# Ammonia Measurements From the NSF/NCAR C-130 Research Aircraft Using a TILDAS Spectrometer with Active Passivation During the WE-CAN Field Campaign

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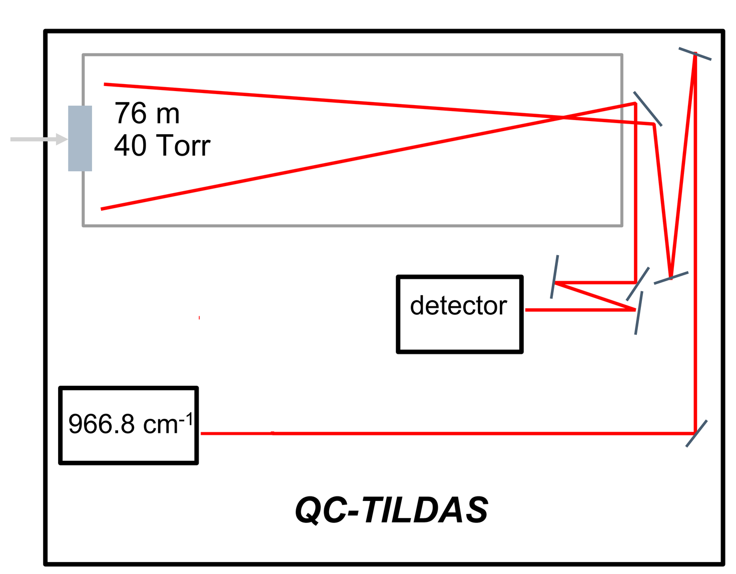
## Introduction

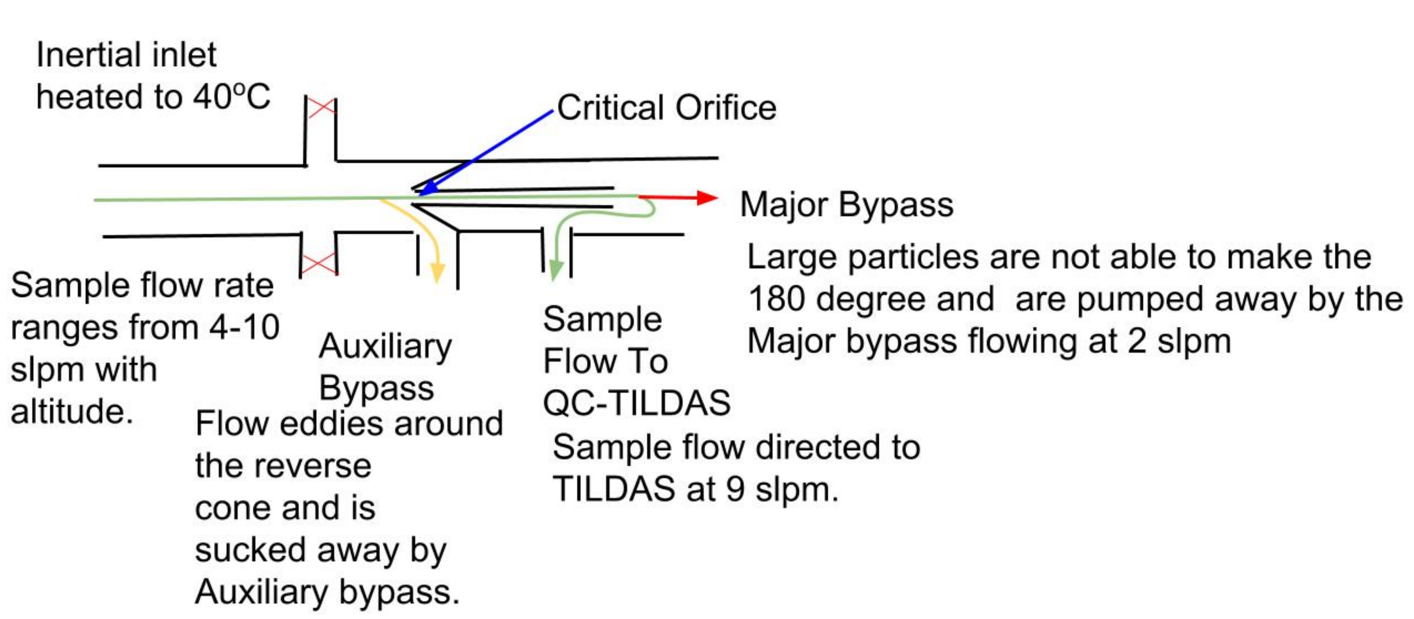
The Western Wildfire Experiment for Cloud Chemistry Aerosol Absorption and Nitrogen (WECAN) is an aircraft campaign focused on measuring the emissions of wildfire smoke in the western U.S. WE-CAN deployed an extensive suite of instrumentation on the NSF/NCAR C-130, and the aircraft was based in Boise, ID for two months during summer 2018. Ammonia ($NH_3$) is a key molecule to measure in order to understand nitrogen chemistry in wildfires. $NH_3$ was measured on the aircraft using a quantum cascade tunable infrared laser direct absorption spectrometer from Aerodyne Research (QC-TILDAS) optimized for use on the C-130. The large dipole moment of $NH_3$ is a basis for its notorious ability to interact with polar molecules on sampling surfaces. This "stickiness' increases instrument time response and can compromise rapid in-situ measurements. To mitigate this 'stickiness', several methods were implemented during WECAN to improve or maintain a sufficient time response. These included: 1) using a heated aircraft inlet block and an inertial inlet, 2) operating with a high sample flow rate (>10 slpm) and 3) employing active continuous passivation of sampling surfaces with 1H,1H-perflourooctylamine. This molecule is a strong perfluorinated base that prevents adsorption of water and other basic species allowing $NH_3$ to easily flow through the inlet to the TILDAS detector. Here, we report on how those techniques were integrated into the instrument system and their benefits with respect to in-situ sampling of $NH_3$ during WE-CAN. $NH_3$ measured with and without passivant addition are compared and contrasted.

