



2016 Environmental Health Public Drinking Water Resampling Analysis

FINAL REPORT

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2016 Environmental Health Public Drinking Water Resampling Analysis: Final Report

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Executive Summary

The Minnesota Department of Health (MDH) has enforcement primacy for the federal Safe Drinking Water Act (SDWA) in Minnesota. To ensure compliance with SDWA requirements, MDH Drinking Water Protection (DWP) Section staff and public water system (PWS) operators collect water samples across the state. The MDH Public Health Laboratory (PHL) analyzes those samples for over 90 contaminants to identify and track trends.

In 2015, a PHL audit revealed potential issues related to the sample collection instructions and thermal preservation of some samples. Specifically, water samples were not consistently thermally preserved (e.g. “iced”) by being received within 24 hours of collection or between 0 and 6 ° C. Very few samples received more than 24 hours after collection were within the required temperature range prior to 2016. Samples not within the temperature range must be qualified and are not valid for supporting enforcement under the SDWA.

To examine uncertainties associated with past samples the DWP, in coordination with the PHL, initiated a project to ensure that all samples have the highest level of quality integrity from sampling to delivery to the laboratory. The project included updating chain-of-custody forms and sampling instructions, aligning data qualifiers, updating sample acceptance criteria, and re-sampling at 919 prioritized locations across the state.

MDH DWP staff established a tiered system that reflected three vulnerability levels based on the estimated impact of potentially invalid data. Highest priority PWSs were grouped within Tier 1. A total of 540, 279, and 100 community and non-community PWSs qualified for Tiers 1, 2, and 3 respectively.

Representative analyte groups were chosen to assess potential systematic bias in water samples caused by changes in preservation temperature: disinfection by-products (DBP), synthetic organic compounds (SOC) and inorganic compounds (IOC), and volatile organic compounds (VOC). Sample result pairs from a specific location were used to compare results prior to 2016 (does not consistently meet required procedures = non-thermally preserved) to those collected in 2016 (does meet required procedures = thermally preserved).

There were 57 target analytes examined, with 33 analytes yielding detectable concentrations at some point. Results indicated:

- For DBPs, the main barriers to a comprehensive assessment of the data were the highly seasonal nature of their occurrence and the variable sampling frequency across the state. Impacts of seasonal variability were somewhat mitigated by only including paired data collected in the same month or one month apart. The DBPs had the highest number of detections of any class (44% of all sample points) with 40% of all systems having some detection. Sixteen systems had single results above the federal maximum contaminant levels (MCL) and two contaminants showed statistically significant differences between thermally preserved and non-thermally-preserved sample pairs. Overall results, however, were comparable to past results across the state and nationwide.

- For SOC/IOCs, detections were very rare with 99.7% of sample points being less than the minimum reporting limit (MRL). No health-based values were exceeded. The few non-tied pairs that were identified had very small differences, indicating that the thermally-preserved and non-thermally preserved samples were very similar. These results were comparable to past results across the state and nationwide.
- For VOCs, detections were rare, with 99% of sample points being less than the MRL for an individual contaminant. Five systems had single results that exceeded federal MCL and five additional systems exceeded state health risk limits (HRLs). While 11 of 18 detected contaminants had higher concentrations in thermally-preserved samples compared to non-thermally preserved samples, the overall low number of detections and small differences between results, combined with a lack of trend seen in scatterplots of concentration difference by sample receiving temperature makes characterizing a trend uncertain. As with the previous two contaminant groups, results were comparable to past results across the state and nationwide.

Immediate impacts from the quality assessment efforts included the creation and use of more robust chain-of-custody forms and sampling instructions, increased understanding of data qualifiers and analytical uncertainty, and the updating and implementation of sample acceptance criteria. Longer-term impacts from quality assessment efforts include the reconstituting of a staff-level DWP/PHL workgroups to promote better understanding of overall processes and improved communication and coordination.

Efforts demonstrated that no additional public health concerns related to drinking water resulted from issues related to thermal preservation. Individual locations that exceeded drinking water standards or guidance MCL and HRL thresholds were already on increased monitoring and known to MDH because they 1) had past elevated results, 2) had a new sampling locations, 3) were highly seasonal or had site specific conditions (DBPs), or 4) had not yet collected a confirmation sample (i.e., subsequent sampling was below the health threshold).

Even though it required a large commitment of time and resources, it was important for DWP to complete the sampling to understand whether previous monitoring failed to identify systems that might be at risk. Because the safety of Minnesota drinking water had been called into question, it was critical to produce valid results to reassure federal agencies, state agency partners, public water systems, and the general public.

This study was part of implementing an ongoing quality improvement process to ensure effective monitoring of public water systems for drinking water contaminants that threaten public health. Additional research may help further clarify acceptable boundaries for valid sample submission with respect to thermal preservation

Introduction

The Drinking Water Protection (DWP) Section in the Environmental Health (EH) Division of the Minnesota Department of Health (MDH) has been granted primacy by the US Environmental Protection Agency (EPA) to implement the Safe Drinking Water Act (SDWA) in Minnesota. The primary means of monitoring public water system (PWS) compliance with the SDWA and its implementing regulations is the review and evaluation of analytical results of water samples. Systems that do not comply with standards and regulations are subject to enforcement actions to ensure that Minnesotans are receiving safe, reliable drinking water. Therefore, it is critical that analytical data is collected, analyzed, and validated consistent with established methods.

Water samples used to show compliance with the SDWA are collected by MDH DWP staff and PWS staff across the state and analyzed for over 90 contaminants by a number of different laboratories. Most samples, however, are analyzed by the MDH Public Health Laboratory (PHL) in St. Paul. The PHL and DWP Section are jointly responsible for ensuring that analytical and regulatory requirements of the SDWA are met.

In 2015 the PHL performed an extensive audit of their policies and procedures in response to concerns over the performance of one of their staff. The PHL audit revealed potential issues related to the thermal preservation of some samples collected by DWP and PWS operators. To address public health and regulatory concerns arising from uncertainty over sample validity MDH took a number of steps, including:

- Updating sampling instructions and training for MDH staff, delegated staff, and public water system personnel to ensure all water samples are properly collected and kept at proper temperature from collection site to laboratory;
- Evaluating past monitoring results to determine which results complied with the temperature requirements;
- Reviewing water systems based on risk factors, including past monitoring results;
- Reviewing and updating water sample handling procedures and practices; and
- Activating the MDH Incident Command System (ICS) to coordinate communication, deployment of resources, and steps to resample potentially affected PWSs.

The ICS was active between February 8 and April 1, 2016. A set of three projects were created to address issues identified during the ICS process. One project involved a review of SDWA Rules to ensure MDH was complying with basic program requirements. Because there are so many SDWA rules, that project only examined MDH activities related to the Surface Water Rule and found we are compliant. Other rules will be reviewed in the future. A second project did a detailed examination of MDH efforts related to the SDWA Lead and Copper Rule to ensure compliance. The 225 line “cross-walk” demonstrated that MDH complies with almost all aspects of the rule (and exceeds requirements in some areas). No critical deficiencies or impacts to public health protection were noted. The Drinking Water Resampling project, the third project and subject of this report, was designed to examine tasks to ensure that all samples have the highest level of quality integrity from sampling to delivery to the laboratory and that no additional public health concerns resulted from issues related to thermal preservation, after the ICS was deactivated.

The Drinking Water Resampling Workgroup was assigned to Karla Peterson and John Freitag, and sponsored by the EH Directors Office. Team members are in Table 1 below. Specific objectives of the project, as documented in the project charter, were to:

1. Work with existing DWP/PHL staff to identify vulnerabilities and process improvement objectives;
2. Identify version control methods for new procedures for internal and external samplers;
3. Develop predetermined responses for situations when samples do not meet sample acceptance criteria; and
4. Complete resampling of designated locations and distribute results.

Table 1: Project Team consisting of staff from both DWP and PHL

DWP Staff	PHL Staff
David Rindal	Cori Dahle
Simon McCormack	Ron Brown
Carol Kephart	Shane Olund
Kyle Johnsen	Jeff Brenner
Jerry Smith	
Rochelle Steinbruckner	Leslie Winter <i>of DWP = Recorder</i>

Routine project meetings were held from April through November, 2016. Objectives 1 and 2 were fulfilled as part of the project. Vulnerabilities and process improvements were implemented in the creation of project deliverables such as a consensus table of data qualifiers with definitions (Appendix A), an updated chain of custody form that better aligns with legal sample security requirements (Appendix B), and implementation of sampling standard operating procedures which have been posted online at [Sample Collection Procedures \(http://www.health.state.mn.us/watersampling\)](http://www.health.state.mn.us/watersampling) for all MDH and PWS staff. Quality improvement was further addressed via a separate project in 2017 that developed metrics for evaluation between DWP and PHL. Version control methods were implemented by the use of SharePoint for all project documents and the placement of version numbers and/or dates on all documents. Both process improvement and version control will be integrated into routine program operations in the future.

To fulfill Objective 3, team members prepared a table of errors most likely to occur for a sample submission along with predetermined responses. Staff from DWP developed a table based on situations encountered in the field while sampling, while staff from PHL developed a table based on issues observed during sample receipt at the laboratory, following EPA requirements. Both tables are found in Appendix C.

The remainder of this report documents efforts to fulfill Objective 4 and also addresses the following objectives identified as part of the ICS:

- Identify and prioritize vulnerable water supplies;
- Identify PHL capacity to test samples and/or an accredited laboratory to perform sub-contract testing; and
- Develop a schedule of water sampling.

Methods

Key aspects of creating and maintaining quality assurance and security for samples are presented below, followed by the process to select locations for re-sampling and the chemicals to be assessed, an overview of temperature trends in samples, and the statistical process for assessing analytical results. For reporting concentrations, a microgram of contaminant per liter of water ($\mu\text{g}/\text{L}$) is assumed to be the same as parts per billion (ppb). The term ppb is used throughout this report.

Quality Assurance

When results do not meet the established criteria of the standard operating procedure for an analytical method or a submission does not meet the sample acceptance policy requirements, data qualifiers are applied to detail the deviation. To fully understand the impacts of the data qualifiers with regards to regulatory compliance, DWP and PHL created a table of qualifiers and the evaluation and response taken when the qualifier is present.

A second critical aspect of obtaining valid sample results is ensuring a consistent chain-of-custody form is maintained from sample collection through delivery to the lab. A series of customized sample request forms were developed by DWP for individual contaminant classes based on existing forms in the Minnesota Drinking Water Information System (MNDWIS). The custom forms are intended to reduce errors in the field by providing specific instructions on sampling, preservation, shipping, and hold times.

A third quality assurance tool developed as part of the incident were sample acceptance criteria. Discussions between DWP and PHL resulted in lists of critical acceptance criteria. The criteria establish the minimum standards for valid sample submission based on federal and state requirements and existing agreements between DWP and PHL.

Sample Locations

Staff reviewed past results, source vulnerability, and nationwide occurrence numbers to estimate impacts to PWSs and guide project scoping and internal and external communication. The established tier system reflected three vulnerability levels. Highest priority PWSs, grouped within Tier 1, shared the following characteristics:

- Had past detections of contaminants;
- Served vulnerable populations such as schools and daycare facilities; and
- Were most likely to have not met temperature requirements due to extended sample transport time or limited access to shipping options.

Other PWSs grouped within Tiers 2 and 3 were less likely to have not met temperature requirements but were still considered vulnerable. In addition, MDH supplemented Tier 3 with

PWSs having special sampling needs. A total of 540, 279, and 100 community and non-community PWSs qualified for Tiers 1, 2, and 3 respectively. MDH developed a project plan to re-collect samples from all 919 PWSs.

Each resampling location was incorporated into the established compliance sampling schedule for 2016 to minimize time, travel, and ensure optimal use of laboratory capacity. Sample collection at Tier 1, 2, and 3 locations began in February, 2016 and was effectively completed by October, 2016. A few additional disinfection byproduct samples were collected from systems that chlorinate, with historical peak concentrations found after October 2016.

Chemicals Analyzed

Regulated SDWA compounds that must be thermally preserved (e.g. “iced”) and received either within 24 hours of collection or at temperatures between 0 and 6 ° C include:

- Organic chemicals, including herbicides, pesticides, solvents, and industrial chemicals. Most organic chemicals regulated by the SDWA are the result of human activities or are associated with plumes from contaminated sources; and
- Inorganic compounds, most often found as naturally occurring contaminants.

Samples taken for the presence of microorganisms, fluoride, nitrate, radionuclides, arsenic, lead, mercury or other heavy metals are not impacted by thermal preservation and were not collected.

There were 57 compounds subject to invalidation due to problems with thermal preservation and included as part of the resampling effort (Table 2). General chemical types included, disinfection byproducts (DBPs) including total trihalomethanes (TTHMs) and haloacetic acids (HAA5s), inorganic compounds (IOCs) and synthetic organic compounds (SOCs), and volatile organic compounds (VOCs). All analytical quantitation was performed at either the MDH PHL in St. Paul, MN or the Eurofins Laboratory in South Bend, IN. Results were reported to DWP and validated using standard methods.

Table 2: Impacted Analytes, Methods, and Chemical Type

Chemical	EPA Method	Chemical Type
Cyanide, Free	SM4500-CN-F	IOC
Cyanide, Total	335.4	IOC
Bromodichloromethane	524.2	DBP - TTHM
Bromoform	524.2	DBP - TTHM
Chlorodibromomethane	524.2	DBP - TTHM
Chloroform	524.2	DBP - TTHM
Dibromoacetic Acid	552.2	DBP - HAA5
Dichloroacetic Acid	552.2	DBP – HAA5

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Chemical	EPA Method	Chemical Type
Monobromoacetic Acid	552.2	DBP – HAA5
Monochloroacetic Acid	552.2	DBP – HAA5
Trichloroacetic Acid	552.2	DBP – HAA5
2,4,5-TP (Silvex)	515.4	SOC
2,4-D	515.4	SOC
Alachlor	525.2/508.1	SOC
Atrazine	525.2/508.1	SOC
Pentachlorophenol (PCP)	515.4	SOC
Simazine	525.2	SOC
Technical Chlordane	508.1	SOC
Toxaphene	508.1	SOC
Benzo(a)pyrene	525.2	SOC
Carbofuran	531.1	SOC
Dalapon	515.4	SOC
Di(2-ethylhexyl) adipate	525.4	SOC
Di(2-ethylhexyl) phthalate	525.4	SOC
Dinoseb	515.4	SOC
Endrin	525.2/508.1	SOC
g-BHC (Lindane)	525.2/508.1	SOC
Glyphosate	547	SOC
Heptachlor	525.2/508.1	SOC
Heptachlor epoxide	525.2/508.1	SOC
Hexachlorobenzene	525.2/508.1	SOC
Hexachlorocyclo-pentadiene	525.2/508.1	SOC
Methoxychlor	525.2/508.1	SOC
Oxamyl	531.1	SOC
Picloram	515.4	SOC

Chemical	EPA Method	Chemical Type
1,1,1-Trichloroethane	524.2	VOC
1,1,2-Trichloroethane	524.2	VOC
1,1-Dichloroethene	524.2	VOC
1,2,4-Trichlorobenzene	524.2	VOC
1,2-Dichlorobenzene	524.2	VOC
1,2-Dichloroethane	524.2	VOC
1,2-Dichloropropane	524.2	VOC
1,4-Dichlorobenzene	524.2	VOC
Benzene	524.2	VOC
Carbon tetrachloride	524.2	VOC
Chlorobenzene	524.2	VOC
cis-1,2-Dichloroethene	524.2	VOC
Ethylbenzene	524.2	VOC
Methylene chloride	524.2	VOC
o-Xylene	524.2	VOC
Styrene	524.2	VOC
Tetrachloroethene	524.2	VOC
Toluene	524.2	VOC
trans-1,2-Dichloroethene	524.2	VOC
Trichloroethene (TCE)	524.2	VOC
p&m-Xylene		VOC
Vinyl chloride	524.2	VOC

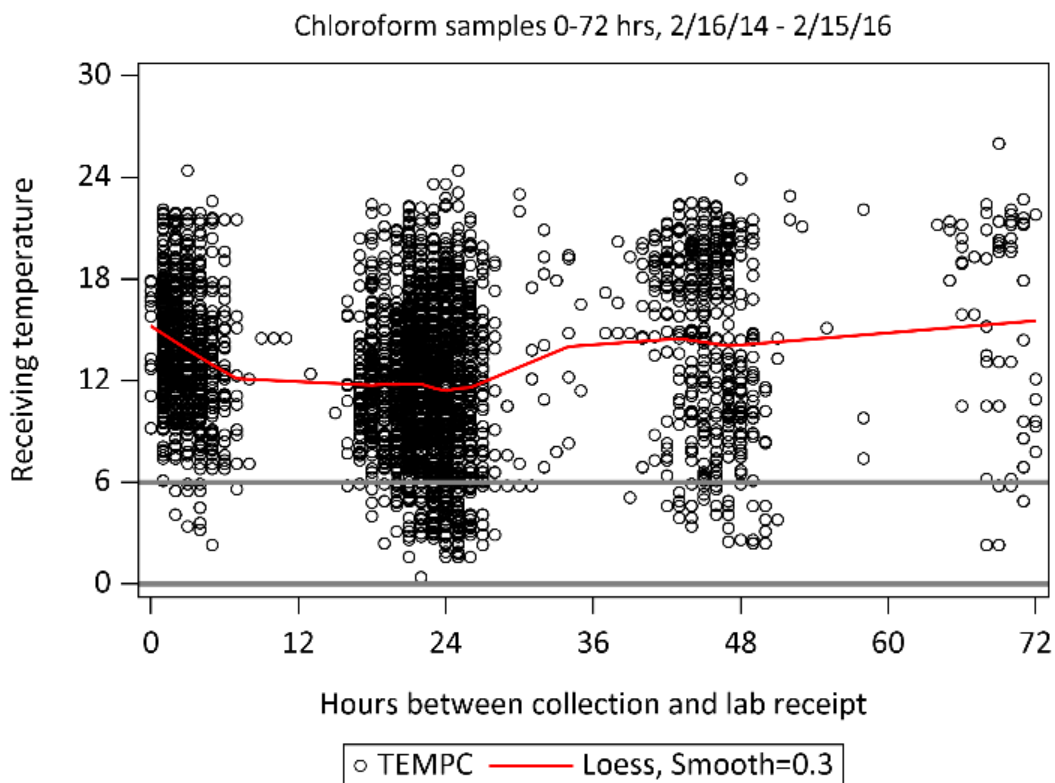
Temperature Assessment

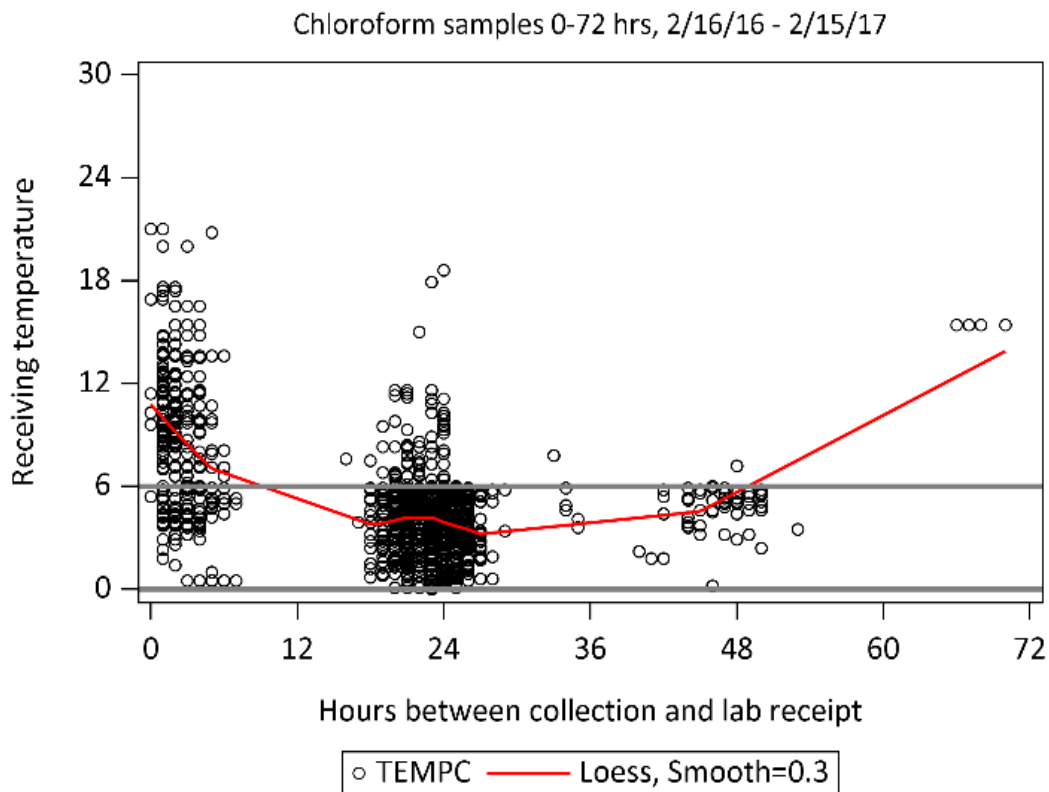
The MDH PHL generally accepts samples between the hours of 8:00 AM and 4:30 PM. Upon receipt of samples, the PHL immediately records the temperature of the samples in the cooler. However, samples may not cool down to 6°C if there is a short interval between collection and receipt. Therefore, the analytical method allows samples to be out of temperature range within the first 24 hours after collection, if the samples are received with evidence of cooling (e.g.,

cooling material present, with material solid or partially thawed). All samples received more than 24 hours after collection must be within 0 and 6 °C.

