DRAFT

Sampling and Analysis Plan:
Phosphorus and Nitrogen Atmospheric Deposition

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Introduction

In just the last few decades, atmospheric deposition of nutrients has been identified as a significant source of nutrients to lakes around the world. More recently, because of the location of Utah Lake, a tiny remnant of ancient Lake Bonneville, and surrounded by hundreds of square miles of remnant playa, agriculture or urbanized landscapes, Wasatch Front Water Quality Council scientists became interested in the contribution of nutrients contained in airborne particles and gases to the overall nitrogen and phosphorus budgets for Utah Lake. The National Atmospheric Deposition Program (NADP) has developed definitive protocols for determining wet deposition of ammonia and other nitrogen compounds. However, because of the variability in types and sources of dry deposition, similar protocols have not been suggested for dry deposition and particularly including that for nutrients. While NADP protocols have focused primarily on regional mobility and deposition of various elements and ammonia, this project is focused on the result of regional and local dusts to Utah Lake and their contribution to the Utah Lake nutrient budget. Moreover, dry deposition is generally considered to be of greater importance in arid regions because of normal dry conditions and lower precipitation, less ground cover, frequent local and regional winds and in the western US, remnant playas from ancient lake Bonneville. Furthermore, stream diversions/dewatering and climate change have exacerbated the mobility of dusts.

This document outlines the study design, the design and operation of the atmospheric deposition samplers, sample handling, laboratory protocols, health and safety concerns and data management.

Objectives

The primary objective of this atmospheric deposition project is to provide quantitative estimates of wet and dry deposition to the surface of Utah Lake. This includes:

1. Adopt National Atmospheric Deposition Program (NADP) protocols where possible for wet deposition while adapting various published protocols for determining dry deposition.

   In addition, two wet/dry samplers, including rain gages, will be obtained from N-CON Automatic Deposition Samplers, the official provider of AD samplers for the NADP. We will also join the NADP program to share data and utilize their laboratory for N and P analysis. One of these samplers will be collocated with one of our modified samplers (1.5-2 m height, installed insect screens, etc.) as well as one of our existing samplers with the original design specifications (i.e. 1 m height, no screen, etc.). This will provide a side-by-side comparison of the three sample designs. This will also provide a comparison between the samplers we have used for the last 3 years against our modified sampler and

the latest NADP design. In addition, we will have completely independent samples of ammonia, nitrate and orthophosphate for each sampling event.

2. Quantify combined local and regional sources of phosphorus and nitrogen, including urban traffic, construction, intense agricultural, as well as regional sources such as the dry lake bed of Sevier Lake.
3. Characterize the importance of insect and plant contamination by including a 500 um screen to prevent insects and other debris from contaminating AD samples and provide a comparison with unscreened (contaminated) samples. This will continue the estimate of annual variability using comparisons with data from the last three years.
4. Determine the decay rate of AD across Utah Lake. This will be accomplished by placing a sampler near the center of the lake.
5. Determine speciation of phosphorus in dusts from urban sources as well as those from the west and southwest deserts in terms of total P, dissolved P and soluble reactive P.

Sampler Design

The current samplers were built following earlier versions of the NADP design and placement of each sampler followed similar protocols established by the NADP (NADP, 2018), (Figures 1 and 2). The Farmington Bay site was chosen to have a control for deposition outside of the Utah Valley as well as to provide initial data for the Farmington Bay nutrient budget that is also being developed.

Each automated sampler consists of two polyethylene buckets on an elevated table with a moveable cover, shown in Figures 1 and 2. These buckets have a 23.5 cm diameter (opening= 0.0434 m^2) and are 35 cm tall. Movement of the cover is initiated by a moisture sensor. This moisture sensor is carefully calibrated to ensure that dew does not trigger the movement of the bucket cover. During dry periods, the cover shields the wet-deposition bucket, and when activated by rain or snow, the cover shifts to shield the dry deposition bucket and exposes the wet deposition bucket. Power for activation of the sensor and transfer of the cover between the wet and dry buckets is provided by a solar panel that maintains a charge on a 12 volt battery. The original design included attaching the solar panel support post to the table with the panel situated about 2 m above the table (Figure 1). However, with concerns over accumulating dust and rain splash potentially adding to the wet sample, we are in the process of reconfiguring this arrangement with the solar panel being placed approximately 5 m away from the table.

In addition, and because there is no current NADP design and protocol for dry deposition sampling, we will increase sample replication by adding three additional dry deposition buckets to the table surface. Thus, in the case that no rain occurs during the sample week, there will be four replicates of dry deposition. With multiple dry weeks expected, this will provide a statistical

measure of onsite variability in dry deposition measurements as part of our quality assurance program.

