Groundwater Quality Evaluation for the Gravel Trend and Battlement Mesa Areas

Garfield County, Colorado

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April 2011

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Table of Contents

Page

LIST OF FIGURES ii
LIST OF TABLES iii
LIST OF APPENDICES iii

1.0 INTRODUCTION 1
1.1. Objectives 1
1.2. Summary of Findings 2

2.0 DATA SOURCES 4

3.0 DATA ANALYSIS 5

4.0 GRAVEL TREND WATER QUALITY CONDITIONS 7
4.1. Groundwater Composition 7
4.2. Health and Drinking Water Standards 9
4.3. Effects of Natural Gas Drilling, Completion, and Production Operations 10
4.3.1. Sodium-Chloride in Groundwater and Produced Water 11
4.3.2. Total Dissolved Solids 12
4.3.3. Chloride 12
4.3.4. Methane 13
4.3.5. Volatile Organic Compounds (VOCs) 14
4.3.6. Dissolved Gases 15

5.0 GROUNDWATER QUALITY AT BATTLEMENT MESA 16

6.0 CONCLUSIONS 18

7.0 REFERENCES CITED 19

LIST OF FIGURES

1.1 Regional Site Location Map

2.1 Gravel Trend Sample Locations
2.2 Battlement Mesa Sample Locations

4.1 Map of TDS Concentrations in the Gravel Trend Area
4.2a Summary of Cation Concentrations in Groundwater in the Gravel Trend Area
4.2b Summary of Anion Concentrations in Groundwater in the Gravel Trend Area
4.3 Piper Diagram of Groundwater in the Gravel Trend Area North of the Colorado River
4.4 Map of Dominant Ions in Groundwater in the Gravel Trend Area
4.5a Groundwater Ion Concentration Relationships for Na/(Na+Cl) vs. TDS – Gravel Trend Area North of the Colorado River
4.5b Groundwater Ion Concentration Relationships Na vs. Cl – Gravel Trend Area North of the Colorado River
4.5c Groundwater Ion Concentration Relationships for Na vs. SO_4 – Gravel Trend Area North of the Colorado River
4.6 Map of Nitrate Concentrations in Groundwater in the Gravel Trend Area
4.7 Map of Methane Concentrations in Groundwater in the Gravel Trend Area
4.8 Groundwater Ion Concentration Relationships for Na/(Na+Cl) vs. TDS in Groundwater and Produced Water –Gravel Trend Area North of the Colorado River
4.9 Na vs. Cl in Groundwater and Produced Water in the Gravel Trend Area
4.10 Piper Diagram of Groundwater Compared to Produced Water in the Gravel Trend Area North of the Colorado River
4.11 Box-and-Whisker Plot Showing TDS Concentrations over Time in the Gravel Trend Area
4.12 TDS Concentrations vs. Distance from Well Pad (up to 1 mile) in the Gravel Trend Area
4.13 Map of Changes in TDS Concentrations between Pre-Drilling and Post-Fracturing Samples in the Gravel Trend Area
4.14 Percentage Changes in TDS Concentrations between Pre- Drilling and Post-Fracturing Samples in the Gravel Trend Area as a Function of Distance from Well Pad (up to 1 mile)
4.15 Box-and-Whisker Plot Showing Chloride Concentrations over Time in the Gravel Trend Area
4.16 Chloride Concentrations vs. Distance from Well Pad (up to 1 mile) in the Gravel Trend Area
4.17 Map of Changes in Chloride Concentrations between Pre- Drilling and Post-Fracturing Samples in the Gravel Trend Area
4.18 Percentage Changes in Chloride Concentrations between Pre- Drilling and Post-Fracturing Samples in the Gravel Trend Area as a Function of Distance from Well Pad (up to 1 mile)

4.19a Box-and-Whisker Plot Showing Methane Concentrations over Time in the Gravel Trend Area

4.19b Box-and-Whisker Plot Showing Methane Concentrations over Time in the Gravel Trend Area North of the Colorado River

4.20 Map of BTEX and MTBE Concentrations in Groundwater in the Gravel Trend

5.1 Piper Diagram of Groundwater and Produced Water in the Battlement Mesa Area

5.2 Map of Dominant Ions in Groundwater in the Battlement Mesa Area

LIST OF TABLES

3.1 Summary of Groundwater Quality Results for Gravel Trend Area for Regulated Drinking Water Constituents

3.2 Summary of Groundwater Quality Results for Battlement Mesa Area for Regulated Drinking Water Constituents

4.1 Summary of Dissolved Gases in Groundwater

LIST OF APPENDICES

A Evaluation of Specific Samples for Potential Impacts from Natural Gas Drilling, Completion, and Production Activities

1.0 INTRODUCTION

Antero Resources Corporation (Antero) has secured a leasehold position in the eastern portion of the Piceance Basin in Garfield County, Colorado, near the towns of Silt and Rifle (referred to herein as *Gravel Trend area*) and also in the central portion of the basin south of the town of Parachute (referred to herein as *Battlement Mesa area*) (Figure 1.1). Antero began natural gas drilling and production from Upper Cretaceous Mesaverde Group strata in the Gravel Trend area in August 2005 and in the Battlement Mesa area in September 2009. Antero currently operates from 42 well pads in the Gravel Trend area and operates from one well pad in the Battlement Mesa area.

Since 2005, Antero has conducted groundwater (and limited spring and surface water) sampling as a routine part of their activities in the vicinity of their well pads. Antero conducts baseline water quality analysis by sampling water wells within ½ mile of its well pad locations before commencement of drilling activities. Samples are analyzed for parameters recommended by the Colorado Oil and Gas Conservation Commission (COGCC) and for other industry-standard constituents. Antero does follow-up water quality sampling within the same ½-mile area after the last anticipated fracture stimulation/completion operation on a well pad. Antero also conducts discretionary sampling upon landowner request if the landowner has reasonable concerns about gas drilling, completion, and production operations in the vicinity of their property.

The majority of the groundwater quality sampling has occurred in the Gravel Trend area where Antero voluntarily began collecting pre-drilling samples in July 2005. Since that time, through December 2010, Antero has sampled 270 different locations in the Gravel Trend area, including many both before and after gas drilling, completion, and production activities. Antero began groundwater quality sampling in the vicinity of their one well pad at Battlement Mesa in July 2009 and since that time samples have been collected from 18 different water supply wells. Two of those wells were sampled again in 2010 following initial drilling, completion, and production activities.

1.1. Objectives

The objectives of this groundwater quality study were to evaluate the overall geochemical composition of groundwater, identify geochemical trends and potential human health concerns, and to determine whether or not Antero's natural gas drilling, completion, and production activities have impacted drinking water quality in the Gravel Trend and Battlement Mesa areas.

1.2. Summary of Findings

A summary of the findings from the evaluation of groundwater quality for the Gravel Trend and Battlement Mesa areas are presented below.

Gravel Trend Area

- The groundwater has naturally high concentrations of total dissolved solids (TDS). The origin of the TDS includes the dissolution of sulfate-rich evaporite minerals within the host aquifers. TDS and/or sulfate exceeded water quality standards published in 5 CCR 1002-41, the Colorado Basic Standards for Ground Water in over 95% of the groundwater samples evaluated.
- Concentrations of arsenic, lead, nitrate, selenium, uranium, chloride, iron, and/or manganese were present above standards in over 30% of the samples evaluated. Many of these elevated levels occur naturally; however, others, such as nitrate, indicate contamination from anthropogenic sources.
- TDS and chloride concentrations are elevated throughout the Gravel Trend area, but are naturally occurring and more closely associated with basin geography than natural gas drilling.
- Selected produced water data from Antero gas wells indicate that the water associated with the Mesaverde Group natural gas deposits is brackish with much higher TDS and chloride, and has distinctively different geochemical signatures than the water supply well and spring-sourced groundwater.
- Neither TDS nor chloride concentrations have increased systematically in concentration in the domestic supply groundwater with time. All increases observed in samples collected prior to drilling compared with those collected subsequent to hydraulic fracturing are attributable to processes not related to Antero natural gas drilling, completion, and production activities.
- Benzene, toluene, ethylbenzene, and xylenes (BTEX) and methane are rare in the groundwater.
  - BTEX concentrations include isolated detects of benzene (1 sample), toluene (3 samples), and xylenes (1 sample), all well below drinking water

standards and most from samples collected prior to natural gas drilling at the nearest Antero well pad.

- Where detected in wells north of the Colorado River, methane concentrations are orders of magnitude lower than COGCC recommended action levels and have not increased with time. There are higher levels of methane (above 1 mg/L) in six of the wells sampled south of the Colorado River, but in all cases methane was present prior to Antero's natural gas drilling, completion, and production activities.

Battlement Mesa Area

- Overall groundwater geochemistry characteristics are similar to the Gravel Trend area; however, trends are not as evolved and only 56% of the wells sampled exceeded the TDS and/or sulfate secondary water quality standards. The Battlement Mesa backup municipal wells located on the south bank of the Colorado River may represent a mixture of Wasatch groundwater and Colorado River water.
- Nitrate was the only compound present above primary drinking water standards; it exceeded the 10 mg/L standard in two wells.
- No BTEX or methane was detected in any of the groundwater samples collected in the vicinity of the Antero well pad.

Based on these results, it is concluded that natural gas production in the Gravel Trend and Battlement Mesa areas has not impacted groundwater quality in the water supply aquifers.

2.0 DATA SOURCES

The water quality data evaluated for this study were obtained from databases developed by the U.S. EPA, the United States Geological Survey (USGS), the COGCC, Antero, and the Battlement Mesa Metropolitan District. Groundwater and spring sample locations and the source of the data are shown in Figure 2.1 for the Gravel Trend area and in Figure 2.2 for the Battlement Mesa area. As shown below, the large majority of the data are from Antero and the COGCC.

Data Source	Pre-Drill Samples	Post-Drill/Pre-Fracture Samples	Post-Fracture Samples	Total Samples
Antero	169	72	86	327
COGCC	181	34	52	267
Other	11	1	2	14
Antero-BM	18	0	2	20
COGCC-BM	3	0	0	3
BM Metro District	4	1	0	5

Antero also provided selected produced water data from their natural gas wells in both the Gravel Trend and Battlement Mesa areas. The produced water analyses provide a comparison between the shallow fresh water aquifers and the deeper non-potable water that is associated with the natural gas-bearing strata.

The Gravel Trend data are from samples that were collected between 1991 and 2011, which is a period that predates and coincides with natural gas production in the area. Battlement Mesa sample results date back to 1977.

3.0 DATA ANALYSIS

Groundwater and spring data were evaluated to characterize its geochemical composition, identify potential human health concerns associated with its use as drinking water, and to determine whether or not there are indications that is has been affected by natural gas drilling, completion, and production activities.

Concentration distribution maps, box-and-whisker plots, ion ratio plots, and Piper diagrams were constructed to evaluate composition and trends. Data for these characterizations were censored first to eliminate replicate and duplicate samples and then to remove samples with charge-balance errors of greater than 10%[1]. For some assessments, samples were grouped based on (1) well depth and/or geologic source, (2) distance from the nearest well pad, or (3) timing relative to gas drilling, completion, and production activities.

Potential human health concerns were assessed by comparing constituent concentrations of uncensored data to the Colorado Basic Ground Water Standards (CBGWS) which are provided in 5 CCR 1002-41, and which are equivalent to Federal Maximum Contaminant Levels (MCLs) in most cases. The primary standards (Table A and Table 1 of 5 CCR 1002-41) are health-based standards that are enforceable by law. The secondary standards (Table 2 and Table 4 of 5 CCR 1002-41) are non-enforceable guidelines for constituents that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. For the case of methane in water, the COGCC recommended action level of 2 mg/L was used as the appropriate screening level. Gravel Trend water quality results are presented in Table 3.1 for the entire area and separately for north of the Colorado River as (1) a statistical summary of concentrations in the Gravel Trend, and (2) the percentage of samples exceeding CBGWS. Battlement Mesa water quality results are summarized in a similar manner in Table 3.2.

Evidence for impacts of natural gas production on groundwater quality in the Gravel Trend area was assessed by (1) comparing the chemical signatures of produced water and

[1] For the charge-balance error calculations and for the ion ratio plots and Piper diagrams, the reactive quantities of the ions measured in either milliequivalents or millimoles per liter (meq/L or mmol/L, respectively) were used rather than mass quantities (milligrams per liter, mg/L).

groundwater using the graphical techniques discussed above, and (2) evaluating changes in concentrations of TDS, chloride, and methane as functions of time and of distance from Antero's natural gas well pads.

4.0 GRAVEL TREND WATER QUALITY CONDITIONS

The groundwater quality evaluation for the Gravel Trend area considers data from sampling locations both north and south of the Colorado River (Figure 2.1). The primary source for groundwater in this area is the Tertiary Wasatch Formation, although in scattered locations (usually near the Colorado River or in upland valleys) relatively thick deposits of saturated Quaternary alluvial materials are also used for water supply. Scattered information regarding well depths was available. The deepest known depth of a sampled well was 440 feet; however, the majority of the wells where depths are known are less than 150 feet deep.

The overall geochemical characteristics of the groundwater in the Gravel Trend area and the presence of constituents that are potential health and aesthetic concerns are discussed; but the primary focus is on determining whether potential impacts have occurred due to Antero's natural gas drilling, completion, and production activities in this area.

4.1. Groundwater Composition

Figure 4.1 shows groundwater and spring TDS concentrations for all sampling locations in the Gravel Trend area relative to CBGWS and drilling well pad locations[2]. As shown in the figure, most groundwater in the study area exceeds the nominal 500 mg/L secondary standard for TDS, with concentrations typically ranging between 500 and 5,000 mg/L. The highest TDS concentrations (1,500 to 9,000 mg/L) occur both inside and outside of areas delineated on the Figure 4.1 as being located within ½ mile of an Antero well pad (dashed circles in the figure).

TDS is comprised of both dissolved cations and anions, and the relative contribution of various ions to TDS is compared in Figures 4.2a and 4.2b. Figure 4.2a shows that for cations, high sodium (Na) concentrations are most strongly correlated with high TDS. This result is consistent with the evolution of groundwater from Ca-Mg- to Na-dominated type either through mineral dissolution or ion exchange (SSPA, 2007). Sulfate (SO_4) is the dominant anion in

[2] Concentrations provided for all evaluations that are not distinguished by whether they are pre-drilling or post-fracturing are averaged. Unless specified, samples do not include produced water samples.

For TDS, a 500 mg/L standard is adopted to be consistent with the Federal Secondary MCL and to serve as an indicator for when cosmetic and/or taste and odor are likely to be issues for the water. The average background concentration for the domestic groundwater in the Gravel Trend area is obviously well above 500 mg/L.

samples with the highest TDS concentrations (Figure 4.2b). The contribution of each ion to the total ionic charge of the samples is illustrated in the Piper diagram[3] shown on Figure 4.3 for samples from north of the Colorado River. The cation base triangle exhibits a trend from calcium-magnesium (Ca-Mg) to sodium (Na) dominated water. The anion base triangle demonstrates that sulfate and bicarbonate (HCO_3) anions are more abundant than chloride (Cl) in all but one sample (which was collected prior to drilling).

The spatial variability in the predominant groundwater ions is shown in Figure 4.4. Samples dominated by Ca-Mg-HCO_3 ions (and lower TDS) are most abundant along the northern and northeastern border of the basin. This result is consistent with the presence of less-evolved groundwater near recharge sources along the northern border of the study area (SSPA, 2007).

Potential sources of groundwater ions are evaluated in Figures 4.5a through 4.5c, by comparing ion concentrations to expected trends from various sources. Figure 4.5a shows that most samples are similar in composition to groundwater that has interacted with an aquifer comprised of evaporite minerals (Herczeg and Edmunds, 2000). Although gypsum ($CaSO_4$) and halite (NaCl) are two of the most common evaporite minerals, Figure 4.5b shows that most of the Gravel Trend groundwater samples plot along a trendline that represents groundwater unrelated to either gypsum or halite, or to carbonate minerals (Chowdhury et al, 2010). Instead, as shown in Figure 4.5c, the samples generally lie along a 2:1 sodium-to-sulfate line, which is consistent

[3] A Piper diagram is a trilinear diagram consisting of two triangular plots and one diamond-shaped plot. Each of the triangular plots depicts either cation or anion data as milliequivalent percentages of the major ions typically found in groundwater. The closer a particular groundwater sample plots to one of the corners of a triangle, the greater the relative abundance of that respective ion in the groundwater sample. Data from the two triangular plots in the diagram are also projected onto the diamond-shaped plot in the figure, thereby providing an additional visual tool to compare geochemical variability between samples.

One important use of the Piper diagram is to compare the major ion chemistry of different groundwater samples. To the extent that these samples plot close to one another, they can be considered as "similar." Another use of a Piper diagram is to determine whether or not a groundwater sample represents a mixture of two or more separate groundwater samples (a mixture will plot on a straight line between end-member components; Hem 1985).

For this study, several changes were made to the layout of a standard Piper diagram. Potassium (K) was removed from the cation group because it constituted very little of the total cation balance. The chloride (Cl) and bicarbonate (HCO_3) axes of the anion base triangle were shifted from the standard layout to allow the differentiation between sulfate (SO_4) and chloride in the diamond portion of the piper diagram. Differentiation is important because the magnitudes of concentrations of these anions vary much more than those of HCO_3.

with the dissolution of the evaporite mineral thenardite (Na_2SO_4) (Mason and Miller 2004) as the groundwater moves on increasingly long flowpaths through the Wasatch Formation.

4.2. Health and Drinking Water Standards

The Gravel Trend groundwater and spring analytical results were screened for exceedances of primary and secondary CBGWS. A summary of the results is presented in Table 3.1 for all the results in the area and separately for those results from north of the Colorado River. The three compounds that most commonly exceeded primary CBGWS (as a percentage of samples analyzed) were nitrate, selenium, and uranium. Both selenium and uranium are present in natural groundwater in several areas of Colorado and their distribution in the Gravel Trend area likely is natural. A similar situation exists for arsenic, although it is present only infrequently above CBGWS in the Gravel Trend area. Of more importance is the relatively large number of wells with nitrates above the CBGWS of 10 mg/L, especially in the western portion of the Gravel Trend area where eight of the 16 sampled wells located within 3,000 feet of the Lundgren "A" well pad had nitrate concentrations that exceeded 10 mg/L in at least one sample (Figure 4.6). Nitrate is rarely found naturally in groundwater at elevated concentrations, and its concentrations in the Gravel Trend area strongly suggest anthropogenic impacts, either from septic systems, livestock wastes, and/or agricultural chemicals.

The water quality results for the five compounds with secondary CBGWS that are normally analyzed for are summarized in Table 3.1. All of the compounds were present above their respective secondary standard in at least 12% of the locations where they were sampled. Of this group of compounds, the one that least frequently exceeded the secondary standard was chloride. In contrast, sulfate exceeded its 250 mg/L standard in 63% of the samples, and TDS exceeded its 500 mg/L standard in 96% of the samples. Because high levels of TDS and sulfate are extremely widespread in Gravel Trend area, domestic groundwater may naturally feel unusual and have strong or unpleasant taste or odors.

Finally, although methane is not a regulated compound, the COGCC has established an informal 2 mg/L concentration in water at which well owners should begin periodic monitoring and/or mitigation efforts in order to prevent the build-up of explosive levels of the gas. As has

been shown in the evaluation of sample results using isotope analyses of methane in the Mamm Creek Field area (URS, 2006; SSPA, 2008), methane in drinking water wells can be from thermogenic sources (such as is produced in the Mesaverde Group natural gas wells), biogenic sources (such as the decay of plant matter in buried organic-rich alluvial sediments), or from a mix of the two. In all cases, the practical avoidance of the build-up of concentrations above 2 mg/L is important.

In the Gravel Trend area, methane was detected in seven of 363 samples from north of the Colorado River at concentrations above the historically-used reporting limit of 0.01 mg/L[4]. These concentrations (0.014 to 0.026 mg/L) are well below the 2.0 mg/L COGCC action guideline. Concentrations in all these samples are too low for practical analysis of carbon and hydrogen isotopes of methane that would allow possible identification of the source of the methane present.

South of the Colorado River in the Gravel Trend area, 19 of 198 groundwater samples analyzed for methane contained the compound above the historically-used reporting limit of 0.01 mg/L. The detections come from 12 different wells and range from 0.035 to 11 mg/L. Levels of methane above 1 mg/L occurred in six of the wells sampled south of the Colorado River, but in all cases methane was present prior to Antero's natural gas drilling, completion, and production activities. No carbon or hydrogen isotopes for methane in any of these groundwater samples were available for this study.

The distribution of methane in the groundwater samples for the Gravel Trend area is shown in Figure 4.7. The spatial and temporal relationship between the methane detections and the drilling at Antero's well pads is discussed in the next section.

4.3. Effects of Natural Gas Drilling, Completion, and Production Operations

The potential effects that Antero's natural gas drilling, completion, and production activities may have on water quality in the Wasatch Formation and alluvial aquifer in the Gravel

[4] The presence of low levels of methane (< 0.002 mg/L) in all of the samples collected for Antero in December 2010 and January 2011 is most likely the result of laboratory instrument background noise quantified because of detection and quantitation limits that were set at unusually low levels by the laboratory.

