An Analysis of Nitrate Groundwater Sample Preservation and Storage Methods

October 2016

Minnesota Department of Agriculture

Pesticide and Fertilizer Management Division

PRIMARY AUTHORS

Kimberly Kaiser, Adam McCullough, Brennon Schaefer, Bill VanRyswyk

CONTRIBUTORS

Nikol Ross (sample collection), Brennon Schaefer (sample collection), Jeff Paddock (sample collection), Treeske Ehresmann (lab planning and analysis), Michele Swarbrick (sample splitting and sample analysis)

REVIEWERS

Dave Tollefson

FUNDING

Clean Water Fund

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Many Minnesotans receive their drinking water directly from underlying aquifers through private wells. Certain aquifers can be susceptible to nitrate leaching from surface activities, including feedlots, fertilizer use, septic systems, among others. The federal maximum contaminant limit (MCL) and state Health Risk Limit (HRL) for nitrate as nitrogen (N) are 10 mg/L, which provides reasonable protection against the negative health effects of nitrate (MDH, 2015). There are many private drinking water wells in Minnesota with nitrate levels that exceed these standards.

In recent years, quantifying the degree of nitrate contamination in groundwater has become an increasing priority for Minnesota. Due to the immensity of such a task, some groundwater samples will inevitably exceed recommended storage times and/or lack recommended preservation techniques. In this study, the effects of various preservation and storage methods on measured nitrate + nitrite as N concentrations were evaluated for groundwater samples collected from three different wells in Minnesota. Nitrogen in groundwater is primarily in the forms of nitrite and nitrate (Warner and Arnold, 2010). Measurements of nitrate + nitrite as N in this report will hereafter be referred to as "nitrate".

BACKGROUND

The Minnesota Department of Agriculture (MDA) established the Township Testing Program (TTP) to assess the extent and magnitude of nitrate contamination in Minnesota's groundwater as measured from private drinking water wells. Specifically, the TTP focused on the nitrate contamination derived from agricultural practices related to nitrogen fertilizer use. As part of the TTP, the MDA estimated that approximately 70,000 private well owners within 250-350 vulnerable townships and cities will be targeted for private well nitrate sampling between 2014 and 2019.

The first phase of the TTP sampling consists of sending homeowners a free nitrate testing kit for their private well. The kit contains a sample bottle, prepaid mailer, and sampling instructions. Homeowners were directed to collect the sample following the instructions and mail the sample to a designated laboratory the same day. It was emphasized that nitrate samples should be mailed the same day, to minimize the holding time between collection and analysis. Standard Methods (APHA, 2005) lists the recommended holding time for nitrate analysis as 48 hours, with refrigeration to four degrees Celsius. The holding time can be extended up to 28 days with the addition of a sulfuric acid preservative. The addition of acid lowers the pH to reduce biological activity. For various reasons, not all of the TTP samples made it to the laboratory at, or below, four degrees Celsius or within the 48 hour holding time. Due to safety concerns, homeowner collected samples were not preserved with sulfuric acid until they arrived at the laboratory. Previous holding time studies conducted by the MDA in 1997, and the Minnesota Department of Health (MDH) in 2009, indicated significant stability in water samples collected for nitrate over

extended periods. Based upon this information, the TTP accepted the homeowner collected samples that arrived at the laboratory after the 48 hour holding time, regardless of temperature. However, the previous studies by the MDA and MDH were not fully documented and, therefore, the MDA elected to conduct a more comprehensive evaluation of nitrate stability in collected groundwater samples utilizing some of the more common preservation and storage methods.

The goal of this study was to demonstrate that nitrate concentrations in groundwater samples collected from private drinking water wells exhibit significant stability for at least 30 days. Specific objectives include:

- An evaluation of high, medium and low nitrate concentration ranges for the preservation and storage methods identified below;
- Evaluation of nitrate concentration stability over-time in groundwater samples refrigerated after collection, with and without acidification via sulfuric acid;
- Evaluation of nitrate concentration stability over time in groundwater samples frozen after collection; and
- Evaluation of nitrate concentration stability over-time in groundwater samples stored at room temperature, in the dark.

PREVIOUS WORK

In 2009, MDH conducted an evaluation of nitrate stability in groundwater samples collected from private drinking water wells located in southeastern Minnesota. Groundwater was collected from three wells, each of which was split into two containers. One container was stored in a refrigerator (7 ºC) and the other at room temperature (24.5 ºC). The intent of the study was to analyze refrigerated and room temperature samples 14 times over a 74-day test period for nitrate concentration. MDH staff used a Hach 4000 spectrophotometer to perform the analysis.

Figure 1 presents nitrate concentration over time for the groundwater samples collected during the MDH nitrate holding study. The nitrate concentrations in groundwater for the two wells with an original nitrate concentration less than 10 mg/L varied within 0.5 mg/L for the two storage methods. Nitrate concentrations for the well with the highest original nitrate content varied by up to 1.0 mg/L for the two storage temperatures, but the variability was not consistant between the storage methods (refrigeration vs. room temperature). The variation in measured nitrate concetration was likely due to normal analytical laboratory variability introduced by sample dilution and/or instrument precision. Measured nitrate concentrations were within 1.0 mg/L of each other for all sample groups, regardless of storage method.

The MDH study concluded that the sample storage temperatures evaluated resulted in little difference in measured nitrate concentrations. Analytical results obtained after a short storage period were similar to those obtained up to 10 weeks later.

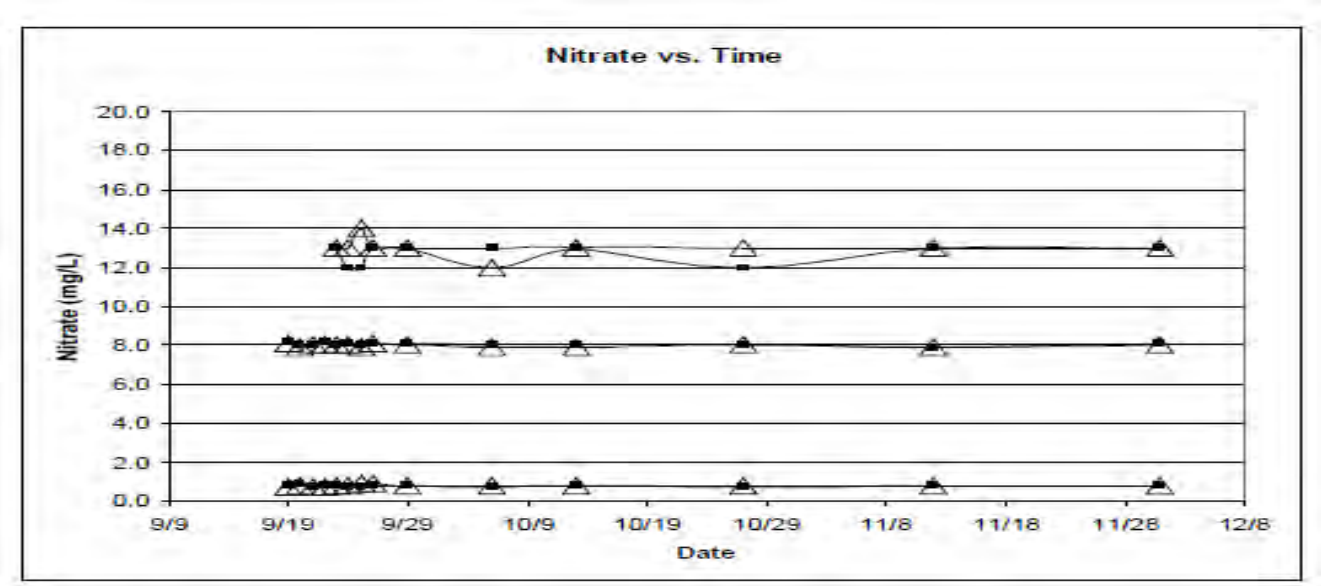


Figure 1. Results of MDH Nitrate Holding Study. NOTE: Triangles denote nitrate concentration for samples stored at room-temperature and squares denote nitrate concentration for refrigerated samples.

