Evaluation of ambient ammonia measurements from a research aircraft using a fast-response QC-TILDAS spectrometer with active passivation

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Some examples of why we need high-sensitivity, fast-response NH_3 measurements:

Test flights were conducted in the Colorado Front Range in Sept 2017 in preparation for WE-CAN in 2018.

Western wildfire Experiment for Cloud chemistry, Aerosol absorption and Nitrogen

For WE-CAN, the instrument must be able to:

- Measure large, rapid gradients in gas-phase NH_3
- Measure over a range of altitudes
- Measure in the boundary layer (turbulence, turns)
- Measure in clouds

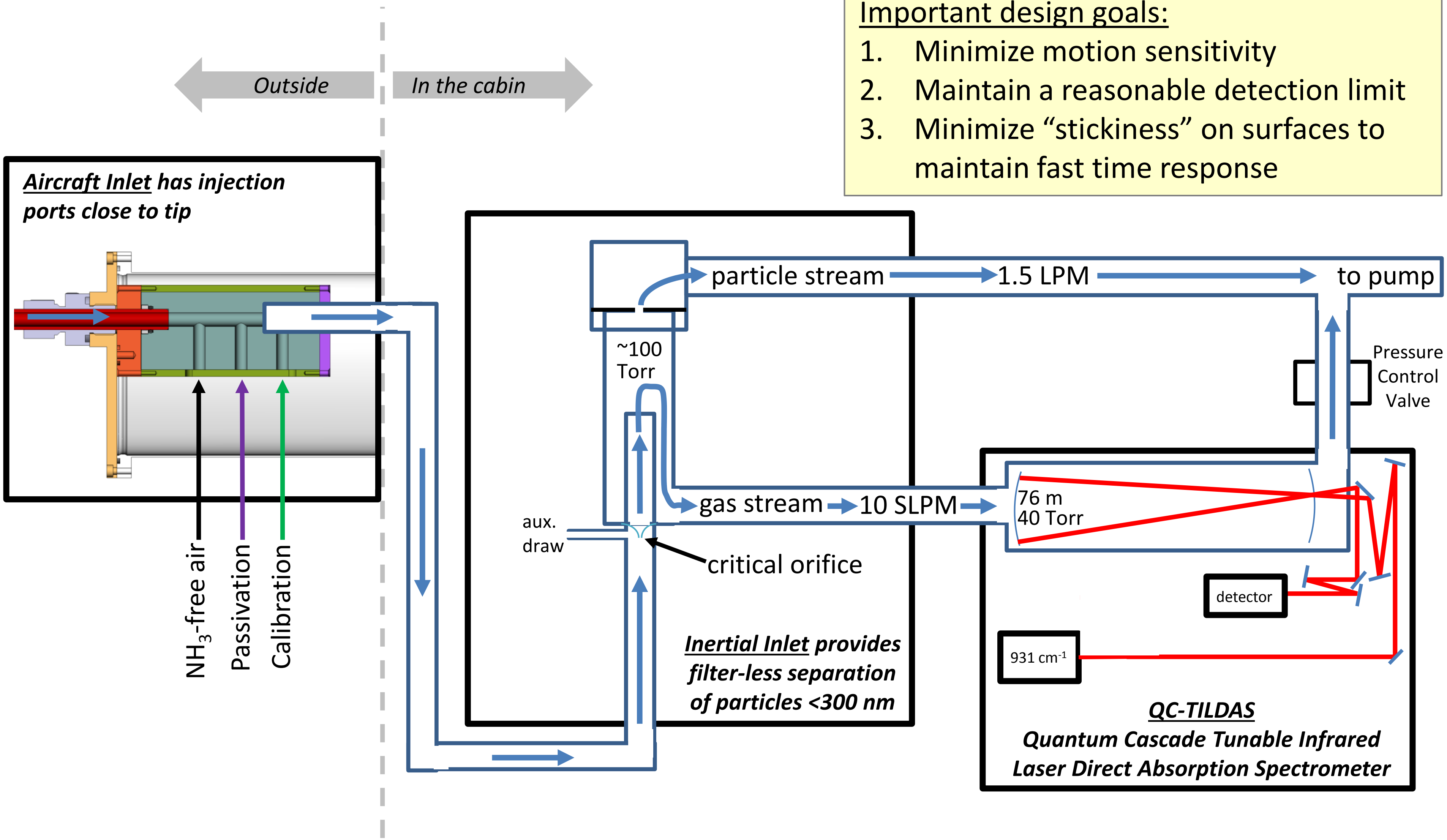
- Measure in smoke (ash, particles)
- Perform in a hot aircraft cabin

This work is supported by the National Science Foundation through grant number AGS-1650786 as part of the WE-CAN field study.

A commercial NH_3 instrument was optimized for the C-130 with WE-CAN objectives in mind.