Using chloroform samples as an example, many samples received by the lab were above the acceptable temperature range but within the first 24 hours after collection (Figure 1). However, comparing samples from 2014-2015 to samples from 2016 shows that more consistent icing of samples reduced the temperature, even within the first 24 hours after collection, and increased the number of samples within the 0 and 6 °C range 24 hours after collection.

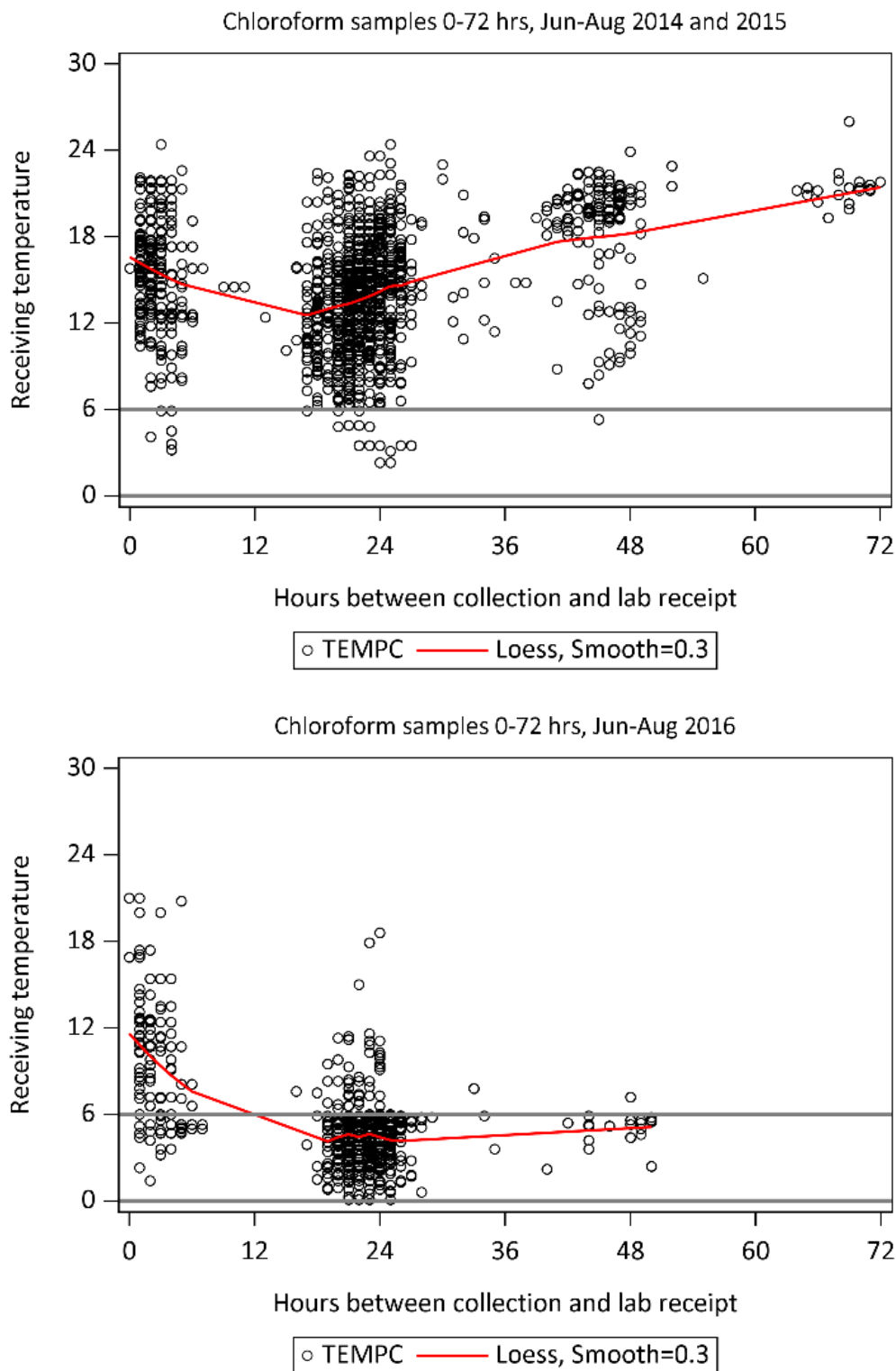
Figure 1: Temperature versus time to receipt at lab for Chloroform (DBP) before and after 2016





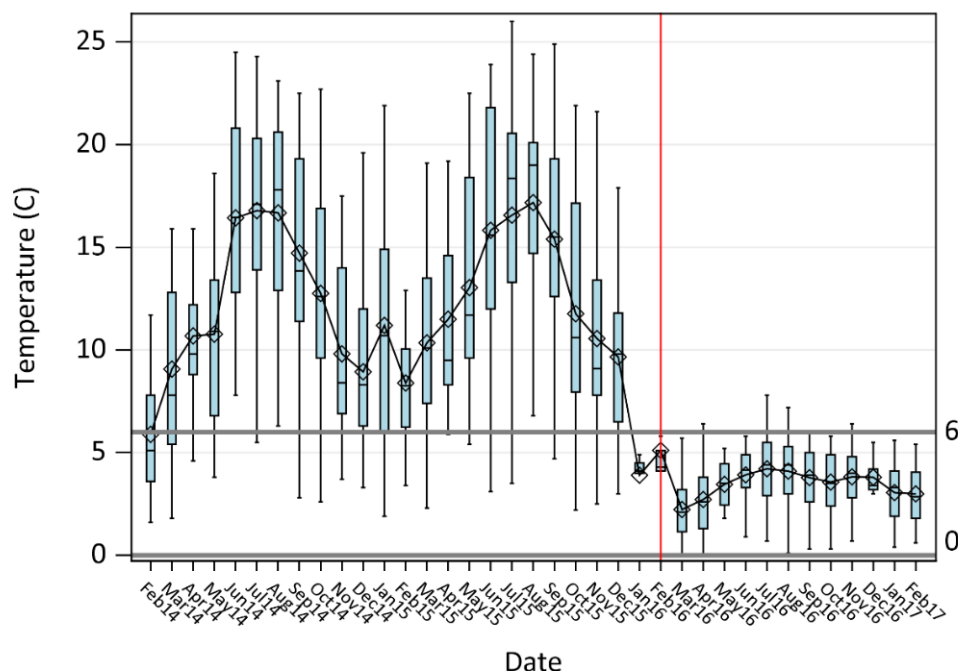
The difference in receiving temperature for chloroform samples is, not surprisingly, most striking during the summer (Figure 2). Prior to 2016 very few samples were within the required 0 to 6°C range during the summer months. While all samples received within 24 hours of collection were valid, regardless of temperature if evidence of cooling was present, after 24 hours all samples should be within the range of 0 to 6°C. Results from 2016 in both Figures 1 and 2 reflect success in submitting samples within the required temperature range.

Figure 2: Temperature versus time to receipt at lab for before and after 2016; summer months



The temperature trend for all chemicals examined in this report are shown in Figure 3. Samples received within 24 hours of collection are excluded to provide a clearer assessment of compliance with temperature requirements. Prior to 2016 the majority of receiving temperatures were well above the acceptable range of 0 to 6° C, with obvious seasonal variation. The thermally preserved samples (to the right of the red vertical line) were generally received at temperatures within the acceptable range. The dramatic improvement in thermal preservation after February 2016, resulted in a significant decrease in samples needing to be qualified for temperature exceedance.

Figure 3: Boxplots of sample receiving temperatures by month and year for samples received >24 hours after collection (1,586 work orders)¹



¹ The length of the box is the interquartile range (distance between the 25th and 75th percentiles). Mean temperatures (diamonds) are connected by a line. The median concentration is the horizontal line within the box. The lower and upper fences (not shown) are located at 1½ x IQR either side of Q3 and Q1. The whiskers are drawn to the value nearest to, but within, each fence. Outliers not shown. Results are from samples received from the following PHL clients: HC - Env Health - Comm Water Supplies (San.); HU - Env Health - Non-Comm - Non-Licensed; HD - Env Health - Non-Comm – Licensed; HW - Env Health - Non-Comm - Non-Transient. Samples analyzed by Eurofins Eaton Analytical, Inc. not included.

In addition to improved thermal preservation, samples were received at the lab more quickly (Table 3) during 2016. Prior to icing, we see that roughly a quarter of samples were received within 12 hours or less; and 65% were received within 24 hours. After icing began, 27% were received within 12 hours or less and 80% were received within 24 hours.

Table 3: Impacted Analytes, Methods, and Chemical Type

Time interval between collection and receipt (hours)	Frequency ² (2/16/14-2/15/16)	Percent (2/16/14-2/15/16)	Frequency ³ (2/16/16-2/15/17)	Percent (2/16/16-2/15/17)
12 or less	810	23.6%	526	27.3%

Time interval between collection and receipt (hours)	Frequency ² (2/16/14-2/15/16)	Percent (2/16/14-2/15/16)	Frequency ³ (2/16/16-2/15/17)	Percent (2/16/16-2/15/17)
>12-24	1,417	41.3%	1,022	53.1%
>24-48	861	25.1%	352	18.3%
>48-72	135	3.9%	23	1.2%
>72	212	6.2%	3	0.2%

² Includes samples from multiple analyte classes (chloroform, TCE, cyanide, atrazine, and bromoform samples) collected during this sampling period.

³ Includes all samples collected during this sampling period. Samples received and analyzed by Eurofins Eaton Analytical, Inc. could not be included.

Chemical Assessment

The primary objective of this assessment was to determine if inconsistent thermal preservation influenced drinking water sampling results by comparing data across a number of years from the same system and sampling point. The goal of this matching assessment was to determine if there is a systematic downwards bias (hypothesized for VOCs/SOCs) or systematic upwards bias (hypothesized for DBPs) in contaminant concentration. If the paired sample results are found to be similar with no bias in one direction or the other, then it can be inferred that thermal preservation did not significantly impact results. If bias is found, it will be necessary to determine if the disagreement is enough to cause differences in interpretation (i.e., is public health action necessary).

The following steps were taken to compare contaminant concentrations in samples that were not consistently thermally-preserved to samples to those collected in 2016 that strictly followed thermal preservation guidelines:

1. Data for thermally preserved samples were extracted using an SQL query of MNDWIS data from the date range 02/16/2016 to 02/15/2017. Data for samples collected prior to strict enforcement of icing requirements were extracted from the previous two years (02/16/2014 – 02/15/2016) and were used as the comparison group. As shown in Figure 3 above, the majority of samples collected during this time period and received more than 24 hours later were not compliant with the receiving temperature range of 0 and 6° C.
2. The purpose of the analysis was to determine whether lack of thermal preservation *after* samples were collected impacted concentration results. *Prior* to sample collection, ambient temperature variation across season may also influence chemical concentrations. Since groundwater temperature is less influenced by ambient air temperature compared to surface water temperature, the analysis was restricted to groundwater systems only. Fewer than 5% of public water systems in Minnesota use a surface water source.
3. Sample results from 02/16/2016 to 02/15/2017 (thermally preserved) were matched to sample results from the previous two years (non-thermally preserved) at the same

system and sampling point. Sampling point results without any matches could not be included. For example, if a thermally preserved sample result was available but the same system-sampling point had not been sampled in the previous two years, no match could be made and that result was not included in the analysis. For DBPs, samples were matched on the same system and *location in the distribution system*. NOTE: Prior to matching, distribution system location name was converted to lower-case text with all spaces removed. Even so, some samples may have been excluded from this analysis due to inconsistencies in the distribution system location name entered in MNDWIS, resulting in mismatches.

4. Many analytes had more than one result per system-sampling point during the comparison timeframes. In cases where there were multiple samples per system-sampling point available for matching, one pair per system-sampling point (the “best match”) was retained using the following criteria:
 - a. Due to the potential for seasonal variation, DBP and current-use pesticide SOC thermally preserved samples were matched with the non-thermally preserved sample that was closest in *month* and then closest in year. Since DBP samples are taken in the distribution system, which further increases the likelihood of seasonal temperature effects on concentration results *prior* to collection, only DBP paired samples collected during the same month, or ± 1 month were analyzed. Due to established sampling schedules, this criteria did not result in the exclusion of many paired samples.
 - b. For VOCs, all other SOCs, and cyanide, the thermally-preserved sample was matched with the non-thermally preserved sample that was closest in time, regardless of season.
5. For analytes with multiple Minimum Reporting Limits (MRLs) (see Table 4), all results were left-censored to the highest MRL in a two-step process to ensure a proper comparison. First, if there were two different method MRLs, any quantitative result that was above the lower MRL but below the higher MRL was set to the higher MRL. For example, if MRLs were 0.5 ppb and 0.1 ppb, and a result of 0.2 ppb was measured using the method with the lower MRL, the result would be set to < 0.5 ppb. In the second step all “less than” results were set to one half of the higher MRL.

Due to their different characteristics, sources, and implications, results are grouped into three main contaminant classes: DBPs, IOCs/SOCs, and VOCs. A summary of results from the matched pair analysis is followed by an assessment of individual compounds detected in the thermally-preserved samples. Scatter plots of the difference in concentration between matched pairs (y-axis) by the temperature of the pre-iced sample (x-axis) in Appendix D are used to visually assess how the post-collection sample temperature may have impacted concentration results. For DBPs with a higher number of detections, additional figures are presented: Either jittered scatterplots⁴ or, if enough detections are available, boxplots of concentration difference by categorical pre-iced sample receiving temperature. In most cases, formal statistical testing of concentration differences between the non-thermally preserved and thermally preserved

samples was not feasible due to the low number of detections found and the resultant number of paired results tied below the MRL. The term “tied” indicates that results from both samples in the pair have the same value. Given the high proportion of left-censored values, the following approaches were taken:

- The number and percent of tied pairs and non-tied pairs are reported along with the number and percent of non-tied pairs in which the thermally-preserved result and non-thermally preserved sample result were higher, and the average concentration difference in non-tied pairs (thermally-preserved – not thermally preserved).

⁴ Jittering adds a little random noise to the data when there are many overlapping points. Adding some jitter turns overlapping points into a cloud to make the overall pattern of points and any trends easier to visualize.

- The difference in concentration between paired results is plotted against the pre-iced sample receiving temperature in Appendix D. The purpose of the plots is to visually examine any relationships that may exist between the concentration difference in matched pairs and the magnitude of the receiving temperature. If there is random variability in concentration difference, data points will be both above and below the zero difference line across the range of temperature. If there is systematic bias in concentration difference due to the influence of the pre-iced sample temperature, data points will be consistently above or below the zero difference line, and/or may show increasing difference in one direction with increasing temperature.
- If greater than 50% of pairs had at least one result above the MRL (which only applies to some DBPs), the Wilcoxon signed-rank test was conducted. This is a non-parametric version of a paired samples t-test. It tests whether the median difference in concentration between iced and non-iced samples is significantly different from zero at $\alpha=0.05$. Note that when the concentration difference between the paired samples is zero, the observation is discarded; meaning the Wilcoxon sign-rank test only considers non-tied pairs.

Results

Quality Assurance

Both DWP and PHL have agreed to use a single list of analytical data qualifiers, which is found in Appendix A. When applying and interpreting these qualifiers it is critical to consider all information provided to ensure an appropriate quality determination. In some cases, a single qualifier may be sufficient to invalidate a results. However, in other cases a series of qualifiers may provide helpful information but not result in invalidation. Processes have been implemented to apply consistent qualifiers that ensure high quality data with minimal sample cancellation.

The DWP chain of custody forms were examined and found to be missing some key fields, most prominent being the “accepted/relinquished” signature blocks for sample sets. The templates were extracted from the DWP database and updated to include a signature block (Appendix B). Training and updated sampling instructions were provided and the new forms were put into production on January 1, 2017. They will be reviewed and updated on an annual basis.

Due to differing priorities (sample collection/delivery vs. sample receipt/analysis) sample acceptance criteria were updated for both DWP and PHL activities (Appendix C). The DWP version emphasizes issues related to missing data fields on the chain-of-custody forms, conditions that mandate re-collection of the sample, and DWP actions resulting from certain situations. The PHL version emphasizes the minimum requirements for a valid sample submission, data qualifiers that will be applied, and actions resulting from certain situations. The recently reconstituted DWP/PHL Workgroup will assess each form and recommend a consensus approach.

Sampling

The sample collection effort in 2016 represented a significant increase in workload for staff throughout the program (Table 4). Training on the updated sampling instructions and thermal preservation occurred throughout 2016 and prompted a number of additional quality improvement steps, including revision of the chain of custody form, clarification of data qualifiers, and improved communication between DWP and PHL.

Table 4: Number of samples collected by MDH annually

Year	Free Cyanide	VOCs	SOCs
2013	270	767	547
2014	333	829	603
2015	254	937	525
2016	523	1604	1510

Letters containing all sampling results and describing impacts on routine sample schedules were sent to each of the systems that were sampled. Because some of the samples were collected within the previously established compliance period they also satisfied the monitoring requirements of SDWA. Facilities were instructed to keep the results on or near the water supply premises and available for public inspection for at least 10 years.

Analytical results

A summary of the contaminants with detections for compliant samples is presented at both the sampling point and system level (Table 5). Of the 57 contaminants assessed, 33 were detected at some point. The first columns provide the minimum reporting limits (MRLs), the number of samples collected, and the total number of detections at each system and sample location. Results that were left-censored are also included.

The largest number of detections, by far, were found for DBPs, where some compounds were detected at over half of the sample points. Almost no SOC's were found, while very few IOC's or VOC's were detected.

The number of systems tested can be less than 919 because some systems were excluded due to no matching results. The number of samples and sampling points can be greater than 919

because some systems were sampled more than once or have multiple sampling locations. When more than one lab analyzed samples, results were left-censored to the higher MRL consistent with step 5 in Chemical Assessment above.

