
Technical Memorandum

Evaluation of “Review of Phase II Hydrogeologic Study” (December 20, 2008) for the Mamm Creek Field Area, Garfield County, Colorado

Prepared for:

State of Colorado Department of Natural Resources,
Colorado Oil and Gas Conservation Commission

Prepared by:



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Technical Memorandum

Date: May 5, 2010
To: Debbie Baldwin – Colorado Oil & Gas Conservation Commission
Subject: **Evaluation of "Review of Phase II Hydrogeologic Study" (December 20, 2008) for the Mamm Creek Field Area, Garfield County, Colorado**

INTRODUCTION

This memorandum provides an evaluation of the assertions made in the December 20, 2008, report "Review of Phase II Hydrogeologic Study," prepared by Geoffrey Thyne for Garfield County, Colorado (Thyne Report). Evaluation of the assertions involved application of statistical analysis to the data discussed in the Thyne Report, as well as to a more extensive database assembled by S. S. Papadopoulos & Associates, Inc. (SSPA) from current Colorado Oil & Gas Conservation Commission (COGCC) data for the Mamm Creek area. This document addresses the following assertions made in the Thyne Report:

- That there is a temporal trend of increasing methane in groundwater with increased drilling for natural gas;
- That there is a temporal trend of increasing chloride in groundwater with increased drilling for natural gas;
- That chloride concentrations above 10 milligrams/Liter (mg/L) in groundwater indicate impacts from water associated with natural gas production; and
- That the stable isotope signatures of methane in groundwater indicate that the methane is thermogenic in origin and is due to the drilling activity.

DATA SOURCES

The COGCC database developed for this study was compiled from data provided to SSPA by the COGCC. The data referred to as the "Albrecht Data" is the data included in analysis for the Thyne Report, and is contained in the appendices of Colorado School of Mines Master's Thesis "Using Sequential Hydrochemical Analyses to Characterize Water Quality Variability at Mamm Creek Gas Field Area, Southeast Piceance Basin, Colorado" (Albrecht, 2007). With the exception of approximately five locations, the COGCC dataset encompasses all of the locations

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contained in the Albrecht dataset and includes new locations sampled after the latest sample from the Albrecht dataset.

The Albrecht methane dataset included 2,188 records, of which 164 were multiple measurements (i.e., duplicates, split samples, other samples collected the same day as the primary sample), with samples collected between 1997 and 2005. Non-detect measurements were generally replaced with values that were 40% of the detection limit. The Albrecht chloride dataset included 1,433 records, of which 121 were multiple measurements, with samples collected between 1997 and 2005. No non-detects were included in the Albrecht chloride data.

The COGCC database included 2,874 records for methane with data collected through early 2009. Of these records, only 2,499 were used to evaluate conditions in the Mamm Creek area. Neither samples from north of the Colorado River and west of the Mamm Creek area towards Battlement Mesa, nor samples from surface water, cisterns/holding tanks, or unknown types of locations were considered. The removal of 857 methane monitoring well samples and 314 multiple measurements left 1,328 results for final trend analysis. Non-detect measurements were replaced with one-half of the detection limit. One very high measurement of 585 mg/L from May of 2003 was considered spurious and removed from the dataset, as there were 11 other measurements reported for the same well, all less than 1 mg/L, including 0.03 mg/L in January 2003 and non-detect in June 2003.

The COGCC chloride dataset consisted of 2,539 records. Removal of measurements from locations outside the Mamm Creek area, wastewater samples, samples from unknown location types, and multiple measurements left 2,027 unique records. Of that amount, 671 chloride measurements from monitoring wells were removed, leaving 1,356 results for final trend analysis. Non-detect measurements, of which there were 3, were replaced with one-half of the detection limit.

It is important to note that neither the Albrecht nor COGCC datasets represent random sampling of groundwater conditions. This is because many wells were either located in targeted areas

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(such as the vicinity of West Divide Creek where a natural gas release from the Schwartz 2-15B well occurred in April 2004), or were specifically selected for sampling or resampling due to prior elevated concentrations of methane and/or inorganic chemical constituents.

DATA ANALYSIS

The assertions of increasing methane and chloride concentrations over time were assessed graphically and statistically using the data available to Thyne (from Albrecht, 2007), as well as more comprehensively, by incorporating more recent COGCC data. The Albrecht data were used as received. Data from the COGCC data were assessed with and without multiple measurements (duplicate sample results, split sample results, etc.) to determine if inclusion of the multiple measurements affected the trend analysis results. Inclusion of multiple measurements had no impact on the trends observed for data distribution, time-series analysis, or box-and-whisker plots; therefore, the analyses presented in this memorandum are for the COGCC dataset without multiple measurements. Furthermore, because the monitoring well data are all related to the West Divide Creek seep and are from a very small area, these results were excluded from the trend analyses of the COGCC data.

Analysis of potential trends was accomplished through data visualization (scatter plots and box-and-whisker plots) and application of statistical tests to quantitatively establish relationships and evaluate inter-annual data trends (Mann-Whitney test¹). Because chloride and methane data are not normally distributed, non-parametric statistical tests were used and graphic results are presented on logarithmic concentration scales.

¹ The Mann-Whitney test is a nonparametric statistical comparison of two populations. The two populations (or sample sets; e.g., two years of sample results) are combined and ranked in order from smallest to largest value. If the samples are drawn from the same population, then it is expected that the rankings will be fairly evenly dispersed, and that the average of the ranks of each sample set will be similar. To test if the sample sets are statistically similar a test statistic is calculated based on the rank of the sample sets. For the Mann-Whitney test, the test statistic is the maximum possible sum of ranks for the larger group minus the actual sum of the ranks of the larger group. This statistic (called U or z, depending on sample size) is then used to determine if the two sample sets are statistically different. Statistical difference is determined by comparing U or z to critical values calculated for a particular confidence level (e.g. 95%), which establishes whether or not the difference between the two sample sets is statistically significant.

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DISCUSSION OF ASSERTIONS

A detailed listing of the assertions made in the Thyne Report is provided in Table 1 of this memorandum. Table 1 also provides a brief evaluation of each, based on SSPA's review of the assertion in light of the data available from the Mamm Creek area. More in-depth evaluation of the primary assertions is provided below.

Methane Trends

The presence of a temporal trend for increasing methane is not supported by analysis of the Albrecht methane data or analysis of the COGCC methane data.

The assertion that methane concentrations in groundwater are increasing with the increasing number of gas wells is presented in Figure 6 of the Thyne Report. This figure presents the geometric mean of methane concentration by year against the cumulative number of wells, and generates an r^2 value of 0.787 with a line of increasing slope². However, based on Albrecht (2007; to which the figure is referenced) these are not actually data from 2000-2007 as indicated. The data are instead from 1997-2005, with the data for the years 1998 and 2000 (two higher mean methane concentration years) excluded³. As will be shown below, inclusion of those data eliminate the apparent time trend. More importantly, this figure belies the actual range of variation of methane concentrations measured within each year, and no analysis is presented on the statistical significance of this trend relative to the intra-annual variability of the data. Also, in examining temporal trends, it is more appropriate to plot concentrations against time as the independent variable, rather than assigning a second dependent variable (i.e., number of gas wells) as the independent variable.

² In regression, or trend, analysis, the r^2 value varies between 0 and 1 and is an indicator of the significance of the apparent trend. The higher the r^2 value the greater the strength of the apparent trend. If $r^2 = 0$, then the data are randomly distributed.

³ Albrecht (p. 68) indicates that "the six values taken in 1998 were removed due to inaccurate recording, and the four values from 2000 were removed based on the low number of data points."

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SSPA reassessed the Albrecht data for time trends in methane concentration. The annual geometric mean concentration was plotted, as reported in Figure 6 of the Thyne Report (but also including data for 1998 and 2000), with the year of sampling as the independent variable, and the geometric standard deviation included as error bars as a measure of within-year variability (Figure 1). Figure 1 clearly shows that changes in the year-to-year geometric mean concentration are small compared to the overall range of variability within each year. The Albrecht methane data were also plotted on a time-series plot to further illustrate the intra-annual variability (Figure 2). A linear trend-line was fitted to the data, but only a weak trend was detected in the data ($r^2 = 0.0018$; $p = 0.049^4$).

Box-and-whisker plots, which allow a visual comparison year-to-year of the median and variability in the data, were also constructed. Figure 3 shows the Albrecht methane data as a box-and-whisker plot with outliers included (i.e., results greater than two standard deviations from the median). Comparison of the interquartile range for each year (i.e. the central 50% of the methane concentration data, as defined by the “box” encompassing the 25th to 75th percentile range) clearly shows that any year-to-year difference in the median values is much smaller than the variability in the data.

Temporal trends in methane concentrations were also assessed with the expanded dataset from the COGCC database, with the monitoring well data removed. Unlike the Albrecht data, the time-series plot shows no significant trend in methane concentration (Figure 4; $r^2 = 0.0022$; $p = 0.089$). Figure 5 is a box-and-whisker plot for the COGCC dataset with outliers for the domestic and irrigation wells only; again, the interquartile ranges show no year-to-year increasing trend.

Mann-Whitney statistical test comparisons were made between each year for which dissolved methane data were available. Tables 2 and 3 summarize the Mann-Whitney tests for the year-to-

⁴ 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.

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year comparisons for the Albrecht and expanded COGCC methane datasets, respectively. The results indicate that the median methane value was significantly different (at the 95% confidence level) between several years for the Albrecht data; however, there were no successive years for the COGCC data where the difference was significant. For the Albrecht data, for years where there was a significant difference in the median value, that difference was not always an increase. In fact, from 2004 to 2005, which represents Albrecht's most recent data, and the years with the greatest number of measurements, there was a significant decrease for methane concentrations. The Mann-Whitney test for the COGCC data, excluding the monitoring wells, suggests that there is not a statistically significant temporal trend for increasing methane concentrations.

The Thyne Report (page 9) states that “pre-drilling methane values did not exceed 1 ppm.... therefore, values above 1 ppm dissolved methane are assumed to indicate impact.” This statement is impossible to support with either the Albrecht or COGCC dataset, as wide-scale methane measurements are only available after drilling was well established in the area. Furthermore, non-drilling impacted groundwater can have methane values in excess of 1 ppm as has apparently occurred in several wells where gas composition and isotopic signatures indicate the presence of biogenic methane (see the “Methane Sources” section, below).

Chloride Trends

The presence of a temporal trend for increasing chloride concentration in groundwater as asserted in the Thyne Report (pages 2 and 23), is not supported by analysis of the Albrecht chloride data or analysis of the COGCC chloride data.

Similar to the dissolved methane concentration results, the data for chloride were assessed for a temporal trend. The Albrecht chloride data were plotted as a time-series (Figure 6). A linear trend-line was fitted to the data, but no significant trend was detected in the data ($r^2 = 0.0002$; $p = 0.625$). Figure 7 shows the Albrecht chloride data as a box-and-whisker plot with outliers. The

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year-to-year difference in the median values is smaller than the variability in the data and the interquartile ranges for each year show no increasing trend with time.

The potential temporal trend in chloride was also assessed with data from the COGCC database. The time-series plot for chloride shows no significant trend in chloride (Figure 8; $r^2 = 0.00003$; $p = 0.831$). Figure 9 shows a box-and-whisker plot for the COGCC chloride data with outliers for the domestic and irrigation wells only. The interquartile ranges again show no year-to-year increasing trend.

Mann-Whitney statistical test comparisons were made between each year for which chloride data were available. Tables 4 and 5 summarize the Mann-Whitney tests for the year-to-year comparisons for the Albrecht and COGCC chloride datasets, respectively. The results indicate that the median chloride value was significantly different (at the 95% confidence level) between several successive years of measurements for the Albrecht data and that the changes included both significant increases and significant decreases. For the COGCC data for the two periods where successive years of chloride measurements were significantly different (1997-1999 and 2007-2008), the trend in both years was for declining concentrations. As with the dissolved methane measurements, the primary difference between the Albrecht and COGCC chloride data is the removal of monitoring well measurements from the COGCC data. The Mann-Whitney test for the COGCC data indicates that there is not a statistically significant temporal trend for increasing chloride concentrations.

Chloride Background Concentrations

The Thyne Report suggests that groundwater chloride concentrations greater than 10 mg/L represent impacts from produced water due to natural gas drilling and production activities (page 16). To evaluate this assertion, and to examine natural background levels of chloride in groundwater in the area, chloride and sulfate concentrations were compared using COGCC data from both north and south of the Colorado River. North of the river, almost all samples represent background conditions prior to natural gas drilling and production. As shown in

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Figures 10 and 11, the median chloride and sulfate concentrations are higher for wells north of the river than wells south of the river.

Because sulfate is commonly reduced in the presence of organic compounds, it is usually absent or present only at very low concentrations in produced water. As such, produced waters from Williams Fork gas-producing zones with relatively high total dissolved solids (TDS) concentrations should have very small sulfate/chloride ratios. All produced water samples collected for the Phase II Hydrogeologic Investigation (SSPA, 2008) had sulfate/chloride ratios of less than 0.003.

