Georgia-Pacific Toledo LLC
1400 SE Butler Bridge Road
Toledo, Oregon 97391

August 25, 2025

Ms. Heather Kuoppamaki
Department of Environmental Quality
700 NE Multnomah Street, Suite 600
Portland, OR 97232

Re:Cleaner Air Oregon (CAO) Emission Inventory Information Request – Liquid Sampling Plans

Dear Ms. Kuoppamaki,

Georgia-Pacific Toledo LLC (GP Toledo) was called into the Cleaner Air Oregon (CAO) program on March 1, 2022, and submitted an Emissions Inventory (Inventory) on May 31, 2022. The Oregon Department of Environmental Quality (DEQ) issued a written request on February 6, 2024, requiring additional information and submittal of a revised Inventory. GP Toledo submitted a revised Inventory and requested information on August 5, 2024. Additional requested information was also submitted by GP Toledo on May 6, 2024, and August 22, 2024.

After reviewing GP Toledo's responses, DEQ provided additional questions on March 24, 2025 in two separate letters. In one of these letters, DEQ requested that the GP Toledo Mill develop liquid sampling plans for the wastewater treatment plant (WWTP) and perform sampling according to those plans. This request was issued based on the DEQ's rejection of emission calculation methodologies in the Inventory for the WWTP proposed by GP Toledo and technical experts. DEQ originally set a due date of May 26, 2025 for submittal of the WWTP sampling plans. After multiple discussions with DEQ, GP Toledo was granted a deadline extension to August 25, 2025.

DEQ requested plans for the following WWTP liquid sampling programs:

1. One year of monthly sampling to assess sulfide and sulfate compounds, flow rate, dissolved oxygen, temperature and pH.
2. One year of quarterly sampling to assess ammonia, purgeables, base/neutrals and acids, and carbonyl compounds.
3. One year of quarterly sampling to assess per- and poly-fluoroalkyl substances (PFAS).

Attached to this letter are the monthly sampling plan and quarterly sampling plan to meet the DEQ's deadline. Although these plans are included, GP has serious concerns about the sampling plan requests. Specifically, GP Toledo is requesting that DEQ delay PFAS liquid sampling until adequate scientific data exists to accurately reflect emissions. Although PFAS sampling is shown in the quarterly sampling plan, this is only in place should PFAS sampling become a feasible option.

In addition, concerns with the logistics of sampling for the requested pollutants are also provided below.

PFAS Technical Issues

In the request dated March 24, 2025, DEQ requested that the Toledo Mill conduct one year of quarterly liquid sampling of mill effluents for PFAS with the intent that the Mill use this information and EPA's WATER9 to estimate emissions of PFAS from the wastewater system. Based on a review of available information and in consultation with the National Council for Air and Stream Improvement (NCASI), GP does not believe there is adequate data to accurately estimate PFAS emissions from the wastewater system. Furthermore, only

perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are currently on the Toxic Air Contaminant Priority List.

WATER9 is a simulation tool that estimates the fate of chemicals in wastewater system process units along several pathways including biological removal and volatilization. Several different empirical models are combined with a mass balance to estimate the emissions. The models require physical parameters as input, and then each calculation is done on a chemical basis. The 3.0 (current) version has many different chemicals built in, along with physical property information. The software allows the user to change parameters for chemicals included in the database. For example, NCASI revised the methanol biorate, since they have data suggesting the default WATER9 value is incorrect. The program also allows users to enter a custom chemical with user-defined properties. The 3.0 version does not include PFOA or PFOS, the two PFAS compounds currently on the Toxic Air Contaminant Priority List. It should also be noted that WATER9's performance has not been evaluated for either of these chemicals or for any other PFAS that NCASI was able to find.

NCASI executed a search to see what, if any, data is available for the physical parameters required by EPA's WATER9 in order to estimate PFOA and PFOS fate in wastewater treatment systems similar to the one operated at GP Toledo. The table below summarizes the information located.

Physical Property	PFOA	PFOS	Notes
Density	Yes, experimental	Yes, modeled	
Vapor Pressure	Yes, experimental	Yes, experimental	Single Temperature, No Temperature Dependence Parameters
Henry's Law Constant	Yes, experimental	Yes, modeled	Single Temperature, No Temperature Dependence Parameters
Molecular Diffusivity in Air	Yes, modeled	No	PFOS - Single Temperature, No Temperature Dependence Parameters
Molecular Diffusivity in Water	Yes, experimental	Yes, experimental	Single Temperature, No Temperature Dependence Parameters
Biodegradation Constant in a wastewater treatment plant	Yes, experimental	Yes, experimental	There are multiple literature values for each, the spread is very large (all the way from inert to a ½ life of about a day)
Octanol-Water ratio	Yes, experimental	Yes, experimental	Large spread in PFOA results

Although WATER9 could generate an output using this data, because the inputs rely on experimental factors and assumptions, the results could not be expected to inform the public or other stakeholders in a reliable or actionable manner.

Furthermore, the lack of temperature-dependent parameters for most of these chemical properties is a significant concern, especially the Henry's Law constant. Therefore, GP requests that DEQ delay PFAS liquid sampling until adequate science exists to accurately reflect emissions.

Sampling Logistic and Technical Concerns

Sulfide Sampling Concerns

NCASI developed a method for measuring sulfide in pulp and paper mill wastewater based on filtration and colorimetric analysis. Release of hydrogen sulfide from aqueous systems such as wastewater treatment plants are a function of sulfide dissolved in the bulk liquid. This method provides a more accurate assessment of sulfide in the aqueous phase that might be emitted to the atmosphere, compared to total sulfide determination which measures dissolved sulfide, sulfide associated with solids, and acid soluble metal sulfides. It provides an

advantage over total sulfide measurements, which can be biased high. Additionally, this methodology takes into account loss of dissolved sulfide due to volatilization, oxidation, etc. by utilization of a special sample collection device and filtration apparatus designed to remove suspended solids larger than 0.70 microns. Samples are preserved within the special sample collection device upon collection, which eliminates atmospheric exposure during preservation that could potentially cause loss of dissolved sulfide. Details can be found in *NCASI Technical Bulletin No. 1027 – Development and Evaluation of a Method for Measuring Dissolved Sulfide in Pulp and Paper Mill Wastewaters* – as well as the attached Monthly Sampling Plan. The NCASI Technical Bulletin is included as an attachment to the Monthly Sampling Plan. Unfiltered samples for total sulfide analysis will also be collected for comparison purposes.

The special sample collection device and filtration apparatus required for the dissolved sulfide sampling consists of reusable syringes, cartridges, stopcocks, and tubing, as well as expendables such as filters and filtration media. An apparatus must be prepared for each sample location prior to going in the field. Syringes for collection of samples for dissolved sulfide must be pre-loaded with preservative just prior to going into the field as well. This preparation and assembly takes several hours and usually two people. Once sample collection is completed, the collection devices and filtration apparatus must be broken down, decontaminated, and placed in a clean place to dry before storage for the next use. The preparation and break down/decontamination step must be done before and after each event and is labor intensive. The sampling equipment that is required is specialized and must be made of specific material, such as Teflon®. It is not easily obtained and is also expensive.

In addition, as previously discussed with DEQ, GP disagrees with the request to conduct sulfide and sulfate sampling. GP has installed and is operating real time H_2S monitors at the facility. This data is more reliable than any data derived from sampling and subsequent modeling. As such, GP reiterates its position that the monitoring data should be utilized in lieu of sampling and modeling data. GP looks forward to further discussions on this issue.

Concerns Regarding Overall Sampling Logistics

Monthly and quarterly sampling efforts will need to be collected by two different sampling teams, consisting of two to three individuals per team, for a variety of reasons. First, with the exception of the Clarifier Inlet or Paper Mill Effluent sampling points, the collection locations DEQ has specified for the monthly and quarterly samples are different. The quarterly sampling locations are accessible from land, however several of the monthly sampling locations can only be accessed by boat. The only way to collect the monthly and quarterly samples on the same calendar day is by engaging two different teams.

Secondly, special sampling protocols must be followed for collection of PFOA and PFOS to minimize cross-contamination. Those protocols and precautions are outlined in the attached Quarterly Sampling Plan and require special planning and preparation prior to sampling. Samples for the other quarterly constituents can be safely sampled at the same time as PFOA and PFOS without concern for interferences.

Monthly sampling for sulfide and sulfate, described in the Monthly Sampling Plan, must be collected by a separate sampling team because much of the special equipment needed for the sulfide sampling is made of Teflon®, which could contaminate samples with PFAS compounds, thus artificially inflating the analytical results. Additionally, all of the preparation and breakdown of the special equipment involved with the monthly sulfide sampling requires that these two teams have no physical contact with one another prior to, during, or after sampling in order to prevent cross contamination.

A third challenge is the nature and volume of sampling equipment required for each effort. Besides special sampling equipment and considerations, the support equipment such as multiple coolers, sample bottleware, containers for clean equipment and used equipment, field meters, will prove challenging to manage by a single team.

We look forward to continued collaboration with DEQ throughout the CAO process. Please contact Logan Vaughan at (503) 240-1627 or logan.vaughan@gapac.com if you have any questions regarding the information provided.

Sincerely,

Mark E. Carden
Vice President– Georgia-Pacific Toledo LLC

Attachments
A—Monthly Sampling Plan
B—Quarterly Sampling Plan

cc: Michael Eisele, DEQ (via email)
J.R. Giska, DEQ (via email)

Attachment A – Monthly Sampling Plan

Georgia-Pacific Toledo Monthly Sampling Plan

Objective:

Samples will be collected monthly for one full year to estimate hydrogen sulfide emissions from the wastewater treatment system at the Georgia-Pacific (GP) Toledo LLC operations, in accordance with the March 24, 2025, request from the Oregon Department of Environmental Quality. Required sample parameters, analyses, and locations were provided in Attachment A of the referenced request. This sampling effort will be conducted in support of the Cleaner Air Oregon (CAO) Emissions inventory for GP Toledo.

Sampling Methodology and Parameters:

Samples for dissolved sulfide will be collected following the protocol described in NCASI Technical Bulletin No. 1027 – *Development and Evaluation of a Method for Measuring Dissolved Sulfide in Pulp and Paper Mill Wastewaters* (**attached**). The method utilizes a special sample collection device and filtration apparatus designed to remove suspended solids larger than 0.70 microns. The filtered sample portions are preserved upon collection for analysis using the colorimetric method for sulfide determination developed by NCASI (DS^{2-}W114.01), which is included as an Appendix to Technical Bulletin No. 1027.

Unfiltered samples for total sulfide analysis will also be collected for comparison purposes. The unfiltered samples will be analyzed for total sulfide using colorimetric method SM 4500-S^{-2} D-2021.

Sulfide samples will be collected in-situ, when possible, by lowering the sample collection tube connected to the special sampling apparatus directly below the water surface and collecting a sample from an approximate depth of one foot below the surface. When it is not possible to collect samples in-situ, a manual sampler capable of collecting a discrete grab sample from approximately one foot below the water surface. Sample collection will then take place directly from the discrete sampling device, using the special sampling apparatus. The filtration step for samples for dissolved sulfide that are collected in-situ will occur as part of the sample collection process. For those samples for dissolved sulfide that require collection of a discrete grab sample, the filtration step will take place immediately after collection of the grab. After the first two rounds of sampling, results for dissolved and total sulfide will be compared to determine if the filtration step associated with the dissolved sample collection is necessary to remove potential interferences with the analytical determination due to suspended solids. Based on the outcome of this comparison, the mill may choose to move forward collecting samples for only one or both.

A grab sample for total sulfate will also be collected at each sample location from a depth of approximately one foot below water surface using the discrete manual sampler.

During sample collection, field tests for dissolved oxygen, temperature, oxidation reduction potential (ORP), and pH will be collected and recorded at each sampling point. The field readings will be collected either in-situ or on an unfiltered discrete grab sample collected from approximately one foot below the water surface. Average wind speed, ambient temperature, and amount of aeration should also be noted for the day of sampling.

Samples will be collected by contracted consultants or mill staff. At least two people will be needed for the sampling effort. A boat will also be needed to reach several sample locations.

Sampling kits, including the appropriate preservatives, will be provided by the analytical laboratory. The sample preservation step is part of the collection method for dissolved sulfide. Sample containers for total sulfide analysis will already contain the appropriate preservative.

A Health and Safety Plan will be prepared prior to initiation of sampling activities.

Sample Locations:

The collection points are (10 sample locations – shown on the attached figure):

1) Clarifier Inlet or Paper Mill Effluent – MSP#1
2) Thermal Pond A – MSP#2
3) Thermal Pond B – MSP#3
4) Thermal Pond C – MSP#4
5) Load Level Pond, Zone 1 – MSP#5
6) Load Level Pond, Zone 2 (hardpipe, LL_{eff}) – MSP#6
7) Treatment Pond A (hardpipe, Seg_{IIIA} or Seg_{IIIB}) – MSP#7
8) Treatment Pond B (hardpipe, Seg_{VIII}) – MSP#8
9) Settling Pond, Zone 1(hardpipe, TP_{eff}) – MSP#9
10) Settling Pond, Zone 2 – MSP#10

A duplicate sample from a random location will be collected during each monitoring event. Samples will be collected from each location, spaced approximately one month apart, for one full year.

In addition to the sample collection locations identified above, flow measurements should be taken at the following locations on the same day as each monthly monitoring event:

- Clarifier Inlet or Paper Mill Effluent
- Thermal Pond A Influent (combined) ***or*** Clarifier Effluent + Recausticizing Sewer Effluent + 30-Acre Pond Effluent
- Recausticizing Sewer Effluent
- 30-Acre Pond Effluent
- 15-Acre Pond
- Load Level Pond Influent (combined) ***or*** Thermal Ponds Effluent + Pulp Mill Effluent
- Pulp Mill Effluent
- Treatment Pond A Influent (combined) ***or*** Load Level Pond Effluent + Pulp Mill Foul Condensate
- Pulp Mill Foul Condensate

Sampling During "Unusual" Conditions

In addition to regular sampling, ODEQ has requested sampling during "unusual" conditions or operating changes. Unusual conditions are defined in the March 24, 2025, letter, Item 1.e. as liquor spills, startup or shutdown of mill equipment, changes to pond configuration or operation and pond dredging activities.