Table 5a: Overview of detected compounds (thermally-preserved sample data: Feb 16, 2016 - Feb 15, 2017) - IOCs

Compound detected	Eurofins and MDH MRLs ⁵ (<i>< ug/L</i>)	# samples	# sampling points tested ⁶	# systems tested	# sampling points with detections	# sampling points with detections <i>left-censored at higher MRL</i>	# systems with detections	# systems with detections <i>left-censored at higher MRL</i>
Cyanide, Free	0.05 (MDH only)	510	495	414	9	N/A ⁷	9	N/A

Table 5b: Overview of detected compounds (thermally-preserved sample data: Feb 16, 2016 - Feb 15, 2017) - DBPs

Compound detected	Eurofins and MDH MRLs ⁵ (<i>< ug/L</i>)	# samples	# sampling points tested ⁶	# systems tested	# sampling points with detections	# sampling points with detections <i>left-censored at higher MRL</i>	# systems with detections	# systems with detections <i>left-censored at higher MRL</i>
Bromodichloromethane	0.5 (MDH only)	1538	1022	768	703	N/A	481	N/A
Bromoform	0.5 (MDH only)	1538	1022	768	264	N/A	151	N/A
Chlorodibromomethane	0.5 (MDH only)	1538	1022	768	526	N/A	382	N/A
Chloroform	0.5 (MDH only)	1538	1022	768	869	N/A	632	N/A
Dibromoacetic Acid	1.0 (MDH only)	1522	1008	756	209	N/A	159	N/A
Dichloroacetic Acid	1.0 (MDH only)	1522	1008	756	706	N/A	498	N/A
Monobromoacetic Acid	1.0 (MDH only)	1522	1008	756	14	N/A	11	N/A
Monochloroacetic Acid	2.0 (MDH only)	1522	1008	756	134	N/A	63	N/A
Trichloroacetic Acid	1.0 (MDH only)	1522	1008	756	603	N/A	395	N/A

Table 5c: Overview of detected compounds (thermally-preserved sample data: Feb 16, 2016 - Feb 15, 2017) - SOCs

Compound detected	Eurofins and MDH MRLs ⁵ ($< \mu\text{g/L}$)	# samples	# sampling points tested ⁶	# systems tested	# sampling points with detections	# sampling points with detections <i>left-censored at higher MRL</i>	# systems with detections	# systems with detections <i>left-censored at higher MRL</i>
2,4-D	E=0.1 M=0.5	1417	1098	790	2	0	2	0
Atrazine	E&M=0.1	1426	1096	789	2	N/A	2	N/A
Endrin	E=0.01 M=0.01; 0.1	1426	1096	789	1	0	1	0
Pentachlorophenol (PCP)	E=0.04 M=0.1	1417	1098	790	1	0	1	0
Picloram	E=0.1 M=0.5	1417	1098	790	3	1	3	1

Table 5d: Overview of detected compounds (thermally-preserved sample data: Feb 16, 2016 - Feb 15, 2017) - VOCs

Compound detected	Eurofins and MDH MRLs ⁵ ($< \mu\text{g/L}$)	# samples	# sampling points tested ⁶	# systems tested	# sampling points with detections	# sampling points with detections <i>left-censored at higher MRL</i>	# systems with detections	# systems with detections <i>left-censored at higher MRL</i>
1,2-Dichloroethane	E=0.5 M=0.2	1484	1239	882	8	5	5	3
1,4-Dichlorobenzene	E=0.5 M=0.2	1484	1239	882	6	3	5	2
Benzene	E=0.5 M=0.2	1484	1239	882	8	1	5	1
Carbon tetrachloride	E=0.5 M=0.2	1484	1239	882	1	1	1	1
cis-1,2-Dichloroethene	E=0.5 M=0.2	1484	1239	882	19	15	9	6
Di(2-ethylhexyl) adipate	E&M: 0.6	1426	1096	789	1	1	1	1

Compound detected	Eurofins and MDH MRLs ⁵ (< ug/L)	# samples	# sampling points tested ⁶	# systems tested	# sampling points with detections	# sampling points with detections left-censored at higher MRL	# systems with detections	# systems with detections left-censored at higher MRL
Di(2-ethylhexyl) phthalate	E=0.6 M=0.6; 1.8	1426	1096	789	59	12	49	10
Ethylbenzene	E&M: 0.5	1484	1239	882	10	N/A	10	N/A
Hexachloro-cyclopentadiene	E=0.1 M=0.1; 0.3	1426	1096	789	1	0	1	0
Methylene chloride	E&M: 0.5	1484	1239	882	4	N/A	4	N/A
o-Xylene	E=0.5 M=0.2	1484	1239	882	19	14	18	13
p&m-xylene	E=0.5 M=0.3	1484	1239	882	19	15	19	15
Styrene	E&M: 0.5	1484	1239	882	5	N/A	5	N/A
Tetrachloroethene	E=0.5 M=0.2	1484	1239	882	8	6	8	6
Toluene	E=0.5 M=0.2	1484	1239	882	13	9	12	8
trans-1,2-Dichloroethene	E=0.5 M=0.1	1484	1239	882	11	6	3	1
Trichloroethene (TCE)	E=0.2 M=0.1	1484	1239	882	25	23	20	18
Vinyl chloride	E&M: 0.2	1484	1239	882	8	N/A	4	N/A

⁵ E = Eurofins; M = MDH PHL; does not include MRLs applicable to $\leq 1\%$ of the samples

⁶ For DBPs, sampling points were different locations within the distribution system

⁷ N/A = Not applicable; only 1 MRL does not require left censoring

Exceedances of Health Based Values

While the samples were collected after treatment (if present), water quality and chemistry can change before being delivered to an individual tap. Therefore, the concentrations discussed below do not necessarily reflect residential exposure levels. In addition, a regulatory exceedance only occurs after a running quarterly average exceeds the MCL, not after a single result.

To investigate potential implications for public health impacts, tables 6 (DBPs) and 7 (IOC/SOCs and VOCs) provide the maximum concentration measured for each analyte with at least one detection, and reports the number of samples that exceeded federal drinking water maximum

contaminant levels (MCLs) or MDH health risk limits (HRLs) at the system and system-location level. The DBPs are listed in a separate table because they are managed differently than the other, single contaminants. Unless a single result is greater than 4 times the MCL, one sample will not result in a violation of the SDWA. Compliance with the SDWA is monitored using running, quarterly average concentrations.

Table 6: DBP concentration results compared to MCLs and MDH health-based guidance values (thermally-preserved sample data: Feb 16, 2016-Feb 15, 2017)

Compound detected	Sample max (ppb) ⁰	MCL (ppb)	# sampling points with sample >MCL*	# systems with sample >MCL*	HRL (ppb)
Bromodichloromethane	48	Sum of 1 – 4 ≤ 80	10	9	6
Bromoform	30	Sum of 1 – 4 ≤ 80	10	9	40
Chlorodibromomethane	43	Sum of 1 – 4 ≤ 80	10	9	-
Chloroform	210	Sum of 1 – 4 ≤ 80	10	9	20
Dibromoacetic Acid	9.2	Sum of 5 – 9 ≤ 60	8	5	-
Dichloroacetic Acid	120	Sum of 5 – 9 ≤ 60	8	5	-
Monobromoacetic Acid	9.1	Sum of 5 – 9 ≤ 60	8	5	-
Monochloroacetic Acid	12	Sum of 5 – 9 ≤ 60	8	5	-
Trichloroacetic Acid	110	Sum of 5 – 9 ≤ 60	8	5	-

*System issues were being addressed prior to re-sampling

Compounds 1 – 4 in Table 6 are collectively known as trihalomethanes (TTHM), while 5 – 9 are collectively known as haloacetic acids (HAA5). According to the federal SDWA, drinking water is regulated for DBPs by monitoring TTHMs and HAA5s.

Assessing health impacts from DBPs is complicated by their seasonal variability, concentration fluctuations, and public health benefits from chlorination. Drinking water treatment operations must often meet competing objectives, including adequate microbial protection (increase chlorination), reduced levels of disinfection by-products (decrease chlorination), and corrosion control-to comply with EPA regulations. The key to treatment is to provide a balance between the health benefits of disinfected drinking water and the creation of by-products from the disinfectants.

Table 7: IOC/SOC and VOC concentration results compared to MCLs and MDH health-based guidance values (thermally-preserved sample data: Feb 16, 2016-Feb 15, 2017)

Compound detected	Sample max (ppb)	MCL (ppb)	# sampling points with sample >MCL*	# systems with sample >MCL*	HRL (ppb)
Cyanide, Free	0.76	200	0	0	100
2,4-D					
Atrazine	0.3*	70	0	0	30
Endrin	0.12	3	0	0	3
Pentachlorophenol (PCP)	0.01*	2	0	0	N/A
Picloram	0.06*	1	0	0	0.3
1,2-Dichloroethane	5	5	0	0	1
1,4-Dichlorobenzene	0.81	75	0	0	10
Benzene	0.5	5	0	0	2
Carbon tetrachloride	15	5	1	1	1
cis-1,2-Dichloroethene	25	70	0	0	50
Di(2-ethylhexyl) adipate	45	400	0	0	N/A
Di(2-ethylhexyl) phthalate	10	6	1	1	7
Ethylbenzene	5.7	700	0	0	50
Hexachloro-cyclopentadiene	0.1*	50	0	0	N/A
Methylene chloride	2.2	5	0	0	5
o-Xylene**	5.5	10000	0	0	300
p&m-xylene**	19	10000	0	0	300
Styrene	11	100	0	0	N/A
Tetrachloroethene	1.5	5	0	0	4
Toluene	3.8	1000	0	0	200
trans-1,2-Dichloroethene	5.1	100	0	0	40
Trichloroethene (TCE)	17	5	2	2	4
Vinyl chloride	2.9	2	1	1	0.2

*Max value < highest MRL

**MCL and HRL are sum of total xylene

* System issues were being addressed prior to re-sampling

Individual Assessment of Exceedances of Health Based Values

Of the 47,913 individual analyte results generated, there were 5 systems with a single result that exceeded the federal MCL. In addition, there were five systems with results above the MDH HRL (not a regulatory standard), excluding the DBPs (Table 8). There were four contaminants with a single result above the drinking water standard: Carbon tetrachloride (1 system), Di (2-ethylhexyl) phthalate (1 system), Trichloroethene (2 systems), and Vinyl chloride (1 system). Five additional contaminants exceeded HRLs but were less than the MCL: 1, 2-Dichloroethane (1 system), Trichloroethene (1 system), and Vinyl chloride (3 systems). Because HRLs are all lower than MCLs, all systems that exceeded MCLs obviously also exceeded HRL limits.

For the five systems that had a sample exceed the federal MCL, none had multiple contaminants, two had follow-up samples that were less than the MRL, and one was a new location. One of the remaining systems has had a carbon filter installed since 2005, and therefore is delivering drinking water with non-detectable levels of TCE (the sample was taken at the entry point, which is before any treatment). The other system has been on increased quarterly monitoring and is adjacent to a Superfund site releasing TCE.

With the exception of one vinyl chloride result, all exceedances were just above the HRL threshold and were in locations that were already on increased monitoring because of a known water quality issue. Two of the systems were connected to community water supplies, one has treatment prior to distribution, one returned a non-detect confirmation sample, and the final location is adjacent to a long-time Superfund site.

Therefore, no additional threats to public health from drinking water were revealed as part of the extended sampling done in 2016.

Table 8a: Exceedances of MCL levels in samples from Feb 16, 2016-Feb 15, 2017, excluding DBPs

County	Contaminant	MCL	2016 Concentration	Date of first exceedance	Comments
St. Louis	Di-2-ethylhexyl phthalate	6 ppb	10 ppb	2006	2016 confirm sample < MCL; surface water system
Wright	Carbon Tetrachloride	5 ppb	15 ppb	NA	New entry point
Washington	Trichloroethene	5 ppb	17 ppb	2016	Carbon filters in use since 2005
Washington	Trichloroethene	5 ppb	8 ppb	2007	Ongoing quarterly monitoring
Hennepin	Vinyl Chloride	2 ppb	5 ppb	2016	Subsequent samples < MDL

Table 8b: Exceedances of HRL levels in samples from Feb 16, 2016-Feb 15, 2017, excluding DBPs

County	Contaminant	HRL	2016 Concentration	Date of first exceedance	Comments
Dakota	1,2-Dichloroethane	1 ppb	1.8 ppb	2008	Reverse osmosis provided at breakroom tap since 2001; first detect in 2004; connected to community PWS in 2018
Houston	Trichloroethene	4 ppb	4 ppb	1995	Air stripper treatment installed prior to 1994; Air stripper treatment replaced June 2017
Dakota	Vinyl chloride	0.2 ppb	0.30 ppb	2016	2016 confirm sample < MRL (< 0.20 ug/L)
Anoka	Vinyl chloride	0.2 ppb	0.32 ppb	2008	Quarterly monitoring performed through July 2017; connected to community PWS in 2017
Hennepin	Vinyl chloride	0.2 ppb	1.90 ppb	2008	Located adjacent to Superfund site

For DBPs there were 14 systems with one result that exceeded a drinking water standard; nine for TTHM and five for HAA5. For the TTHM locations one system with past elevated results exceeded based on an average quarterly concentration and the other eight had a single result above the MCL, ranging from 80.5 ppb to 215 ppb and located all across the state. For the HAA5 locations one system with past elevated results exceeded based on an average quarterly concentration and the other four had a single result above the MCL, ranging from 62 ppb to 242 ppb and located all across the state.

Typically, approximately one PWS exceeds the TTHM MCL based on average quarterly concentration per calendar year. Recent numbers of TTHM MCL violations have been: one (2016), three (2015), one (2014), one (2013), 0 (2012), one (2011), zero (2010), three (2009), and one (2008). HAA5 average quarterly concentrations exceeding the MCL are less common, occurring approximately every three years: one in 2016, one in 2014, one in 2008, one in 2007, one in 2005, and one in 2004. Therefore having one exceedance each for TTHM and HAA5 in the compliant set is consistent with past results.

For individual DBP results exceeding MCLs, the 2016 values (eight for TTHM and four for HAA5) are consistent with results from the previous year (14 for TTHM and five for HAA5). Therefore the number of violations in the compliant sample set is consistent with past results.

Paired Sample Analysis: DBP Results

It is expected that non-thermally preserved DBP levels may be higher than thermally-preserved DBP levels because, typically, DBPs form at faster rates and reach higher equilibrium concentrations in warmer water. Factors such as biodegradation and volatilization, which would also be expected to increase with increasing temperatures and therefore lower some DBP concentrations, are not thought to impact all samples and to the same extent. Biodegradation is a process that would affect the haloacetic acids and not the trihalomethanes, thus reducing their prevalence and impact on DBPs as a whole.

Detections in the total sample set were highest for the DBPs, with five of the nine DBPs having over 50% of paired results with detections (Table 9). The difference in paired samples was not biased in the same direction for all DBPs, with four of the nine DBPs showing a higher number of non-thermally preserved sample results among non-tied pairs. The mean difference between thermally-preserved and non-thermally preserved samples was highest for dichloroacetic acid and trichloroacetic acid, which both had higher non-thermally preserved concentrations overall, and the difference between the samples was statistically significant in the Wilcoxon signed-rank test. The differences could be the result of changes in thermal preservation methods during sample collection and shipping.

However, the statistically significant differences in two DBPs are overshadowed by the overall variability in the results (caused by specific, local conditions and approaches) and seasonal nature of the occurrences (they are more likely to appear in late summer or early fall). The observed trend does not reflect a major change in expected public health condition of drinking water with respect to DBPs: they can occur in vulnerable systems during high risk seasons and must be managed according to local/regional needs and resources.

Table 9: Summary of iced and non-iced paired DBP results from same system and location in the distribution system

Compound	# Sample point pairs ¹	Tied pairs # (%)	Non-tied pairs # (%)	Non-tied pairs Higher iced concentration # (%)	Non-tied pairs Higher non-iced concentration # (%)	Non-tied pairs Mean difference (iced – non-iced) ²	Non-tied pairs Wilcoxon Signed Rank Test
Bromodichloromethane	704	<MRL: 184 (26%) >MRL: 23 (3%)	497 (71%)	264 (38%)	233 (35%)	-0.06 ppb	Z=3102.5 P=0.3333
Bromoform	704	<MRL: 521 (74%)	172 (24%)	103 (15%)	69 (10%)	0.05 ppb	N/A

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Compound	# Sample point pairs ¹	Tied pairs # (%)	Non-tied pairs # (%)	Non-tied pairs Higher iced concentration # (%)	Non-tied pairs Higher non-iced concentration # (%)	Non-tied pairs Mean difference (iced – non-iced) ²	Non-tied pairs Wilcoxon Signed Rank Test
		>MRL: 11 (2%)					
Chlorodibromomethane	704	<MRL: 281 (40%) >MRL: 27 (4%)	396 (56%)	216 (31%)	180 (26%)	-0.14 ppb	Z=2717.5 P=0.2336
Chloroform	704	<MRL: 66 (9%) >MRL: 24 (3%)	614 (87%)	328 (47%)	286 (41%)	-0.16 ppb	Z=4802 p=0.2752
Dibromoacetic Acid	649	<MRL: 466 (75%) >MRL: 6 (1%)	177 (27%)	86 (13%)	91 (14%)	-0.03 ppb	N/A
Dichloroacetic Acid	649	<MRL: 152 (23%) >MRL: 14 (2%)	483 (74%)	212 (33%)	271 (42%)	-0.46 ppb	Z=-9838 P=0.0013
Monobromoacetic Acid	649	<MRL: 635 (98%) >MRL: 0 (0%)	14 (2%)	10 (2%)	4 (1%)	0.33 ppb	N/A
Monochloroacetic Acid	649	<MRL: 594 (92%) >MRL: 2 (<1%)	53 (8%)	26 (4%)	27 (4%)	0.23 ppb	N/A
Trichloroacetic Acid	649	<MRL: 153 (24%) >MRL: 15 (2%)	481 (74%)	210 (32%)	271 (42%)	-0.39 ppb	Z=-7314.5 P=0.0163

¹ Groundwater system samples only, collected during same time of year (±1 month)

² Mean difference among non-tied pairs only. Results <MRL were assigned a value of ½ MRL

Scatter plots, and in some cases boxplots, of the paired data are presented in Appendix D. Individual contaminant results are discussed below.

Bromodichloromethane

Of 704 paired samples, 74% had at least one result greater than the MRL. Of non-tied pairs, there was a higher percent with a higher thermally-preserved concentration. Overall mean difference between the paired results was small (-0.06 ppb). The Wilcoxon signed-rank test was not statistically significant indicating that the iced and non-iced concentration results are not significantly different from one another. No bias is visually apparent in the scatterplot of paired sample concentration difference by pre-icing sample receiving temperature; nor in the boxplot (Appendix D). However, since the number of pairs in which the pre-iced sample receiving temperature was 6 °C or below were sparse, the boxplot and descriptive statistics should be interpreted with caution.

Bromoform

Of 704 paired samples, 26% had at least one result greater than the MRL. The difference between the non-tied samples overall was small, with a mean difference of 0.05 ppb, indicating that iced and non-iced samples were very similar. No visual pattern in concentration difference by temperature is seen in Appendix D, except perhaps an increase in overall variability above 12 °C.

Chlorodibromomethane

Of 704 paired samples, 60% had at least one result greater than the MRL. Among non-tied pairs, there was a greater number with a higher iced sample concentration. The mean difference between the iced and non-iced samples overall was small (-0.14 ppb). The Wilcoxon signed-rank test was not statistically significant ($p=0.238$), indicating that the thermally preserved and non-thermally preserved results are not significantly different from one another. Visually, no obvious bias is seen in the scatterplot/jittered scatterplot (Appendix D).