Figure 12 shows that the median sulfate/chloride ratio south of the river is lower than the median ratio for samples from north of the river. This may suggest different sources for the groundwater, including possible influences on the groundwater from deeper sources, or local impacts due to anthropogenic sources such as road salt contamination or agricultural water recharge. However, as shown in Figure 13 by the overlap in sulfate and chloride concentrations (i.e., sulfate/chloride ratios) between many of the wells north of the Colorado River and south of the river, especially for higher TDS waters, elevated chloride concentrations alone are not a definitive indicator for produced water impacts. Figure 13 shows 1) that high chloride concentrations can occur naturally in the groundwater in the Mamm Creek area and 2) that sulfate/chloride ratios can help distinguish between groundwater that is likely not influenced by produced waters and groundwater that may be, and the possible degree to which mixing of the different water sources may be occurring. What cannot be ascertained from Figure 13 is whether influences that may be from deeper waters are natural or caused by natural gas drilling and production activities.

Methane Sources

While analysis of the available data for groundwater in the Mamm Creek area does not indicate that a statistically significant increase is occurring in methane concentrations with time and increased drilling, methane is present in many wells in the area. The potential sources of

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methane have been addressed in previous reports (“Phase I Hydrogeologic Characterization of the Mamm Creek Field Area in Garfield County,” URS, 2006; and “Phase II Hydrogeologic Characterization of the Mamm Creek Field Area, Garfield County, Colorado,” SSPA, 2008). This section is meant to revisit the sources of methane in light of the expanded COGCC database and comments in the Thyne Report.

Methane in groundwater can be biogenic, thermogenic, or abiotic in origin. Biogenic methane is produced either by microbial fermentation of acetate or by microbial reduction of carbon dioxide through a process called methanogenesis. Thermogenic (or thermocatalytic) methane is produced during the thermal breakdown of higher molecular weight hydrocarbons, including crude oil and coal. Abiotic methane is produced at great depths in the earth under highly reducing conditions.

The origin of methane, as well as the loss of methane by microbial oxidation is reflected in the stable isotope signatures for deuterium (^2H or D) and carbon-13 (^{13}C) of the methane (Figure 14). Thermogenic methane tends to be depleted in ^{13}C and D , but to a lesser extent than biogenic methane. Biogenic methane generation by acetate fermentation is a process that occurs in the presence of organic matter after all alternate electron acceptors have been depleted. Methane produced by acetate fermentation (e.g., swamp gas, landfill gas) is highly depleted in both ^{13}C and D , although this depletion is to some extent dependent on the depletion of the original organic matter. Biogenic methane generated by carbon dioxide reduction is highly depleted in ^{13}C , but less depleted in D than methane generated by acetate fermentation (Krzycki et al, 1987). Methane can be generated by both acetate fermentation and carbon dioxide reduction in groundwater (Hansen et al, 2001, Schlesinger, 1991). The D signature of methane (D_{CH_4}) generated by carbon dioxide reduction is somewhat dependent on the deuterium signature of the water ($\text{D}_{\text{H}_2\text{O}}$). The ^{13}C fractionation is dependent on the concentration and $^{13}\text{C}/^{12}\text{C}$ ratio of inorganic carbon constituents (dissolved carbon dioxide, bicarbonate, and carbonate) which supply carbon for reductive methanogenesis.

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Bicarbonate is usually the dominant anion in groundwater due to the dissolution of carbonate minerals (e.g. Langmuir, 1997). In addition to carbonate mineral dissolution, inorganic carbon can be incorporated into groundwater from atmospheric carbon dioxide (more important near recharge zones) and degradation of organic carbon, which releases carbon dioxide as a byproduct. Much of the groundwater utilized for domestic supply purposes in the Mamm Creek area has bicarbonate as the major anion (URS, 2006; SSPA, 2008), indicating that carbon dioxide is available for methanogenesis. Inorganic carbon that arises from carbonate weathering tends to have $^{13}\text{C}/^{12}\text{C}$ ratios similar to carbonate minerals, while inorganic carbon arising from degradation of organic matter would be depleted in ^{13}C .

The COGCC database includes 602 groundwater gas samples that provide $^{13}\text{C}/^{12}\text{C}$ and D/ ^1H isotopic ratios ($\delta^{13}\text{C}$ and δD , respectively) for methane. (For an explanation of the measurement of isotope ratios, see Clark and Fritz, 2000; SSPA, 2008.) These sample results are plotted on Figure 14 against the regions predicted for biogenic and thermogenic methane.

As microbial processes that generate methane (“C1”) tend to do so without the concurrent generation of higher carbon number hydrocarbons (e.g., ethane, or “C2”; propane, or “C3”), the ratio of C1 to C2+C3 hydrocarbons can also be used to distinguish between methane sources. In the COGCC database, hydrocarbon gas composition samples and $\delta^{13}\text{C}$ results were available for 171 domestic well samples, 313 monitoring well samples, 67 gas well samples (including production gas and gas from produced water), 49 seep samples, and 4 surface water samples. These data are plotted in Figure 15 on a Bernard diagram (Whiticar, 1990, after Bernard et al., 1978), with regions expected for thermogenic gas (“wetter”, i.e. more C2+C3 hydrocarbons, and less depleted in ^{13}C) and biogenic gas (low C1/(C2+C3) ratio, more depleted in ^{13}C).

Methane is stable under very reducing conditions which may not be present everywhere within an aquifer. As groundwater containing dissolved methane flows into areas where conditions are less reducing or where mixing with oxidized recharge waters occurs, the methane becomes unstable and can be oxidized to carbon dioxide. This conversion can occur both abiotically as

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well as through bacterial mediation. As the methane is oxidized to carbon dioxide, the remaining methane becomes progressively enriched in ^{13}C . In some cases, this isotopic fractionation can make oxidized bacterial methane isotopically indistinguishable from thermogenic methane, thereby complicating interpretation of methane sources by stable isotope signatures alone. Therefore, trends showing increasing $\delta^{13}\text{C}$ of methane with increasing carbon dioxide to methane ratio can be used to identify methane oxidation. Figure 16 plots $\delta^{13}\text{C}$ against carbon dioxide/methane and illustrates the trend that results from the oxidation of methane to carbon dioxide.

Evaluation of Figures 14 through 16 for data from the Mamm Creek area indicates the following:

- There is very little groundwater used for domestic supplies that contains methane formed by biogenic fermentation processes. The cluster of monitoring well samples in the biogenic fermentation field likely results from proximity to buried and decaying plant mass associated with West Divide Creek.
- Samples with isotopic signatures in both the thermogenic and biogenic carbonate reduction fields show distinct indications of oxidation. This is apparent for several domestic wells and monitoring wells that have been sampled multiple times over the last 5 years. The oxidation shifts do not mask the origin of the gases in these samples.
- There is no basis for the assertion in the Thyne Report that reduction of Williams Fork Formation thermogenic carbon dioxide is producing methane with a biogenic signature. Contrary to Thyne's suggestion that carbon dioxide proportions of greater than 20% may occur in Williams Fork gas from the Mamm Creek area, the highest proportion measured in analyses from the COGCC database was 3.5%, with the majority of analyses being less than 1%. (Four natural gas samples collected for the Phase II Hydrogeologic Investigation in 2007 contained from 24 to 134 times more methane than carbon dioxide on a molar percent basis; much more than the 3.5 times or smaller value for methane/carbon dioxide that would occur if 22% of the gas were carbon dioxide.)

Since the methane and carbon dioxide would migrate together, the impact of the methane formed from reduced thermogenic carbon dioxide on the overall $\delta^{13}\text{C}$ of the methane in groundwater would be minimal. In other words, methane plotting in the carbonate reduction field is of biogenic origin; it is not from impacted water containing only reduced thermogenic carbon dioxide with no accompanying thermogenic methane, because that situation is extremely unlikely to occur.

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- There is methane in several domestic and monitoring wells that appears to be of thermogenic origin or of mixed thermogenic and biogenic origin. With the exception of two known wells and the area affected directly by the leak from the Schwartz 2-15B well, however, it is difficult to show a cause-effect relationship between drilling and the presence of methane in the wells. This is especially true in the southeast portion of the Mamm Creek area near the axis of the Divide Creek Anticline where several water wells contained dissolved methane concentrations greater than 1 mg/L. At the time they were initially sampled many of these wells were ½ to 1 mile from the nearest existing gas wells (most of which had been plugged and abandoned for many years). Gas composition and isotope samples collected from five of these wells for the Phase II Hydrogeologic Investigation in 2007, indicated that based on $\delta^{13}\text{C}$ and δD values that thermogenic methane may be a component of the gas; although a comparison of methane to heavier hydrocarbons indicates that the gas is likely not the same as the conventional natural gas produced from the Williams Fork Formation in the Mamm Creek area. Since this area is known to be hydrostatically overpressured (URS, 2006), it is possible that the migration of thermogenic methane and deeper groundwater into water supply aquifer occurs naturally in the area.
- Dissolved methane in a number of wells is enriched in ^{13}C relative to thermogenic and/or biogenic gases in the area. These samples also have elevated carbon dioxide to methane ratios, indicating that the original methane isotope signature has been modified by oxidation. In examining the systematic variations in $\delta^{13}\text{C}$ of methane versus carbon dioxide to methane ratios, the vast majority of these samples are more consistent with oxidation of bacterial methane than of thermogenic methane.

CONCLUSIONS

The Thyne Report makes several assertions that water quality conditions are changing as a direct result of natural gas drilling and production activities in the Mamm Creek area. As the report correctly points out, however, and as was pointed out in the Phase II Hydrogeologic Investigation (SSPA, 2008), it is difficult to confidently show that water quality conditions and trends in the region are directly impacted by the gas drilling and production activities without having the benefit of comparing pre-drilling baseline data against data collected over the last eight-plus years. Nonetheless, there are several points which should be reiterated.

- The apparent trends of increasing methane and chloride with increasing natural gas drilling are not statistically valid when the variability of the sample results is considered. Additionally, the focus of sampling on known or suspected trouble areas likely contributes to what the Thyne Report considered to be increasing percentages of methane samples with concentrations above 1 mg/L.

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- Statements asserting that elevated chloride concentrations in groundwater are a direct result of increasing natural gas drilling and production are not strictly correct based on a comparison of sulfate/chloride ratios for sample from north of the Colorado River with those from the Mamm Creek area. As stated in SSPA (2008), there appear to be two distinct groundwater sources in the Mamm Creek area. While the higher TDS (and sulfate and chloride) water in the eastern half of the area may indicate a mixing of groundwater from deeper in the Wasatch or in the Williams Fork Formation in some cases, it does not *a priori* indicate that this mixing is due to natural gas production. The region in the eastern half of the Mamm Creek area with relatively high TDS groundwater is extensive and includes areas of little or no drilling (see Figure 5-14 in URS, 2006).
- Natural gas drilling and production is distributed across much of the Mamm Creek area while methane is present in groundwater primarily in the eastern half of the area. With the exception of two known domestic wells impacted with thermogenic methane and the West Divide Creek seep area, however, the groundwater samples containing methane with a possible thermogenic signature are located in the southeast corner of the Mamm Creek area. This is an area close to the axis of the Divide Creek Anticline where the depth to the Williams Fork Formation is shallow and where known hydrostatic overpressure conditions exist (URS, 2006). It is also an area where thermogenic methane was detected in water supply wells prior to the increased natural gas drilling of the last five years. Additionally, gas composition and isotope analyses taken together indicate that while the gas may be thermogenic or contain a thermogenic component, it is distinct from the conventional natural gas produced from the Williams Fork Formation in the Mamm Creek field.

REFERENCES

- Albrecht, T. R., 2007. Using Sequential Hydrochemical Analyses to Characterize Water Quality Variability at Mamm Creek Gas Field Area, Southeast Piceance Basin, Colorado. Colorado School of Mines Thesis.
- Clark, I. D., and P. Fritz, 2000. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York. 328 p.
- Hansen, L. K., R. Jakobsen, and D. Postma, 2001. Methanogenesis in a shallow sandy aquifer, Romo, Denmark. *Geochimica et Cosmochimica Acta*: 65(17), pp. 295-2935.
- Krzycki, J. A., W. R. Kenealy, M. J. DeDiro, and J.G. Zeikus, 1987. Stable carbon isotope fractionation by *methanosarcina barkeri* during methanogenesis from acetate, methanol, or carbon dioxide-hydrogen. *Applied and Environmental Microbiology*: 53(10), pp. 2597-2599.

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Langmuir, D., 1997. *Aqueous Environmental Chemistry*. Prentice Hall, New Jersey. 600 p.

Schlesinger, W. H., 1991. *Biogeochemistry: An Analysis of Global Change*. Academic Press, Inc., San Diego. 443 p.

