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Nitrile Gloves Are a Potential Source of Nitrate + Nitrite (NO_x) Contamination in Water Quality Samples

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SUMMARY

The South Florida Water Management District (SFWMD or District) Water Quality Monitoring Section (WQM) Quality Assurance Team initiated an investigation with three main objectives: (1) determine if nitrile or vinyl gloves are a potential source of ammonia (NH_3-N) or nitrate + nitrite (NO_x) contamination, (2) determine the relative ease that contamination may occur, and (3) determine the efficacy of rinsing nitrile gloves to mitigate NO_x contamination. This is of particular concern to the District's sample collection practices because of the relatively high percent of NH_3-N and NO_x data qualified compared to other water quality analytes. Exposure testing of gloves found that nitrile gloves have the potential to contaminate samples with NO_x but not with NH_3-N. The level of NO_x contamination increased with the level of sample exposure to the nitrile glove. No contamination was found from vinyl gloves for either analyte. Rinsing the gloves was found to reduce contamination substantially.

Given the potential for NO_x contamination from nitrile gloves, guidance was issued to District samplers to thoroughly rinse nitrile gloves with analyte free water (AFW) prior to handling samples or to use non-nitrile gloves. Since this new sampling protocol was adopted, the rate of NO_x contamination detected in quality control (QC) blank samples dropped tenfold. Although there are and always will be other sources of contamination, the reduction in QC blank contamination since the adoption of the new sampling protocol indicates that nitrile gloves were the most widespread source of NO_x contamination.

INTRODUCTION

Part of SFWMD's mission is to manage and protect water resources within its 16-county region, stretching from Orlando to the Florida Keys (**Figure 1**). The collection and measurement of water quality data are essential to the management and protection of these water resources. The Florida Department of Environmental Protection's (FDEP's) Quality Assurance (QA) Rule, Chapter 62-160, Florida Administrative Code (F.A.C.), as amended on April 16, 2018, requires these data to be scientifically valid and defensible. To meet this regulatory requirement, SFWMD implemented a quality management plan (QMP) that covers all aspects of sampling, from study design, field collection, field measurement, and analyses, to data generation, reduction, reporting, and database management (SFWMD 2014). The QMP requires data with known and documented quality have acceptable completeness, representativeness, and comparability.

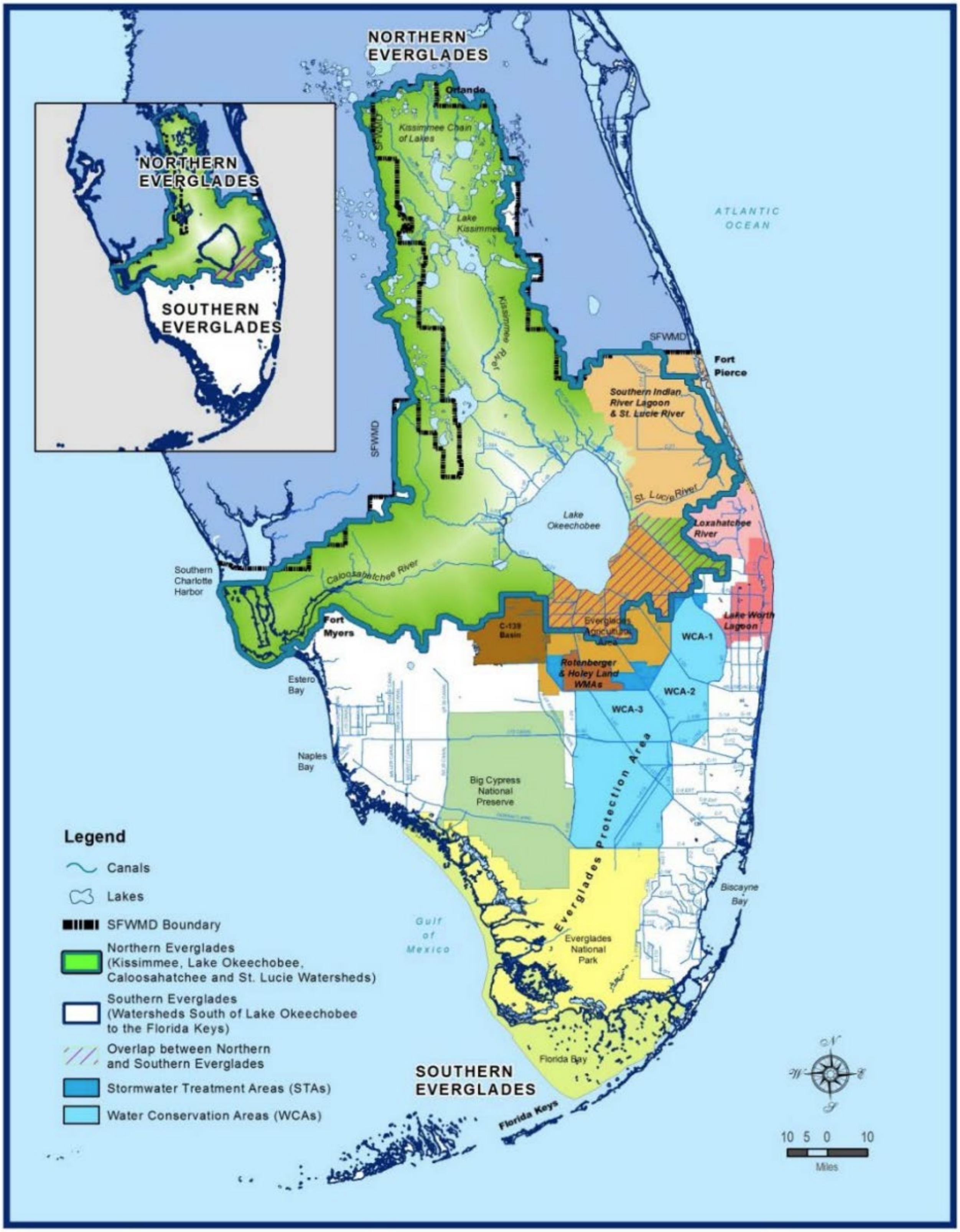

Figure 1. SFWMD boundary with major geographic features.