METHODS

SAMPLE COLLECTION AND PREPARATION

Three wells located in Dakota County, Minnesota were sampled by MDA field staff on June 1st, 2015. The wells were selected based upon historic nitrate concentration so that three different concentration ranges could be evaluated, including a low (0.4 to 3 mg/L), medium (3 to 10 mg/L), and high (>10 mg/L) concentration range. Prior to sampling, all three wells were purged for at least 15 minutes until all field parameters stabilized (e.g., temperature, pH, specific conductivity, dissolved oxygen, and water appearance). Stabilized field parameters for each well are presented in Table 1. Once field parameters stabilized, 3-5 gallons of water were collected into a five gallon polyethylene carboy from each well.

Table 1. Well sampling field parameters after stabilization.

Well Conc. Range	Discharge (gal/min)	Length of Well Purge (min)	Temperature (^{0}C)	pH	Specific Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Water Appearance
Low	3	15	10.52	7.78	510	0.08	Clear
Medium	5.5	19	10.49	7.61	637	7.68	Clear
High	9	20	10.19	7.61	755	8.67	Clear

Samples were transported on ice and delivered to the MDA laboratory the same day by MDA staff. Once the samples reached the laboratory, water from each well was mixed and split into 40 equivalent sub-samples using a Teflon Dekaport Cone Splitter. An initial set of four sub-samples, and their corresponding replicates, was analyzed within 48 hours for each well. The remaining 32 sub-samples were then stored at varying temperatures, including: refrigeration (~4

ºC), freezing (~-15 ºC), and room - in the dark - temperature (~23ºC). Half of the refrigerated samples had a sulfuric acid preservative added, which represented a "control" group. Table 2 outlines the study design by the different preservation and storage methods and the corresponding time (in days) between sample collection and laboratory analysis. The study design in Table 2 was used for all three nitrate sample concentration ranges. All samples were analyzed in replicate for each preservation and storage method.

Table 2. Study preservation/storage method and analytical frequency.

Preservation Method	Laboratory Analysis Day from Receiving Samples									
	Day 2	Day 3	Day 4	Day 5	Day 8	Day 9	Day 10	Day 11	Day 15	Day 30
Refrigeration and Sulfuric Acid (Control)	x	x	x	x	x	x	x	x	x	x
Room Temperature	x	x	x	x	x	x	x	x	x	x
Refrigeration	x	x	x	x	x	x	x	x	x	x
Frozen	x	x	x	x	x	x	x	x	x	x
Control Replicate	x	x	x	x	x	x	x	x	x	x
Room Temp Replicate	x	x	x	x	x	x	x	x	x	x
Refrigeration Replicate	x	x	x	x	x	x	x	x	x	x
Frozen Replicate	x	x	x	x	x	x	x	x	x	x

LABORATORY ANALYSIS

Samples were analyzed for nitrate + nitrite as nitrogen by the MDA Laboratory Services Division (MDA laboratory). Nitrate concentrations were determined by an automated colorimetric method, which uses flow injection analysis (FIA), manufactured by Lachat Instruments, Inc. (LAB-Mth-0041). The FIA system is designed to deliver and react reagents with the sample in the required order and ratios. The equipment configuration for this method includes a copperized cadmium reduction column which converts nitrate into nitrite for analysis. For this method the MDA laboratory reports an estimated uncertainty of 8%, due to normal analytical variability, with a method reporting limit (MRL) of 0.4 mg/L.

DATA ANALYSIS

To determine the appropriate statistical methods for this study, an evaluation of the data was first performed through data summaries and graphical exploratory data analysis procedures. Statistical summary values were calculated and, following recommendations in Helsel and Hirsch (2002), histograms, boxplots, quantile plots, and probability plots were generated for each data set. Upon evaluation of this information, it was determined that, due to the small number of sample points in each data set and the fact that the distributions of several of the data sets were not normally distributed, nonparametric procedures would be utilized to compare each of the groups (Helsel and Hirsch, 2002). Also, the relative percent difference measure was used to evaluate the precision of each result compared to the replicate samples that were collected for quality assurance/quality control (QA/QC) purposes.

RESULTS AND DISCUSSION

Nitrate concentration results for all samples are presented in Figure 2. Results have been presented by nitrate concentration range, preservation method, and the day of analysis. All sample results, including replicates, can be found in Appendix A.