Trend area are evaluated below by reviewing concentrations and trends for specific compounds relative to the timing of and distance to these operations. Results are evaluated both on a geographic basis and on changes in concentrations in specific wells for samples collected prior to drilling and samples collected after fracture stimulations[5]. This evaluation examines in detail the distribution and changes for TDS, chloride, and methane in the groundwater in the Gravel Trend area.

4.3.1. Sodium-Chloride in Groundwater and Produced Water

Elevated levels of TDS, chloride, and methane in groundwater are presumed to be indicative of produced water associated with natural gas production (Thyne, 2008). For the Gravel Trend area, this hypothesis was tested by plotting TDS vs. Na/(Na+Cl) for the subset of the produced water samples obtained from Antero that were collected at least 6 months after the date of fracture stimulation operations for the gas well. Since most fracture stimulation fluid flowback is complete within a 6-month period (Antero Resources, personal communication, February 1, 2011), this restriction assures that the produced water samples will be representative of the actual formation waters associated with the gas producing strata. As shown in Figure 4.8, TDS concentrations in produced water are a factor of 10-100 times the concentrations of Gravel Trend area drinking water, which is consistent with this hypothesis.

Evidence that groundwater has not been impacted by produced water can be seen in Figure 4.9 by observing that very few groundwater samples lie along the 1:1 Na:Cl line of the produced water (which is representative of brackish near-marine water that dominated during the time of sediments of the Mesaverde Group). In Figure 4.9, the groundwater samples with the highest Na-Cl concentrations are samples that were collected prior to drilling at the nearest Antero well pads. Additional evidence is the lack of correlation between the major ion chemistry of the groundwater and produced water shown in the Piper diagram in Figure 4.10. This result

[5] To establish a standardized method to determine the cut-off dates for pre-drilling and post-fracturing sampling, each well was associated with the nearest Antero well pads. The earliest spud-date and earliest approximate fracture date was identified for each pad. A groundwater or spring sample was determined to be pre-drilling if it predated the earliest spud date and post-fracturing if it was collected after the earliest fracture date. Samples collected in the interim period were not used in pre-post analyses for a given sample location. This reduced the number of comparisons that could be made, but ensured that there was no ambiguity in the comparisons that were made.

suggests mixing between end-member components (water supply aquifers and produced water) is insignificant.

4.3.2. Total Dissolved Solids

TDS concentrations from Gravel Trend groundwater samples were assessed for a temporal trend, with the assumption that a higher concentration as a function of time potentially indicates natural gas production impacts. Figure 4.11 shows produced water and groundwater TDS data grouped by year on box-and-whisker plots. As expected, produced water TDS concentrations are significantly higher than from the drinking water aquifers. Also, the year-to-year difference in the median values in groundwater is smaller than the variability in the data, and the interquartile ranges for each year show no increasing trend with time. Further, TDS concentrations for all groundwater and spring samples collected in the Gravel Trend area do not increase with proximity to the well pads (Figure 4.12), with the linear trend-line fit to the data exhibiting no statistically significant trend (r^2 = 2x10-5; p = 0.945[6]).

Percentage changes in TDS concentrations in paired samples (pre-drilling and post-fracturing) in the Gravel Trend area are shown geographically on Figure 4.13 and as a function of the distance from the nearest Antero well pad on Figure 4.14. There are no systematic changes (indicative of impacts) evident in the data. In order to evaluate whether those instances where there were increases of greater than 50% in TDS, each was evaluated individually by considering the full set of parameters for the paired samples (see Appendix A). In no case did the effects of gas drilling, completion, and production activities appear to be the cause of the increases.

4.3.3. Chloride

As for TDS, chloride concentrations from Gravel Trend groundwater samples were assessed for a temporal trend, with the assumption that a higher concentration as a function of time potentially indicates natural gas drilling, completion, and production impacts. Figure 4.15

[6] The value of p provides an indication of whether the trend identified has statistical significance. At the 95% confidence level, any p-value less than or equal to 0.05 is considered to reject the assertion or hypothesis (known as the null hypothesis) that there is no statistical significance to the calculated trend; conversely, a value of p greater than 0.05 supports the assertion that there is no statistical significance to the calculated trend.

shows produced water and groundwater chloride data grouped by year on box-and-whisker plots. Similar to TDS, produced water chloride concentrations are significantly higher than water from the drinking water aquifers. Also, the year-to-year differences in the median values in groundwater are fairly constant until 2009 and 2010 when they drop significantly. Further, chloride concentrations for all groundwater and spring samples in the Gravel Trend area do not increase with proximity to the well pads (Figure 4.16) with the linear trend-line fitted to the data exhibiting no statistically significant trend ($r^2 = 0.0003$; $p = 0.747$).

Percentage changes in chloride concentrations in pre-drilling and post-fracturing paired samples from both north and south of the Colorado River are presented geographically on Figure 4.17 and as a function of the distance from the nearest Antero well pad on Figure 4.18. While there are more sample pairs with greater than 50% increases in chloride concentrations than for TDS, there are no systematic changes (indicative of impacts) evident in the data. As for TDS, the specific instances where there were increases of greater than 50% in chloride were evaluated individually and there were no incidences found that suggested impacts due to gas drilling or production activities (see Appendix A).

4.3.4. Methane

Methane occurrence in groundwater can be a good early indicator of impacts from oil and gas drilling, completion, and production activities due to the fact that methane will migrate rapidly through existing pathways from deep high pressure reservoirs to shallow low pressure environments. Whether originally present as a gas or exsolved from produced water, methane as a free-phase gas can travel easily and increase in concentration quickly in shallow fresh water aquifers. However, since biogenic methane that has no relation to methane from deep natural gas deposits can also occur in aquifers, it is important that its presence be evaluated carefully so that its source is not misinterpreted.

Dissolved methane concentrations presented on a temporal basis are shown in the box-and-whisker plot on Figure 4.19a for the Gravel Trend area and in Figure 4.19b for the area north of the Colorado River. There is no temporal trend of increasing methane concentrations in groundwater in the Gravel Trend area. As shown in Figure 4.19b, the presence of methane north

of the Colorado River is so sparse that increasing concentrations of methane in drinking water aquifers in future sampling should be easily identified.

The location and concentrations of methane in groundwater samples in the Gravel Trend area are shown on the map on Figure 4.7. Methane occurs at very low levels above 0.01 mg/L at only five locations north of the Colorado River, at four locations it was present prior to drilling and at the fifth location it was present at a concentration of 0.016 mg/L at a well near the Colorado River and almost 3,500 feet from the nearest Antero well pad. South of the Colorado River, methane occurred at 12 locations at concentrations above 0.01 mg/L. There is no indication that any of the occurrences are related to activities at Antero well pads:

- Except for three samples with no pre-fracture stimulation operation results, all detections of methane occurred in pre-drilling samples or at locations where pre-drilling samples contained methane.
- For the three locations where samples were collected only after fracture stimulation operations had taken place, one was greater than 1 mile from the nearest Antero well pad and the other two were more than ½ mile from the nearest well pad and had very low methane concentrations (0.035 and 0.35 mg/L).

There are four locations that have methane concentrations above the COGCC recommended action level of 2 mg/L and all contained elevated concentrations prior to drilling at the adjacent Antero well pads. All of the wells with the elevated methane concentrations are located in valleys adjacent to perennial streams (from west to east, Mamm Creek, Dry Hollow Creek, and Divide Creek). Dissolved gas compositional and isotopic analyses were not available for this study, but such analyses would be valuable in evaluating the source of methane in these wells.

4.3.5. Volatile Organic Compounds (VOCs)

The presence of volatile organic compounds (VOCs) in groundwater potentially indicates the influence of anthropogenic activities on groundwater. In the case of natural gas production, BTEX compounds may occur in the produced fluids from the oil- or gas-bearing intervals being produced or they may be contained in some of the fluids that have historically been used in some areas as an additive to fracture stimulation fluids or drilling muds. As shown in Figure 4.20, BTEX compounds were detected in only five widely spaced samples in the Gravel Trend area at

concentrations well below CBGWS. The sources of the VOCs cannot be determined based on these results, but they do not appear to be related to natural gas drilling, completion, and production activities.

4.3.6. Dissolved Gases

Water or headspace gas samples were collected for chromatographic gas composition and stable isotopes from several locations north of the Colorado River in 2006 (SSPA 2007). A summary of these results is presented in Table 4.1. Although methane was detected at low concentrations (maximum of 0.04%) in five samples, the only two samples collected from wells closer than one mile to the nearest Antero well pad were collected prior to drilling. None of the samples contained sufficient methane to warrant methane isotopic analyses.

Stable isotopes of carbon in carbon dioxide (CO_2) were also measured for the samples in which gas composition was analyzed (SSPA, 2007). Oxidation of methane is not suggested by the $\delta^{13}C$ values of any of the samples. This result is consistent with the general absence of dissolved methane in the sampled wells.

5.0 GROUNDWATER QUALITY AT BATTLEMENT MESA

The location of Battlement Mesa groundwater samples are shown in Figure 2.2. The preponderance of the samples are pre-drilling samples, one of which is from 1977 and four from 1980-81 from the four backup water supply wells maintained by the Battlement Mesa Metropolitan District. Most of the samples were collected in 2009 by Antero prior to drilling at the Watson Ranch Well pad. Two samples, both collected by Antero's third party contractor, were collected in 2010 subsequent to fracture stimulation operations at the Watson Ranch well pad. In addition to drinking water aquifer samples, three produced water samples were available for this study, two of which are from wells on the Watson Ranch well pad.

The major ion compositions for the groundwater samples from the Battlement Mesa area are plotted on the Piper diagram of Figure 5.1 and the spatial distribution of the groundwater types is shown on Figure 5.2. The three produced water samples from the area are also plotted on the Piper diagram. The relative concentrations of the dominant ions show that the water in the Battlement Mesa overall is not as evolved as in the Gravel Trend area (Figure 4.3). At Battlement Mesa, the predominant water types are sodium-magnesium-bicarbonate (Na-Mg-HCO_3) and sodium-bicarbonate (Na-HCO_3), especially in the water with lower levels of TDS. As TDS increases, the water from the sampled wells has increasing dominance of sulfate; at all six locations with TDS greater than 1,000 mg/L, sulfate is the dominant anion.

The lower TDS, sodium, and sulfate concentrations that are characteristic of the Battlement Mesa groundwater are likely the result of shorter subsurface flowpaths in alluvial deposits and/or the Wasatch Formation than is the case for much of the Gravel Trend area. The four Battlement Mesa backup municipal wells, which are located adjacent to the south bank of the Colorado River, are completed in Quaternary alluvial deposits that are in direct communication with the river. These wells have intermediate TDS concentrations and are slightly enriched in calcium and chloride compared to the wells completed further from the river on Battlement Mesa and they probably represent a mixture of Wasatch groundwater and Colorado River water. As would be expected, the domestic groundwater is distinctly different than the produced water.

The primary differences between the water quality in the Battlement Mesa and the Gravel Trend Areas are that (1) there is a lower abundance of TDS in the former (median values of 570 mg/L versus 1,200 mg/L, respectively), and (2) exceedances of drinking water standards are less frequent (Table 3.2). Based on 27 groundwater samples, the only compound exceeding a health-based primary CBGWS was nitrate, which was above 10 mg/L in two samples. For secondary CBGWS, TDS exceeded 500 mg/L in 56% of the samples in the Battlement Mesa area as opposed to more than 95% of the samples in the Gravel Trend area, and the chloride standard of 250 mg/L was not exceeded in any of the Battlement Mesa samples. No BTEX or methane were detected in any of the samples in the Battlement Mesa area.

In the Watson-1 well which was sampled both prior to drilling and after fracture stimulation operations, there were significant increases in the concentrations of manganese and iron (manganese increased from non-detection at a level of 0.010 mg/L to 0.082 mg/L and iron increased by a factor of almost 14 from 0.25 mg/L to 3.5 mg/L). Turbidity, measured in the field during sample collection, was also approximately 30 times higher in the second sample compared to the first. All other constituents increased by no more than a factor of two and many were similar or decreased between the first and second samples. The Watson-1 well is located in an empty field and has low-carbon steel casing, a broken well cap, and no pump; the depth to water in the well is approximately 120 feet. Both times the well was sampled, the sample was collected from a bailer and the well was not purged. Iron and manganese are components of low carbon steel and it is likely that during the second sample event that rust particles from the well casing were entrained in the bailer during sampling. Since the samples were not filtered in the field or the lab prior to sampling, these materials would have ended up being measured during analysis.

The groundwater quality results collected from wells in the vicinity of the Watson Ranch well pad provide a robust baseline dataset for the area and will be useful in the future for evaluating the potential effects from natural gas drilling, completion, and production activities.

6.0 CONCLUSIONS

Results of the present investigation are similar to the baseline water quality study presented in SSPA (2007). Groundwater in the Gravel Trend area has a naturally-high concentration of TDS. These concentrations are similar to 2006 levels, despite increased natural gas drilling, completion and production operations in the area. Chloride and methane concentrations have not increased over time, as might be expected if impacts had occurred. Finally, baseline water quality of the aquifer is impaired for several human health and aesthetic effects in Gravel Trend, and given the natural origin of the drinking water contaminants, conditions are unlikely to improve.

The Battlement Mesa groundwater quality dataset collected from Antero sampling in the vicinity of the Antero Watson Ranch drill pad does not contain any indication of impacts from natural gas drilling, completion, and production activities and it provides a good baseline that will allow potential effects of future activities at the well pad to be evaluated.

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Figures

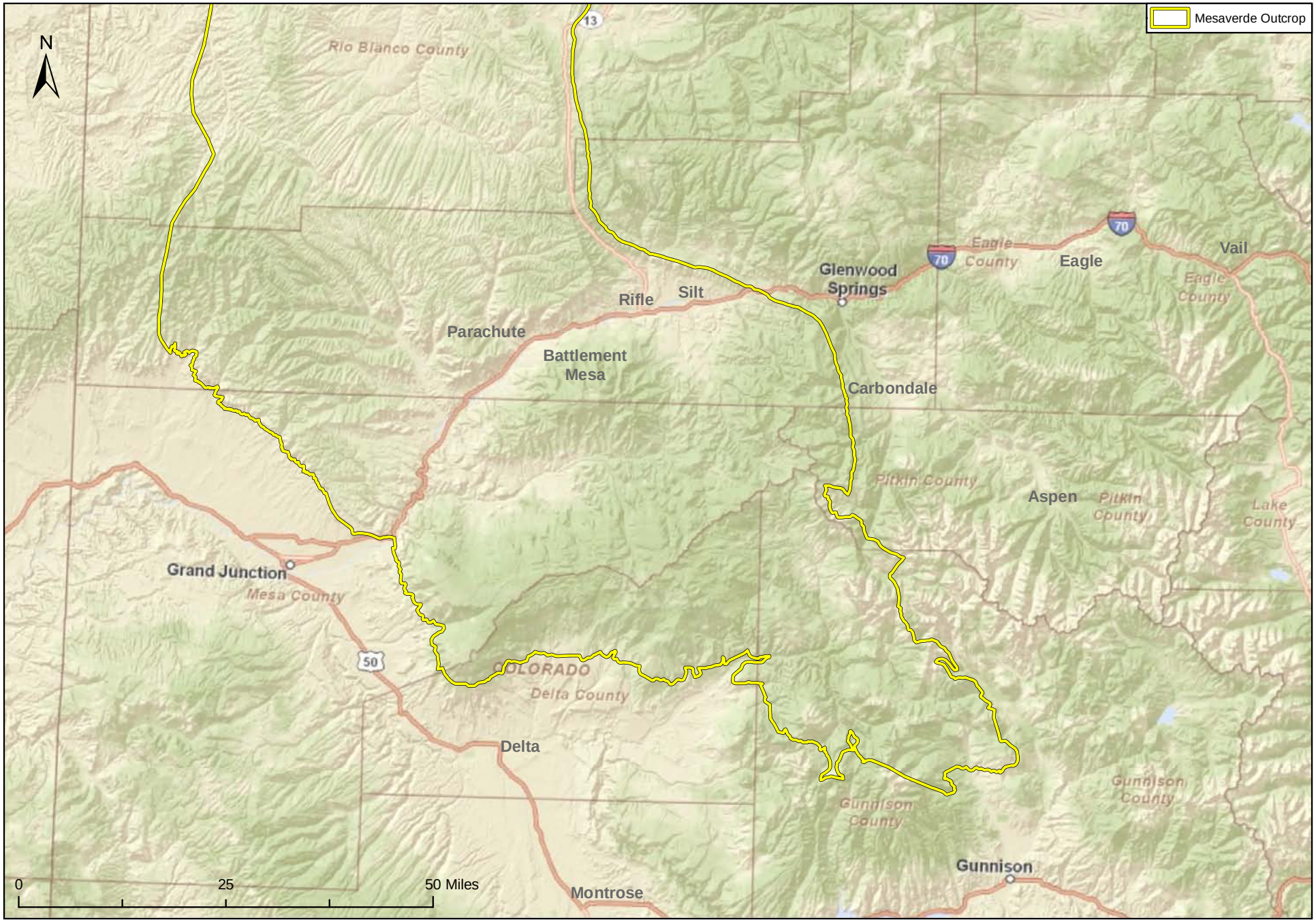

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Figure 1.1 Regional Site Location Map

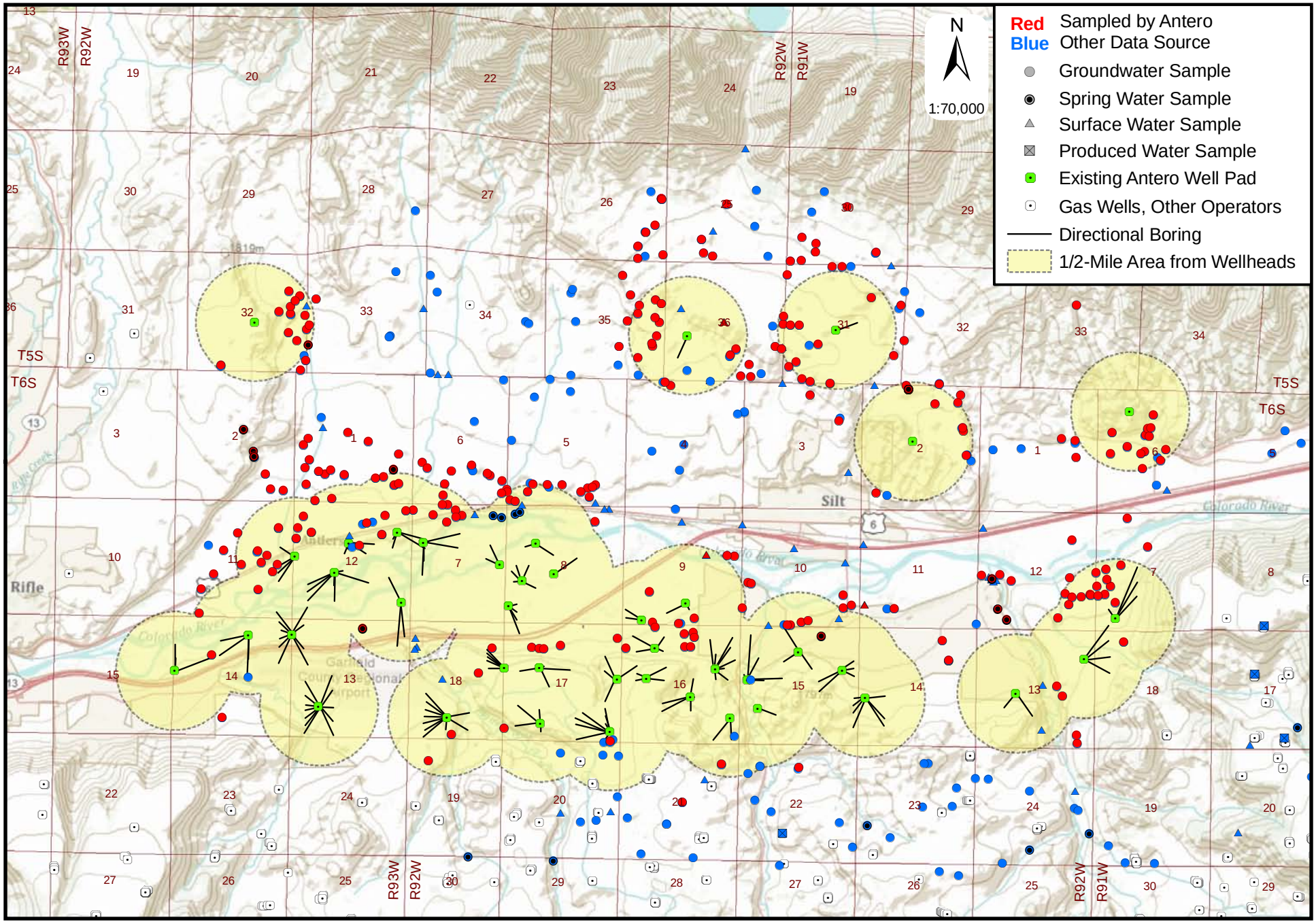

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Figure 2.1 Gravel Trend Sample Locations