To ensure data with "known and documented quality", data are systematically evaluated for quality. An evaluation of QC blanks[1] found that NH_3-N and NO_x were detected in QC blanks at a higher frequency than other analytes, indicating potential contamination from either field collection or laboratory analysis of these samples. From a review of scientific literature, nitrile gloves were identified as a potential source of NH_3-N and NO_x contamination. During sample collection, gloves are used to protect SFWMD samplers from harmful substances (i.e., acid) and protect the sample from contamination by the sampler's sweat, oil, skin cells, etc. Nitrile gloves were the most common type used by SFWMD field personnel for the collection of water samples. Studies have found that nitrile gloves can be potential sources of contamination for nitrogen, carbon, and various trace elements (Strohmeier 2012, Belzile 2014). In their *National Field Manual for the Collection of Water-Quality Data* (Wilde 2014), the United States Geological Survey (USGS) required its staff to rinse gloved hands with deionized water (DIW) while gently rubbing hands together to remove any surface residue prior to handling sampling equipment. While SFWMD's sample collection standard operating procedures (SOPs) stipulates gloves should never contact a sample, the consistent blank contamination suggested that all possible methods of contamination should considered. The amount of effort and cost to collect and analyze these samples for NO_x (9,607 samples from 617 stations in calendar year 2020) and NH_3-N (7,350 samples from 596 stations in 2020), and the importance of the data, compelled this quality assurance (QA) study to investigate possible causes of contamination and recommend processes to reduce contamination when collecting water quality samples for NH_3-N or NO_x.

Following findings from the literature, two experiments were designed to test whether nitrile gloves were a source of sample contamination. The first experiment was a preliminary test using minimal resources, conducted to evaluate whether nitrile gloves had the potential to contaminate a sample under a worst-case scenario. The second experiment was designed to detect contamination under different glove exposure scenarios. In this exposure test, samples were exposed to different levels of glove contact and glove decontamination procedures. The results of these experiments are documented herein. Additionally, findings from these experiments were used to improve sample collection procedures. The effectiveness of these procedural improvements is documented in *Evaluating the Effectiveness of Changes to Sample Collection Protocol* section of this report.

BACKGROUND

HISTORICAL DATA EVALUATION

Three types of QC blanks are collected for QA: (1) equipment blanks (EBs), (2) field blanks (FBs), and (3) field cleaned equipment blanks (FCEBs). Blank types are intended to evaluate different stages of the sampling process and may be used to infer at what stage of the sampling process contamination occurs. For the purposes of providing the frequency of contamination by analyte, these three blank types were grouped together and defined as QC blanks. QC blanks are collected during each sampling event and undergo the same collection process and analysis as the samples collected for that event. Contamination in a QC blank, colloquially called a "blank hit", occurs when an analyte is detected at or above the method detection limit (MDL). If a sample result is within an order of magnitude QC blank, the sample receives a 'G' qualifier code indicating that QC blank associated with the reported value failed to meet the established QC criteria (SFWMD 2021a). Data qualifiers are standardized comments regarding data quality to aid the end user with determining the usability of the data.

To evaluate which analytes had the greatest rate of contamination, QC blank data from SFWMD's environmental database, DBHYDRO (SFWMD 2020a), were evaluated. To screen out noise from small

[1] The SFWMD Laboratory also collect QC blanks for purposes of measuring analytical error, but for the purposes of this report, QC blanks are field QC blanks intended to measure potential contamination from collection, processing, and preservation of samples in the field.

sample sizes, analytes with fewer than 100 QC samples were removed from the analysis. Data were limited to those collected by WQM staff from January 1, 2015, to September 30, 2021, which was the most recent data available at the time of analysis. **Figures 2** and **3** contain data from 2015 through 2019 as that was the period used to establish baseline rates of contamination in QC blanks and the percentage of qualified data. All samples were collected following the sampling protocol described in the *Field Sampling Manual*[2] (SFWMD 2020b) and analyzed following the *Chemistry Laboratory Quality Manual*[2] (SFWMD 2021). Overall, the frequency of QC blank contamination ranged from near 0% to just slightly over 10% (**Figure 2**). Contamination of NH_3-N and NO_x QC blanks were seen at a frequency of slightly over 10% and 6%, respectively. Although frequencies of QC blank contamination for dissolved organic carbon (DOC) and other analytes are higher than NO_X (**Figure 2**), concern of contamination for these other analytes is lower because the level of contamination in their QC blanks is lower relative to the sample. Consequently, low level contamination would not meaningfully affect their samples, resulting in less qualified data (**Figure 3**). Specifically, because both NH_3-N and NO_x have a large percentage of sample results within an order of magnitude of their MDL values (5 micrograms nitrogen per liter (µg N L^{-1})), even a small fraction of contaminated QC blanks will result in higher associated samples qualified compared to analytes with low MDLs relative to their background concentration (e.g., DOC).

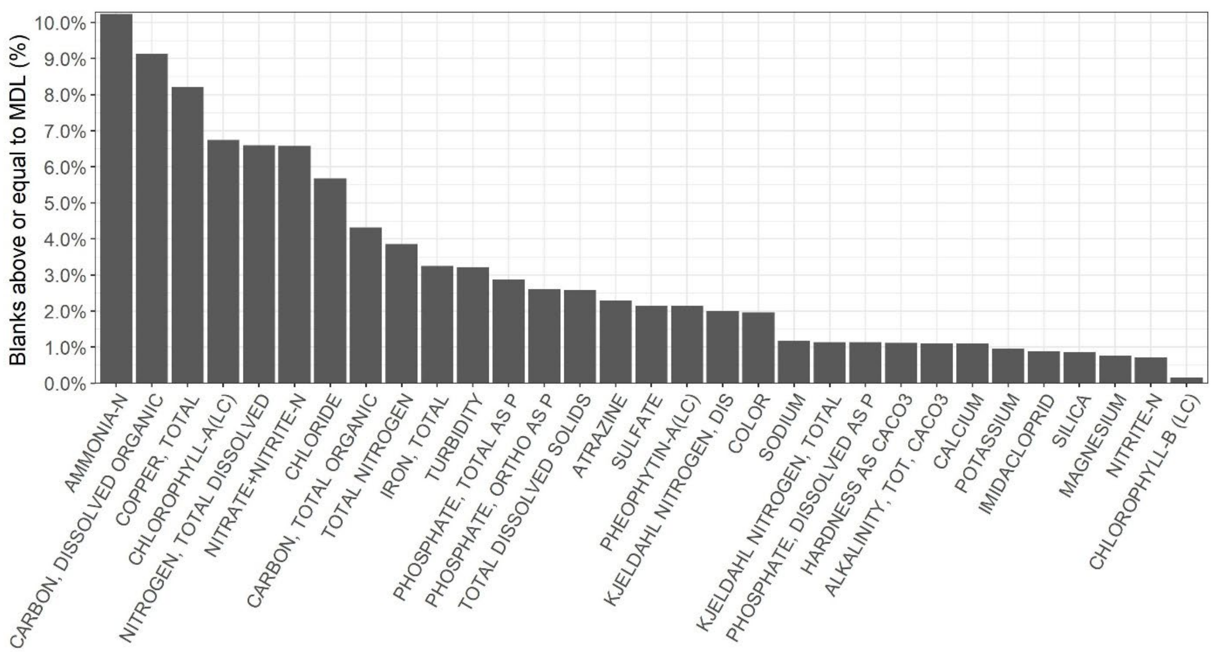

Figure 2. Percentage of blanks by analyte, greater than their MDL (2015–2019).