Due to the complex nature of the sampling, contracted personnel with specialized equipment and training will be utilized to complete the work. For transient events such as black liquor spills, there will be insufficient time to get the proper resources onsite before the event is over.

For planned startup or shutdown events, every effort will be made to schedule the contracted testing to coincide with the startup or shutdown event.

In the remote chance that there are any changes to pond configuration, samples will be captured before and after the changes occur.

Safety is a top priority at GP Toledo. During dredging events, personnel not associated with the dredging effort are not allowed on the ponds as the safety risk is too great, therefore sampling during dredging will not be possible.

Sampling Protocol:

From each sample location:

1. Collect a sample for dissolved sulfide, following the procedures described in NCASI Technical Bulletin No. 1027 and method DS^{2-}W114.01 (attached). The samples will be collected using the collection device and filtration apparatus described in the technical bulletin as part of the sample collection procedure. Two 40-ml volatile organic analysis (VOA) vials will be collected for each dissolved sulfide sample.
    - One 25 mL sample will be preserved during collection using the syringe preloaded with 2 mL of the zinc acetate/sodium hydroxide preservation solution described in the attached technical bulletin. The actual sample volume collected for each location should be recorded in the field notes.
    - A second, unpreserved reference sample will be collected following the same procedures as the first, minus addition of the preservation solution. This sample will be used by the laboratory to correct the overall dissolved sulfide concentration for background and color.

2. Collect a sample for total sulfide, using the collection device in the NCASI technical bulletin and method (attached), omitting the sample filtration step. Two 40-ml VOA vials will be collected for each total sulfide sample.
    - One VOA vial will be preloaded by the lab with zinc acetate/sodium hydroxide preservation solution and should be filled to near the top and mixed thoroughly.
    - A second, unpreserved reference sample will be collected following the same procedures as the first, minus addition of the preservation solution. This sample will be used by the laboratory to correct the overall dissolved sulfide concentration for background and color.

3. Please note that sample collection procedures should be followed only through the second sentence of Section 11.11 of method DS^{2-}W114.01 (attached). Sample reaction and analysis will be performed by the analytical laboratory.

4. Collect a sample for total sulfate by filling the laboratory-provided sample container and capping tightly.

5. All samples should be placed in a cooler with ice after collection.

6. During sample collection, field tests for dissolved oxygen, temperature, and pH should also be collected and recorded at each sampling point either in-situ or on an unfiltered grab sample.

Analytical Methods, Container Type, Preservation, and Holding Time

Analyte	Analytical Method	Container Type/Preservative	Holding Time
Dissolved Oxygen	SM 4500-O G-2021 or H-2021	Field reading - immediate	
pH	SM 4500-H+ B-2021	Field reading - immediate	
Temperature	SM 2550 B-2021	Field reading – immediate	
Oxidation Reduction Potential	SM 2580 as a reference	Field reading - immediate	
Dissolved Sulfide	Collection, filtration, and analysis NCASI DS^{2-}W114.01	1 – 40 mL glass vial*, to pH > 9 with zinc acetate/sodium hydroxide preservation, 1-40 mL glass vial**, no preservative A duplicate sample from a random location will be collected each day.	14 days***
Total Sulfide	Collection NCASI DS^{2-}W114.01 Analysis SM 4500-S^{-2} D- 2021	1 – 40 mL glass vial*, to pH > 9 with zinc acetate/sodium hydroxide preservation, 1- 40 mL glass vial**, no preservative Cool to ≤ 6 degrees C	7 days
Total Sulfate	To be determined SM 4500-SO_4^{2-} or 300.0	1 - Polyethylene, no preservative Cool to ≤ 6 degrees C	28 days

SM = Standard Methods Online
NCASI = National Council for Air and Stream Improvement
EPA = Environmental Protection Agency test method
*The ideal sample volume is 25 mL. Record the actual sample volume in the field notes.
**Vials should be filled near the top and mixed thoroughly with the preservative
***Holding time based on discussions with Diana Cook of NCASI. The holding time has proven to be greater than as specified in NCASI DS^{2-}W114.01

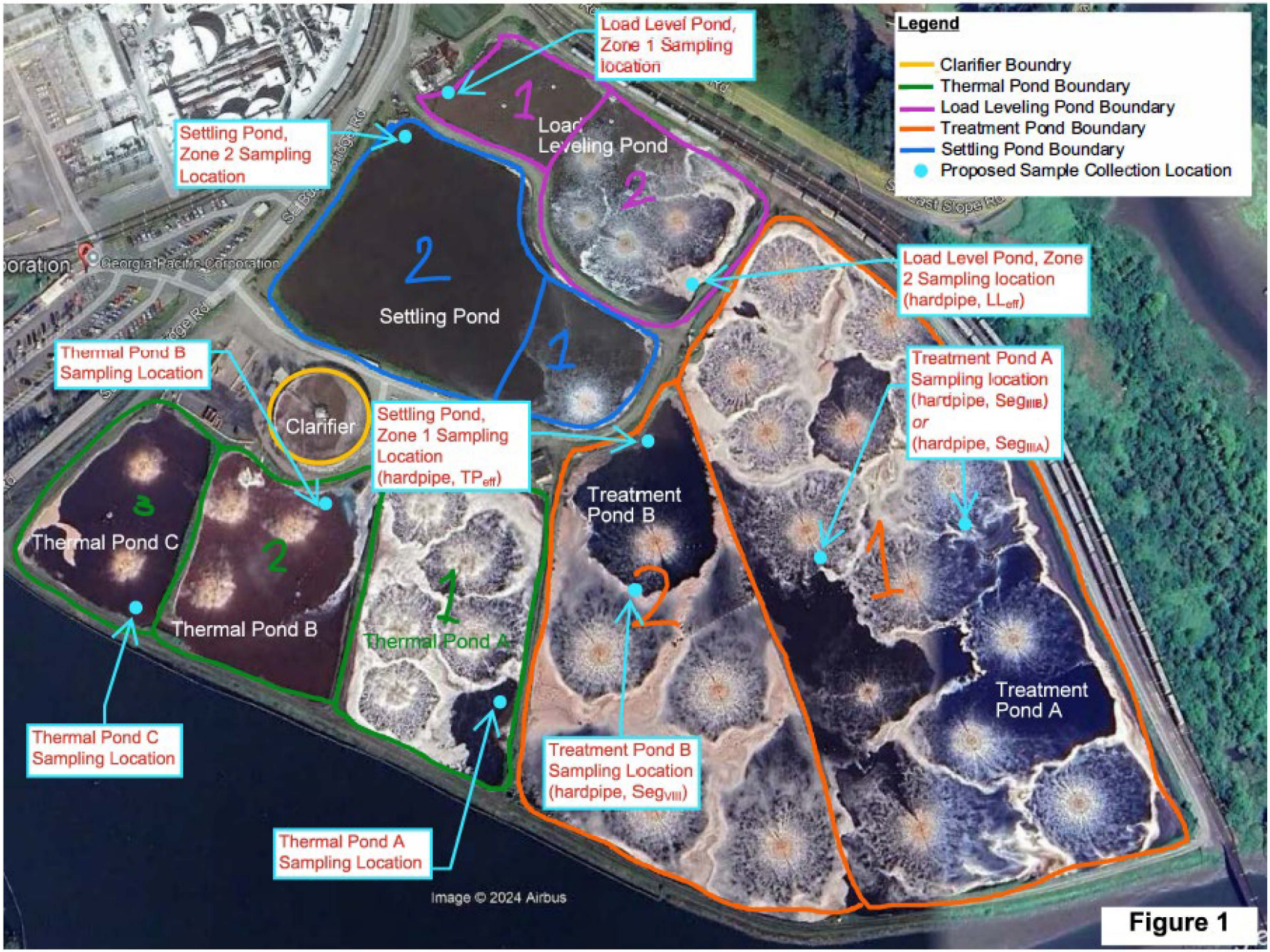
Load Level Pond, Zone 1 Sampling location
Legend
Clarifier Boundry
Thermal Pond Boundary
Load Leveling Pond Boundary
Treatment Pond Boundary
Settling Pond Boundary
Proposed Sample Collection Location
Settling Pond, Zone 2 Sampling Location
Load Leveling Pond
Settling Pond
Load Level Pond, Zone 2 Sampling location (hardpipe, LL$_{eff}$)
Thermal Pond B Sampling Location
Clarifier
Settling Pond, Zone 1 Sampling Location (hardpipe, TP$_{eff}$)
Treatment Pond A Sampling location (hardpipe, Seg$_{IIIB}$) or (hardpipe, Seg$_{IIIA}$)
Thermal Pond C
Thermal Pond B
Thermal Pond A
Treatment Pond B
Treatment Pond A
Thermal Pond C Sampling Location
Treatment Pond B Sampling Location (hardpipe, Seg$_{VIII}$)
Thermal Pond A Sampling Location
Image © 2024 Airbus

Figure 1

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NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

DEVELOPMENT AND EVALUATION OF A METHOD FOR MEASURING DISSOLVED SULFIDE IN PULP AND PAPER MILL WASTEWATERS

TECHNICAL BULLETIN NO. 1027

MARCH 2015

by
Diana Cook, David Campbell, and Ron Messmer
NCASI West Coast Regional Center
Corvallis, Oregon

Acknowledgments

This report was written by Diana Cook, Principal Research Scientist, with assistance from David Campbell, Research Associate, and Ron Messmer, Senior Research Associate, at NCASI's West Coast Regional Center. Steve Stratton, Regional Manager, provided review and comment. Karen Phelps assisted with document preparation and literature retrieval. NCASI member companies provided assistance with sampling and site selection for the field work.

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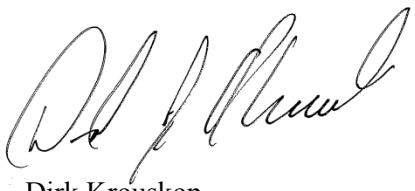
PRESIDENT'S NOTE

NCASI has a long history of research focused on understanding the sources and fates of reduced sulfur compounds in forest products industry wastewaters. In the more recent past, mechanistic and correlative approaches to estimating hydrogen sulfide emissions from wastewater treatment basins have been developed based on measured concentrations of total sulfide in wastewater because analytical approaches capable of yielding accurate and reproducible measures of dissolved sulfides were lacking. Total sulfide measurements may overstate the amount of sulfide that can be readily evolved from basins and thus may result in high-biased estimates of hydrogen sulfide emissions. This bias is of greatest potential concern in basins containing high concentrations of suspended solids.

This report summarizes research to develop an effective and reproducible method for measuring dissolved sulfide in mill wastewaters. The method (provided as an appendix) employs a special sample collection device designed to remove suspended solids larger than 0.70 μm and to immediately preserve filtered portions for later analysis using standard total sulfide analysis methods. The method was shown to have reasonable recovery, precision, and accuracy in the laboratory and in the field, although field recoveries of matrix spikes were affected by both oxygen and solids in the native samples. Comparison of total and dissolved sulfides in samples collected at five mills indicated that dissolved concentrations ranged from 0 to 82% of the total sulfide concentrations.

The information contained in this report will be useful to those interested in developing or refining measurements of dissolved sulfide in wastewater and/or estimated emissions of hydrogen sulfide from pulp and paper mill wastewater treatment systems.



Dirk Krouskop

March 2015

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NOTE DU PRÉSIDENT

NCASI possède une longue tradition de recherche sur les sources et le devenir des composés de soufre réduit dans les eaux usées de l'industrie des produits forestiers. Plus récemment, des méthodes mécanistes et corrélatives basées sur la mesure des sulfures totaux dans les eaux usées ont été développées pour estimer les émissions de sulfure d'hydrogène générées par les bassins des systèmes de traitement des eaux usées parce qu'il n'y avait pas de méthodes analytiques capables de mesurer des concentrations précises et reproductibles des sulfures dissous. La mesure de la concentration des sulfures totaux peut cependant surévaluer la quantité de sulfures émis par les bassins et, par conséquent, donner des estimations hautement biaisées des émissions de sulfure d'hydrogène, ce qui peut être très problématique dans le cas des bassins dont la concentration en matières en suspension est élevée.

Le présent rapport résume les travaux de recherche sur le développement d'une méthode de mesure efficace et reproductible des sulfures dissous dans les eaux usées des usines. La méthode (décrite dans l'annexe) fait appel à un dispositif spécial de prélèvement des échantillons conçu pour retirer les matières en suspension dont le diamètre est supérieur à 0,70 μm et de conserver instantanément les portions filtrées pour qu'elles soient ultérieurement analysées à l'aide des méthodes standards d'analyse des sulfures totaux. Les travaux ont montré que le pourcentage de récupération, la précision et l'exactitude de la méthode étaient satisfaisants à la fois en laboratoire et dans des conditions réelles, bien qu'en conditions réelles l'oxygène et les particules solides dans les échantillons d'origine ont eu un effet sur les pourcentages de récupération des matrices enrichies. Des échantillons prélevés dans cinq usines ont montré que la concentration des sulfures dissous se situait entre 0 et 82% de la concentration des sulfures totaux.

Les renseignements dans le présent rapport seront utiles à ceux et celles qui désirent mesurer la concentration des sulfures dissous dans les eaux usées ou les émissions estimées de sulfure d'hydrogène générées par les systèmes de traitement des eaux usées des usines de pâtes et papiers, ou qui désirent améliorer leur méthode de mesure.

Dirk Krouskop

Mars 2015

DEVELOPMENT AND EVALUATION OF A METHOD FOR MEASURING DISSOLVED SULFIDE IN PULP AND PAPER MILL WASTEWATERS

TECHNICAL BULLETIN NO. 1027
MARCH 2015

ABSTRACT

A method for measuring dissolved sulfide in pulp and paper mill wastewater based on filtration and colorimetric analysis was developed, then evaluated using wastewater samples collected at five mills. Compared to total sulfide determinations that measure dissolved sulfide, sulfide associated with solids, and acid soluble metal sulfides, this method provides a more accurate assessment of sulfide in the aqueous phase that might be emitted to the atmosphere from wastewater treatment systems. The method evaluation demonstrated good reproducibility (<15% relative standard deviations) in wastewaters for replicates collected throughout wastewater treatment systems. Method accuracy was assessed by conducting initial and ongoing precision and recovery experiments in reagent grade water, yielding recoveries ranging from 80.3 to 95.4%. Matrix spikes conducted in the field yielded poor recoveries suggestive of losses due to oxidation and sorption onto solids. Laboratory experiments to validate the mechanism of these losses were conducted using nitrogen-purged samples and surrogate stocks spiked with lignin solids. Field measurements indicated that dissolved sulfide concentrations for wastewater samples were lower than total sulfide concentrations at the five mills sampled during this evaluation.