Chloroform

Of 704 paired samples, 91% had at least one result greater than the MRL. Among non-tied pairs, there was a greater number with a higher iced sample concentration. The mean difference between paired samples was small (-0.16 ppb). The Wilcoxon signed-rank test was not statistically significant ($Z=280$, $p=0.9630$) indicating that, even though there were a large number of detections, the iced and non-iced results are not significantly different from one another. The boxplot in Appendix D shows a slight decrease in mean concentration difference with increasing temperature. However, since the number of pairs in which the pre-iced sample receiving temperature was 6 °C or below were sparse, the boxplot and descriptive statistics should be interpreted with caution.

Dibromoacetic Acid

Of 649 paired samples, 28% had at least one result greater than the MRL. The mean difference between the non-tied paired samples was small (-0.03 ppb), indicating that concentration

results were similar. No trend is seen in median or mean concentration difference with increasing temperature (Appendix D).

Dichloroacetic acid

Of 649 paired samples, 77% had at least one result greater than the MRL. Among non-tied pairs, the non-iced sample result was higher more frequently with a mean difference of -0.46 ppb.

The Wilcoxon signed-rank test was statistically significant ($p=0.001$) indicating that the concentration in iced and non-iced samples is significantly different. While no difference in median concentration by temperature category was seen in the boxplot, there was a decrease in mean concentration difference seen in the highest temperature category, indicating that that the pre-iced concentration may have increased slightly as the temperature increased. Since paired results in which the pre-iced sample receiving temperature was 6 ° C or below were sparse, the boxplot and descriptive statistics in this first temperature category should be interpreted with caution.

From a public health standpoint, if the lack of thermal preservation resulted in a slightly higher reported concentration for dichloroacetic acid, past results would be overestimates, rather than underestimates, of concentration.

Monobromoacetic Acid

Of 649 paired samples, monobromoacetic acid was rarely detected, with only 2% of paired samples having at least one result greater than the MRL. The mean difference in concentration in the paired samples was small (0.33 ppb). In the 14 non-tied pairs, the iced concentration was higher than the non-iced concentration more often. The scatterplot does not show that this bias increased in frequency or magnitude with increasing temperature. Due to the high number of pairs <MRL, no further analysis could be done.

Monochloroacetic acid

Of 649 paired samples, 9% had at least one result greater than the MRL. The mean difference between the iced and non-iced non-tied pairs overall was small (0.23 ppb). Approximately the same number of pairs had a higher iced or non-iced concentration, and the scatterplot shows no consistent bias. Due to the high percent of pairs <MRL, no further analysis could be done.

Trichloroacetic acid

Of 649 paired samples, 76% had at least one result greater than the MRL. Of the non-tied pairs, there were more occurrences of a higher non-iced concentration (42% vs. 32%). The Wilcoxon signed-rank test was statistically significant indicating that the concentration in iced and non-iced samples is different. While no difference in median concentration by temperature category was seen in the boxplot, there was a decrease in mean concentration difference in the highest temperature category, indicating that that the pre-iced concentration may have increased slightly as the temperature increased. Since paired results in which the pre-iced sample receiving temperature was 6 C or below were sparse, the boxplot and descriptive statistics in this first temperature category should be interpreted with caution. From a public health

standpoint, if the lack of thermal preservation resulted in a higher reported concentration of trichloroacetic acid, past results would be overestimates, rather than underestimates, of concentration.

IOC and SOC Results

Iced and non-iced paired results for cyanide and the SOCs were equivalent in almost all cases, with nearly all results both below the MRL (97-100% of pairs) (Table 10). All non-tied pair samples were close to the zero difference line, with concentration differences of ≤ 1 ppb (Appendix D).

There was no evidence of a consistent upwards or downwards bias in SOC concentration results between iced and non-iced paired samples. However, the comparison was hindered by the very high percent of results less than the MRL. Three of the six compounds did not have a single detection.

The observed results do not reflect a major change in expected public health condition of drinking water with respect to IOCs or SOCs: detections are very rare and generally at very low concentrations.

Table 10: Summary of thermally-preserved and non-thermally-preserved paired IOC and SOC results at same system and sampling point

Compound	# Sample point pairs ¹	Tied pairs # (%)	Non-tied pairs		Non-tied pairs Mean difference (iced – non-iced) ²
			Higher iced concentration # (%)	Higher non-iced concentration # (%)	
Cyanide, Free	133	<MRL: 128 (96%) >MRL: 0	1 (<1%)	4 (3%)	-0.04 ppm ²
2,4-D	All results <MRL	All results <MRL	All results <MRL	All results <MRL	All results <MRL
Atrazine	684	<MRL: 679 (99%) >MRL: 0	4 (1%)	1 (<1%)	-0.03 ppb
Endrin	All results <MRL	All results <MRL	All results <MRL	All results <MRL	All results <MRL
Pentachlorophenol (PCP)	All results <MRL	All results <MRL	All results <MRL	All results <MRL	All results <MRL
Picloram	705	<MRL: 703 (>99%) >MRL: 0	1 (<1%)	1 (<1%)	0.23 ppb

¹ Mean difference among untied pairs only. Results <MRL were assigned a value of $\frac{1}{2}$ MRL

² ppm = parts per million = mg/L

Scatter plots of concentration difference between paired results by non-iced sample receiving temperature for IOC/SOCs are presented in Appendix D. Individual contaminant results are discussed below.

Cyanide, free

Only five pairs out of 133 (3%) had at least one result greater than the MRL. The mean difference between the iced and non-iced non-tied pairs overall was small (-0.04 mg/L), indicating that the results were very similar. Due to the high percent of pairs <MRL, no further analysis could be done.

Atrazine

Only five pairs out of 684 (1%) had results greater than the MRL. The mean difference between the iced- and non-iced non-tied samples overall was small (-0.03 ppb), indicating that the results were very similar. Due to the high percent of pairs <MRL, no further analysis could be done.

Picloram

Only two pairs out of 705 (<1%) had results greater than the MRL. The mean difference between the iced and non-iced non-tied pairs overall was higher compared to the other SOCs, but still very small (0.23 ppb), indicating that the results were very similar. Due to the high percent of pairs <MRL, no further analysis could be done.

VOC Results

Thermally-preserved/non-thermally preserved paired results for VOCs were equivalent in almost all cases, with nearly all paired results (97% - 99%) below the MRL (Table 11). Many of the VOC non-tied pairs had a mean difference in concentration of less than 1 ppb. However, there were several instances of single outliers in the pairs with unusually large concentrations, which resulted in a higher mean difference. At least a subset of these outliers are expected to represent external contamination of the sample. For example, one system (1020017) had an entry point result of 45 ug/L di(2-ethylhexyl) adipate. The result from a thermally-preserved sample taken two months later at this same entry point was below the MRL.

Overall, there were more cases in which the thermally-preserved result was higher than the non-thermally preserved result (11/18 analytes) among non-tied paired samples, which would be the expected outcome if thermal preservation had an influence on concentration. However, an increase in concentration difference with increasing sample receiving temperature was not seen in the scatterplots (Appendix D). For 4/18 analytes, the number of pairs in which the iced- and non-iced samples were higher were equal, and for 3/18 analytes, there were more non-iced results that were higher in the pair.

For VOCs overall detections were rare, with 99% of sample points being less than the MRL for an individual contaminant. The low number of detections and small differences between results, combined with a lack of trend seen in scatterplots of concentration difference by sample receiving temperature makes characterizing a trend uncertain. As with the previous two contaminant groups, results were comparable to past results across the state and nationwide.

The observed results do not reflect a major change in expected public health condition of drinking water with respect to VOCs: detections are unusual and generally occur at very low concentrations.

Table 11: Summary of thermally-preserved and non-thermally preserved paired VOC results at same system and sampling point

Compound	# Sample point pairs ¹	Tied pairs # (%)	Non-tied pairs	Non-tied pairs	Non-tied pairs
			Higher iced concentration # (%)	Higher non-iced concentration # (%)	Mean difference (iced – non-iced) ²
1,2-Dichloroethane	781	<MRL: 777 (>99%) >MRL: 0	1 (<1%)	3 (<1%)	-0.04 ppb
1,4-Dichlorobenzene	781	<MRL: 780 (>99%) >MRL: 0	1 (<1%)	0 (0%)	0.38 ppb (1 pair only)
Benzene	781	<MRL: 780 (>99%) >MRL: 0	0 (0%)	1 (<1%)	-1.05 ppb (1 pair only)
Carbon tetrachloride	781	<MRL: 780 (>99%) >MRL: 0	1 (<1%)	0 (0%)	14.75 ppb (1 pair only)
cis-1,2-Dichloroethene	781	<MRL: 769 (99%) >MRL: 1 (<1%)	7 (<1%)	4 (<1%)	0.12 ppb
Di(2-ethylhexyl) adipate	684	<MRL: 682 (>99%) >MRL: 0	1 (<1%)	1 (<1%)	22.20 ppb
Di(2-ethylhexyl) phthalate	683	<MRL: 677 (99%) >MRL: 0	4 (<1%)	2 (<1%)	0.77 ppb
Ethylbenzene	781	<MRL: 776 (>99%) >MRL: 0	3 (<1%)	2 (<1%)	1.03 ppb
Hexachloro-cyclopentadiene		All results <MRL	All results <MRL	All results <MRL	All results <MRL
Methylene chloride	781	<MRL: 778 (>99%) >MRL: 0	2 (<1%)	1 (<1%)	0.26 ppb
o-Xylene	781	<MRL: 771 (99%) >MRL: 0	6 (<1%)	4 (<1%)	0.49 ppb
p&m-xylene	781	<MRL: 767 (98%) >MRL: 0	7 (<1%)	7 (<1%)	1.34 ppb
Styrene	781	<MRL: 778 (>99%) >MRL: 0	3 (<1%)	0 (0%)	2.23 ppb
Tetrachloroethene	781	<MRL: 773 (99%)	4 (<1%)	4 (<1%)	0.04 ppb

Compound	# Sample point pairs ¹	Tied pairs # (%)	Non-tied pairs	Non-tied pairs	Non-tied pairs
			Higher iced concentration # (%)	Higher non-iced concentration # (%)	Mean difference (iced – non-iced) ²
		>MRL: 0			
Toluene	781	<MRL: 770 (99%) >MRL: 0	7 (<1%)	4 (<1%)	-0.33 ppb
trans-1,2-Dichloroethene	781	<MRL: 778 (>99%) >MRL: 0	2 (<1%)	1 (<1%)	0.10 ppb
Trichloroethene (TCE)	781	<MRL: 758 (97%) >MRL: 1 (<1%)	9 (1%)	13 (2%)	-0.37 ppb
Vinyl chloride	781	<MRL: 774 (99%) >MRL: 0	4 (<1%)	3 (<1%)	0.07 ppb

¹ Mean difference among non-tied pairs only. Results <MRL were assigned a value of ½ MRL

Scatter plots of concentration difference between paired results by non-iced sample receiving temperature for VOCs are presented in Appendix D. Individual contaminant results are discussed below.

1, 2-Dichloroethane

Only four pairs out of 781 had a result greater than the MRL. In three out of the four cases, the iced sample was lower than the non-iced sample by an average of -0.04 ppb, which is a very small difference. Therefore there is not enough evidence to show a meaningful difference between iced and non-iced samples. No samples exceeded the MCL but one system had results at the HRL of 5 ppb. DWP will follow up to further document trends and take appropriate action.

1, 4-Dichlorobenzene

Only one pair out of 781 had a result greater than the MRL. In that single pair, the iced sample result was slightly above the non-iced sample (0.38 ppb), there are not enough detections to show a difference between the samples.

Benzene

Only one pair out of 781 had a result greater than the MRL. In that single pair the iced sample was lower than the non-iced sample (-1.05 ppb). There are not enough detections to show a difference between iced/non-iced samples.

Carbon tetrachloride

Only one pair out of 781 had a result greater than the MRL. In that single pair, the iced sample was much higher than the non-iced sample (14.7 ppb versus <MRL). However, there are not enough detections to show a difference between iced- and non-iced samples. The single result is above both the MCL (5 ppb) and HRL (2 ppb) and occurred at a new sample location. DWP will follow up with this facility to further document trends and take appropriate action.

cis -1, 2-dichloroethene

Twelve pairs out of 781 had a result greater than the MRL. The iced and non-iced results only differed by an average of 0.12 ppb, indicating that the samples were very similar.

Di (2-ethylhexyl) adipate

Only two pairs out of 684 had a result greater than the MRL. In a single pair, the iced sample was much higher than the non-iced sample (45 ppb versus <MRL). As noted above, the result from a thermally-preserved sample taken two months later at this same entry point was below the MRL. There are not enough detections to show a difference between the samples based on thermal preservation.

Di (2-ethylhexyl) phthalate

Six pairs out of 683 had a result greater than the MRL. The detections were close to the MRL of 1.8 ppb in 5/6 cases. In addition, iced and non-iced results only differed by an average of 0.77 ppb, indicating that they were very similar. One result is above both the MCL (6 ppb) and HRL (7 ppb). DWP will follow up with this facility to further document trends and take appropriate action.

Ethylbenzene

Five pairs out of 781 had at least one result greater than the MRL. The iced and non-iced results were similar and close to the MRL in four out of five non-tied pairs. One non-tied pair showed a larger difference (non-detect in non-iced sample vs. 5.7 ug/L in the iced sample). The two following iced samples from this same system/sampling point were non-detects.

Hexachlorocyclopentadiene

As all paired results were less than the highest MRL of 0.3 ppb, no further analysis was possible. The reason it is included is that some results were above the lower MRL.

Methylene chloride

Three pairs out of 781 had at least one result greater than the MRL. The paired results were close to the MRL of 0.5 ppb (all <1 ppb), indicating that iced and non-iced samples were very similar.

o-xylene

Ten pairs out of 781 had at least one result greater than the MRL. The concentration was higher in the iced sample in 6/10 pairs. One pair includes an outlier (see Appendix D), with a non-iced sample concentration below the MRL and an iced sample concentration of 5.5 ppb. Two later iced samples taken at this same system-sampling point were both below the MRL.

p&m-xylene

Sixteen pairs out of 781 had at least one result greater than the MRL. Half of pairs had a higher iced result. There was one iced sample outlier at the same system-sampling point as the o-xylene outlier discussed above. Two later iced samples taken at this same location had detectible results that were much lower than 19 ppb (0.67 and 1.0 ppb). Given the lack of a trend in iced/non-iced differences and outlier follow-up samples that were near the MRL, there was no evidence that lack of thermal preservation influenced the results.

Styrene

Only three pairs of 781 had at least one result greater than the MRL. All three iced samples were greater than the non-iced samples, and they differed by an average of 2.23 ppb. Three non-tied pairs is an extremely small sample size to make a general conclusion about whether improper thermal preservation influenced analytical results for styrene. Regardless, results are all orders of magnitude below both the MCL (10,000 ppb) and HRL (300 ppb). At no time did levels approach a public health concern.

Tetrachloroethene

Eight pairs out of 781 had at least one result greater than the MRL. Half of the samples had higher iced sample concentrations, while the other half had higher non-iced samples. In addition, the iced and non-iced results only differed by an average of 0.04 ppb, indicating that they were very similar.

Toluene

Eleven pairs out of 781 had results greater than the MRL, with 7/11 having a higher iced sample concentration. The difference in concentration between iced and non-iced sample pairs was less than 2 ppb in all cases except one pair in which the non-iced result was 7 ppb and the iced result was below the MRL. If this larger difference was due to lack of thermal preservation, we would expect to see the opposite; i.e., a higher concentration in the iced sample.

trans -1, 2-Dichloroethene

Three pairs out of 781 had at least one result greater than the MRL; 2/3 had a higher iced sample concentration. Iced- and non-iced paired results only differed by an average of 0.10 ppb, indicating that they were very similar.

Trichloroethene (TCE)

Twenty-three pairs out of 781 had at least one result greater than the MRL, with 13/22 non-tied pairs having a higher non-iced concentration. The non-tied paired results were very similar except for one pair in which the iced result was <MRL and the non-iced result was 10 ppb (see outlier in Appendix D). If this larger difference was due to lack of thermal preservation, we would expect to see the opposite; i.e., a higher concentration in the iced sample. Results from two systems were above the MCL (5 ppb) and one above the HRL (4 ppb). DWP will follow up with these facilities to further document trends and take appropriate action.

Vinyl chloride

Seven pairs out of 781 had at least one result greater than the MRL. The iced and non-iced paired results only differed by an average of 0.07 ppb, indicating that the samples were very similar. One system was above the MCL (5 ppb) and four systems were above the HRL (0.2 ppb). However, all subsequent samples all came back below MRL. Regardless, DWP will follow up with these facilities to further document trends and take appropriate action.

Discussion

As the program responsible for implementing the SDWA in Minnesota and the agency committed to protecting, maintaining and improving the health of all Minnesotans and ensuring that drinking water is safe for everyone, everywhere, the most critical question was if the systems impacted by potential thermal preservation issues were delivering safe drinking water.

Given the way the situation unfolded in early 2016 after standing up the ICS, it was necessary to aggressively respond to questions raised regarding the overall performance of the drinking water assessment/enforcement system across the state. Representatives from both the MDH Executive Office and Governor's Office demanded a comprehensive accounting of system performance that went beyond the data routinely reported to EPA. They wanted to be able to assure Minnesotans that all legal and public health requirements were being met and drinking water was safe. The best way to provide that assurance at that point was to gather additional data at the most vulnerable locations.

The results from Tier 1, 2, and 3 locations were all subject to the same quality assessment and validation procedures as any data reported to MDH. If a specific sample location was previously scheduled for sampling during 2016 and results met quality criteria, the results were used to fulfill routine compliance sampling requirements. If a location was not previously scheduled for sampling during 2016, the result was acted upon only if it exceeded HRLs or MCLs. Locations not previously scheduled for sampling with results below health-based standards were entered into MNDWIS but regularly scheduled sampling will continue in future years.

An overview of the data collected between 02/16/2016 and 02/15/2017 (Table 12) reflects the high quality of drinking water in Minnesota, with 99% or higher of the VOC and IOC/SOC results being non-detect. A large number of samples collected for assessment were DBPs and VOCs because those are the most likely to be impacted by differences in thermal preservation. An

overall assessment of results demonstrates that there were no new public health concerns found and confirmed the fact that Minnesota has one of the highest compliance rates with requirements of the SDWA.

Table 12: Summary of results by contaminant class

Contaminant Class	# of results	% of sample points with detections	% of systems with detections*	# systems exceeding MCL*
DBP	9,128	44 %	40%	14
IOC/SOC	5,981	0.3 %	0.4 %	0
VOC	21,873	1.0 %	1.1 %	5

* System issues were being addressed prior to re-sampling.

Individual locations that had single results that exceeded MCL and HRL thresholds were either already known to MDH, new sampling locations, highly seasonal and site specific (DBPs), or lacking in a confirmation sample (e.g. subsequent sampling was below the health threshold). MDH will continue to work with each of these locations to track contaminant trends and implement steps necessary to ensure safe drinking water is delivered to all Minnesotans. Compliance with SDWA is determined by a rolling quarterly average of results and is not usually based on a single sample result.

Disinfection Byproducts

In disinfection, gaseous chlorine or liquid sodium hypochlorite is added to, and reacts with, water to form hypochlorous acid. In the presence of bromine, hypobromous acid is also formed. Hypochlorous and hypobromous acid form strong oxidizing agents in water and react with a wide variety of compounds, which is why they are such effective disinfectants. Hypochlorous acid and hypobromous acid also react with naturally occurring organic matter to create many water DBPs, including four primary trihalomethanes (TTHMs):

1. Chloroform – CHCl_3
2. Bromodichloromethane (BDCM) – CHCl_2Br
3. Dibromochloromethane (DBCM) – CHClBr_2
4. Bromoform – CHBr_3

The two most commonly found TTHMs in iced samples were #1 and #2 above, which is expected given the routine use of chlorine in drinking water systems in Minnesota. Dichloroacetic acid (DCA) and Trichloroacetic acid (TCA) were significantly higher in non-iced compared to iced samples, indicating that thermal preservation may have impacted sample results. Both DCA and TCA has no bromide and therefore has a greater opportunity to form in higher temperatures and/or longer reaction times because chloride is a better electrophile and can remove bromide and iodide. If the lack of thermal preservation was responsible for the higher concentrations of DCA and TCA in non-iced samples, past results would have been overestimates, rather than underestimates, of concentration, which is important from a public health action standpoint.

