TEMPORAL VARIABILITY OF THE PIEBER EFFECT AND SOME NOTES ON AMS DETECTION LIMITS

Pedro Campuzano Jost

& the CU Boulder Aircraft Crew

CU Boulder

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EXPLORING THE VARIABILITY OF THE PIEBER EFFECT, FOR ONE INSTRUMENT OVER TIME

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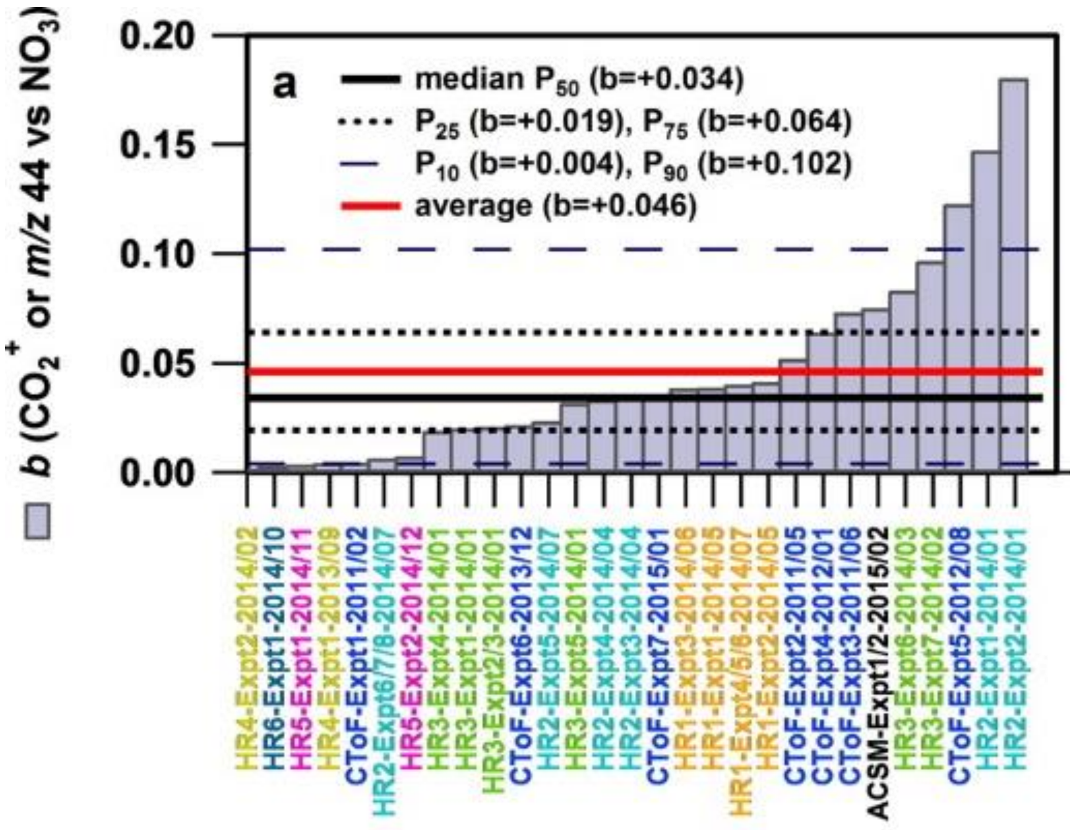

Pieber et al, ES&T 2016

Pieber Effect: Charred OA residue on the vaporizer reacting with nitrate salts to form excess CO_2^+

Can severely impact f_{44}/ O:C Ratio (Froehlich et al, AMT 2015), but also quantification

Severity of effect depends on the particular vaporizer, possibly tuning and instrument history, with a wide range of conversion efficiencies reported

Can a detailed analysis of instrument history give insight into both sources of the residue and recovery times?

