# Scope

This document describes the details of operation, methodology, assembly and modification of a denuder-based relaxed eddy accumulation (REA) system.

# Principle of Operation

Relaxed eddy accumulation is a sampling method which is conceptually similar to methods such as eddy covariance, disjunct eddy covariance and eddy accumulation. The system evaluates micrometeorological data to conditionally sample ascending or descending air parcels into one of two denuders. Denuders are advantageous because slow-response equipment is permissible for analysis and samples can be stored prior to analysis. After a sampling run, the amount of compound trapped in up and down parcels is evaluated; the mass difference and micrometeorological data are used in conjunction to determine an overall flux.

Because of variability in eddy velocity and compound concentration, a composite sample proportioned upon actual eddy velocity would be desirable. However, the sampling rate of this system is too high to make gathering a sample in this manner possible. The term ‘relaxed’ indicates the sampling rate is chosen independently from the instantaneous vertical eddy velocity *w*. The vertical flux estimate *F* is then determined by an empirical coefficient *β*, the standard deviation of vertical wind velocity σw and the difference in mean concentrations between ascending c+ and descending c- samples (Businger & Oncley, 1990). In most situations, the coefficient *β* is roughly 0.6. Over-bars denote a mean quantity.

The mean concentration of each sample depends upon the total sampling duration *t*, mass collected in the up *m*+ and down *m*- reservoirs, up *f*+ and down *f*- sample flow rates, and the fraction of total time duration in which up *α*+ and down *α*- sampling occurs (Baum and Ham, 2007). Expressing the flux in terms of these known quantities:

The quantities in the above equation are determined from micrometeorological data gathered by the data logger and from a mass analysis of the denuders for the desired compound.

# Applicability to Ammonia

Ammonia (NH3) is a naturally occurring compound and important source of nitrogen for living systems. At high concentrations, however, NH3 becomes a public health and environmental nuisance: high exposure levels irritate or even burn skin, eyes and respiratory tissues[[1]](#footnote-1), deposition and runoff contribute to soil & water body eutrophication[[2]](#footnote-2),[[3]](#footnote-3), and it promotes fine particulate matter (PM2.5) formation[[4]](#footnote-4),[[5]](#footnote-5). Further, volatilization of NH3 from applied fertilizers reduces the nitrogen available to crops[[6]](#footnote-6).

A significant proportion of NH3 emissions originate from agricultural fields treated with NH3-based fertilizers and from waste produced within confined animal feeding operations (CAFOs). Quantifying NH3 emissions from land sources such as these will substantially contribute to the overall understanding of ammonia’s behavior in the atmosphere. Such knowledge is needed as a basis for addressing the challenges above through regulatory changes and/or modifications in agricultural practices.

Direct measures of NH3 fluxes are hindered by a lack of fast-response instrumentation and by ammonia’s reactive nature. The use of honeycomb denuders to trap gaseous NH3 satisfies the need for slow-response analytical techniques since extraction and analysis can occur at a later place and time. To ensure only gaseous NH3 is collected, the system draws samples at a fairly consistent, relatively high flow rate so liquid and particulate forms diffuse too slowly and become trapped in a filter pack. Sampling directly into the denuders minimizes possible losses due to NH3 adsorption on sampling lines. The precautions in design were made considering NH3 but should improve the quality of sampling for any gaseous compound.

# Usage Procedures

## Sampling Site Setup

The sampling site must be equipped with a 120vAC power source capable of providing up to 8A during typical operation and up to 20A for pump start-up. Additional instruments such as laptops or separate weather monitoring instruments will increase the power requirements.

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| **CSAT3 Sonic Anemometer [Sensor Head]**   1. Position the horizontal arm in the channel on top of the Bosch square tube so the sensor head mounting bolt is accessible at the end of the boom. Secure the horizontal arm using U-bolts. 2. Mount the sensor head to the horizontal arm and finger-tighten the bolt underneath the block. 3. Rotate the sensor head so when the boom is mounted on the tower, the predominant wind direction is into the sensors. Adjust for terrain as well, if necessary:    1. For flat level terrain, level the block using the bubble level located on top of the block.    2. For sloping terrain, adjust the block so the top block surface is parallel to the terrain. 4. Secure the lower bolt with a 9/16” wrench. |
| **Denuder Mounting Plate**   1. Secure the T-nuts on the back of the denuder mounting plate in a channel on the anticipated wind-ward side of the Bosch tubing. 2. Locate the denuder mounting plate relatively close to the sonic. A distance of ≤1 ft is recommended. 3. Secure the mounting plate by tightening the hex bolts holding the T-nuts. |

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| **Boom (Bosch tubing) Mounting**   1. Orient the boom so the instruments, particularly the sonic anemometer, are facing into the predominant wind direction. If the anemometer sensor head is not adequately oriented upwind, it should be adjusted before mounting the boom. 2. Ensure the denuders are safely within reach to facilitate swapping cartridges. 3. Attach the boom securely to the tower using straps, clamps, U-bolts or another robust method. |