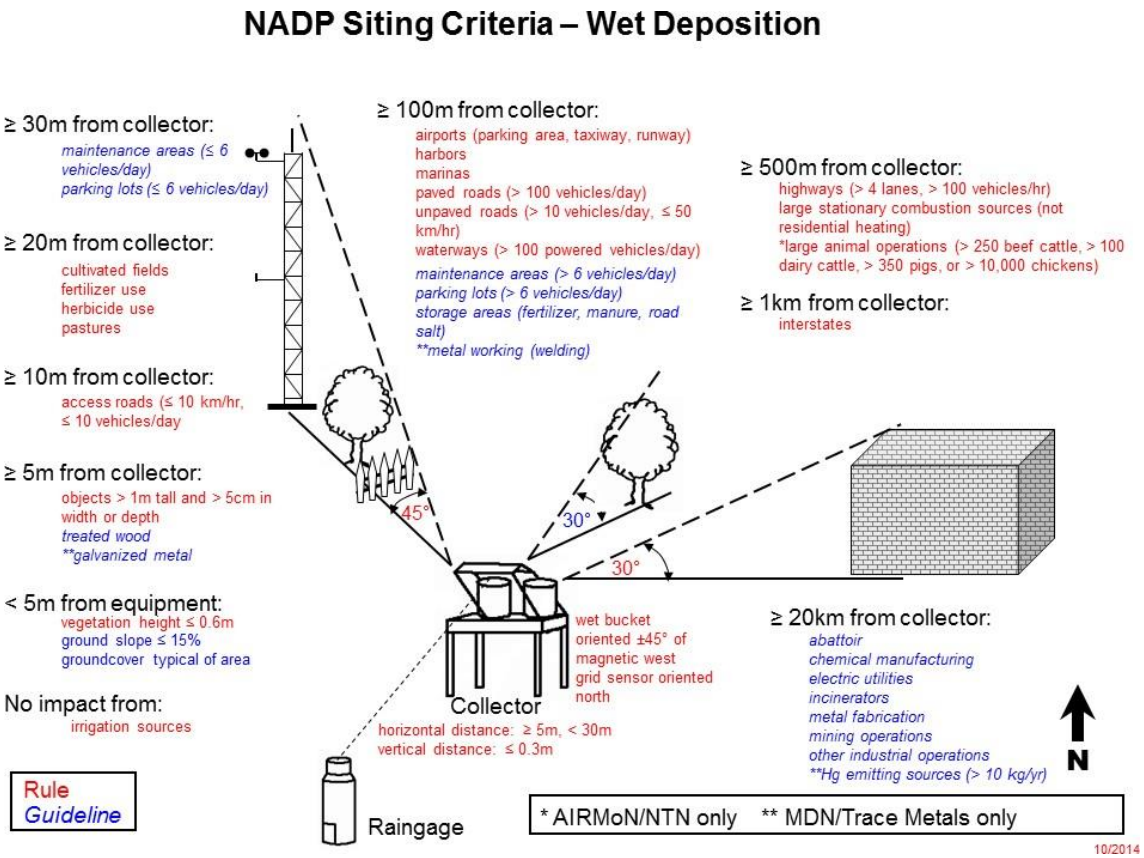

Figure 1. Diagram of sample collector apparatus including rules and guidelines included in the siting criteria for NADP sample sites. From NADP, 2018.

In addition, the table surface that supports the sampling buckets will be raised approximately ½ m so that the top of sampling buckets will be located 1.5 to 2 m above the ground surface. Additional modifications include: 1) fixing a vertical “splash guard” on the side of the cover to reduce rain drops from splashing and adding additional material to wet deposition sample; 2) Similarly, we are currently testing the efficacy of adding a loosely meshed material (Miner’s Moss©) for its ability to dampen the impact, and hence reduce the splash of raindrops, further reducing the potential contamination. If useful, this material will be fixed to the cover as well as to the splash guard and table surface that would be exposed to rain. 3) Heated moisture sensors will be installed. This will facilitate drying immediately at the completion of a rain event; hence closing the wet deposition cover immediately after the rain event – further limiting the potential for sample contamination; 4) A 500 um – mesh screen will be positioned within the dry side buckets near the surface of the water or about 10 cm from the bottom of bucket. These will

exclude unwanted debris such as insects, seeds and other plant parts. Screens will not be added to the wet side buckets. Experience has demonstrated that insect contamination during a rain event is rare, occurring in about 1 in 50 wet sample collections and includes only 1 – 2 insects when it does happen. Moreover, this is just as likely as that which occurs over the lake. Therefore, wet samples that contain insects will be noted on the sample label and chain of custody sheet that accompanies samples to the NADP lab. This notation will accompany all sample result reporting. 5) The solar panel will be placed 5 m from the table to avoid any splash contamination; 6) The samplers will be fitted with a bird repellant device to prevent birds from perching and contaminating the sampling buckets.