[2] Note that SFWMD's *Field Sampling Manual* and *Chemistry Laboratory Quality Manual* are updated annually and changes to field or laboratory procedures may occur from year to year.

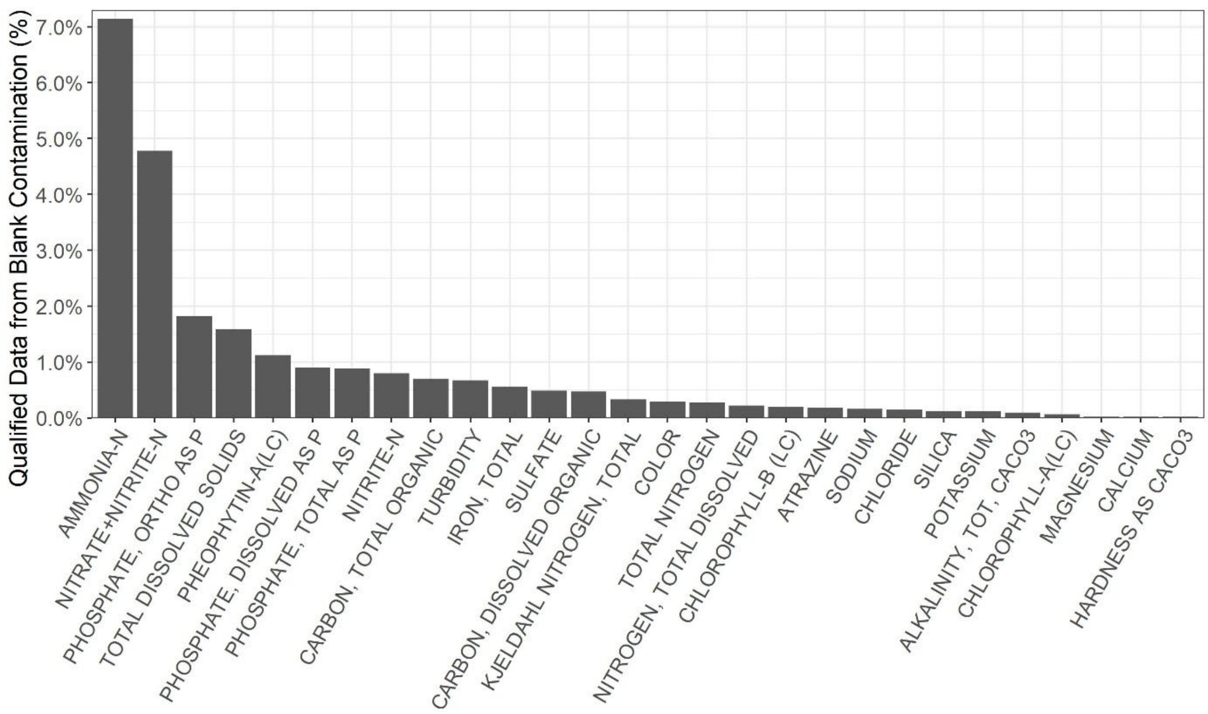

Figure 3. Percentage of qualified data by analyte (2015–2019).

GLOVE EXPERIMENTS

Two experiments were designed to test whether nitrile glove contamination is possible and if so, to what degree contamination occurs. In the first experiment, a preliminary test was conducted to find if nitrile gloves had the potential to contaminate samples in a worst-case scenario. The second experiment was designed to measure the degree of contamination under different glove exposure scenarios and to test glove rinsing as a possible mitigation strategy. Analytical methods for both experiments were identical. The laboratory analytical method for NO_x is based on Standard Method (SM) 4500 NO3 F (Automated Cadmium Reduction Method) (Janson 2019). The analytical method for NH_3-N is based on SM 4500 NH3-H (Automated Phenate Method) (Janson 2019). Descriptive statistics were calculated using the R programming language (R Core Team 2020) with figures constructed using the R packages *ggplot2* (Wickham et al. 2021) and *plotrix* (Lemon 2006). Fisher's Exact Test was run using R package *RVAideMemoire* (Hervé 2021) and pairwise comparisons using R package *rcompanion* (Mangiafico 2021).

EXPERIMENT 1: WORST-CASE SCENARIO STUDY

Experimental Design

To determine the potential for NH_3-N or NO_x contamination from nitrile gloves, a preliminary test was conducted where four glove brands: three nitrile and one vinyl (used as a control), were used: Uline Blue Nitrile, Safety Choice Blue Nitrile™, Purple Nitrile, and Fisher Safety Choice Vinyl™. A single glove of each brand was used. Each glove was placed in separate 1-liter bottles containing 50 milliliters (mL) of AFW. Each bottle was shaken for 10 seconds, and water was decanted into a 60 mL sample bottle and analyzed.

Results

The resulting NO_x concentrations in these test samples were as high as 1,900 µg N L^{-1}, with all nitrile glove brands having contamination above 600 µg N L^{-1} (**Appendix A, Figure 1**). NH_3-N was detected at 25 µg N L^{-1}, which was well above its 5 µg N L^{-1} MDL. However, NH3-N was also found in the control blank at a level greater than any of the glove tests, resulting in inconclusive findings for NH_3-N (Figure A-2 in Appendix A). While this preliminary test did not include replicate samples, results strongly suggested nitrile gloves had the potential for NO_x contamination, providing the impetus for Experiment 2. This preliminary test resulted in recommendations issued to SFWMD samplers on April 1, 2020, urging them to use caution when using nitrile gloves and to not cover AFW carboy spigots with nitrile gloves. The impact of this guidance is described in *Evaluating the Effectiveness of Changes to Sample Collection Protocol* section of this report.

EXPERIMENT 2: GLOVE EXPOSURE STUDY

Experimental Design

This study comprised three different experiments consisting of non-nitrile glove exposure, unrinsed nitrile glove exposure, and rinsed nitrile glove exposure (**Table 1**). Treatments within each experiment were replicated five times. In Experiment 1, other potential contamination sources were assessed, four treatments consisted of (1) an unrinsed sample bottle, (2) a sample bottle rinsed with AFW, (3) tip of the index finger of a single vinyl glove dipped into rinsed sample bottles for 1 second, and (4) tip of the index finger of a single vinyl glove dipped into rinsed sample bottles for 10 seconds. In Experiment 2, unrinsed nitrile gloves were included in similar Experiment 1 treatment specifically by (1) rubbing a nitrile glove inside a dry, unrinsed sample bottle prior to sample collection, (2) turning a glove inside out and rubbing it on the inside of a dry, rinsed sample bottle prior to sample collection, (3) dipping the nitrile gloves into a rinsed sample bottle for 1 second, and (4) dipping the nitrile gloves into a rinsed sample bottle for 10 seconds. Experiment 3 repeated the second experiment's treatments using nitrile gloves rinsed vigorously with AFW for five seconds.