KEYWORDS

dissolved sulfide, emissions, filtration, hydrogen sulfide, total sulfide, wastewater

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 1000 (December 2012). *Mechanistic approach for estimating hydrogen sulfide emissions from wastewater treatment plants.*

Technical Bulletin No. 997 (August 2012). *The presence, fate, and ecological significance of hydrogen sulfide in pulp and paper mill effluents.*

Technical Bulletin No. 933 (June 2007). *Development and application of a method for measuring reduced sulfur compounds in pulp and paper mill wastewaters.*

Special Report No. 06-02 (February 2006). *An evaluation of a colorimetric method for the determination of total sulfide in pulp and paper mill wastewaters.*

DÉVELOPPEMENT ET ÉVALUATION D'UNE MÉTHODE DE MESURE DES SULFURES DISSOUS DANS LES EAUX USÉES DES USINES DE PÂTES ET PAPIERS

BULLETIN TECHNIQUE N^{O} 1027
MARS 2015

RÉSUMÉ

NCASI a développé une méthode pour mesurer la concentration des sulfures dissous dans les eaux usées des usines de pâtes et papiers basée sur des techniques de filtration et de colorimétrie, puis l'a évaluée au moyen d'échantillons d'eaux usées prélevés dans cinq usines. Cette méthode évalue plus précisément la quantité de sulfures dans la phase aqueuse qui pourrait être émise dans l'atmosphère par les systèmes de traitement des eaux usées comparativement aux méthodes de détermination des sulfures totaux qui mesurent la concentration des sulfures dissous, des sulfures associés à des matières solides et des sulfures métalliques solubles dans l'acide. Les résultats de l'évaluation de la méthode montrent une bonne reproductibilité (écarts types relatifs <15%) dans les eaux usées compte tenu des résultats obtenus avec les échantillons prélevés dans les systèmes de traitement des eaux usées couverts par la présente étude. NCASI a aussi vérifié l'exactitude de la méthode en évaluant sa précision et son pourcentage de récupération (au début puis de manière continue) avec de l'eau de qualité réactif. Les résultats ont montré que le pourcentage de récupération se situait entre 80,3% et 95,4%. L'analyse des matrices enrichies provenant d'échantillons prélevés sur le terrain a révélé de faibles pourcentages de récupération en raison probablement de pertes causées par l'oxydation et la sorption sur des matières solides. Pour confirmer le mécanisme causant ces pertes, NCASI a réalisé des essais en laboratoire avec des échantillons purgés à l'azote et des solutions-mères enrichies avec des solides de lignine. Les mesures sur le terrain ont montré que la concentration de sulfures dissous dans les échantillons d'eaux usées des cinq usines évaluées dans la présente étude était plus basse que la concentration de sulfures totaux.

MOTS-CLÉS

eaux usées, émissions, filtration, sulfure d'hydrogène, sulfures dissous, sulfures totaux

AUTRES PUBLICATIONS DE NCASI

Bulletin technique n^{o} 1000 (décembre 2012). *Approche mécaniste pour estimer les émissions de sulfure d'hydrogène de systèmes de traitement des effluents* (seul le résumé est en français)

Bulletin technique n^{o} 997 (août 2012). *La présence, le devenir et l'importance écologique du sulfure d'hydrogène dans les effluents des usines de pâtes et papiers* (seul le résumé est en français)

Bulletin technique n^{o} 933 (juin 2007). *Développement et application d'une méthode pour mesurer les composés de soufre réduit dans les eaux usées des fabriques de pâtes et papiers* (seul le résumé est en français)

Rapport spécial n^{o} 06-02 (février 2006). *Évaluation d'une méthode colorimétrique pour la détermination des sulfures totaux dans les eaux usées de fabriques de pâtes et papiers* (seul le résumé est en français)

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DEVELOPMENT AND EVALUATION OF A METHOD FOR MEASURING DISSOLVED SULFIDE IN PULP AND PAPER MILL WASTEWATERS

1.0 INTRODUCTION

Reduced forms of sulfur (i.e., sulfides) are common in many wastewaters, including some from pulp and paper mills. Sulfur chemistry in aqueous systems is complex because of the various oxidation states of sulfur and its ability to form soluble and particulate complexes as well as volatile hydrogen sulfide. Releases of hydrogen sulfide from aqueous systems such as wastewater treatment plants are a function of sulfides dissolved in the bulk liquid. Unfortunately, accurate quantification of dissolved sulfide (H_2S, HS^-, and S^{-2}) concentrations in wastewater samples is fraught with challenges because of its unstable nature. Dissolved sulfide can volatilize, oxidize, sorb onto organic solids, precipitate with metals, and be readily transformed to other sulfur species such as thiosulfate and sulfate under aerobic conditions in the presence of biological solids (Yongsiri et al. 2003). Due to this instability, samples collected from wastewater treatment systems must be preserved or analyzed immediately to yield consistent results. Another problem is that standard laboratory manipulations (e.g., centrifugation and flocculation) used to separate dissolved and insoluble forms can result in significant losses of dissolved sulfide from samples. As a consequence of these difficulties, a total sulfide measurement technique (e.g., Standard Method 4500-S^{2-} D; APHA 2005) is typically used as a surrogate for dissolved sulfide. Such methods measure sulfide associated with suspended solids and acid soluble metal sulfides as well as dissolved forms. These methods overstate the amount of dissolved sulfide in samples in which a significant fraction of the total sulfide is associated with the solid phase. A simple and accurate method for measuring dissolved sulfide could improve the accuracy of hydrogen sulfide emissions estimates developed from models that link emissions to dissolved sulfide concentrations.

Standard Methods (APHA 2005) defines dissolved sulfide as the sulfide remaining after suspended solids have been removed by flocculation and settling. NCASI previously investigated the use of flocculation, centrifugation, and direct filtration to assess dissolved sulfide, but losses of sulfide were high during sample manipulations and poor reproducibility was observed. NCASI continued to research techniques for measuring dissolved sulfide that would be reproducible and would more accurately measure the concentration of dissolved sulfide present at the time of sample collection. A method was developed that employs a special sampling device that includes a filtration system to remove suspended solids and immediately preserve the filtered portion for subsequent analysis using standard total sulfide analysis methods.

Current EPA-approved methods for determination of total sulfide are based on methylene blue, iodometric titrations, or an ion selective electrode (USEPA 2004). These are all method-defined assessments, and concentrations can vary depending on the approaches utilized to collect, preserve, and analyze samples. NCASI experience has indicated that the methylene blue method yields results comparable to those from NCASI RSC 02.02 for total sulfide concentrations in biologically treated final effluents when the concentration is greater than 0.04 mg S/L (NCASI 2006). Use of the ion selective electrode method to directly measure sulfide ions was also evaluated by NCASI. Large changes in sulfide concentrations (i.e., greater than 40%) occurred during the sample manipulations needed to add the highly alkaline buffer and stir the solution prior to reading the sulfide level with the ion selective electrode. The method also gave variable results in pulp and paper mill wastewaters, and membrane fouling was common due to solids. Experiments conducted during the study reported herein utilized the methylene blue method for sample analysis because it provides a rapid, easy, and cost effective way to react samples in the field and uses instrumentation that is readily available at many mill laboratories.

This report summarizes laboratory and field experiments conducted to develop and evaluate NCASI Method DS^{2-}-W114.01 for determination of dissolved sulfide in pulp and paper mill wastewaters.

2.0 METHOD DESCRIPTION

Initial experiments focused on designing a sampling apparatus and filter arrangements that would allow rapid collection, filtration, and preservation of about 25 mL of untreated or biologically treated wastewaters while minimizing sulfide losses due to oxidation that can occur upon contact with air. Numerous trials using five different wastewaters led to the final design, shown in Figure 2.1. The types and combinations of filters investigated during initial experiments are summarized in Table 2.1 and Table 2.2, respectively. The initial design goal was a final filter pore size of 0.45 µm because this is the cutoff often cited in the literature for defining dissolved components (e.g., dissolved phosphorus). However, filtration to a pore size of 0.45 µm was not consistently achieved with any of the filtering combinations assessed. The filtering apparatus did not pull a vacuum strong enough for the various membrane filters examined, and a glass fiber filter with a 0.45 µm pore size was not commercially available. The smallest practicable filter pore size was 0.7 µm. The final design utilized a coarse filtration with glass wool followed by a layered filter arrangement with graduated filtration from ~10 to 1 µm pore sizes followed by a 0.7 µm glass fiber filter (Figure 2.1).

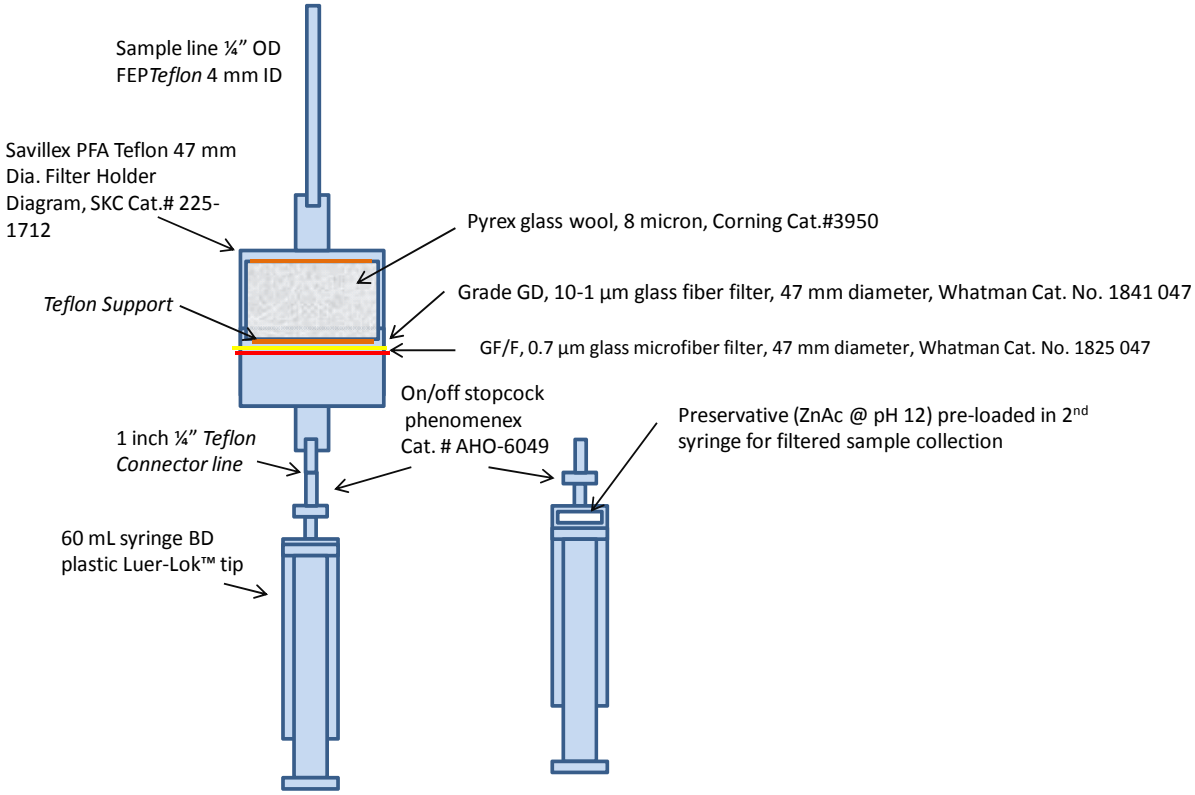

Figure 2.1 Syringe Filtration Apparatus

Table 2.1 Filter Types Investigated

Filter	Filter Pore Size (μm)
Polytetrafluoroethylene (PTFE)	60
Multilayer glass microfiber	10 to 1
Versapor-3000T supported membrane	3.0
Glass microfiber	2.7
Versapor-1200 supported membrane	1.2
Glass fiber	1.0
Nylon membrane	0.8
Glass microfiber	0.7
Cellulose nitrate membrane	0.45
Nitrocellulose membrane	0.45
Nylon membrane	0.45

Table 2.2 Filtration Combinations Investigated and Sample Volumes Filtered

Filter Combinations (filter pore size in μm)	Sample Volume Filtered[a] (mL)
60 + 1.0	5
60 + 2.7 +1.0	10
60 + 3.0 + 0.45	0
10-1 + 2.7 + 0.45	0
10-1	>25
10-1 + 0.7	>25
10-1 + 0.45	<1
3.0 + 1.0	10
3.0 + 2.7	>25
3.0 + 2.7 +1.0	<5
3.0 + 2.7 + 0.45	<2
2.7 + 1.2	>25
2.7 + 1.2 + 0.45	<5
2.7 + 1.0	<20
2.7 + 1.0 +0.45	<1
2.7 + 0.45	<1
2.7 + 0.8	<1

[a] Volume filtered for most challenging matrix.

Sample collection is achieved by inserting a Teflon™ sample line into the matrix to be sampled and evacuating the device by pulling the plunger on the syringe until all void spaces are filled with sample. The stopcock to the filtration device is then closed and the initial 60 mL sampling syringe is replaced by a syringe containing 2 mL zinc acetate preservative at pH >10. Approximately 25 mL of sample is pulled through the sampling device and into the syringe containing the preservative. This syringe is then removed from the filtration apparatus and the sample is placed in a 40 mL VOA vial, where it is reacted immediately with sulfuric acid to acidify the sample, followed by reaction with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the methylene blue color is proportional to the sulfide concentration and is measured on a spectrophotometer at a wavelength of 665 ηm after a minimum of five minutes. Dissolved sulfide concentration is calculated based on a calibration curve prepared using sodium sulfide nanohydrate. A full description of this procedure is provided in Appendix A.

