Wood Buffalo Environmental Association

**Program Description**

# Denuder Program

*Last Updated: November 2025*

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# Program Overview

The Annular Denuder and Filter Pack (Denuder) sampling program is a part of a collection of integrated monitoring programs operated by the WBEA Deposition (DEP) monitoring group (formerly the Terrestrial Environmental Effects Monitoring [TEEM] group). The Denuder program provides measurements of key atmospheric pollutants in remote areas around the Regional Municipality of Wood Buffalo. The monitoring network aims to accurately determine the spatial and temporal distribution of atmospheric pollutants for air quality and deposition modeling and evaluation of ecosystem responses.

The Denuder program was established to address specific monitoring questions:

- Can uncertainty in regional passive air measurements be reduced?
- Can nitric acid (HNO3) and ammonia (NH3) concentrations be continuously measured–and deposition concentrations inferred–using these systems?
- Can additional components of pollution–specifically particulate matter (PM) and sulphur dioxide (SO2)—be measured without compromising HNO3 and NH3 data?

*(adapted from Edgerton, 2015)*

## Sampling Environment

Denuders are placed either on a 30-m tower or on a tripod.

At tower sites (Figure 1), the Denuder is installed so that the sample inlet is positioned approximately 5 meters above the canopy and offset 1 meter from the tower. A winch and pulley system allows the sampler to be lowered to the ground for monthly sample changeouts.

Denuders are placed on tripods for two main reasons: (1) instalment of a tower at that location is not possible, or (2) it is co-location at an ambient Air Monitoring Station (AMS). At AMS locations (Figure 2), Denuders are mounted on a tripod on an elevated sampling deck so that the sample inlets are positioned approximately 3 meters above the ground surface. At other tripod locations not at AMS sites, the Denuder is placed on a tripod in an open area. The tripod is placed on a wood deck at ground level.

*Figure 1. Denuder sampler (left) and an aerial photo of a MET tower site (right). The aerial photo shows the Denuder suspended in the air adjacent to the right side of the tower.*

*Figure 2. Photo of four Denuder samplers at BGFM (AMS01) in March 2021. Two samplers are mounted back-to-back on each tripod for colocation comparison purposes.*

## History

Below is a timeline of major network developments.

- 2013 – Frist five samplers constructed by Atmospheric Research and Analytics. These were deployed by BioSynch at four locations. Samplers integrated with MET towers at sites 1004 (co-located), 1007, 2001, and 2013
- 2014 - Winch systems added to lower samplers for media changeout
- 2015 - Testing of dual-stage filter for PM analysis using the second sampler at site 1004
- 2017 - Dual-stage filter for PM analysis added to all sites, testing of sodium carbonate coated denuder for $SO_2$ capture using the second sampler at site 1004
- 2018 - All samplers upgraded (datalogger added), contract laboratory transitioned from ARA to DRI, two new samplers built for sampling colocation prior to lab transition.
- 2020 - Sampler added to site STMT
- 2021 – Six additional samplers constructed for network expansion to 3011 and 3016, and for a colocation study at three sites in preparation for lab transition from DRI to WBEA ASG.
- 2022 – Pulley system upgrades to sites: 2001, 2013, 3011, 3016 (safer design)
- 2023
    - Pulley system upgrades to sites: 1004, 1007 (safer design)
    - Pump upgrade from T2-03 Micro Diaphragm Pump / #T3CP-1HE-04-2SEB to T2-03 Micro Diaphragm Pump / #T3CP-1HE-04-1SNB. This is to achieve the desired particulate matter size of 2.5 micron within the sharp cut cyclone.
    - Introduction of metering needle valve to control pump flow rate
    - Retrofit / Redesign: both the pump and the flowmeter, which both have a temperature dependence, are housed in a small, heated enclosure located beneath the datalogger. The heating routine turns the heater on if the enclosure temperature falls below a given value (currently 5C). The datalogger is capable of running the pump, flowmeter, and heater, this simplifies things within the enclosure immensely.
    - New sites established and deployed to include greater network coverage: 1002, 1023, 2005, 3009
    - Site establishment at 3017 as part of expansion – deployment TBD
    - Addition of sulphur dioxide ($SO_2$) annular denuder tube to collect better quantitative data (trial began in September)
- 2024 – Removal of needle valve from redesign to allow unrestricted pump flow rate. There were variances found in the denuder flow rate via the data logger and Alicat flow meter. Removal of the needle valve allowed for less resistance leading to flow meter.
- 2025 – Addition of denuder at site 3017.

