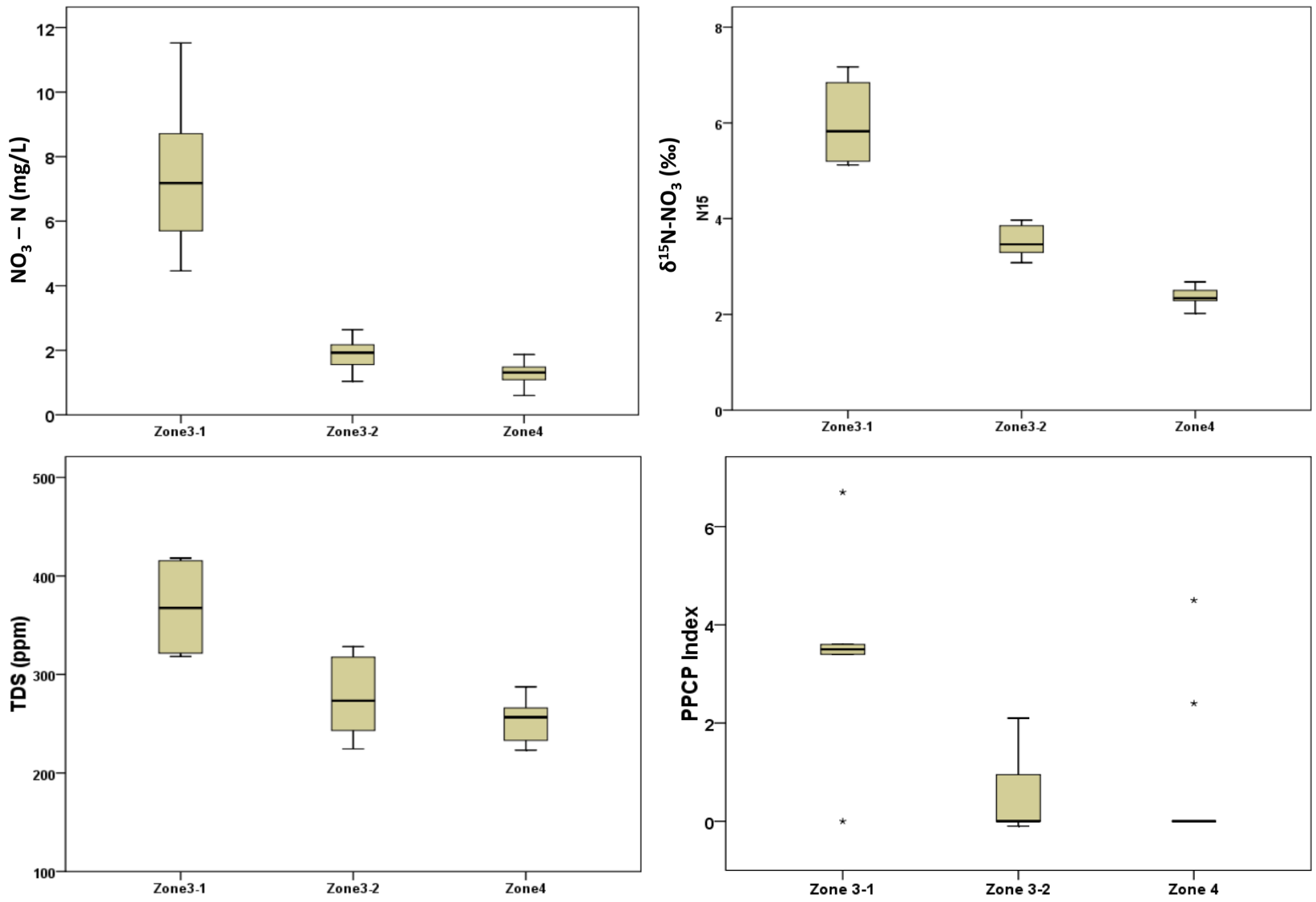

Figure 45. Comparison of groundwater nitrate concentration, nitrogen isotope, total dissolved solids and PPCP index in Zone 3-1, Zone 3-2 and Zone 4.