The treatments dipping the fingertip of a nitrile glove for a duration of 1 or 10 seconds provided a good approximation for potential contamination in the real world, with limited exposure areas and times. Dry contact for nitrile, rinsed nitrile, and inside-out nitrile gloves of the interior of a dry bottle prior to filling the bottle with AFW provided insight about the potential for dry contact transfer of NO_x contamination, which could occur if the sampling equipment were handled improperly.

Samples were preserved to a pH between 1.3 to 2.0 with 4 drops of sulfuric acid utilizing the single lot number for consistency. Vinyl gloves were worn for all sample handling steps when samples were not undergoing their treatment. This was done based on the preliminary test showing vinyl gloves were likely not a significant source of NH_3-N and NO_x. Fisher Safety Choice Vinyl™ and Fisher Safety Choice Blue Nitrile™ gloves were used as glove types in the exposure study.

Table 1. Glove Exposure Study experimental design.

Experiment	Treatment	Treatment Steps	Purpose
Non-nitrile Glove	Bottle Unrinsed	Unrinsed bottle filled with AFW.	Test sample bottle for contamination.
	Bottle Rinsed	Bottle rinsed 1 time with AFW then filled with AFW.	Test AFW for contamination.
	Vinyl Gloves, 1-Second Dip	Bottle rinsed 1 time with AFW, filled with AFW, and finger dipped for 1 second.	Limited exposure test for vinyl glove contamination.
	Vinyl Gloves, 10-Second Dip	Bottle rinsed 1 time with AFW, filled with AFW, and finger dipped for 10 seconds.	Long exposure test for vinyl glove contamination.
Unrinsed Nitrile Glove	Bottle Dry Rubbed with glove	Dry gloved finger rotated 1 time around entire interior surface of empty dry bottle, then filled with AFW.	Dry contact contamination test.
	Bottle Dry Rubbed with Inside Out Gloves	Finger in an inside-out dry glove rotated 1 time around entire interior surface of empty dry bottle then filled with AFW.	Dry contact contamination test. Proxy for glove over carboy spigot.
	1-Second Dip	Bottle rinsed 1 time with AFW, filled with AFW, and finger dipped for 1 second.	Limited exposure test for glove contamination.
	10-Second Dip	Bottle rinsed 1 time with AFW, filled with AFW, and finger dipped for 10 seconds.	Long exposure test for glove contamination.
Rinsed Nitrile Glove	Rinsed Nitrile Gloves, Bottle Dry Rubbed	Finger in a rinsed glove rotated 1 time around entire interior surface of empty dry bottle then filled with AFW.	Test for effectiveness of rinsing for mitigating dry contact contamination.
	Rinsed Nitrile Gloves, 1-Second Dip	Bottle rinsed 1 time with AFW, filled with AFW, and finger in rinsed glove dipped for 1 second.	Test the effectiveness of rinsing for reducing glove contamination.
	Rinsed Nitrile Gloves, 10-Second Dip	Bottle rinsed 1 time with AFW, filled with AFW, and finger in rinsed glove dipped for 1 second.	Test the effectiveness of rinsing for reducing glove contamination.

Statistical Analysis of Glove Exposure Test Data

Values below the MDL (5 µg N L^{-1}) were reported at the MDL and given a “U” qualifier. Because such a large proportion of these data were below their MDL (approximately 70% of NO_x and 98% of NH_3-N), the data were transformed to frequencies before running statistical analyses (Helsel 2012). Specifically, the numeric NO_x and NH_3-N data were dichotomized to a binominal category of “Detected” or “Undetected” depending on whether the result was equal to or greater than the MDL. A contingency table of detected and undetected for each treatment was created and Fisher’s Exact Test used to calculate the statistical difference between treatments for each analyte. A post-hoc pairwise comparison of treatments was used when a significant difference was found using Fisher’s Exact Test. Significant differences among treatments across all experiments are denoted by “a”, “b”, and “ab” (**Table 2**). Treatments without statistical differences share the same letter. Treatments that do not share a common letter are significantly different. The Benjamini–Hochberg method (Benjamini and Hochberg 1995) of controlling for false discovery rate in multiple comparison tests was used to adjust probability (p)-values. All results from glove exposure studies are reported in Tables B-1 and B-2 in Appendix B.

NO_x Glove Exposure Study Results

Detectable concentrations of NO_x were not found in the non-nitrile glove experiment (**Table 2** and **Figure 4**). Contamination was detected in three of the four treatments involving unrinsed nitrile gloves. In the nitrile bottle dry rub treatment, mean NO_x was measured at 15 µg N L^{-1}, this is above the practical quantitation limit (PQL) of 10 µg N L^{-1}. The PQL is the minimum value of an analyte that can be measured with a high level of confidence. Mean NO_x was well above the PQL for the nitrile 1-second dip and nitrile 10-second dip treatments at 202 and 242 µg N L^{-1}, respectively. In the rinsed nitrile glove experiment, only one 10-second dip sample was above the MDL, and this detection was below the PQL. All others were below detection.

Table 2. Glove Study sample results for NO_x.

Experiment	Treatment	Range (µg N L^{-1})	Mean (µg N L^{-1}) [a]	Median (µg N L^{-1})	Percent of results equal or greater than MDL (%) [b, c]
Non-nitrile Glove	Unrinsed Bottle	< 5	< 5	< 5	0 a
	Bottle Rinsed	< 5	< 5	< 5	0 a
	Vinyl 1-Second Dip	< 5	< 5	< 5	0 a
	Vinyl 10-Second Dip	< 5	< 5	< 5	0 a
Unrinsed Nitrile Glove	Nitrile Bottle Rub	11-17	15	15	100 b
	Nitrile 1-Second Dip	174 - 239	202	189	100 b
	Nitrile 10-Second Dip	224 - 263	242	242	100 b
	Nitrile Inside Out Rub	< 5	< 5	< 5	0 a
Rinsed Nitrile Glove	Nitrile Rinsed Rub	< 5	< 5	< 5	0 a
	Nitrile Rinsed 1-Second Dip	< 5	< 5	< 5	0 a
	Nitrile Rinsed 10-Second Dip	<5-7	< 5	< 5	20 ab

a. Mean reported as < 5 µg N L^{-1} when at least 4 of 5 values were below the MDL and the detected value was no larger than 7 µg N L^{-1}.

b. Treatments not connected by common letter are significantly different.

c. MDL for NO_X is 5 µg N L^{-1}.