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| **CSAT Sonic Anemometer [Cable Box]**   1. Mount the anemometer electronics box securely to the tower near the boom. 2. Connect the cable from the anemometer sensors to the *Transducer Head* input. 3. Connect the dual gray cables from the data logger field box to the *+12V SDM* input of the electronics box. |

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| **Sampling Valves**   1. The sampling valves on the denuder mounting plate connect to the data logger using the cable shown at right. 2. The white fitting connects inside the data logger field housing. 3. The bulkhead fitting connects to the denuder mounting plate |

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| **HMP45AC Temp/RH Sensor**   1. Remove the split nut on the bottom of the radiation shield. 2. Remove the protective yellow cap on the sensor and insert fully into the split nut. 3. Screw the split nut into the shield and tighten. 4. Affix the radiation shield mounting bracket to a tower leg using the supplied U-bolt. Position so the upper half of the radiation shield is roughly the same elevation as the boom. 5. The sensor is hard-wired into the data logger but if wiring is necessary, refer to Components Description & Assembly. |

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| **Sampling Tubing**   1. Make the following connections from the pump box:    1. DOWN-INLET to ‘down’ denuder    2. UP-INLET to ‘up’ denuder    3. DOWN-OUTLET to field box DOWN-INLET    4. UP-OUTLET to field box UP-INLET 2. Make these connections from the field box:    1. DOWN-OUTLET to ‘down’ valve COM port    2. UP-OUTLET to ‘up’ valve COM port    3. PURGE GAS to zero air tank 3. Connect exhaust tubes to the NC ports of the ‘up’ and ‘down’ valves and route away from the sampling inlets. |

## Data logger program setup

The data logger program file ends in *.cr5* and is editable either in LoggerNet or in MS Notepad. If another program is used, ensure the file remains text-only. The variables below should be reviewed and edited for each new sampling position. Short descriptions are included in the program file too.

1. FLUX\_INTERVAL: Specifies how frequently covariance & flux data are calculated and saved; also used to calculate necessary reserved space for data tables. Default value: **30**
2. NUM\_DAY\_CPU: Specify how many days worth of data should be stored in the data logger unit. Default value: **1**
3. NUM\_DAY\_CRD: If the data logger is equipped with a card, specify how many days of data should be stored on the card; enter **0** if no card is present.
4. CSAT3\_ AZIMUTH: Describe the orientation of the sonic sensor head by compass azimuth where north is 0, increasing clockwise (E=90, S=180, W=270 or -90). The program will normalize any negative values.
5. zm: Enter the height (meters) of the sampling inlets above the measured surface.
6. zo: Enter the surface roughness length (meters).
7. x\_east\_max: Enter the distance from tower to longitudinal, eastern sampling boundary (m).
8. x\_south\_max: Enter the distance from tower to lateral, southern sampling boundary (m).
9. x\_west\_max: Enter the distance from tower to longitudinal, western sampling boundary (m).
10. x\_north\_max: Enter the distance from tower to lateral, northern sampling boundary (m).
11. wdir\_min: Specify the lower boundary of the sampling wedge, as described by compass azimuth. Range: **0-359** Default: **0**
12. wdir\_max: Specify the upper boundary of the sampling wedge, as described by compass azimuth. Range: **1-360** Default: **360**

The numerical and hard-wired constants are listed immediately after the user-defined constants but editing these is not advised since they are not site-dependent and some constants are critical to proper data collection.

## Field verification prior to sampling run

* include any procedures which may need to be performed for calibration
* provide checklist of things to verify before running for data
* clearing out old/test data and initializing system
* what to watch for when monitoring a data run
* why & how to end a data run

## Denuder preparation

*Originally from PILS Manual, Appendix 26: Inorganic Vapors Denuder Rejuvenation Procedures*

For collection of acids (nitric, nitrite, sulfur dioxide, acetate, HCl, formic and oxalic acid) one recommended coating solution contains 2% sodium carbonate in solution of:

500mL deionized water

20mL glycerol

750mL methanol

For collection of bases (ammomia), phosphoric acid is substituted for sodium carbonate.

1. Prepare the appropriate solution and obtain four solid denuder end caps.
2. Ensure denuders & end caps are clean and dry.
3. Place one end cap on each denuder.
4. Add 50mL of the appropriate coating solution to the denuder and secure an end cap over the remaining end of each denuder.
5. Rotate for one minute before removing & properly disposing of excess liquid.
6. Allow denuder to dry under clean laminar flow hood or use dry, filtered, chemically-scrubbed air to induce drying.