SSPA, 2008. Phase II Hydrogeologic Characterization of the Mamm Creek Field Area, Garfield County, Colorado. Prepared for: Board of County Commissioners, Garfield County, Colorado.

Thyne, G. 2008. Review of Phase II Hydrogeologic Study. Prepared for Garfield County.

URS Corporation, 2006. Phase I hydrogeologic characterization of the Mamm Creek field area in Garfield County. Prepared for Board of County Commissioners, Garfield County, Colorado.

Whiticar, M. J., 1990. A geochemical perspective of natural gas and atmospheric methane. *Advances in Organic Geochemistry*, Vol. 16, Nos. 1-3, pp. 531-547.

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FIGURES

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- Figure 3 Box-and-whisker plot of Albrecht methane data, outliers included.
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- Table 3 Year-to-year comparison of COGCC methane data using Mann-Whitney test.
- Table 4 Year-to-year comparison of Albrecht chloride data using Mann-Whitney test.
- Table 5 Year-to-year comparison of COGCC chloride data using Mann-Whitney test.



FIGURES



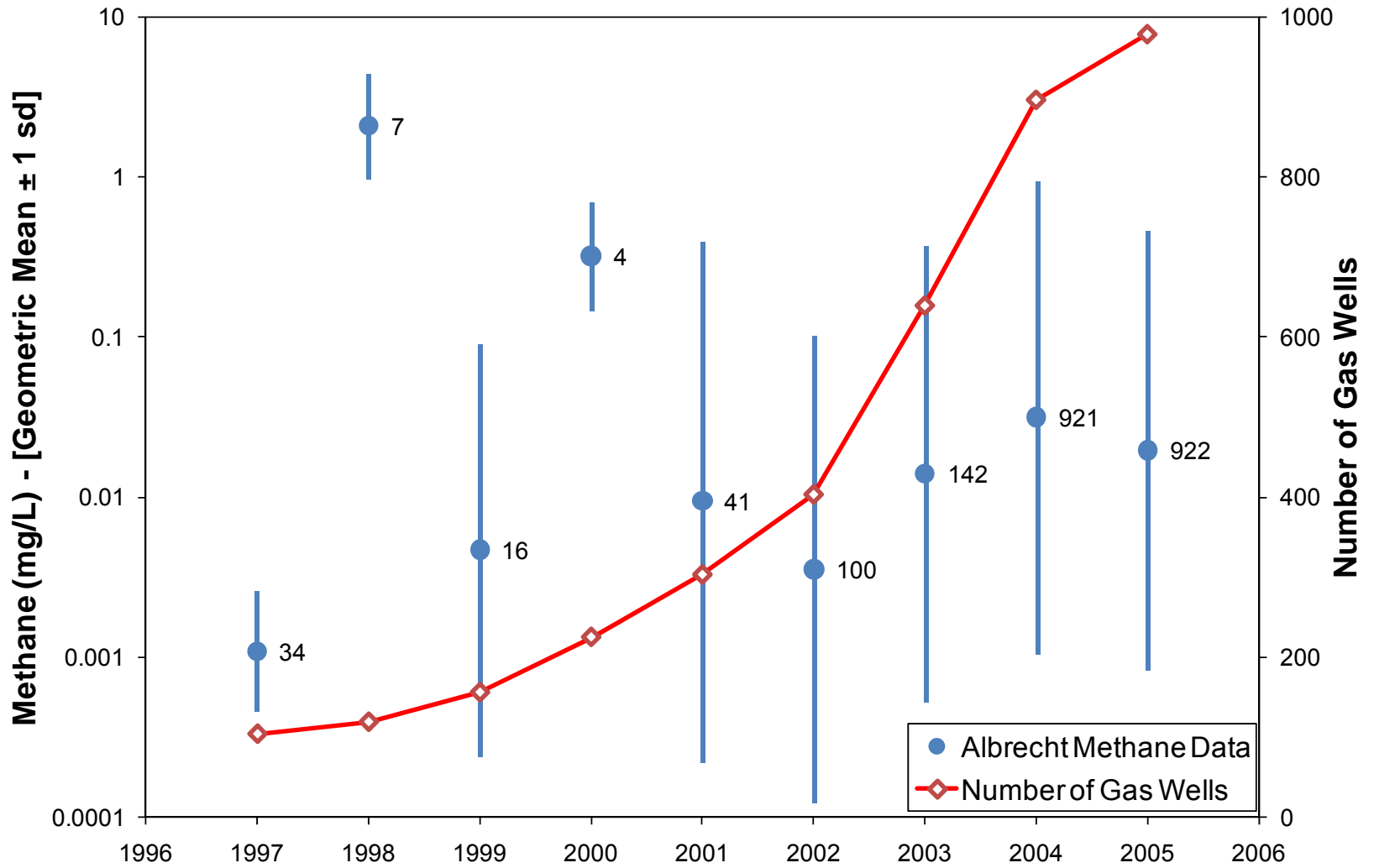
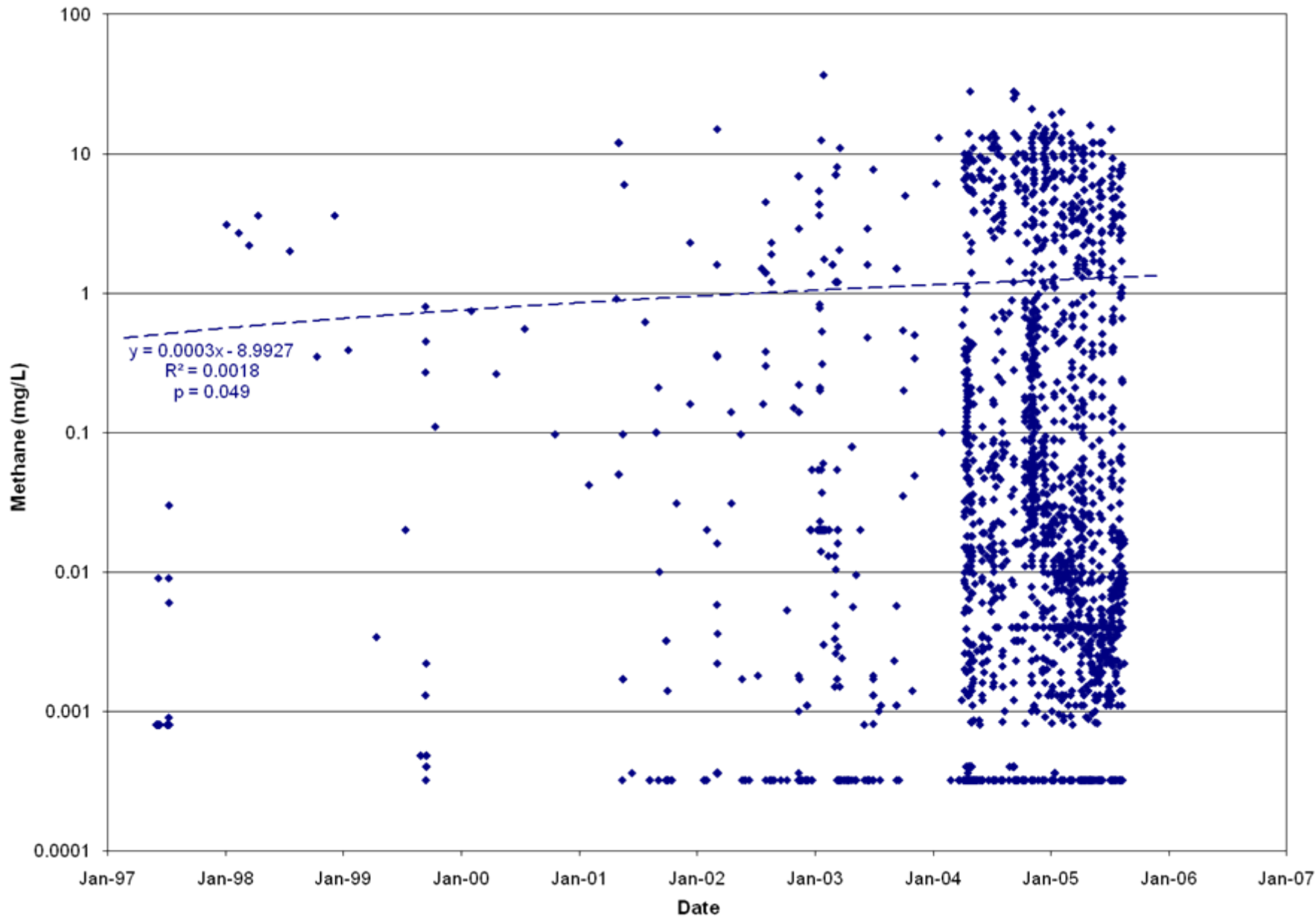


Figure 1. Geometric mean and geometric standard deviation of the Albrecht (2007) data.



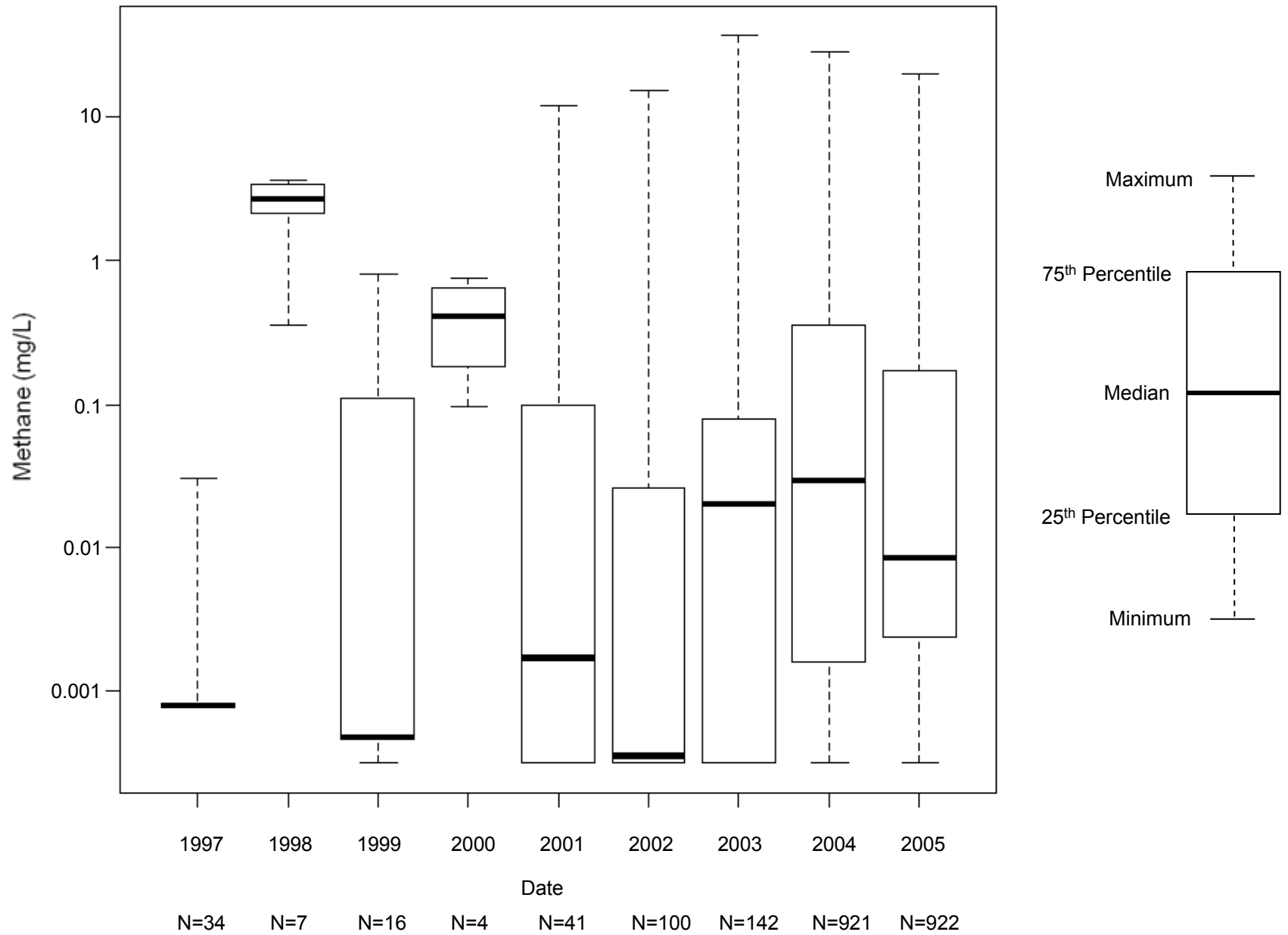


Figure 3. Box-and-whisker plot of Albrecht methane data, outliers included.