Samples are collected weekly from each location. To save time and to reduce the potential for contamination, the sampling buckets will be lined with plastic bags to reduced contamination and eliminate the need for extensive bucket cleaning. During the weekly sampling all buckets are replaced with clean ones. In order to emulate the adhering properties of a wet lake surface, the dry-deposition buckets at each site are pre-loaded with 3 L of deionized water (Anderson & Downing, 2006; Jassby et al., 1994). This volume of water was chosen as compromise between simulating water surface in the context of this standard sampling device while offering low evaporative loss and sample volume small enough to yield detectable concentrations and deposition rates.

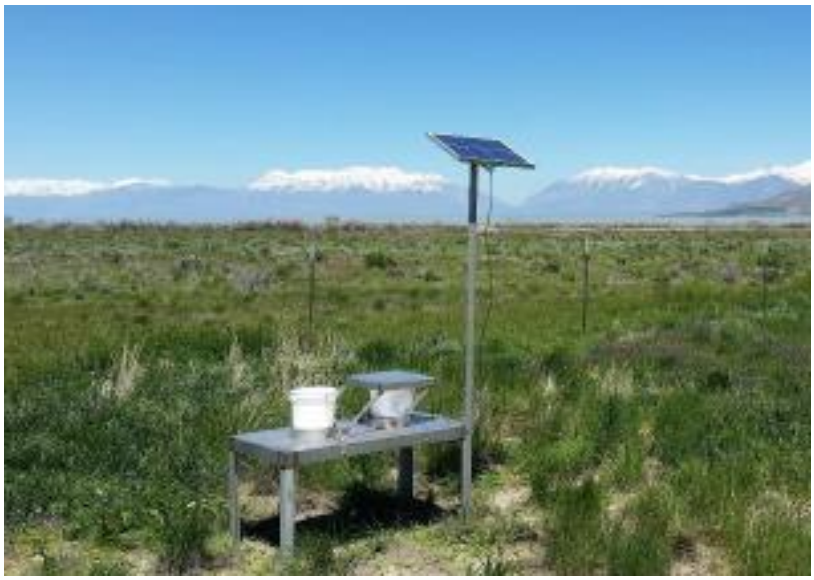

Figure 2: Automated Sampler at Mosida on May 4, 2017. The solar panel post will be situated 5 m from the table. The table surface will be modified to minimize the surface area exposed to splashing rain drops. The legs will be extended to position the top of the sample bucket at 2 m above the ground level and the table surface will be modified to minimize the surface area exposed to potential splash.

Sample Locations

Samplers are being placed at five sites around Utah Lake and at two sites near Farmington Bay.

Sample sites were selected with the goal of measuring AD from undisturbed, agricultural, rural and urban landscapes while still providing measurements from around the lake and which are very near the lake's edge (Figure 2). This is intended to provide the most accurate estimates of dust/nutrients that is reaching the lake surface. These locations are sites where historical AD data has been collected for three consecutive years.

Figure 3. Location of sample sites surrounding Utah Lake. The sampler at Saratoga Springs is currently missing but will be replaced.

The exact locations are:

Near the Orem POTW, UTM = 40.27595 N, -111.7372 W. This location is about 50 feet from a storage shed and about 20 ft from an unused asphalt road located west of the sampler. There is

a vacant field north of the sampler with little plant growth. The entire site is located within a light industrial area in Orem. The site is 110 meters from the edge of Utah Lake.

Lakeshore/Lincoln Point, UTM = 40.11291 N, -111.78893 W. Located on the southern edge of a property with light farm traffic. Site was relocated on August 18, 2018 to > 100 ft from that farm road. An open field lies to the south with light brush and there is a wetland just to the east. . The site is approximately 200 meters from the edge of Utah Lake.

Mosida, UTM = 40.07712 N,-111.92574 W. Surrounded by a large field with low-lying scattered brush. In 2017 it was located approximately 140 ft from the nearest road. On August 18, 2018 it was moved to a location 500 ft from that road and it is > 1100 ft from center pivot sprinkler irrigated fields, . The site is 750 meters from the edge of Utah Lake.

The southern edge of Saratoga Springs UTM = 40.28234 N, -111.8706 W. The southern outskirts of Saratoga Springs UTM = 40.28234 N, -111.8706 W, is located at the edge of a property (abandoned since late summer of 2018) approximately 500 ft from the highway. A small dirt road leading to the property is rarely used. There are small structures just over 50 ft away to the south, east and north. A large unused field borders the site on the south and west. This sampler was recently lost or destroyed as the property recently changed owners and apparently is being developed. The site is approximately 110 meters from the edge of Utah Lake but we may need to change the siting for this sampler.