Important design goals:

1. Minimize motion sensitivity
2. Maintain a reasonable detection limit
3. Minimize “stickiness” on surfaces to maintain fast time response



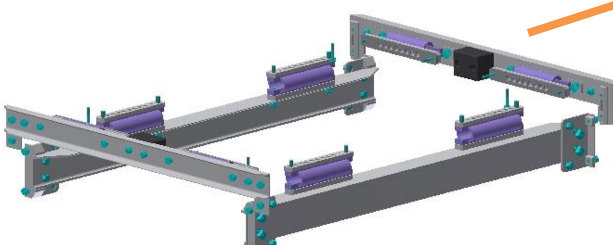
Individual components are commercially available from Aerodyne Research Inc.

To meet these goals, we tested a few unique features in flight.

To reduce motion sensitivity:

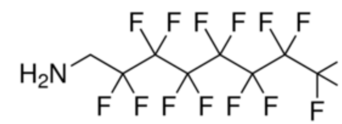
1) Laser objective is vibrated at ~200 Hz to wash out etalon fringe motion

2) TILDAS mounted on custom-designed vibration isolation plate



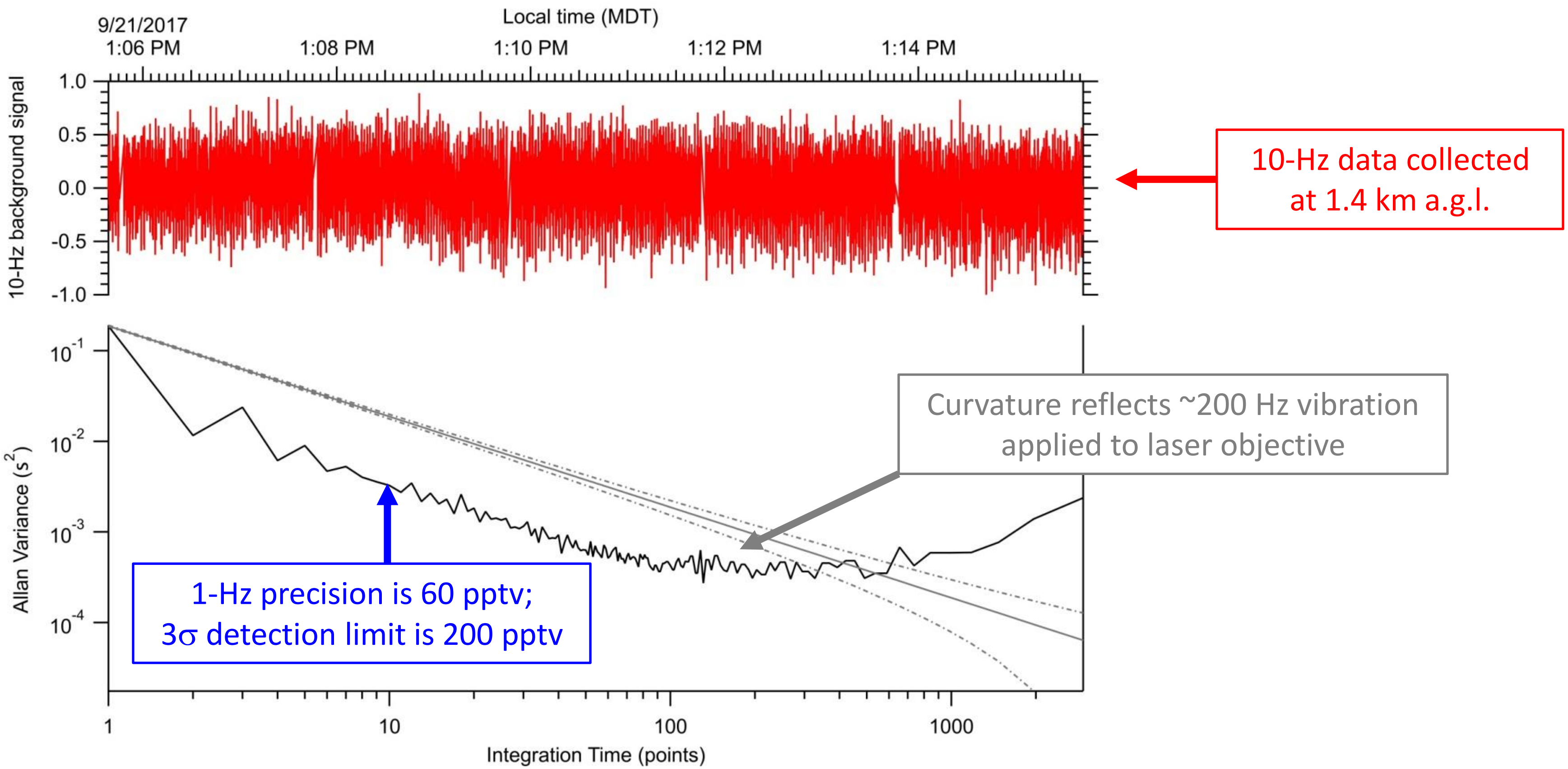
To ensure fast time response:

3) Active passivation with a strong perfluorinated base that prevents adsorption of both water and basic species to sampling surfaces