KORUS-AQ: 20 FLIGHTS IN POLLUTED CONDITIONS WITH POST-FLIGHT IE CALIBRATION

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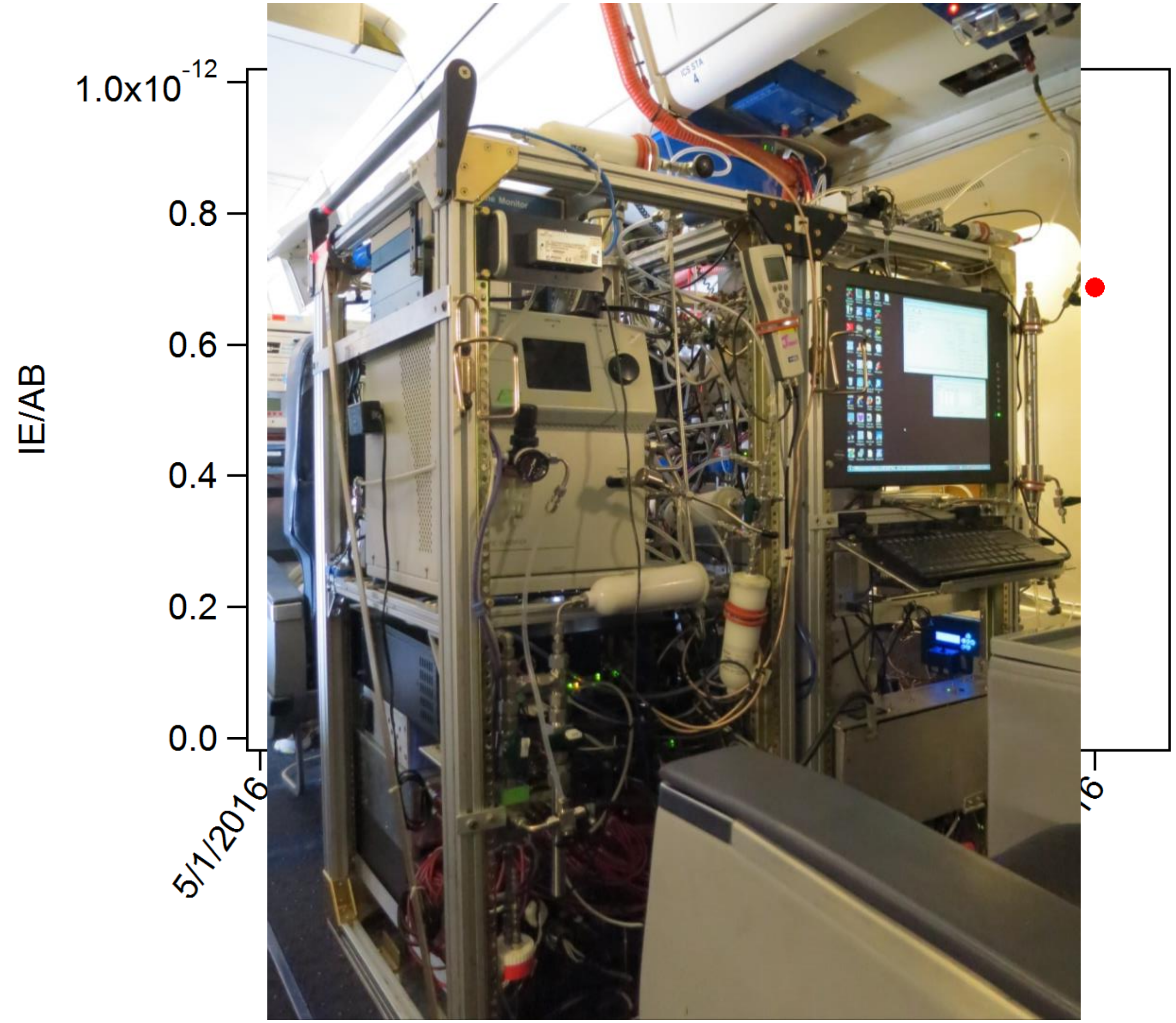