In general, sampling locations tested at wastewater treatment plants (WWTPs) are not readily accessible for direct use of the filtration apparatus. Consequently, an extractive sampling device was used to draw wastewater from the treatment system into a reservoir from which a sample aliquot could be easily collected. The extractive device (Figure 2.2) consists of a submersible pump, a 10 L wide-mouth carboy (reservoir), inlet and outlet connections, and a sampling port. The submersible pump is placed into the WWTP unit approximately one to two feet below the liquid surface and turned on for five to ten minutes in order to clear the system of air and flush it with fresh sample. It is then turned off and the filtration apparatus sample line is inserted into a port on the reservoir. A sample is immediately drawn through the filter system and into the collection syringe.

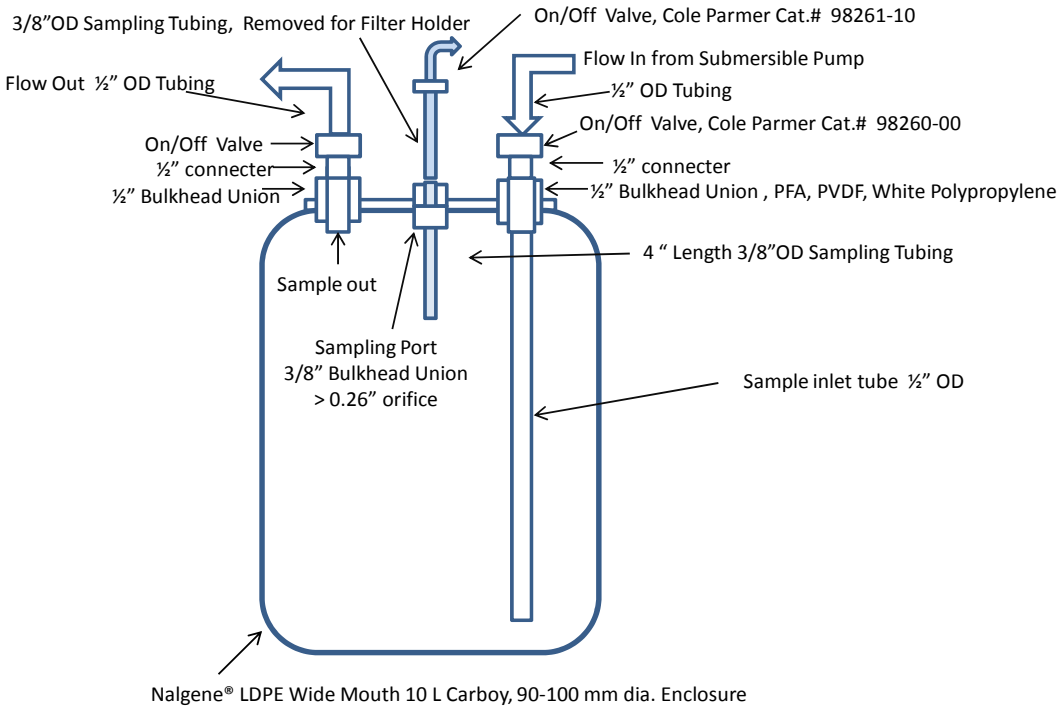

Figure 2.2 Extractive Sampling Apparatus

3.0 METHOD DEVELOPMENT AND EVALUATION

The filtration apparatus (Figure 2.1) was initially evaluated in the laboratory to determine if accurate and reproducible results could be obtained. The sampling apparatus (Figure 2.2) and the filtration technique were then tested at five pulp and paper mills. The overall study included measurements of method blanks, background samples for color and turbidity correction, calibrations, calibration verifications with each sample set, initial and ongoing precision and recovery standards, sample replicates to assess method precision, and measurements of samples fortified with sulfide to determine matrix impacts on recovery. Experiments to investigate losses of sulfide spikes in the wastewater samples were also performed. These included purging samples to remove oxygen prior to conducting matrix spikes to investigate oxidation losses, and addition of dissolved organic matter (soluble lignin) and suspended solids (Sigma Cell) to examine the role of dissolved and particulate solids in matrix spike recoveries.

Method blanks were prepared using aliquots of reagent water that were treated exactly the same as the samples, including exposure to all glassware, filtration equipment, and reagents.

The methylene blue method for determination of sulfide is based on a colorimetric assessment of the sample that can be biased due to sample color and turbidity. This interference is corrected for by preparing a sample in which the sulfide has been removed by pre-treatment with bromine and phenol. The result for sulfide in the sample is then corrected by this background amount prior to reporting.

Method linearity across the working range was determined by preparing and analyzing a five-point calibration curve (0.0, 0.03, 0.09, 0.30, 0.60, and 0.99 mg S/L). The calibration curve was plotted to serve as a visual verification of linearity. A linear regression was used to verify curve fit and calculate the R-squared value. This calibration was verified with each sample set by preparing a fresh single standard and analyzing it in the same manner used for samples from which the initial calibration curve was prepared.

Initial precision and recovery were determined by analyzing four replicates of sulfide-fortified reagent water. The relative standard deviation (RSD) of the replicates was calculated in order to assess the precision of the method. Criteria for precision and accuracy associated with the methylene blue colorimetric methods currently approved by EPA are limited. Standard Method 4500-$S2^-$ B or D and EPA Method 376.2 do not list precision data and state an accuracy ±10%. In this study, 15% RSDs for precision and a recoveries between 90 and 110% were considered acceptable criteria during method evaluation.

Ongoing precision and accuracy was evaluated by measuring the recovery of a sulfide-fortified blank processed using the same apparatus as for the field and laboratory samples.

To determine sample precision, replicates of all samples were collected and either a relative percent difference (RPD) from two replicates or an RSD from more than two replicates was calculated. Method accuracy was investigated by conducting replicates of sulfide-fortified samples in the field or laboratory and determining percent recovery of the added sulfide.

Unless otherwise noted, all samples were preserved by addition of zinc acetate at pH >10 prior to analysis (NCASI 2006).

4.0 RESULTS

4.1 Quality Control and Assurance

The methylene blue analytical method was calibrated over a range of 0.03 to 0.65 mg S/L using a standard of sodium sulfide nonahydrate. This standard was prepared using cold degassed reagent grade water to extend its stability. Aliquots of standard were not preserved and therefore were presumed to be in dissolved sulfide form. Calibration curve aliquots were reacted as specified in Appendix A and absorbance was determined at a wavelength of 665 ηm. A plot of absorbance versus sulfide concentration yielded an R-squared of 0.9993, indicating that the method was linear across the working range (Figure 4.1, diamonds). Samples outside the working range were diluted prior to measuring absorbance. Calibration was compared to the calibration curve for determination of total sulfide in which the standard is preserved with zinc acetate at pH >9.5. This curve yield an R-squared of 0.9979 (Figure 4.1, squares). As the figure shows, slopes and y-intercepts were nearly identical for preserved and unpreserved sulfide standards.

Throughout this study, calibration was verified by analyzing a freshly prepared calibration standard with each set of samples on each day of the study. Targeted spiking concentrations varied to validate calibration at various concentrations across the calibrated range. This also served to validate the stability of the sodium sulfide nonahydrate spiking stocks used during experiments and field sampling. Calibration verification results are summarized in Table 4.1 and indicate that the calibration curve was valid and that the sulfide standards utilized during field work were stable.

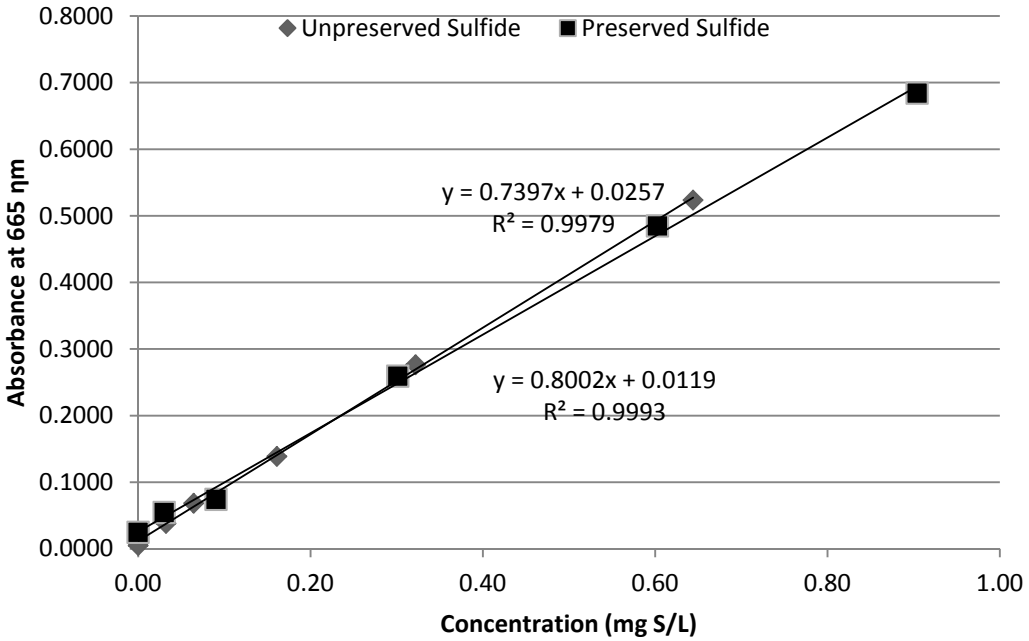

Figure 4.1 Sulfide Calibration Curves

Table 4.1 Calibration Verification Results

Average Rec. (%)	Range of Rec. (%)	Number of Calibration Verifications	Conc. Range Assessed (mg S/L)
97.1	80.0 to 109	13	0.17 to 0.64

All standard stocks stored at 4°C prior to use.

All reagent blanks were <0.01 mg S/L throughout the course of this evaluation. All filtration device blanks (method blanks) were <0.01 mg S/L (n=10).

Background correction samples ranged from <0.01 to 0.09 mg S/L with an average of 0.02 mg S/L, indicating that most of the samples processed via filtration had little remaining turbidity or color to interfere during dissolved sulfide measurements.

A summary of initial precision and recovery (IPAR) and ongoing precision and recovery (OPAR) experiments is provided in Table 4.2. Four replicate IPARs yielded an average recovery of 87.4% and an RSD of 4.2%. These results illustrate that sulfide losses were minimal and good precision and accuracy were observed in reagent grade water when the dissolved sulfide filtration device was utilized.

Table 4.2. Initial and Ongoing Precision and Recovery: Reagent Water

	Spike Level (mg S/L)	Average Rec. (%)	RSD (%)
Initial Precision and Recovery	0.80	87.4	4.2
Ongoing Precision and Recovery	0.53 to 0.85	88.4	7.0

All standard stocks stored at 4°C prior to use.

4.2 Field Testing for Precision

Replicate samples were collected at various locations at five mills to assess the precision of the dissolved sulfide method, as shown in Table 4.3. Four replicates were collected for dissolved sulfide after flushing the sample collection reservoir with fresh sample. RSDs obtained for the four replicates collected at each sampling location ranged from 4.0 to 14.3% with an average of 9.3%, indicating good precision for the method. The exception to this was the low level replicates collected at the pond outlet of Mill A. The high RSD observed for these replicates indicates a lack of precision near the detection limit of the method. Dissolved sulfide levels were below the lower calibration limit of the method for six of the locations and therefore could not be used to evaluate method precision.

Table 4.3 Method Reproducibility in Pulp and Paper Mill Wastewaters

Mill Code	Sampling Location[a]	RSD (%)	Ave. Conc. (mg S/L)
A	Primary clarifier outlet	8.0	3.40
A	Pond outlet	66	0.05
A	Caustic sewer	NA	ND
B	Front of AS	NA	ND
B	Upwell of AS	NA	ND
C	Primary clarifier outlet	4.0	2.42
D	Primary clarifier outlet	6.9	0.96
D	Front of ASB	13.2	0.93
D	Final effluent	NA	ND
E	Primary clarifier outlet	14.3	0.28
E	Front of ASB	NA	ND

[a] AS = activated sludge; ASB = aerated stabilization basin.
NA = not available due to lack of detection for dissolved sulfide in sample.
ND = not detected above lower calibration limit of method.

4.3 Field Testing for Accuracy

The collection process was repeated and four spiked replicates were assessed at each site to characterize the accuracy of the method. For the spiking study, the 10 L extractive sampling reservoir was replaced with a 1 L reservoir in order to minimize volumes of sulfide spiking solution required. As shown in Table 4.4, spike recoveries averaged 42.7% and ranged from 15.7 to 80.7%, indicating significant losses of sulfide during sampling.

An additional 1 L sample was collected to determine dissolved oxygen (DO), pH, total suspended solids (TSS), and volatile suspended solids (VSS). This information was collected in an effort to examine the impact these parameters might have on sulfide spike recoveries, as prior work showed low recoveries of spikes when analyzing samples containing high TSS concentrations for total sulfide. Results of these data are also provided in Table 4.4.

Losses of added sulfide (low spike recoveries) could result from reactions of sulfide with the spiking apparatus or sample collection surfaces, oxidation, volatilization, or sorption onto dissolved or particulate solids in the matrix. These potential causes were investigated in order to form a weight of evidence approach for the validity of the method, as spikes were not adequately recovered in the matrices tested. Data for average field spike recoveries were regressed to each of the variables in Table 4.4 in an effort to determine if the parameters correlated to the low recoveries. A simple regression analysis indicated that there was not a statistically significant relationship between matrix spike recoveries and the other parameters in the table at a confidence level of 95%.