The Jordan River Pump Station UTM = 40.35931 N, -111.8963 W. This is perhaps the least representative site for Utah Lake for “global” AD due to the thick phragmites beginning at about 10 m away on two sides. Small particles from the plants have occasionally been captured in the samples, although elevating the platform and addition of a screen should reduce contamination significantly. This will be one site where a sampler with the original design will be placed side by side with the new sampler design. The site is 10 meters from the edge of Utah Lake.

Sample Handling

The following is a step by step procedure with precautions for sample collection and handling.

Step 1. Approach sampler from the downwind direction. In the field notebook, record the location, arrival time to the site, how much rain was in the gauge, status of the electronics, bug and other contaminants on the table or in the screen, and other pertinent information Note the condition of the collection site and equipment. (i.e. equipment malfunction, weather conditions, signs of human activity and other relevant notes: (see Field Logbook section below). Ensure to not lean over the either sample bucket so that no human hair, clothing fibers, or other contaminants get in the sample.

Step 2. Put on latex gloves before working with the sample.

Step 3. For the dry side bucket, carefully lift the screen out and away from the bucket. With forceps, carefully remove all insect and plant debris from the screen and place in separate sampling jar. Appropriately label this jar (see sample labeling and containers below).

Step 4. Replace screen into dry side bucket. Use a small, acid-rinsed brush and approximately 100 mL DI water, delivered using a squirt bottle (measure actual amount used), to lightly scrub and rinse the screen and sides of the plastic bag – allowing this rinse water to add to the water sample remaining in the bucket. This dust, etc. in this rinse water is retained in the sample because it contains any true deposition material that may have adhered to the screen or side of the sample bag. The screen is then removed from the sample bag and bucket to prevent any damage to the sample bag during further handling and transport to the lab.

Step 5. Seal and properly label the plastic bags and retain in the sampling bucket to prevent damage during transport and secure an acid washed, DI-rinsed lid over the buckets.

Step 6. For the wet side bucket, if a precipitation event has occurred since the last sampling event, proceed to sealing and labeling the sample. Screens are not used in the wet side buckets because bug contamination is minimal during a rain event and this design more-exactly emulate the NADP samplers. Therefore, the screen and bag rinsing step is not required.

Step 7. Wash the table top, bucket cover, debris screens, and all other equipment near the sampling buckets with phosphorus-free detergent and rinsed with DI water to reduce contamination during future weather events.

Step 8. Put on new pair of latex gloves. Place a new plastic bag into clean sampling buckets and place 3 L distilled water in the dry side bucket and reposition the screen. Secure buckets in proper position.

Step 9. place a drop of water on the rain sensor to assure the collector will open to the other side, followed by allowing it to dry and close the wet side bucket.

Step 10. At the lab, the NADP samples are packaged and shipped according to NADP instructions.

Step 11. At the lab the screen and sampling buckets are washed with phosphorus-free detergent, rinsed with DI and stored in clean plastic bags in preparation for the next week's sampling event.

Health and Safety

The potential for hazardous conditions exists during any field activities. A hazard analysis and Health and Safety Plan (HSP) has been prepared for all field activities associated with the South Davis Sewer District staff and WFWQC field technicians (SDSD employees). The objective is for the field sampling team to discuss planned activities, identify potential safety hazards (specific activities and potential water and chemical hazards) and determine a plan to mitigate those hazards. While possible hazards include accessing water and working in and around open water, the field sampling team has experience assessing all hazards and will address them in the context of the HSP before going to the field. All staff involved with field sampling activities will follow the HSP. Precautions and hazards include, but are not limited to:

1. Health risk awareness, appropriate planning, following safety procedures is critical. Sampling teams will be aware of hazards such as heat exhaustion and dehydration and will be

equipped with safety equipment such as extra drinking water, first aid kits, cell phones, sunscreen, hats, chest waders, neoprene or latex gloves, insect repellant, etc.