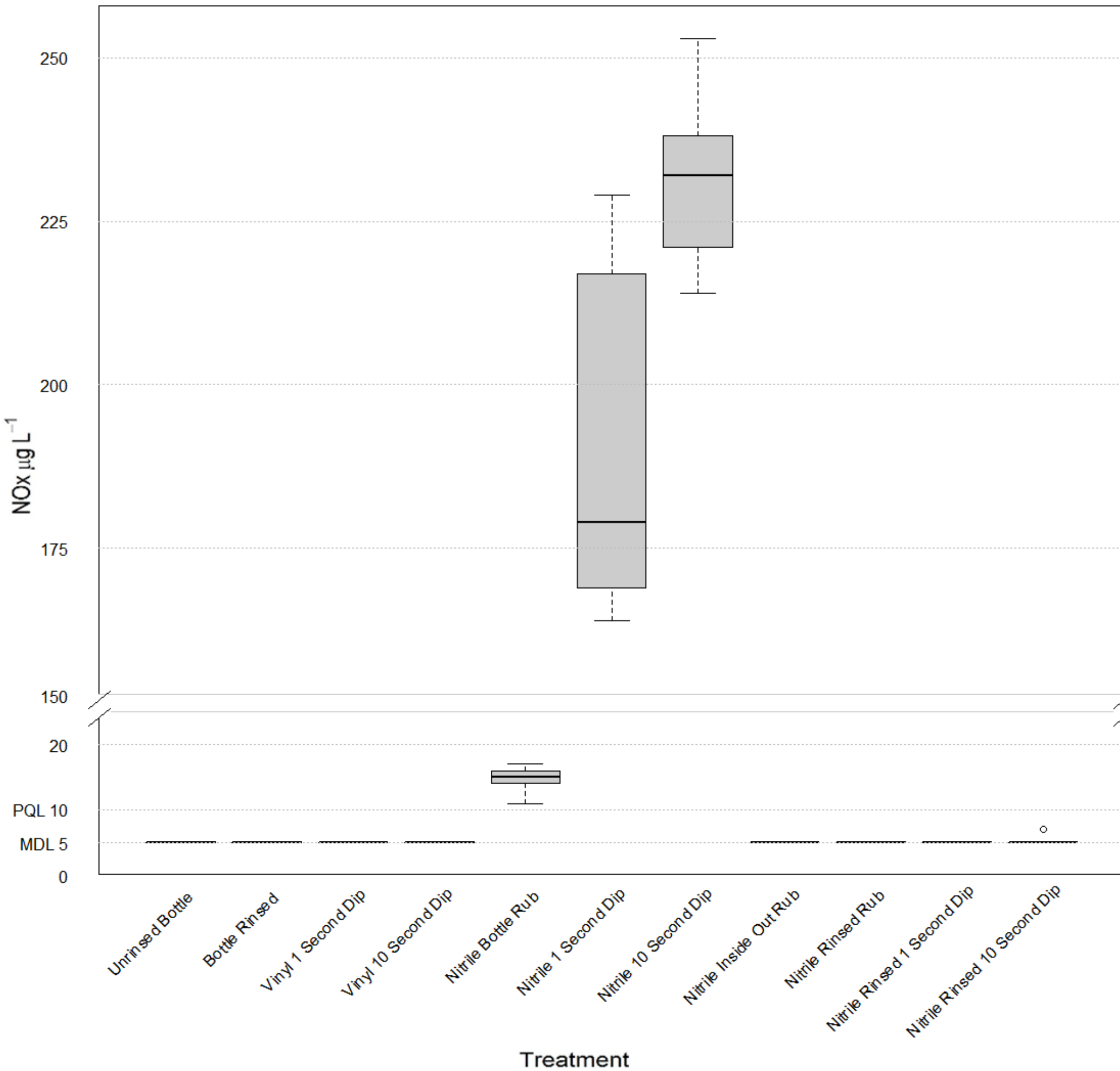

Figure 4. NO_x contamination by treatment. Ordinate broken between 30 and 150 µg N L^{-1} so all differences among treatments are visible.

NH_3-N Glove Exposure Test Results

Ammonia (NH_3-N) concentrations did not exceed the MDL in any treatments (Table B-2 in Appendix B). A single test detected ammonia in the Nitrile 1-Second Dip treatment at the MDL of 5 µg N L^{-1}. No statistically significant differences were detected among the NH_3-N treatments.

EVALUATING THE EFFECTIVENESS OF CHANGES TO SAMPLE COLLECTION PROTOCOL

Realizing the potential for nitrile glove NO_x contamination from the findings of the worst-case scenario test, interim guidance was issued to sample collectors to reduce the potential for contamination on April 1, 2020. After the glove exposure test, the degree to which even a slight one second contact would contaminate a sample was understood so an additional mandatory sample collection guidance was issued on March 1, 2021. This guidance instructed samplers to either rinse nitrile gloves thoroughly with AFW while rubbing hands together to ensure the entire surface of both gloves were flushed with free flowing AFW, or to use non-nitrile gloves when collecting samples to be analyzed for any nitrogen species. Use of other non-nitrile gloves has always been allowed. NH_3-N was not included in this analysis because nitrile gloves were not found to contaminate NH_3-N samples in the glove exposure test.

METHODS

To evaluate the effectiveness of the changes made to the sampling protocol by the issuance of interim and mandatory guidance, the frequency of NO_x contamination in blanks was compared from the periods before interim guidance (2015 through 2019), to the period of interim guidance (2020), and the period after mandatory guidance was issued (2021). These periods are irregular, starting and ending at different times of the year. The interim guidance period starts April 1, 2020, and runs to the start of the mandatory guidance period. The post-mandatory guidance period starts March 1, 2021, and up to September 30, 2021, the date of the latest data available when this paper was written. To remove the potential confounding effects from these irregular periods, data used in this evaluation were limited to days of the year that these periods have in common, April 1–September 30. Data from the years prior to interim guidance being issued were similarly filtered to only include days from this time period. The frequency of contamination was calculated by the number of QC blanks from routine sampling trips where NO_x was at or above the MDL; these “Detected” blanks were compared to the number of QC blanks where NO_x was below the MDL (i.e., “Undetected”). Statistically significant difference in the proportion of NO_x detections between the pre-interim, interim, and post-mandatory guidance periods were made by pairwise comparison between periods using the G-Test of independence using the null hypothesis of no difference in the proportion of QC blanks with detectable NO_x between periods.

To avoid Type I error (false positive), which incorrectly rejects the null hypothesis when there is a finding of no significant effect, the Bonferroni correction was applied to the p-value. This was calculated by dividing the original significance (α)-value, 0.05, by the number of comparisons, 21, which gives a Bonferroni-adjusted p-value of 0.0023.