## Instrument configuration for flight

The detector is a QC-TILDAS trace gas monitor from Aerodyne Research Inc. This instrument employs direct absorption spectroscopy in the infrared (~967 cm$^{-1}$) to measure $NH_3$. The optical path length of the spectrometer is 76 m. The optical cell is typically held at a constant pressure of 40 Torr and a constant temperature of 300 K.

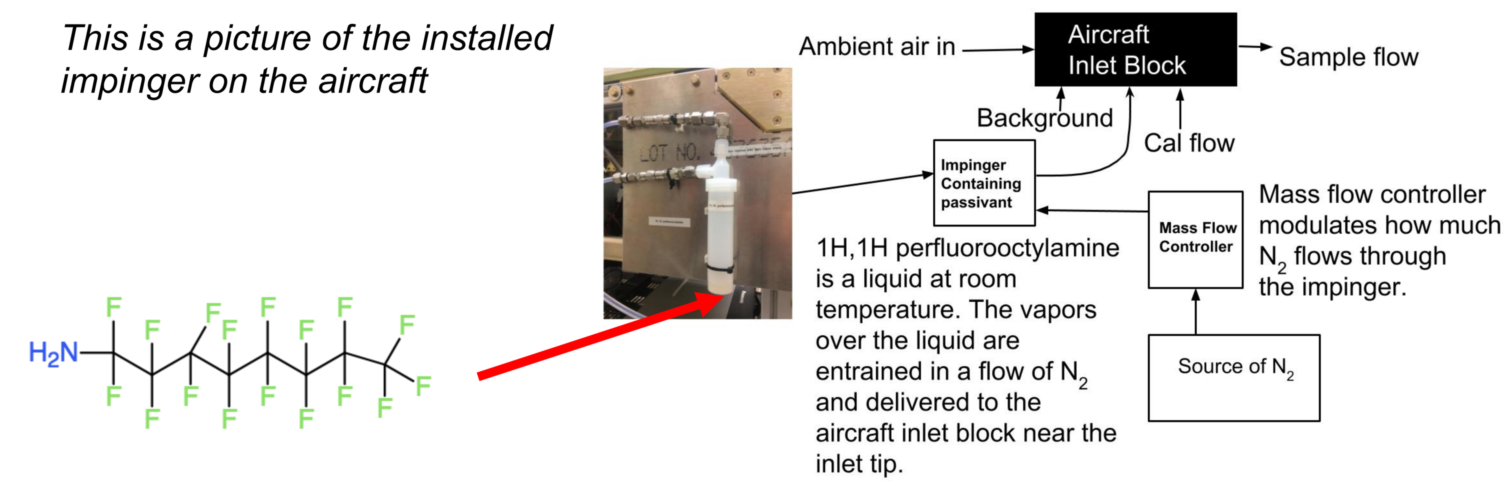



### Inertial Inlet allows for filter-less separation of aerosols from the sample stream




Thermal decomposition of ammonium species (e.g. $NH_4NO_3$) could result in a measurable gas phase $NH_3$ signal. Inertial inlet can efficiently separate particles with sizes greater than 300 nm without a filter. Particulate species involving $NH_4^+$ typically range from 100 μm and 1 μm in size. Thus, we expect these particles to be sufficiently filtered by the inertial inlet.