Table 4.4 Sample Results: Matrix Spike Recovery and Characterization

Mill Code	Sampling Location[a]	Ave. Field Spike Rec. (%)	Spike Conc. (mg S/L)	TSS (mg/L)	VSS (%)	DO (mg/L)	pH	Temp. (˚C)
A	Primary clarifier outlet	NA	NA	37.1	83.8	1.55	6.5	41.7
A	Pond outlet	NA	NA	96.5	53.4	2.07	7.0	30.2
A	Caustic sewer	NA	NA	2522	83.0	NA	NA	NA
B	Front of AS	55.8	0.32	1925	80.2	4.5	7.0	24.7
B	Upwell of AS	80.7	0.32	1514	45.8	5.9	7.0	23.8
C	Primary clarifier outlet	31.9	0.80[b]	43.1	79.2	4.57	7.0	37.7
D	Primary clarifier outlet	56.1	0.80	162	31.8	1.51	8.0	48.4
D	Front of ASB	15.8	0.80	71.7	53.7	NA	7.5	NA
D	Final effluent	53.9	0.80	6.6	63.2	4.93	7.5	25.5
E	Primary clarifier outlet	31.4	0.80	17.8	78.9	1.04	7.0	36.5
E	Front of ASB	15.7	0.80	25.5	86.7	4.63	6.5	38.4
	AVERAGE	42.7						

[a] AS = activated sludge; ASB = aerated stabilization basin.
[b] Insufficient spike level compared to sample concentration.
NA = not available due to field sampling issues with spiking apparatus.

Method IPARs were conducted using the field sampling equipment with deionized water as the matrix. Four replicates yielded excellent spike recoveries for dissolved sulfide (see Table 4.2), indicating that spiking apparatus, sample collection surfaces, and volatilization during spiking and sample processing could not account for losses of the sulfide spikes during field testing. Thus, oxidation and reactions with solids were investigated further.

Experiments were conducted using pulp and paper mill wastewaters purged with nitrogen to investigate the potential for oxidative losses. Portions of samples were purged with nitrogen for >60 minutes or until DO measured in the samples was <0.2 mg/L. This also purged sulfide from the sample, and most concentrations of sulfide for the purged matrices were less than 0.60 mg S/L prior to matrix spike addition. Matrix spiking experiments were then performed using the nitrogen-purged effluents. Improved recoveries were observed, ranging from 45 to 105% and averaging 74.8% (as shown in Table 4.5), indicating that oxidation was an important source of sulfide loss but did not explain all of the losses observed.

Table 4.5 Spike Recoveries after Nitrogen Purging of Samples

Mill Code	Sampling Location[a]	Matrix Spike Rec. (%)	Spike Conc. (mg S/L)
A	Primary clarifier outlet	45.0	0.77
A	Pond outlet	39.8	1.11
B	Front of AS	82.2	0.98
B	Upwell of AS	105	0.97
C	Primary clarifier outlet	88.6	0.84
D	Primary clarifier outlet	63.6	0.94
D	Front of ASB	80.0	0.98
E	Primary clarifier outlet	85.6	0.95
E	Front of ASB	83.5	0.97

[a] AS = activated sludge; ASB = aerated stabilization basin.

The impacts of solids on matrix spike recoveries were investigated using spiking experiments that utilized solutions of deionized (DI) water spiked at known concentrations using commercially available water soluble lignins as surrogates for dissolved pulp and paper mill wastewater organics. An experiment was also conducted using non-soluble Sigma Cell type 20 cellulose as a surrogate for particulate solids in mill wastewaters. Lignin A was an alkali carboxylated lignin and Lignin B was an alkali low sulfonate lignin. The impacts of these solids on sulfide spike recovery are illustrated in Figure 4.2 for Lignin A (diamond), Lignin B (square), and Sigma Cell (triangle). Spike recoveries decreased when lignin solids were present in reagent water above concentrations of ~50 mg/L. Cellulose did not appear to impact spike recoveries across the concentration range assessed. The lignin impacts on recoveries demonstrate that losses of sulfide during spiking experiments may be related to sorption onto lignin-type solids in the matrix and subsequent removal by the filtration device. The nature of the response to increasing doses of lignin also indicates that only a portion of sulfide present was reactive towards lignin.

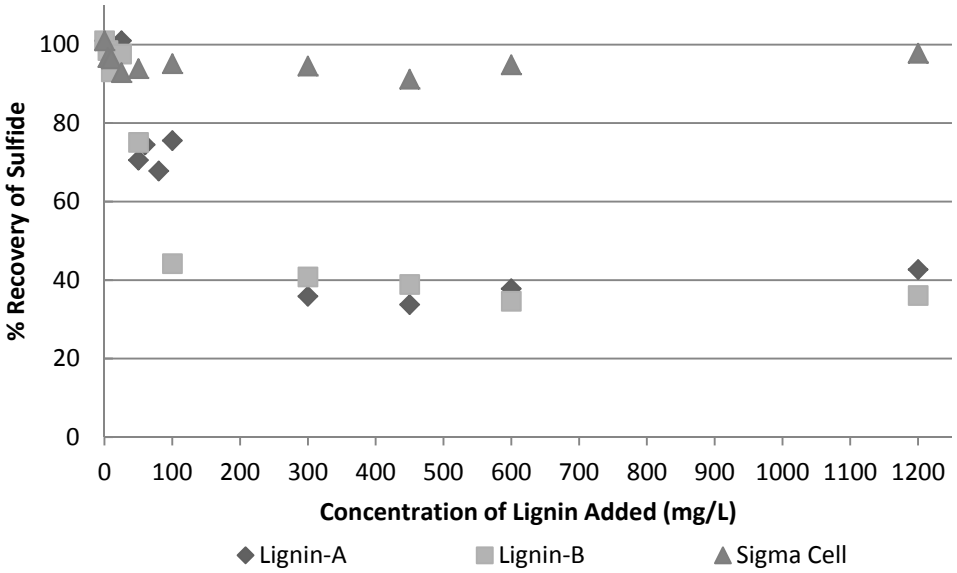

Figure 4.2 Sulfide Spike Recoveries in Solutions of Lignins and Sigma Cell at Various Concentrations

This information, together with experiments indicating increased recoveries of spikes observed in nitrogen-purged matrices, supports a hypothesis that sulfide spikes in wastewater samples were lost during matrix spiking experiments due to oxidation and sorption onto dissolved organics in the matrix.

4.4 Comparison of Dissolved and Total Sulfide

During each assessment, four replicate aliquots of the whole (not filtered) sample were collected from the exit port of the sampling reservoir (Figure 2.2) and preserved on site with zinc acetate at pH >10. These samples provided a concentration of total sulfide for comparison to results obtained using the filtration device. Comparison of total and dissolved sulfide results (Figure 4.3) indicates that concentrations of dissolved sulfide at various sampling locations are lower (ranging from 18 to 100% lower) than total sulfide concentrations at the same locations. The large differences observed for many of these samples suggests that using dissolved sulfide measurements may yield more accurate estimates of hydrogen sulfide emissions from wastewater treatment operations.

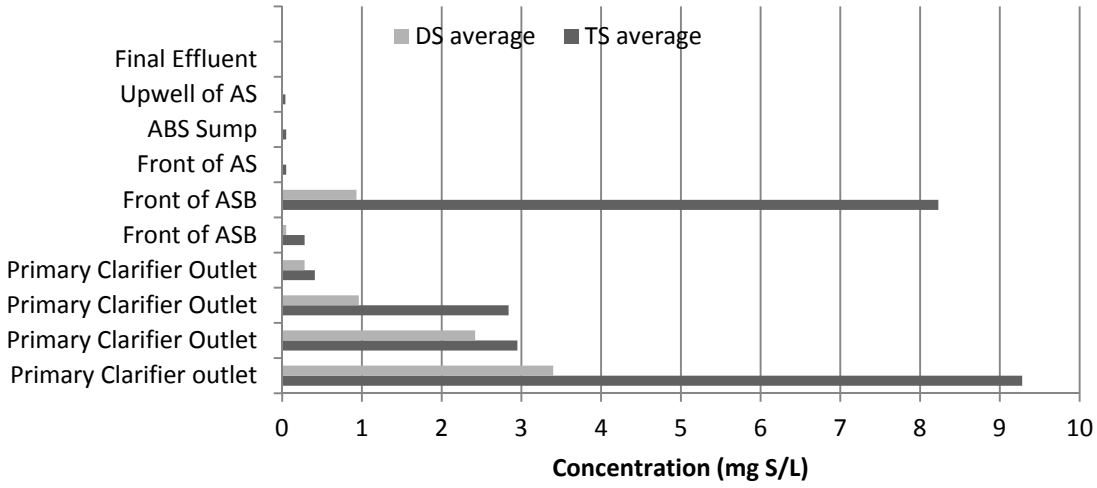

Figure 4.3 Average Total Sulfide (TS) and Dissolved Sulfide (DS) Concentrations

5.0 SUMMARY AND CONCLUSIONS

An ability to measure dissolved sulfide in wastewaters is desirable for purposes of estimating sulfide emissions from wastewater treatment plants. It provides an advantage over total sulfide measurements, which are biased high due to inclusion of metal sulfides and sulfides associated with solids. A sample collection device and a filtration apparatus were developed and tested to provide a system for collecting and measuring dissolved sulfide in pulp and paper mill wastewaters. The evaluation included experiments to characterize the accuracy and precision of the method in laboratory studies and field application at five mills.

- Replicate samplings (n=4) yielded relative standard deviations from 4.0 to 14.3% with an average of 9.3% for dissolved sulfide.
- Method accuracy as assessed by initial and ongoing precision and recovery experiments ranged from 80.3 to 95.4% with an average of 88.4%.
- Ongoing calibration verifications indicated the stability of this analysis, yielding recoveries ranging from 80.0 to 109% with an average of 97.1%.
- Matrix spiking experiments during field evaluation indicated losses of sulfide. Further experiments to investigate the reasons for losses of sulfide spikes indicated that oxidation in the matrix and sorption by dissolved organic matter (using lignin surrogates) were apparently the main loss mechanisms.
- The method yielded substantially lower values for dissolved sulfide than for total sulfide in a majority of the samples assessed.

This dissolved sulfide method for collecting and analyzing wastewater samples could provide a more accurate assessment of sulfide species that have the potential to be emitted to the atmosphere from wastewater treatment systems in the form of hydrogen sulfide.

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APPENDIX A

NCASI METHOD DS^{2-}-W114.01

NCASI METHOD DS^{2-}-W114.01

TOTAL DISSOLVED SULFIDE IN PULP AND PAPER MILL WASTEWATERS BY SPECTROPHOTOMETRY

NCASI

West Coast Regional Center

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To serve the forest products industry as a center of excellence for providing technical information and scientific research needed to achieve the industry's environmental goals.

NCASI METHOD DS^{2-}-W114.01

TOTAL DISSOLVED SULFIDE IN PULP AND PAPER MILL WASTEWATERS BY SPECTROPHOTOMETRY

1.0 SCOPE AND APPLICATION

1.1 This method is used for determination of dissolved sulfide [CAS 18496-25-8] in wastewaters from pulp and paper mills. Dissolved sulfide is measured by collecting a sample and removing suspended solids via filtration. The sample is preserved immediately after filtration and dissolved sulfide is measured using a spectrophotometer.

1.2 The concentration of sulfide measured using this method represents the dissolved amount of sulfide in the sample following collection and filtration via a 0.7 μm pore size filter using the apparatus illustrated in Section 17, Figures 1 and 2. Quantification of dissolved sulfide in the collected and preserved sample involves acidification to release sulfide in the form of hydrogen sulfide that subsequently reacts with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue (Section 17, Figure 3). The intensity of the color is directly proportional to the concentration of sulfide in the sample.

1.3 The method has been applied to influent to wastewater treatment, samples from within the wastewater treatment system, and effluent from wastewater treatment at pulp and paper mills.

1.4 This method has been validated for a single laboratory.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in use of spectrophotometers and skilled in interpretation of colorimetric data. Each analyst must demonstrate an ability to generate acceptable results with this method.

2.0 SUMMARY OF THE METHOD

2.1 Samples are collected directly from the aqueous wastewater stream or wastewater basin using the sample collection vessel illustrated in Section 17, Figure 1. After filtration using the apparatus illustrated in Section 17, Figure 2, immediately preserve samples using a solution of zinc acetate to stabilize dissolved sulfide as zinc sulfide. Acidify the preserved sample and immediately react it with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. Measure the absorbance of this chromophore using in a spectrophotometer at a wavelength of 665 nanometers (ηm).

2.2 The quantity of dissolved sulfide is determined by utilizing the measured absorbance value and the linear regression equation derived from the calibration curve developed in Section 7.2.2.

2.3 The method detection limit was calculated using the USEPA procedure in 40CFR Part 126 Appendix B (Federal Register 1984) in reagent grade water and was determined to be 0.01 mg S/L.

2.4 Data quality is assured with initial and ongoing recovery assessments, duplicate analyses, blank analyses, and reproducible calibration and testing of sample collection, filtration, and spectrophotometer systems. A calibration check is analyzed with each sample set. A complete description of quality control procedures, calculations, and method performance criteria are listed in Section 9.

3.0 DEFINITIONS

3.1 The definitions herein are specific to this method, but conform to common usage as much as possible.

3.1.1 µg/L – micrograms of compound per liter

3.1.2 µg S/L – micrograms of sulfide per liter

3.1.3 May – this action, activity, or procedural step is neither required nor prohibited

3.1.4 Must – this action, activity, or procedural step is required

3.1.5 Should – this action, activity, or procedural step is suggested but not required

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagents, glassware, filters, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the method by analyzing method blanks.

4.2 Interferences will vary considerably from source to source, depending on the diversity of the site being sampled. Strong reducing substances such as sulfite, thiosulfate, and hydrosulfite above a concentration of ~10 mg/L can prevent or reduce color development. High concentrations of sulfide may limit color development, and sample dilution may be required following preservation but prior to formation of the chromophore. Turbidity and color can also impact overall results. A sulfide-free blank must be prepared for each matrix assessed, and its results subtracted from dissolved sulfide determined in the sample to correct for interference due to color and particulates smaller than the 0.7 µm pore size used to filter samples.

5.0 SAFETY

5.1 All chemicals should be treated as potential health hazards. Prudent practices for handling chemicals in the laboratory are recommended (NRC 1995).

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material Safety Data Sheets (MSDSs) and Safety Data Sheets (SDSs) should be available to all personnel involved in these analyses. All SDSs for chemicals used in the method must be reviewed prior to use.