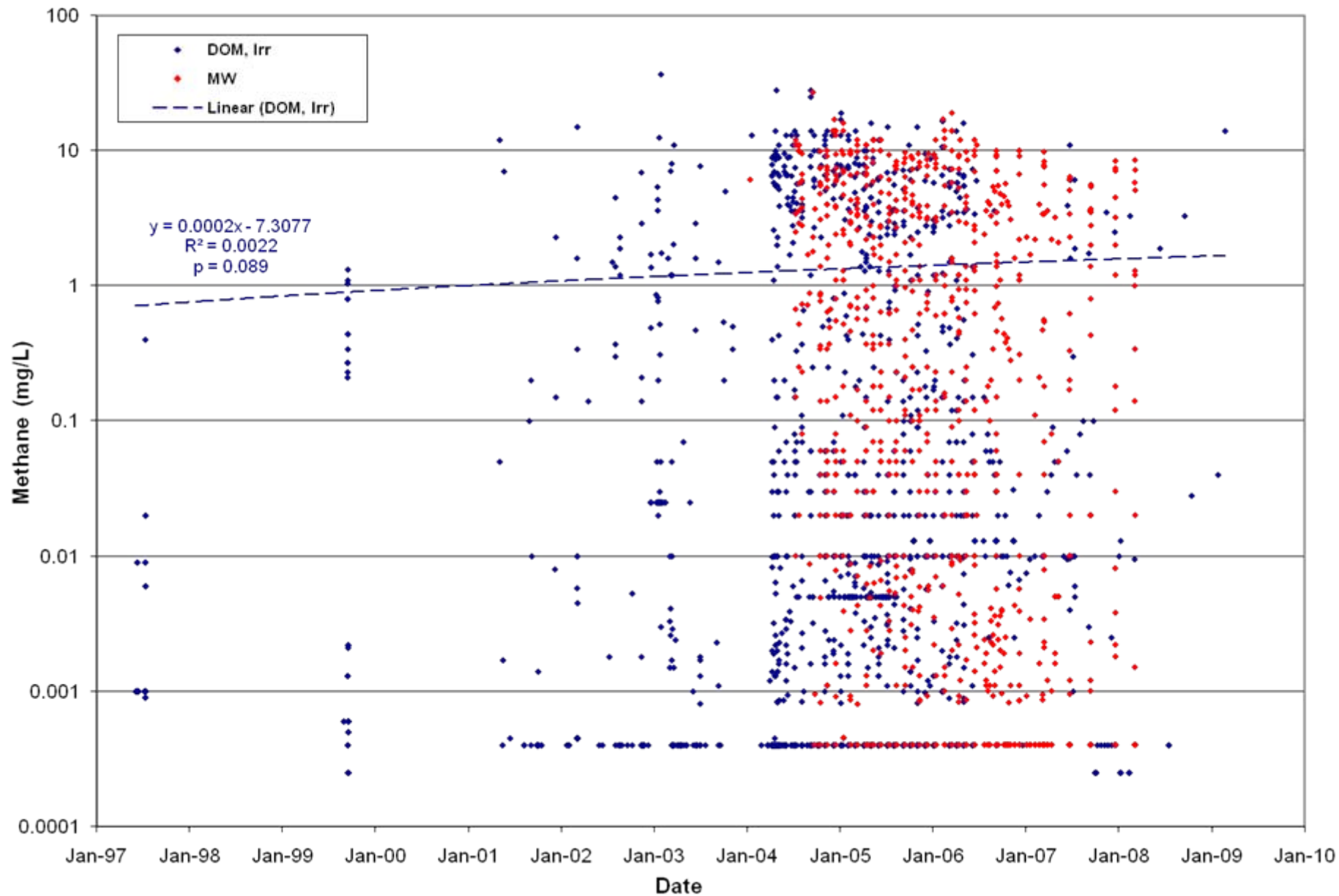


Figure 4. Time series plot of COGCC methane data.

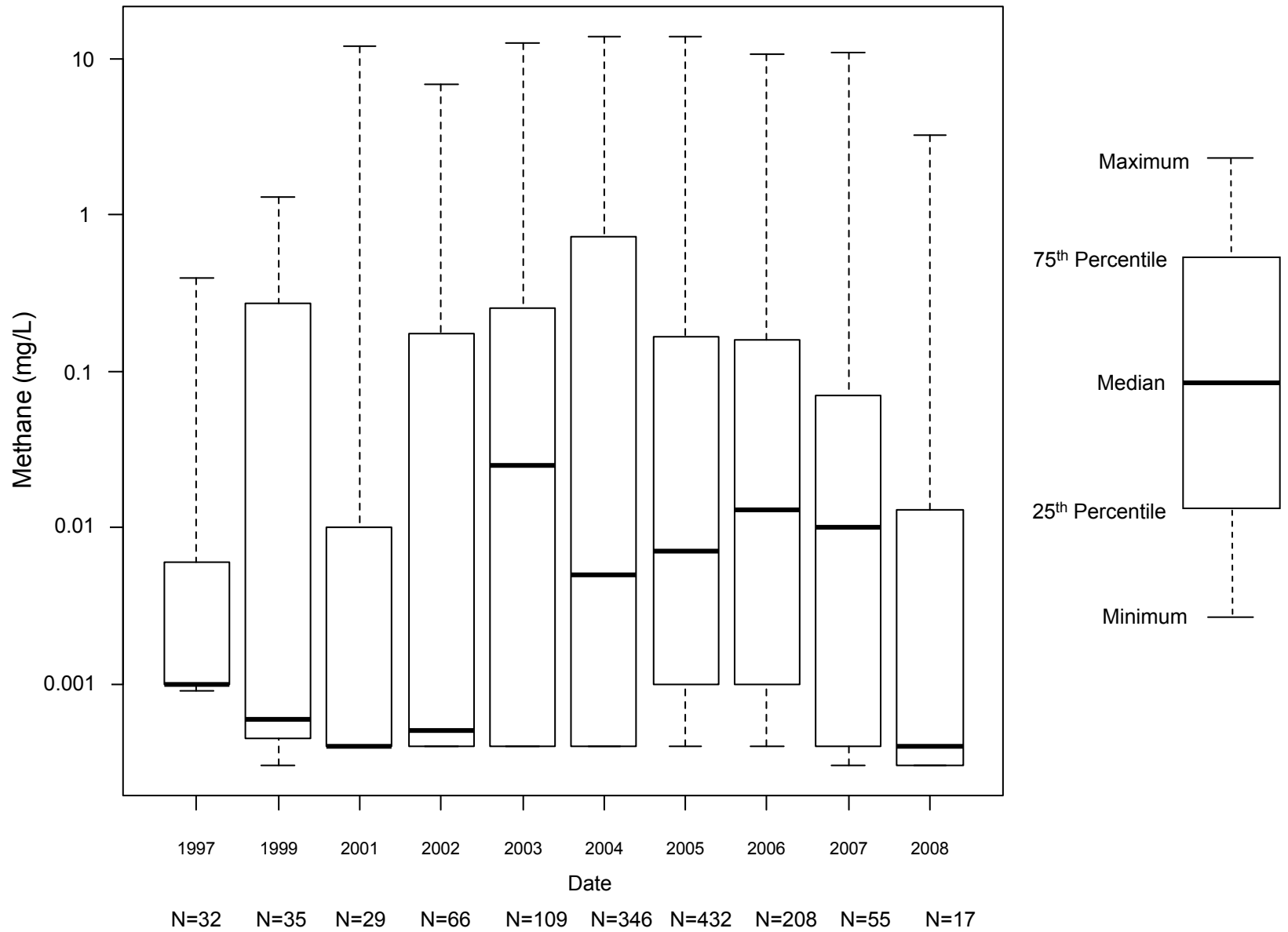


Figure 5. Box-and-whisker plot of COGCC methane data, outliers included.

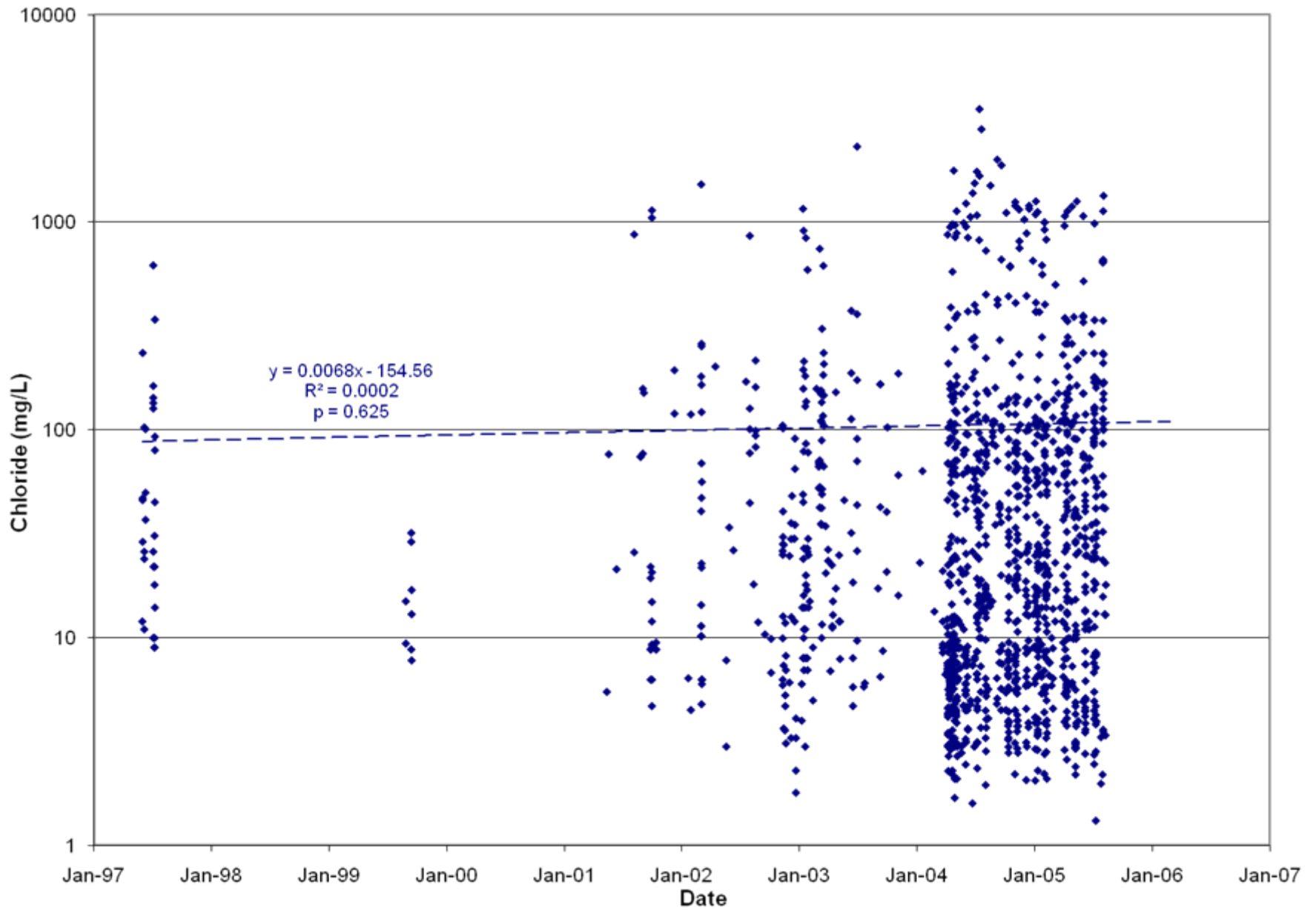


Figure 6. Time series plot of the Albrecht chloride data.