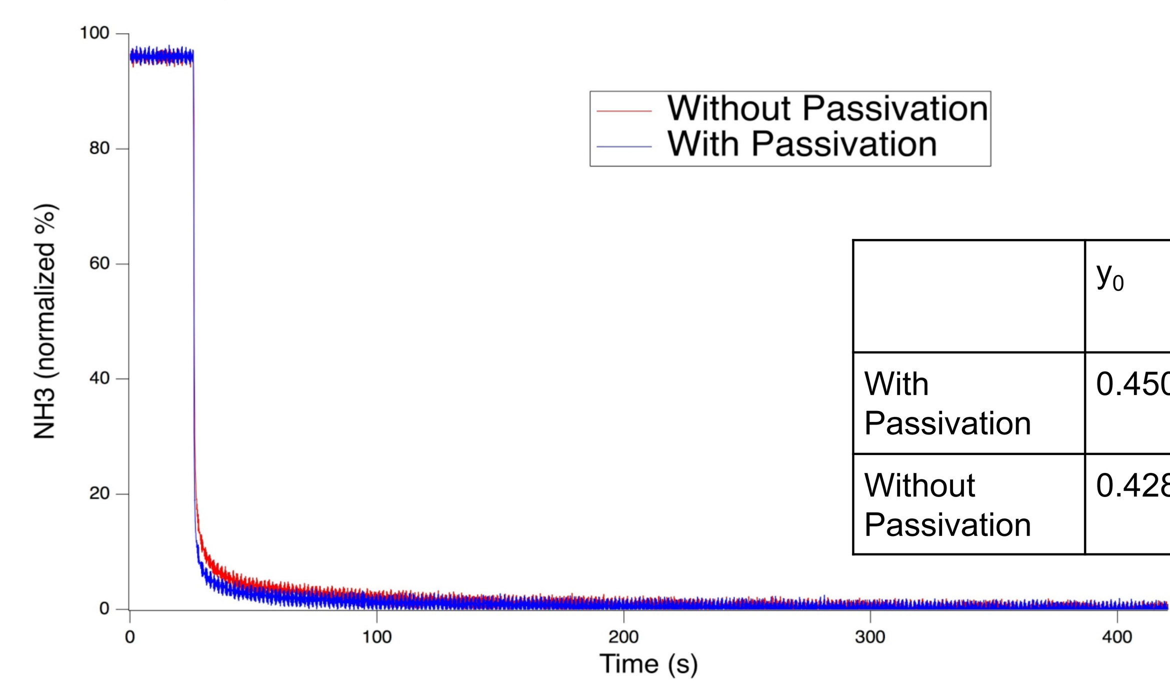
## Active Continuous Passivation with a Strong Base Improves Time Response




1H,1H-Perflourooctylamine is injected directly into the sample stream as close as possible to the inlet tip. The amine group sticks to water and other basic species adsorbed to sampling surfaces and presents a nonpolar tail to other molecules (like $NH_3$) in the ambient sample stream. The passivant coating prevents further adsorption of water and $NH_3$, and thus allows $NH_3$ in an ambient air sample to pass through without sticking.

A double exponential decay function of the form, $NH_3(t) = y_0 + A_1 * e^{-(t-t_0)/\tau_1} + A_2 * e^{-(t-t_0)/\tau_2}$, is used to quantify instrument time response. This equation represents the $NH_3$ mixing ratio (in ppbv) as a function of time (in seconds) and contains two time constants ($\tau$1 and $\tau$2) that represent two contributing factors to the time response. $\tau$1 is typically smaller and represents the gas exchange rate through the instrument flow path. $\tau$2 is typically larger and is related to the stickiness of $NH_3$ on sampling surfaces.