2. Sampling will be performed in and around open water, possibly involving the use of boats or kayaks. Sampling personnel should not wade into water deeper than waist-high. If water is deeper than waist-high, a boat or kayak shall be used to perform sampling. Sampling personnel always work in groups of two, at a minimum, when obtaining samples and wear all appropriate safety gear, including a personal flotation device (PFD) when using a boat or kayak. All boats should be equipped with safety equipment such as PFDs, oars, air horn, etc. and staff will always possess cell phones. The sampling team shall follow all Utah boating laws and rules.
3. During and after sample collection, personnel will wear PPE gloves, keep their hands away from their eye and mouth areas and always wash their hands with soap and water after sampling. Field personnel will be careful to avoid contact with preservatives such as acids, Lugol's and alcohol or dry ice. Rinse skin with water if minor skin contact occurs or seek medical attention if preservatives are consumed, contact eyes or skin irritation occurs.
4. Staff will be watchful for sharp objects, such as broken glass, and should not pick up suspicious objects. Take care while walking; running water, barbed wire, large rocks, and slippery mud will likely be encountered.
5. Appropriate clothing will be worn; preferably wide-brimmed hats, long sleeved shirts and full-length pants. Dehydration, sun exposure, insect stings are potential hazards.

Field Logbook

Field activities will be documented in a bound field logbook, which is dedicated to this project. The field logbook will be water-resistant, the pages will be sequentially numbered, and all entries will be made in indelible ink. Each page of the field logbook will be dated and signed by the person making the entry. Field notes will contain all pertinent information about sampling activities, site conditions, field equipment and methods used, times of placement and retrieval of sample bags and which ones contained debris or other types of contamination, general observations, and other pertinent technical information. Examples of typical field entries include the following:

- Date and time of sampling
- Name of personnel present
- Exact location and duration/distance that each type of equipment was used
- Referenced sampling location description (in relation to a stationary landmark), GPS coordinates, and maps
- Daily temperature, wind and other climatic conditions
- Field measurements, activities, and observations
- Types of sample containers used
- Sample identification and cross-referencing with containers/buckets

- Types of analyses to be performed
- Site sketches/ any changes to site configuration
- Visitors to the site

Additional Sampling to Characterize Insect Contribution

There is much controversy surrounding the presence of insects in the samples, whether they should be included in the sample, the degree of depuration/leaching of nutrients into the sample and how they could be prevented/screened from the sample without upsetting air flow patterns in the sample bucket and allowing remobilization of dust which has entered to bucket. While we think this has only minimal effect on the wet deposition samples (i.e. very seldom find even one insect), insect contamination in the dry deposition samples is common. While inserting screens into the dry side bucket will minimize this potential contamination, in the past, any insects or plant debris present in samples were removed before sample processing.

To this end we will perform some experiments to characterize the importance of insects:

Nutrient content of insects

Three measures of nutrient content of insects and their potential for adding to the phosphorus content in the samples will be performed.

1. An additional dry deposition sample bucket will be deployed, without the screen), at each sample site for two to three weeks. On a daily basis the number of insects in the sample will be noted, their basic taxonomy (at least to order) and a 200 mL aliquot will be removed and preserved for P and N (ammonia and NO3) analysis. This is intended to emulate the effect of accumulating insects over the weekly interval and provide an estimate of nutrient loss from insects. The sampling period is extended beyond the typical one-week sampling period to measure changes in actual depuration rates. At the conclusion, the insects will be collected, dried, weighed and analyzed for nutrient content. This will provide for a mass balance measurement between insect weight and nutrient loss, the addition of nutrients to the sample from nutrients leaching from the carcasses and natural dry deposition rates (obtained from the normal dry deposition sampler, which serves as control in this experiment).
2. Similarly, a sample of insects will be collected near each sample site using sweep nets. Approximately 100 insects (1 g) will be collected and identified. Wet weight will be recorded followed by submersing the sample in 3 L of water. A 200 mL aliquot will be removed each day to track the loss of N and P to the water sample. A second sample of approximately 100 insects (1 g) will be weighed (wet weight), then dried (@ 70 C for at least 24 hours, reweighed and digested to determine total P per mg wet and dry weight,
3. The insects and plant debris retrieved from the screens in the dry side buckets will be sorted according to plant and animal material, weighed and identified to lowest taxonomic

level possible. This will provide a weekly measured of contamination to the dry side bucket and also a comparison with the results of steps 1 and 2.

These experiments are intended to provide insight into the actual degree of insect "contamination" to the samples.

Field Quality Control

The tubs, table tops, funnels, bottles, buckets, and all equipment in contact with the samples are cleaned with phosphorus-free detergent, acid-washed with 10% HCl solution, and kept in plastic bags until they are used for sample collection. Each batch of deionized water added to samplers is analyzed along with the deposition samples and this serves as a field blank. Contaminated samples are removed from analysis. For this exercise, contaminated samples are described as overlapped samples (dry buckets that collected some rainwater; a combination of wet and dry deposition sample due to sampler malfunction), samples with contaminants (bird droppings, obvious algal growth, insect or plant debris). In the case where the sampling interval has exceeded 7 days, nitrogen measurements will be removed from analysis. Only data from non-contaminated samples are used for all deposition calculations and concentration data.