RESULTS: FREQUENCY OF BLANK CONTAMINATION BY PERIOD

The interim guidance and post-mandatory guidance periods had the lowest frequency of QC blank contamination of the seven periods evaluated. Only seven NO_x detections were found in the QC blanks in 2021 and 34 from the 2020 interim guidance period. Approximately the same number of total blanks were collected in the same time period from each year (**Table 3**).

There were statistically significant differences between the interim guidance period in 2020 and each of the pre- and post-interim periods: 2016, 2017, 2019, and 2021 (**Table 4**). There were statistically significant differences with the post-mandatory guidance period in 2021 and every other year. In the pre-interim guidance periods in the years 2015 to 2019, there were significant differences found between 2015 and 2017 as well as between 2017 and 2018.

Table 3. NOx detections in QC blanks by year. [a]

Period	Total QC Blanks	Detected	Undetected	Percent Detections (%)
2015	1,041	63	978	6.05%
2016	942	74	868	7.86%
2017	901	95	806	10.54%
2018	908	52	856	5.73%
2019	810	53	757	6.54%
2020	987	34	953	3.44%
2021	1,050	7	1,043	0.67%

a. Data used from April 1 through September 30 of each year. Periods are represented by the year they occurred.

Table 4. P-values of pairwise yearly comparisons using G-Test of Independence. [a,b]

Period	2015	2016	2017	2018	2019	2020	2021
2015	NA	-	-	-	-	-	-
2016	0.11398	NA	-	-	-	-	-
2017	**0.00031**	0.04548	NA	-	-	-	-
2018	0.76117	0.06846	**0.00016**	NA	-	-	-
2019	0.66568	0.28952	0.00305	0.48111	NA	-	-
2020	0.00555	**<0.0001**	**<0.0001**	0.01692	**0.00237**	NA	-
2021	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	NA

a. Significant in p-values in bold. Bonferroni correction applied to critical values; p-value must be less than 0.00238 to be significant.

b. Data used from April 1 through September 30 of each year. Periods are represented by the year they occurred.

DISCUSSION

In the worst-case scenario test, three brands of nitrile gloves were found to have the potential for NO_x contamination. The level of this potential contamination was high, with all brands having sample concentrations above 600 µg N L^{-1} (Figure A-1 in Appendix A). Because the potential was found for nitrile gloves to contaminate samples a follow up experiment was designed to expose the samples to a more realistic levels of contact with the sample. In this glove exposure experiment, treatments where the outside of an unrinsed nitrile glove contacted the sample or sample bottle, NO_x contamination was found (**Table 2** and **Figure 4**), and the level of contamination increased with the degree of sample contact. When samples were exposed to a nitrile gloved finger for 1 second, the level of NO_x contamination averaged 202 µg N L^{-1}, increasing to an average of 242 µg N L^{-1} when the length of exposure was increased to 10 seconds. This is 40 times greater than the MDL for the 1-second exposure and 48 times greater for the 10-second exposure. Contamination at this level is a significant concern, particularly when ambient concentrations of dissolved inorganic nitrogen (DIN) from sampling areas such as Everglades National Park, Water Conservation Area 2, and Water Conservation Area 3 are typically below 100 µg N L^{-1} (Julian et al. 2021). The source for nitrile glove NO_x contamination is likely from various inorganic salts, such as calcium nitrate, used during the glove manufacturing process (Strohmeier et al. 2012). These salts are easily dissolved in water where they are readily transferable to the sample or sampling equipment. This is evident in the treatment where a short 1 second exposure of nitrile glove contaminated samples to a much higher degree than a dry glove finger rubbed around the inside of a sample bottle. Because the contaminant is easily soluble, rinsing with

AFW was hypothesized to be an effective way to decontaminate the gloves. This is borne out in the results of the glove exposure test. It was evident in this experiment that a thorough 5 second rinse was enough to reduce NO_x contamination. There were no statistically significant differences between the control treatments and treatments where rinsed gloves were rubbed in a dry bottle, dipped for 1 second in a filled bottle, and dipped for 10 seconds in a filled bottle. There was a single instance of detectable NO_x in the rinsed glove treatments when a rinsed glove was dipped for 10 seconds into the sample resulting in a detection of 7 µg N L^{-1}, this is above the MDL but below the PQL. This study found that rinsing gloves with AFW is an effective decontamination procedure as demonstrated by the low frequency of contamination after rinsing and low level of contamination found in the single sample where NO_x was detectable.

There were two changes in sampling protocol as result of the nitrile glove experiments. The first change came after the worst-case scenario test when interim guidance was issued. In this guidance, SFWMD samplers were urged to use caution when using nitrile gloves and instructed that a glove was not to be used to cover the spigots of AFW containers; gloves were being used to cover the spigot in an effort to protect the spigot from contamination. In the second change to sampling protocol, SFWMD samplers were directed to follow specific instructions to rinse nitrile gloves or use non-nitrile gloves when collecting samples to be analyzed for NO_x. This change was incorporated in the *Field Sampling Manual* (SFWMD 2020b). Although the first change did not give specific decontamination instructions, the result was a reduction in QC blank contamination. In the periods analyzed from 2015 through 2019 approximately 6% to 10.5% of QC blanks had detectable quantities of NO_x (**Table 3**). This dropped to 3.44% detections in the 2020 period, a statistically significant difference from previous periods (**Table 4**). This frequency dropped even lower after nitrile glove decontamination procedures were mandated. Detectable NO_x was only found in 0.67% of QC blanks in the 2021 period, a statically significant difference from every other period. This greater than tenfold reduction in detectable NO_x in QC samples led to a substantial reduction in sample data being qualified.

Results for NH_3-N in the worst-case scenario study were inconclusive since NH_3-N was found in the control treatment. However, in the glove exposure study, no significant differences occur between treatments for NH_3-N. In the only a single instance where NH_3-N was detected, the amount detected was 5 µg N L^{-1}, equal to the MDL, the lowest detectable quantity possible. Therefore, evidence does not support nitrile gloves as a source of NH_3-N contamination.

CONCLUSION

Evidence from the worst-case scenario glove study, glove exposure study, and an analysis of the effects from changes in the sample collection procedure support the hypothesis that nitrile gloves are a potential source of NO_x contamination. This contamination risk can be reduced by rinsing nitrile gloves with AFW or using vinyl gloves. It should not be inferred that nitrile gloves were responsible for all previous instances of contamination, but it is clear from the order of magnitude reduction in the frequency of NO_x contamination in QC blank samples after changes were made to the sampling protocol that nitrile gloves were a major contributor to NO_x contamination. Nitrile gloves can still be used if rinsed thoroughly before being used to collect for samples. However, non-nitrile gloves are a preferable alternative especially when collecting samples for NO_x, as they are not potential sources of contamination. Adoption of these recommendations will reduce the amount of data qualified as a result of NO_x contamination in QC blanks and improve overall data quality.