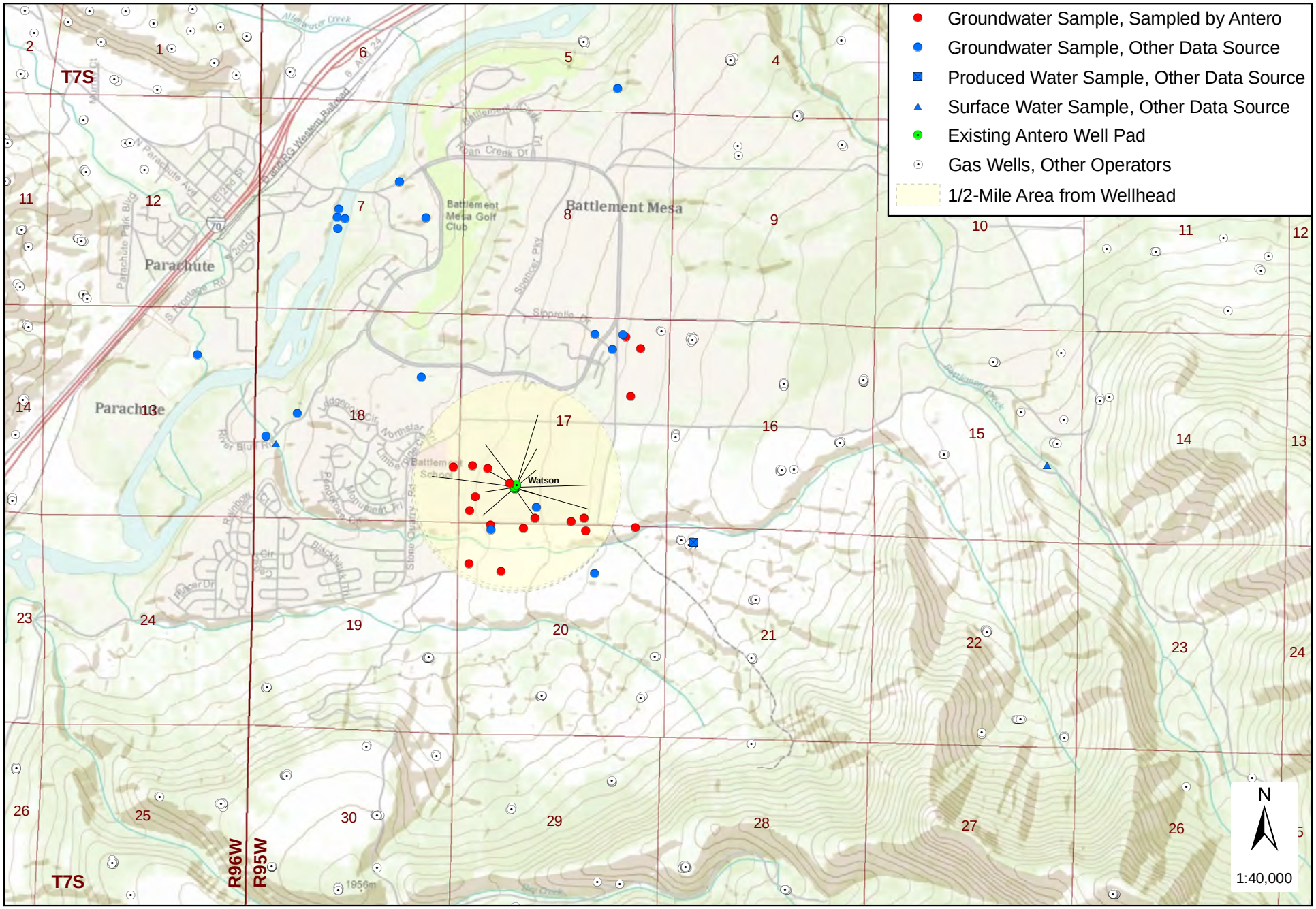

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Figure 2.2 Battlement Mesa Sample Locations

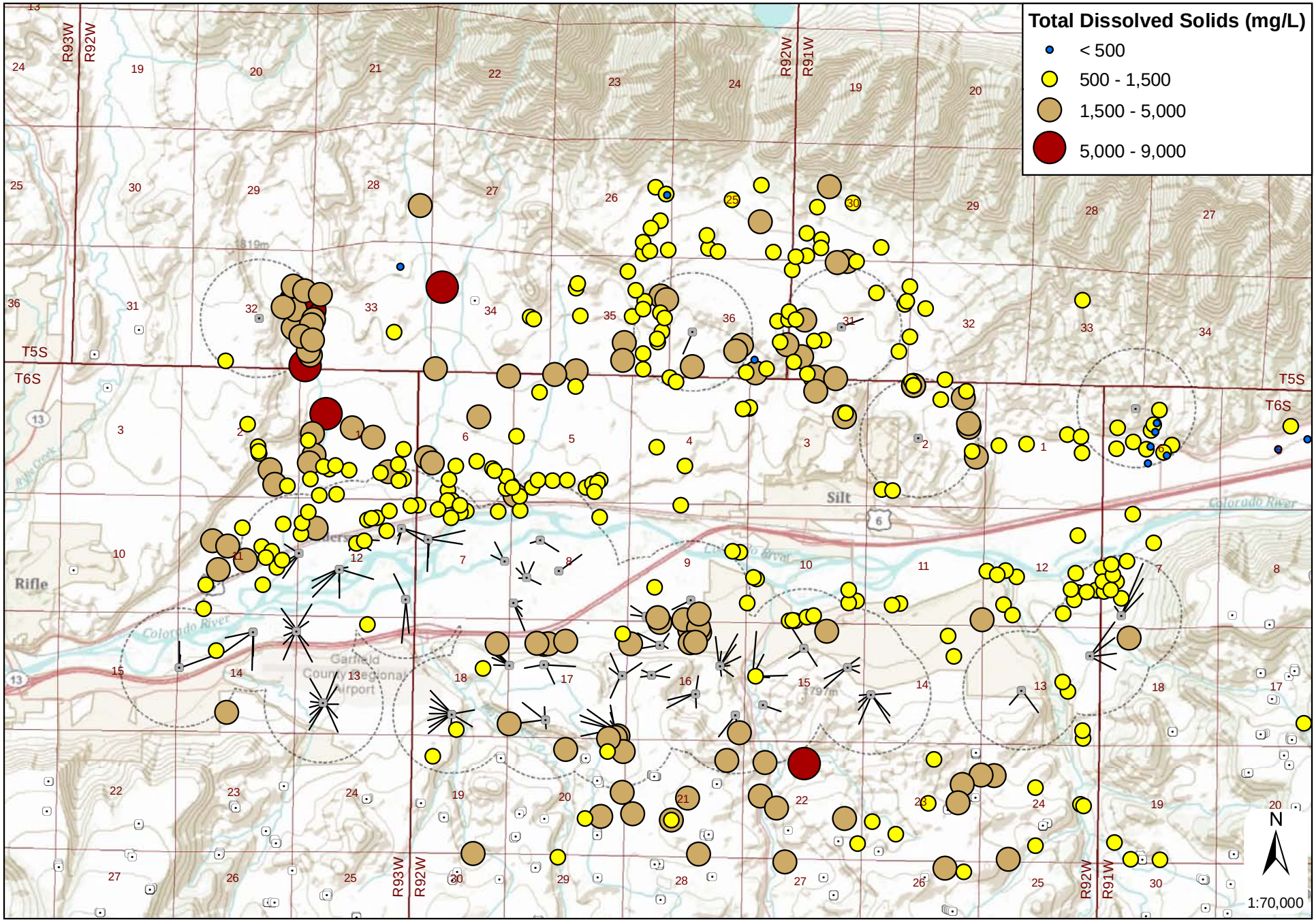

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Figure 4.1 Map of TDS Concentrations in the Gravel Trend Area

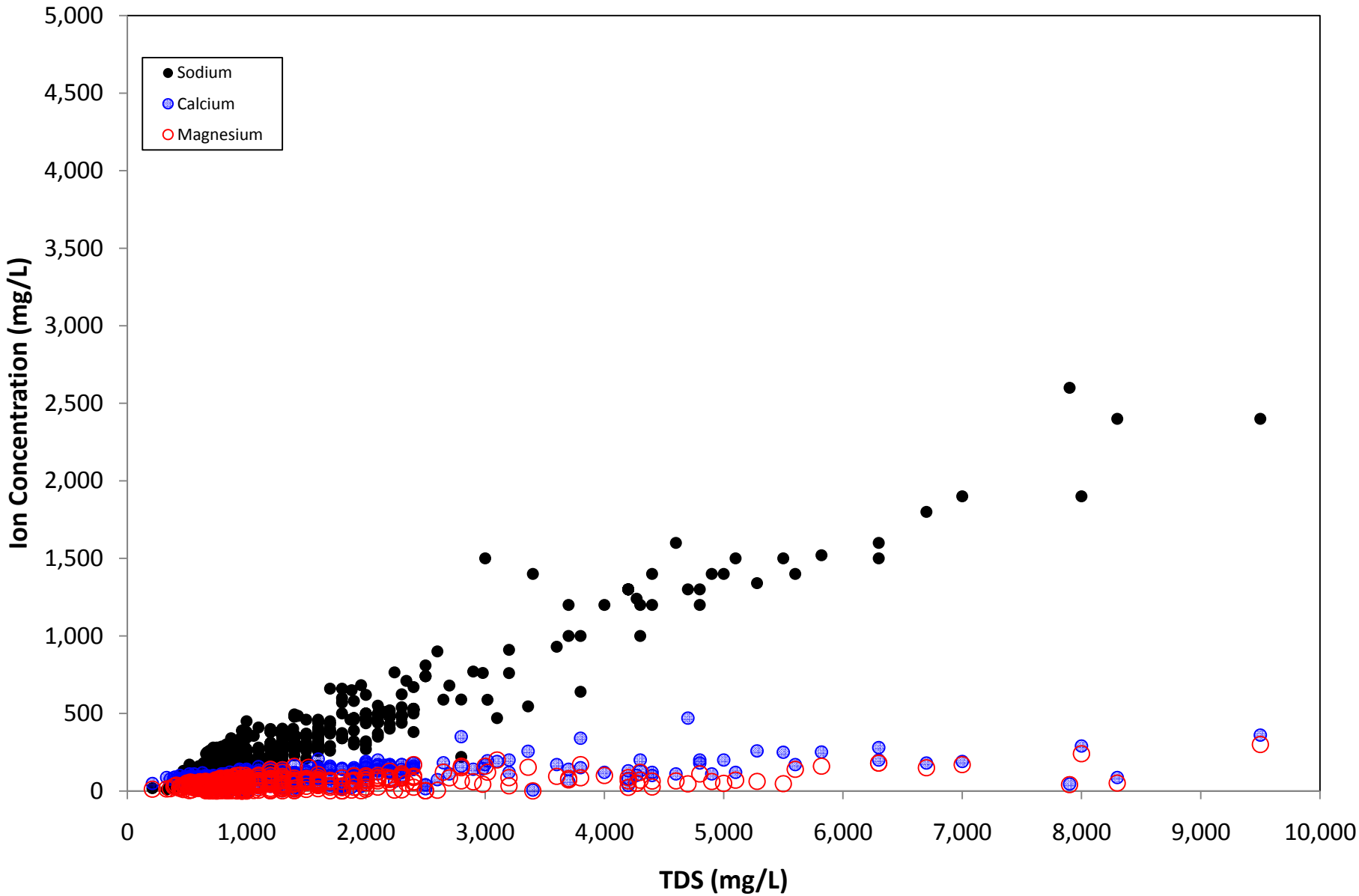

Figure 4.2a Summary of Cation Concentrations in Groundwater in the Gravel Trend Area

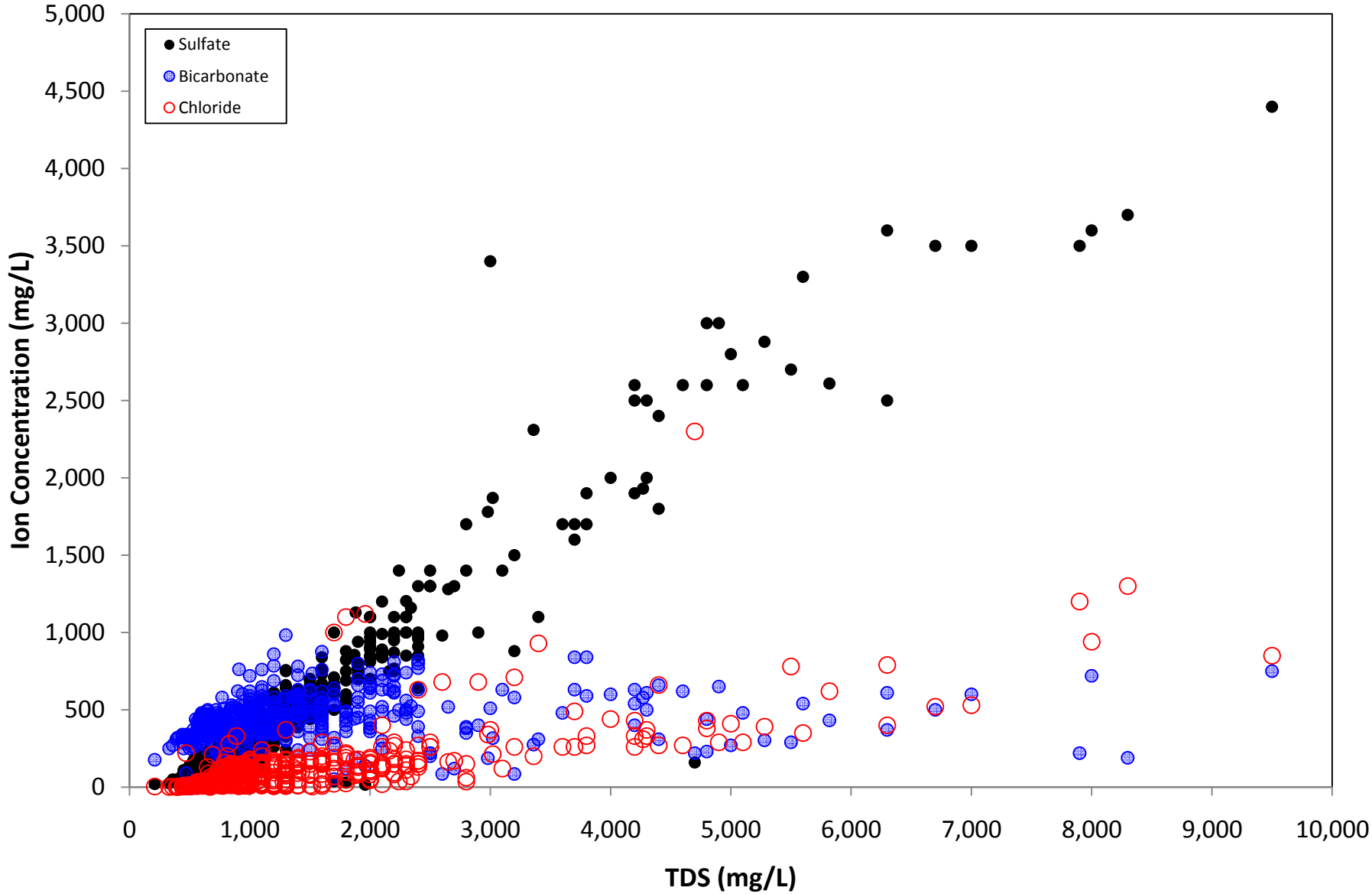

Figure 4.2b Summary of Anion Concentrations in Groundwater in Gravel Trend Area

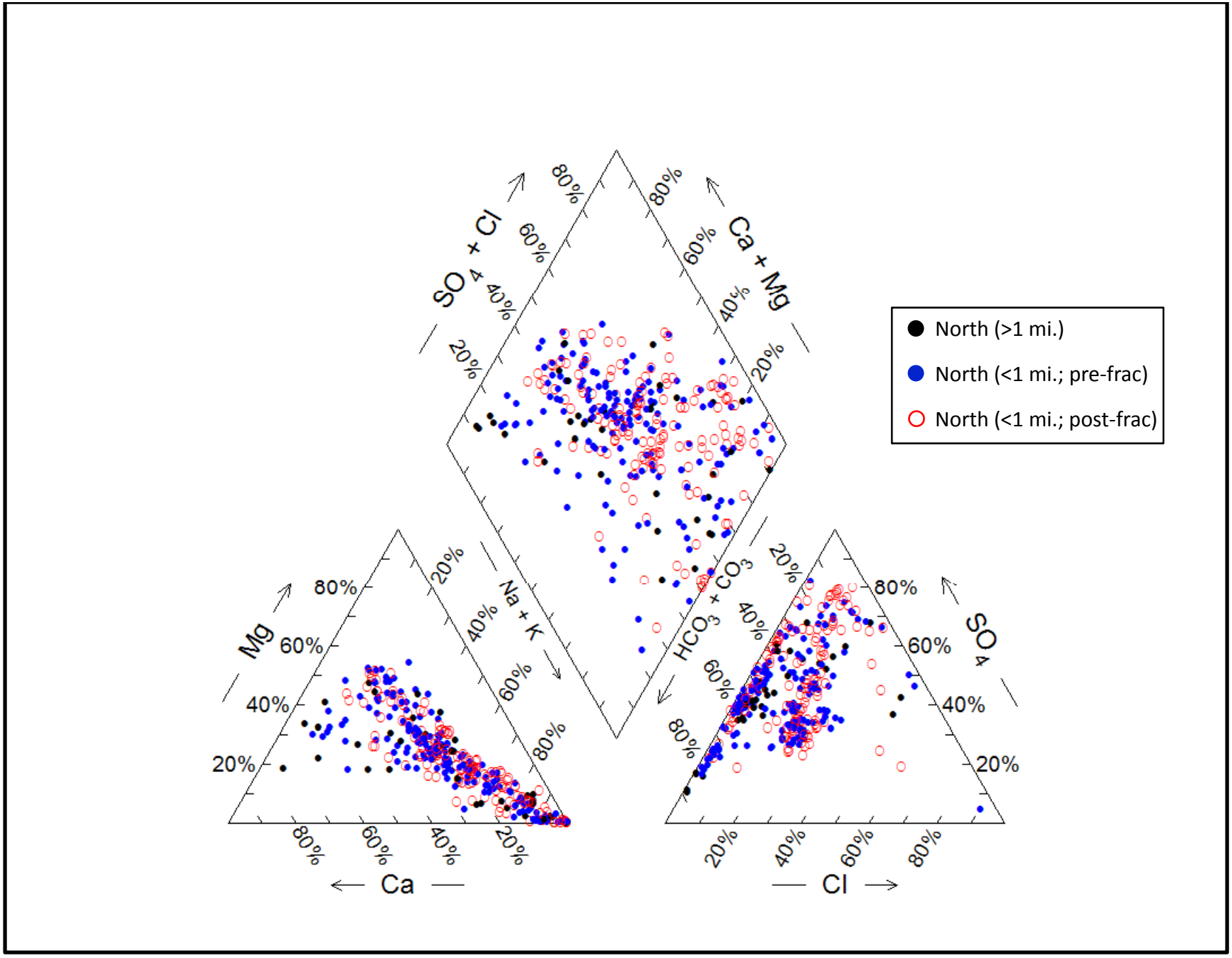

Figure 4.3 Piper Diagram of Groundwater in the Gravel Trend Area North of the Colorado River