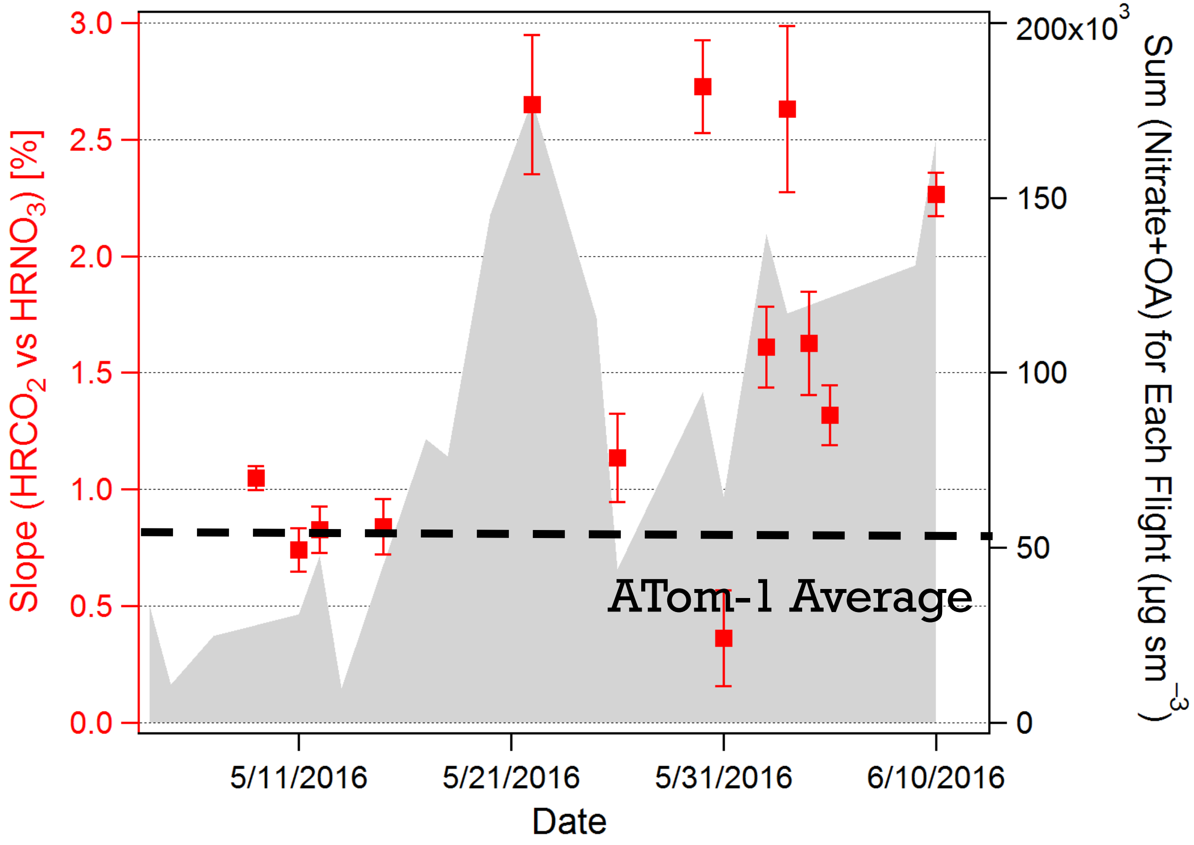
Any NH_4NO_3 calibration provides an easy check on the overall magnitude of the Pieber Effect.