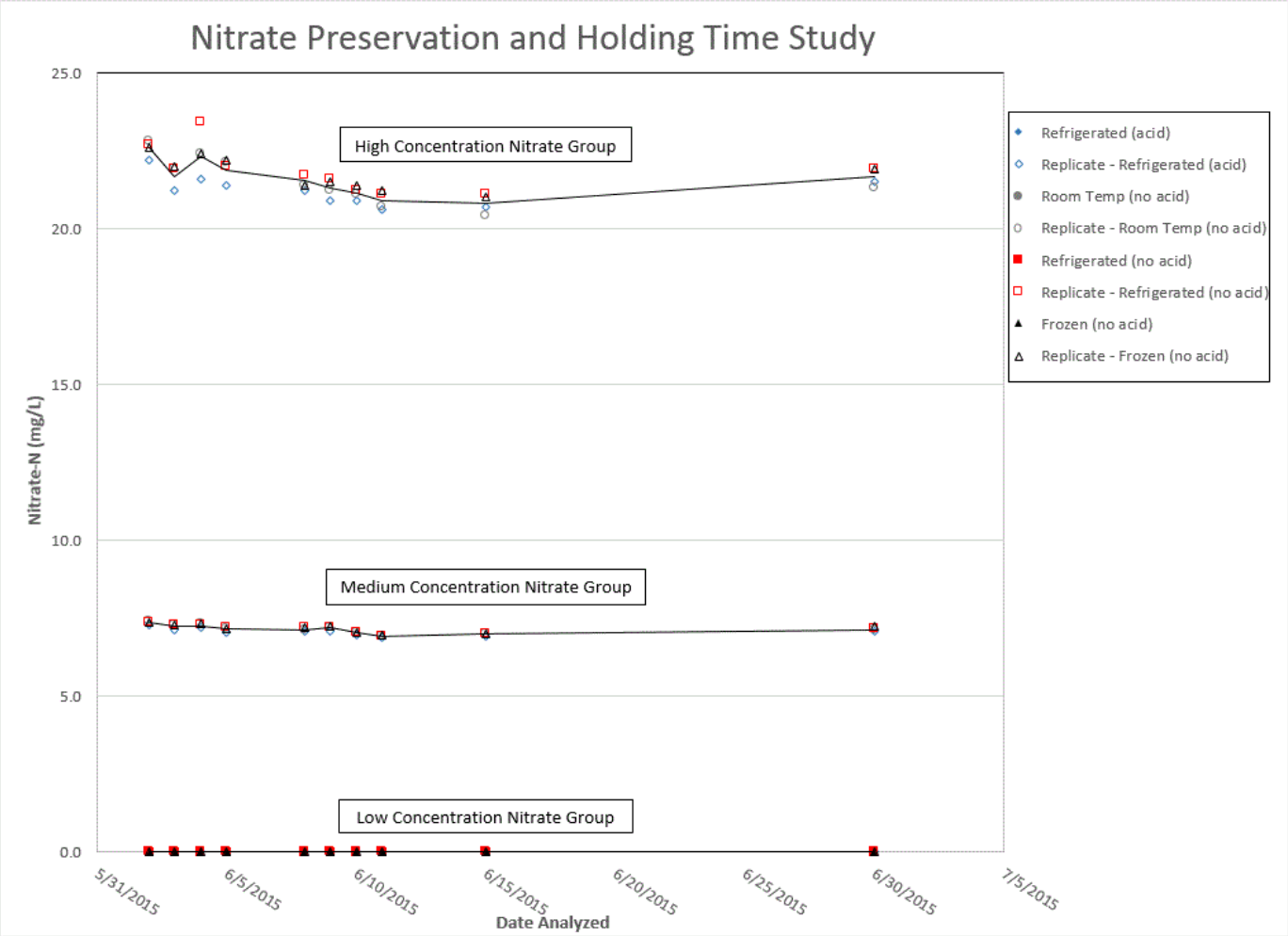


Figure 2. Nitrate concentrations over-time for all groups.

Nitrate concentration results for the three concentration ranges are presented in Table 3. Preservation and storage methods did not have any measurable effect on the results over the 30-day study period for the low concentration samples, as the samples were all reported at a concentration below the method reporting limit of 0.4 mg/L. **Thus, this group has been excluded from further analysis in this report.**

Table 3. Nitrate results for the different preservation methods and holding times. NOTE: The values presented are the mean concentration of the sample and the corresponding replicate.

Sample Type			Nitrate-N Results (mg/L) by Day									
Nitrate-N Concentration Range	Preservation and Storage Method	Code	2	3	4	5	8	9	10	11	15	30
Low	Standard Method Refrigerated (acid)	L1	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Room Temp (no acid)	L2	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Refrigerated (no acid)	L3	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Frozen (no acid)	L4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Medium	Standard Method Refrigerated (acid)	M1	7.3	7.1	7.1	7.1	7.0	7.1	7.0	6.9	6.9	7.0
	Room Temp (no acid)	M2	7.4	7.3	7.2	7.1	7.1	7.2	7.0	6.9	7.0	7.1
	Refrigerated (no acid)	M3	7.4	7.3	7.3	7.2	7.2	7.2	7.1	6.9	7.0	7.2
	Frozen (no acid)	M4	7.4	7.3	7.3	7.2	7.2	7.3	7.1	7.0	7.0	7.2
High	Standard Method Refrigerated (acid)	H1	22.1	21.2	21.6	21.4	21.3	21.0	20.9	20.6	20.7	21.4
	Room Temp (no acid)	H2	22.8	21.8	22.4	22.0	21.6	21.2	21.1	20.8	20.5	21.4
	Refrigerated (no acid)	H3	22.8	21.9	22.9	22.0	21.9	21.6	21.3	21.1	21.1	22.0
	Frozen (no acid)	H4	22.7	21.9	22.5	22.2	21.6	21.5	21.4	21.2	21.0	22.0

Figures 3 and 4 present the nitrate concentration results for the medium and high concentration groups, respectively, for each preservation and storage method over time. It should be noted that the concentrations presented in these graphs represent the mean of the sample and associated replicate. Figures 3 and 4 indicate that the results for each method fluctuated slightly, either upward and downward, between each day of analysis. In addition, it was found that the fluctuation was generally consistent between the different methods, with the majority of the results uniformly fluctuating upward or downward relative to the previous day. This relationship between the different sample groups analyzed on a given day can likely be attributed to the variability of the laboratory method, rather than the storage method.

Furthermore, a decrease in nitrate concentrations would be expected over time due to various processes, such as denitrification, microbial uptake, and absorption and adsorption onto bottle surfaces (Kotlash and Chessman, 1998). However, there were multiple occasions in the medium and high concentration data sets where nitrate concentrations increased between certain holding times. For example, between Day 15 and Day 30, which represented the largest gap in holding times between analyses, there was a consistent increase in nitrate concentrations for each preservation and storage method. This uniform increase in concentrations between Day 15 and Day 30, and other holding times, further suggests that this variability can be attributed to the normal day-to-day analytical or laboratory variability rather than holding times or preservation methods.