No evidence was found that nitrile gloves have the potential to cause NH_3-N contamination. Since NH_3-N contamination was the analyte with the greatest proportion of qualified data among commonly collected analytes (**Figure 3**), further study to find the source of this contamination should be undertaken.

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APPENDIX A: WORST-CASE SCENARIO TEST RESULTS

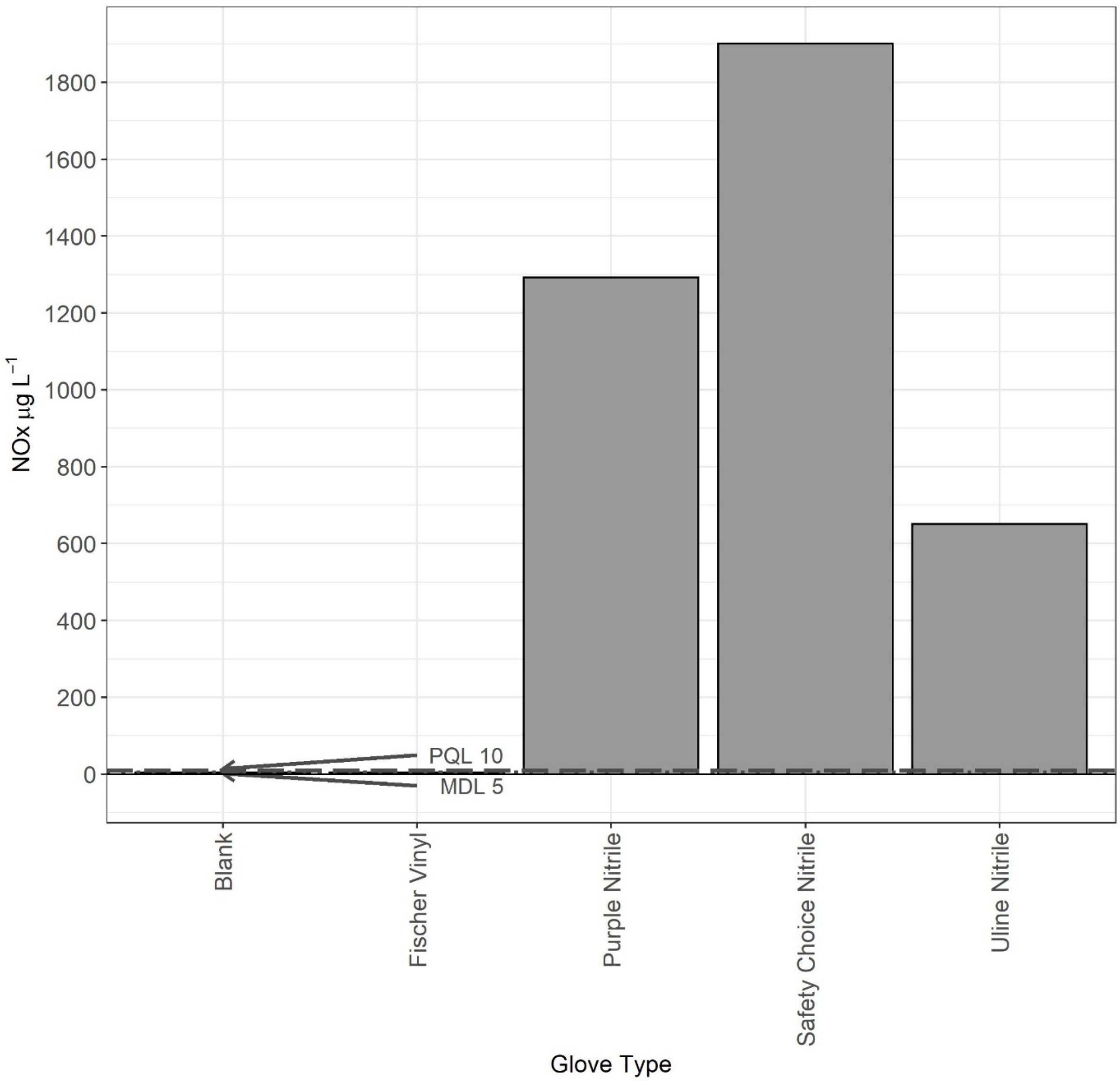

Figure A-1. NO_x contamination in worst-case scenario glove test.