For a recent aircraft campaign, KORUS-AQ, we were calibrating the instrument after each flight

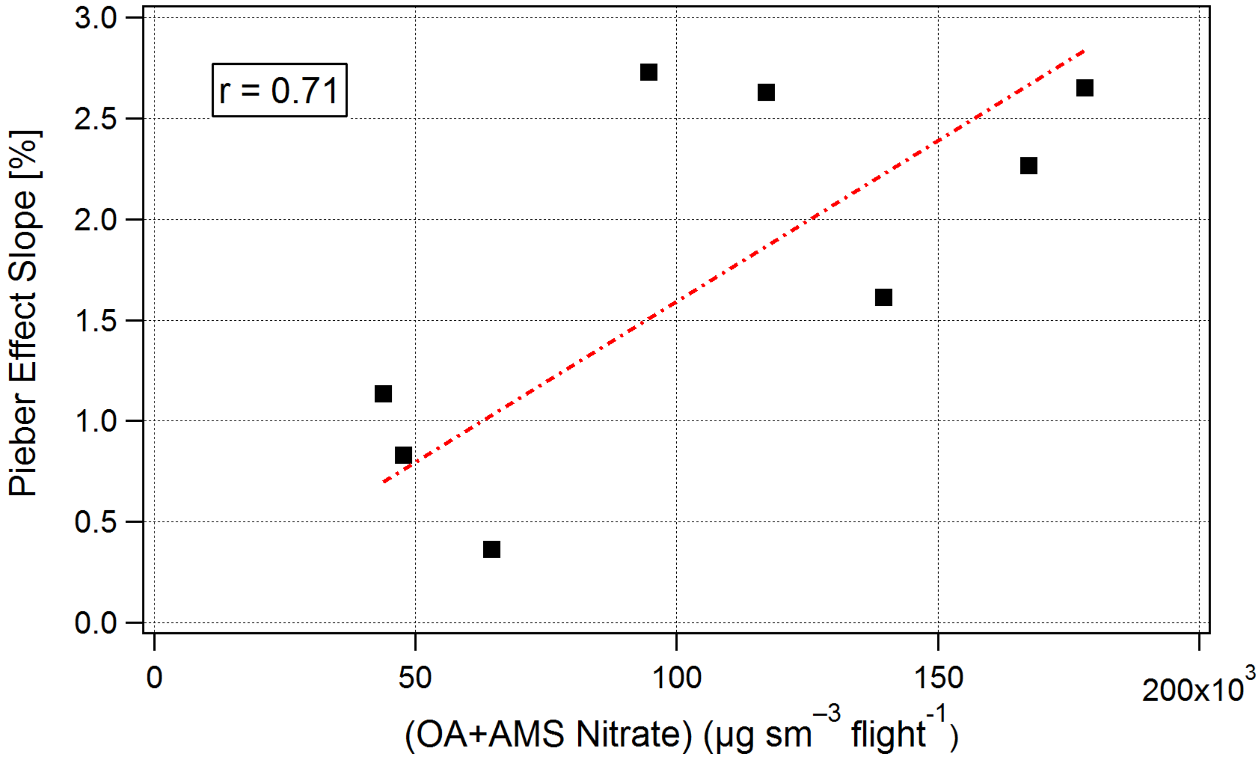
This allows us to directly relate any changes to the aerosol sampled on that day

KORUS-AQ: RESULTS

Pieber Plot Average



- Correlates with BC as well
- No obvious specific correlation with HOA or BBOA
- Lots of nitrate in this campaign!



SUMMARY (I)

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- The magnitude of the Pieber Effect correlated fairly well with total sampled mass over the course of an individual flight during KORUS-AQ.
- Recovery, at least for this instrument (which has always exhibited a very low Pieber effect to begin with) is in general swift.

COMPARING TWO WAYS TO ESTIMATE AMS DETECTION LIMITS

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Standard Analytical Chem Definition:

$DL(Species) = A * \sigma_{dev}(Species(Blank))$, with typically A=3

However: Filters reduce measurement time

Hence N is often too small for an accurate estimate of σ_{dev}

Does not account for time-varying backgrounds

Drewnick et al (AMT, 2009):