Managing DBPs is one of the most challenging aspects of assuring compliance with the SDWA. The main barriers to a comprehensive assessment of DBPs in drinking water include the highly seasonal nature of their occurrence (primarily in Fall), the need for very specific conditions for their creation (chlorination and organic matter present), the variable sampling frequency across the state (ranging from quarterly to every three years), and limited toxicological information.

Balancing the creation of DBPs and the need for chlorination is an example of the complexity of managing drinking water systems. Bacteriological contamination is one of the greatest threats to safe drinking water, yet one of the most effective means of protection (chlorination) creates residual problems.

IOCs and SOCs

Given the overwhelming number of non-detects for this class it is difficult to assess the impacts of lack of thermal preservation. However, the absence of detections reflects the low potential for a public health impact from IOCs and SOCs in Minnesota drinking water.

The most significant improvement resulting from the resampling effort was a closer examination of the procedure used to sample for cyanide. Options for chemical preservation were examined in collaboration with PHL and a pilot study conducted in 2017. A final procedure, with different approaches for PWSs that do or do not chlorinate, was set in 2018 and implemented statewide.

VOCs

The word volatile comes from the Latin term “volatilis”, which means fleeting or transitory. The dictionary defines volatile as “evaporating readily at normal temperatures and pressures.” The VOCs are the most likely to be impacted by a lack of thermal preservation.

Numerically, 11 of 18 VOCs showed that the iced samples were higher more often than the non-iced samples in non-tied pairs, indicating a potential impact from lack of thermal preservation. However, the number of samples with detections were very small (typically less than 10 out of nearly 800 samples) and the difference between concentrations was generally small (less than 1 ppb). A few contaminants showed elevated single results, which may be related to external contamination of the samples themselves. No relationship between concentration difference by increasing non-iced temperature was seen in the scatterplots. Further, the one compound with more than 20 pairs that had detections (TCE) showed a lower concentration in the iced samples occurred more often. For all these reasons, no obvious bias in concentration due to lack of thermal preservation was apparent from the available data.

Quality Assessment

Immediate impacts from the quality assessment efforts included the creation and use of more robust chain-of-custody and sample request forms, increased understanding of data qualifiers and analytical uncertainty, and the application and implementation of sample acceptance criteria. The improved forms have reduced potential vulnerability in future enforcement cases by more clearly documenting methods and requirements. Discussions of data quality and sample acceptance procedures have improved communication and collaboration between DWP and PHL.

Longer-term impacts from quality assessment efforts include the reconstituting of a staff-level DWP/PHL workgroups to promote better understanding of overall process and improve communication and coordination. The group will work in partnership to enhance cross-section understanding of roles in shared activities, build collective ownership of outcomes for program customers, and build strong ties and systems for sustaining the partnership.

Conclusions

The immediate goal of the 2016 sampling effort was to confirm the safety of Minnesota drinking water for contaminants that may be impacted by varying degrees of thermal preservation. Sample locations were chosen to cover the most vulnerable PWSs. Results were overwhelmingly “non-detect” and, with few exceptions, below health based standards. Therefore, public health was protected before, during, and after the 2016 compliance sampling event.

Even though there were a large number of samples, the high percentage of non-detects made it very difficult to perform statistical analysis for possible trends. A statistically significant difference that may be linked to thermal preservation was found in two DBPs, supporting the need for attention to thermal preservation methods. Unfortunately, DBPs are notoriously variable depending on specific site conditions and season. The way MCL exceedances are calculated and the lack of HRLs for many DBP makes it difficult to connect potential health impacts to the individual differences identified. However, given that samples not collected according to required procedures were likely overestimating actual concentrations, there is assurance that public health was protected from DBPs throughout.

Even though it required a large commitment of time and resources, it was very important for DWP to complete the necessary sampling to understand whether previous monitoring using less stringent thermal preservation failed to identify systems that might be at risk. Because the safety of Minnesota drinking water had been called into question, it was critical to communicate these findings to reassure federal agencies (who are responsible for oversight), state agency partners (who coordinate on water issues), public water systems (who need to document compliance with regulations), and the general public (who have high expectations of consistently safe drinking water).

In addition to confirming the high quality of Minnesota drinking water, the resampling effort helped support ongoing improvements in methods and coordination among partners. Ultimately it has helped support the development of a strong continuous improvement culture in both DWP and PHL that will examine and improve business processes into the future.

The results of this effort will be reported to EPA so that all partners in drinking water protection can benefit from lessons learned. For example, if the currently required thermal preservation ranges can be expanded even slightly, significant savings/benefits from reduced sample recollection, increased staff time available, and avoided analytical costs may be realized. Therefore, additional research is needed to further clarify acceptable boundaries for valid sample submission with respect to thermal preservation.

Appendices

Appendix A1 – A5: Data Qualifiers and definitions

Appendix B: Updated Chain of Custody sample request form

Appendix C1 and C2: Sample Acceptance Criteria

Appendix D: Scatter Plots of concentration difference among paired samples versus receiving temperature of the non-thermally preserved sample

Appendix A1: Data Qualifiers Evaluation Guidance – used regularly

DQs – Used regularly by PHL and DWP	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
B1	Target analyte detected in method blank at or above the method reporting limit. See comments or additional qualifiers.	Receive MNDWIS Report. (1) If target analyte result <RL, result can be accepted with no further action. (2) If target analyte result is between RL and MCL, system is placed on DB. (3) If target analyte is not confirmed, documentation is added to original result stating "Detect due to suspected contamination of sample in laboratory." RCB per protocol and do not use original result in peak quarter determination. (4) For 2 and 3, because contamination of sample can't be confirmed, it should not be marked invalid. (4) If sample is rejected, arrange to have sample recollected.
D1	Sample required dilution due to matrix. Reporting limit has been raised.	Receive MNDWIS Report. (1) If RL(new) < DL required by rule, results can be accepted as is. (2) If RL(new) > DL required by rule and target analyte result <RL(new), new sample is to be collect to confirm result. (3) If RL(new) > DL required by rule and target analyte result >RL(new), result can be accepted as is. (4) If sample is rejected, arrange to have sample recollected.
D2	Sample required dilution due to high concentration of target analyte(s). Reporting limit has been raised.	Accept result as is. Evaluate new RL in relationship to trigger and/or MCL of target analyte and target analyte result. Target analyte result use in compliance determination is not affected by this data qualifier.
E4	Concentration estimated. Internal standard recoveries did not meet method acceptance criteria. See comments or additional qualifiers.	Receive MNDWIS Report. Make scientific decision based on comments/additional qualifiers, target analyte, analyte result, MCL, and methodology to accept or reject. If sample is rejected, arrange to have sample recollected.
F1	Sample received in inappropriate sample container.	Receive email. Depending on container/analysis requested, i.e. non-MDH container, inappropriate preservative. Micro: Reject sample. Inorganics/organics: Make scientific decision based on target analyte, analyte result, MCL, methodology, vulnerability, and potential health risk to accept or reject. If sample is rejected, arrange to have sample recollected.
H5	This test is specified to be performed in the field within 15 minutes of sampling; sample was received and analyzed past the regulatory holding time.	Receive MNDWIS Report. Accept result as is, since qualifier indicates sample is non-field filtered.
L1	The spike recovery was above laboratory acceptance limits for the associated laboratory control sample and/or laboratory control sample duplicate.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject [usually high bias with a detect, and may be rejected, if appropriate]. If sample is rejected, arrange to have sample recollected.
L2	The spike recovery was above laboratory acceptance limits for the associated laboratory control sample and/or laboratory control sample	Receive MNDWIS Report. Target analyte result use in compliance determination is not affected by this data qualifier.

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DQs – Used regularly by PHL and DWP	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
	duplicate. Target analyte was not detected in the sample.	
M1	Matrix spike and/or matrix spike duplicate recovery was high; the associated laboratory control sample and/or laboratory control sample duplicate recovery was acceptable.	Receive MNDWIS Report. (1) If target analyte result <RL, result can be accepted with no further action. (2) If target analyte result is between RL and MCL, system is placed on DB. If target analyte is not confirmed, documentation is added to original result stating "Detect due to suspected contamination of sample in laboratory." RCB per protocol and do not use original result in peak quarter determination. (3) If target analyte result >MCL, collect validation sample ASAP. If confirmed, proceed according to rule. If unconfirmed, documentation is added to original result stating "Detect due to suspected contamination in laboratory."
M2	Matrix spike and/or matrix spike duplicate recovery was low; the associated laboratory control sample and/or laboratory control sample duplicate recovery was acceptable.	Receive MNDWIS Report. (1) If target analyte result <MCL, system is placed on DB. (2) If target analyte result >MCL, collect validation sample ASAP. If confirmed, proceed according to rule. If unconfirmed, documentation is added to original result stating "Original result (MM/DD/YY) exceedance due to suspected matrix interference."
S2	Surrogate recovery was below laboratory/method acceptance limits. Unable to confirm matrix effect.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If MS was performed on sample for target analyte and was acceptable, result could be accepted. Laboratory should be communicated with, and MS on confirmation sample requested. If sample is rejected, arrange to have sample recollected.
V1	Calibration verification standard recovery was above method acceptance limits. This target analyte was not detected in the sample.	Receive MNDWIS Report. Target analyte result use in compliance determination is not affected by this data qualifier.
V3	Calibration verification standard recovery was above method acceptance limits. This target analyte was detected in the sample, but the sample was not reanalyzed. See comments or additional qualifiers.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. (1) If target analyte result is between RL and MCL, system is placed on DB. If target analyte is not confirmed, documentation is added to original result stating "Detect due to CVS failure." RCB per protocol and do not use original result in peak quarter determination. (3) If sample is rejected, arrange to have sample recollected.
V4	Calibration verification standard recovery was below method acceptance limits. See comments or additional qualifiers.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If sample is rejected, arrange to have sample recollected.
W6	Laboratory control sample/laboratory control sample duplicate relative percent difference exceeded the laboratory acceptance limit. Recovery met acceptance criteria.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. May indicate system failure - evaluation of other batch QC data is required. If sample is rejected, arrange to have sample recollected.

Appendix A2: Data Qualifiers Evaluation Guidance – not used regularly

DQs – Not used regularly by PHL and DWP	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
B4	Target analyte detected in method blank at or above method reporting limit. Concentration found in the sample was at least 10 times the concentration found in the method blank.	Receive MNDWIS Report. Scientific based decision needs to be made based on target analyte, analyte result, MCL, and methodology. [Depending on target analyte result, it's trigger, it's MCL this may not be that large of difference in which case follow up may be required.]
H2	Initial analysis within holding time. Reanalysis for the required dilution was past holding time [additional comments usually provided with DQ].	Receive email. If result is within duplicate range ($\pm 10\%$), accept result. If not, reject sample and arrange to have sample recollected.
H7	The sample was re-extracted past the recommended holding time for confirmation [additional comments usually provided with DQ].	Receive MNDWIS Report. If result is within duplicate range ($\pm 10\%$), accept result. If not, reject sample and arrange to have sample recollected.
H8	Initial analysis within holding time. Reanalysis for confirmation was past holding time [additional comments usually provided with DQ].	Receive MNDWIS Report. If result is within duplicate range ($\pm 10\%$), accept result. If not, reject sample and arrange to have sample recollected.
M3	The spike recovery value is unusable since the analyte concentration in the sample is disproportionate to the spike level. The associated laboratory control sample and/or laboratory control sample duplicate recovery was acceptable.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If sample is rejected, arrange to have sample recollected.
M4	The analysis of the spiked sample required a dilution such that the spike recovery calculation does not provide useful information. The associated laboratory control sample and/or laboratory control sample duplicate recovery was acceptable.	Receive MNDWIS Report. If due to result/spike ratio, then result can be accepted depending on analyte. If due to matrix/spike ratio, then recollection may be necessary.
M6	Matrix spike and/or matrix spike duplicate recovery was outside laboratory limits, the associated standard reference material recovery was acceptable.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If sample is rejected, arrange to have sample recollected.
M7	Laboratory control sample and/or laboratory control sample duplicate were analyzed in place of matrix spike/matrix spike duplicate due to insufficient sample	Receive MNDWIS Report. Target analyte result use in compliance determination is not affected by this data qualifier.

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DQs – Not used regularly by PHL and DWP	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
	provided for method required quality control.	
Q4	Sample received and analyzed without chemical preservation.	Receive email or MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject (typically accept). If sample is rejected, arrange to have sample recollected.
Q5	Sample received with inadequate chemical preservation, but preserved by the laboratory.	Receive email or MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject (typically accept). If sample is rejected, arrange to have sample recollected.
Q9	Insufficient sample received to meet method quality control requirements [usually linked to M7].	Target analyte result use in compliance determination is not affected by this data qualifier.
R2	The reporting limits have been raised due to limited sample volume.	Receive MNDWIS Report. (1) If RL (new) < DL required by rule, results can be accepted as is. (2) If RL (new) > DL required by rule and target analyte results <RL (new), collect a new sample to confirm result. (3) If RL (new) > DL required by rule and target analyte is >RL (new), result can be accepted as is. (4) If recollection is required, entire set (ex. BNAs) would need to be recollected, not just analyte in question. If sample is rejected, arrange to have sample recollected.
R3	The reporting limit for this analyte has been raised to account for interference from coeluting organic compounds present in the sample.	Receive MNDWIS Report. (1) If RL (new) < DL required by rule, results can be accepted as is. (2) If RL (new) > DL required by rule and target analyte results <RL (new), collect a new sample to confirm result. (3) If RL (new) > DL required by rule and target analyte is >RL (new), result can be accepted as is. (4) If recollection is required, entire set (ex. BNAs) would need to be recollected, not just analyte in question. If sample is rejected, arrange to have sample recollected.
R4	The reporting limits for this analysis have been raised due to sample foaming.	Receive MNDWIS Report. (1) If RL (new) < DL required by rule, results can be accepted as is. (2) If RL (new) > DL required by rule and target analyte results <RL (new), collect a new sample to confirm result. (3) If RL (new) > DL required by rule and target analyte is >RL (new), result can be accepted as is. (4) If recollection is required, entire set (ex. BNAs) would need to be recollected, not just analyte in question. If sample is rejected, arrange to have sample recollected.
R5	The reporting limits for this analyte has been raised to account for the reporting limit verification standard.	Receive MNDWIS Report. (1) If RL (new) < DL required by rule, results can be accepted as is. (2) If RL (new) > DL required by rule and target analyte results <RL (new), collect a new sample to confirm result. (3) If RL (new) > DL required by rule and target analyte is >RL (new), result can be accepted as is. (4) If recollection is required, entire set (ex. BNAs) would need to be recollected, not just analyte in question. If sample is rejected, arrange to have sample recollected.
S1	Surrogate recovery was above laboratory/method acceptance limits. No target	Receive MNDWIS Report. Target analyte result use in compliance determination is not affected by this data qualifier.

DQs – Not used regularly by PHL and DWP	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
	analytes were detected in the sample.	
S3	Surrogate recovery was below laboratory/method acceptance limits. Reextraction and/or reanalysis confirms low recovery caused by matrix effect.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If MS was performed on sample for target analyte and was acceptable, result could be accepted. Laboratory should be communicated with, and MS on confirmation sample requested. If sample is rejected, arrange to have sample recollected.
S4	Surrogate recovery was above laboratory/method acceptance limits. Reextraction and/or reanalysis confirms high recovery caused by matrix effect.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. (1) If target analyte result <RL, result can be accepted with no further action. (2) If target analyte result is between RL and MCL, system is placed on DB. If target analyte is not confirmed, documentation is added to original result stating "Detect due to matrix interference." RCB per protocol and do not use original result in peak quarter determination. (3) If target analyte result >MCL, collect validation sample ASAP. If confirmed, proceed according to rule. If unconfirmed, documentation is added to original result stating "Detect due to matrix interference." (4) If sample is rejected, arrange to have sample recollected.
S5	The analysis of the sample required a dilution such that the surrogate recovery calculation does not provide useful information. The associated laboratory control sample/blank spike recovery was acceptable.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If due to result/surrogate ratio, then result can be accepted depending on analyte. If due to matrix/surrogate ratio, then recollection may be necessary. If sample is rejected, arrange to have sample recollected.
S6	Surrogate recovery was above laboratory/method acceptance limits. See comments or additional qualifiers.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, other QC data, and methodology to accept or reject. If sample is rejected, arrange to have sample recollected.
S7	Surrogate recovery was below laboratory/method acceptance limits. See comments or additional qualifiers.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, other QC data, and methodology to accept or reject. If sample is rejected, arrange to have sample recollected.
V2	Calibration verification standard recovery was above method acceptance limits. This target analyte was detected in the sample. The sample could not be reanalyzed due to insufficient sample.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. (1) If target analyte result is between RL and MCL, system is placed on DB. If target analyte is not confirmed, documentation is added to original result stating "Detect due to CVS failure." RCB per protocol and do not use original result in peak quarter determination. (2) If target analyte result >MCL, collect validation sample ASAP. If confirmed proceed according to rule. If unconfirmed documentation is added to original result stating "Detect due to CVS failure." (3) If sample is rejected, arrange to have sample recollected.
V5	Calibration verification standard recovery was above	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology

DQs – Not used regularly by PHL and DWP	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
	method acceptance limits. This target analyte was detected in the sample. The sample could not be reanalyzed within holding time.	to accept or reject. (1) If target analyte result is between the RL and MCL, system is placed on DB. If target analyte is not confirmed, documentation is added to original result stating "Detect due to CVS failure." RCB per protocol and do not use original result in peak quarter determination. (2) If target analyte result >MCL collect a validation sample ASAP. If confirmed proceed according to rule. If unconfirmed documentation is added to original result stating "Detect due to CVS failure." (3) If sample is rejected, arrange to have sample recollected.
W4	Matrix spike/matrix spike duplicate relative percent difference exceeded the laboratory acceptance limit. Recovery met acceptance criteria.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If target analyte result is low, this can account for poor RPD in spikes. If target analyte result is not low, poor RPD can indicate a non-homogeneous sample or system failure - evaluation of other batch QC data is required. If resampling is determined necessary, communicate with laboratory and request assistance investigating failure. If sample is rejected, arrange to have sample recollected.
W8	Sample/sample duplicate relative percent difference exceeded the laboratory acceptance limit.	Receive MNDWIS Report. Make scientific decision based on target analyte, analyte result, MCL, and methodology to accept or reject. If target analyte result is low, this can account for poor RPD in spikes. If target analyte result is not low, poor RPD can indicate a non-homogeneous sample or system failure - evaluation of other batch QC data is required. If resampling is determined necessary, communicate with laboratory and request assistance investigating failure. If sample is rejected, arrange to have sample recollected.