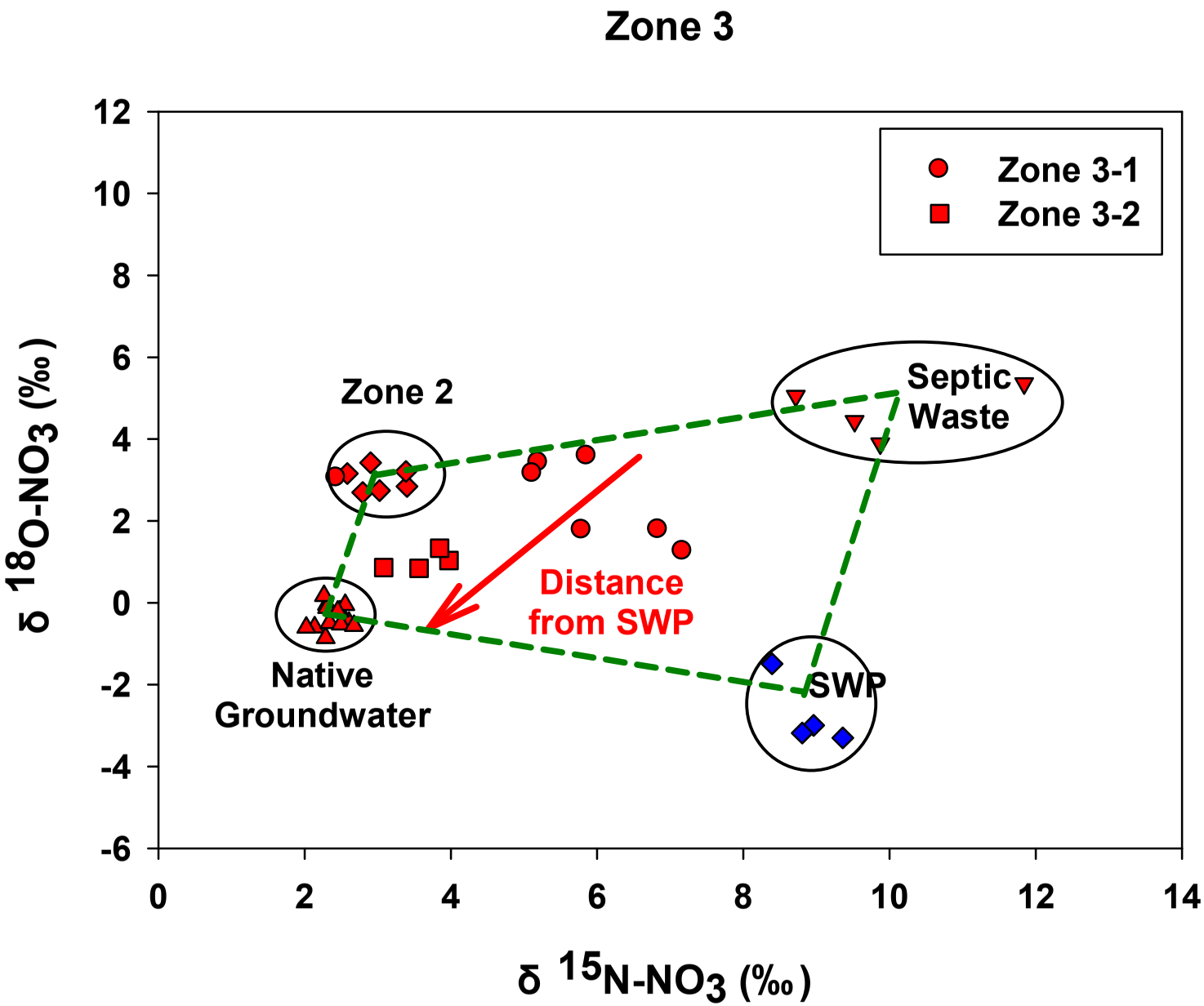

Figure 46. Relationship between $\delta^{15}N$ and $\delta^{18}O$ of nitrate in Zone 3. The septic waste endmember was estimated to be equal to WWTP #1 effluent measured in Zone 1. The green box denotes the 2-dimensional space defined by the four end members used in the isotope mixing analyses (Figures 47 and 48).