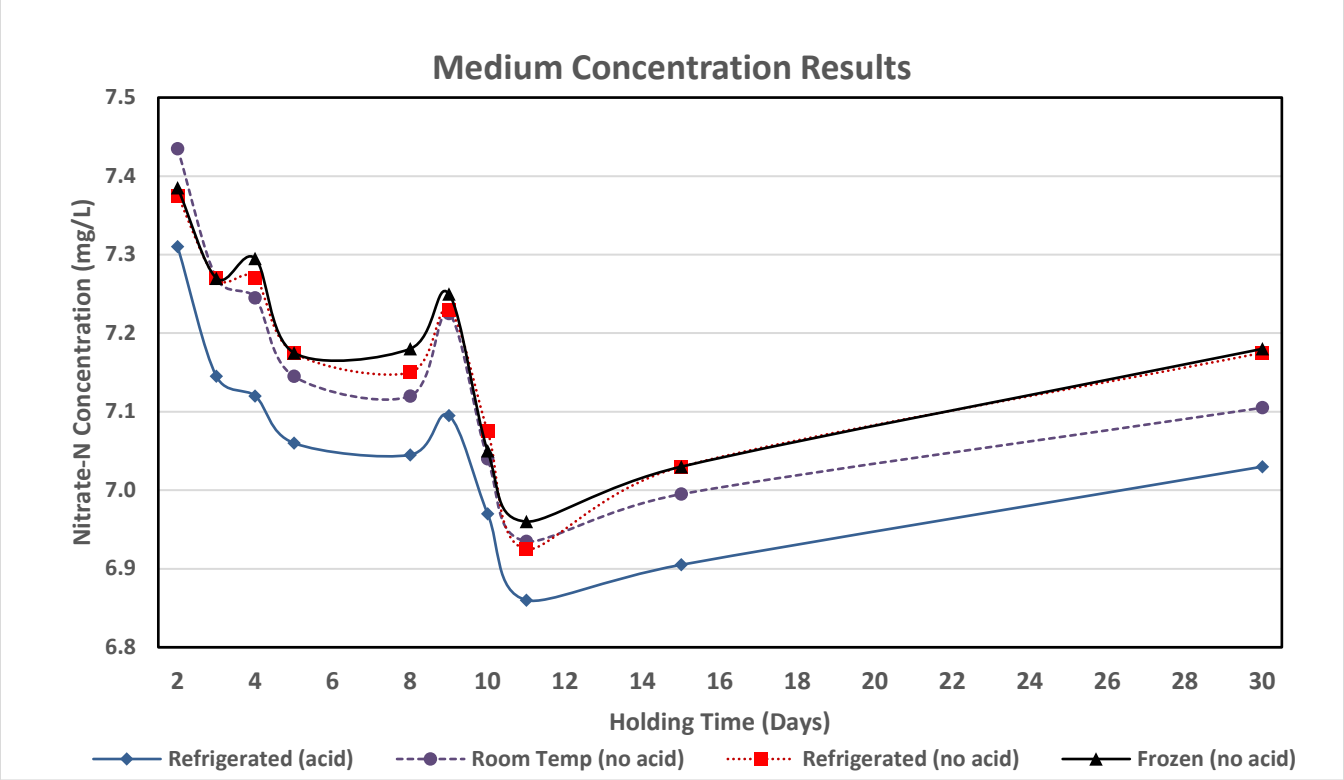


Figure 3. Medium nitrate concentrations for the different preservation and storage methods.
NOTE: Results represent the mean concentration of the sample and the associated replicate.

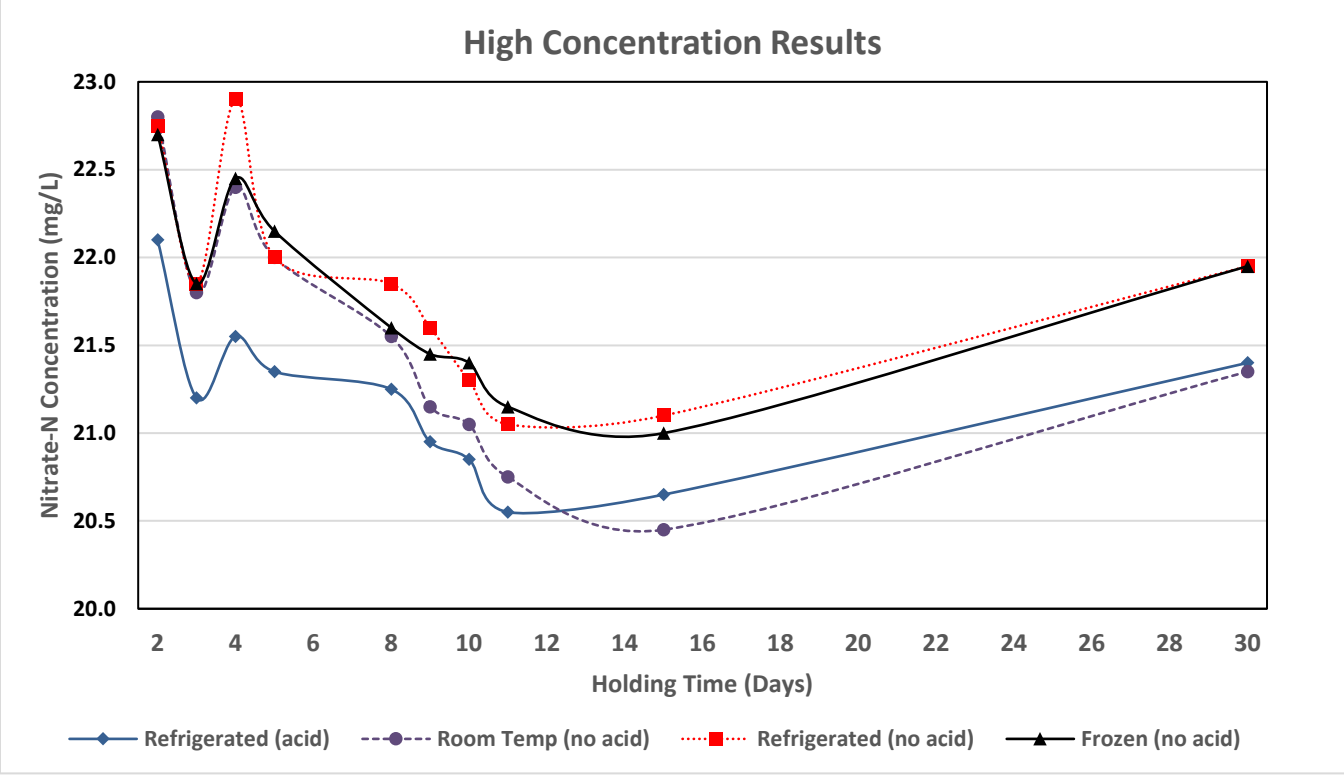


Figure 4. High nitrate concentrations for the different preservation and storage methods. NOTE: Results represent the mean concentration of the sample and the associated replicate.

Various statistical analyses and data summary techniques were performed to evaluate the variability and distribution of the data. Table 4 presents the summary statistics for the medium and high concentration nitrate groups. Figures 5 and 6 present boxplots for the medium and high concentration nitrate group sample data, as examples of graphical exploratory data analysis procedures. Other graphical summaries (histograms, quantile plots, and probability plots) have been included in Appendix B. This information shows that the number of sample points in each data set was very small and that the distributions of several of the data sets were not normally distributed.

Table 4. Medium and high concentration nitrate groups' summary statistics. NOTE: Replicates were not included in this analysis.

Nitrate-N Range	Preservation and Storage Method	Number of Samples	Min	Max	Range	Median	Mean	Standard Deviation
			Nitrate-N (mg/L)					
Medium (3<10 mg/L)	Control	10	6.9	7.3	0.4	7.0	7.1	0.1
	Room Temp (no acid)	10	6.9	7.5	0.6	7.1	7.2	0.2
	Refrigerated (no acid)	10	6.9	7.4	0.5	7.2	7.2	0.1
	Frozen (no acid)	10	7.0	7.4	0.4	7.2	7.2	0.1
High (≥10 mg/L)	Control	10	20.5	22.0	1.5	21.3	21.2	0.4
	Room Temp (no acid)	10	20.5	22.8	2.3	21.6	21.5	0.7
	Refrigerated (no acid)	10	21.0	22.8	1.8	21.9	21.8	0.5
	Frozen (no acid)	10	21.0	22.8	1.8	21.8	21.8	0.6