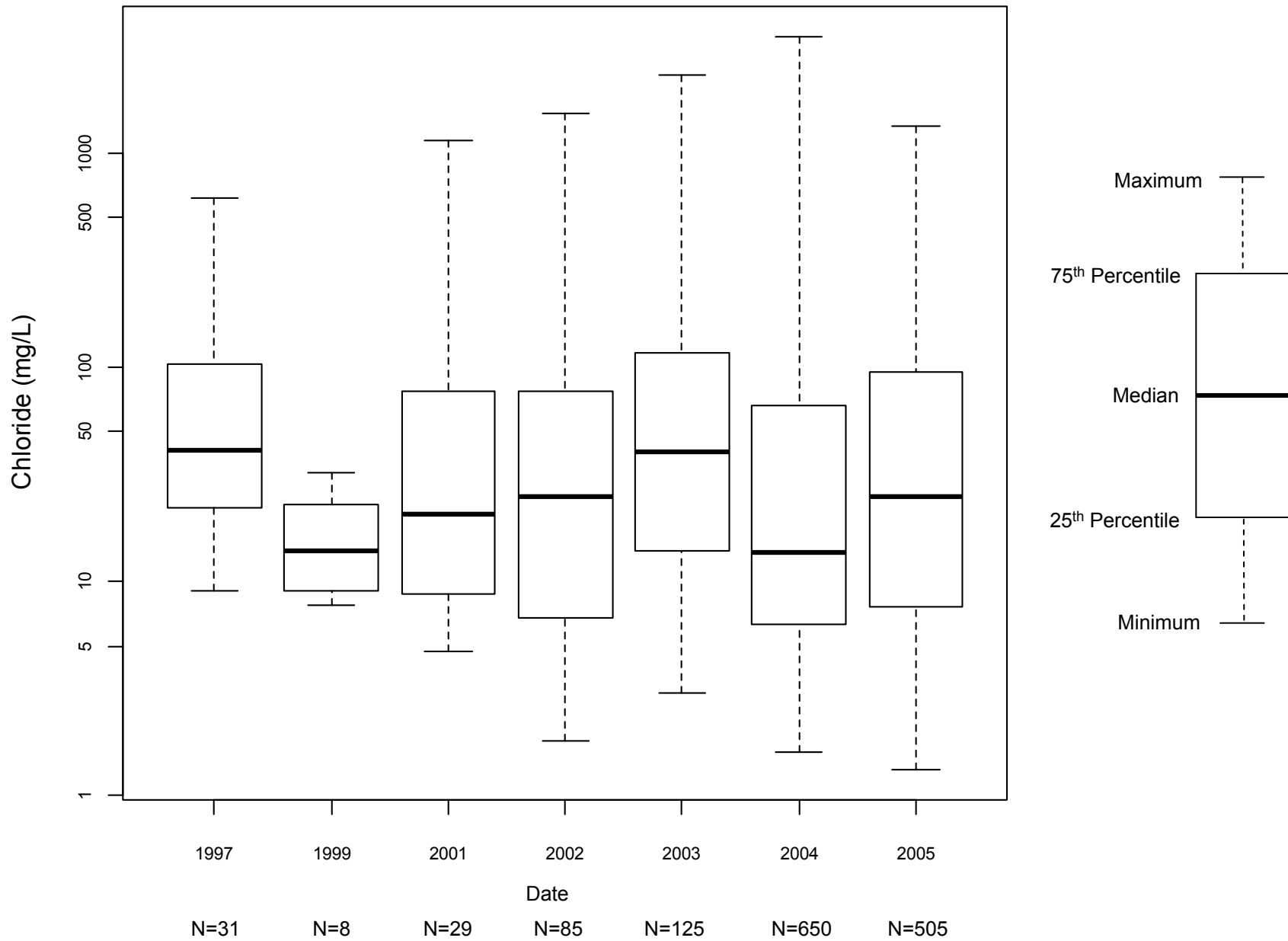


Figure 7. Box-and-whisker plot of Albrecht Chloride data, outliers included.

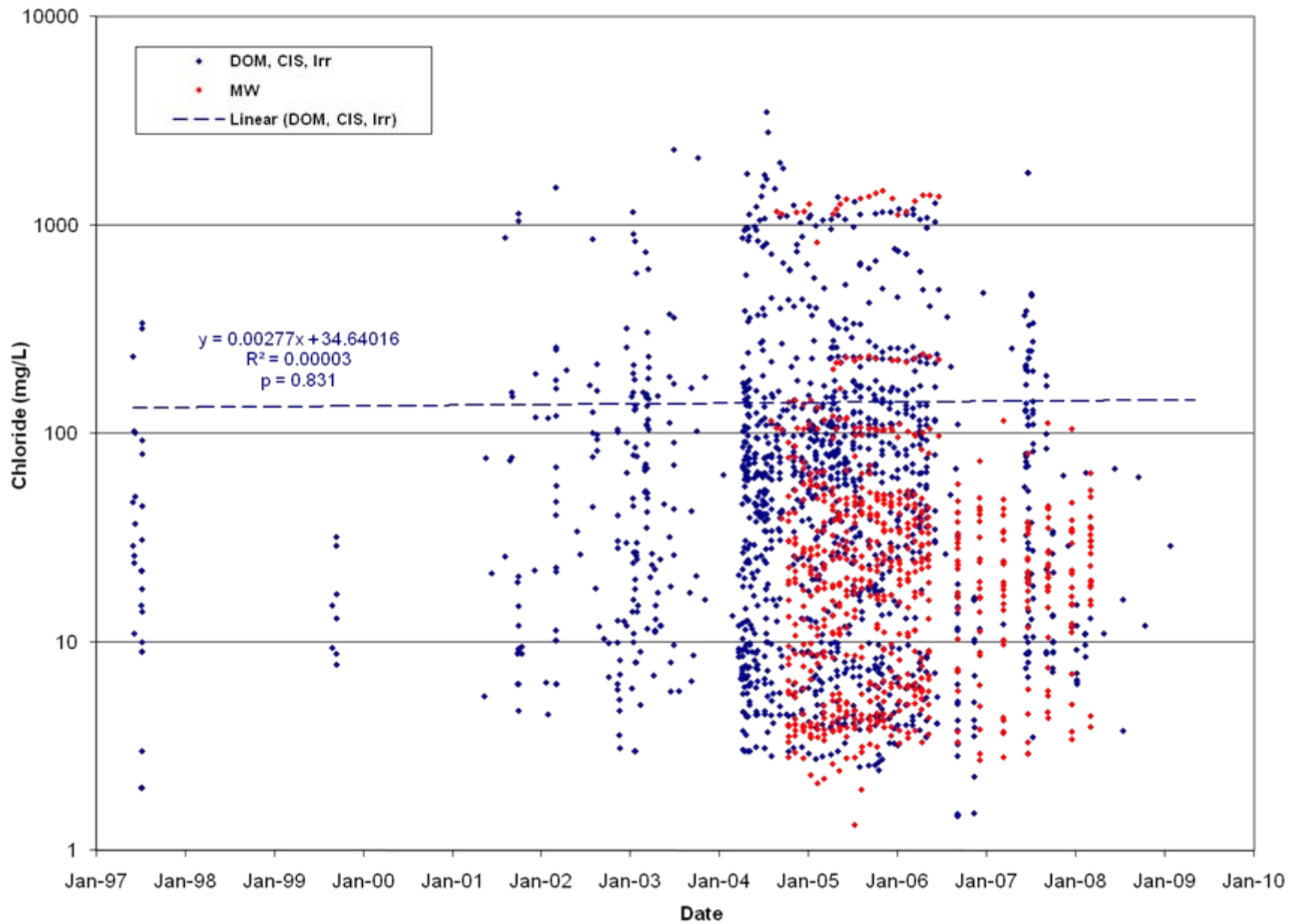


Figure 8. Time series plot of COGCC chloride data.

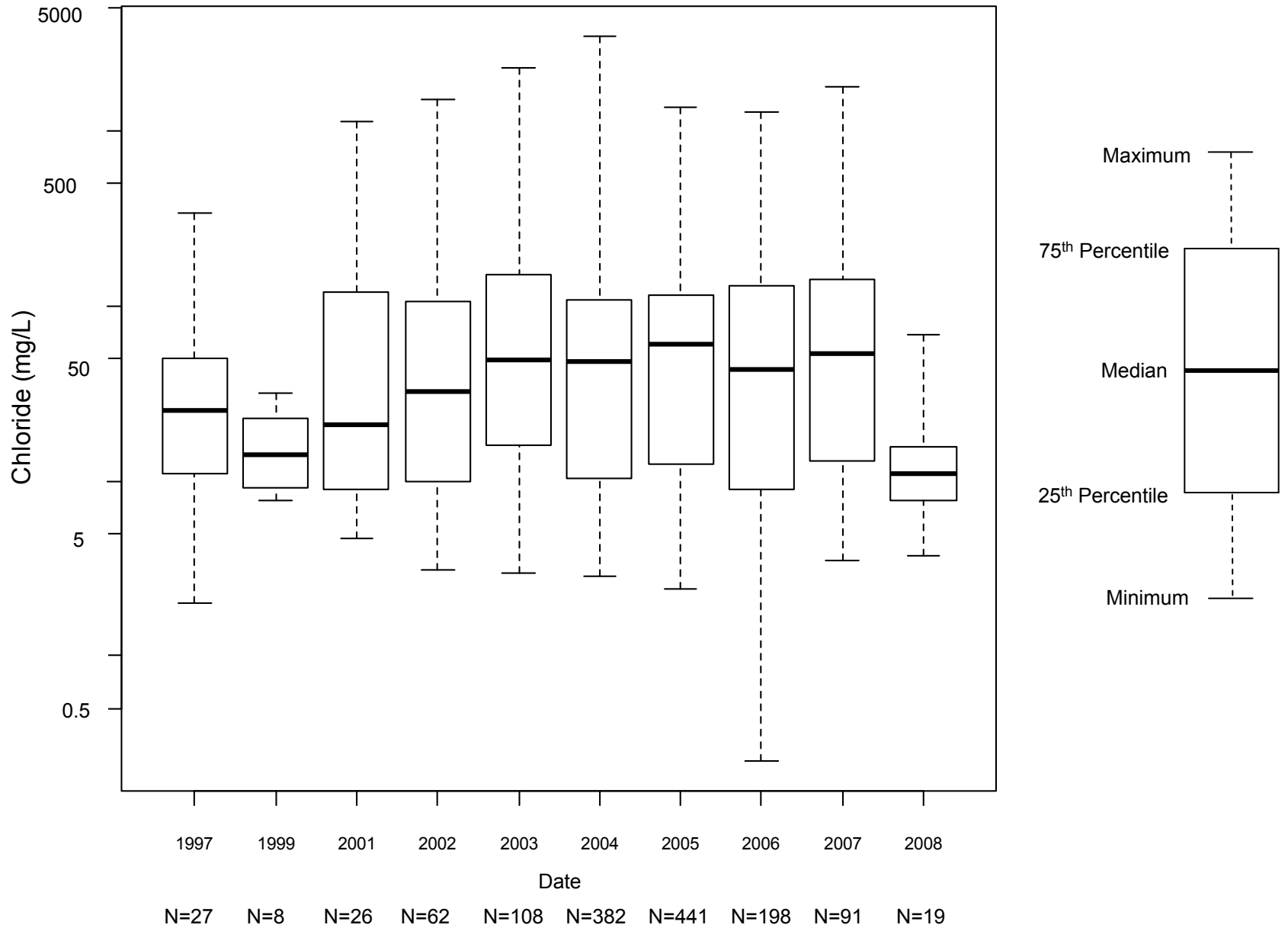


Figure 9. Box-and-whisker plot of COGCC chloride data, outliers included.

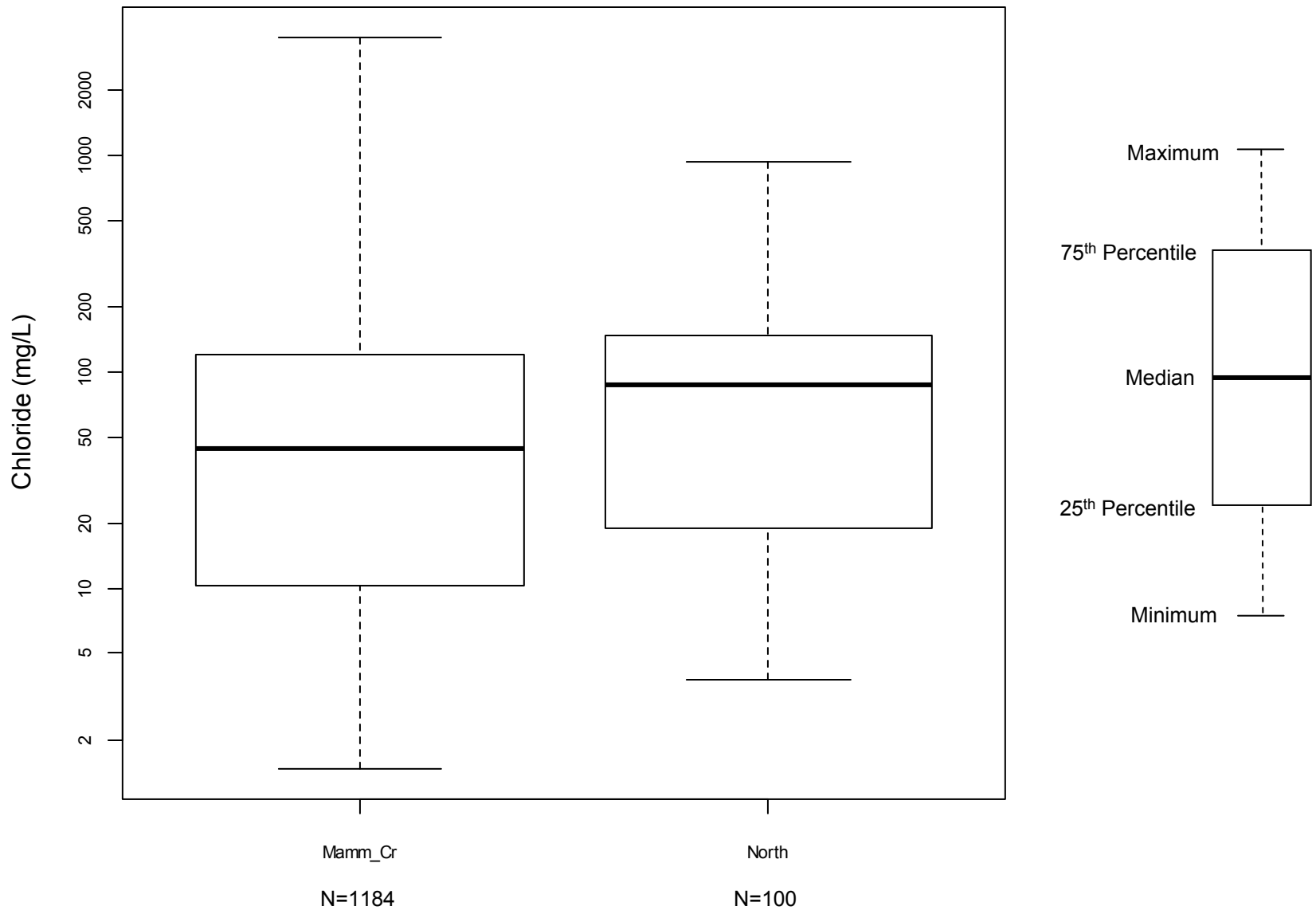


Figure 10. Box-and-whisker plot of chloride concentration for wells located North and South of the Colorado River.