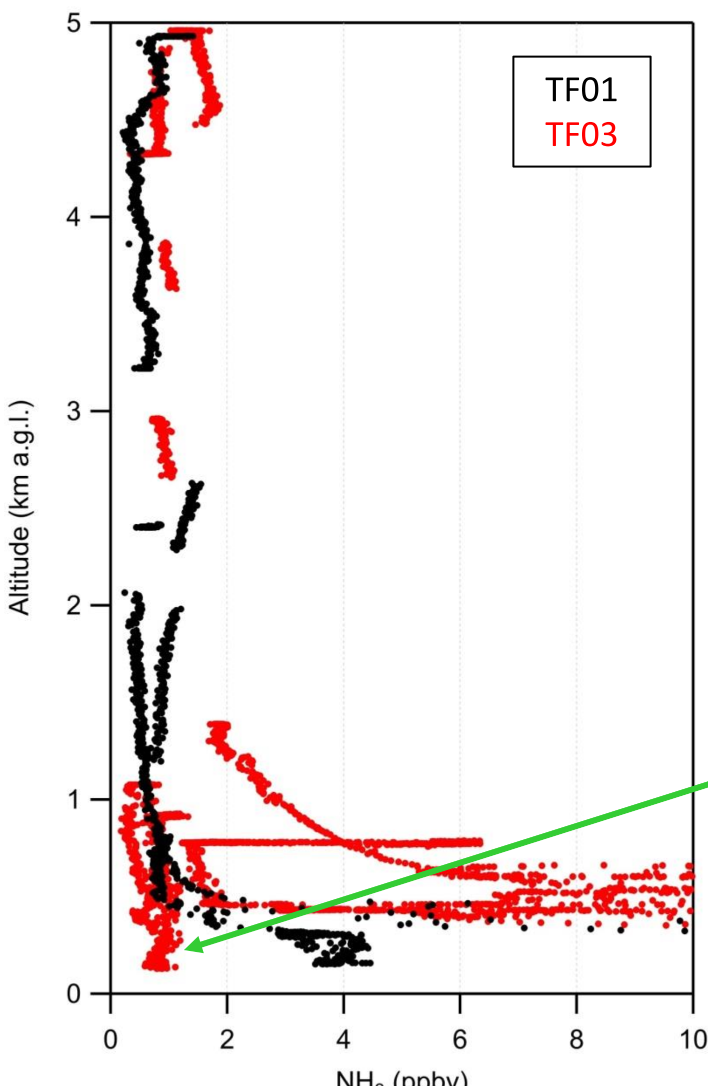
1H,1H perfluorooctylamine

Data collected while overblowing NH_3-free air showed an in-flight detection limit of 200 pptv at 1 Hz.



- No detectable change in zero signal level with altitude (0-5 km a.g.l.) nor with fluctuations in cabin pressure (±10 Torr) and temperature (±5˚C)
- Zero levels measured with a chemical scrubber compared well with a synthetic bottled source of NH_3-free air, but only when followed in series by 4 Angstrom molecular sieve

The 200 pptv detection limit allowed measurement over a range of altitudes.



Ambient measurements were always above zero signal levels, even in the free-troposphere

NH_3 in the free troposphere was frequently 1 ppbv or less

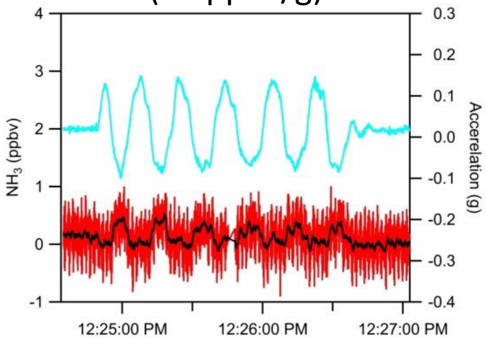
Boundary layer near Akron, CO was pretty clean after a few days of rain.

NH_3 as much as 80 ppbv during missed approaches at Greeley and when flying low over Northeastern Colorado

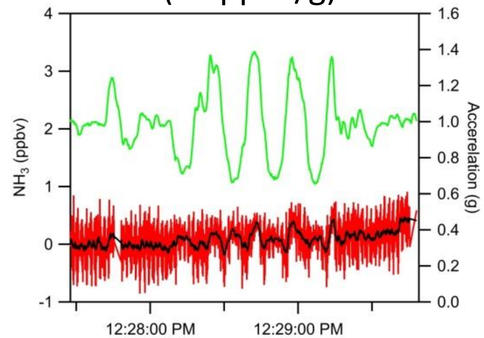
Variations in NH_3 associated with turbulence and turns are within the detection limit.