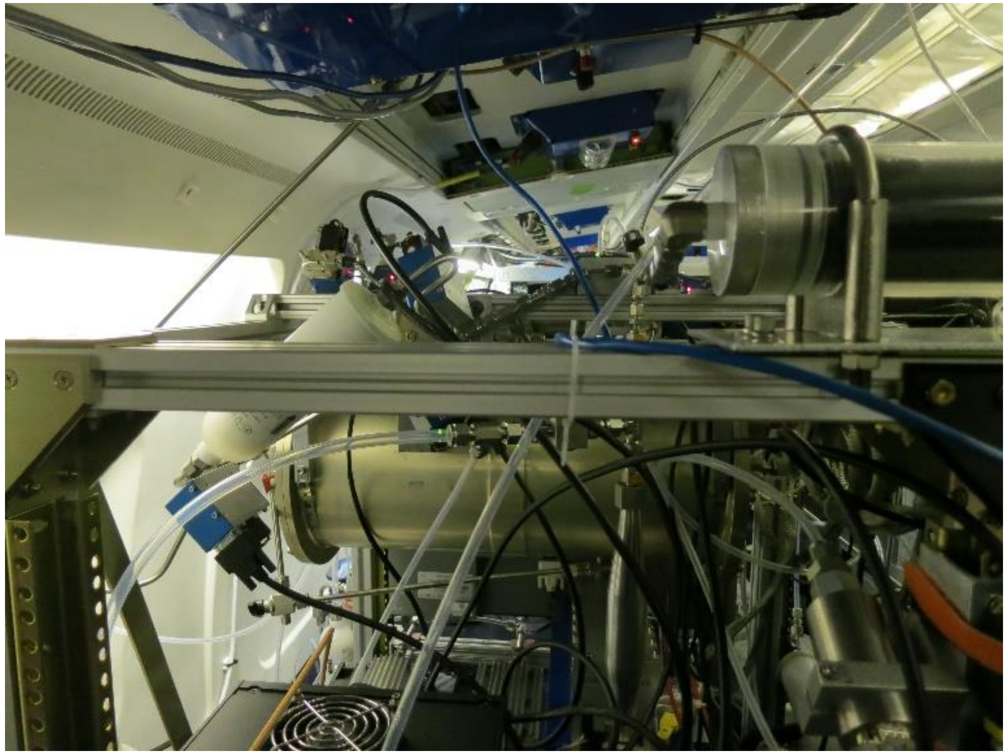
- Assuming counting statistics as only source of noise
- Assuming Open-Closed ~ Closed
- Assuming $\tau_{open} = \tau_{closed}$

$$DL(Species) = A * \left(\frac{\sqrt{C_{species}}}{C_{species}}\right)_{OMinusC} = A * \left[\left(\frac{\sqrt{C_{species}}}{C_{species}}\right)_{closed} + \left(\frac{\sqrt{C_{species}}}{C_{species}}\right)_{open}\right] \sim A * \sqrt{2} * \left(\frac{\sqrt{C_{species}}}{C_{species}}\right)_{closed}$$