## Denuder extraction

*Originally from PILS Manual, Appendix 26: Inorganic Vapors Denuder Rejuvenation Procedures*

1. Obtain four clean & dry solid denuder end caps.
2. Place one end cap on each denuder.
3. Fill each denuder with MQ water before securing the other cap and rotate such that water reaches all the inside surfaces; roughly 30 times over 1 minute;

removal of denuders from instrumentation

procedures for transportation/storage

how to extract the captured ammonia

any intermediate preparation steps prior to…

performing ion chromatography (instructions for)

descriptions/instructions of other wet chemistry analytical techniques

## Storage & maintenance

* which if any instruments should be disconnected
* checklist for storage hoods/containers/etc
* maintenance associated with components
  + annual pump diaphragm maint
  + periodic replacement of tubing?
  + scheduled calibrations of included equipment

# Components List & Descriptions

This system is composed of the following components. A full breakdown of denuder parts is on the following page. Serial numbers are available in the appendices.

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| **Qty** | **Component** | **Part Name/#** | **Manufacturer** |
| **1** | 3D sonic anemometer | CSAT3 | Campbell Scientific; Logan, UT |
| **1** | LI-7500 |  |  |
| **1** | Barometric pressure transmitter | PTA-427 A | Campbell Scientific; Logan, UT |
| **1** | Temp & relative humidity probe | HMP45AC | Vaisala (Vendor: Campbell Sci. ) |
| **1** | Tank containing ‘zero’ air |  |  |
| **1** | Dual-head gas diaphragm pump | R221-AT-AA1 | Air Dimensions Deerfield Beach, FL |
| **4** | Electropolished stainless steel cans used as ballasts |  |  |
| **2** | Three-way 12V solenoid valves (VAC-100 PSIG, DC 12V) | 091-0094-900 | Parker Hannifin Corp.  Cleveland, OH |
| **2** | PTFE inlet tees | K-31320-35 | Cole Parmer; Vernon Hills, IL |
| **2** | Quick-disconnect denuder fitting | K-31404-09 | Cole Parmer; Vernon Hills, IL |
| **2-4** | Honeycomb denuder cartridges | ChemComb 3500 \*see next page | Thermo Scientific Waltham, MA |
| **1** | 4-channel relay rack | G4PB4R | Opto 22; Temecula, CA |
| **1** | Bipolar +/-15V power supply | REL110-2005 | Astrodyne; Mansfield, MA |
| **1** | External 13.8V power supply |  |  |
| **1** | Solid state relay for pump, 120VAC | 120D10 | Opto 22; Temecula, CA |
| **1** | Field housing case with 12V fan |  |  |
| **1** | Fast-response data logger | CR5000 | Campbell Scientific; Logan, UT |
| **2** | Mass flow controllers, 0-10 sLPM | AFCS-010001  (AFC26S-VADN5-C0/air) | Aalborg  Orangeburg, NY |
| **1** | Mass flow controller, 0-5 sLPM | FC-260 | Millipore (Tylan General)  Allen, TX |
| **1** | Two-way NC 12V solenoid valve | C-01367-70 | Cole Parmer; Vernon Hills, IL |
| **1** | Mounting tripod & arms |  |  |
| **-** | Misc. “Swagelok” fittings |  |  |
| **-** | 3/8” tubing |  |  |
| **-** | 1/4" tubing |  |  |

Each ChemComb 3500 denuder is composed of the following parts:

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| **Qty** | **Component** | **Thermo Part #** | **Quantity per cartridge** |
| **1** | Inlet Cap | 30-006127 | 1 |
| **1** | PM2.5 inlet, 10L/min, PTFE | 55-006038-T100 | 1 |
| **1** | Impactor plate | 55-006040 | 1 |
| **1** | Long length housing | 55-008909 | 1 |
| **3** | Glass stand-off | 24-006041 | 1-5\* |
| **5** | Spacer | 36-006042 | 5 |
| **2** | Honeycomb denuder, glass | 55-006171 | 2-4\* |
| **1** | Spring | 30-006044 | 1 |
| **3** | 47mm filter stage assm, Teflon | 55-006169 | 3 |
| **1** | 47mm filter holder, thread exit | 36-006048 | 1 |
| **1** | Filter holder housing (outlet) | 55-006049-0004 | 1 |
| **1** | Male fitting for thread exit | 32-003178 | 1 |
| **1** | Outlet plug | 30-006128 | 1 |

\*holds 5 total: *X* denuders (up to 4) and [5 minus *X*] glass stand-offs

1. (Agency for Toxic Substances and Disease Registry, 2004) [↑](#footnote-ref-1)
2. (Doorn & Natschke, 2002) [↑](#footnote-ref-2)
3. (U.S. Environmental Protection Agency, 2007) [↑](#footnote-ref-3)
4. (Krauter, Potter, & Klooster, 2003) [↑](#footnote-ref-4)
5. (Sharma, Kishore, Tripathi, & Behera, 2007) [↑](#footnote-ref-5)
6. (Zhu, Pattey, & Desjardins, 2000) [↑](#footnote-ref-6)