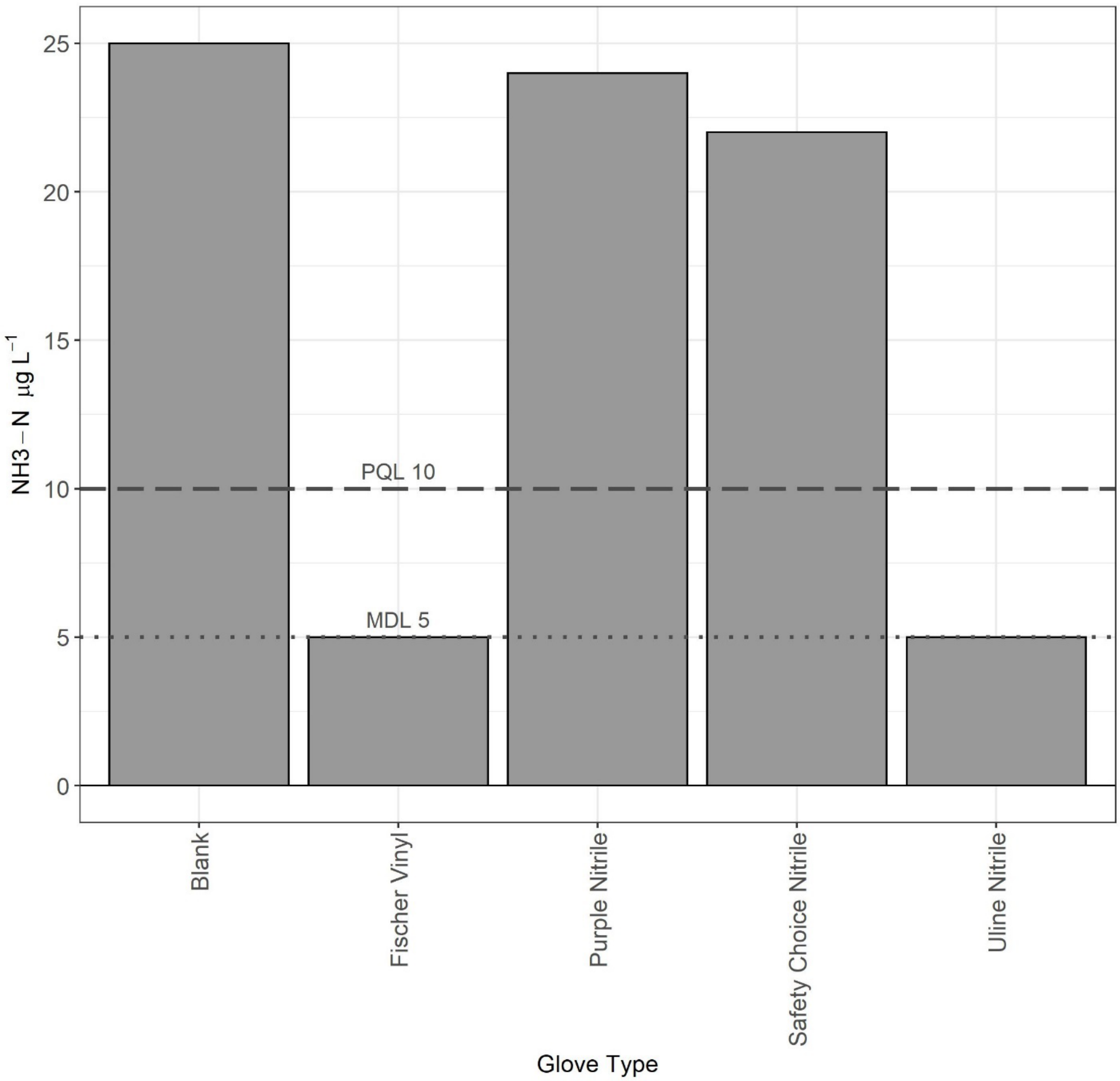

Figure A-2. NH_3-N Contamination in worst-case scenario glove test.

APPENDIX B: GLOVE EXPOSURE STUDY DATA

In **Tables B-1** and **B-2**, samples qualified with a 'U' have concentrations below the MDL and are essentially non-detects and samples qualified with a 'I' have concentrations between the MDL and PQL.

Table B-1. NO_x data with qualifier codes.

Treatment	SAMPLE_ID	VALUE	UNITS [a]	MDL	Qualifier
Unrinsed Bottle	P121273-52	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-53	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-54	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-55	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-56	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-2	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-3	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-4	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-5	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-6	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-7	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-8	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-9	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-10	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-11	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-12	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-13	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-14	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-15	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-16	0.005	mg/L	0.005	U
Nitrile Bottle Rub	P121273-37	0.017	mg/L	0.005	
Nitrile Bottle Rub	P121273-38	0.015	mg/L	0.005	
Nitrile Bottle Rub	P121273-39	0.016	mg/L	0.005	
Nitrile Bottle Rub	P121273-40	0.014	mg/L	0.005	
Nitrile Bottle Rub	P121273-41	0.011	mg/L	0.005	
Nitrile 1-Second Dip	P121273-17	0.174	mg/L	0.005	
Nitrile 1-Second Dip	P121273-18	0.239	mg/L	0.005	
Nitrile 1-Second Dip	P121273-19	0.179	mg/L	0.005	
Nitrile 1-Second Dip	P121273-20	0.189	mg/L	0.005	
Nitrile 1-Second Dip	P121273-21	0.227	mg/L	0.005	
Nitrile 10-Second Dip	P121273-22	0.242	mg/L	0.005	
Nitrile 10-Second Dip	P121273-23	0.248	mg/L	0.005	
Nitrile 10-Second Dip	P121273-24	0.263	mg/L	0.005	
Nitrile 10-Second Dip	P121273-25	0.231	mg/L	0.005	
Nitrile 10-Second Dip	P121273-26	0.224	mg/L	0.005	
Nitrile Inside Out Rub	P121273-42	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-43	0.005	mg/L	0.005	U

Table B-1. Continued.

Treatment	SAMPLE_ID	VALUE	UNITS [a]	MDL	Qualifier
Nitrile Inside Out Rub	P121273-44	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-45	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-46	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-47	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-48	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-49	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-50	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-51	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-27	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-28	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-29	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-30	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-31	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-32	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-33	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-34	0.007	mg/L	0.005	I
Nitrile Rinsed 10-Second Dip	P121273-35	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-36	0.005	mg/L	0.005	U

a. mg/L – milligrams per liter.

Table B-2. Ammonia data with qualifier codes.

Treatment	SAMPLE_ID	VALUE	UNITS [a]	MDL	Qualifier
Unrinsed Bottle	P121273-52	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-53	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-54	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-55	0.005	mg/L	0.005	U
Unrinsed Bottle	P121273-56	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-2	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-3	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-4	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-5	0.005	mg/L	0.005	U
Bottle Rinsed	P121273-6	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-10	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-11	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-7	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-8	0.005	mg/L	0.005	U
Vinyl 1-Second Dip	P121273-9	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-12	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-13	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-14	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-15	0.005	mg/L	0.005	U
Vinyl 10-Second Dip	P121273-16	0.005	mg/L	0.005	U
Nitrile Bottle Rub	P121273-37	0.005	mg/L	0.005	U
Nitrile Bottle Rub	P121273-38	0.005	mg/L	0.005	U
Nitrile Bottle Rub	P121273-39	0.005	mg/L	0.005	U
Nitrile Bottle Rub	P121273-40	0.005	mg/L	0.005	U
Nitrile Bottle Rub	P121273-41	0.005	mg/L	0.005	U
Nitrile 1-Second Dip	P121273-17	0.005	mg/L	0.005	U
Nitrile 1-Second Dip	P121273-18	0.005	mg/L	0.005	U
Nitrile 1-Second Dip	P121273-19	0.005	mg/L	0.005	U
Nitrile 1-Second Dip	P121273-20	0.005	mg/L	0.005	U
Nitrile 1-Second Dip	P121273-21	0.005	mg/L	0.005	I
Nitrile 10-Second Dip	P121273-22	0.005	mg/L	0.005	U
Nitrile 10-Second Dip	P121273-23	0.005	mg/L	0.005	U
Nitrile 10-Second Dip	P121273-24	0.005	mg/L	0.005	U
Nitrile 10-Second Dip	P121273-25	0.005	mg/L	0.005	U
Nitrile 10-Second Dip	P121273-26	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-42	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-43	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-44	0.005	mg/L	0.005	U

Table B-2. Continued.

Treatment	SAMPLE_ID	VALUE	UNITS [a]	MDL	Qualifier
Nitrile Inside Out Rub	P121273-45	0.005	mg/L	0.005	U
Nitrile Inside Out Rub	P121273-46	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-47	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-48	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-49	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-50	0.005	mg/L	0.005	U
Nitrile Rinsed Rub	P121273-51	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-27	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-28	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-29	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-30	0.005	mg/L	0.005	U
Nitrile Rinsed 1-Second Dip	P121273-31	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-32	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-33	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-34	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-35	0.005	mg/L	0.005	U
Nitrile Rinsed 10-Second Dip	P121273-36	0.005	mg/L	0.005	U

a. mg/L – milligrams per liter.