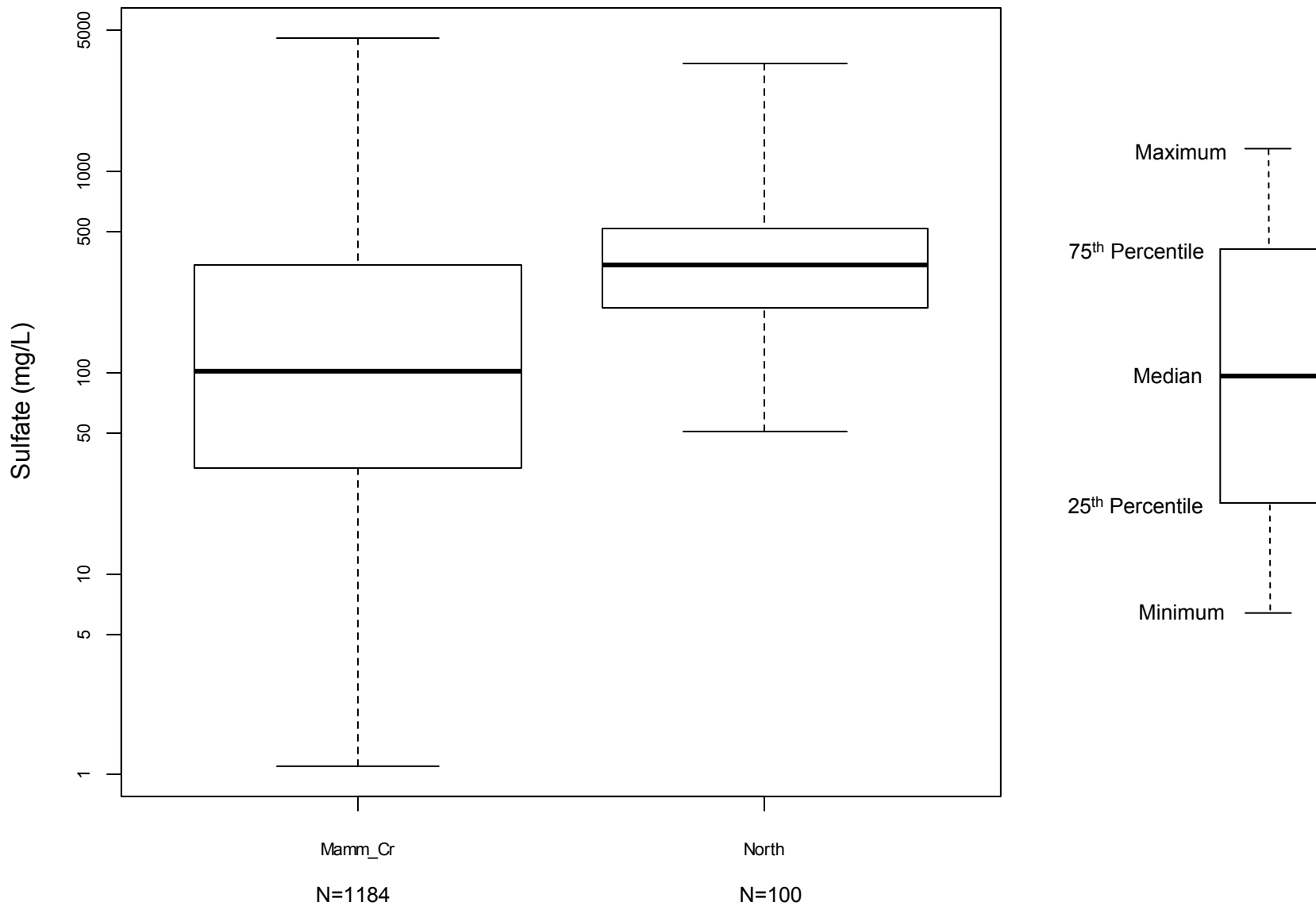


Figure 11. Box-and-whisker plot of sulfate concentration for wells located North and South of the Colorado River.

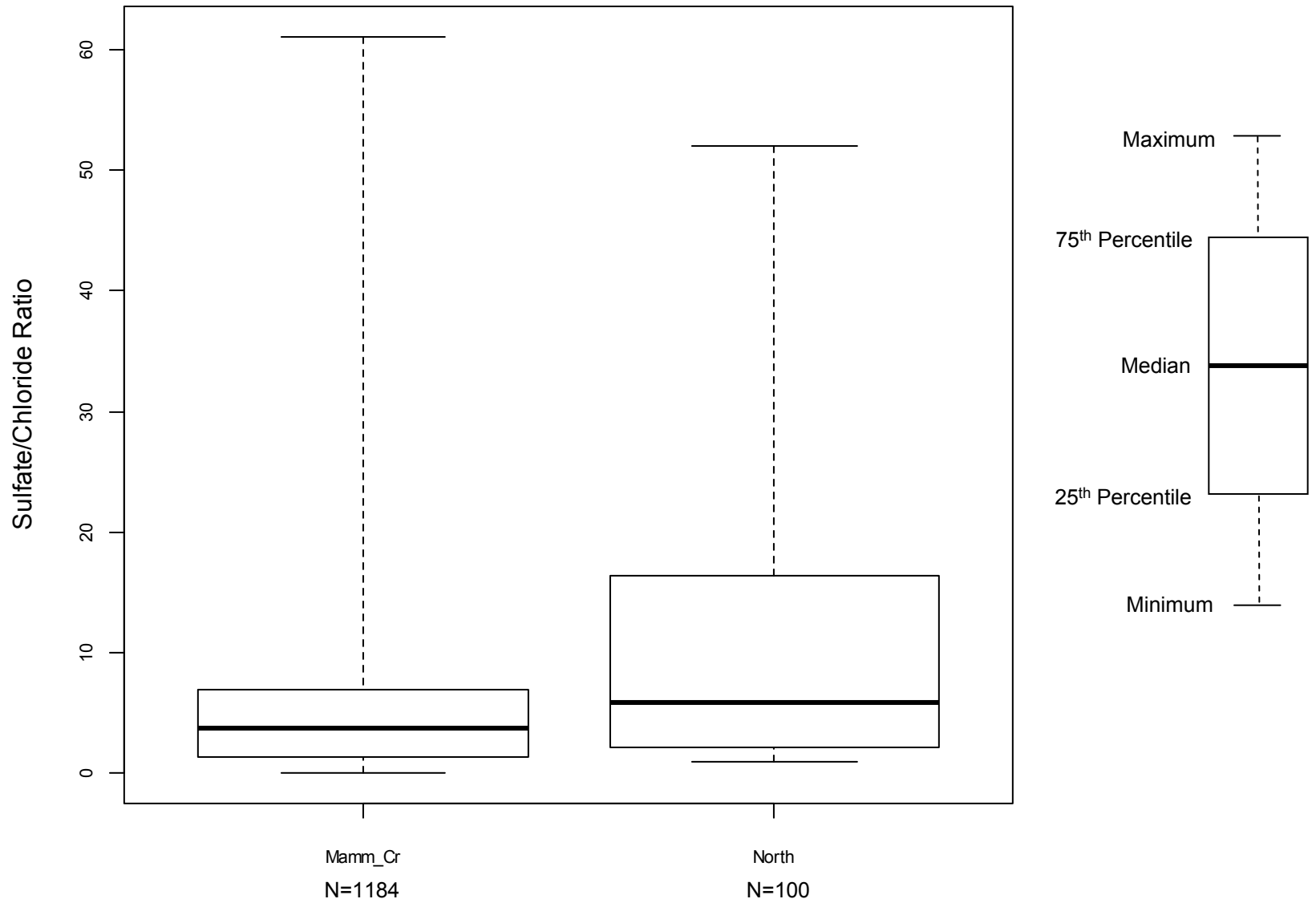


Figure 12. Box-and-whisker plot of the ratio of sulfate to chloride concentration for wells located North and South of the Colorado River.

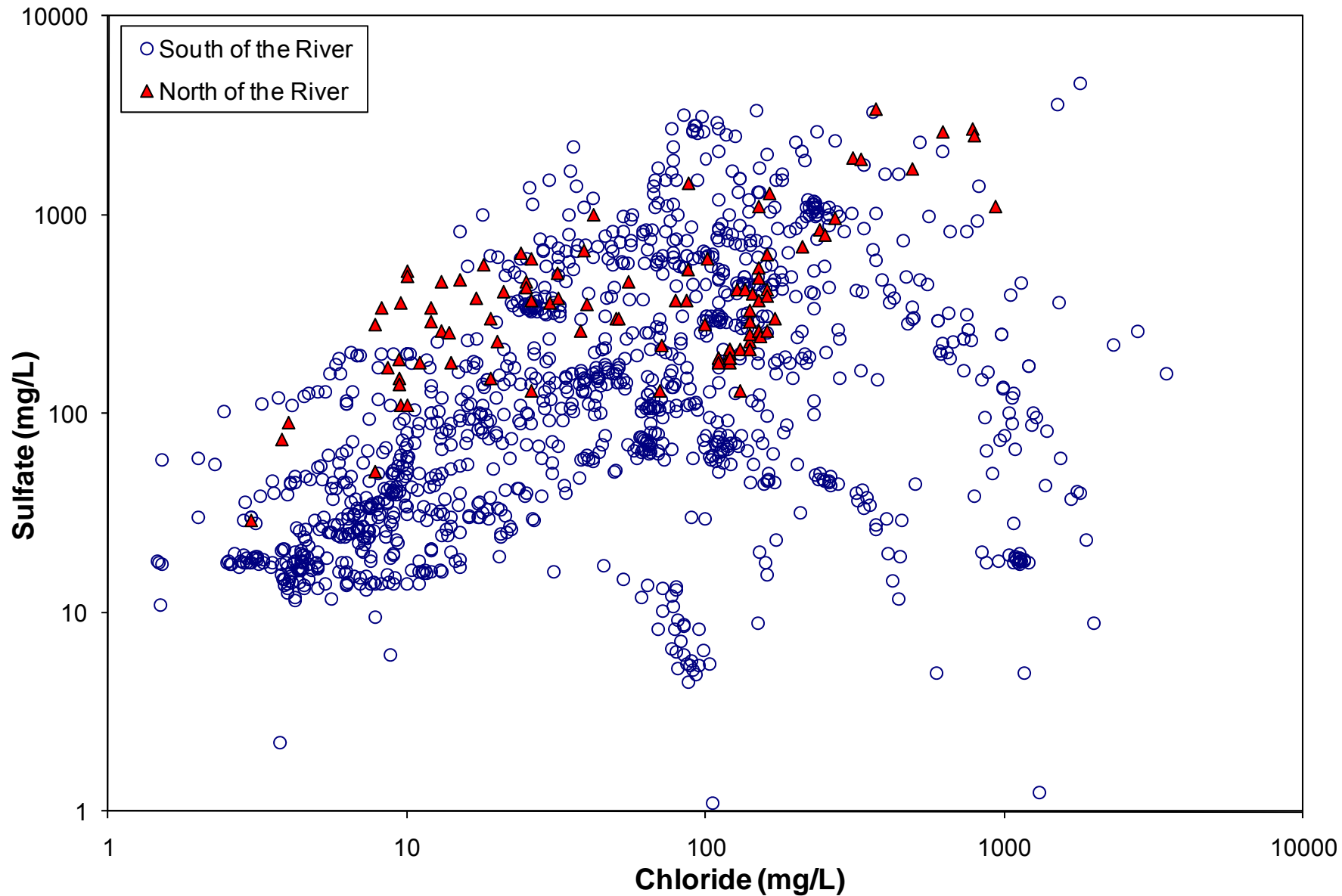


Figure 13. Relationship between sulfate and chloride concentrations in wells located North and South of the Colorado River.