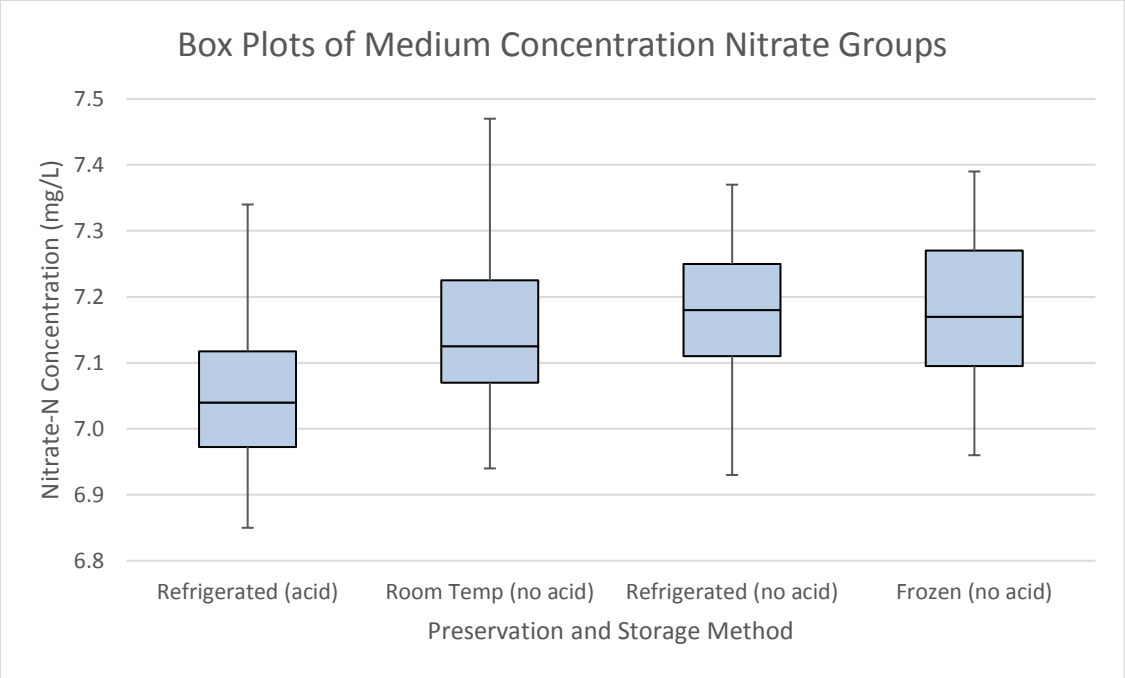


Figure 5. Box plots of medium concentration nitrate groups. NOTE: Replicates were not included in this analysis.

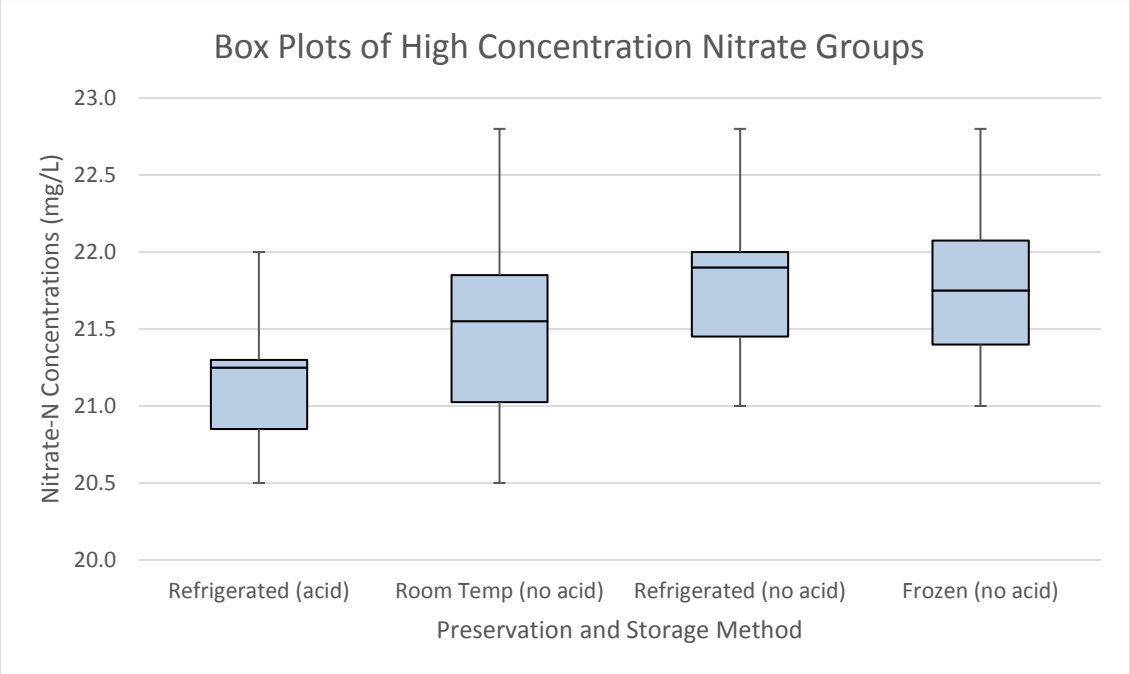


Figure 6. Box plots of high nitrate concentration results. NOTE: Replicates were not included in this analysis.

The nonparametric Kruskal-Wallis test was utilized to compare the central tendency (median values) of the results from each of the storage method groups, in the medium and high nitrate concentration ranges, for determining if the differences were significant. The test results were evaluated at the 95 percent confidence level. It was found that there was a significant difference between the standard method and the refrigerated and frozen storage methods for both of the concentration groups, but not between the standard method and room temperature storage method. However, the difference in the medians between these group pairings was less than 0.14 mg/L of nitrate for the medium concentration samples and less than 0.65 mg/L nitrate for the high concentration samples (Table 5). Additionally, when the room temperature, refrigerated and frozen samples were compared to each other, there was no significant difference in the median values.

Table 5. Medium and high median difference and associated p-values.

Sample Description	Median Difference	Statistic	p-value
Medium Concentration			
Standard Method vs. Room Temp	-0.1	1.54	0.133
Standard Method vs. Refrigerated	-0.2	2.04	0.049
Standard Method vs. Frozen	-0.2	2.18	0.036
Room Temp vs. Refrigerated	-0.1	0.50	0.623
Room Temp vs. Frozen	-0.1	0.65	0.523
Refrigerated vs. Frozen	0.0	0.15	0.882
High Concentration			
Standard Method vs. Room Temp	-0.3	1.38	0.177
Standard Method vs. Refrigerated	-0.6	2.60	0.013
Standard Method vs. Frozen	-0.5	2.48	0.018
Room Temp vs. Refrigerated	-0.3	1.22	0.229
Room Temp vs. Frozen	-0.2	1.10	0.279
Refrigerated vs. Frozen	0.1	0.12	0.903

QA/QC

The Relative Percent Difference (RPD) is a standard equation used to compare the precision of an original sample to a replicate sample. Generally, for nitrate measurements, a RPD of less than 10% is within acceptable limits. All of the RPDs were less than 5% in both the medium and the high nitrate concentration sample groups (Table 6).

Table 6. Medium and high absolute relative percent difference.