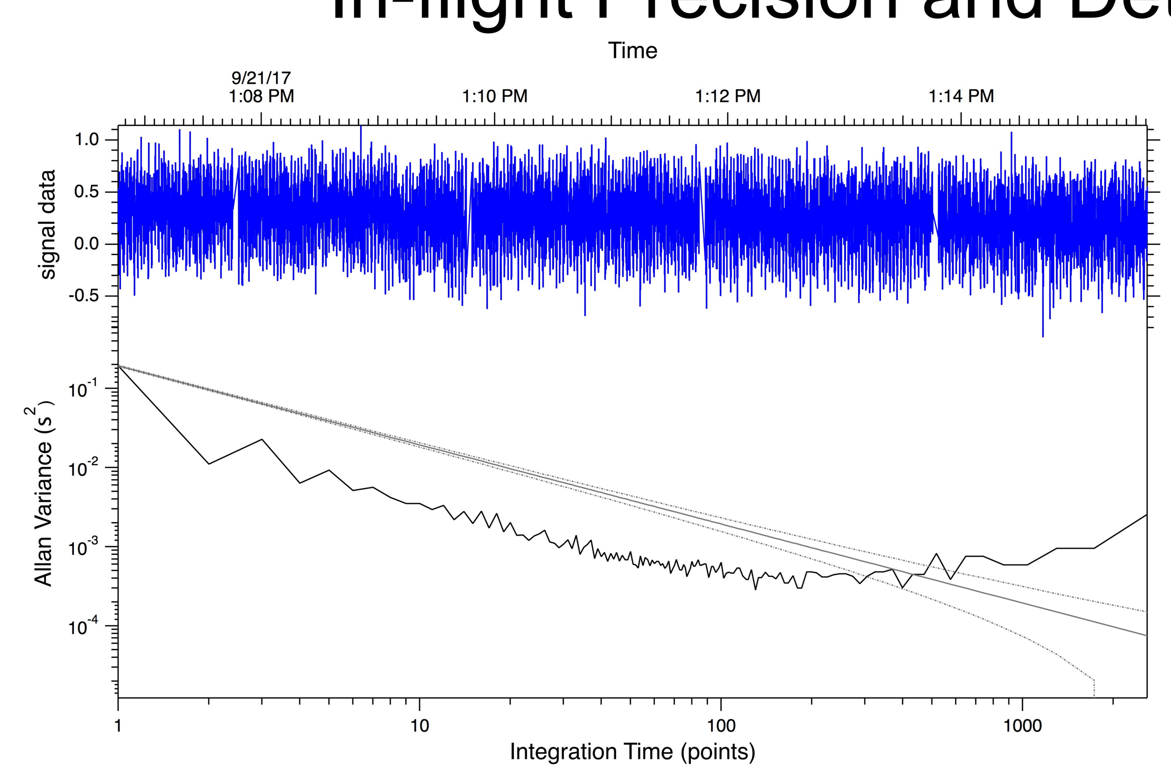
Time response profiles are created at 10 Hz data collection rate by turning the calibration gas off while overblowing the inlet tip with $NH_3$-free air. As shown below, when sample surfaces are relatively clean, passivant only results in a small improvement in time response.




**Coefficient Values**

| | $y_0$ | $A_1$ | $\tau_1$ | $A_2$ | $\tau_2$ | D ($A_2$/($A_1$+$A_2$)) |
|---|---|---|---|---|---|---|
| With Passivation | 0.450 | 104 | 0.662 | 8.17 | 41.2 | 0.0728 |
| Without Passivation | 0.428 | 104 | 0.663 | 8.14 | 41.8 | 0.0726 |

## In-flight Precision and Detection Limit




**Calculated precision and detection limit for 1 Hz and 10 Hz acquisition**

| | |
|---|---|
| 1 Hz Precision | 0.0594 ppb |
| 1 Hz Detection Limit | 0.178 ppb |
| 10 Hz Precision | 0.440 ppb |
| 10 Hz Detection Limit | 1.32 ppb |