Appendix A3: Data Qualifiers Evaluation Guidance – prior to analysis

DQs – typically addressed prior to analysis, and not attached to final results	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
A2	Sample incubation period exceeded method requirement.	Receive email from PHL. Reject sample, and arrange to have sample recollected.
A3	Sample incubation period was shorter than method requirement.	Receive email from PHL. Reject sample, and arrange to have sample recollected. If the sample is TC and E. coli present acceptance of the sample is allowed
A4	Target organism detected in associated method blank.	Receive email from PHL. Reject sample, and arrange to have sample recollected.
A5	Incubator/water bath temperature was outside method requirements.	Receive email from PHL. Reject sample, and arrange to have sample recollected.
A7	Micro sample received without adequate headspace.	Receive email from PHL. Reject sample, and arrange to have sample recollected.
A9	Insufficient sample volume to perform proper sample analysis.	Receive email from PHL. Reject sample, and arrange to have sample recollected.
J	Analyte was present between the method detection limit and reporting limit and should be considered an estimated value ['J' flag results, often used for PFC or CEC analysis].	Receive MNDWIS Report. Accept results if used as non-compliance samples, i.e. PFCs. Will only appear on reports if project was set up to have data reported to MDL, at client's request. It is not standard practice for PHL to report results <RL
N3	Accreditation authority does not offer certification for this parameter.	Some samples do not have an EPA method, or a lab accredited for the analysis, because they are often CECs or investigative. This would be known upfront and factored into the project. These samples are not used as SDWA compliance samples.
Q1	Sample integrity was not maintained. See comments or additional qualifiers.	Receive email. Reject and arrange for sample recollection.
Q2	Sample received with head space [applies primarily to VOCs].	Receive email. Reject and arrange for sample recollection.
Q3	Sample received with improper chemical preservation [i.e. not preserved, or pH is incorrect].	Receive email. Reject and arrange for sample recollection.
Q6	Sample was received above recommended temperature [in future, add DQ for 'below recommended temperature'].	Receive email. Reject and arrange for sample recollection.
Q7	Sample inadequately dechlorinated.	Receive email. Reject and arrange for sample recollection.
T1	Method approved by EPA, but not yet available for	Some samples do not have an EPA method, or a lab accredited for the analysis, because they are often CECs or investigative. This would be known upfront and

DQs – typically addressed prior to analysis, and not attached to final results	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
	accreditation by accreditation authority.	factored into the project. These samples are not used as SDWA compliance samples.
T2	Cited accreditation authority method does not contain this analyte as part of method compound list.	Some samples do not have an EPA method, or a lab accredited for the analysis, because they are often CECs or investigative. This would be known upfront and factored into the project. These samples are not used as SDWA compliance samples.
T3	Method not approved or finalized by EPA.	Some samples do not have an EPA method, or a lab accredited for the analysis, because they are often CECs or investigative. This would be known upfront and factored into the project. These samples are not used as SDWA compliance samples.
T4	Laboratory not accredited for this parameter.	Some samples do not have an EPA method, or a lab accredited for the analysis, because they are often CECs or investigative. This would be known upfront and factored into the project. These samples are not used as SDWA compliance samples.
T5	The reported result cannot be used for compliance purposes.	Some samples do not have an EPA method, or a lab accredited for the analysis, because they are often CECs or investigative. This would be known upfront and factored into the project. These samples are not used as SDWA compliance samples.

Appendix A4: Data Qualifiers Evaluation Guidance – after initial analysis

DQs – typically addressed after initial analysis	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
E1	Concentration estimated. Analyte exceeded calibration range. Reanalysis not possible due to insufficient sample.	Receive MNDWIS Report. Confirmation/Validation sample is required. If C/V sample result confirms original result proceed per rule requirements. If C/V sample result does not confirm original result, document original result as unconfirmed. Based on analyte, invalidation may be appropriate, a science based decision is required taking into account factors such as target analyte, persistence in environment, mode of transport, lapsed time between samples, environmental conditions, etc. If sample is rejected, arrange to have sample recollected.
E2	Concentration estimated. Analyte exceeded calibration range. Reanalysis not performed due to sample matrix problems.	Receive MNDWIS Report. Confirmation/Validation sample is required. If C/V sample result confirms original result proceed per rule requirements. If C/V sample result does not confirm original result, document original result as unconfirmed. Based on analyte, invalidation may be appropriate, a science based decision is required taking into account factors such as target analyte, persistence in environment, mode of transport, lapsed time between samples, environmental conditions, etc.
E3	Concentration estimated. Analyte exceeded calibration range. Reanalysis not performed due to holding time requirements.	Receive MNDWIS Report. Confirmation/Validation sample is required. If C/V sample result confirms original result, proceed per rule requirements. If C/V sample result does not confirm original result, document original result as unconfirmed. Based on analyte, invalidation may be appropriate, a science based decision is required taking into account factors such as target analyte, persistence in environment, mode of transport, lapsed time between samples, environmental conditions, etc.
H1	Sample analysis performed past holding time [usually associated with samples that have 48 hour holding time].	Receive email. Reject and arrange to have sample recollected.
H3	Sample was received or analysis requested past holding time but analyzed at the clients request [typically associated with emergency response].	Receive email. Applies to a sample that was analyzed, rather than rejected. Qualifier specifically states that the sample was analyzed at client request,
H4	Sample was extracted past required extraction holding time, but analyzed within analysis holding time.	Receive email. Reject and arrange to have sample recollected.

Appendix A5: Data Qualifiers Evaluation Guidance – informational only


DQs – typically informational only, and do not require DWP action, other than normal SDWA compliance actions	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
Z01	Example: Colisure media used for analysis.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions. Z-01 is a free text qualifier and may be highly varied.
C4	Confirmatory analysis was past holding time.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.
H8	Initial analysis within holding time. Reanalysis for confirmation was past holding time.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.
W4	Matrix spike/matrix spike duplicate relative percent difference exceeded lab acceptance limit. Recovery met acceptance criteria.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.
WB	Relative percent difference exceeded the laboratory acceptance limit. Result less than 5 times the RL.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.
MC	Result greater than the MCL.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.
QT	RPD between sample duplicates not within acceptance limits. Analyte concentration within range for RER comparison and RER within acceptance limits.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.
WP	Sample preserved more than 5 days after collection.	Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.

DQs – typically informational only, and do not require DWP action, other than normal SDWA compliance actions	Description and PHL/DWP comments	Proposed Action (Guidance Only) - DWP
<p>W8</p>	<p>Sample/sample duplicate relative percent difference exceeded lab acceptance limit.</p>	<p>Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.</p>
<p>L3</p>	<p>The spike recovery was below laboratory acceptance limits for the associated laboratory control sample and/or laboratory control sample duplicate.</p>	<p>Receive result with attached DQ. These DQs are typically informational only, and do not require DWP action, other than normal SDWA compliance actions.</p>

Appendix B: Sample Request/Chain of Custody Forms

1	2	3	4
Minnesota Department of Health			Matrix
Chain-of-Custody Form			Drinking Water
«sample_date»			
Program Code «pws_program_»	PWSID «pws_id»	System Name «pws_name»	City, Town, Township «city»
Date Collected (for all samples on form)	Collector ID «collector_id»	Collector Name (please print) «collector_name»	Original Sample Number «original sample nbr»
Sample Type «sample_type»	Your Chlorine Residual Result _____ mg/l	Sampler Comments	

1	Field Number	Time Collected am <input type="checkbox"/> pm <input type="checkbox"/>	Location ID «sp1_id»	Sampling Point «sp1_name»
2	Field Number	Time Collected am <input type="checkbox"/> pm <input type="checkbox"/>	Location ID «sp2_id»	Sampling Point «sp2_name»
3	Field Number	Time Collected am <input type="checkbox"/> pm <input type="checkbox"/>	Location ID «sp3_id»	Sampling Point «sp3_name»
4	Field Number	Time Collected am <input type="checkbox"/> pm <input type="checkbox"/>	Location ID «sp4_id»	Sampling Point «sp4_name»

INORGANIC	1	2	3	4	METALS	1	2	3	4	ORGANIC	1	2	3	4
<i>Unpreserved</i>					<i>HNO₃ Preserved</i>					BNA (Na ₂ SO ₃ /HCl) EPA 508.1/525.2				
Alkalinity SM 2320B					Arsenic EPA 200.8					Carbamates (Na ₂ S ₂ O ₃) EPA 531.1				
Bromide EPA 300.1					Copper EPA 200.8					Glyphosate (Na ₂ S ₂ O ₃) EPA 547				
Chloride EPA 300.1					Iron EPA 200.7					Herbicides (Na ₂ SO ₃) EPA 515.4				
Conductivity SM 2510B					Lead EPA 200.8					VOCs, Low Level (Ascorbic/HCl or HCl) EPA 524.2				
DOC SM 5310C					Manganese EPA 200.8									
Fluoride SM 4500-F-C					Sodium EPA 200.7					THMs (Ascorbic/HCl or HCl) EPA 524.2				
Nitrite-N SM 4500-NO ₂ B					Ca as CaCO ₃ EPA 200.7					HAA (NH ₄ Cl) EPA 552.2				
pH SM 4500-H+B					Mg as CaCO ₃ EPA 200.7					PFC Expanded (Unpreserved) MDH 555				
Silica SM 4500-SiO ₂ C					Hardness EPA 200.7									
Sulfate EPA 300.1					Metals Scan (Non-Regulatory)									
UV254 SM 5910B					IOC (As,Ba,Be,Cd,Cr,Ni,Se,Sb,Tl) EPA 200.8					RADIATION CHEMISTRY				
SUVA (UV abs., UV254, DOC)										<i>Unpreserved</i>				
					<i>NaOH Preserved</i>					Radium-226, -228 EPA 903.0/904.0				
<i>H₂SO₄ Preserved</i>					Cyanide, Free SM 4500-CN F					Gross Alpha EPA 900.0				
Ammonia-N EPA 350.1					Cyanide, Total EPA 335.4									
Nitrate+Nitrite-N SM 4500-NO ₃ F					<i>HNO₃/HCl Preserved</i>					SUBCONTRACT				
Total Phosphorus SM 4500P I					Mercury EPA 245.2, 1631					Bromate/Bromide EPA 300.1				
TOC SM 5310C										Bromate EPA 300.1				
					MICROBIOLOGY					Chlorite EPA 300.1				
					<i>Sterile, Na₂S₂O₃</i>					OTHER				
Lab Use Only					Coliform-PA SM 9223B									
					Coliform-MPN-OT SM 9223B									

The sampler has collected, preserved, and shipped these sample(s) according to instructions currently found at www.health.state.mn.us/divs/eh/water/forms/sampproc/index.html.

Relinquished by: _____ Date: _____ Time: _____

Accepted by: _____ Date: _____ Time: _____

Appendix C1: DWP Sample Acceptance Criteria – if COC fields are blank

COC Field	Supporting Documentation Can Be Supplied	E-mail from PHL	Response/Supporting Documentation Needed/Affidavit Required	Justification
Program Code	Yes	Yes	E-mail notification from DWP	No more documentation needed - this is a business requirement that does not affect sample integrity.
PWSID	If missing, but PWSName is present, yes. If the bottle and COC do not match the sample needs to be canceled.	Yes	E-mail notification from DWP	
PWSName	If missing, but PWSID is present, yes. If the bottle and COC do not match the sample needs to be canceled.	Yes	E-mail notification from DWP	
City, Town, Township	Yes	Yes	E-mail notification from DWP	No more documentation needed - this does not affect sample integrity.
Date Collected	Yes	Yes	Copy of Field Logbook if DWP staff collected; Email procedure if PWS collected.	
Collector ID	Yes	Yes	E-mail notification from DWP	No more documentation needed - this does not affect sample integrity.
Collector Name	Yes	Yes	E-mail notification from DWP	No more documentation needed - this does not affect sample integrity.
Original Sample ID	Yes	Yes	E-mail notification from DWP	No more documentation needed - this does not affect sample integrity.
Sample Type	Yes	Yes	E-mail notification from DWP	No more documentation needed - this does not affect sample integrity.
Field Number	Yes	Yes	Copy of Field Logbook if DWP staff collected; Email procedure if PWS collected.	

COC Field	Supporting Documentation Can Be Supplied	E-mail from PHL	Response/Supporting Documentation Needed/Affidavit Required	Justification
Sampling Point	Yes	Yes	Copy of Field Logbook if DWP staff collected; Email procedure if PWS collected.	
Time Collected	Yes	Yes	Copy of Field Logbook if DWP staff collected; Email procedure if PWS collected.	
Signature	Yes	Yes	Email notification from DWP	

Email notification procedure:

1. PHL emails DWP Compliance Officers when there is missing or incorrect COC information;
2. DWP Compliance Officers contact collectors;
3. DWP Compliance Officers respond to PHL with an email that contains the following:
 - a. Work Order #; PWSID #, PWS Name; Confirmation of corrected data; Date; Collector; Compliance Officer; statement indicating 'The sample was collected [insert corrected information] as per the collector', with the Compliance Officer's electronic signature (email address)
4. PHL keeps a copy of this email correspondence as part of the amended COC.

Appendix C2: DWP Sample Acceptance Criteria – for other issues

Issue	Response	Notes
Expired Bottle	Cancel Sample and Recollect	
No analysis requested for bottle received	Reply with analysis required or dispose of the bottle	
No container received for analysis requested	Cancel Sample and Recollect	
Incorrect container received for analysis requested	Cancel Sample and Recollect OR request a different/appropriate analysis using email procedure	
Temperature >6.0 degrees AND >24 hours since collection	Cancel Sample and Recollect	
Out of Hold	Cancel Sample and Recollect	
Container cannot be linked to COC	Cancel Sample and Recollect OR Go to PHL and make corrections, date/initial, and supply copy of field log book	Cannot use "None" on a new COC form
Unlabeled container with COC in single mailer	Email DWP to call collector and then respond as directed	May proceed with analysis
Labeled container without COC	Email DWP to call collector and then respond as directed; label should include xxxxxxxx	May proceed with analysis
Unlabeled container without COC	Cancel Sample and Recollect	
Compromised Container	Response based on analysis requested	
Non-MDH container	Response based on analysis requested	
Received with Evidence of Freezing	Cancel Sample and Recollect	

December 2016

Minnesota Department of Health Environmental Laboratory

Sample Acceptance Policy

The Environmental Laboratory (ENV) defines the minimum level of acceptability by the requirements in federal and state laws and regulations, and agreements established with clients and/or projects. ENV used the most stringent requirements from these sources to create this Sample Acceptance Policy.

The acceptance criteria for valid submissions are listed below. If a submission is missing required information or contains discrepant information, ENV will note that the submission does not conform to this sample acceptance policy and, if appropriate, holds the sample(s) in a secure area of the lab under proper environmental conditions. ENV staff will contact the responsible party and attempt to resolve the issues, if possible, otherwise the laboratory must reject the sample(s). ENV may be able to test the sample(s) after obtaining more information from the submitter, however not all issues will be able to be resolved, as identified below. Samples authorized for analysis while not meeting these requirements will result in data qualifiers as indicated.

The following items are required for a valid sample submission. Samples authorized for analysis while failing to include this information with a submission will result with data qualified as not meeting this sample acceptance policy.

- A properly completed chain of custody form (COC) must be submitted with the associated sample containers.
 - At a minimum, a properly completed COC must include the following information:
 - Sample ID and/or location
 - Date and time of collection (a.m./p.m. clearly identified or 24-hour clock is assumed)
 - Collector's name
 - Preservation type
 - Sample type
 - Sample matrix
 - Sample analysis specified
 - Sample comments, if applicable
- Samples must be relinquished to ENV through signature manifest on COC.

The following items are required to analyze samples and supply valid results. Collector/project manager will be notified of failure(s), and if sample(s) are authorized for analysis while failing to adhere to these requirements, it will result in data qualified indicating results cannot be used for compliance purposes.

- Sample containers must be appropriate for the requested analyses, and undamaged or uncompromised.
- Sample containers must be received within the method-specified holding time.
- Sample containers must be properly chemically and thermally preserved, per method-specified requirements.
- Sample vials must be submitted without headspace (air bubbles exceeding 6mm in diameter), per method-specified requirements.
- Sample collection must occur before the expiration date listed on container.
- Sample containers submitted for legal chain-of-custody must be received with no evidence of tampering (e.g. broken custody seals).

The following items are required to analyze samples and supply valid results. Failure to adhere to these requirements will result in samples being rejected and a resample requested. If resampling is not feasible and analysis proceeds, it will result in data qualified indicating results cannot be used for compliance purposes.

- Sample container(s) must be labeled with unique identifying information that clearly links the container(s) to one, and only one, sample point on the COC.
- Sample containers must be properly filled and sufficient sample volume received to perform analyses requested.

The following items will be recorded and retained by ENV, but will not result in client communication or data qualifiers.

- No collection year on COC – ENV will assume the sample was collected within the past 12 months.
- Blank fields on a COC that are not identified as a requirement for a valid submission will be left blank in the ENV LIMS.
- Container labels should be water-resistant. Both labels and COC should be completed using indelible ink.
- Incorrect edits on the COC and/or sample labels. Edits must be done using a single strike-through, initialed and dated.

If you have questions or comments about this policy or about samples you have submitted to ENV, please contact the Operations Unit at 651-201-5300, or by email at health.PHL-Environmental-Lab@state.mn.us.

Appendix D: Scatter Plots of concentration difference among paired samples versus receiving temperature of the non-thermally preserved sample

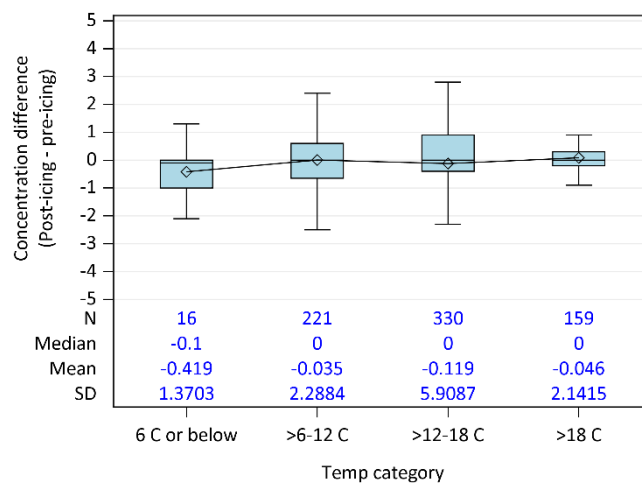
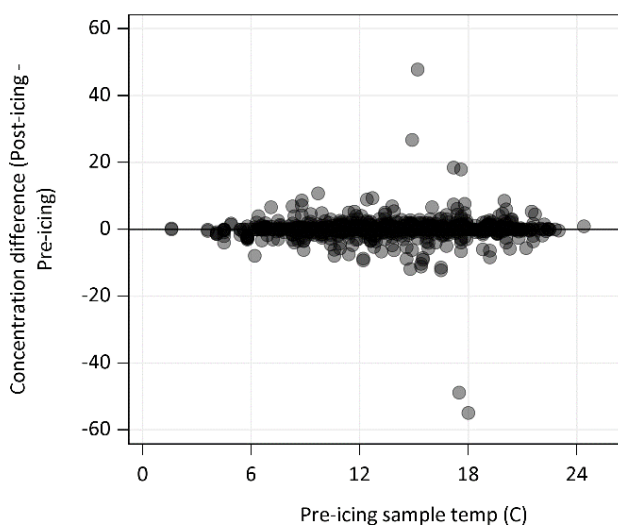
Disinfection By-Products

DBP results are for groundwater systems only, where the difference in month between paired results is 0 or ± 1 . In addition to a scatterplot of concentration difference by receiving temperature from non-thermally preserved results (e.g. 2014 – 2015), boxplots are shown when there is a sufficient number of non-paired results. Otherwise, jittered scatterplots with mean (SD) and median are shown.