Maneuvers show changes in NH_3 with accelerations

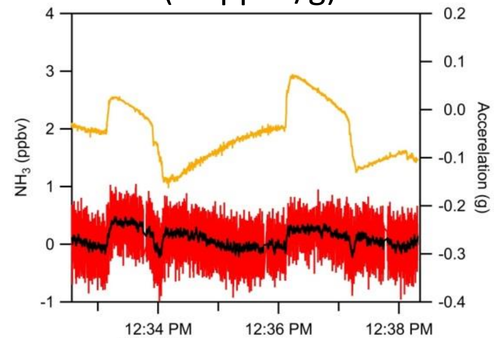
Side-side
(~3 ppbv/g)



Up-down
(~1 ppbv/g)

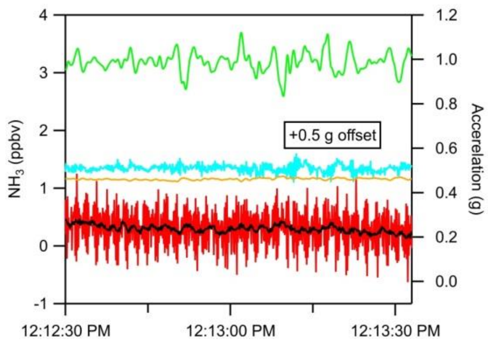


Fore-aft
(~5 ppbv/g)



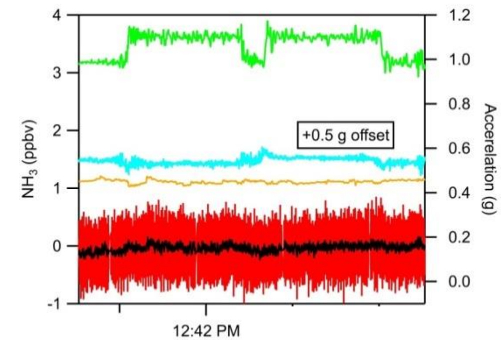
(Data collected while measuring NH_3-free air)

Straight and level in the boundary layer
(0.3 km a.g.l.)



Largest accelerations in the vertical plane

During turns
(2.6 km a.g.l.)



Changes in NH_3 are ≤ 50 pptv during turbulence and turns (within 200 pptv detection limit).

But, as often happens in field work, we had complications just before our most interesting test – passivation.

Our instrument was compromised by contamination from the chemical scrubber.

- *Cool and rainy weather during the test flight period were unfavorable conditions for the chemical scrubbing media*
- *We did not diagnose the problem until it was too late*
- *The instrument could not be properly cleaned in time prior to our third and final flight*

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Not recommended

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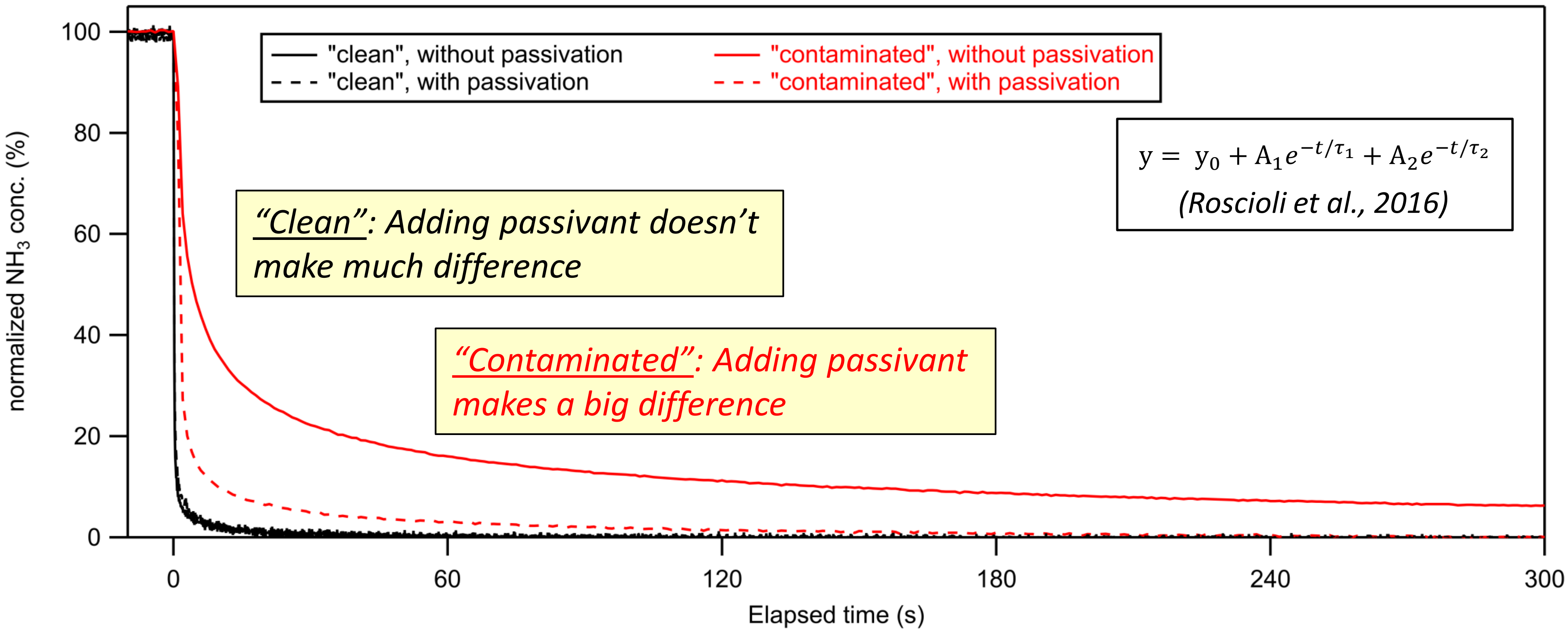
- *Cool and rainy weather during the test flight period were unfavorable conditions for the chemical scrubbing media*
- *We did not diagnose the problem until it was too late*
- *The instrument could not be properly cleaned in time prior to our third and final flight*
- *In the end, we learned a lot from this…*