Zone 3-1

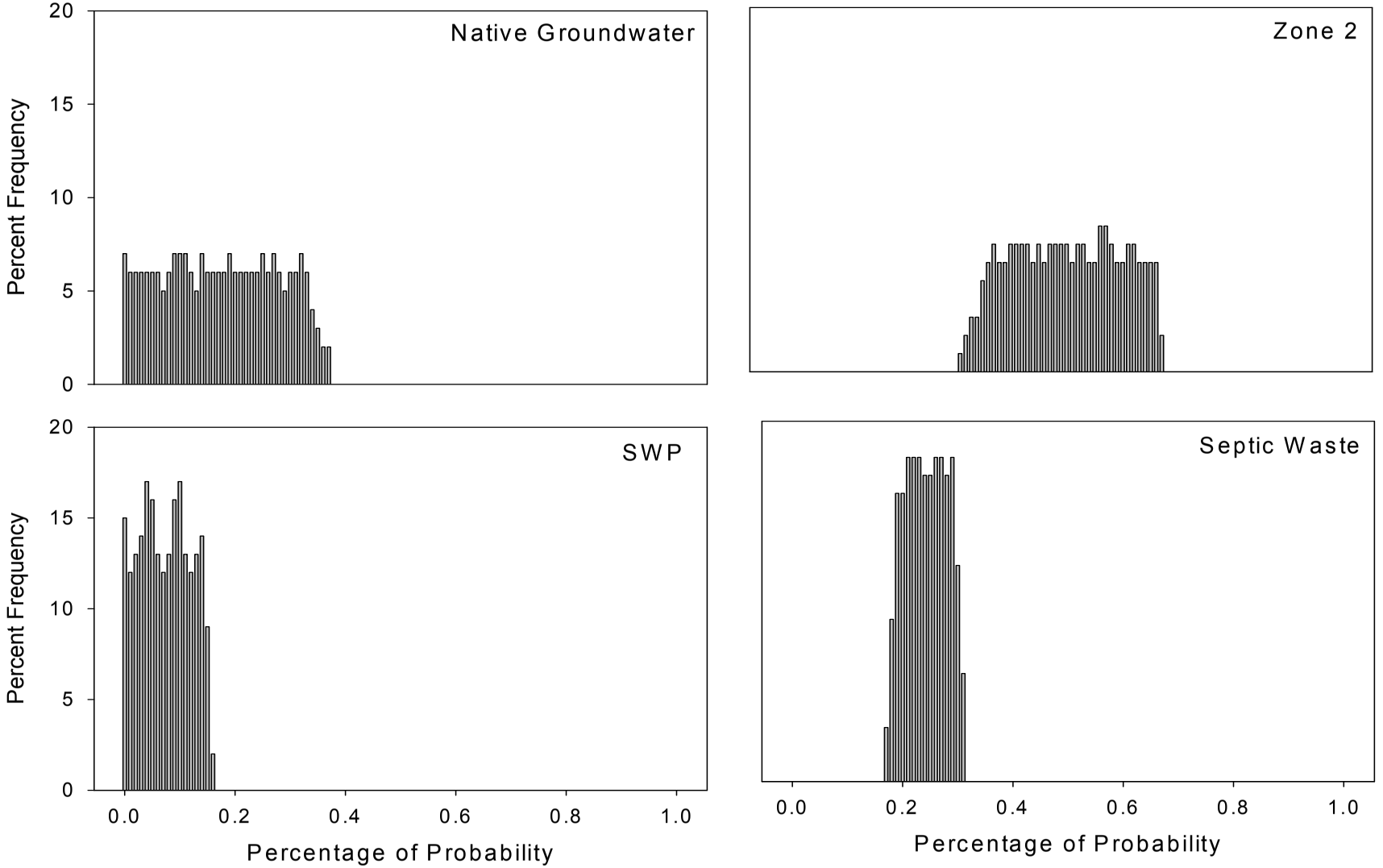

Figure 47. Nitrate contribution by different water sources in Central Cherry Valley, Zone 3-1: native groundwater; (estimated from Zone 4), mountain-front flow groundwater (estimated from Zone 2); SWP recharge; and septic waste (estimated to equal the isotopic composition of nitrate discharged from the City of Beaumont Wastewater Treatment Plant).