5.3 Hydrogen sulfide gases or liquids may be harmful if inhaled or ingested. This compound can also cause a considerable nuisance odor. Use it in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

5.4 The sulfide 2 reagent used to form methylene blue contains potassium dichromate. Therefore the final solution will contain hexavalent chromium (D007) at a concentration regulated as a hazardous waste by federal RCRA. Hazardous waste must be managed and disposed of according to federal, state and local regulations.

6.0 EQUIPMENT AND SUPPLIES

***Note**: Brand names and suppliers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and material other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Sampling Equipment

This section describes the equipment needed to collect samples in the field when inserting the filtration apparatus directly into the sample may not be practical or will result in collection of samples that are not representative of the sampling location.

6.1.1 Nalgene® LDPE wide mouth 10 L carboy, 90-100 mm diameter enclosure/cap

6.1.2 ½ inch OD (HDPE) tubing, ⅜ inch inside diameter

6.1.3 ½ inch bulkhead union, PFA, PVDF, white polypropylene (2-3)

6.1.4 on/off valve, Cole Parmer Catalog No. 98260-00 (2)

6.1.5 ⅜ inch OD (HDPE) tubing, ¼ inch inside diameter

6.1.6 ⅜ inch bulkhead union for sampling port, >0.26 inch orifice (1)

6.1.7 on/off valve, Cole Parmer Catalog No. 98261-10 (1)

6.1.8 12 volt DC submersible pump, 1 to 2 inch diameter, Proactive®

6.1.9 portable 12 volt DC power supply, NAPPA Power Boost™ 400

6.2 Filtration Equipment

6.2.1 filter holder(s) (with wrenches), Savillex® PFA, 47 mm, SKC Catalog No. 225-1712

6.2.2 grade GD 10 to 1 µm glass fiber filter, 47 mm diameter, Whatman Catalog No. 1841 047

6.2.3 GF/F 0.7 µm glass microfiber filter, 47 mm diameter, Whatman Catalog No. 1825 047

6.2.4 Pyrex® glass wool, 8 'micron,' Corning Catalog No. 3950

6.2.5 60 mL BD plastic syringe(s), Luer-Lok™ tip

6.2.6 on/off Luer stopcock(s), Phenomenex Catalog No. AHO-6049

6.2.7 1-5 mL adjustable volume pipette or 200-1000 µL adjustable volume pipette

6.2.8 40 mL clear glass VOA vials with Teflon™ lined caps

6.2.9 30 mm rack(s) for vials and 60 mL plastic syringes

6.3 Analytical Equipment

This section describes the equipment needed to collect and analyze dissolved sulfide.

6.3.1 Cary 100 spectrophotometer or equivalent UV spectrophotometer capable of measuring absorbance at a selected wavelength of 665 ηm with a light path length of 10 mm.

6.3.2 Syringe filters: 1.0 µm GMF-150, Whatman Cat No. 6783-2510

6.3.3 10 mL syringe with Luer fitting

6.3.4 Lint-free wipes for cleaning cuvette prior to measurement

6.3.5 Volumetric pipettes to dispense 1-10 mL

6.3.6 40 mL vials, EPA/VOA certified; borosilicate glass with polypropylene closed caps with PTFE-faced silicone liner ensures airtight seal of sample and reduced light exposure

6.3.7 Assemble the collection apparatus illustrated in Section 17, Figure 1 as described here.

6.3.7.1 Drill a ⅜ inch hole in the center of the Nalgene LDPE wide mouth 10 L carboy, 90-100 mm diameter cap and attach the ⅜ inch bulkhead union (>0.26 inch orifice). Connect a 4 inch length of ⅜ inch outside diameter HDPE to the inside portion of the bulkhead union. Attach a 3 inch length of ⅜ inch outside diameter HDPE tubing to the inside portion of the bulkhead union and attach an on/off valve to the top section of the tubing.

6.3.7.2 Drill two ½ inch holes on each side of the center ⅜ inch bulkhead union. Allow enough space for addition of the bulkheads and easy access to the valves. Fit the ½ inch holes with ½ inch bulkhead unions and fit the outside portion with an on/off valve. Add a 10 feet section of ½ inch outside diameter HDPE tubing to the outside of one of the on/off valves. This will be the exit tube for excess sample and for purging the apparatus of oxygen prior to sample collection. It should be an appropriate length to return excess sample to the treatment unit being sampled or to a temporary reservoir.

6.3.7.3 Add a length of ½ inch HDPE tubing that extends almost to the bottom of the 10 L carboy to the inside of the other ½ inch bulkhead union. Add an on/off valve and then a length (50 to 100 feet) of ½ inch HDPE tubing that extends to the submersible pump to the outside of this same ½ inch bulkhead union.

6.3.8 Assemble the filtration apparatus illustrated in Section 17, Figure 2 as described here.

6.3.8.1 Attach a 6 to 7 inch length of ¼ inch outside diameter (OD) Teflon tubing to the inlet side of the filter holder and a 1¼ inch length of ¼ OD, 4 mm inside diameter (ID) Teflon tubing to the outlet of the filter holder.

6.3.8.2 Using forceps or clean gloves, place a GF/F 0.7 µm glass microfiber filter on the Teflon support screen in the back half of the filter holder, followed by the Grade GD 10 to 1 µm glass fiber filter. The Grade GD is a graduated filter with flow direction, and the face toward the flow must be the 10 µm side. This is marked on the filter package when received. Alternatively, stack the filters before placing them in the filter holder if static electricity becomes problematic.

6.3.8.3 Use scissors to cut off a 2 inch length of glass wool from the end of the glass wool rope.

6.3.8.4 Using clean gloves, open the outside end of the glass wool with a rounded flower-shaped opening by inverting the near end, then slightly compress the mass of glass wool into the inlet half of the filter holder. Gently push any overhanging glass wool completely inside the holder.

6.3.8.5 Carefully assemble the two halves of the filter holder and tighten with the two large plastic filter holder wrenches.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Sodium sulfate nanohydrate ($Na_2S.H_2O$: FW 240.2) CAS No. 1313-84-4, ACS; reagent grade ≥98.0%

7.1.2 Deionized (DI) water should be tested immediately before use to verify the absence of sulfide. If the water is contaminated, it may be necessary to prepare fresh DI water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.1.3 Zinc acetate dehydrate, reagent grade ($Zn(C_2H_3O_2)_2 \cdot 2\ H_2O$; FW 219.5); CAS No. 5970-45-6.

7.1.4 Prepare 1 N NaOH by dissolving 40 g of pellets (97+%, CAS No. 1310-73-2) in approximately 800 mL of DI water in a 1 L volumetric flask. Use caution and appropriate PPE when transferring NaOH to the flask containing water, as considerable heat is liberated by the exothermic reaction. The flask should be kept in a cold-water bath until the NaOH is dissolved and cool. When cool, finish adding DI water to the mark. Allow to cool again, add DI water to the mark if necessary, and mix well.

7.1.5 Prepare zinc acetate preservation solution (~40 mmole/L) by adding approximately 180 mL of DI water and a magnetic stir bar to a 200 mL beaker. Vigorously stir while gradually adding 1.75 g of zinc acetate dihydrate until dissolved. Slowly add 1N NaOH solution dropwise until pH 8.0 is achieved (this process should take 15 to 20 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt that will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is no longer required. Adjust final pH to 12 ±0.5 using 1N NaOH solution (total 1N NaOH required is approximately 20 mL). This solution should produce a fine, even suspension that does not settle rapidly. If you shake the container and then let it sit, it will usually remain in suspension for over 20 minutes.

7.1.6 Reagent set (HACH Catalog No. 22445-00); includes Sulfide Reagent 1 (~50% sulfuric acid, CAS No. 7664-93-9) and Reagent 2 (<1% potassium dichromate, CAS No. 7778-50-9)

7.1.7 Bromine water (HACH Catalog No. 211-20, CAS No. 7726-95-6)

7.1.8 Phenol solution 30 g/L (HACH Catalog No. 2112-20, CAS No. 108-95-2)

7.2 Calibration Standards

7.2.1 Sulfide calibration standard is prepared in DI water that has been sparged with nitrogen (to remove oxygen) for 1 hour then chilled at 4°C. Dissolve a stock solution of 150 ±0.1 mg of sodium sulfide nonahydrate in 100 mL of the sparged/chilled DI water diluted to the mark in a 100 mL volumetric flask. When completely dissolved, transfer the solution quickly into three 25 mL VOA vials with Teflon lined screw caps. Fill the vials completely, leaving no headspace, and store at 4°C until used within three days. The concentration in the solution will be nominally ~200 µg S/mL. Use equation 1 to calculate the actual concentration.

Equation 1

$$\text{Concentration } \mu g\ S/mL = \frac{mg\ (Na_2S\,9H_2O) \times MW\ (S) \times 1000\ \mu g}{MW\ (Na_2S.9H_2O) \times mL \times 1\ mg}$$

where: $\mu g\ (Na_2S.9H_2O)$ = *mass of compound*
$MW\ (Na_2S.9H_2O)$ = *240 mg/mmol*
$MW\ (S)$ = *32 mg/mmol*
mL = *total volume of DI water*

7.2.2 Prepare a multilevel calibration curve by diluting 0, 5, 10, 15, 25, 50, 75, 100, and 125 µL of 200 µg S/mL sulfide stock in separate 25 mL aliquots of DI water. This provides 0.00, 0.04, 0.08, 0.12, 0.20, 0.40, 0.60, 0.80, and 1.0 mg S/L calibration standards. These standards must be reacted to form the methylene blue chromophore as soon as possible, as specified in Section 11. Once reacted, the standards can be stored at room temperature for three days.

7.3 Initial and Ongoing Precision Standards

7.3.1 Prepare a sulfide spiking solution at a concentration of 0.18 mg S/mL by adding 250 ±0.1 mg of sodium sulfide nanohydrate to a 200 mL volumetric flask containing ~180 mL of chilled/nitrogen sparged DI water. Dilute to the mark and cap. When the sulfide crystals are completely dissolved transfer to six 25 mL VOA vials. Pour slowly and leave no head space in the vials. Store at 4˚C and use within three days.

7.3.2 Use the sulfide spiking solution (Section 7.3.1) for initial precision and recovery (IPR) and ongoing precision and recovery (OPR) testing, targeting a final concentration range from 0.2 to 0.8 mg S/L in 1 L volumes of sample (matrix spike, MS) or DI water (IPR and OPR). For example, 3.0 mL of spiking stock (Section 7.3.1) at a concentration of 0.18 mg S/mL added to 1 L will yield a spiking concentration of 0.49 mg S/L. Filter and analyze this sample as described in Section 11.

8.0 SAMPLE COLLECTION

8.1 Sample collection is one of the most important aspects of determining dissolved sulfide. Sulfide can easily be lost via volatilization, oxidation, or reaction with metal surfaces. To reduce these losses this method employs the sample collection apparatus and filtration device described in Sections 6.3.7 and 6.3.8. The sample collection procedure is described in Section 11 in which samples are preserved as collected using a zinc acetate preservation solution (Section 7.1.5).

8.2 Preserved samples can be stored cold for up to four hours or reacted in the field to form the methylene blue chromophore and stored at room temperature for up to three days.

9.0 QUALITY CONTROL

A method blank, independent standard check, calibration verification checks, IPR, OPR, and duplicates should be performed to control the quality of data generated using this method.

9.1 Method Blanks

9.1.1 Prepare method blanks using the procedures outlined in Section 11 utilizing DI water as the sample.

9.2 Independent Standard Check

9.2.1 A primary standard prepared for calibration and matrix spike experiments should be compared to an independent standard either prepared from another source of the compound or obtained from a certified standard vendor.

9.3 Calibration Verification Checks

9.3.1 Prepare and analyze a mid-level calibration point on every day samples are analyzed. Percent recovery of each compound in the standard should be within 20% of the percent recovery of the same calibration level in the multipoint calibration. If the daily calibration check fails, it should be repeated. If it fails a second time, the standards should be re-prepared. If it continues to fail, the multipoint calibration should be repeated. A summary of single laboratory daily calibration checks for this method is provided in Section 17, Table 1.

9.4 Initial and Ongoing Precision and Recovery

9.4.1 Complete a demonstration of initial precision and recovery (IPR) prior to analyzing samples. The IPR consists of analyses of four replicates of reagent water spiked with dissolved sulfide using the procedures specified in Section 11. Ongoing precision and recovery (OPR) is assessed using this process with each sample set analyzed.

9.5 Duplicate Analyses

9.5.1 A duplicate sample should be analyzed with each set of samples (batch of samples no greater than 20). Duplicate analysis requires analyses of separate aliquots of the sample. The relative percent difference between the two samples should be calculated and charted to estimate the method's precision. Section 17, Table 2 lists relative percent differences found during a single laboratory validation of the method.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Spectrophotometer Operating Conditions

10.1.1 Turn on the instrument and its operating hardware (computer) and warm them up for at least 15 minutes or as recommending in the instrument manual.

10.1.2 Use these instrument settings for sulfide measurements:

Wavelength (nm)	665.00
Ordinate mode	abs
SBW (nm)	1.5
Ave time (sec)	0.100
Beam mode	single front
Curve fit	linear, Min R^2: 0.9500
Concentration units	mg S/L

10.1.3 Zero the instrument with DI water before analyzing samples and standards.

10.1.4 Use these cuvettes: Brand polystyrene (PS) cuvettes, Cat. No. 759071D, cuvette path length 10 mm

10.2 Initial Multipoint Calibration

10.2.1 Prepare and analyze calibration standards covering the working range of the method (Section 7.2.2) in order to establish a calibration function for the method. React the samples as specified in Sections 11.12, 11.13, and 11.14 and measure the absorbance for each calibration point and a method blank at a wavelength of 665 ηm. Plot the absorbance reading (y-axis) obtained for each calibration level versus the concentration (x-axis) in the standard assessed. Use a linear regression to determine the slope and y-intercept of the line. R-squared for the linear regression line should be greater than 0.9500. A typical calibration curve is illustrated in Section 17, Figure 4.