Adding passivant to a “contaminated” instrument brings back the time response.

Step change response initiated by switching off calibration gas at t_0 while measuring NH_3-free air:



“Clean”: Adding passivant doesn’t make much difference

“Contaminated”: Adding passivant makes a big difference

$$y = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

(Roscioli et al., 2016)

- Under these “contaminated” conditions, NH_3 accumulation on sampling surfaces was severe *In fact, it was so bad that we couldn’t measure it – the red time profiles are after one cleaning!*
- NH_3 accumulation should be avoidable during normal operation (even in polluted environments) with frequent checks of the step-change time response and cleanings
- Adding passivant can recover instrument response when cleaning is not possible (e.g., when contamination occurs in flight or just prior)

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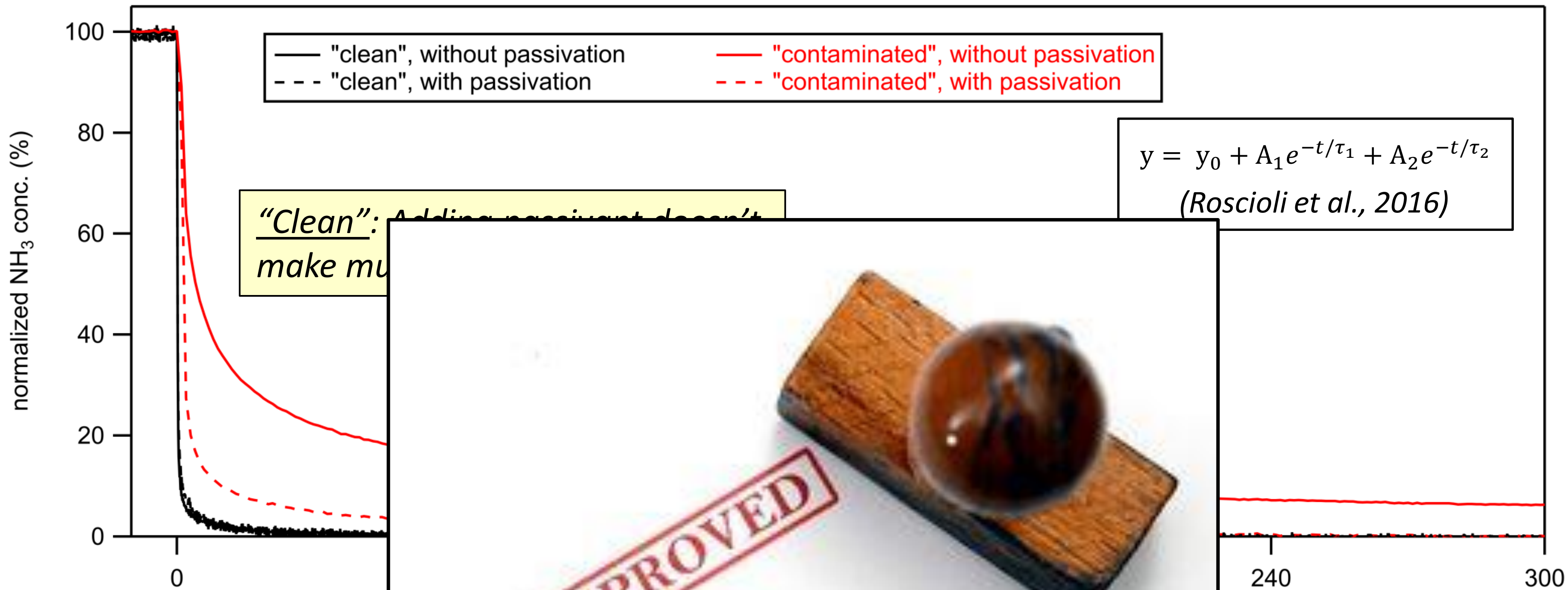