Zone 3-2

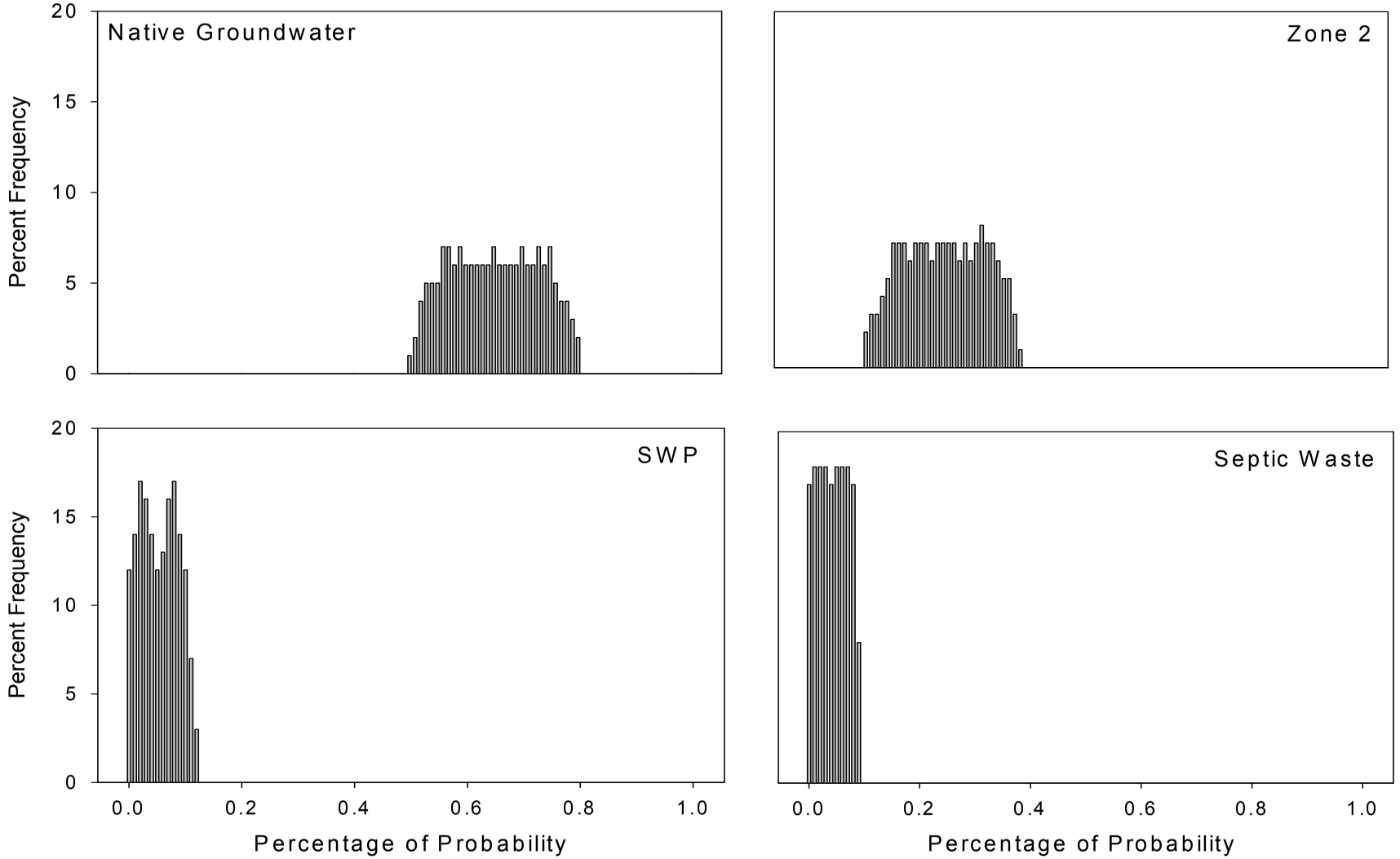

Figure 48. Nitrate contribution by different water sources in well peripheral to Cherry Valley, Zone 3-2: natural groundwater; (estimated from Zone 4), mountain-front flow groundwater (estimated from Zone 2); SWP recharge; and septic waste (estimated to equal the isotopic composition of nitrate discharged from the City of Beaumont Wastewater Treatment Plant).