That said, we are currently designing a protocol whereby contributions by insects or plant debris (whether considered contamination or not) can be accounted for (See Contamination section).

Clearly, measurements aimed at providing estimates of dry deposition are controversial and remains the subject of much debate – so much so that the NADP itself has been unable to agree on standard methods or equipment. Moreover, placement of wet and dry samplers in a manner that surrounds a particular lake in question is nearly unprecedented. Therefore, particular attention to QA/QC procedures is warranted and should be carefully documented. Table 1 summarizes these procedures. Typically, the NADP analyzes for ortho-P but does not perform the digestion for total phosphorus measurement. We are currently in discussion with NADP to perform this additional analysis to complete our analytical spectrum.

Table 1. Summary of specific measurements and practices aimed at minimizing and quantifying potential sample contamination and onsite variability during sample collection and handling.

Type of Measurement	How often	Number	Reason	Analytes	Number expected for project year
Glove contamination	Each lot	2 per	Check for contamination	Total N, total P	20
Field cleaning water for dilution	weekly	1			40
DI water for cleaning	weekly	1			
Dry deposition replicates	weekly	3	Determine within site variability of dry deposition mass		50
Collocated NADP Samples	Weekly at two sites	1	Check of method versus national network	Total N, ortho-phosphate	75
Bags	2 per lot		Blank for contamination		5
Loss to bags	Monthly	2	Loss to bag walls		10

Labeling and containers for samples

These atmospheric deposition samples are in aqueous solution (collected as rain or as particulates and aerosols accumulated in the distilled water provided in the dry deposition side) and will be collected directly into new clean plastic bags that have been inserted into the collection buckets. The plastic bags will be sealed but will be retained in the pre-labeled sampling buckets to prevent damage during transport to the lab.

Self-adhesive sample labels will be provided and affixed to each plastic bag and bucket. This may be done by the sampling team or the laboratory. These sample labels will be completed using indelible ink and will include the following information:

- Project name
- Sample identification number
- Location identification (site description or UTM coordinates)
- Date and time of sample collection (added in field)
- Sampler's initials (added in field)
- Analyses requested

Sample labels will be affixed to the sample containers and covered with clear tape.

Laboratory Procedures

Currently, the samples are analyzed in BYU's Environmental Analytics Lab. Analysis includes total P, soluble reactive P, total dissolved P, and dissolved organic P.

Upon arrival at the Water Lab, gather fourteen 500-milliliter plastic bottles, purchased from the Eyring Science Center Stores.

Label each bottle with the date, time, location and type of sample (wet, dry, or bulk)

Always wear latex gloves while handling samples. For each new lot of gloves, one pair will be soaked in 10% HCL to extract any N or P contamination. This sample will be analyzed with the run to identify any N or P contamination.

For sample retrieval, place each sample bucket in a lab sink and remove the sample bucket lid carefully.

Using a graduated cylinder, measure 500 mL from the sample bag and place in labeled 500 mL lab sample bottle. Using the graduated cylinder measure and note in the field notebook the remaining volume in the "dry" sample bucket.

The precipitation (wet) bucket is then retrieved. If there is enough water to make a sample that the Environmental Lab can test (200 mL), proceed with scrubbing and rinsing the sample bag. Pour sample into the appropriately labeled 500-mL bottle.

The volume is noted and the sample is ready for additional processing. If there is not enough precipitation in the bucket, use a measured amount of deionized water hose to spray the sides of the bag and the screen to collect any dust/phosphorus that may have stuck to the bucket wall. After spraying a sufficient amount (generally 100 mL), add additional DI water, if nnecssary, to dilute to 200 mL. Measure using a graduated cylinder, record the volume and pour into a sample bottle.

Repeat until all samples are processed, ensuring that the graduated cylinder and screen is rinsed between each sample.

Cleaning

Note: put on a lab coat, safety goggles and latex gloves.

Following sample removal, the buckets are washed and prepared for the next week of sampling. Because new sample bags will be inserted into the buckets, cleaning of buckets will only require washing with phosphorus-free detergent and a DI water rinse. The sink in the Water Lab is filled with warm tap water mixed with phosphate-removing soap. Each bucket is immersed and scrubbed with a variety of bristle brushes to remove all remaining contaminants inside and outside the buckets. The same procedure is followed for the lids. After drying, the buckets are placed in clean plastic bags for transport to the field.