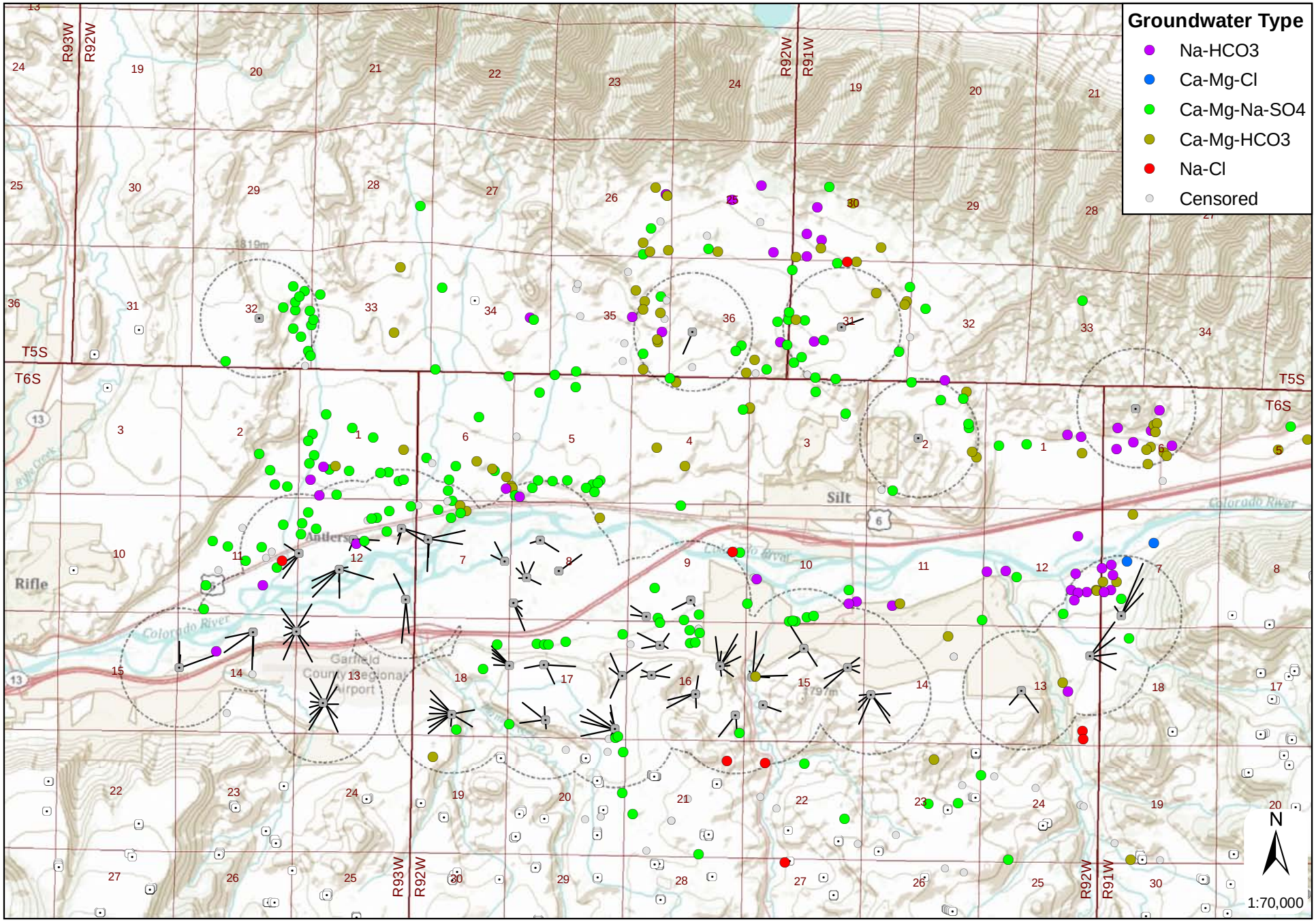

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Figure 4.4 Map of Dominant Ions in Groundwater in the Gravel Trend Area

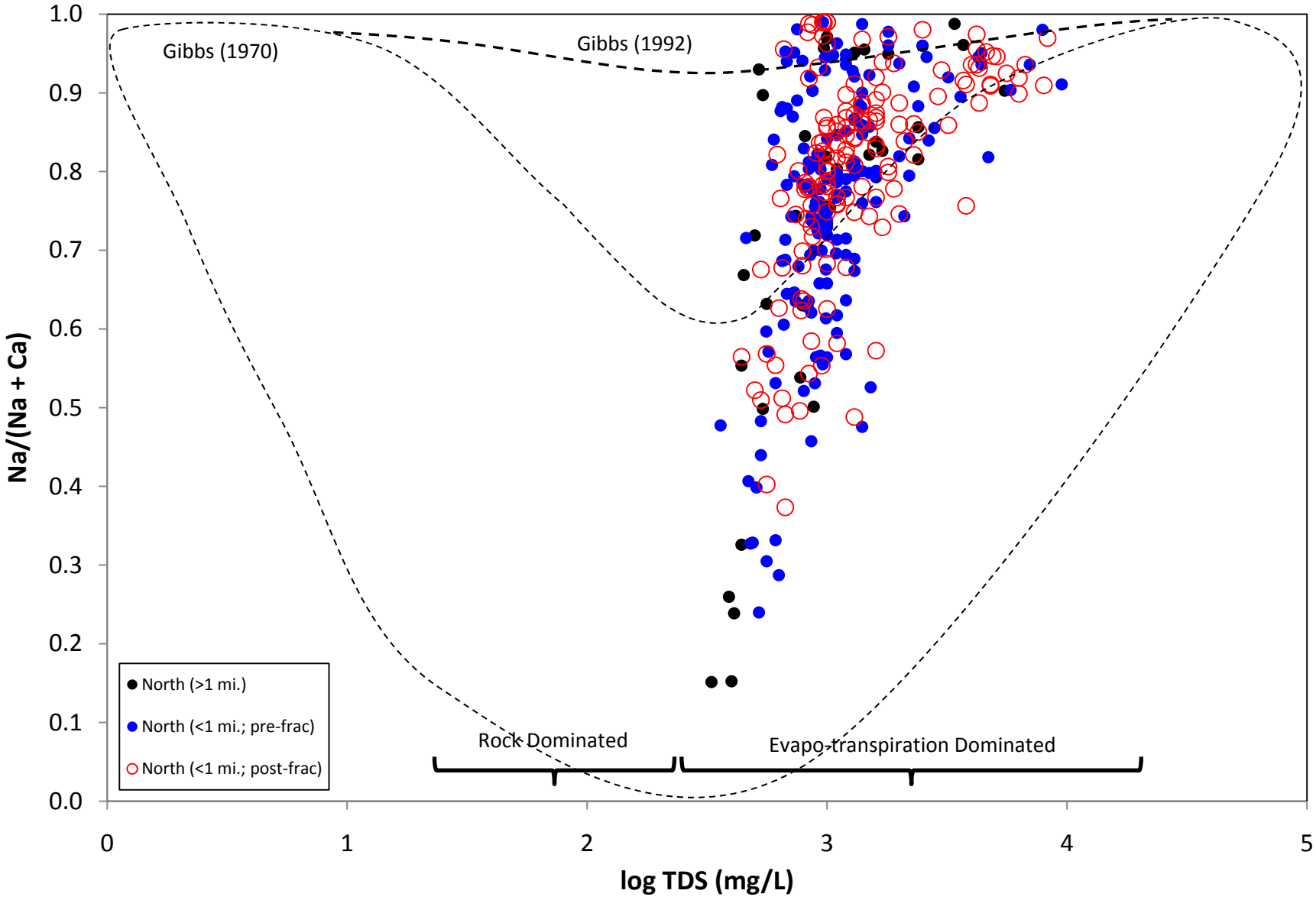

Figure 4.5a Groundwater Ion Concentration Relationships for Na/(Na+Ca) vs. TDS - Gravel Trend North of Colorado River

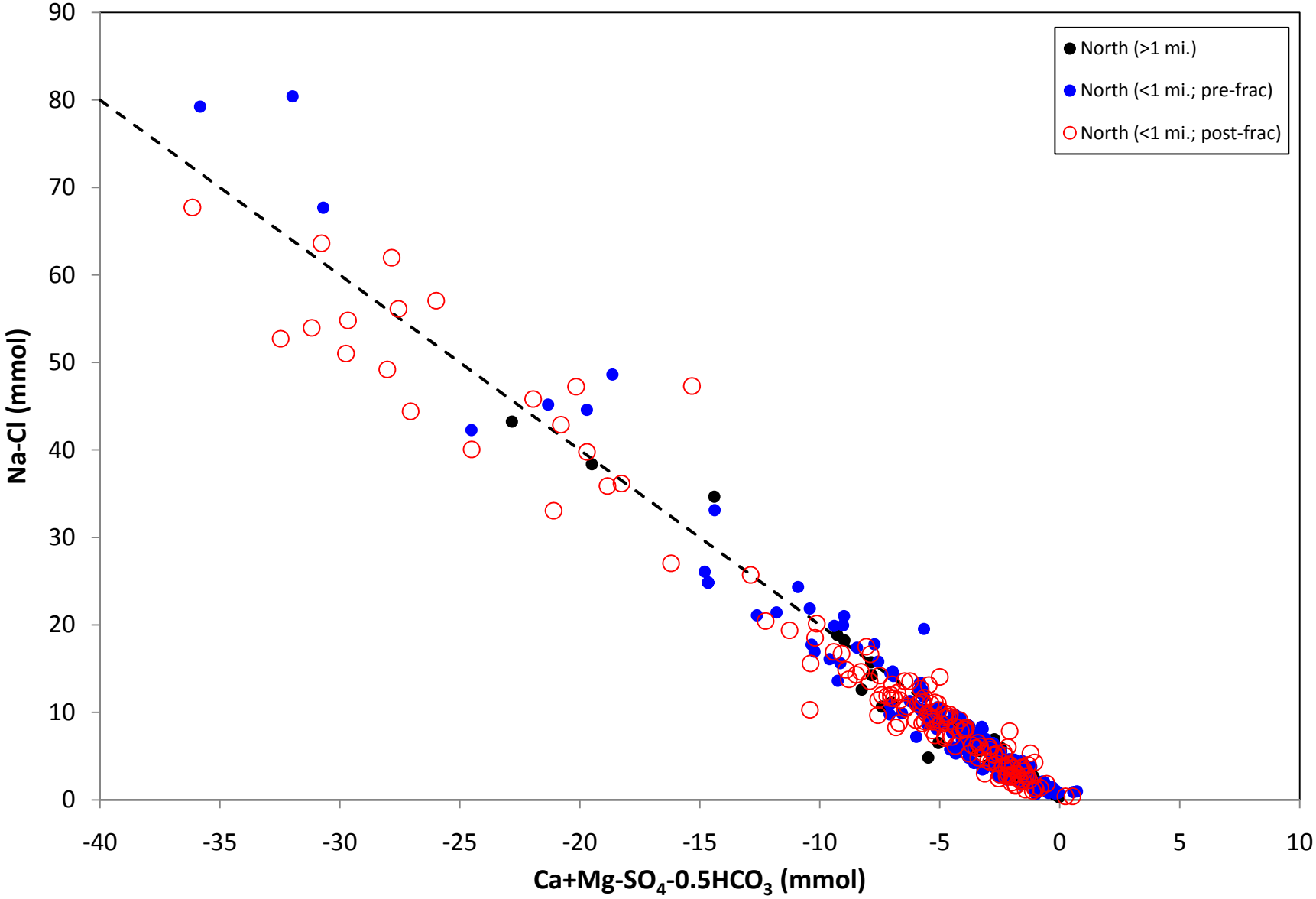

Figure 4.5b Groundwater Ion Concentration Relationships for Na vs. Cl - Gravel Trend North of Colorado River

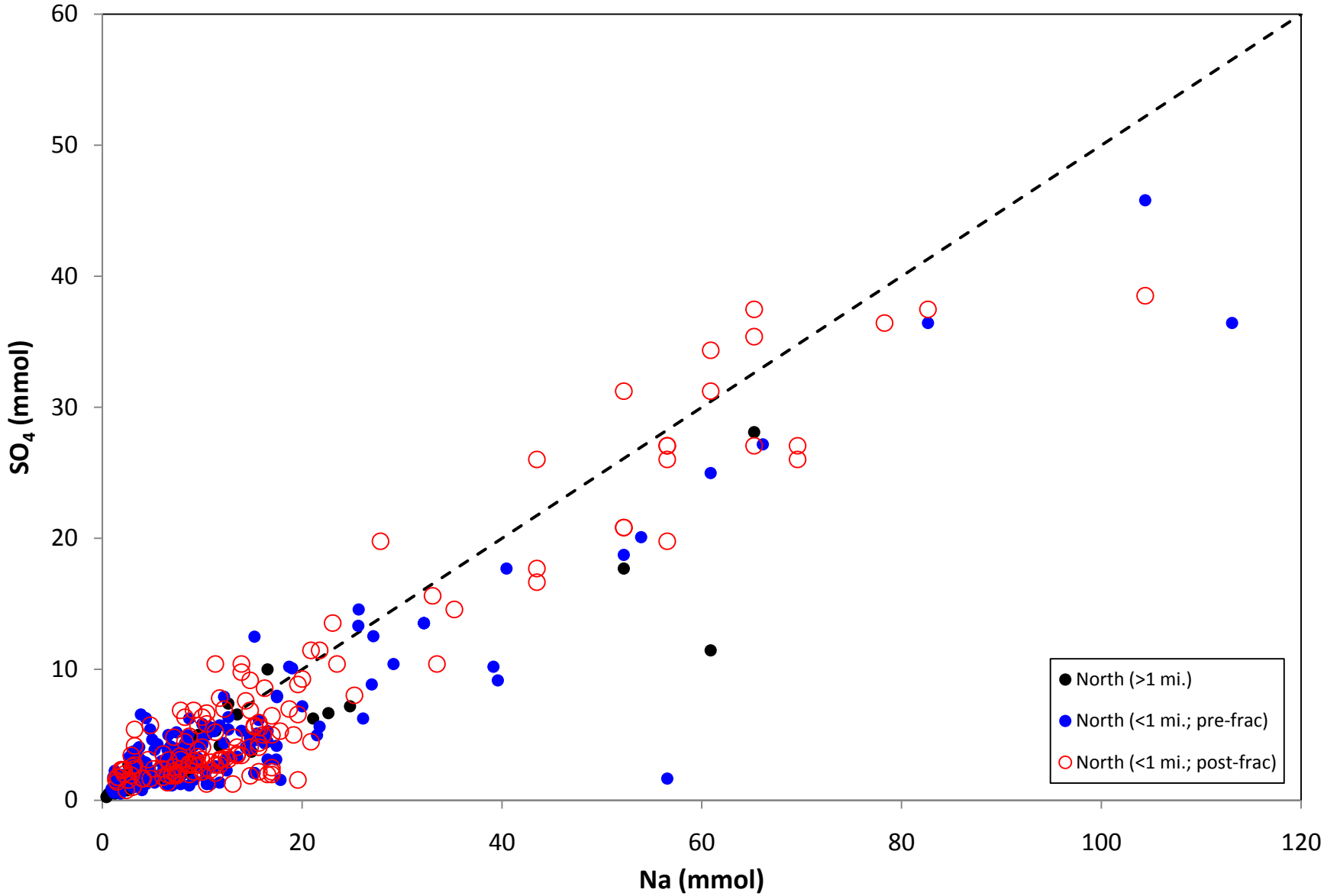

Figure 4.5c Groundwater Ion Concentration Relationships for Na vs. SO_4 - Gravel Trend North of Colorado River

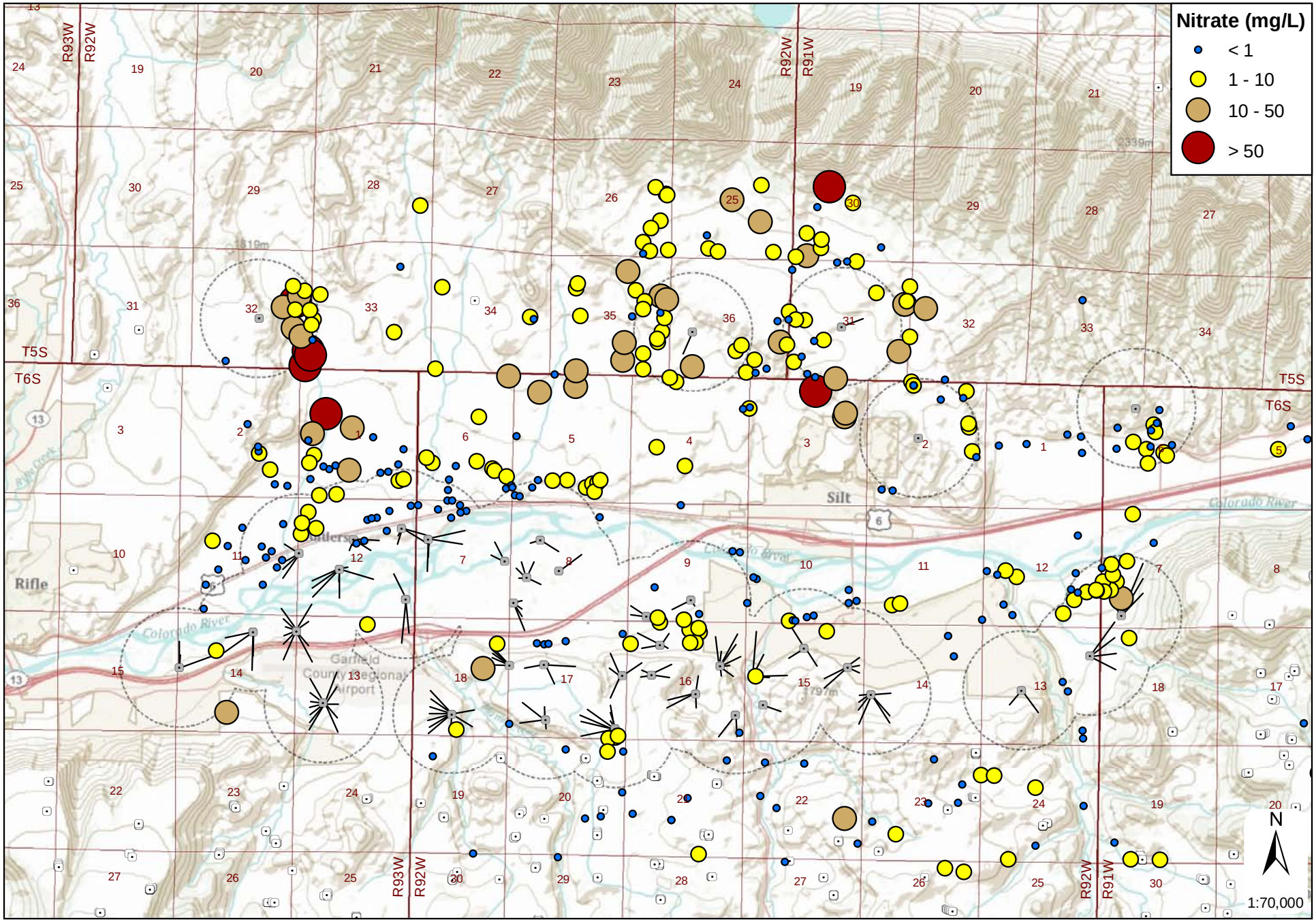

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Figure 4.6 Map of Nitrate Concentrations in Groundwater in the Gravel Trend Area

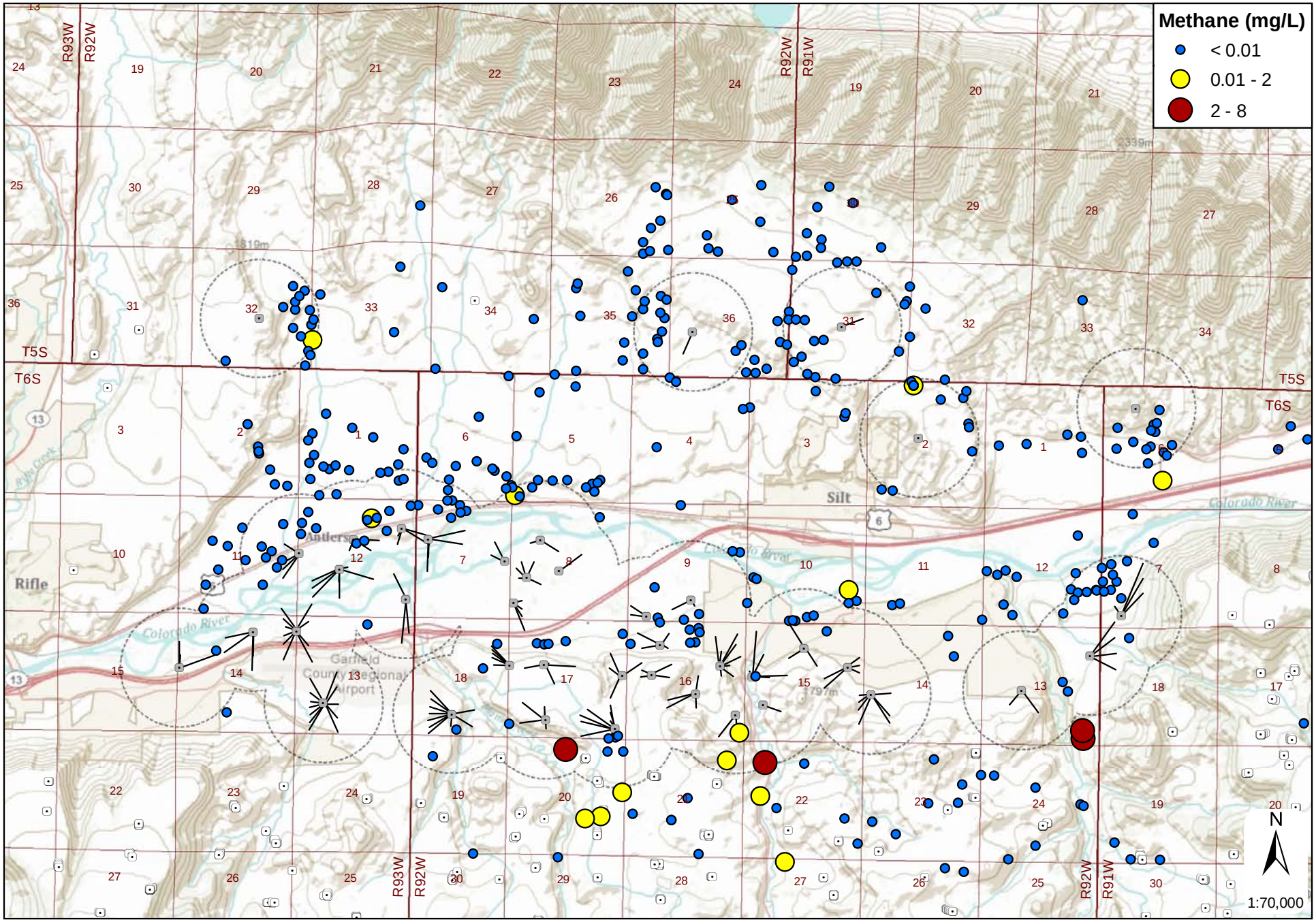

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Figure 4.7 Map of Methane Concentrations in Groundwater in the Gravel Trend Area