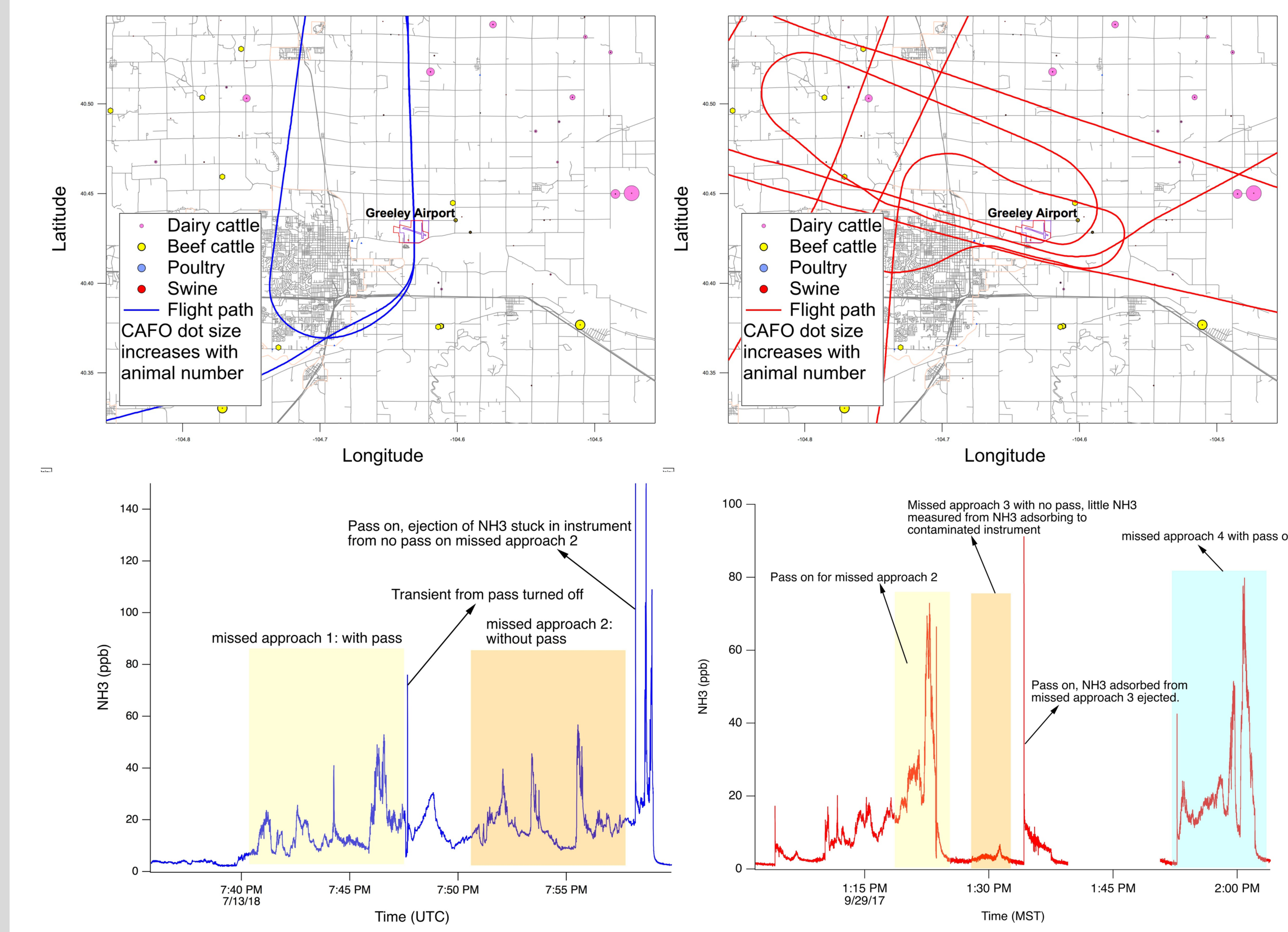
Allan variance is distorted because of a high frequency vibration deliberately applied to the laser objective to dampen the instrument's sensitivity to aircraft accelerations and vibrations.

Instrument precision is determined from a 10-minute segment of data collected at 10 Hz, in flight, and while measuring instrument background. Precision, or the 1-sigma Allan deviation, is defined here as the square root of the Allan variance. Detection limit is estimated as three times the precision (or 3-sigma).

## Passivation ensures collection of high-quality, fast-response $NH_3$ data in flight

2018 Test Flight 01
Missed approach at Greeley Airport
with a clean instrument

2017 Test Flight 03
Missed approach at Greeley Airport
with a contaminated instrument




Concentrated animal feeding operations (CAFOs) are a large source of $NH_3$ in the Colorado Front Range. Missed approaches at Greeley Regional Airport during WE-CAN test flights provided an opportunity to sample large and rapid changes in $NH_3$ mixing ratios when operating the instrument with passivant ("pass") and without passivant ("no pass").

The time series from these missed approaches shows that passivant addition is less important for clean instruments (e.g., TF01 in 2018). In contrast, passivant addition makes a dramatic difference when added to a contaminated instrument system (e.g., very little $NH_3$ was observed during the missed approach on TF03 in 2017 when no passivant was added).

Therefore, passivant addition is a unique technique for ensuring fast time response of mission critical instrumentation, especially when instrument sampling surfaces cannot be cleaned before flight.

In the case of the contaminated instrument system that could not be cleaned in time before flight, high accuracy and rapid response measurements of $NH_3$ could still be collected by adding passivant (e.g., TF03 in 2017, when passivant is re-added to the instrument system).

## References

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