# Equipment Details

## Sampler Description

The annular denuder and filter pack sampling system is based on the USEPA Compendium Method IO4.2, a proven annular denuder technology for the determination of gasses and fine particles (<2.5 µm). The samplers are custom-built for low power consumption so they can be operated in remote locations without access to grid power.

The components of the sampling unit can be grouped into four sub-systems: the flow system (pump and plumbing), the sampling media, the data acquisition system (datalogger and telemetry), and the power system. Sampler components are housed within a weatherproof enclosure (fiberglass, 12”x14”x6”), with the inlet protruding from the bottom of the enclosure (Figure 3). A detailed list of parts is provided in the WBEA SOP (2023).

In 2023, the system was upgraded to a new, simplified design (Figure 4). The old design (Figure 4) was more crowded in the housing.

## Flow System

A micro-diaphragm pump (controlled at 0.91 liters per minute flow) draws ambient air through the sampling media where pollutants of interest are retained. A flow sensor positioned after the sample media measures the sampling rate. The known sampling rate allows for the accurate calculation of sample volume, an improvement over passive sampling methodologies typically used in remote environments that rely on empirically derived sampling rates.

The pump is housed within a small, thermostatically controlled enclosure inside the sampler enclosure which keeps the pump warm and allows the sampler to operate throughout the year in a range of ambient temperatures (-35 to +35 deg C). The pump is replaced in each sampler on an annual basis, usually concurrent with other fall maintenance activities (MET sensor changeouts) so that each sampler has a low-hour pump entering the winter sampling period.

The flow sensor is calibrated against an external flow calibrator device (Alicat FP-25) prior to installation and on an annual basis. The relationship between the flow sensor output voltage and the flow rate is represented by a multiplier that must be updated in the datalogger program after each calibration. Typically, the flow sensor is calibrated at the WBEA Center using a rebuilt pump enclosure assembly (pump, heater, thermostat) and new plumbing (all plumbing after the sample media train), and the entire suite of components is replaced in the field.

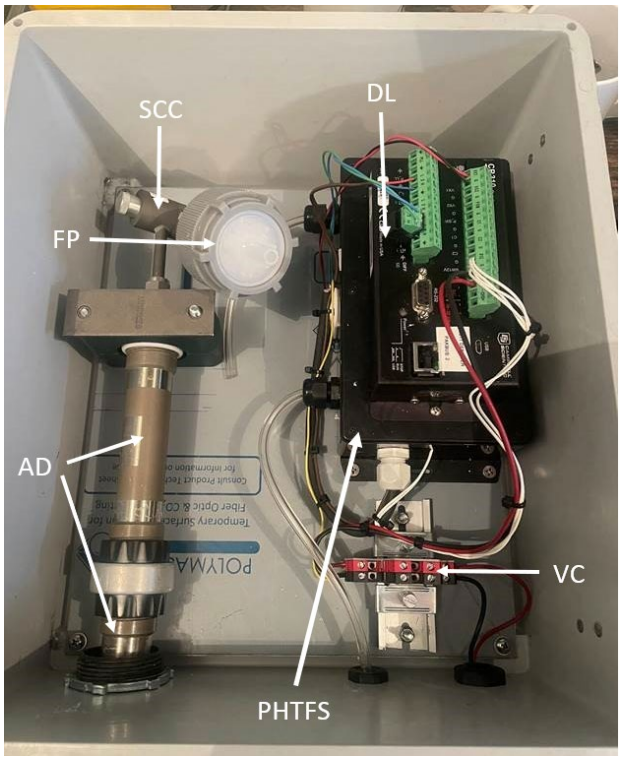


*Figure 3 - Inside the upgraded Denuder sampler enclosure. Components labeled clockwise from top left: sharp-cut cyclone (SCC), datalogger (DL), voltage converter (VC), pump-heater-thermostat-flow sensor assembly (PHTFS), annular denuders (AD), and filter pack (FP).*