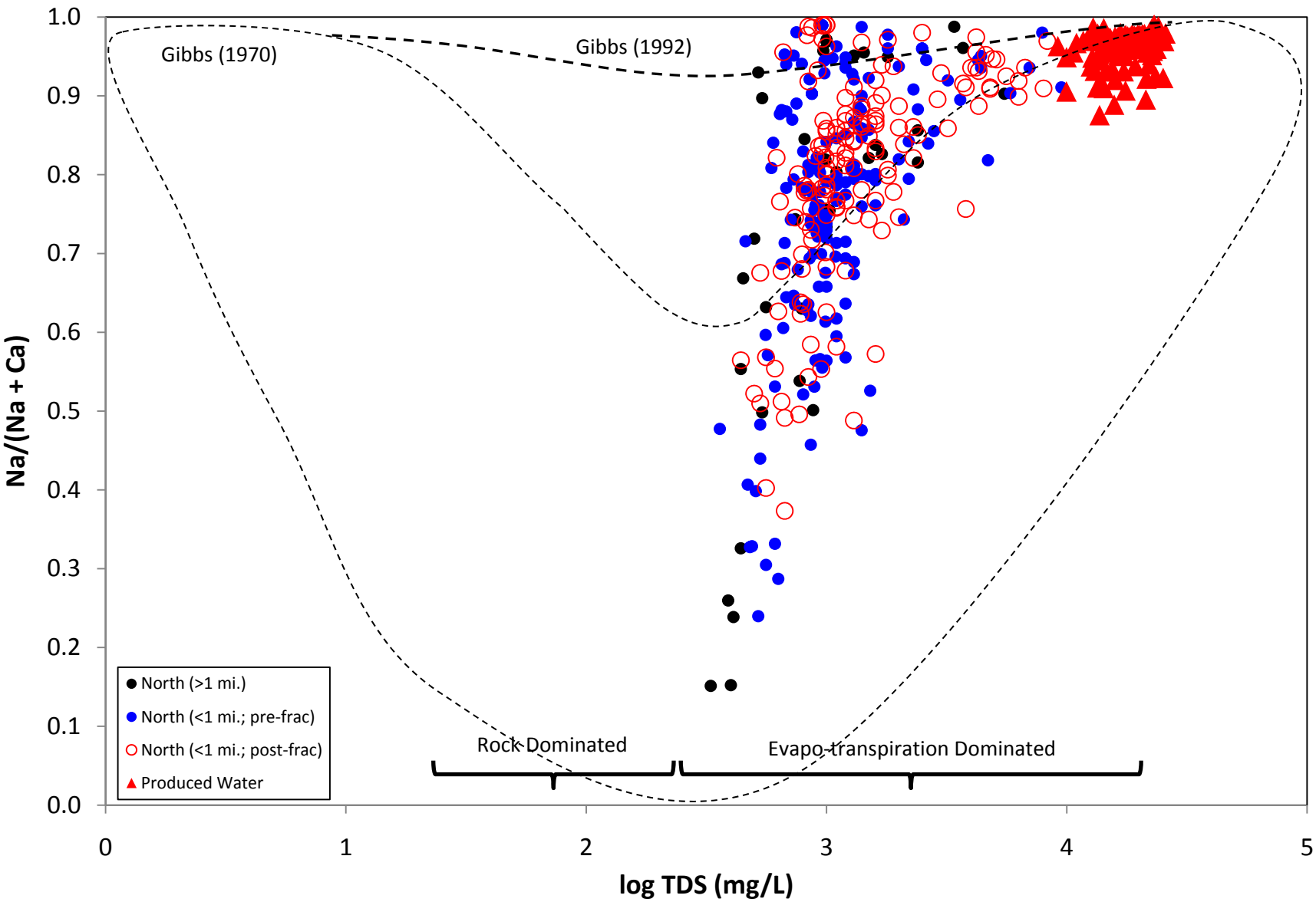

Figure 4.8 Groundwater Ion Concentration Relationships for Na/(Na+Ca) vs. TDS in Groundwater and Produced Water - Gravel Trend Area North of the Colorado River

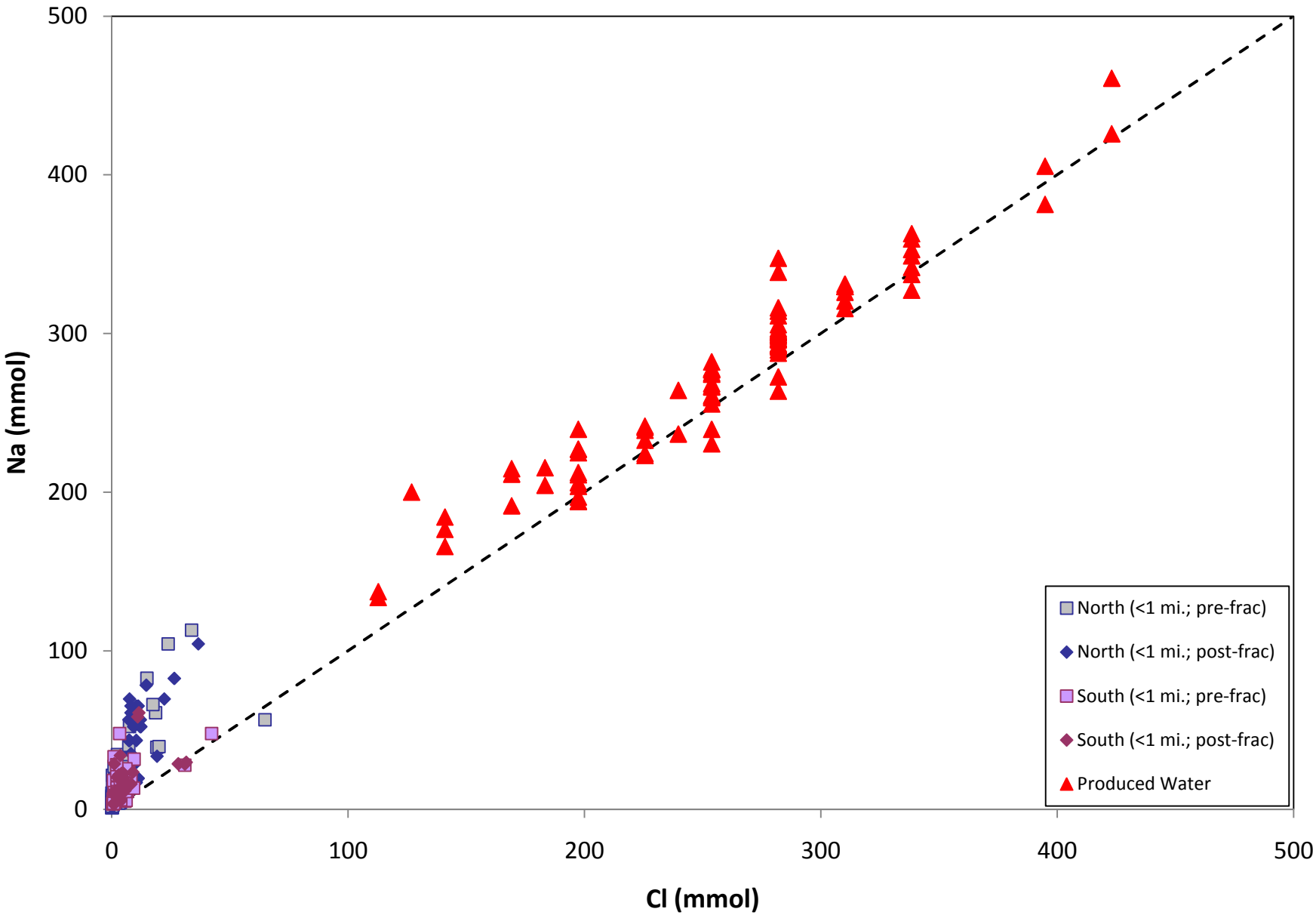

Figure 4.9 Na vs. Cl in Groundwater and Produced Water in the Gravel Trend Area

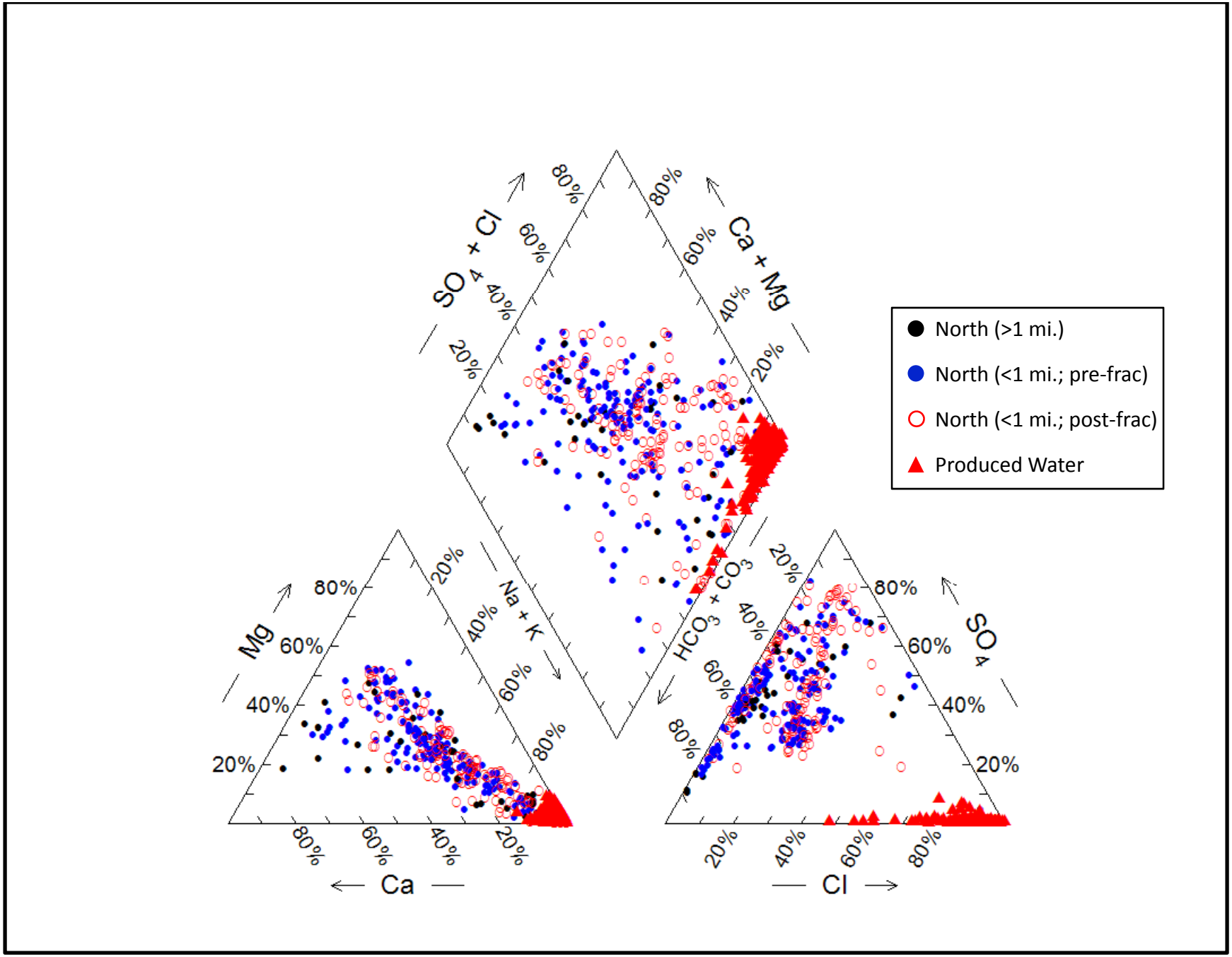

Figure 4.10 Piper Diagram of Groundwater Compared to Produced Water in the Gravel Trend Area North of the Colorado River

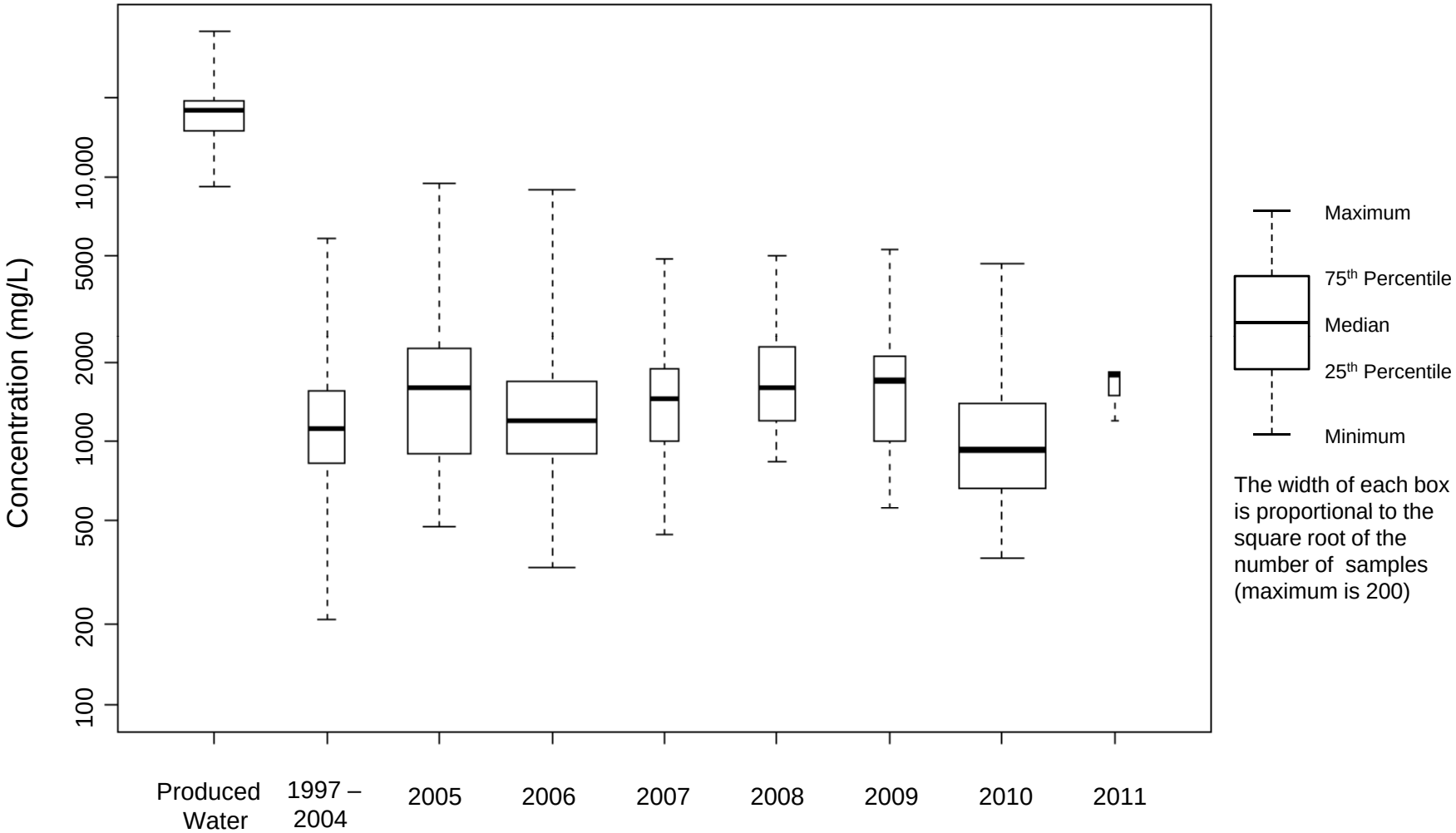

Figure 4.11 Box-and-Whisker Plot Showing TDS Concentrations over Time in the Gravel Trend Area

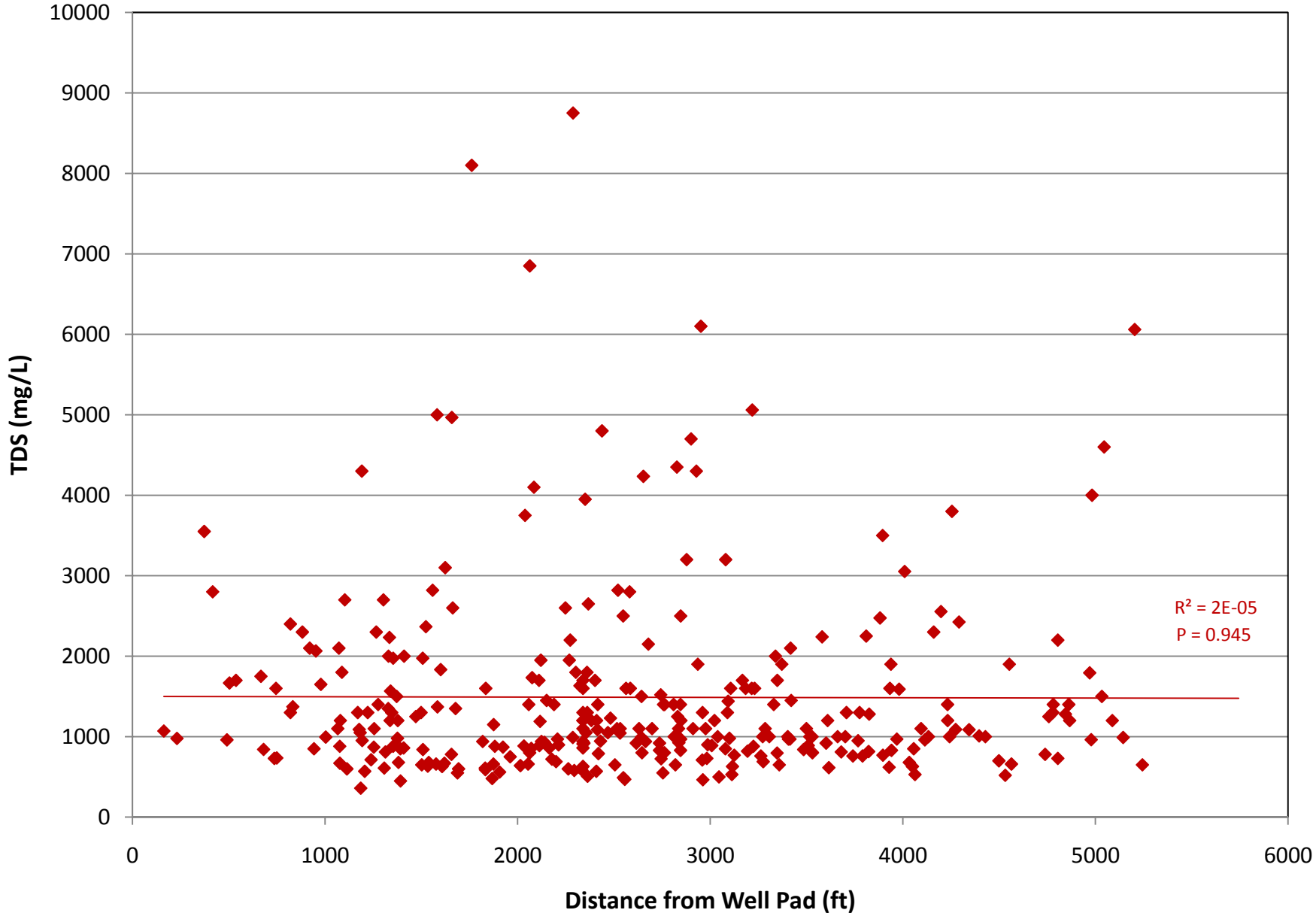

Figure 4.12 TDS Concentrations vs. Distance from Well Pad (up to 1 mile) in the Gravel Trend Area