Nitrate-N Range	Sample Description	Absolute Relative Percent Difference	
		Average	Range (min,max)
Medium (3<10 mg/L)	Standard Method	0.70	(0.00, 1.69)
	Room Temp	0.54	(0.14, 1.79)
	Refrigerated	0.49	(0.14, 1.12)
	Frozen	0.46	(0.00, 1.11)
High (≥10 mg/L)	Standard Method	0.52	(0.00, 0.93)
	Room Temp	0.56	(0.00, 1.39)
	Refrigerated	0.85	(0.00, 4.37)
	Frozen	0.64	(0.00, 1.85)

CONCLUSIONS

Results of this study indicate minimal variation in nitrate concentrations between different preservation and storage methods with analysis occurring from two to 30 days after collection. Although Kruskal-Wallis comparison analysis showed significant differences between the refrigerated and frozen groups when compared against the standard method samples, the differences were very small and may be related to the different levels of pH associated with the addition of sulfuric acid in the control group. For the practical purposes of MDA sampling programs, any of the tested preservation and storage methods would be acceptable for nitrate analysis within 30 days of collection.

REFERENCES

Helsel, DR. and Hirsch, R.M (2002). *Statistical Methods in Water Resources. Techniques of Water-Resources Investigations of the United States Geological Survey.* http//water.usgs.gov/pubs/twri/twri4a3/.

Kotlash, A. R., and Chessman, B. C. (1998). *Effects of water sample preservation and storage on nitrogen and phosphorus determinations: implications for the use of automated sampling equipment.* Water Research, *32*(12), 3731-3737.

MDH (Minnesota Department of Health) (2015). *Nitrate in Well Water*. Minnesota Department of Health Well Management Section. Retrieved March 25, 2016, from: http://libguides.gwumc.edu/c.php?g=27779&p=170369.

American Public Health Association (APHA) (2005). *Standard Methods for the Examination of Water and Wastewater*, 21st edition.

Warner, K.L., and Arnold, T.L. (2010). *Relations that Affect the Probability and Prediction of Nitrate concentration in Private Wells in the Glacial Aquifer Systems in the United States*. U.S. Geological Survey Scientific Investigations Report 2010-5100, 55 p. plus appendices.

APPENDIX A

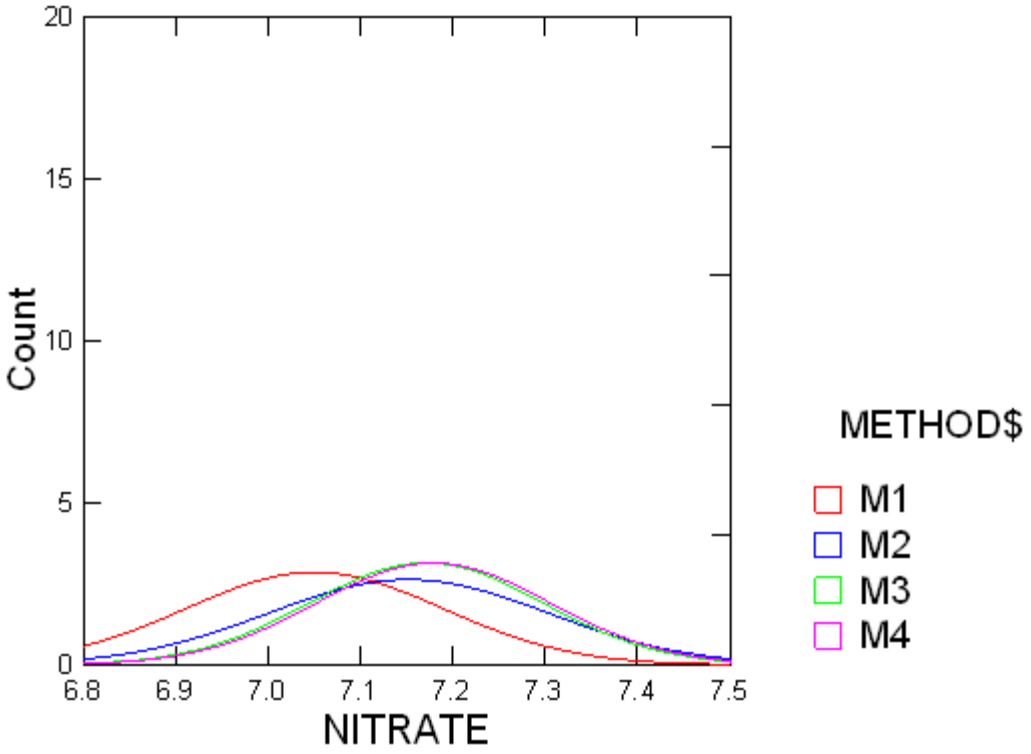
Complete results of study with replicates.

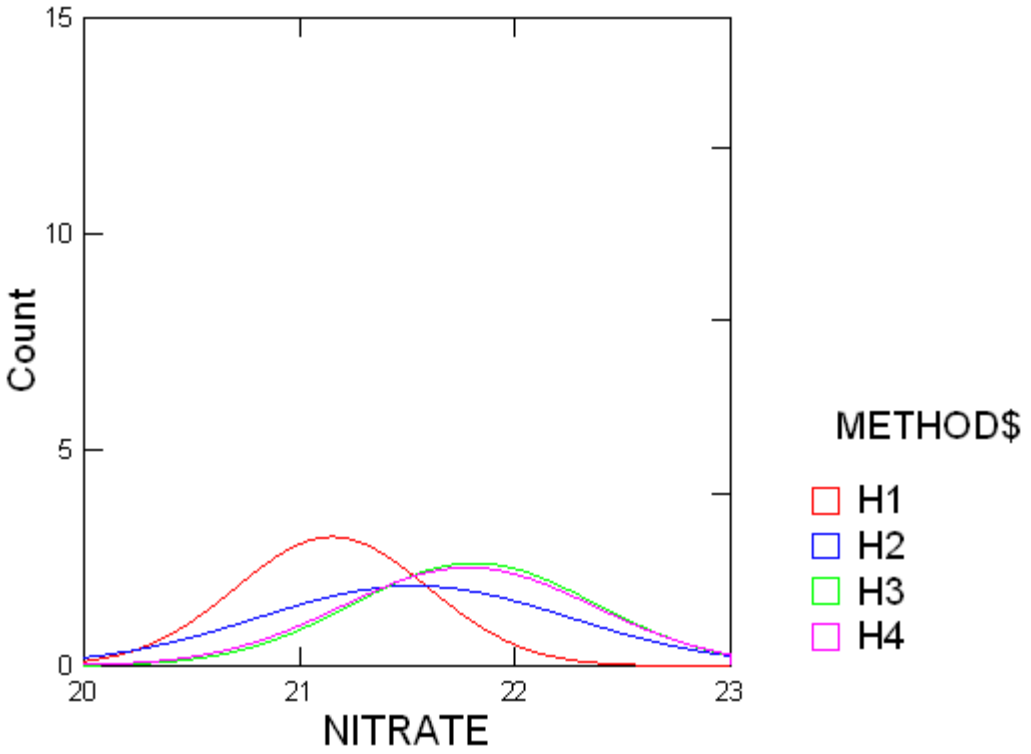
Sample Type			Nitrate-N (mg/L) by Day									
Nitrate Concentration Range	**Preservation and Storage**	**Code**	**2**	**3**	**4**	**5**	**8**	**9**	**10**	**11**	**15**	**30**
Low (0.4<3 mg/L)	**Control (Standard Method) Refrigerated (acid)**	**L1**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Raw Room Temp (no acid)	**L2**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Refrigerated (no acid)	**L3**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Frozen (no acid)	**L4**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Replicate Control (Standard Method) Refrigerated (acid)	**L5**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Replicate Raw Room Temp (no acid)	**L6**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Replicate Refrigerated (no acid)	**L7**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
	Replicate Frozen (no acid)	**L8**	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Medium (3<10 mg/L)	**Control (Standard Method) Refrigerated (acid)**	**M1**	**7.3**	7.2	7.1	7.1	7.0	7.1	7.0	6.9	6.9	7.0
	Raw Room Temp (no acid)	**M2**	**7.5**	7.3	7.2	7.1	7.1	7.2	7.1	6.9	7.0	7.1
	Refrigerated (no acid)	**M3**	**7.4**	7.3	7.3	7.2	7.1	7.3	7.1	6.9	7.1	7.2
	Frozen (no acid)	**M4**	**7.4**	7.3	7.3	7.2	7.2	7.3	7.1	7.0	7.1	7.1
	Replicate Control (Standard Method) Refrigerated (acid)	**M5**	**7.3**	7.1	7.2	7.0	7.1	7.1	7.0	6.9	6.9	7.1