Quality assurance/quality control procedures

1. Field Blanks on the DI water. For each week's sampling event, an acid-washed and DI rinsed 2- gallon container is filled with DI water for replacement of the 3 L of water that is placed in the dry deposition buckets. At one of the sites that is visited, a 200 mL sample of this DI water will be collected during the time when the 3 L aliquot is added to the bucket. This sample will serve as a field blank.
2. Blank plastic bag sample. At least once each month or each new lot, one of the new plastic insert bags will be rinsed with approximately 1 L DI water. The DI water will be saved and analyzed for total P, nitrate and ammonia.
3. QA in the Lab
    a. Perform Method Detection Limit procedure at least once each month or as required by analytical method.
    b. A standard curve is prepared for each analyte for each sample analytical run
    c. An instrument blank, standard or spiked sample is analyzed every 10 sample
    d. Calibration standards MDL and MRL and spike/recovery results are reported for each sampling run.

The attached appendices describe the laboratory procedures for these different fractions.

References

NADP. 2018. NADP site selection and installation manual. Version 3.0.

Anderson, K. A., and Downing, J. A. (2006). "Dry and wet atmospheric deposition of nitrogen, phosphorus and silicon in an agricultural region." Water, Air, & Soil Pollution, 176(1), 351-374.

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Appendix I

Soluble Reactive Phosphorous (SRP or DRP)

Additional PPE: gloves

Reagents:

Reagent A:

1. Dissolve 0.2908 g of antimony potassium tartrate in 100 ml of Milli-Q water.
2. Dissolve 12 g of ammonium molybdate in 250 ml of Milli-Q water.
3. Make 1000 ml of 5 N H_2SO_4 by adding 141 ml of concentrated H_2SO_4 to Milli-Q water and bringing to a volume of 1 liter.
4. Add these three solutions together and bring to a volume of 2000 ml with Milli-Q water. Store in a Pyrex bottle in a dark, cool place.

Reagent B: This solution needs to be made fresh immediately before use.

ml Reagent A	g Ascorbic acid
50	0.264
100	0.528
200	1.056
250	1.320

Procedure:

1. Fill a 20-25 mL syringe with sample
    - Sample bottles should be shaken before/during syringe filling so as to collect a representative sample (especially if sample contains sediments)
    - Make sure there are no air bubbles in the syringe once filled
2. Attach a 0.45 µm membrane filter to the syringe
3. Filter 10.0 mL of sample into a clean tube
    - Use the 60 tube racks for the ICP/Lachat
4. Add 1.0 mL of combined reagent (Reagent B)
5. Add the green/silicone stoppers to all the tubes, and invert samples 4 times.
6. Wait 10-15 minutes for color to develop.
    - Do not wait more than 30 minutes
7. Invert samples twice right before measuring
8. Measure absorbance on the spectrophotometer at 880 nm
    - Use the pure water with reagent as the calibration/process blank

Notes

- Samples should be at room temperature before analysis.
- Use Milli-Q water for the process blank.
- Syringes and tubes should all be acid-washed with HCL
- Calculation curve created using standards at 0, 0.02, 0.025, 0.04, 0.05, 0.06, 0.08, 0.10, 0.20, 0.50,

2.0, 5.0 ppm PO4-P

Source: Pote, D.H., Daniel, T.C. 2005. Dissolved Phosphorus in Water Samples. In: Methods for Phosphorus Analysis, Kovar and Pierzynski (eds).

Appendix II

Nitrate and Ammonium Analysis by Lachat

Sample Preparation:

1. Fill a 20-25 mL syringe with sample
    - Sample bottles should be shaken before/during syringe filling so as to collect a representative sample (especially if sample contains sediments)
    - Make sure there are no air bubbles in the syringe once filled
2. Attach a 0.45 µm membrane filter to the syringe
3. Filter 10.0 mL of sample into a clean tube
    - Use the 60 tube racks for the ICP/Lachat

Analysis (Lachat QuickChem 8500):

Ammonium:

1. Prepare standards of 2, 1, 0.5, 0.1, 0.05, 0 ppm NH_4-N. Use Milli-Q water to dilute the standards.
2. Prepare sodium hypochlorite solution: In a 200 ml volumetric flask, add 100 ml 5.25 % sodium hypochlorite (NaOCl) and dilute to the mark with Milli-Q water. Invert to mix.
3. Ensure the ammonium manifold is installed. Move tubes to appropriate reagents and check for flow (See Lachat instructions for details).
4. Analyze samples using the 'Ammonium low' method.

Nitrate:

Prepare standards of 2,1,0.5,0.1,0.05, 0 ppm NO_3-N. Use Milli-Q water to dilute the standards.

1. Ensure the nitrate manifold is installed. Move tubes to ppropriate reagents and

check for flow (See Lachat instructions for details) .

2. Analyze samples using the 'Nitrate low' method.

Method sources:

Flow injection analysis is used to determine nitrate-N and ammonium-N (QuickChem 8500, Lachat Instruments, Loveland, CO). The concentration of NO_3-N is determined using the cadmium reduction method (Keeney & Nelson, 1982), and the concentration of NH_4-N is determined by the sodium salicylate-sodium nitroprusside method (Rowland, 1983).