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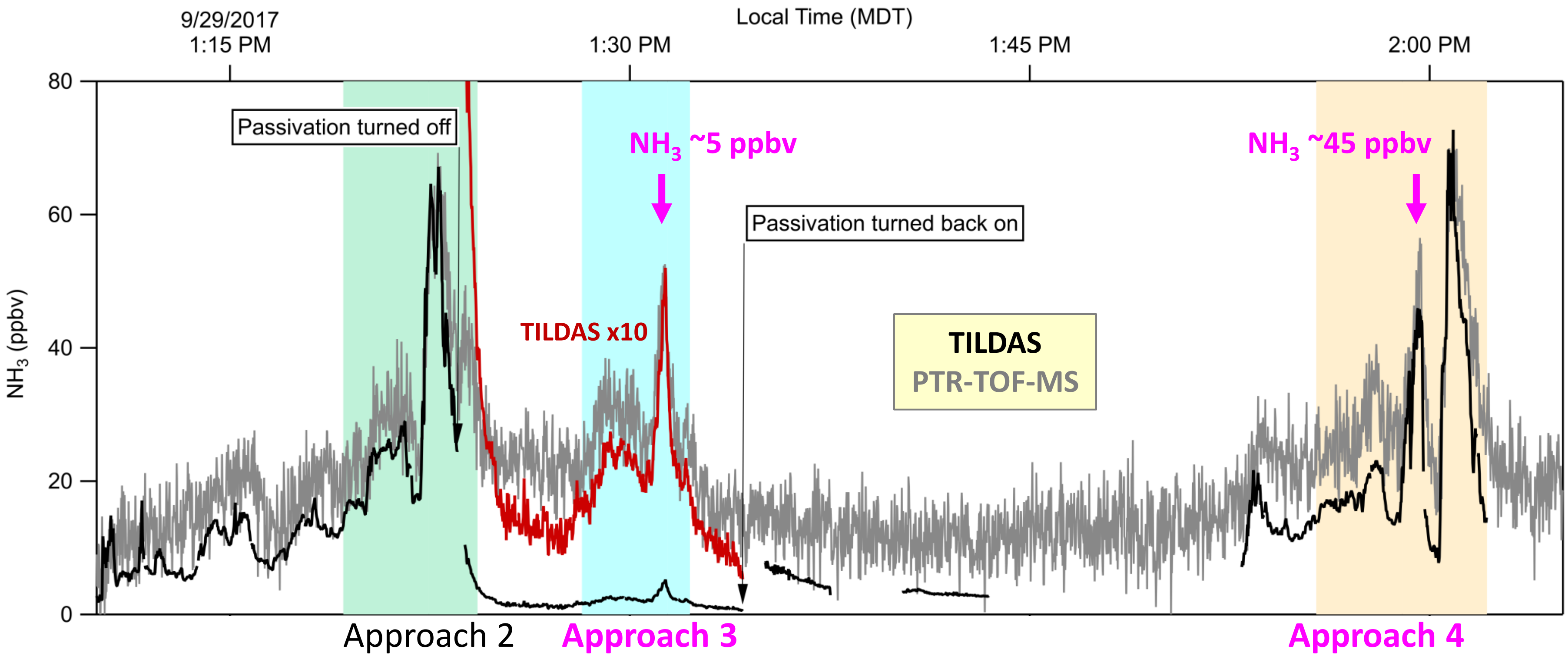
Adding passivant enabled our "contaminated" instrument to continue to collect useful, high-quality data in flight.