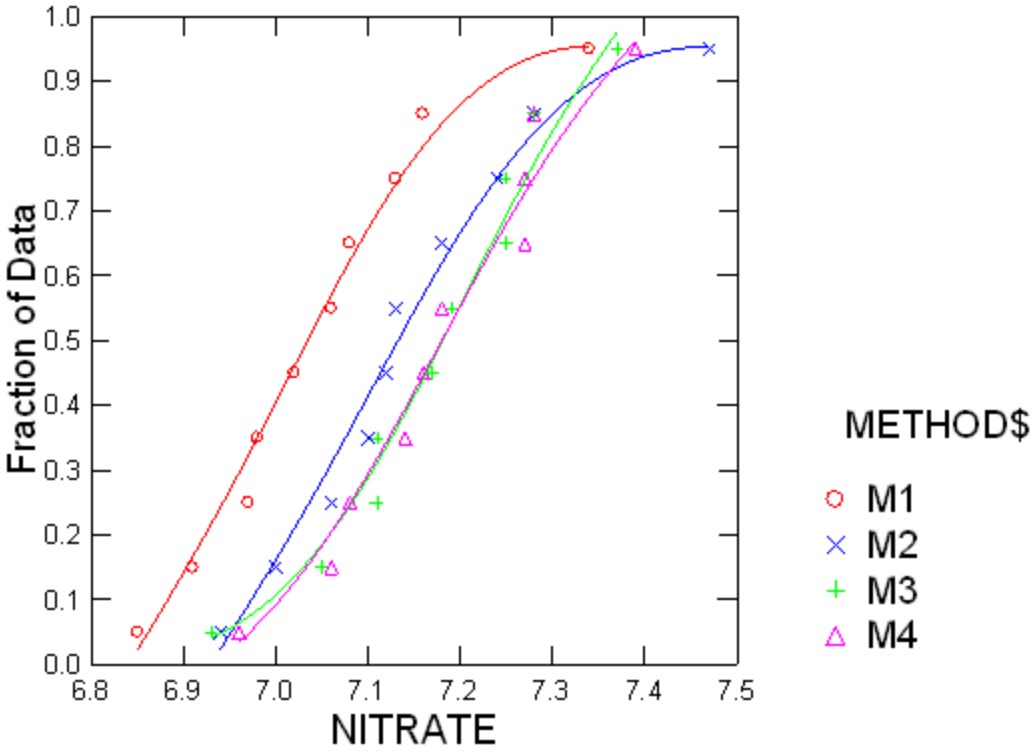
Sample Type			Nitrate-N (mg/L) by Day									
Nitrate Concentration Range	**Preservation and Storage**	**Code**	**2**	**3**	**4**	**5**	**8**	**9**	**10**	**11**	**15**	**30**
	Replicate Raw Room Temp (no acid)	**M6**	**7.4**	7.3	7.3	7.2	7.1	7.2	7.0	6.9	7.0	7.1
	Replicate Refrigerated (no acid)	**M7**	**7.4**	7.3	7.3	7.2	7.2	7.2	7.0	6.9	7.0	7.2
	Replicate Frozen (no acid)	**M8**	**7.4**	7.3	7.3	7.2	7.2	7.2	7.0	7.0	7.0	7.2
High (≥10 mg/L)	**Control (Standard Method) Refrigerated (acid)**	**H1**	**22.0**	21.2	21.5	21.3	21.3	21.0	20.8	20.5	20.6	21.3
	Raw Room Temp (no acid)	**H2**	**22.8**	21.7	22.4	21.9	21.7	21.1	21.0	20.8	20.5	21.4
	Refrigerated (no acid)	**H3**	**22.8**	21.8	22.4	22.0	22.0	21.6	21.4	21.0	21.1	22.0
	Frozen (no acid)	**H4**	**22.8**	21.7	22.5	22.1	21.8	21.4	21.4	21.1	21.0	22.0
	Replicate Control (Standard Method) Refrigerated (acid)	**H5**	**22.2**	21.2	21.6	21.4	21.2	20.9	20.9	20.6	20.7	21.5
	Replicate Raw Room Temp (no acid)	**H6**	**22.8**	21.9	22.4	22.1	21.4	21.2	21.1	20.7	20.4	21.3
	Replicate Refrigerated (no acid)	**H7**	**22.7**	21.9	23.4	22.0	21.7	21.6	21.2	21.1	21.1	21.9
	Replicate Frozen (no acid)	**H8**	**22.6**	22.0	22.4	22.2	21.4	21.5	21.4	21.2	21.0	21.9