D.R., and D.W. Nelson. Nitrogen - Inorganic forms. pp. 643-698. *In*: A.L. Page (ed.), Methods of Soil Analysis Part 2. 1982. American Society of Agronomy, Inc. Madison, WI.

Rowland, A.P. (1983). An automated method for the determination of ammonium-N in ecological materials. Commun. Soil Sci. Plant Anal. 14:49–63.

Appendix III

Total Dissolved Phosphorus

Additional:

PPE gloves

Procedure

Sample Preparation:

1. Fill a 20-25 mL syringe with sample
    - Sample bottles should be shaken before/during syringe filling so as to collect a representative sample (especially if sample contains sediments)
    - Make sure there are no air bubbles in the syringe once filled
2. Attach a 0.45 µm membrane filter to the syringe
3. Filter 10.0 mL of sample into a clean tube
    - Use the 60 tube racks for the ICP/Lachat

Analysis:

Run samples on ICP-OES under the 'Phosphorus' method (iCAP 7400, Thermo Scientific, Madison, WI). Phosphorus is determined at 178.2 nm.

Appendix IV

Total Phosphorus
(Water)

Additional PPE: gloves, goggles, chemical

apron Reagents:

Nitric Acid, 69.6% (concentrated)

Hydrogen peroxide, 50%

Batch size: 24: 22 samples, 1 standard, 1

blank Procedure:

Set up:

1. Shake sample vigorously. Use a syringe to pull out 20 ml of sample. Record the ml and tube number for each sample on the datasheet. Be sure to include a known check (0.1 ppm P, tube 1) and a process blank (last tube).

2. Place in a white Teflon vessel.

3. Add 2 ml nitric acid (1 pump from the repipette).

4. Add 1 ml hydrogen peroxide (1 pump from the repipette, this is stored in the fridge).

5. Using the reshaping tool, recondition the white Teflon cap.

6. Place the Teflon cap on the vessel, and make sure that it fits well.

7. Place the vessel inside the safety shield (brown).

8. Tighten the safety valve (lid) by hand.

For the sample in tube 1 (reference vessel).

- Do not put the safety valve on yet.
- Place the thermowell into the Teflon cap.

9. Once you have completed this for all samples, place the carousel lid in place above the samples.

10. Take the samples to the microwave.

For the sample in tube 1 (reference vessel).

- Slide the ATC sensor through the safety valve (make sure the valve does not have a TFM foil in it).
- Slide the ATC sensor through a TFM foil.
- Place the sensor into the thermowell and tighten the safety valve.

Instrument (Milestone Ethos EZ Microwave Digestor):

1. Place the rotor inside the microwave and ensure that it locks into place.

2. Plug in the jumper of the ATC sensor.

3. Place exhaust tube in fume hood.

4. Turn on the microwave.

5. Login.

6. Go to program, select “epa.2”.

7. Press start.

8. Check on the temperature profile about every 20 minutes to make sure it is working properly.

9. The run should take about an hour. When the temperature is 40°C or lower, the samples can be removed from the microwave.

Sample transfer:

1. Collect the following items:

    - Purple centrifuge rack
    - Small distilled water wash bottle
    - 2 L 10% Nitric acid bath
    - Pressure release tool
    - Vessel removing tool
    - Washable marker

2. Retrieve the carousel containing samples from the microwave digester and place in the fume hood.

3. Number the centrifuge tubes using the washable marker.

4. Working inside the hood, use the pressure relief tool to release excess pressure from the safety valve.

5. Carefully remove the safety valve from the first brown safety shield.

6. Using the vessel removing tool, pop the vessel out of the shield by lining up one of the two holes in the bottom of the shield with the two projections in the tool and pressing down.

7. Remove the white Teflon cap from the vessel.

8. Using distilled water, quantitatively transfer the contents of the vessel to the corresponding centrifuge tube.

9. Dilute the sample up to the 25 ml mark on the centrifuge tube, also mark the dilution on the sample sheet.

10. Cap the tube and invert it 3 times. Repeat with remaining samples.

Analysis:

Run samples on ICP-OES under the 'Phosphorus' method (iCAP 7400, Thermo Scientific, Madison, WI).

Clean up:

1. Place white Teflon vessels and caps in a 10% Nitric acid bath (let sit for 30 minutes- 1 hour).

2. Rinse the white Teflon vessels and caps with DI water.

3. Rinse safety shields and safety valves with DI water be sure to tap additional water out of safety valves.

4. Return sample carousel to the microwave digester.