Bromodichloromethane

Bromodichloromethane paired results (ppb)

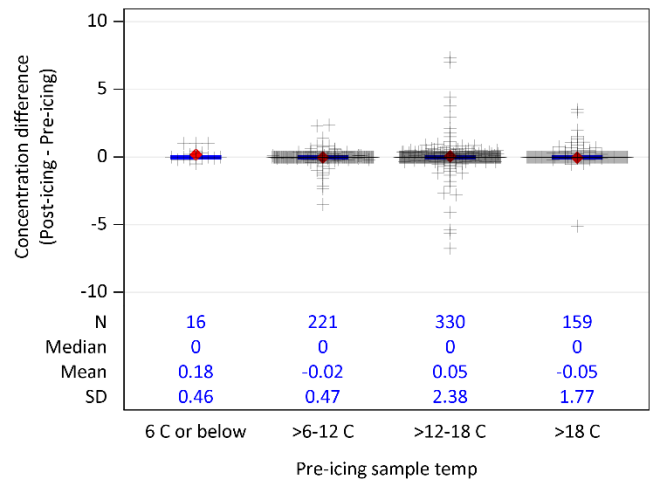
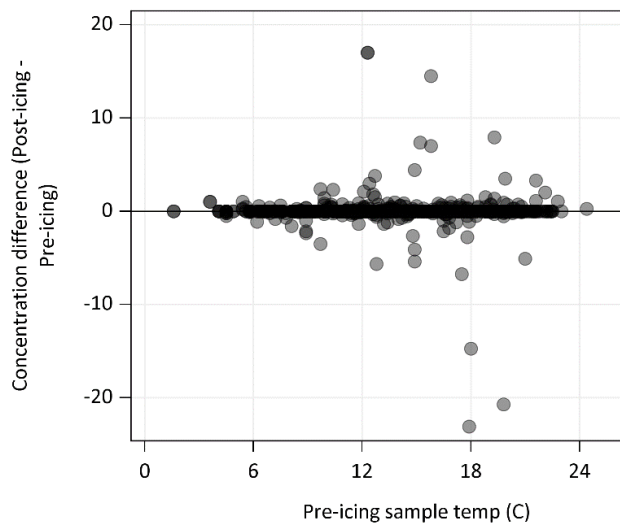
- Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line
- Boxplot of concentration difference by categorical pre-icing receiving temperature, box= Interquartile Range (IQR = 25th-75th percentile), whiskers=upper and lower fence ($\pm 1.5 \times$ IQR), outliers not shown, means connected by line



Bromoform

Bromoform paired results (ppb)

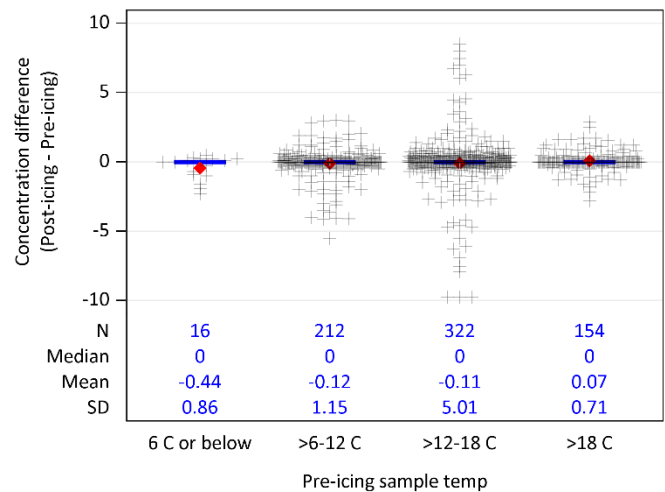
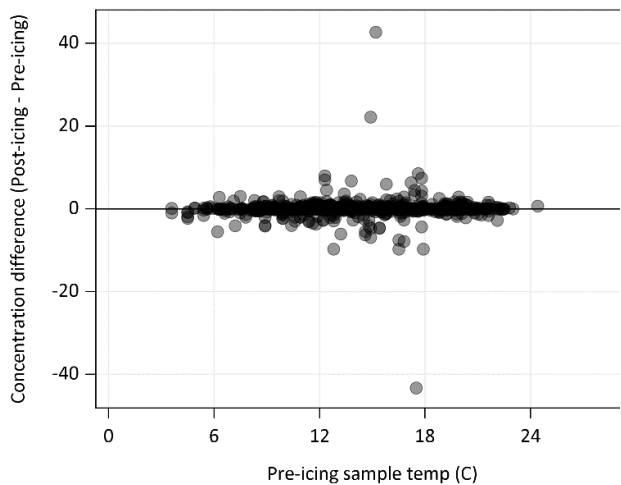
- Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line
- Bromoform jittered scatterplot of concentration difference by categorical temperature, with mean (red diamond) and median (blue bar) shown



Chlorodibromomethane

Chlorodibromomethane paired results (ppb)

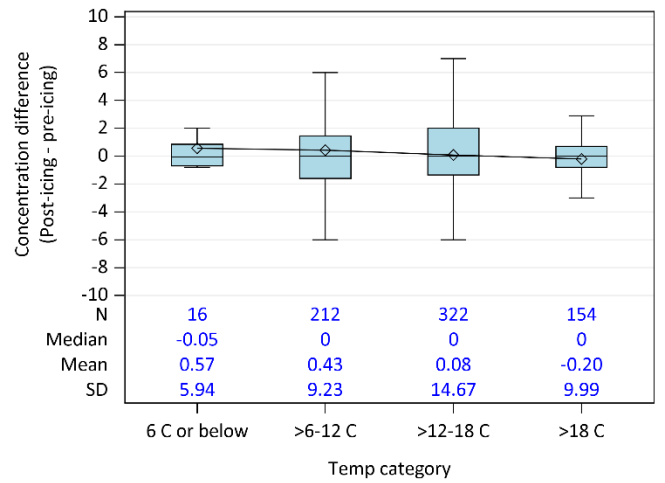
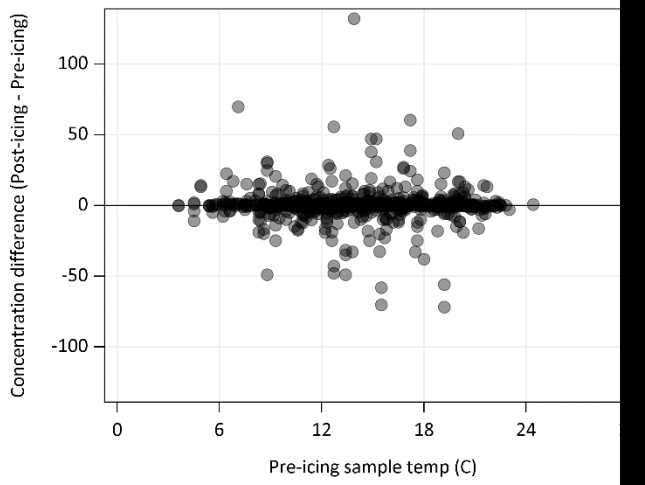
- Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line
- Jittered scatterplot of concentration difference by categorical temperature, with mean (red diamond) and median (blue bar) shown; truncated at ± 10 .



Chloroform

Chloroform paired results (ppb)

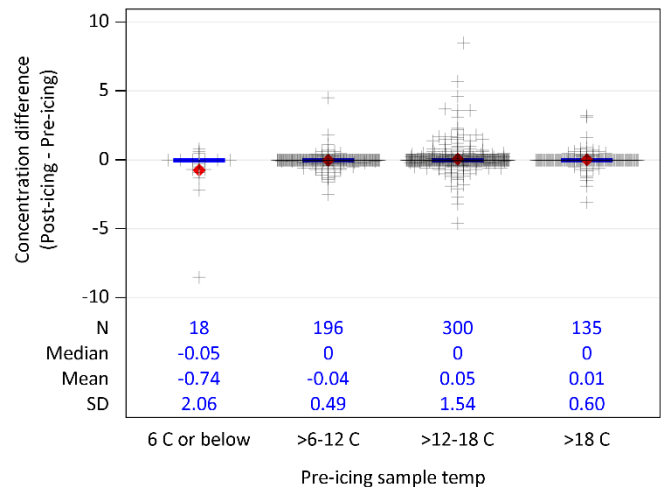
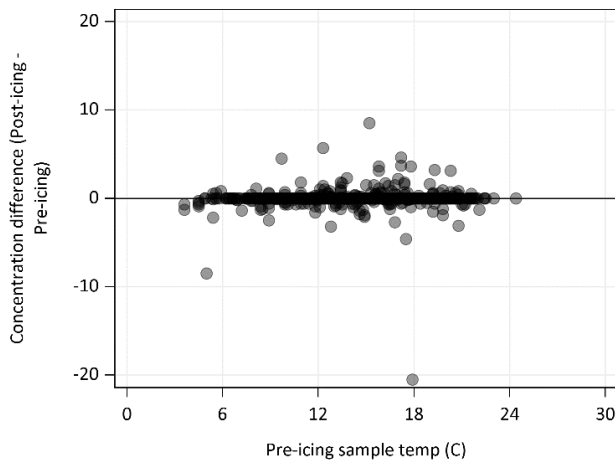
- Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line
- Boxplot of concentration difference by categorical pre-icing receiving temperature, box=IQR (25th-75th percentile), whiskers=upper and lower fence ($\pm 1.5 \times$ IQR), outliers not shown, means connected by line



Dibromoacetic Acid

Dibromoacetic acid paired results

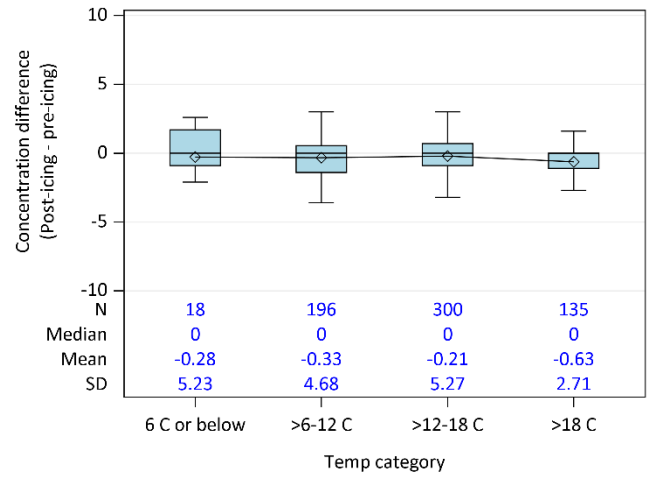
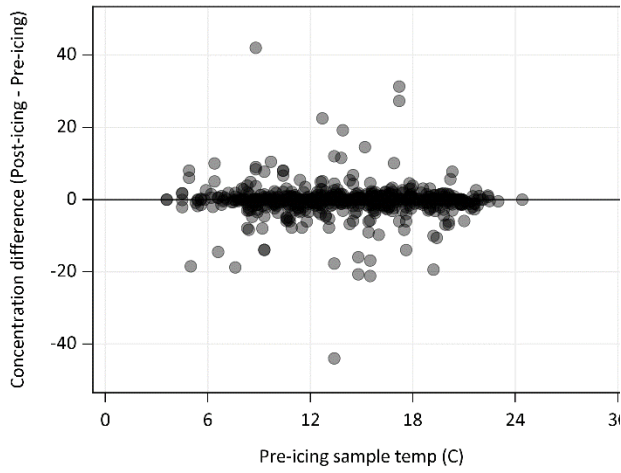
- Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line
- Jittered scatterplot of concentration difference by categorical temperature, with mean (red diamond) and median (blue bar) shown



Dichloroacetic acid

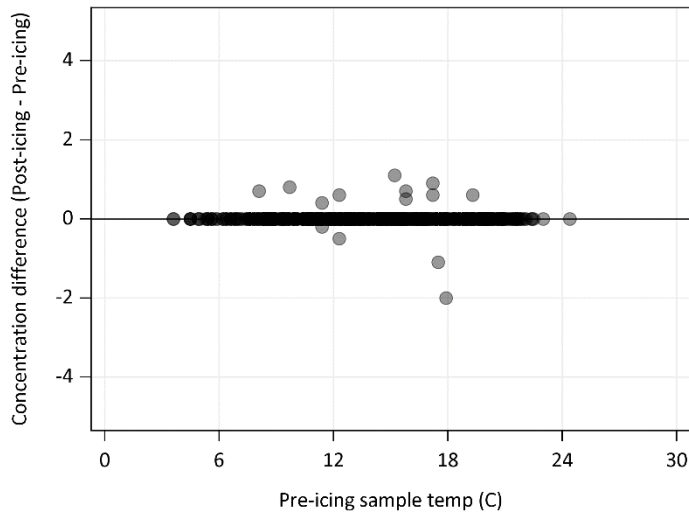
Dichloroacetic acid paired results (ppb)

- Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line; statistically significant trend
- Boxplot of concentration difference by categorical pre-icing receiving temperature, box=IQR (25th-75th percentile), whiskers=upper and lower fence ($\pm 1.5 \times$ IQR), outliers not shown, means connected by line



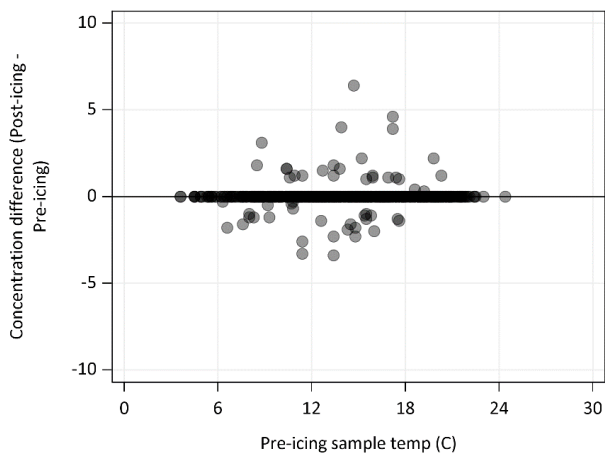
Monobromoacetic acid paired results (ppb)

Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line



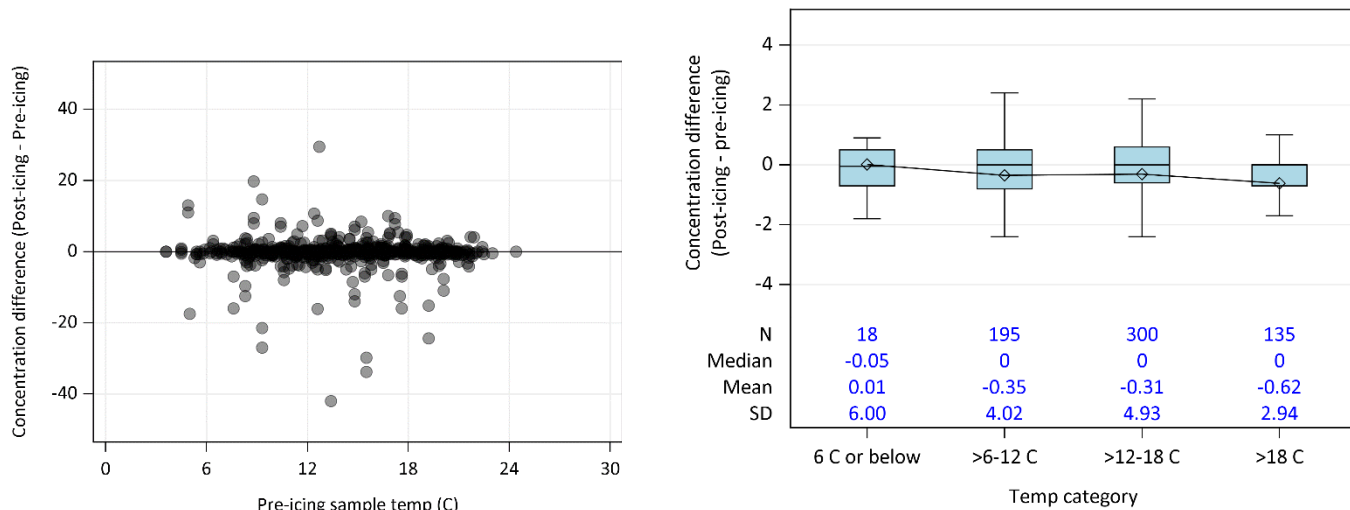
Monochloroacetic acid paired results (ppb)

Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line



Trichloroacetic acid paired results (ppb)

- a) Scatterplot of concentration difference by pre-icing receiving temperature with zero difference line¹; statistically significant trend.
- b) Boxplot of concentration difference by categorical pre-icing receiving temperature, box=IQR (25th-75th percentile), whiskers=upper and lower fence ($\pm 1.5 \times$ IQR), outliers not shown, means connected by line¹

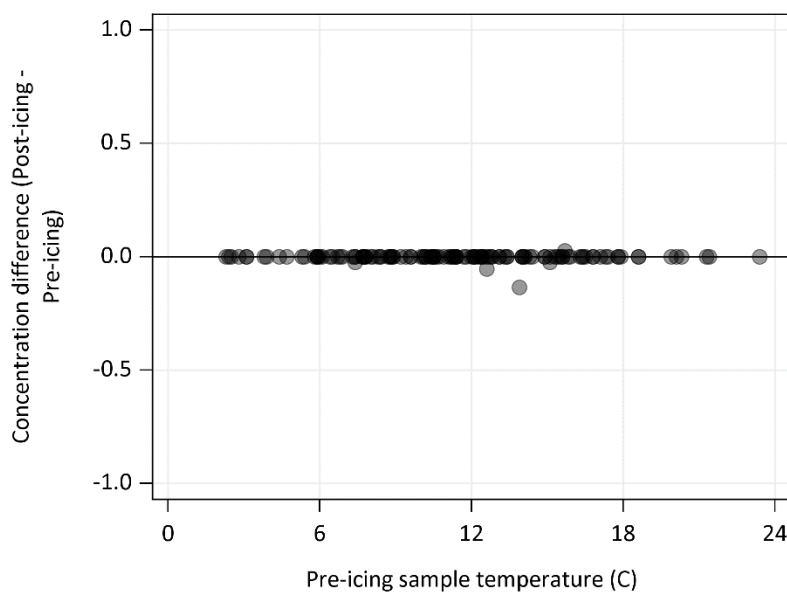


¹ One outlier (difference=81 ppb, receiving temperature=8.8 C) excluded

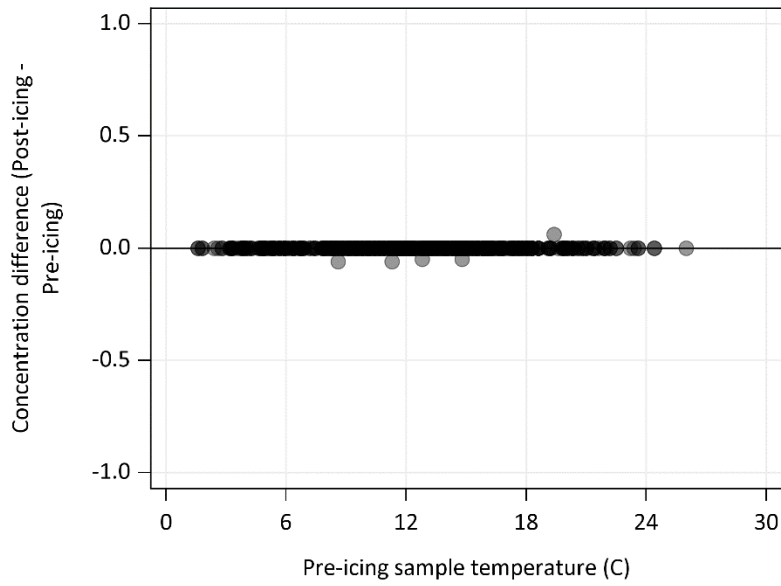
IOC and SOC Results

Scatterplots of concentration difference by pre-icing receiving temperature with zero difference line