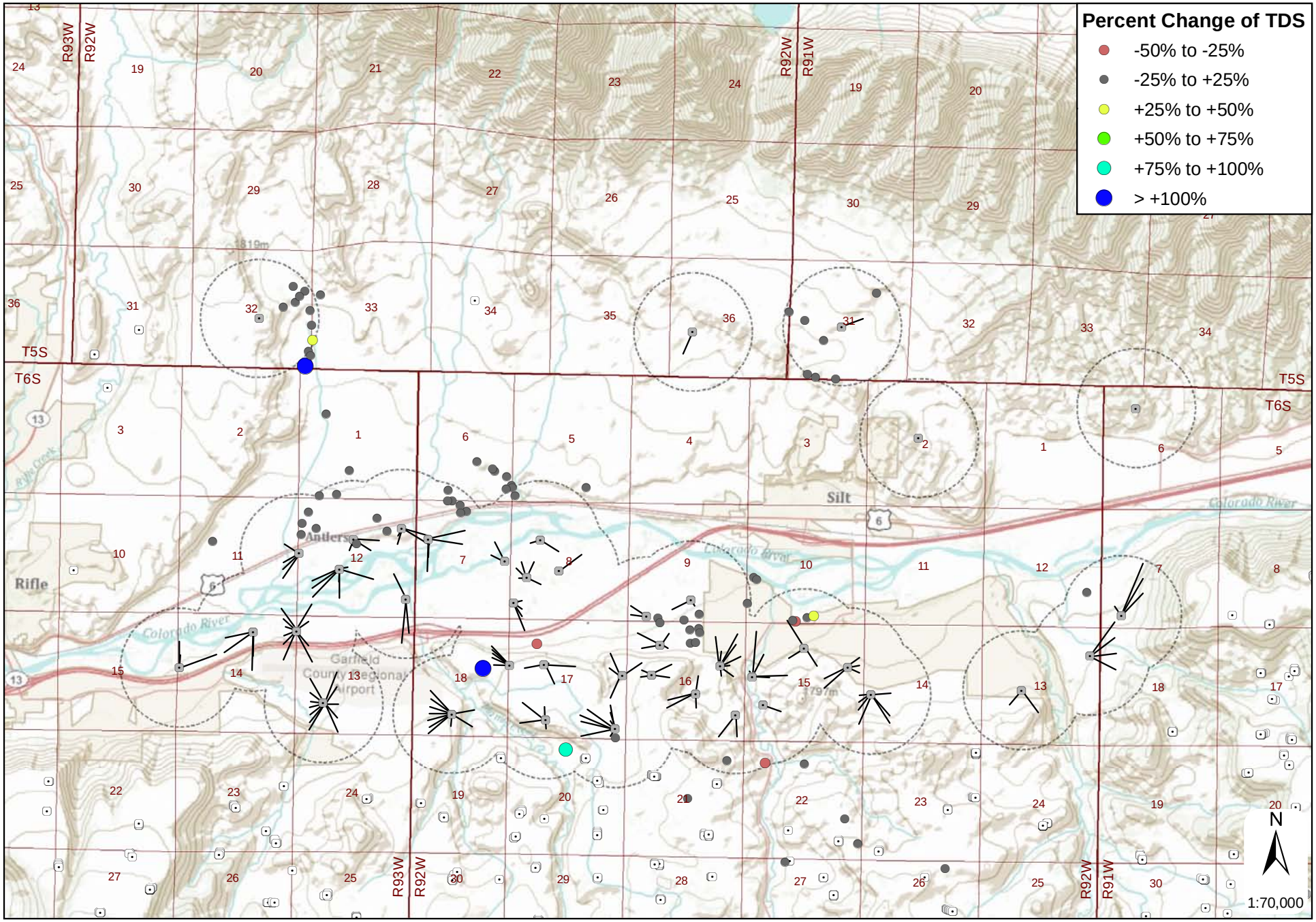

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Figure 4.13. Map of Changes in TDS Concentrations Between Pre-Drill and Post-Fracturing Samples in the Gravel Trend Area

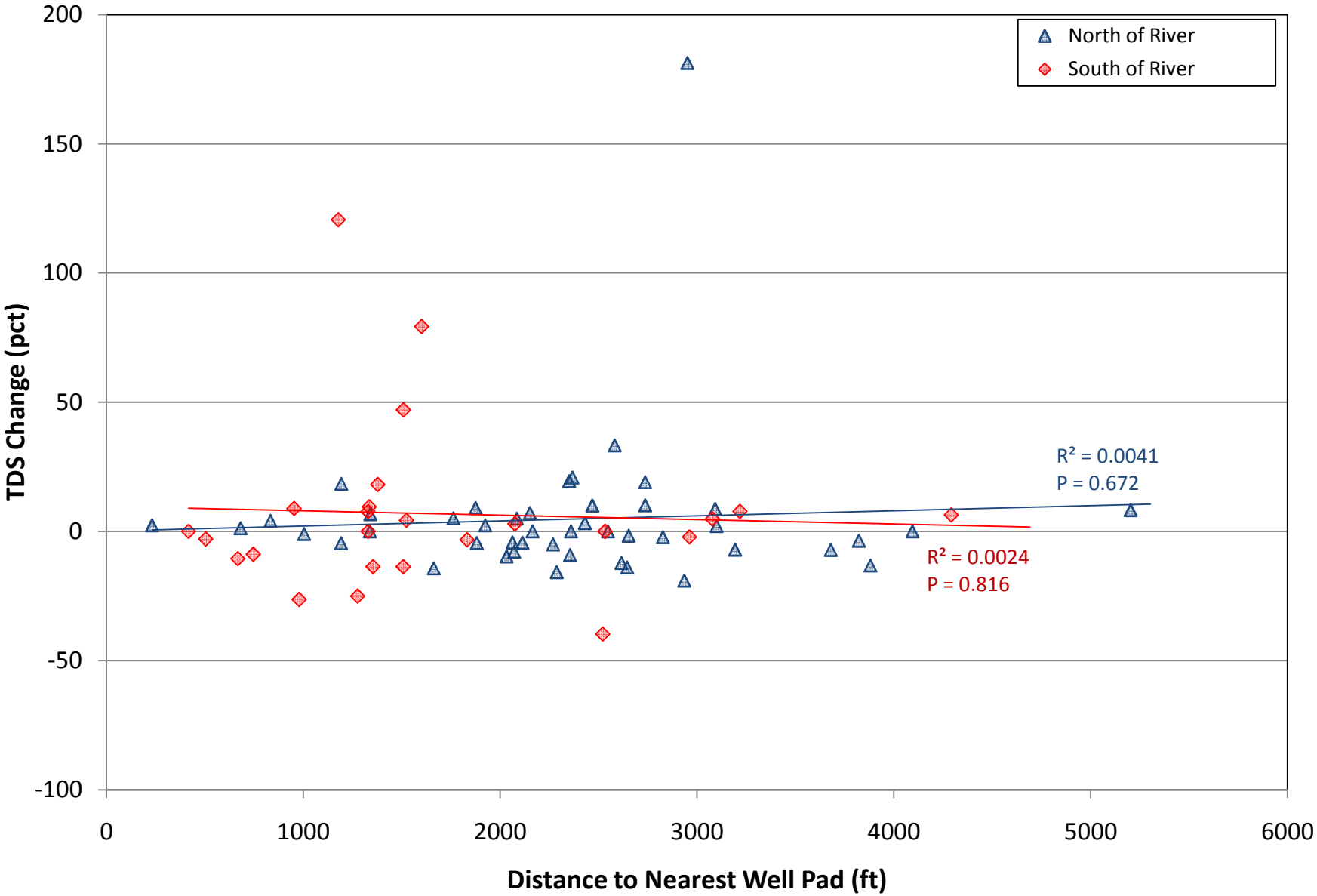

Figure 4.14 Percentage Changes in TDS Concentrations Between Pre-Drilling and Post-Fracturing Samples in the Gravel Trend Area as a Function of Distance from Well Pad (up to 1 mile)

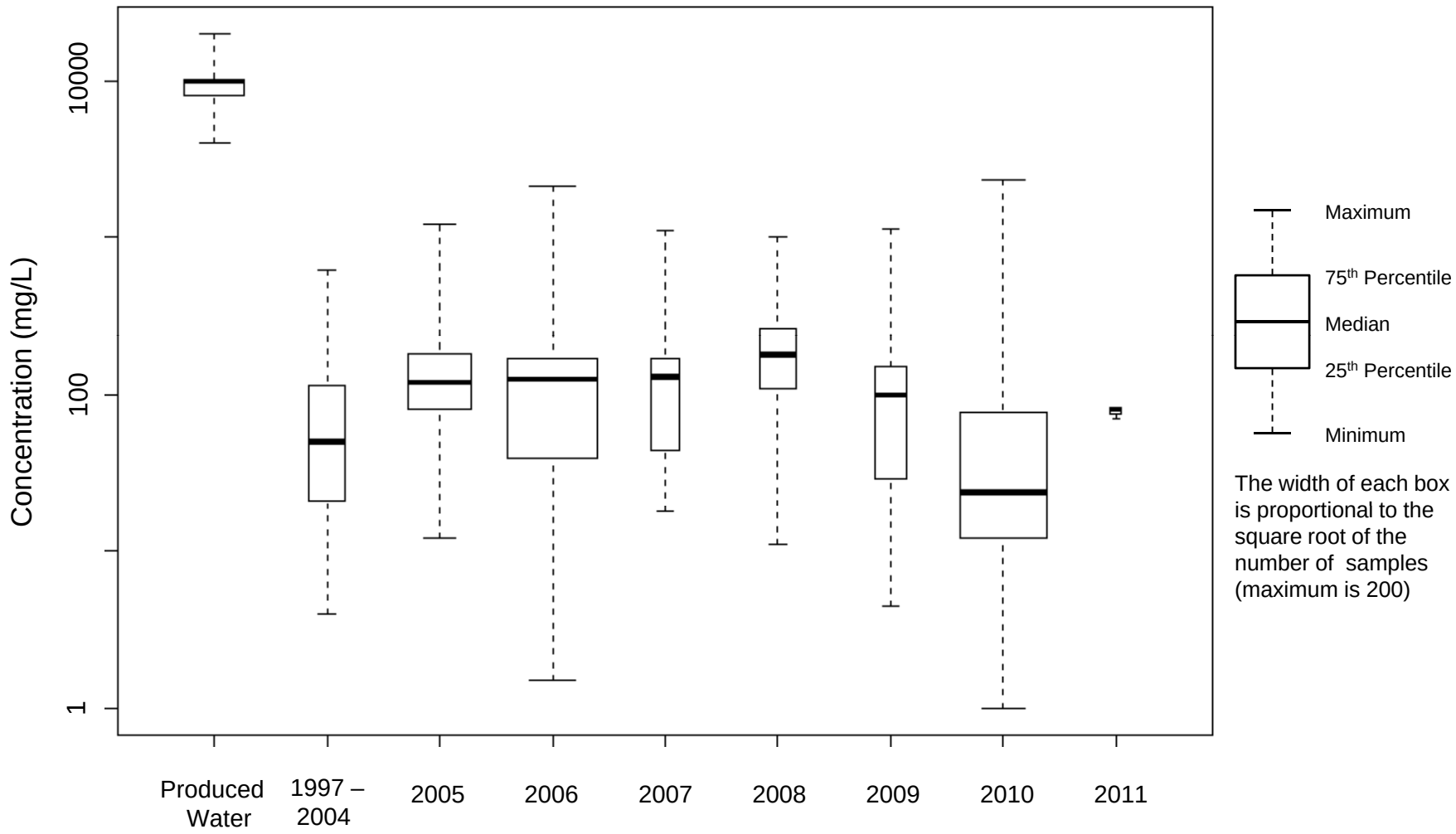

Figure 4.15 Box-and-Whisker Plot Showing Chloride Concentrations over Time in the Gravel Trend Area

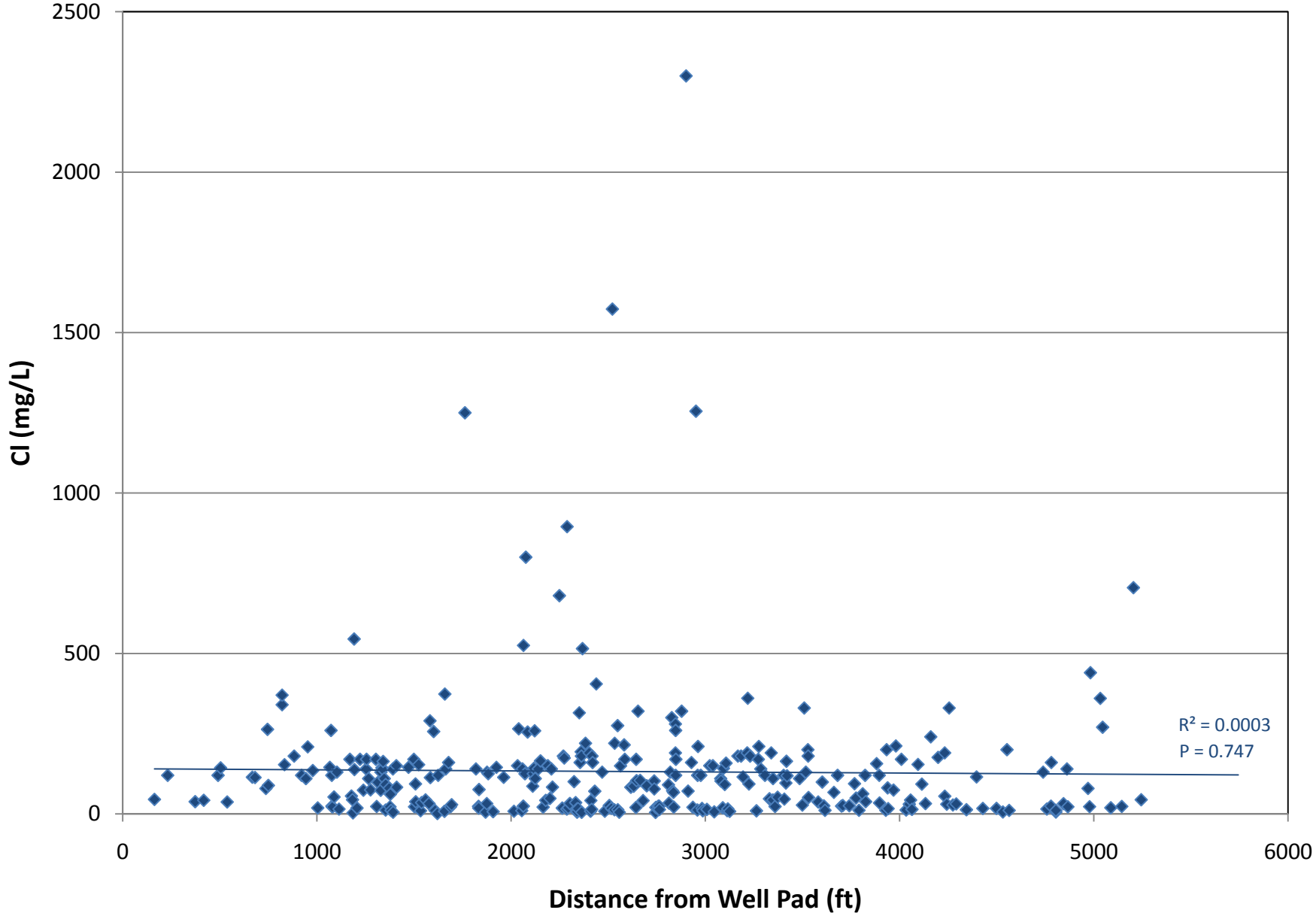

Figure 4.16 Chloride Concentrations vs. Distance from Well Pad (up to 1 mile) in the Gravel Trend Area

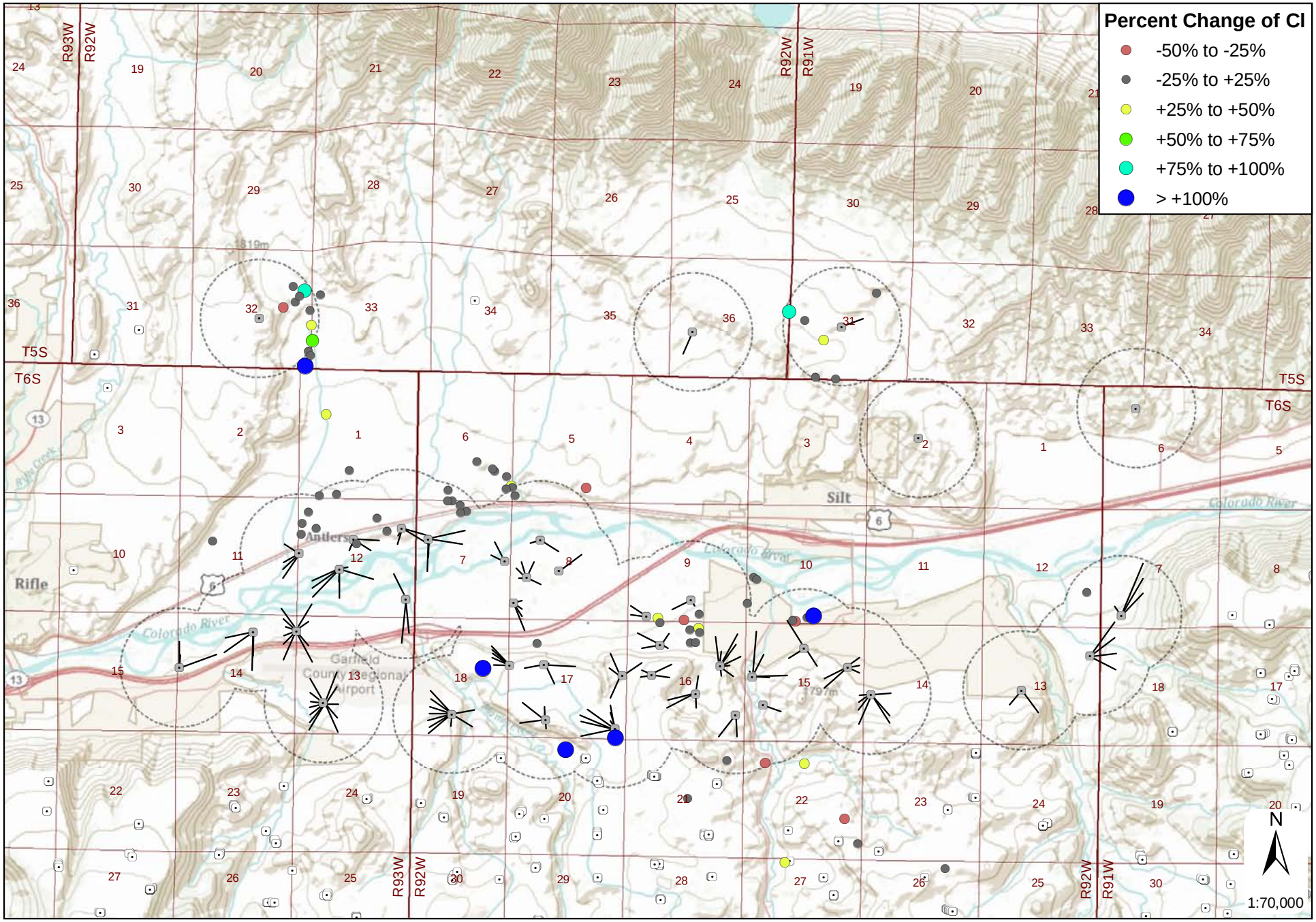

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Figure 4.17 Map of Changes in Chloride Concentrations Between Pre-Drill and Post-Fracturing Samples in the Gravel Trend Area

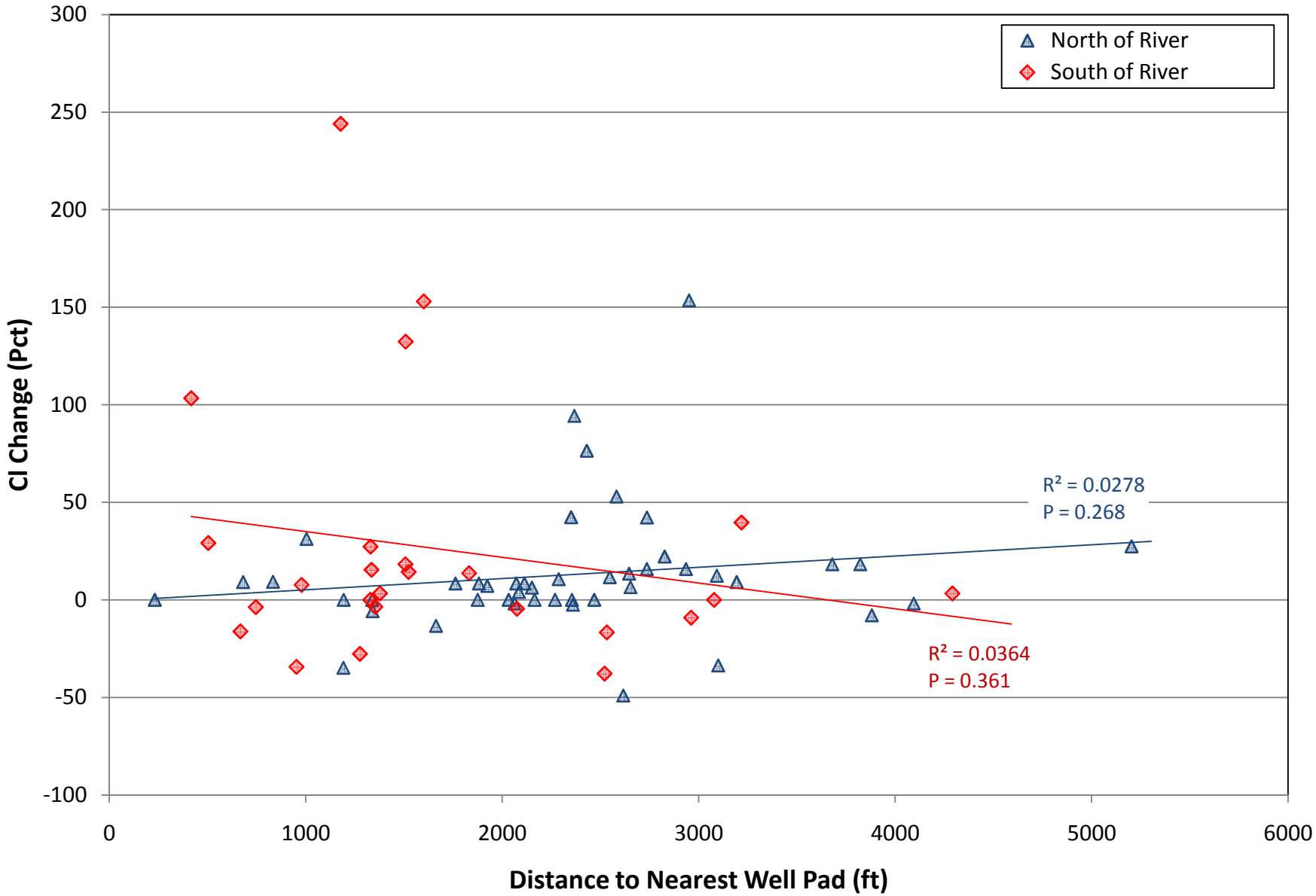

Figure 4.18 Percentage Changes in Chloride Concentrations Between Pre-Drilling and Post-Fracturing Samples in the Gravel Trend Area as a Function of Distance from Well Pad (up to 1 mile)