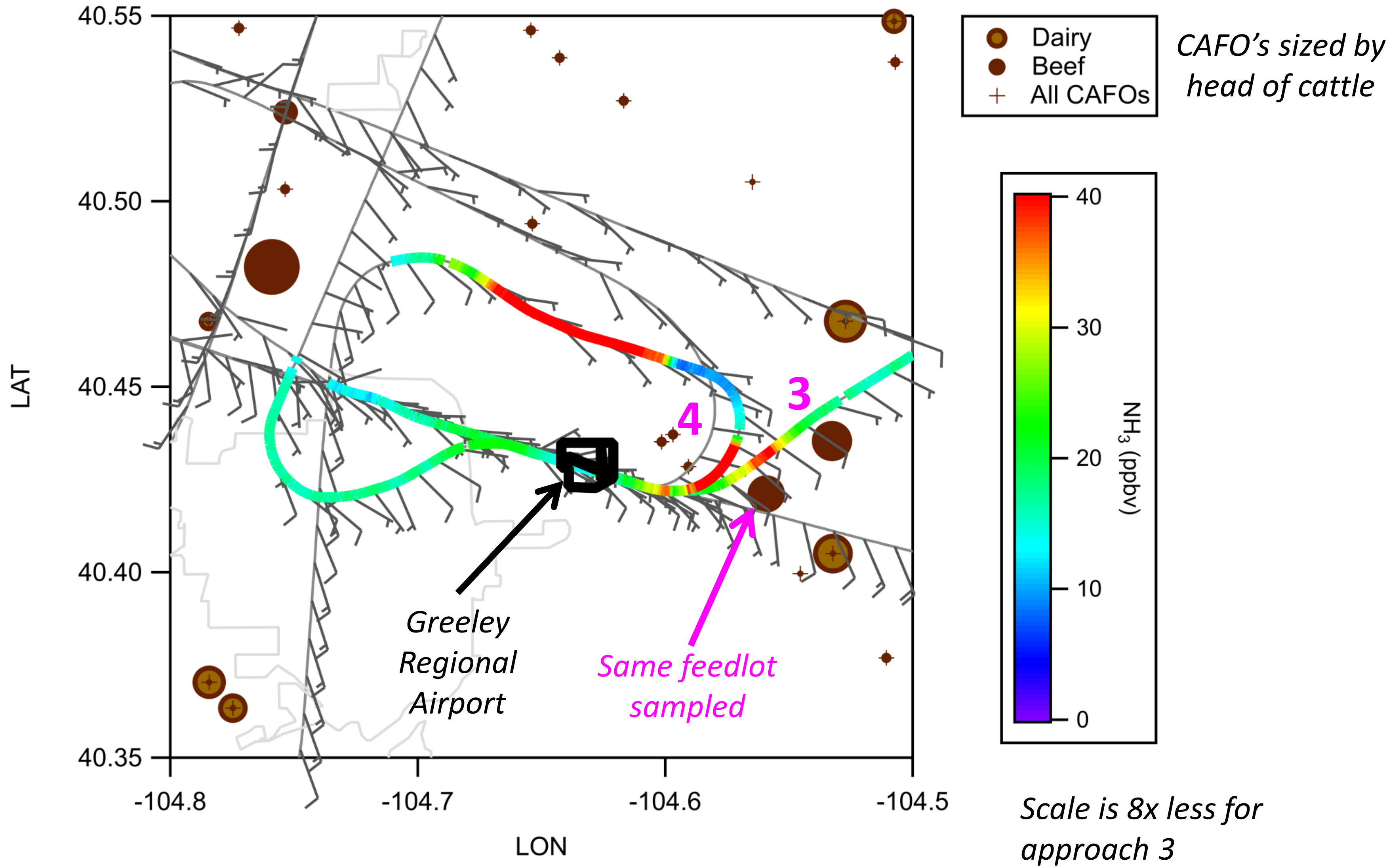


<u>Without passivation</u>, a large portion of NH_3 sticks to "contaminated" inlet surfaces instead of being transmitted to the detector.

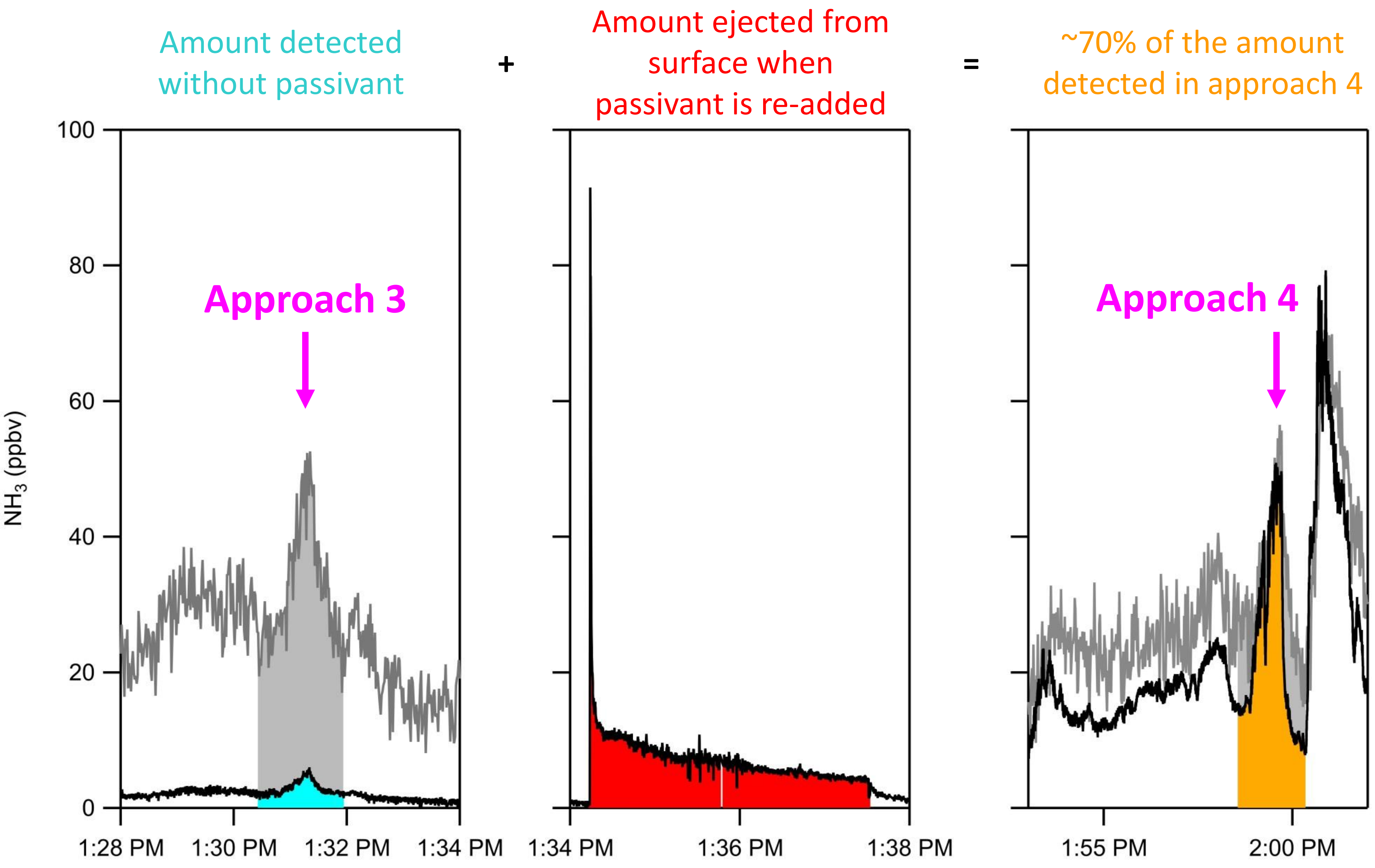
<u>With passivation</u>, an expected amount of NH_3 is observed.