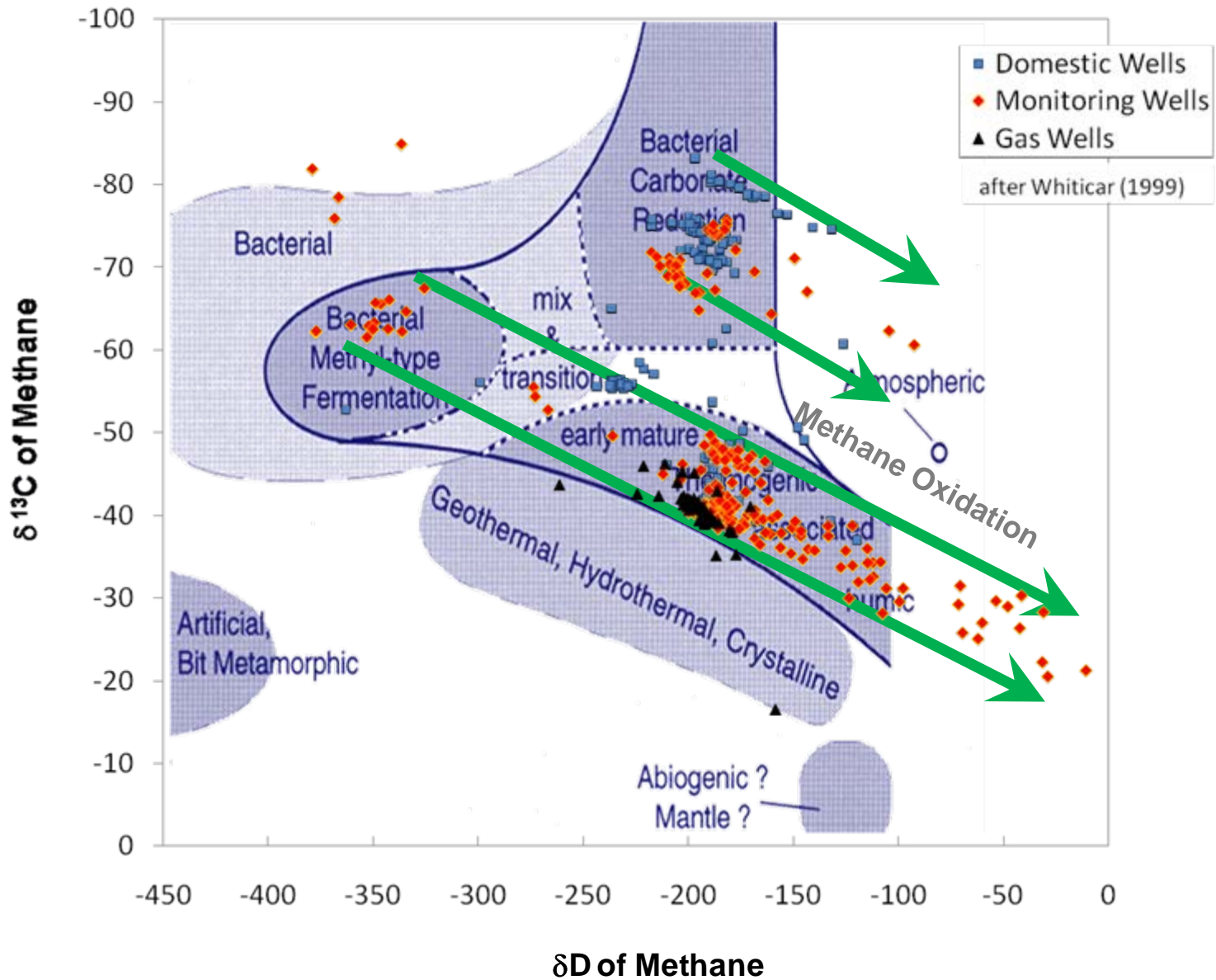


Figure 14. Carbon and hydrogen isotopes of methane with regions of biogenic and thermogenic natural gases.

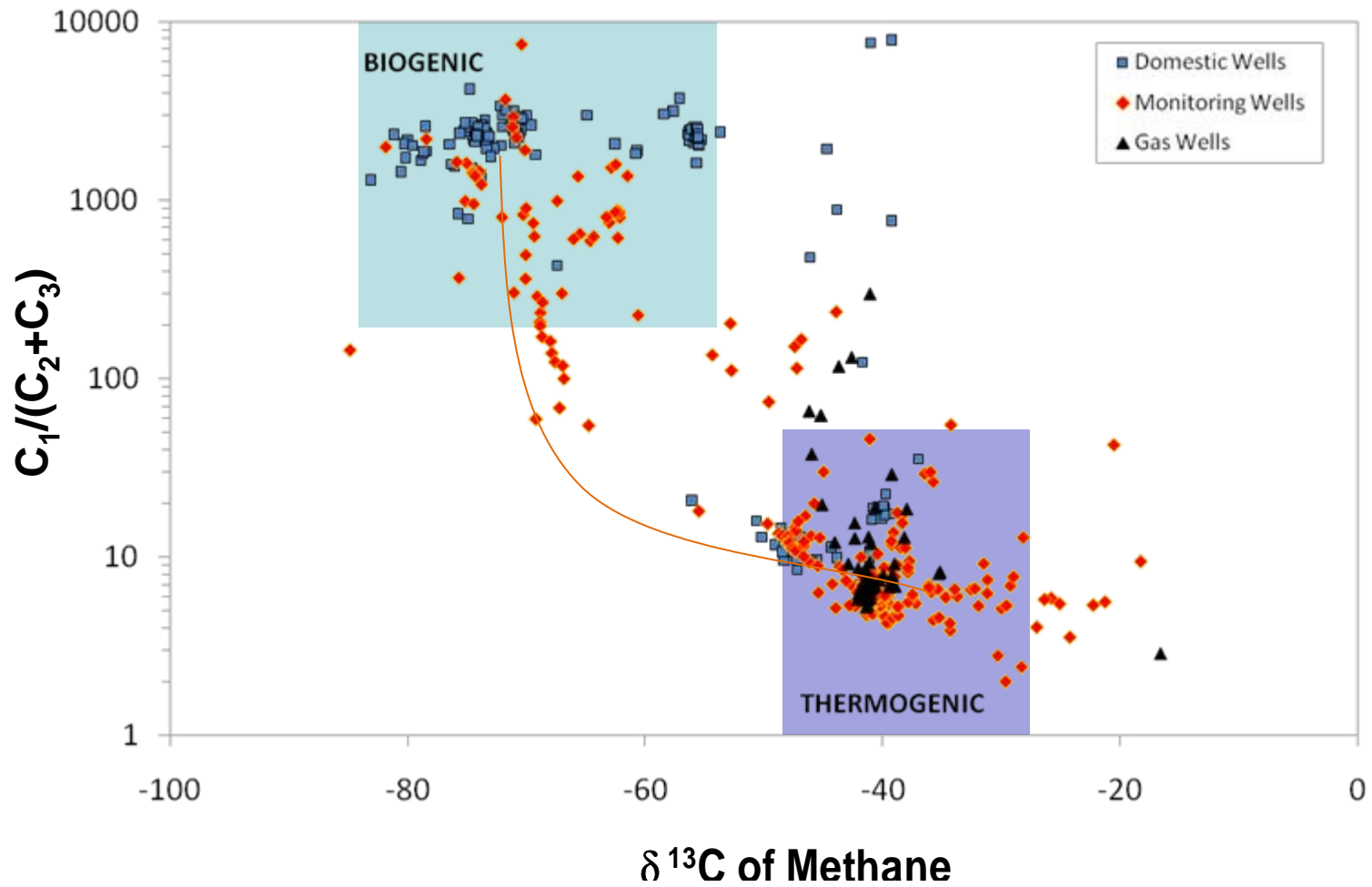


Figure 15. Bernard Diagram showing comparative molecular and isotopic compositions of biogenic and thermogenic gases.

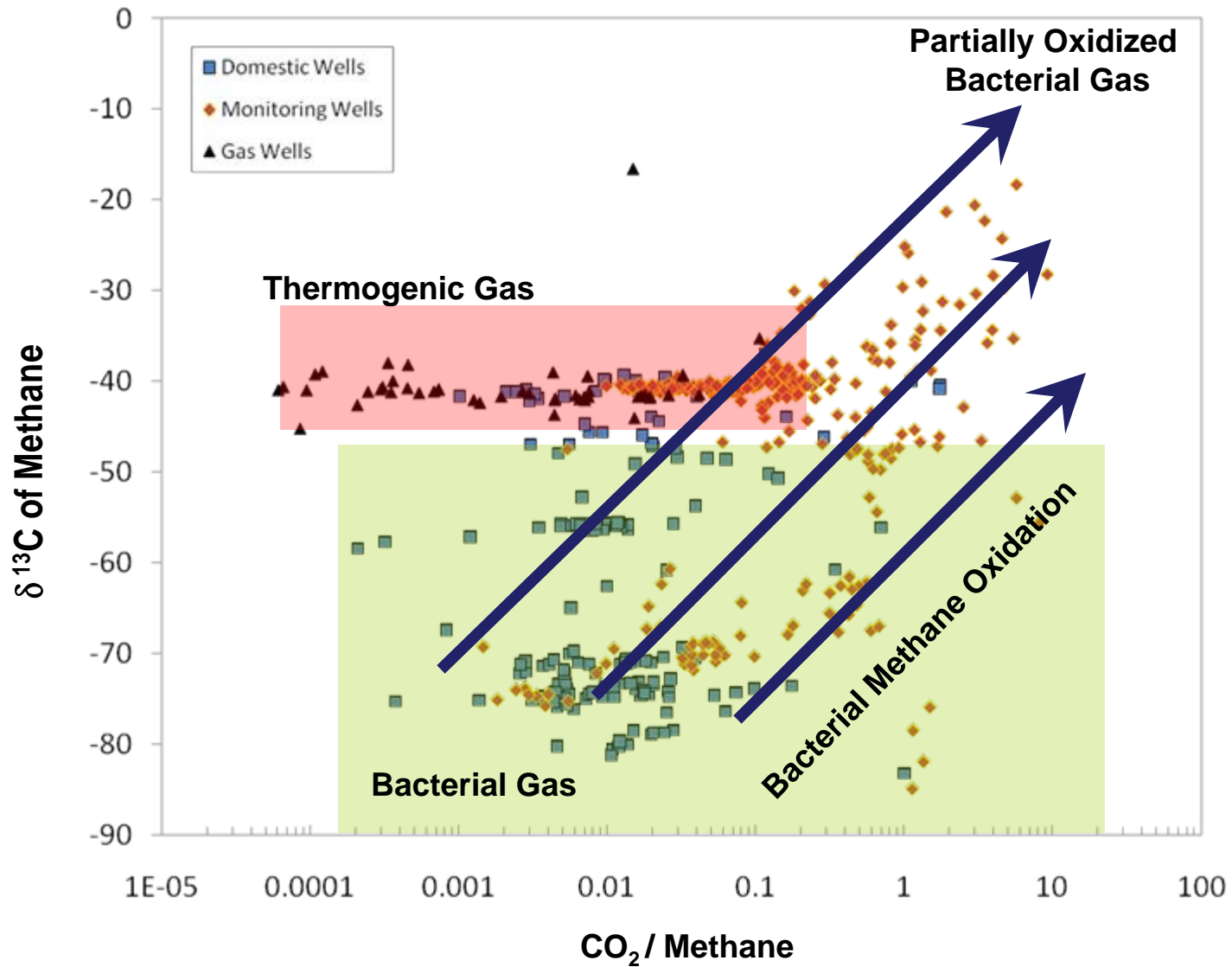
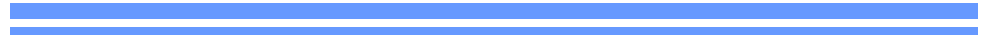


Figure 16. Plot of $\delta^{13}\text{C}$ of methane against gas compositional carbon dioxide to methane ratio.