10.3 Daily Calibration Check

10.3.1 Prior to analyzing samples each day, prepare and analyze a daily calibration check from a sulfide stock standard (Section 7.2.1) using the same process used to prepare the initial multipoint calibration curve. Calculate the sulfide concentration in this standard using the equation developed in Section 10.2. Calculate percent recovery of the standard using Equation 2. In-house percent recovery control limits should be determined, and should not exceed ±20%. If the calibration check does not pass, a fresh stock should be prepared and analyzed. If these fail, a fresh stock of sulfide (Section 7.2.1) should be prepared and the initial multipoint calibration should be repeated. Section 17, Table 1 summarizes results for daily calibration checks during method evaluation and subsequent single laboratory evaluation.

Equation 2

$$\%R = \left(\frac{C_i}{C} \right) \times 100$$

where: $\%R$ = *percent recovery*
C_i = *concentration measured for continuing calibration standard (mg S/L) using multipoint calibration curve*
C = *gravimetric concentration (mg S/L)*

10.4 Method Blank Analysis

10.4.1 A method blank should be prepared and analyzed with each sample set using DI water as the sample and conducting the filtration and analysis procedures specified in Section 11. The method blank is especially important when a change in reagents, DI water, and filter lots occurs.

11.0 PROCEDURE

11.1 Insert the submersible pump approximately 1 foot below the surface of the treatment unit aqueous phase being assessed. Secure all tubing as needed to protect from accidental loss to the treatment unit.

11.2 Prepare a syringe with preservative to collect a filtered sample by attaching a Luer stopcock to a 60 mL BD plastic syringe. Open the stopcock and pull out the plunger. Close the stopcock and place the syringe barrel upright in a rack.

11.3 Add 2 mL of zinc acetate preservative (Section 7.1.5) to the syringe. Remove the syringe from the rack and insert the plunger about ½ inch.

11.4 Holding the syringe upright, gently tap on the stopcock to allow any preservative that may be in the tip of the stopcock to drop into the syringe. Open the stopcock and slowly push the plunger in until the headspace above the preservative is removed. Close the stopcock.

11.5 Attach a 60 mL syringe that does not contain preservative to the Luer lock port of the filter holder.

11.6 Connect the submersible pump to the power supply and turn on the pump to fill the sample collection device and purge it of air. Close all valves while turning off the power to the pump. This will leave a representative portion of sample in the 10 L carboy that has been purged of air. Immediately insert the filter holder's inlet tubing down into the sampling port of the sample collection apparatus (Section 17, Figure 2) and slowly pull (~1 min) the syringe plunger out until the stop is met. Allow several seconds for the vacuum to lessen in the syringe. Filtered sample should now fill the filter holder and some should have entered the syringe. Close the stopcock. For method blanks, IPRs, and OPRs the inlet tubing can be placed into the sampling port of a 1 L container to minimize the amount of DI water and spiking stocks required.

11.7 If the filter holder has not been purged of air, the syringe can be removed from the stopcock on the filter holder and the plunger pushed back into the syringe. Reattach this syringe to the stopcock, open the stopcock, and pull additional sample into the filter holder until approximately 5 mL of sample is drawn into the syringe. Close the stopcock and remove the syringe.

11.8 Immediately attach the stopcock on the second syringe that has been pre-loaded (Section 11.2) with zinc acetate preservative to the stopcock on the filter holder. Apply a small amount of vacuum to the syringe and then open the stopcock on the filter holder. Pull the specified volume of sample into the syringe with the preservative. Close the stopcock. Remove the syringe.

11.9 Holding the syringe upright, determine the volume of sample filtered; record the volume. **Note**: The inside of the first seal on the plunger is accurate to 0.5 mL.

11.10 Transfer the sample from the syringe to a 40 mL glass VOA vial.

11.11 An additional sample must be collected in order to correct the overall concentration for background color and turbidity. Use the same procedure described in Sections 11.2 and 11.4 through 11.10 to collect the sample, omitting the addition of zinc acetate preservative in Section 11.3. Prepare a sample for matrix background correction: remove the native dissolved sulfide that may be present in the collected sample by adding 8 drops of bromine water (Section 7.1.7); mix the solution; add 4 drops of phenol solution (Section 7.1.8); and mix.

11.12 React the sample by adding 1 mL of Sulfide Reagent 1 to each 40 mL VOA vial containing the filtered sample and swirling gently to mix.

11.13 Immediately add 1 mL of Sulfide Reagent 2 to each vial, cap, and invert three to four times.

11.14 Allow the sample to react for a minimum of 5 minutes. Filter a portion of the reacted sample using a syringe filter (1.0 µm GMF-150, Section 6.3.2) and a 10 mL syringe into the 10 mm light path length cuvette. Read the absorbance at a wavelength of 665 µm. Experiments indicate that, once reacted, samples can be stored at room temperature for up to three days prior to reading the absorbance.

11.15 Apply the dilution factor from the volume determined in Section 11.9 corrected for dilution of the sample by the preservative. For example, if 24 mL of sample was filtered and collected in the syringe with 2 mL of preservative for a total of 26 mL, the measured concentration must be multiplied by a factor of 1.04 (26/25; 25 mL is the standard sample volume).

11.16 A dilution is necessary if color absorption is greater that the upper calibration point. For dissolved sulfide analysis dilutions are made from the reacted sample with DI water and the absorption is re-measured. This dilution factor must be applied to the final concentration calculation.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculations

12.1.1 Calculate the sulfide concentration in each background and sample using the linear equation derived from the calibration curve. Apply the dilution factors determined in Sections 11.15 and 11.16.

12.1.3 Subtract the appropriate background result from each sample to correct for turbidity and color.

12.2 Duplicate Precision

Duplicate samples should be analyzed with each set of samples. Calculate relative percent difference (RPD) for each duplicate pair as shown in Equation 3.

Equation 3

$$RPD = \frac{ABS\left|C_1 - C_2\right|}{\left(C_1 + C_2\right)/2} \times 100$$

where: RPD = *relative percent difference in two determinations*
C_1 = *concentration measured in sample (mg S/L)*
C_2 = *concentration measured in duplicate (mg S/L)*
ASB = *absolute value*

12.3 Ongoing Accuracy and Precision

An OPR standard should be analyzed with each sample set to assess the accuracy of the method. Calculate percent recovery using Equation 4.

Equation 4

$$R = \frac{\left(C_{opar}\right)}{C_S} \times 100$$

where: R = *percent recovery*
C_{opar} = *concentration measured in OPR sample (mg S/L)*
C_S = *theoretical concentration of spiked compound (mg S/L)*

13.0 METHOD PERFORMANCE

13.1 Single laboratory performance of this method is detailed in Section 17, Tables 1, 2, and 3. Single laboratory precision expressed as the pooled relative standard deviation of replicates is

estimated to be 7.0% in reagent grade water (n = 4) and 9.3% in pulp and paper mill wastewaters (n = 5 sets of four replicates in each wastewater). All method blanks were <0.01 mg S/L (n = 10).

14.0 POLLUTION PREVENTION

14.1 Pollution prevention approaches have not been evaluated for this method. The laboratory should check state and local requirements to determine if pollution prevention equipment is required or recommended in its area.

15.0 WASTE MANAGEMENT

15.1 It is the responsibility of the laboratory to comply with all federal, state, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 REFERENCES

16.1 Federal Register. 1984. Rules and Regulations, Appendix B to Part 136, Definition and procedure for the determination of the method detection limit – Rev. 1.11. *Federal Register* 49(209).

16.2 National Council for Air and Stream Improvement, Inc. (NCASI). 2014. *Development and evaluation of a procedure for measuring dissolved sulfide in pulp and paper mill wastewaters*. Technical Bulletin No. 1027. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

16.3 National Research Council (NRC). *Prudent practices in the laboratory*. Washington DC: National Academy Press.

17.0 TABLES AND DIAGRAMS

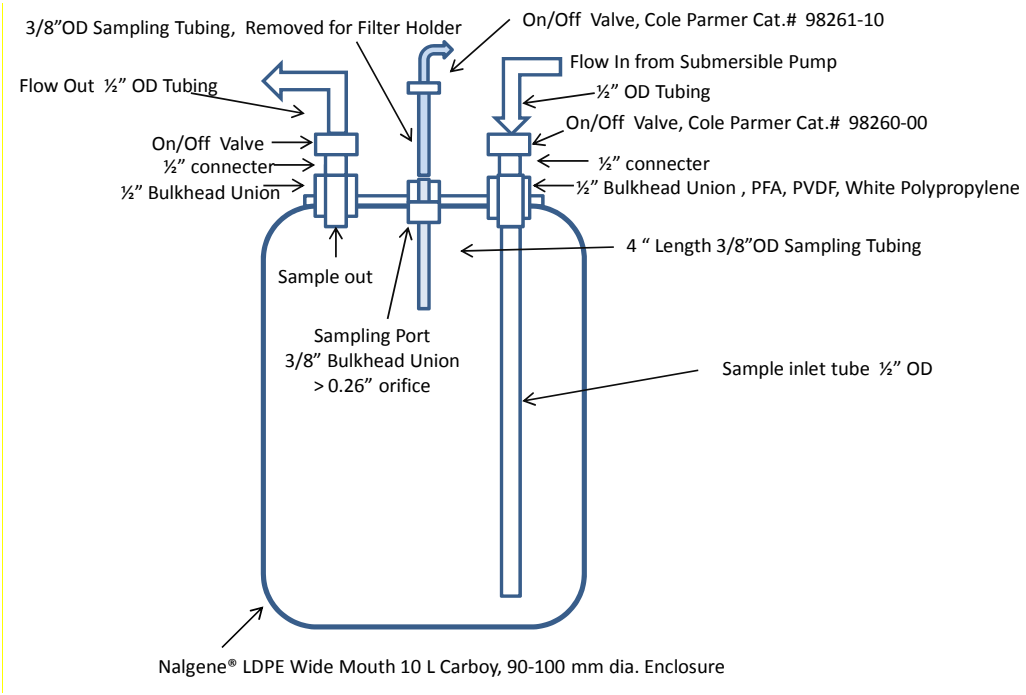

Figure 1. Sample Collection Apparatus

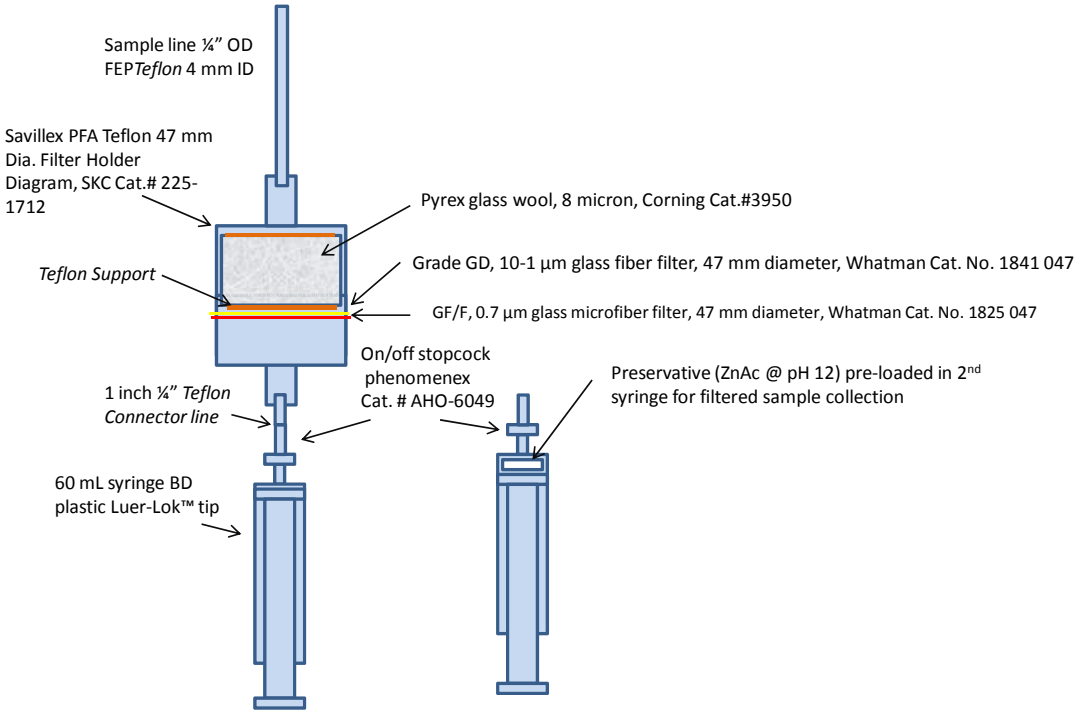

Figure 2. Syringe Filtration Apparatus

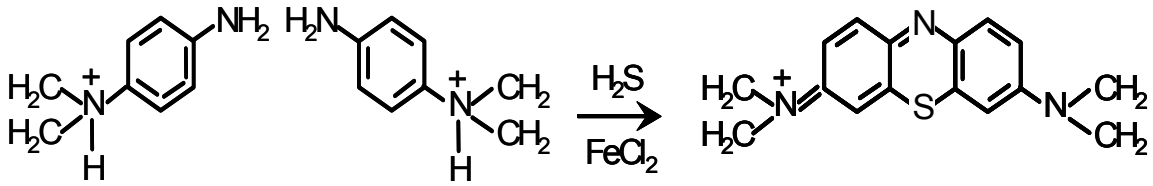

Figure 3. Methylene Blue Formation

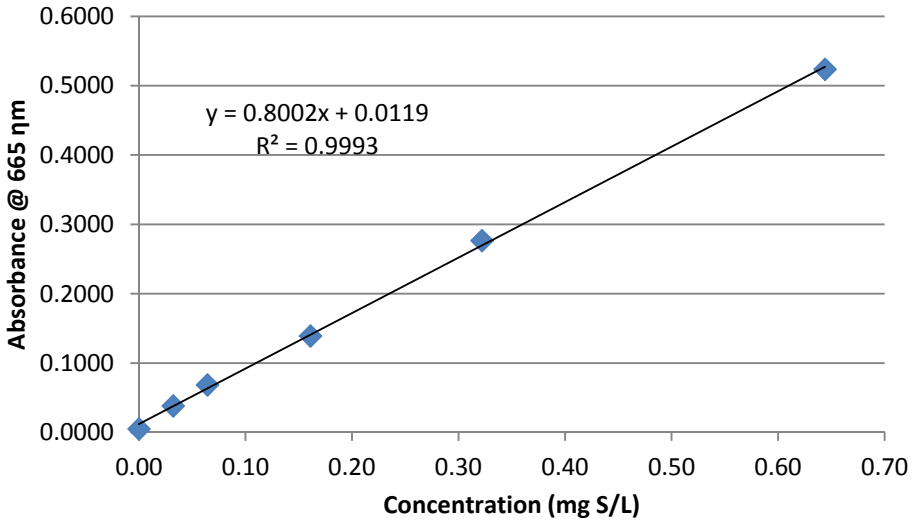

Figure 4. Dissolved Sulfide Linear Calibration Curve

Table 1. Single Laboratory Evaluation: Daily Calibration Checks

Parameter	Mean Recovery	Recovery Range	RSD (%)	n
Dissolved sulfide	99.6%	79.9 to 116%	10.4	16

Table 2. Single Laboratory Evaluation: Initial and Ongoing Precision and Recovery

Dissolved Sulfide	n	Average Recovery (%)	Relative Standard Deviation (%)	Range of Recoveries (%)
Initial precision and recovery	4	87.4	4.2	83.4 to 92.2
Ongoing precision and recovery	6	88.4	7.0	80.3 to 95.4

Table 3. Single Laboratory Evaluation: Matrix Reproducibility

Dissolved Sulfide	Matrix n	Replicates per Matrix	Average RSD (%)	Range of RSDs (%)
Pulp and paper mill wastewaters	5	4	9.3	4.0 to 14.3

Attachment B – Quarterly Sampling Plan

Georgia-Pacific Toledo Quarterly Sampling Plan

Objective:

Samples will be collected quarterly for one full year to support Water9 modeling of the wastewater treatment system at Georgia-Pacific (GP) Toledo LLC, in accordance with the March 24, 2025, request from the Oregon Department of Environmental Quality (DEQ). Required sample parameters, analyses, and locations were provided in Attachment A of the referenced request. This sampling effort will be conducted in support of the Cleaner Air Oregon (CAO) Emissions inventory for GP Toledo.