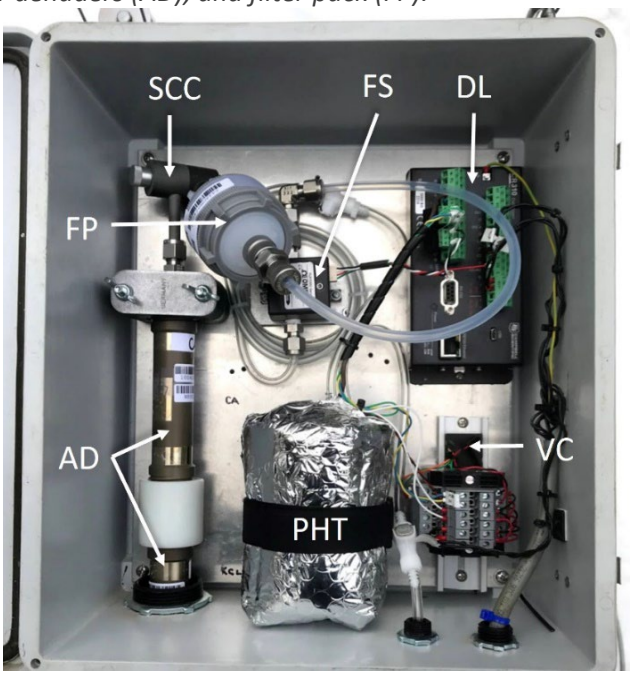


*Figure 4 - Inside the old version of the Denuder sampler enclosure. Components labeled clockwise from top left: sharp-cut cyclone (SCC), flow sensor (FS) datalogger (DL), voltage converter (VC), pump-heater-thermostat (PHT), annular denuders (AD), and filter pack (FP).*

## Sampling Media

The sampling media train is plumbed in series (connected consecutively) and consists of:

- a 150mm annular denuder coated with citric acid for the capture of gaseous ammonia,
- a 150mm annular denuder coated with potassium chloride for the capture of gaseous nitric acid,
- a sharp-cut cyclone for exclusion of particles > 2.5 microns [µm], and
- a dual-stage filter pack for the capture of particles ≤ 2.5 µm with:
    - a Teflon filter for particulate nitrate, sulfate, ammonium, and trace metals, and
    - a nylon filter for capture particulate nitrate that is lost from the Teflon filter

In 2023, a 150 mm annular denuder coated with sodium carbonate for the capture of gaseous sulphur dioxide was trialed to ensure that adding a denuder to the sampling train would not impact the other samples. The trial was inconclusive and the WBEA maintained the two-denuder system.

The sharp-cut cyclone is not currently extracted and analyzed. Sampling media details are located below in Table 1.

*Table 1. Target analytes from sampling media currently processed (adapted from WBEA SOP)*

| Media | Target Analyte |
|---|---|
| Annular Denuder – coated with citric acid ($C_6H_8O_7$) | Ammonium ($NH_4^+$), some nitrate ($NO_3^-$) is also captured |
| Annular Denuder – coated with potassium chloride (KCl) | $NO_3^-$, some $NH_4^+$ is also captured |
| Dual Stage Filter Pack – Teflon Filter | Particulate $NO_3^-$, Sulfate ($SO_4^{2-}$), $NH_4^+$, Trace Elements |
| Dual Stage Filter Pack – Nylon Filter | Particulate $NO_3^-$ |

Sampling media is prepared and packaged by the laboratory, deployed, and retrieved by WBEA staff or contractors, and returned to the laboratory for analysis. See Appendix 1 for a list of analytes analyzed for by WBEA Analytical Services Group (ASG) laboratory for denuders. Media is typically deployed for one-month period and other monitoring activities (PAS and IER sampling, MET maintenance, or troubleshooting) are typically scheduled concurrently with media changeouts.

Field blanks are collected at the time of changeout by deploying and collecting a set of media in a sampler while leaving the pump powered off. Field blank media is stored on-site, capped, and contained in the plastic bag, for the sampling period and returned to the lab with the sampled media.

The annular denuders are extracted with ASTM Type I ultra-pure water and extracts are analyzed by ion chromatography (IC) for nitrate ($NO_3^-$), ammonium ($NH_4^+$), and sulfate ($SO_4^{2-}$) for the determination of nitric acid ($HNO_3$), ammonia ($NH_3$), and sulfur dioxide ($SO_2$) respectively.

The Teflon filter is cut in half with ceramic scissors. One-half is extracted with deionized (DI) and the extract is analyzed for ions by IC. The other half is subjected to microwave-assisted extraction in an acid-peroxide cocktail and is analyzed by dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICPMS) for the determination of trace elements.

The entire nylon filter is extracted with deionized water and the extract is analyzed for $NO_3^-$.

From program kickoff in summer 2013 to March 2018, sampling media was prepared and analyzed by the laboratory staff at Atmospheric Research and Analytics (ARA). Media preparation and analysis was contracted to Desert Research Institute laboratory (DRI) when the ARA laboratory closed in 2018.