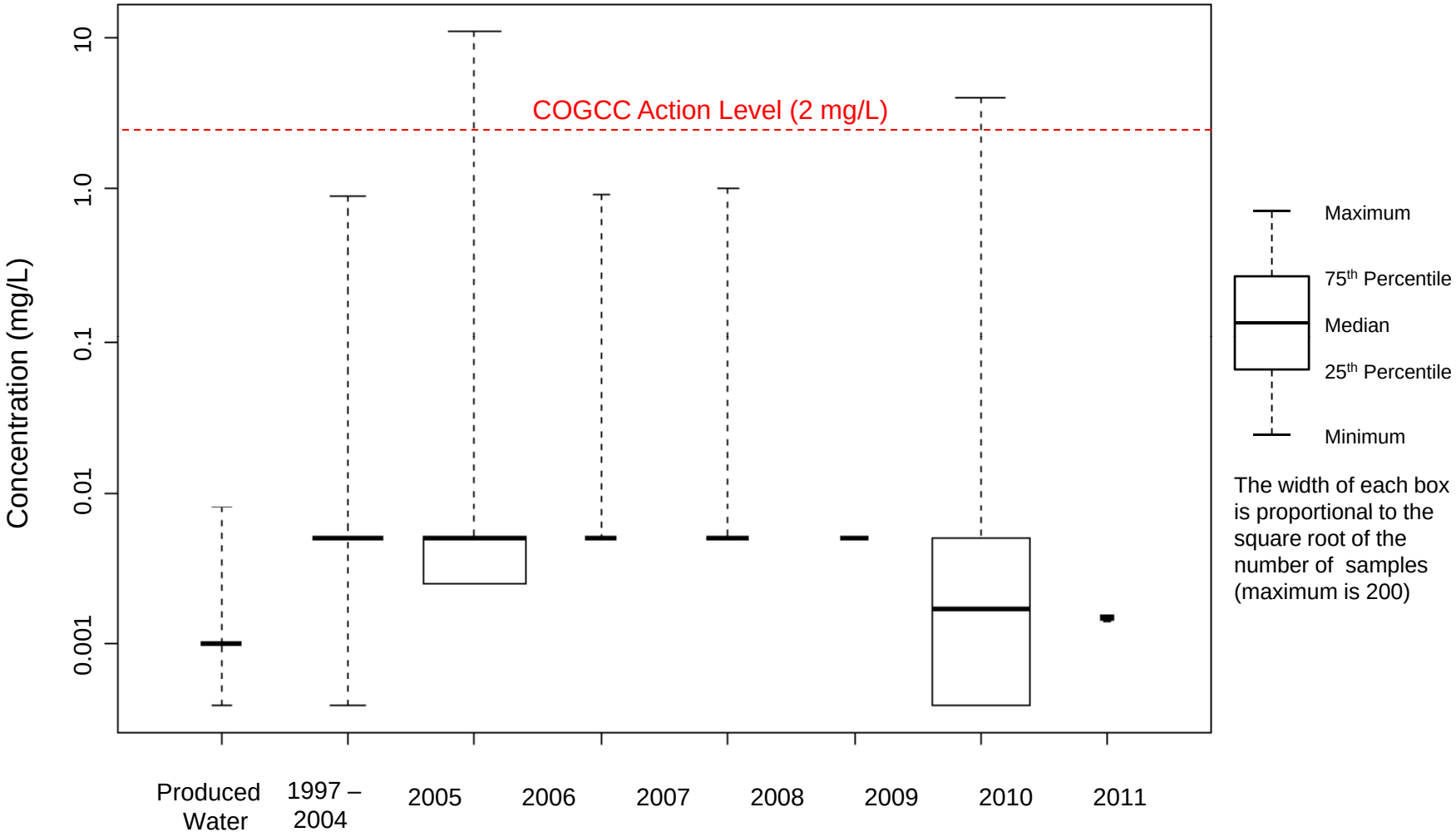

Figure 4.19a Box-and-Whisker Plot Showing Methane Concentrations over Time in the Gravel Trend Area

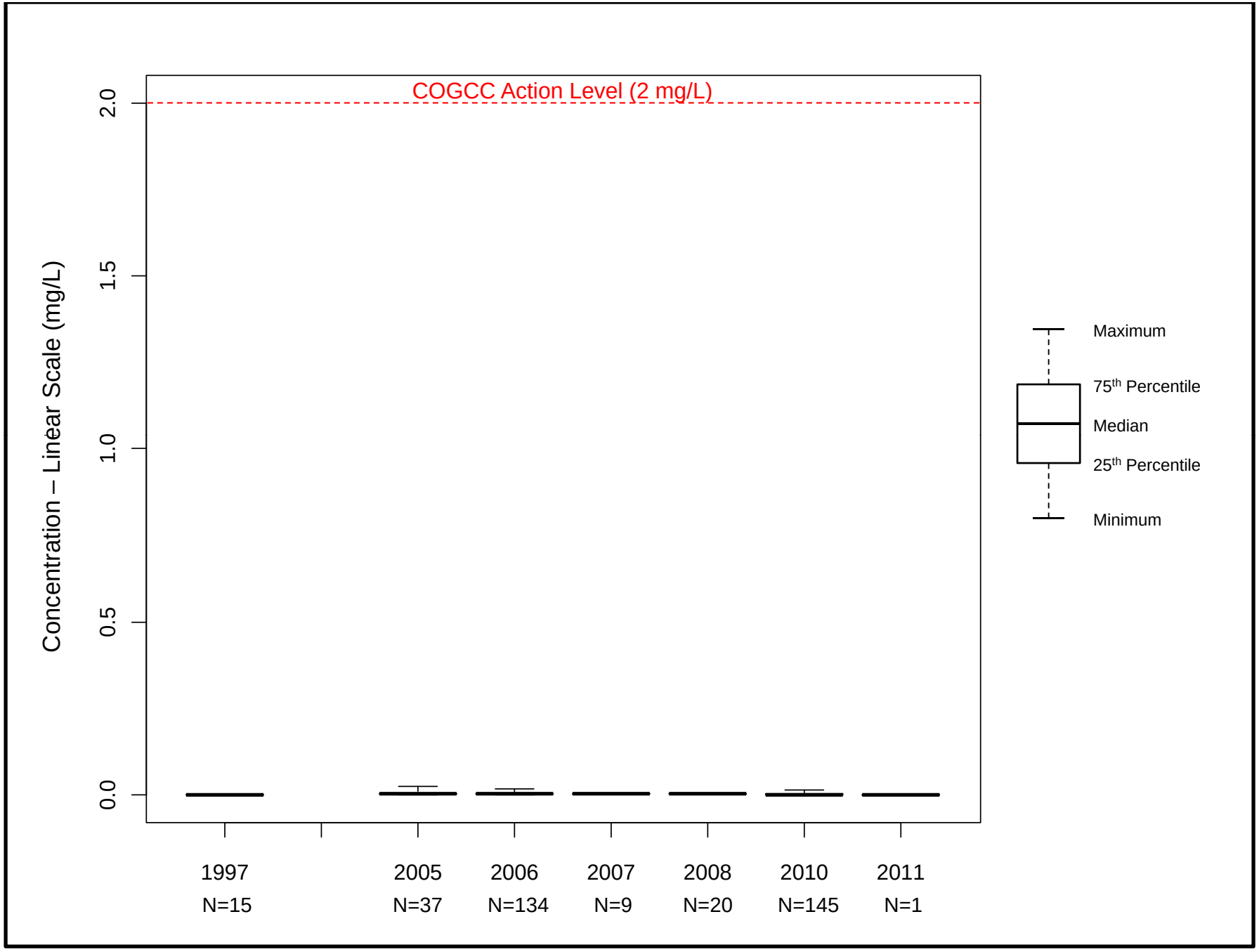

Figure 4.19b Box-and-Whisker Plot Showing Methane Concentrations over Time in the Gravel Trend Area North of the Colorado River

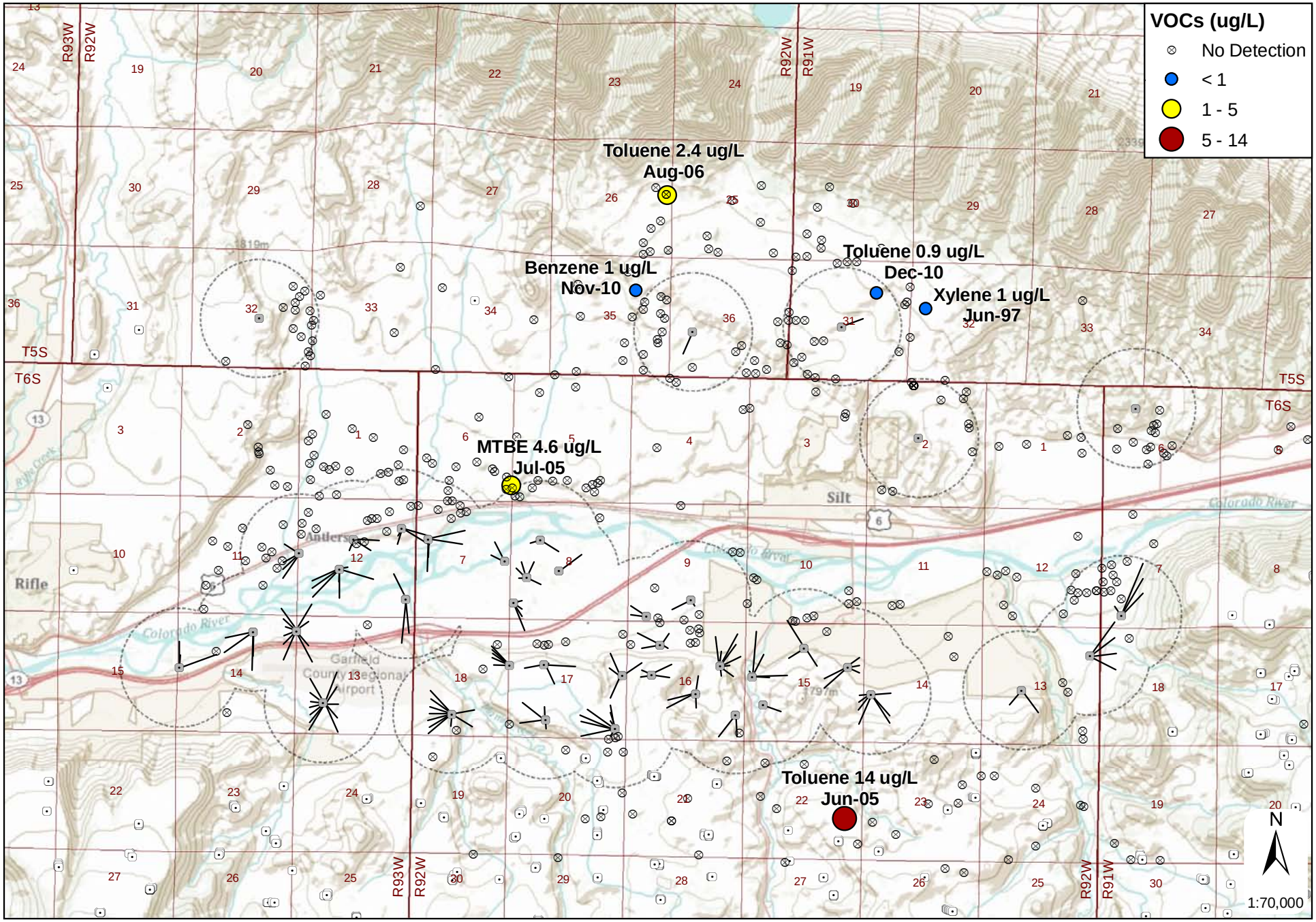

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Figure 4.20 Map of BTEX and MTBE Concentrations in Groundwater in the Gravel Trend Area

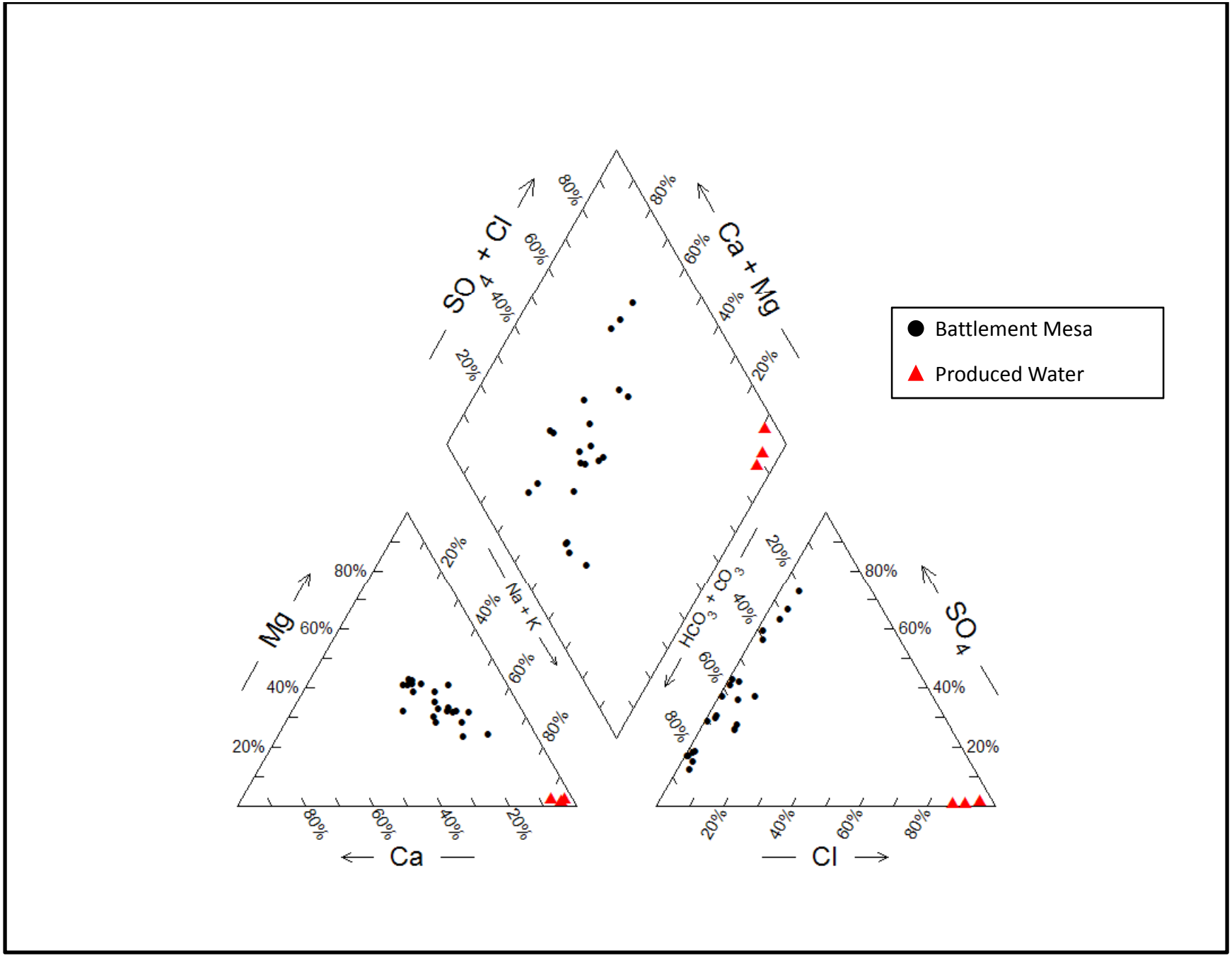

Figure 5.1 Piper Diagram of Groundwater and Produced Water in the Battlement Mesa Area

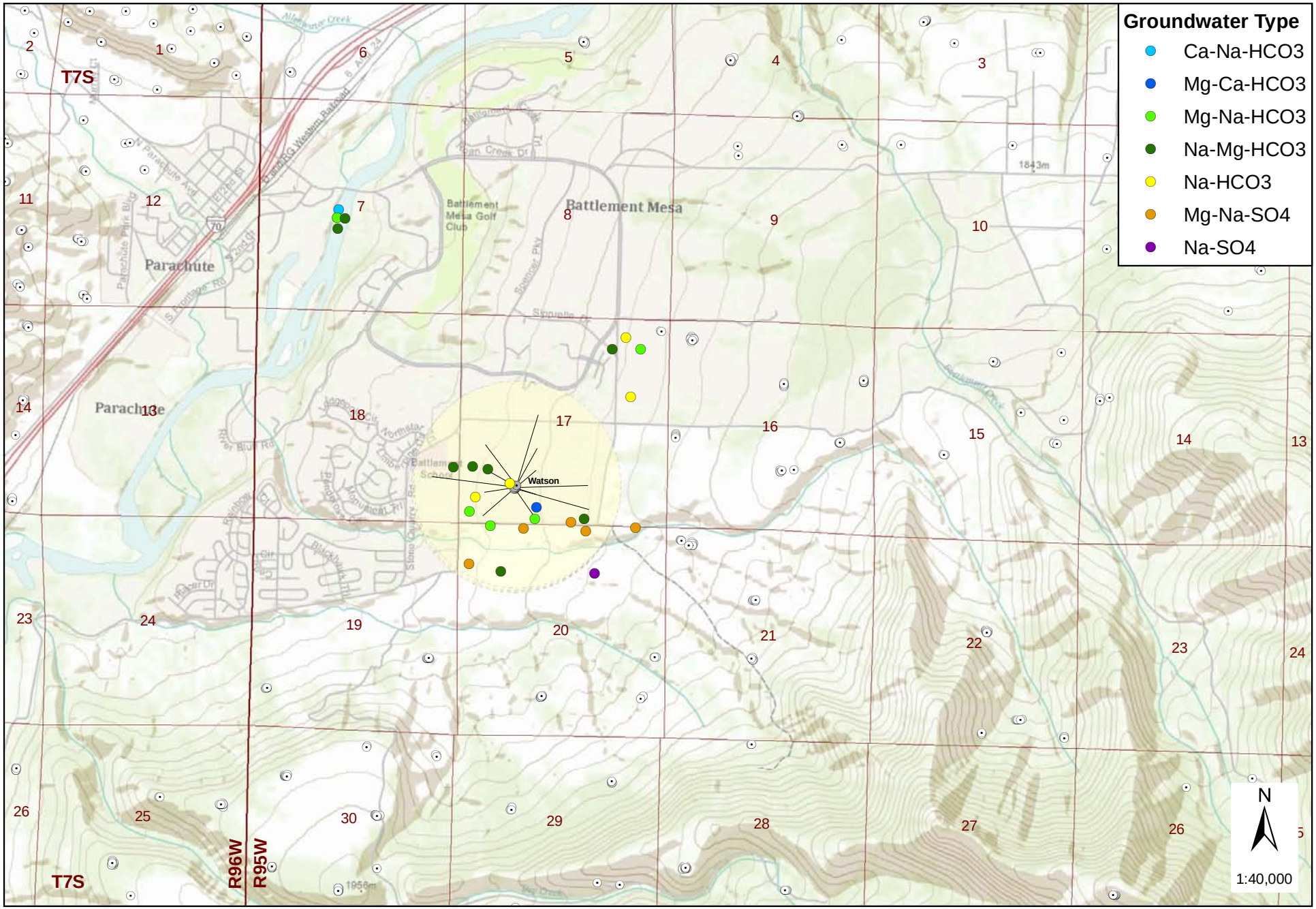

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Figure 5.2 Map of Dominant Ions in Groundwater in the Battlement Mesa Area

Tables

Table 3.1 Summary of Groundwater Quality Results for Gravel Trend Regulated Drinking Water Constituents