Sampling Methodology and Parameters:

Quarterly grab samples for the constituents listed below will be collected in accordance with the sampling requirements outlined in the various analytical methods and following the protocol described in this sampling plan.

- Ammonia (EPA Method 350.1)
- Purgeables (Volatile Organic Compounds – VOCs) by GC/MS (EPA Method 624.1)
- Base/Neutrals and Acids (BNA) by GC/MC (EPA Method 625.1)
- Carbonyl Compounds by HPLC (EPA Method 8315A)
- *PFOA and PFOS by LC-MS/MS (Method 1633A)*[1]

Special sampling protocols must be followed for collection of the per-and polyfluoralkyl substances (PFAS) perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) to minimize cross-contamination. Those protocols and precautions are outlined in this sampling plan. Samples for the other constituents listed above can be safely sampled at the same time as PFOA and PFOS without concern for interferences. Monthly sampling for sulfide and sulfate, described in the Monthly Sampling Plan, must be collected by a different sampling team because much of the special equipment needed for the sulfide sampling is made of Teflon®, which could contaminate samples with PFAS compounds, thus artificially inflating the analytical results.

Quarterly samples will be collected by contracted consultants. At least two people will be needed for the sampling effort.

Sampling kits, including the appropriate preservatives, will be provided by the analytical laboratory(ies) (To be determined).

A Health and Safety Plan will be prepared prior to initiation of sampling activities.

[1] Sampling information for PFOA and PFOS is provided for completeness. However, as detailed above, GP is requesting to not complete this sampling due to sampling and technical issues.

Sample Locations:

Sample Location	Sample ID	Required Sampling (1)	Required Sampling (2)
Clarifier Inlet or Paper Mill Effluent	QSP#1	X	X
Recaustizing Sewer Effluent	QSP#2	X	X
30-Acre Pond Effluent	QSP#3	X	--
15-Acre Pond	QSP#4	X	--
Pulp Mill Effluent	QSP#5	X	X
Pulp Mill Foul Condensate	QSP#6	X	X

(1) Ammonia, VOCs, BNA, Carbonyl Compounds
(2) PFOA and PFOS

A duplicate sample from a random location will be collected during each monitoring event. Samples will be collected from each location, spaced approximately three full months apart, for one full year.

Sampling During "Unusual" Conditions

In addition to regular sampling, ODEQ has requested sampling during "unusual" conditions or operating changes. Unusual conditions are defined in the March 24, 2025 letter, Item 1.e. as liquor spills, startup or shutdown of mill equipment, changes to pond configuration or operation and pond dredging activities.

Due to the complex nature of the sampling, contracted personnel with specialized equipment and training will be utilized to complete the work. For transient events, such as black liquor spills, there will be insufficient time to get the proper resources onsite before the event is over.

For planned startup or shutdown events, every effort will be made to schedule the contracted testing to coincide with the startup or shutdown event. This will not be in addition to the regularly required samples.

In the remote chance that there are any changes to pond configuration, samples will be captured before and after the changes occur.

Safety is a top priority at GP Toledo. During dredging events, personnel not associated with the dredging effort are not allowed in the ponds as the safety risk is too great, therefore sampling during dredging will not be possible.

Quality Assurance/Quality Control:

The purpose of the Quality Assurance/Quality Control (QA/QC) during sample collection is to confirm the accuracy of laboratory analysis or as a check on field sampling methods and equipment. During each quarterly sampling event, the following QA/QC samples should be collected, in addition to the compliance sample, in accordance with:

- **Trip Blank -** When samples for VOCs are collected, the contract laboratory will prepare and include one or more trip blanks (samples) with the outgoing shipment of fresh sample containers to the field team for analysis with the primary well samples. Trip blanks will

consist of sealed, laboratory prepared 40-milliliter VOC vials of organic-free deionized water. The trip blank(s) will accompany all containers and collected samples throughout the field sampling and return laboratory shipping process. Trip blank analytical results will be used to evaluate primary sample results for contamination potentially introduced during field sample collection and handling, return shipment to the laboratory, or laboratory processing of samples for analysis.

- **Field Equipment Blank (FEB)** – Field equipment blanks are prepared in the field using laboratory-supplied organic and PFAS-free reagent water. At the sampling site, the sampler must open the laboratory-supplied reagent water, pour into or over sample collection equipment, collect this water into other laboratory-provided pre-preserved sample containers, seal, and label these containers as the FEB. The FEB is returned to the laboratory along with the other samples and analyzed to ensure that target constituents were not introduced into the sample during sample collection/handling. FEBs must be prepared using the same batch of bottle ware and preservative as the regular sample and must be prepared and collected in the field, at the facility.

- **Field Duplicate** – A field duplicate sample collected at the same time and place as the regular samples, under identical circumstances, and treated exactly the same throughout field and analytical procedures. A field duplicate will be collected at a random sample location during each monitoring event. Analysis of field duplicate samples gives a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

PFAS Sampling Precautions and Best Practices:

During sample collection for PFOA and PFOS, care should be taken to minimize cross-contamination of the sample. PFAS are widely ubiquitous and are found in many household, consumer, and industrial products. Incidental cross-contamination could potentially be introduced while the sample bottle is open or during sample collection. Potential sources of PFAS cross-contamination include a multitude of personal care products, clothing, dust or soil particles, food packaging, and plumbing and piping materials such as pipe thread tape, valves, gaskets, and some hoses and tubing.

As a precaution, all persons involved in sample collection should minimize exposure to the following products, ensure proper hand washing, and wear powderless nitrile gloves that are known to be PFAS-free.

- *On the day of sampling (preferably 24 hours prior to the event), minimize use of cosmetics, moisturizers, sun blocks, insect repellants, fragrances, creams, or other personal care products (including hair products), unless the products are known to be 100% natural.*
- *Other items that are likely to contain PFAS and should be avoided include:*
    - *Powdered nitrile gloves.*
    - *Pre-packaged food, fast food or items wrapped in aluminum foil.*
    - *New, unwashed clothing.*
    - *Clothing washed with chemically treated fabric softeners or dried with anti-static sheets.*

- *Synthetic water-resistant/or stain-resistant materials (such as waterproof clothing and shoes such as Gore-Tex®), waterproof or coated Tyvek® material (special attention to boots), or chemicals that provide UV protection or insect repulsion.*
- *Teflon® and other fluoropolymer containing materials.*
- *Waterproof /treated paper in field notebooks.*
- *Waterproof markers unless proven to be PFAS-free. Indelible pens that are ballpoint or gel and pencils are acceptable. Fine or ultra-fine Sharpies are also acceptable. Standard Sharpies are not.*
- *Adhesive paper products (such as Post-It® Notes or Scotch® tape).*
- *Sealable bags (e.g., Ziploc® plastic bags) that are not provided by the laboratory. (Note: only ultra-clean polypropylene or high-density polyethylene [HDPE] material sealable bags are allowed).*
- *Chemical ice or blue ice packs, unless provided by the approved laboratory and certified to be PFAS-free.*
- *Duct tape and electrical tape.*

The following additional considerations should be taken during sample collection to prevent contamination:

- *Only use laboratory-provided, HDPE sample bottles, with linerless HDPE or polypropylene screw caps.*
- *Attention should be given such that no dust or fibers fall into the HDPE sample bottle during collection.*
- *Never set the cap down, touch any part of the cap that contacts the bottle, or let anything touch the rim of the bottle or inside the cap.*
- *Use PFAS-free markers to label the empty sample bottle prior to or immediately after the sample collection. Make sure the cap is on the sample bottle and gloves are changed after sample bottle labeling. Allow the ink to dry completely before proceeding. Preprinted labels from the laboratory can also be used.*
- *Ensure that the interior of the cooler is clean.*
- *Ensure an adequate number of resealable PFAS-free bags are available. Preferably, these should be provided by the laboratory.*
- *Sampling equipment, such as dipper poles, dipper cups, tubing, etc. should be certified PFAS-free or tested for PFAS.*

Sampling Equipment and Decontamination

Samples should be collected using a telescoping dipper pole and a new, disposable dipper cup made of polypropylene. Prior to collecting the first sample, a FEB should be collected, as described in the QA/QC section above, by pouring laboratory-provided reagent over or into the sampling equipment and then decanting into the appropriate laboratory-provided sample containers.

When possible, single-use (disposable) field sampling equipment should be utilized. Non-disposable equipment, such as telescoping dipper pole, should be decontaminated after use at

each sample location using Alconox or Liquinox detergent or deionized water. Equipment should be thoroughly washed, rinsed, and wiped dry with paper towels and properly stored in clean containers such as cardboard containers, HDPE buckets, or LDPE bags before initial use and between sample locations.

Sampling Protocol

From each sample location (*please note that samples for PFOA and PFOS should be collected first, followed by samples for the other constituents*):

1. *Using the telescoping dipper pole and a new, disposable dipper cup, collect a sample for PFOA and PFOS, considering the precautions outlined in the PFAS Sampling Precautions and Best Practices section of this sampling plan. At least two unpreserved laboratory-provided PFAS-free HDPE sample bottles (one 125 mL bottle and one 500 mL bottle (or other size and quantity as determined by the laboratory) will be collected at each sample location for PFOA and PFOS.*
    - *Sample bottles for PFOA and PFOS should be double-bagged in PFAS-free resealable plastic bags and immediately placed in a clean cooler with sufficient wet ice, also double-bagged in PFAS-free resealable plastic bags.*
    - *Samples for PFOA and PFOS should be stored in a separate cooler from the samples for other constituents.*
2. Repeating the procedure with the telescoping dipper and dipper cup, collect a sample for VOCs. At least two laboratory-provided 40-ml VOC vials, preserved with hydrochloric acid, will be collected for each VOC sample. Care should be taken to collect the samples with zero headspace and without overfilling the vials and flushing out the preservative. Vials should be capped tightly after collection.
3. Repeating the procedure with the telescoping dipper and dipper cup, collect a sample for BNAs. At least two laboratory-provided unpreserved 1-liter amber glass jars will be collected for each BNA sample. The bottles should be filled completely and capped tightly after collection.
4. Repeating the procedure with the telescoping dipper and dipper cup, collect a sample for Carbonyl Compounds. At least one laboratory-provided unpreserved 1-liter amber glass jar will be collected for each Carbonyl Compounds sample. The bottle should be filled completely and capped tightly after collection.
5. Repeating the procedure with the telescoping dipper and dipper cup, collect a sample for Ammonia. One laboratory-provided 250 mL (or greater) polyethylene bottle, preserved with sulfuric acid, will be collected for each Ammonia sample. The bottle should be filled completely, taking care not to overfill and flush out the preservative, and capped tightly after collection.
6. All samples should be placed in a cooler with ice after collection.

Analytical Methods, Container Type, Preservation, and Holding Time

Analyte	Analytical Method	Container Type/Preservative	Holding Time
Ammonia	EPA Method 350.1	1 – 250 mL (or greater) polyethylene bottle, to pH < 2 with sulfuric acid Cool to ≤ 6 degrees C.	28 days
Purgeables (Volatile Organic Compounds – VOCs)	EPA Method 624.1	At least 2 – 40 mL glass vials, to pH < 2 with hydrochloric acid Cool to ≤ 6 degrees C	14 days
Base/Neutrals and Acids (BNA)	EPA Method 625.1	At least 2 – 1-liter amber glass jars - no preservative Cool to ≤ 6 degrees C	7 days to extraction, 40 days to analyze after extraction
Carbonyl Compounds*	EPA Method 8315A	At least 1 – 1-liter amber glass jar - no preservative Cool to ≤ 6 degrees C	3 days to extraction, 3 days to analyze after extraction
PFOA and PFOS	*Method 1633A*	*1 – 125 mL HDPE bottle and at least 1 - 500 mL (or smaller) HDPE bottle, with linerless HDPE or polyethylene screw caps* *Cool to ≤ 6 degrees C*	*28 days, extracts may be held for up to 90 days*

*Note: Cleaner Air Oregon carbonyl compounds suitable for aqueous testing are Acetaldehyde, Formaldehyde, Propionaldehyde, and Crotonaldehyde. These are the compounds which will be analyzed by GP Toledo in relation to this sampling plan.