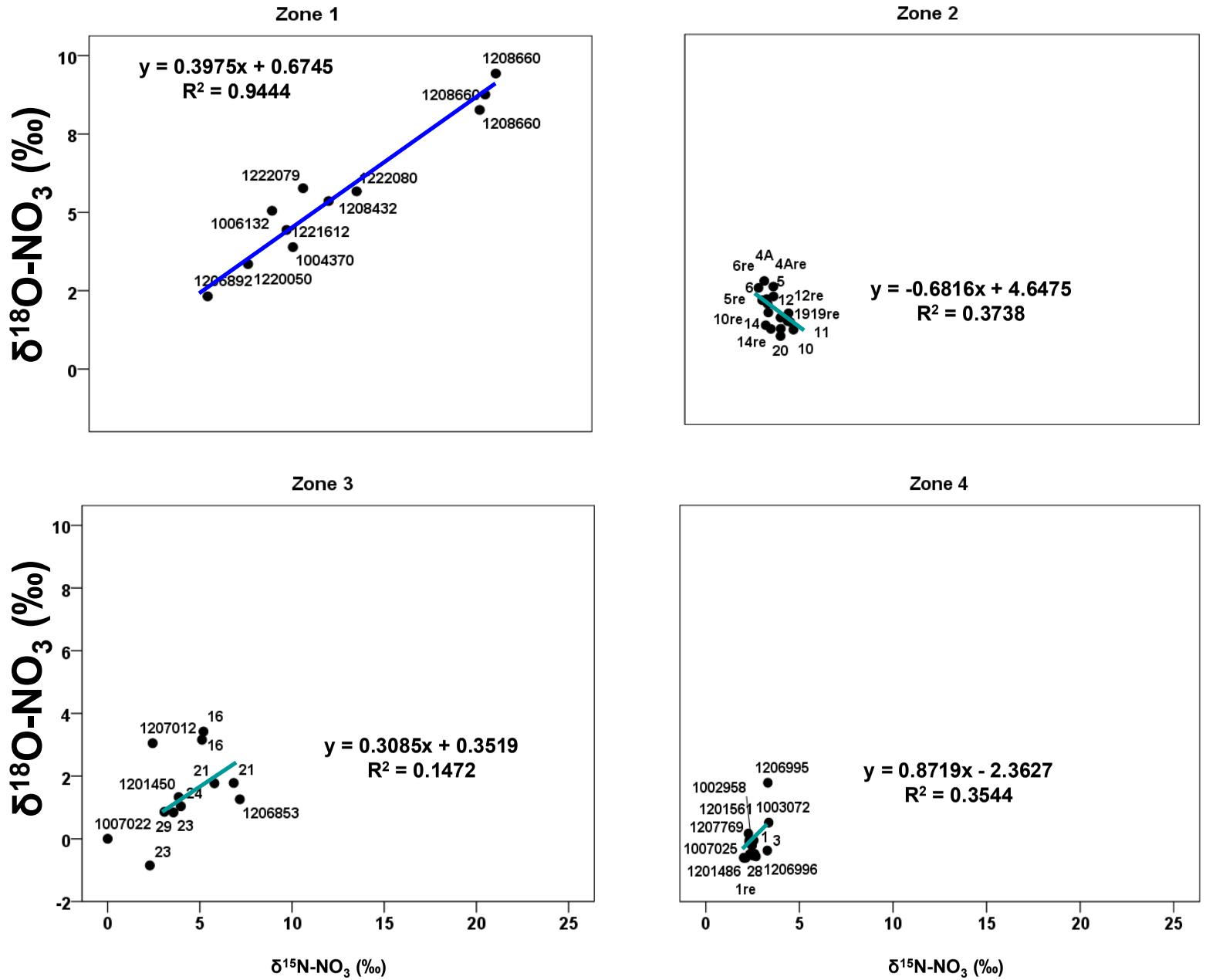

Figure 49. Summary of bi-plots of the isotopes of nitrate measured in groundwater zones within the BMZ. Labeled with sample ID.