TABLES



Table 1: Summary of Assertions in Thyne (2008)

Thyne Report	SSPA Comment	SSPA Figure or Table Reference
1. (ES-1) Water quality data is sufficient to establish the range of natural background chemistry and to delineate the impact of petroleum activities. The impacts are mainly elevated methane (CH ₄) and chloride (Cl ⁻).	While it is true that background water quality data for the area north of the Colorado River is sufficient to establish a reasonable range for natural background chemistry, the situation is not as clear for the Mamm Creek area. Statistical analysis for the Mamm Creek area suggests that either background data is not sufficient OR that there is no significant increase CH ₄ and Cl ⁻ in with time.	Figures 1-13 Tables 2-5
2. (ES-2a) CH ₄ is increasing over last 7 years coincident with increase in number of gas wells.	Statistical analysis does not support increasing CH ₄ and Cl ⁻ with increasing natural gas drilling and production.	Figures 1-9 Tables 2-3
3. (ES-2b) Pre-drilling CH ₄ is <1 mg/L in GW, except for biogenic CH ₄ which is confined to pond and stream bottoms.	Groundwater samples from the southeast portion of the Mamm Creek area prior to 2003 contain probable thermogenic CH ₄ that may occur due to the natural upward migration of Williams Fork formation natural gas.	
4. (ES-2c) CH ₄ isotopic data show that most samples with elevated CH ₄ are thermogenic in origin.	There are several groundwater wells with CH ₄ that is not of thermogenic origin. The signature of this CH ₄ cannot be due to the reduction of thermogenic carbon dioxide (CO ₂) because there is not sufficient CO ₂ in the Williams Fork gas to produce a shift in isotopic composition.	Figures 14-16
5. (ES-3) Cl ⁻ is increasing over time with increase in number of gas wells. This Cl ⁻ is from produced water.	There is not a statistically significant increase in Cl ⁻ concentration over time; further Cl ⁻ concentrations well in excess of 10 mg/L can occur naturally in groundwater in the Mamm Creek area.	Figures 8-13 Tables 4-5
6. (ES-4) CH ₄ and Cl ⁻ concentrations do not trigger regulatory action; however, Cl ⁻ may reach regulatory limits as more gas wells are drilled.		
7. (ES-5) The number of domestic wells and their distribution is inadequate to monitor and locate potential source(s) of contamination from gas wells and produced water pits.		
8. (p. 7) Elevated initial bradenhead pressures in wells are related to recognized geologic faults and fractures.	For the operators to address, especially as it relates to shallow structures and whether they extend upwards into the Wasatch Formation.	

Table 1: Summary of Assertions in Thyne (2008) – Continued

Thyne Report	SSPA Comment	SSPA Figure or Table Reference
9. (p. 8) Increased fracturing near the Divide Creek Anticline may cause higher incidence of drilling and completions problems, which may in turn affect water resources by allowing introduction of gas or other fluids into the water supply aquifer.	Fracturing due to tensile stress regimes along the anticlinal axis may also result in the natural migration of natural gas and deep groundwater into the water supply aquifer (as is suggested by groundwater sampling in the southeast corner of the Mamm Creek area).	
10. (p. 9) Pre-drilling CH ₄ in wells is <1 mg/L; therefore values >1 mg/L are assumed to indicate impact, with most likely source being produced natural gas.	See Item 3, above.	
11. (p. 9) There is a trend of increasing dissolved CH ₄ with time that is positively correlated with the number of gas wells.	See Item 2, above. Also consider bias of sampling conducted beginning in 2004 after the discovery, investigation, and remediation of the West Divide Creek gas seep.	
12. Figure 6	The numbers of wells and dates in this chart do not correspond either with Figure 2 or with URS Table 4-1.	
13. (p. 10) All 7 domestic wells sampled for isotope data by SSPA indicated thermogenic origin.	Two samples definitely do not indicate thermogenic origin. The other 5 wells are in the same area in the southeast. Two wells appear to be thermogenic and 3 wells may be coalbed gas or include coalbed gas based on the high C-1/(C-2+C-3) ratios.	Figures 14-16
14. (p. 10-11) Domestic wells are inadequate as monitoring points to determine CH ₄ or other contamination due to gas drilling and production, and sampling domestic wells constitutes an invasion of privacy that can be problematic for government agencies conducting the sampling.		
15. (p. 11, Fig. 8) CH ₄ from domestic wells plotting in the microbial CO ₂ reduction field is attributed to the reduction of thermogenic CO ₂ due to the high concentrations (up to 22%) of CO ₂ present in Williams Fork Formation gas (presumably in the Mamm Creek area).	The highest CO ₂ proportion measured to date from Williams Fork Formation gas wells is 3.5 %. Since CO ₂ and CH ₄ would migrate together, there is insufficient CO ₂ in the gas to shift the signature from the thermogenic into the microbial CO ₂ reduction field.	Figures 14-16
16. (p. 12) Samples 703996 and 704023 from SSPA (2008) cannot be from the oxidation of fermentation gas.	There is no disagreement with this assertion (as is concluded by Figure 4-21 of the SSPA report), although oxidation processes and/or the presence of coalbed gases may be affecting the signature of the CH ₄ . It is similarly concluded that other wells in the southeast portion of the Mamm Creek area may include coalbed gas.	Figures 14-16

Table 1: Summary of Assertions in Thyne (2008) – Continued

Thyne Report	SSPA Comment	SSPA Figure or Table Reference
17. (p. 13) Production of elevated bicarbonate (HCO_3^-) due to CH_4 oxidation is not seen in West Divide Creek seep samples.	HCO_3^- concentrations in groundwater are too high to determine if oxidation of CH_4 has affected the overall HCO_3^- concentration. As the report states, analysis of stable isotopes of the HCO_3^- would be a better way to evaluate the sample.	
18. (p. 15) Unlined pits are (still) used to store produced water or to allow it to infiltrate into the shallow aquifer.	This should be addressed by the COGCC and the operators.	
19. (p. 16) Statement reporting the volume of water produced from the Mamm Creek Field in 2007 indicates all the water is saline.	This is not accurate. Of the 16 produced water samples collected by SSPA in 2007 (SSPA, 2008), had one with TDS of 690 mg/L, and two had less than 9,000 mg/L TDS and sodium-bicarbonate (not sodium-chloride) geochemical signatures..	
20. (p. 16) High TDS water from samples collected from wells located at the base of Grass Mesa are associated with mapped basement faults.	While deep faults are not known to cut the surface in this area of Piceance Basin, the sodium-chloride (Na-Cl) signatures of the water are interesting and may indicate influence of deeper water in these wells. There is very little CH_4 (ND or <0.005 mg/L) in these wells (URS, 2006), so any association with gas wells or gas production is suspect, unless the Na-Cl is from leaking pits.	
21. (p. 16 and Fig. 12) Water with >10 mg/L Cl^- has some degree of “impact” from gas drilling and production.	The comparison of Mamm Creek area groundwater sulfate and Cl^- concentrations with concentrations from north of the Colorado River shows that high Cl^- concentrations can exist without gas drilling and production impacts.	Figure 13
22. (p. 16 and Fig. 13) Lower salinity produced waters are due to dilution of saline water with condensed water from production-induced cooling. The SSPA interpretation of water as brackish is incorrect.	<p>This assertion depends on the amount of condensation water that would be necessary to reduce Cl^- and TDS concentrations significantly. The high Cl^- and TDS samples that do not fall on the produced water “mixing line” may represent natural bicarbonate- or sulfate-rich waters.</p> <p>The brackish water interpretation is correct and is supported in the literature. Seawater has a Cl^- concentration of 19,000 mg/L (Hem, 1985), well above any of the produced water samples plotted on Fig. 13 or measured in most of the produced water samples collected by SSPA (2008).</p>	Figure 13

Table 1: Summary of Assertions in Thyne (2008) – Continued

Thyne Report	SSPA Comment	SSPA Figure or Table Reference
<p>23. (p. 19) The groundwater clusters with 1) high TDS and elevated sodium, Cl⁻ and CH₄, and 2) high TDS and elevated Na, Cl⁻, and sulfate are impacted by produced water.</p>	<p>This cannot be proven for all cases. See Items 21 and 22. The high TDS water that contains elevated Na-Cl-SO₄ but not CH₄, may include deeper formation water, but the lack of CH₄ indicates this water may not be associated with gas drilling and production.</p>	
<p>24. (p. 21) Sub-regulatory impact trend is best delineated by increasing CH₄ and Cl⁻ in groundwater samples.</p>	<p>See Items 1, 2 and 5, above. The increasing trend in CH₄ and Cl⁻ is not supported by statistical analysis that takes into consideration sample variability.</p>	<p>Figures 1-13 Tables 2-5</p>
<p>25. (p. 21) 1) While “some small amount” of vertical migration of gas occurs naturally, the trend of increasing CH₄ with increasing drilling indicates that drilling and production activities are the cause.</p> <p>2) Most affected locations “are near structural features where the faults and fractures maximize the vertical mobility of the gas, however it is not possible at this time to identify if leaking production tubing, leaking top-of-gas casing or un-cased Wasatch interval is the primary source of methane.”</p>	<p>Both of these statements acknowledge, but then do not consider, that migration of CH₄ into the groundwater aquifer may be a natural process that in certain areas does not require conduits provided by gas wells.</p>	

Table 2: Year-to-year comparison of Albrecht methane data using the Mann-Whitney test

	N	Median (mg/L)	1997	1998	1999	2000	2001	2002	2003	2004
1997	34	0.0008								
1998	7	2.7	0 0.0000 /							
1999	16	0.00089		2 0.0006 <i>D</i>						
2000	4	0.4082			8 0.0720					
2001	41	0.0014				29 0.1186				
2002	100	0.00036					1701 0.1566			
2003	142	0.02						9978 0.0000 /		
2004	921	0.027							74646 0.0038 /	
2005	922	0.0084								382430 0.0003 <i>D</i>

N = number of sample results from each year used in Mann-Whitney test.

Median = median methane concentration in water in mg/L.

Mann-Whitney statistics:

xx.
0.yyyy
<i>I/D</i>

Value of Mann-Whitney test statistic U, where xx. is the smaller of U1 and U2.

Significance of the differences between median methane values from one year to the next.

Whether methane is **Increasing** or **Decreasing** when median methane values are significantly different (at the 95% confidence level).

Boldface values indicate comparisons where median methane values are significantly different (at the 95% confidence level).

Table 3: Year-to-year comparison of COGCC methane data using the Mann-Whitney test (excluding duplicates and MWs)

	N	Median (mg/L)	1997	1999	2001	2002	2003	2004	2005	2006	2007
1997	25	0.0004									
1999	14	0.0004	112 0.0920								
2001	28	0.0004		146 0.3270							
2002	57	0.0004			819 0.4800						
2003	108	0.0023				3220 0.3890					
2004	310	0.0023					18536 0.0510				
2005	402	0.0098						59482 0.3433			
2006	191	0.0103							35784 0.2160		
2007	52	0.0075								4941 0.8237	
2008	27	0.0004									495 0.0710

N = number of sample results from each year used in Mann-Whitney test.

Median = median methane concentration in water in mg/L.

Mann-Whitney statistics:

xx.

Value of Mann-Whitney test statistic U, where xx. is the smaller of U1 and U2.

0.yyyy

Significance of the differences between median methane values from one year to the next.

I/D

Whether methane is **Increasing** or **Decreasing** when median methane values are significantly different (at the 95% confidence level).

Boldface values indicate comparisons where median methane values are significantly different (at the 95% confidence level).

Table 4: Year-to-year comparison of Albrecht chloride data using the Mann-Whitney test

	N	Median (mg/L)	1997	1999	2001	2002	2003	2004
1997	31	37						
1999	8	14	167 0.0170 <i>D</i>					
2001	29	20.7		119 0.3860				
2002	85	24.8			1063 0.4476			
2003	125	40.4				6381 0.0060 <i>I</i>		
2004	650	26					28308 0.0000 <i>D</i>	
2005	505	35						145198 0.0010 <i>I</i>

N = number of sample results from each year used in Mann-Whitney test.

Median = median chloride concentration in water in mg/L.

Mann-Whitney statistics:

xx.
0.yyyy
<i>I/D</i>

Value of Mann-Whitney test statistic U, where xx. is the smaller of U1 and U2.

Significance of the differences between median chloride values from one year to the next.

Whether chloride is **Increasing** or **Decreasing** when median chloride values are significantly different (at the 95% confidence level).

Boldface values indicate comparisons where median chloride values are significantly different (at the 95% confidence level).

Table 5: Year-to-year comparison of COGCC chloride data using the Mann-Whitney test (excluding duplicates and MWs)

	N	Median (mg/L)	1997	1999	2001	2002	2003	2004	2005	2006	2007
1997	22	30									
1999	8	14	112 0.0410 D								
2001	26	21.1		109 0.3268							
2002	56	32.3			699 0.9050						
2003	107	49				333 0.1670					
2004	343	46.7					16943 0.3100				
2005	403	60.7						70806 0.4800			
2006	175	40.1							35751 0.0670		
2007	75	63								5706 0.1570	
2008	15	11									859 0.0001 D

N = number of sample results from each year used in Mann-Whitney test.

Median = median chloride concentration in water in mg/L.

Mann-Whitney statistics:

xx.

Value of Mann-Whitney test statistic U, where xx. is the smaller of U1 and U2.

0.yyyy

Significance of the differences between median chloride values from one year to the next.

I/D

Whether chloride is **Increasing** or **Decreasing** when median chloride values are significantly different (at the 95% confidence level).

Boldface values indicate comparisons where median chloride values are significantly different (at the 95% confidence level).