TEST SETUP

CU Aircraft AMS 1 min acq cycle

BackG 6 s		Filter	Filter Blar	Filter Blank		ePToF ~5 s



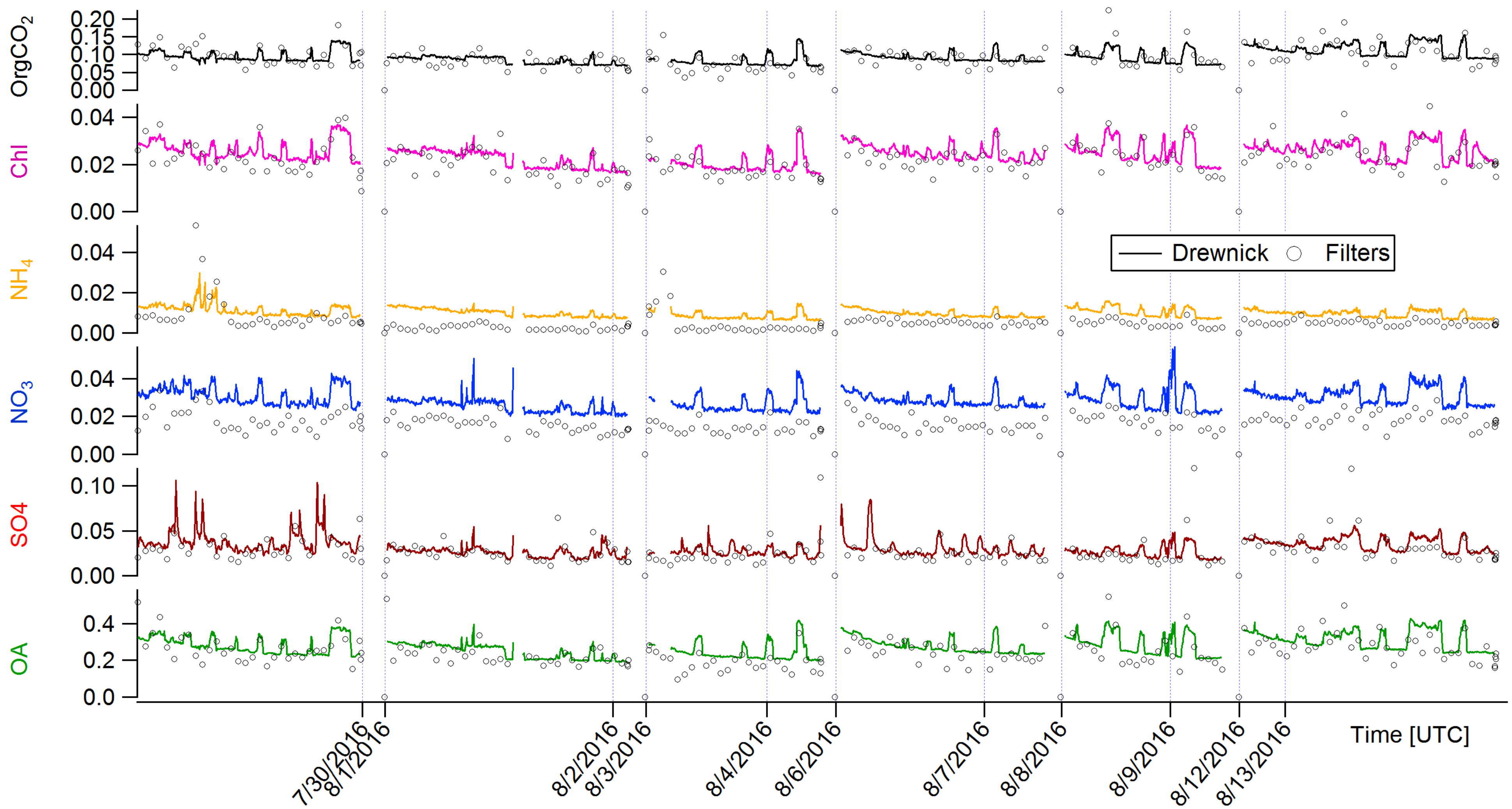
Fast switching, fully automated blank setup

20 s filters (1 Hz) are recorded every 18 min

This provides:

- Sufficient points for a good standard deviation calc
- Direct comparison to the Drewnick DL calculated from closed signal for the same cycle
- Blanks taken over a vast array of conditions

DREWNICK'S DETECTION LIMITS FOR ATOM-1 FLIGHTS RF01-RF06



AS A CORRELATION PLOT:

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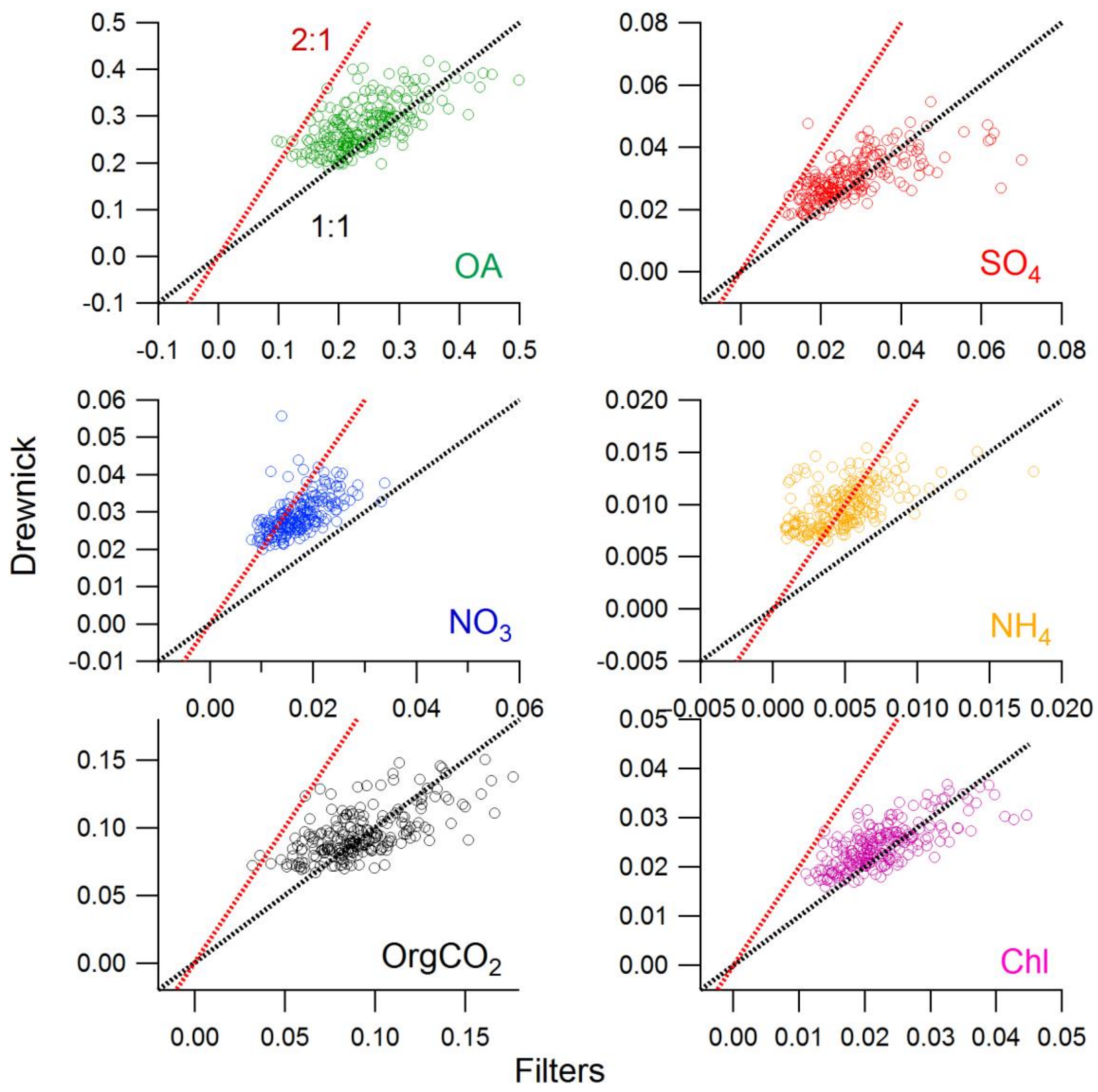

- Using fast filters, we get reasonable closure between the two methods to estimate DL.
- However, DLs estimated from the closed spectrum (Drewnick et al) seem high, the opposite was expected.
- While the absolute scaling factor might be wrong, the fact that we get different ratios for different species seem to imply some subtle analysis effect (likely HRFrag Table related) that needs to be explored further.

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- Using fast filters, we get reasonable closure between the two methods to estimate DL.
- However, DLs estimated from the closed spectrum (Drewnick et al) seem high, the opposite was expected.
- And I vote for a CO_2 free atmosphere!