<u>PTR-TOF-MS</u> Data courtesy of Lu Hu and Wade Permar from Univ. of Montana
(1-Hz mixing ratios kinetically calculated from raw instrument signal; inlet is non-specific and instrument is uncalibrated for NH_3)

Flight tracks, winds, and PTR data indicate that the same feedlot was sampled on approach 3 and 4.

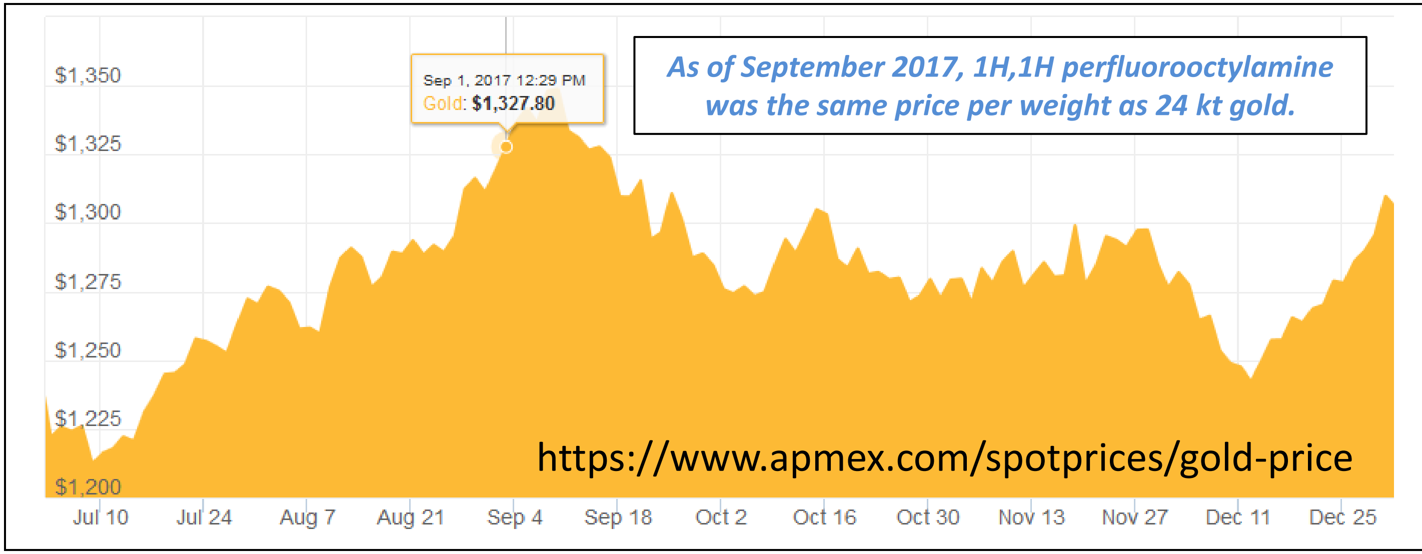


An interesting observation: the amount of NH_3 recovered from surface ejection adds up.



PTR detected ~85% of NH_3 observed on approach 4 during approach 3

So, is passivation of NH_3 instruments worth the cost?



Answer: It depends on how/what/where you want to measure…

- Recommended when rapid (> 1 Hz) collection of NH_3 is mission critical (e.g., measuring fluxes, sampling from aircraft or another mobile lab)

  1 oz. of passivant at $1400 lasts for 120 flight hours

- Can be useful *(insurance policy)* for maintaining optimum operation in NH_3-rich/humid environments or when contamination of sampling surfaces is likely, yet frequent cleaning is not possible

- May not be necessary for fast operation (even in polluted environments) if sampling surfaces can be cleaned whenever a step-change response to NH_3 shows time response has degraded

- Does not seem cost effective for measurements where response time is not critical (e.g., sites reporting hourly data)

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