Analyte	Water Quality Criteria[a]			Groundwater Concentrations				No. of	Percent
	Primary	Secondary	Units	Average[b]	Median[b]	Minimum	Maximum	Samples	Exceed
Arsenic	0.01		mg/L	0.0043	0.0025	<0.0006	0.049	363	3.6
			North of River	0.0046	0.0025	<0.0006	0.049	294	4.1
Barium	2		mg/L	0.044	0.022	0.00003	3.6	372	0.3
			North of River	0.04	0.021	0.00003	3.6	299	0.3
Cadmium	0.005		mg/L	0.0014	0.0025	<0.00006	0.0059	369	0.3
			North of River	0.0012	0.0005	<0.00006	0.0059	300	0.3
Chromium	0.1		mg/L	0.0051	0.005	0.0008	0.21	357	0.3
			North of River	0.0053	0.005	0.0008	0.21	285	0.4
Fluoride	4		mg/L	0.9	0.67	<0.09	5.8	586	1.4
			North of River	0.88	0.71	<0.09	5.28	387	0.8
Lead	0.05		mg/L	0.12	0.0025	<0.00006	41	339	0.6
			North of River	0.15	0.0014	<0.00006	41	275	0.7
Molybdenum	0.035		mg/L	0.0052	0.002	<0.002	0.035	21	0
			North of River	0.0055	0.002	<0.002	0.034	19	0
Nitrate	10		mg/L	7.0	1.1	<0.09	562	583	9.4
			North of River	7.5	1.2	<0.09	410	375	11
Nitrite	1		mg/L	<0.03	<0.03	<0.002	0.23	567	0
			North of River	<0.03	<0.03	<0.002	0.23	377	0
Selenium	0.05		mg/L	0.04	0.01	<0.0008	1.4	520	16
			North of River	0.037	0.01	<0.0008	1.4	359	12
Silver	0.05		mg/L	0.0041	0.005	<0.00003	0.081	275	0.4
			North of River	0.0038	0.005	<0.00003	0.081	212	0.5
Uranium	0.03		mg/L	0.019	0.021	0.0015	0.047	19	16
			North of River	0.019	0.021	0.0015	0.047	19	16
Benzene	5		ug/L	0.04	0.01	<.0008	1	567	0
			North of River	0.38	0.5	<0.03	1	372	0
Ethylbenzene	700		ug/L	0.38	0.5	<0.001	1	567	0
			North of River	0.38	0.5	<0.03	1	372	0
Toluene	1000		ug/L	1.8	2.5	<0.005	14	567	0
			North of River	1.5	2.5	<0.04	2.5	372	0
Xylenes, Total	10000		ug/L	0.9	0.75	<0.003	1.5	566	0
			North of River	0.78	0.5	<0.06	1.5	372	0
Methane		2[c]	mg/L	0.061	0.005	<0.0008	11	578	0.9
			North of River	0.0034	0.0025	<0.0008	0.026	363	0
Chloride		250	mg/L	141	93	1	2300	587	12
			North of River	138	97	1	2300	385	13
Iron		0.3	mg/L	1.6	0.05	<0.005	300	554	20
			North of River	1.4	0.05	<0.005	300	377	15
Manganese		0.05	mg/L	0.15	0.005	<0.0001	16	537	30
			North of River	0.19	0.005	<0.0001	16	370	34
Sulfate		250	mg/L	624	365	<0.01	4400	590	63
			North of River	600	320	<0.01	4400	387	64
TDS		500	mg/L	1564	1200	210	9500	591	96
			North of River	1514	1100	330	9500	388	96

Notes: [a]Colorado Primary and Secondary Basic Groundwater Standards

[b]Average and median values were calculated assuming non-detected analytes were present at 1/2 of the laboratory reporting limit

[c]COGCC recommended action level

Table 3.2 Summary of Groundwater Quality Results for Battlement Mesa Regulated Drinking Water Constituents

Analyte	Water Quality Criteria[a]			Groundwater Concentrations				No. of Samples	Percent Exceed
	Primary	Secondary	Units	Average[b]	Median[b]	Minimum	Maximum		
Arsenic	0.01		mg/L	0.0036	0.0035	<0.001	0.0089	24	0
Barium	2		mg/L	0.092	0.05	0.014	0.6	24	0
Cadmium	0.005		mg/L	<0.0050	<0.0050	<0.0050	<0.01	24	0
Chromium	0.1		mg/L	<0.010	<0.010	<0.010	<0.010	24	0
Fluoride	4		mg/L	0.35	0.33	0.03	1.0	26	0
Lead	0.05		mg/L	0.0032	<0.005	<0.005	0.0054	24	0
Molybdenum	0.035		mg/L	<0.1	<0.1	<0.1	<0.1	4	0
Nitrate	10		mg/L	2.2	0.56	<0.1	17	27	7.4
Nitrite	1		mg/L	<0.10	<0.10	<0.10	<0.10	20	0
Selenium	0.05		mg/L	<0.020	<0.020	<0.01	<0.020	24	0
Silver	0.05		mg/L	<0.010	<0.010	<0.010	<0.010	24	0
Uranium	0.03		mg/L						
Benzene	5		ug/L	<1.0	<1.0	<0.5	<1.0	21	0
Ethylbenzene	700		ug/L	<1.0	<1.0	<0.5	<1.0	21	0
Toluene	1000		ug/L	<5.0	<5.0	<0.5	<5.0	21	0
Xylenes, Total	10000		ug/L	<3.0	<3.0	<0.5	<3.0	20	0
Methane		2[c]	mg/L	<0.010	<0.010	<0.002	<0.010	23	0
Chloride		250	mg/L	19	8	1.8	60	27	0
Iron		0.3	mg/L	0.31	<0.10	0.01	3.4	27	19
Manganese		0.05	mg/L	0.1	<0.010	<0.005	0.87	27	19
Sulfate		250	mg/L	255	150	20	1340	27	26
TDS		500	mg/L	769	570	340	2670	27	56

Notes: [a]Colorado Primary and Secondary Basic Groundwater Standards

[b]Average and median values were calculated assuming non-detected analytes were present at 1/2 of the laboratory reporting limit

[c]COGCC recommended action level

Table 4.1 Summary of Dissolved Gases in Groundwater (North of Colorado River)

Drilling Status	Station[a]	Gas Phase Composition (Mole %)														$\delta^{13}C$ of CO_2[b]
		Ar	CO	CO_2	H	He	N	O_2	CH_4	C_2H_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	
Pre-Spud	703102	1.54	ND	8.6			72.74	17.12	ND	ND	ND	ND	ND	ND	ND	-20.97
	704709	1.04	0.011	0.68	ND	0.0029	89.32	8.94	0.0049	ND	ND	ND	ND	ND	ND	-18.84
	704710	1.33	0.072	4.88			76.13	17.59	ND	ND	ND	ND	ND	ND	ND	-19.14
	704712	1.42	ND	5.54			76.4	16.64	ND	ND	ND	ND	ND	ND	ND	-20.29
	704714	1.35	0.028	7.47			72.9	18.25	ND	ND	ND	ND	ND	ND	ND	-22.27
	704716	1.5	0.039	11.79			83.17	3.5	ND	ND	ND	ND	ND	ND	ND	-21.16
	704719	1.45	ND	3.08			70.37	25.1	ND	ND	ND	ND	ND	ND	ND	-18.61
	704732	1.04	ND	1.26	ND	0.0019	78.63	19.07	ND	ND	ND	ND	ND	ND	ND	-19.24
	704733	1.35	ND	2.55			85.06	11.04	ND	ND	ND	ND	ND	ND	ND	-21.66
	704734	1.27	ND	11.97			76.08	10.68	ND	ND	ND	ND	ND	ND	ND	-20.9
	704738	1.39	0.055	5.31			76.15	17.1	ND	ND	ND	ND	ND	ND	ND	-20.48
	704739	1.16	ND	1.83	ND	0.0021	85.71	11.3	ND	ND	ND	ND	ND	ND	ND	-20.07
	704743	1.29	ND	3.07	ND	0.0288	90.57	5.04	0.0044	ND	ND	ND	ND	ND	ND	-21.57
	704744	1.45	ND	5.67			91.01	1.83	0.0393	ND	ND	ND	ND	ND	ND	-21.47
	704747	1.29	ND	6.41			68.27	24.03	ND	ND	ND	ND	ND	ND	ND	-20.72
	704749	1.48	ND	11.22			73.82	13.48	ND	ND	ND	ND	ND	ND	ND	-21.47
	704752	1.51	0.054	6.94			74.27	17.23	ND	ND	ND	ND	ND	ND	ND	-20.65
	704753	1.33	ND	12.74			72.01	13.92	ND	ND	ND	ND	ND	ND	ND	-22.39
	704754	1.46	0.06	11.65			73.32	13.51	ND	ND	ND	ND	ND	ND	ND	-21.67
Post-Frac	703107	0.938	ND	2.24	ND	0.002	96.27	0.554	ND	ND	ND	ND	ND	ND	ND	-21.38
	703109	1.49	ND	6.89			89.73	1.89	ND	ND	ND	ND	ND	ND	ND	-21.54
	704720	1.3	ND	6.62			82	10.07	0.0092	ND	ND	ND	ND	ND	ND	-16.6
	704724	1.26	ND	7.13			83.48	8.13	ND	ND	ND	ND	ND	ND	ND	-20.8
	704729	0.832	ND	1.3	ND	0.13	95.37	2.37	0.0022	ND	ND	ND	ND	ND	ND	-20.95
	704762	1.39	ND	6.88			89.04	2.69	ND	ND	ND	ND	ND	ND	ND	-21.8

Notes: [a]All samples collected between 7/21/2006 and 8/15/2006

[b]$\delta^{13}C$ of CO_2 in units of per mil

Appendix A

Evaluation of Specific Samples for Potential Impacts from Natural Gas Drilling and Production Activities

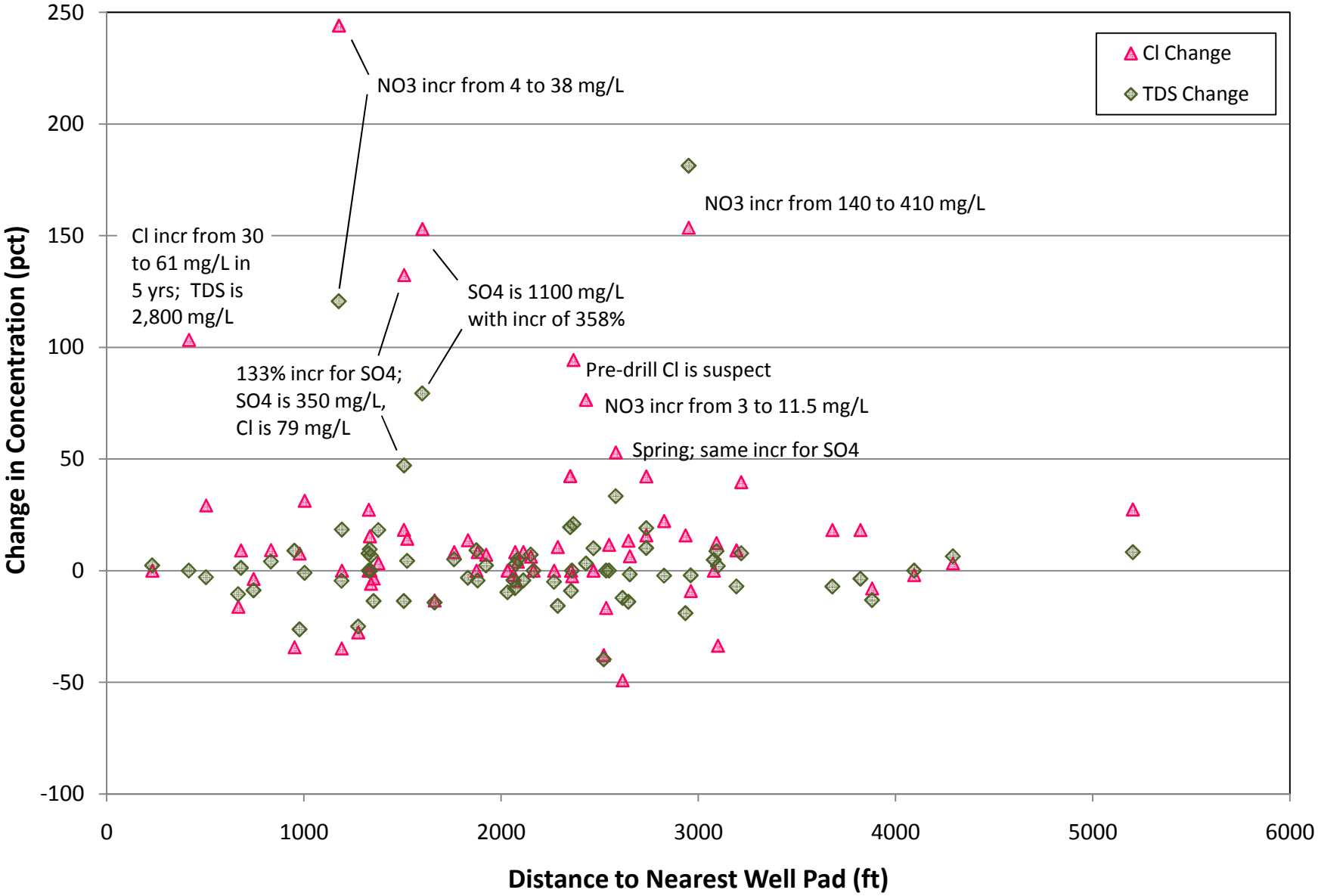

Figure A-1 Pre-Drilling to Post-Fracturing Changes in Concentration for TDS and Chloride in the Gravel Trend Area as a Function of Distance to Well Pad

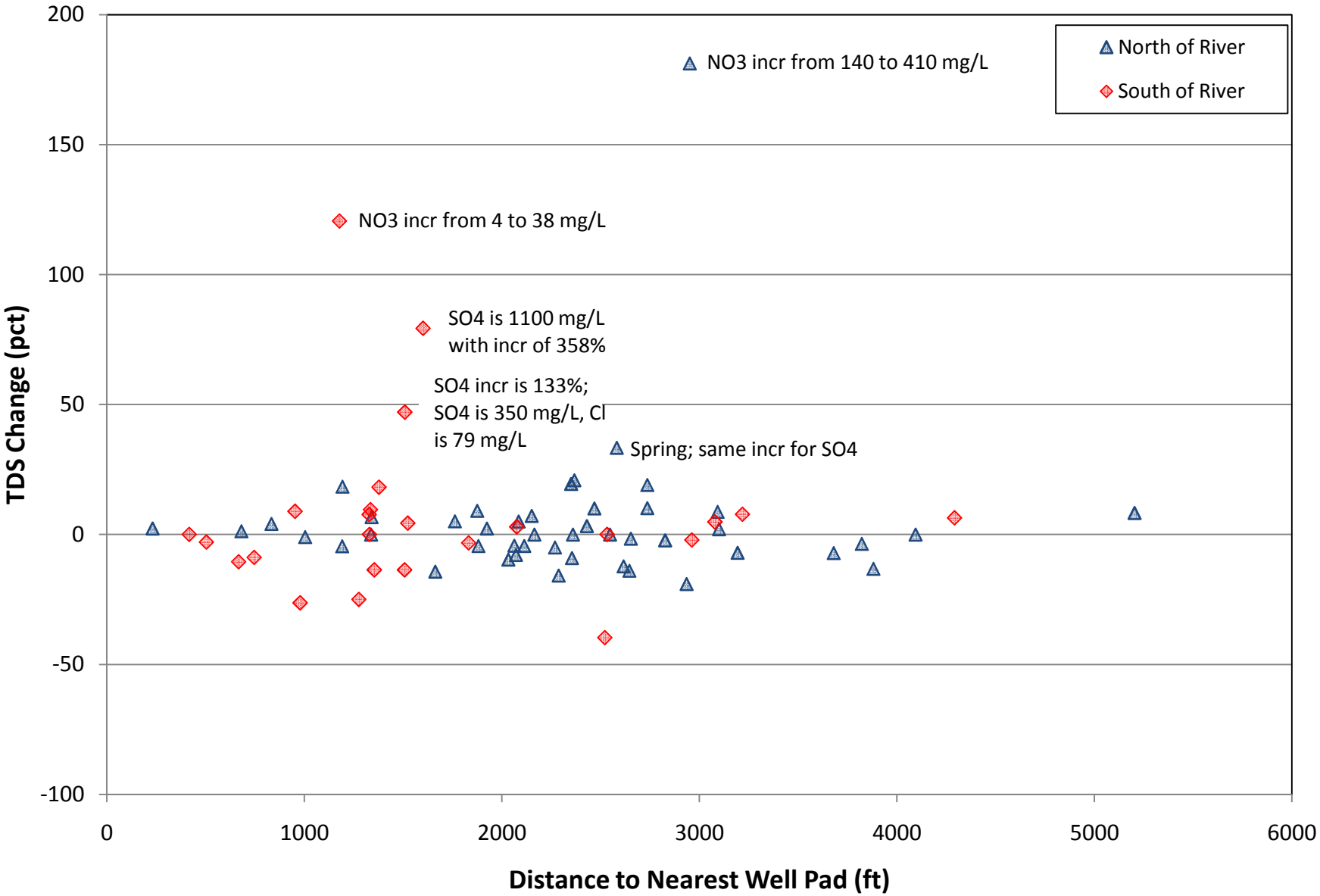

Figure A-2 Pre-Drilling to Post-Fracturing Changes in Concentration for TDS in the Gravel Trend Area as a Function of Distance to Well Pad

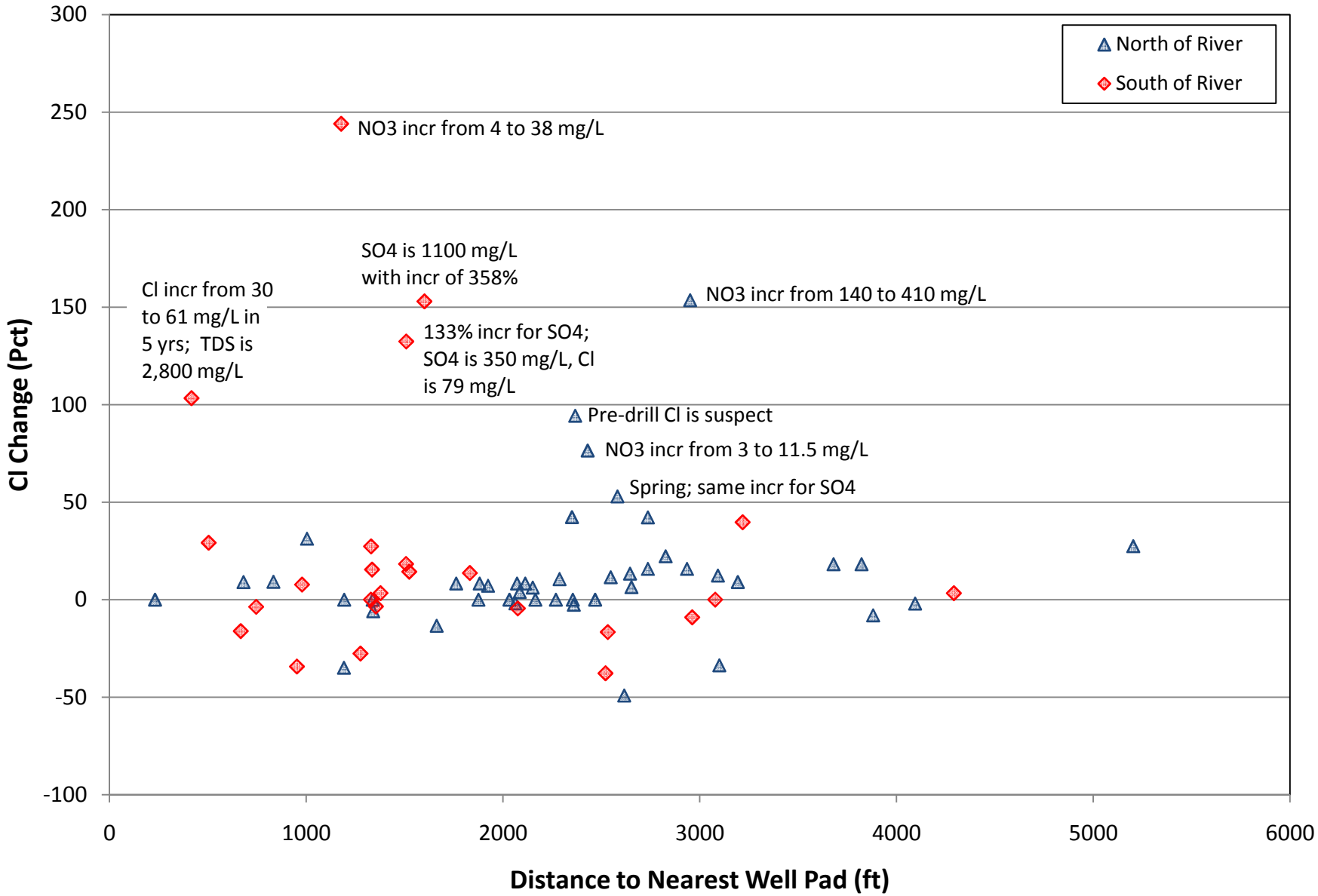

Figure A-3 Pre-Drilling to Post-Fracturing Changes in Concentration for Chloride in the Gravel Trend Area as a Function of Distance to Well Pad