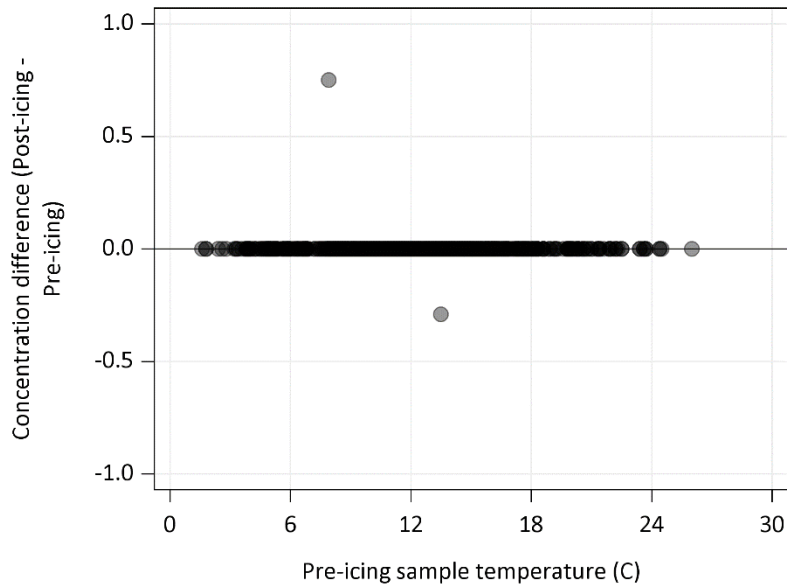
Cyanide paired results (ppm)



Atrazine paired results (ppb)



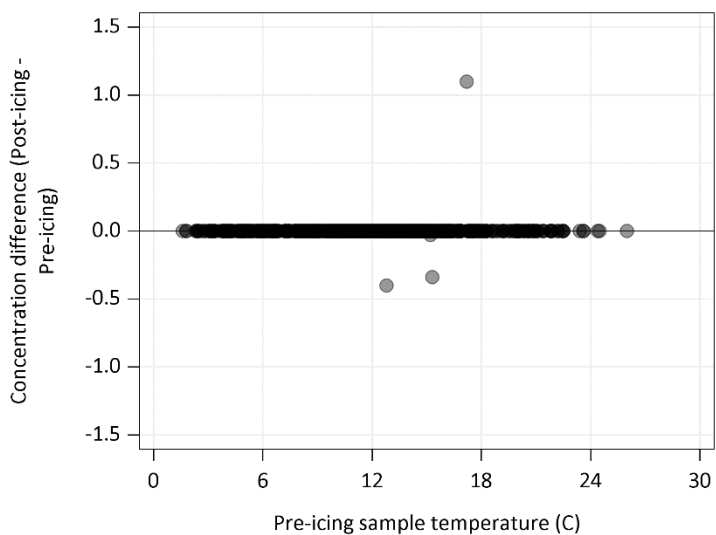
Picloram Paired Results (ppb)



VOC Results

Scatterplots of concentration difference by pre-icing receiving temperature with zero difference line

1, 2-Dichloroethane paired results (ppb)



1, 4-Dichlorobenzene

No figure shown (only 1 non-tied pair)

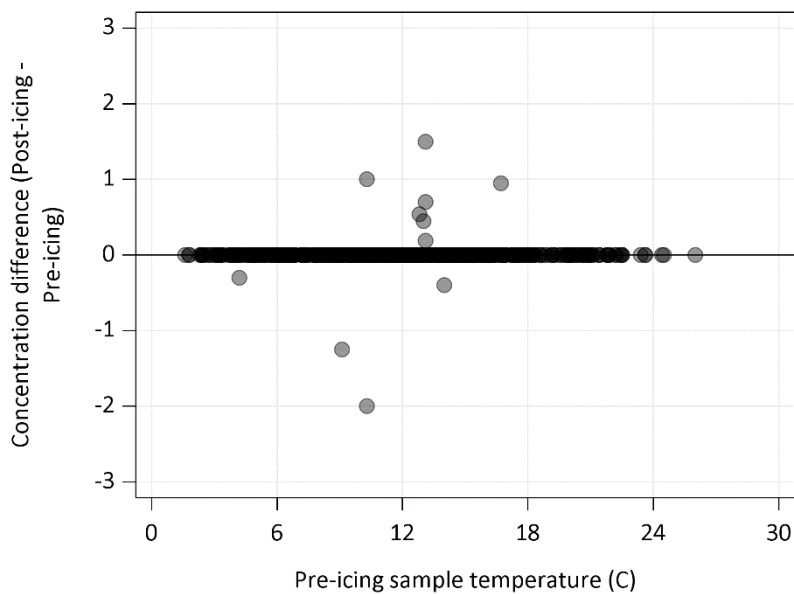
Benzene

No figure shown (only 1 non-tied pair)

Carbon tetrachloride

No figure shown (only 1 non-tied pair)

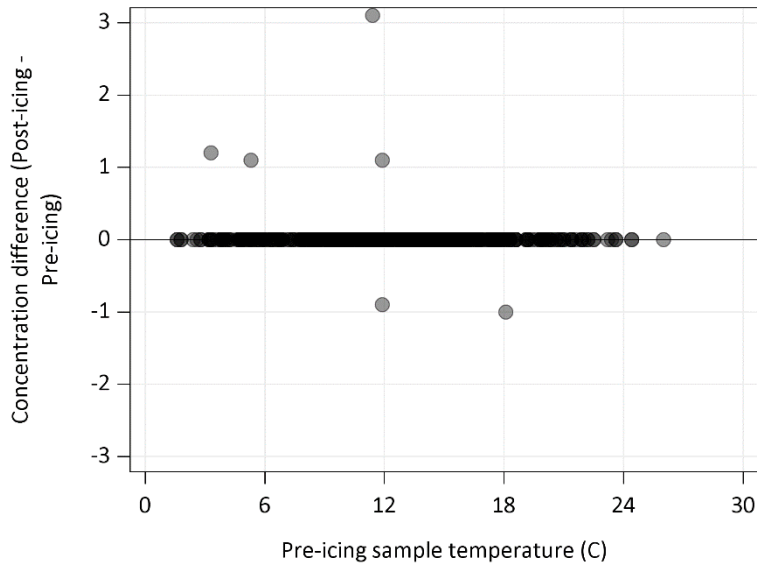
cis -1,2-dichloroethene paired results (ppb)



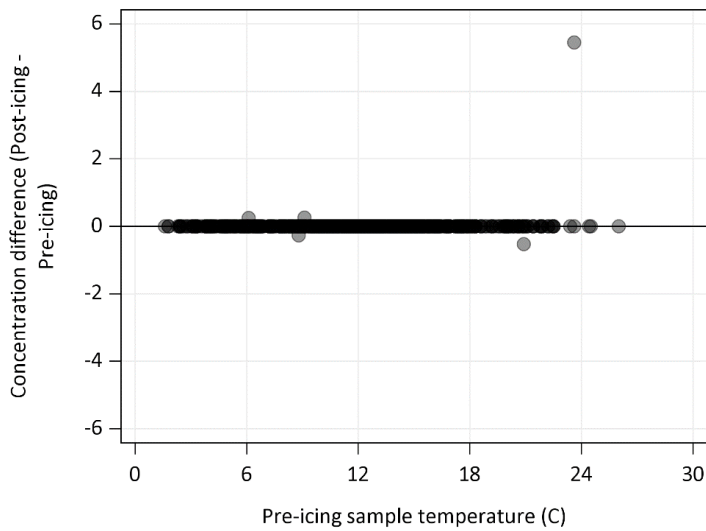
Di (2-ethylhexyl) adipate

All results < MRL. No figure shown

Di(2-ethylhexyl) phthalate paired results (ppb)



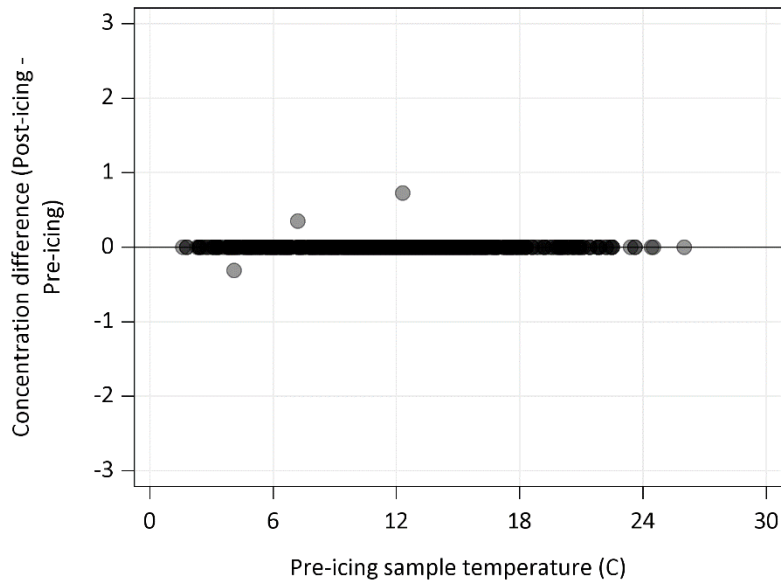
Ethylbenzene paired results (ppb)



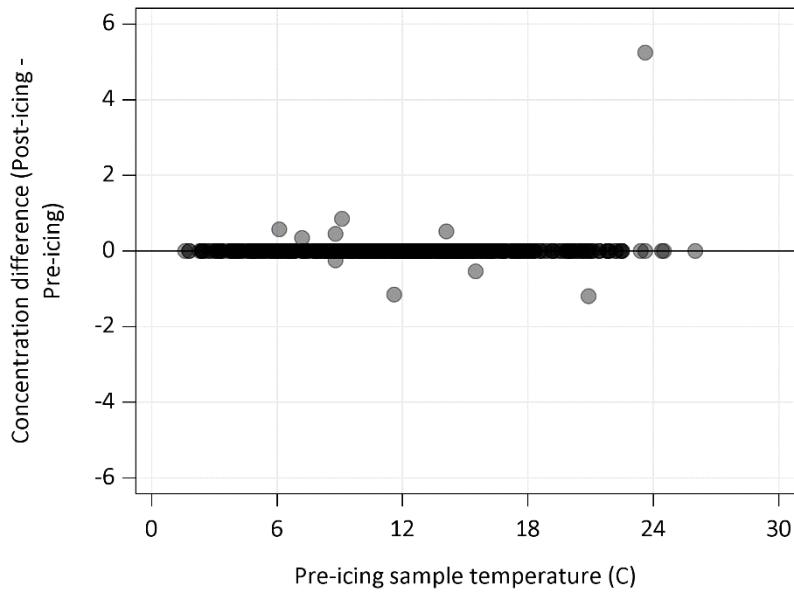
Hexachlorocyclopentadiene

All results < MRL. No figure shown

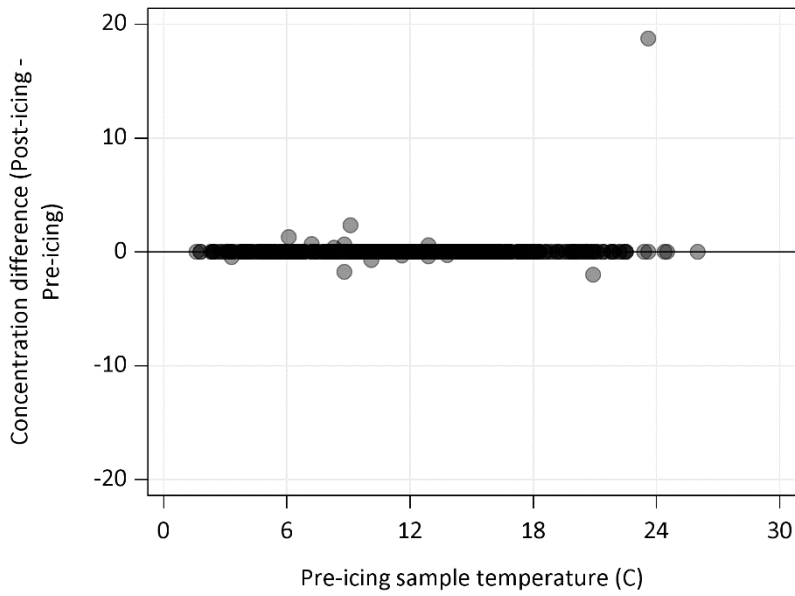
Methylene chloride paired results (ppb)



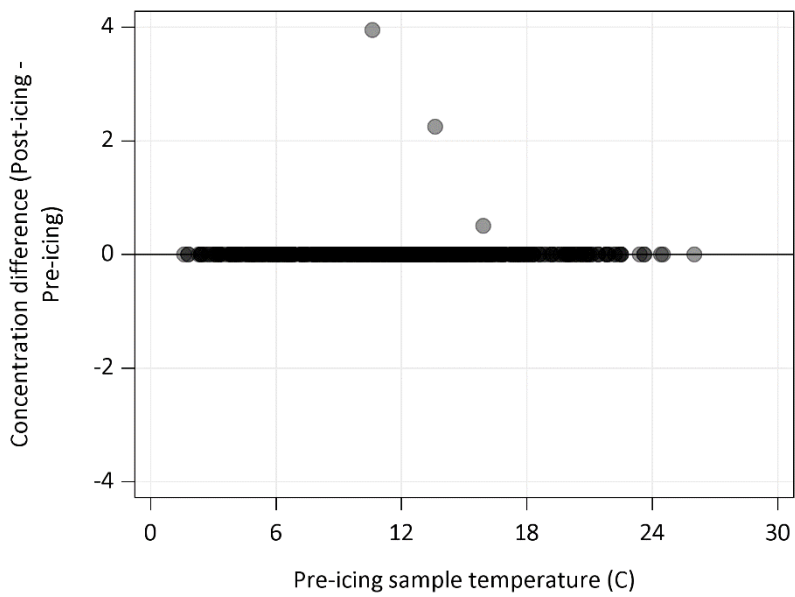
o-xylene paired results (ppb)



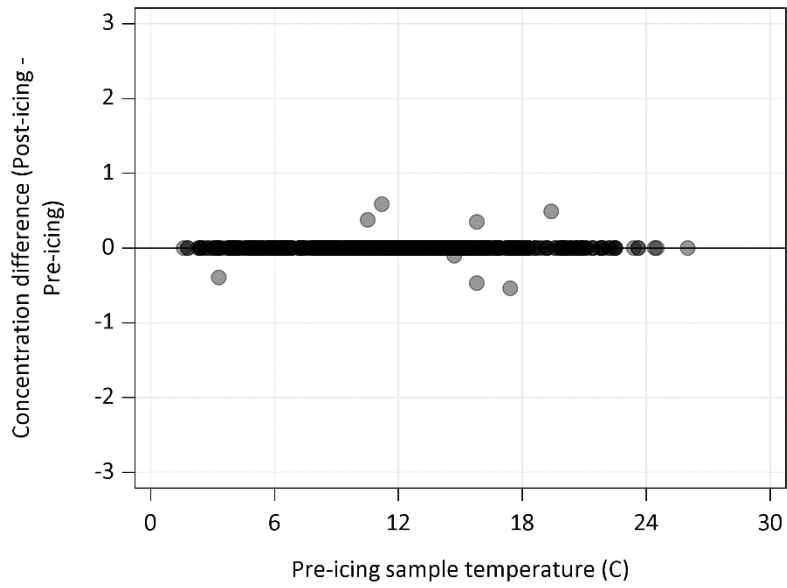
p&m-xylene paired results (ppb)



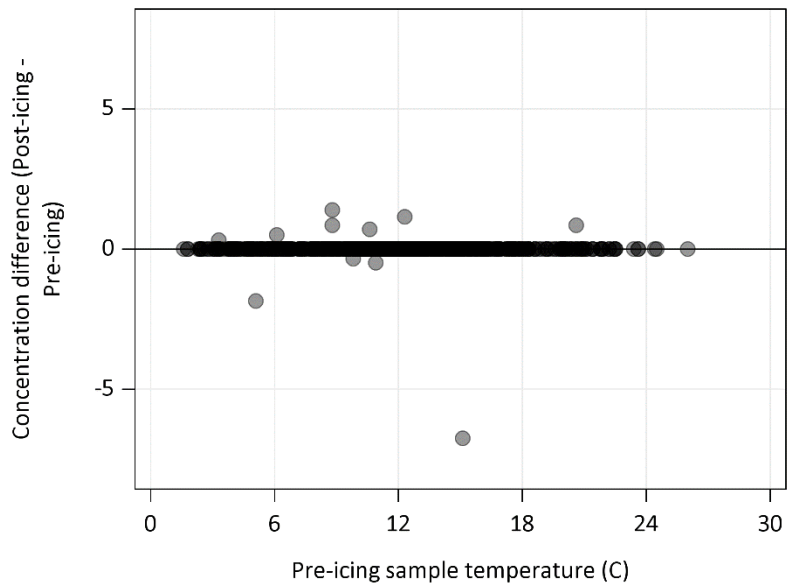
Styrene paired results (ppb)



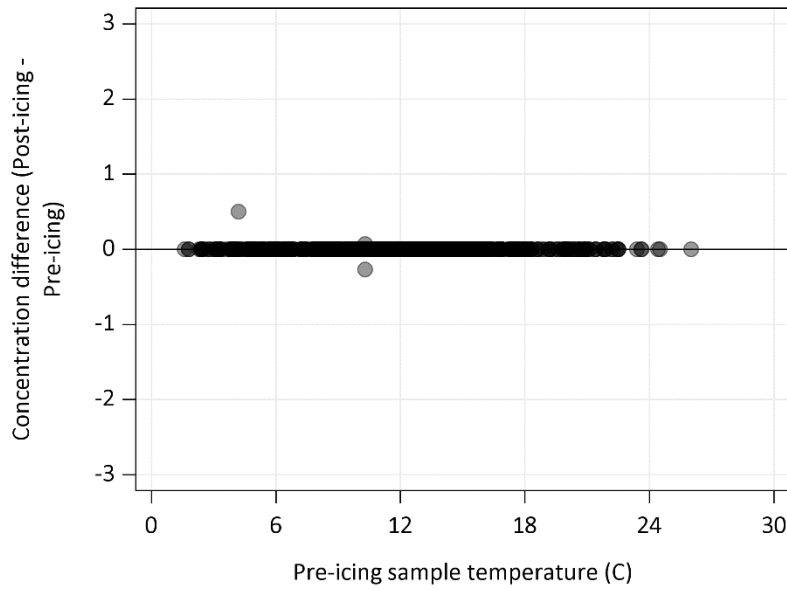
Tetrachloroethene paired results (ppb)



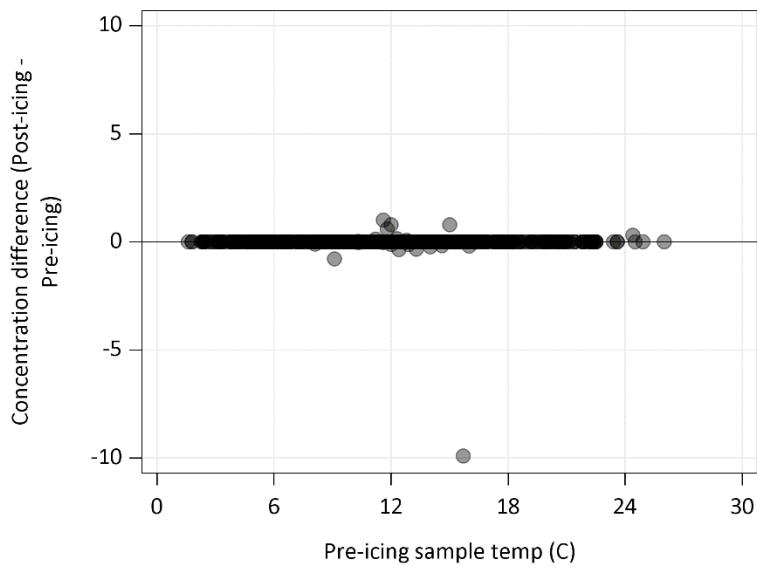
Toluene paired results (ppb)



trans -1,2-Dichloroethene paired results (ppb)



Trichloroethene (TCE) paired results (ppb)



Vinyl chloride paired results (ppb)