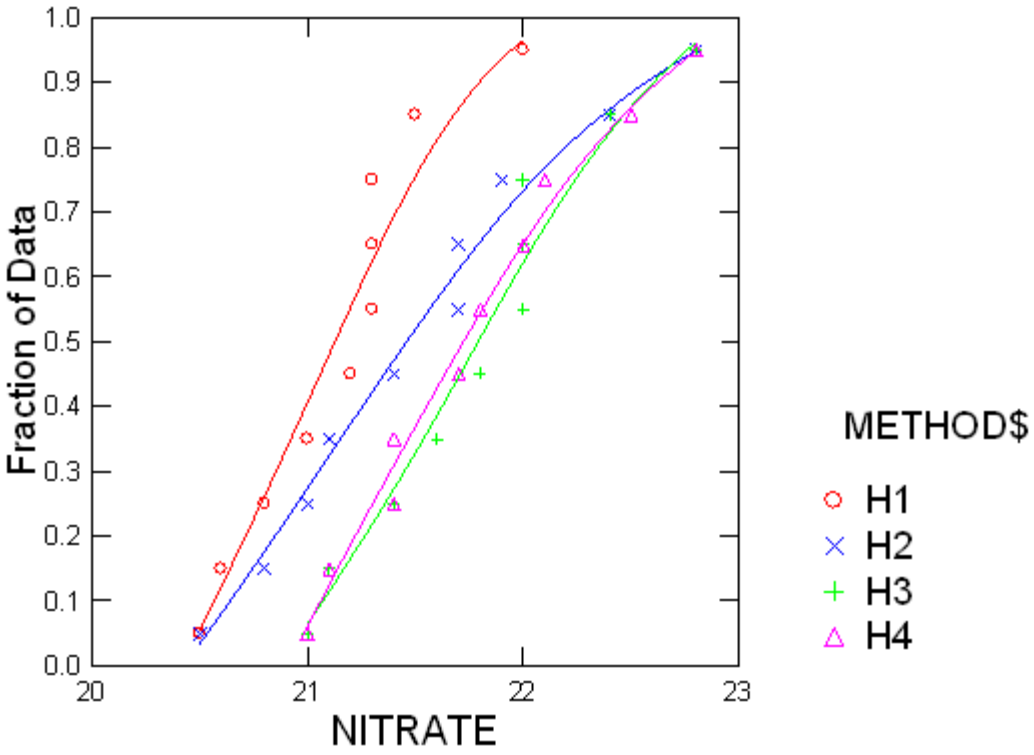
APPENDIX B

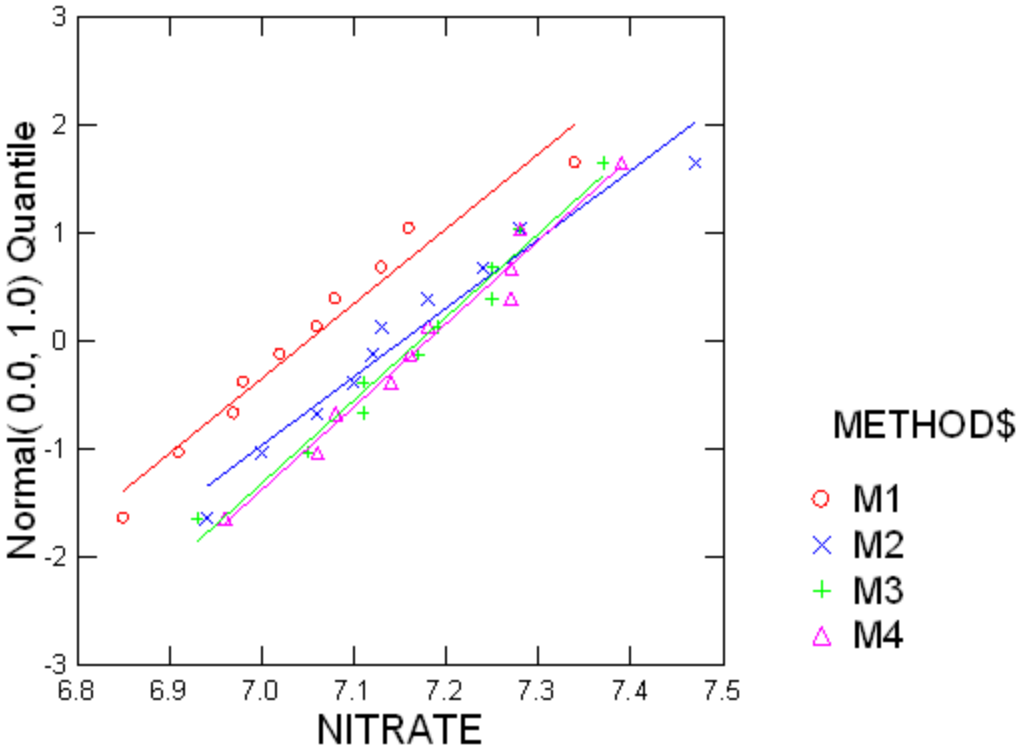
Histogram, quantile and probability plots for medium and high nitrate concentration group data.

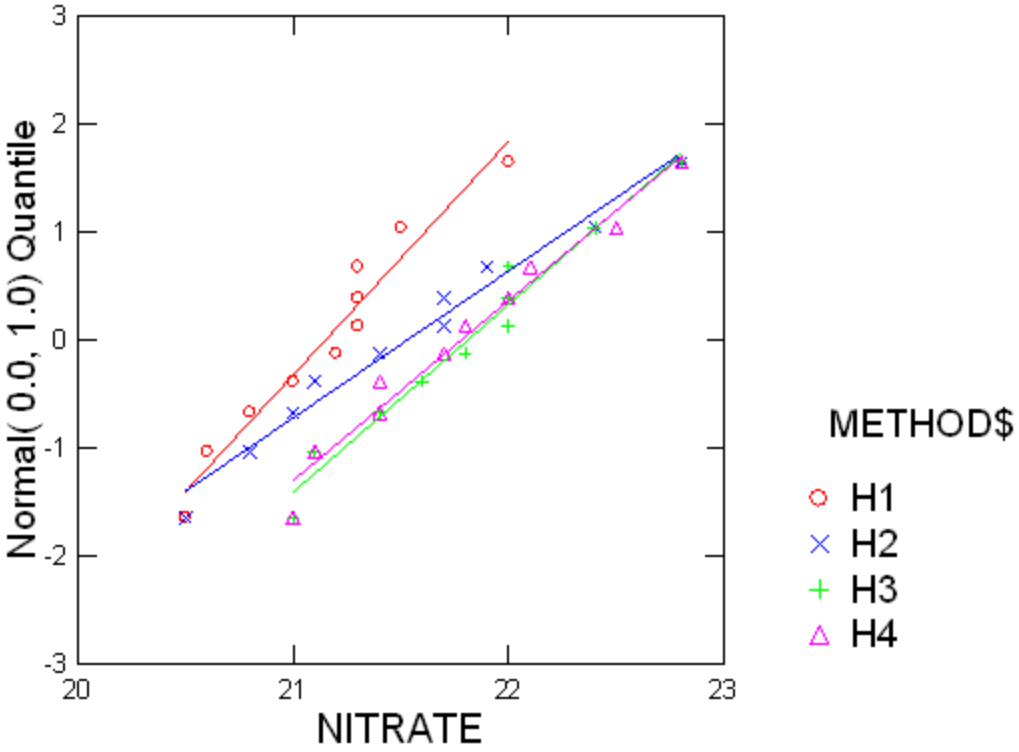





Fraction of Data
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
NITRATE
METHOD$
M1
M2
M3
M4


Fraction of Data
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
20
21
22
23
NITRATE
METHOD$
H1
H2
H3
H4


Normal(0.0, 1.0) Quantile
NITRATE
3
2
1
0
-1
-2
-3
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
METHOD$
M1
M2
M3
M4


Normal(0.0, 1.0) Quantile
NITRATE
3
2
1
0
-1
-2
-3
20
21
22
23
METHOD$
H1
H2
H3
H4