In summer 2021, a co-located sampling project was initiated in preparation of Denuder analyses to be moved in-house to the WBEA ASG Lab. Media prepared by each laboratory was deployed at 3 sites across the deposition gradient (Site 1004, BGFM, and STMT) to ensure alignment of results among laboratories. Please refer to WBEA Project Plan 049-2021 for project details including a timeline and site-specific sampling details. In 2022, the WBEA ASG laboratory began to take full responsibility of DEN media preparation and analyses. By 2023, all Denuder media preparations and analyses were conducted in house.

## Data Acquisition

The data acquisition system consists of a Campbell Scientific datalogger (CR310 or CR310-Cell205) that records flow data and sampler diagnostics (pump temperature and supply voltages). The first version of the sampler (2013) relied on the datalogger of the host station for recording flow rates, but a sampler redesign in 2018 incorporated the small CR310 which has improved data reliability and allowed for monitoring of sampler diagnostics.

There are various options for telemetry connection for automated data collection and remote monitoring of flow rates and diagnostics. Existing field installations rely on the host station modem for telemetry. At MET tower sites the Denuders are connected to the modem through the host station datalogger by a Tx/Rx configuration of the C terminals on both loggers. At AMS sites the Denuders are connected to the modem through Wi-Fi bridges. At the denuder sites established from 2023 and onward, a CR310-Cell205 datalogger is used for telemetry. A CR310-Cell205 datalogger has a built in SIM card option and does not require an additional modem.

There are currently no documents that outline steps for networking DEN samplers with existing station telemetry; however, those technical details can be found within the datalogger programming and LoggerNet Setup on the Q9 server.

## Power Systems

Denuders operate on 12 VDC power systems. The datalogger is powered with 12V directly from the power distribution terminals inside the sampler. The flow module is powered with 12V from

the SW12V channel on the datalogger. A DC-DC converter within the sampling unit supplies the micro-diaphragm pump with the required 5 VDC.

All tower stations have a dedicated solar power system for the Denuders, separate from the telemetry power system and main datalogger and sensor system. The Denuder power system consists of a solar array (mounted to the solar tower), battery bank, and solar charge controller.

At AMS sites, the Denuders are connected to line power through a receptacle on the sampling deck and an AC-DC converter that converts the grid-supplied 120V AC to 12V DC.

## Timeline of Activities

- Data checks – done remotely, 2 times per week
- Monthly changeouts -
    - Confirm the sampler is operating properly at time of arrival
    - Confirm flow rates using Alicat
    - Retrieve sampling media from previous month
    - Deploy sampling media for the current month (and any field blanks) and verify that all connections are tight
    - Confirm the sampler is operating properly prior to departure
    - Replace the pump assembly, flow module, and plumbing in each sampler and update the multiplier within each datalogger program, as needed
- Ad-hoc site visits - to troubleshoot and resolve any emergent issues
- At the WBEA Center throughout the year
    - Rebuild pump enclosure assembly by installing a new pump and replacing the heater or thermostat, if necessary
    - Rebuild the flow module assembly with new plumbing from sample media train to pump enclosure, if necessary
    - Calibrate the flow module with the new pump and plumbing

# Appendix 1

List of analytes WBEA ASG laboratory reports:

Ions

| | | | | |
|---|---|---|---|---|
| Ammonium | Calcium | Chloride | Fluoride | Magnesium |
| Phosphate | Potassium | Nitrate | Sodium | Sulphate |

Elements

| | | | | |
|---|---|---|---|---|
| Ag (silver) | Co (cobalt) | Mn (manganese) | Pr (praseodymium) | Sr (strontium) |
| Al (aluminum) | Cr (chromium) | Mo (molybdenum) | Pt (platinum) | Ta (tantalum) |
| As (arsenic) | Cs (cesium) | Na (sodium) | Rb (rubidium) | Th (thorium) |
| Ba (barium) | Cu (copper) | Nb (niobium) | S (sulphur) | Ti (titanium) |
| Be (beryllium) | Fe (iron) | Nd (neodymium) | Sb (antimony) | Tl (thallium) |
| Bi (bismuth) | K (potassium) | Ni (nickel) | Se (selenium) | U (uranium) |
| Ca (calcium) | La (lanthanum) | P (phosphorus) | Si (silicon) | V (vanadium) |
| Cd (cadmium) | Li (lithium) | Pb (lead) | Sm (samarium) | W (tungsten) |
| Ce (cerium) | Mg (magnesium) | Pd (palladium) | Sn (tin) | Zn (zinc) |