Evaluation of Uncertainties and Introduction of Tools for Quantification of Bulk Particle-phase Organic Nitrates Using Real-time Aerosol Mass Spectrometry

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University of Colorado Boulder

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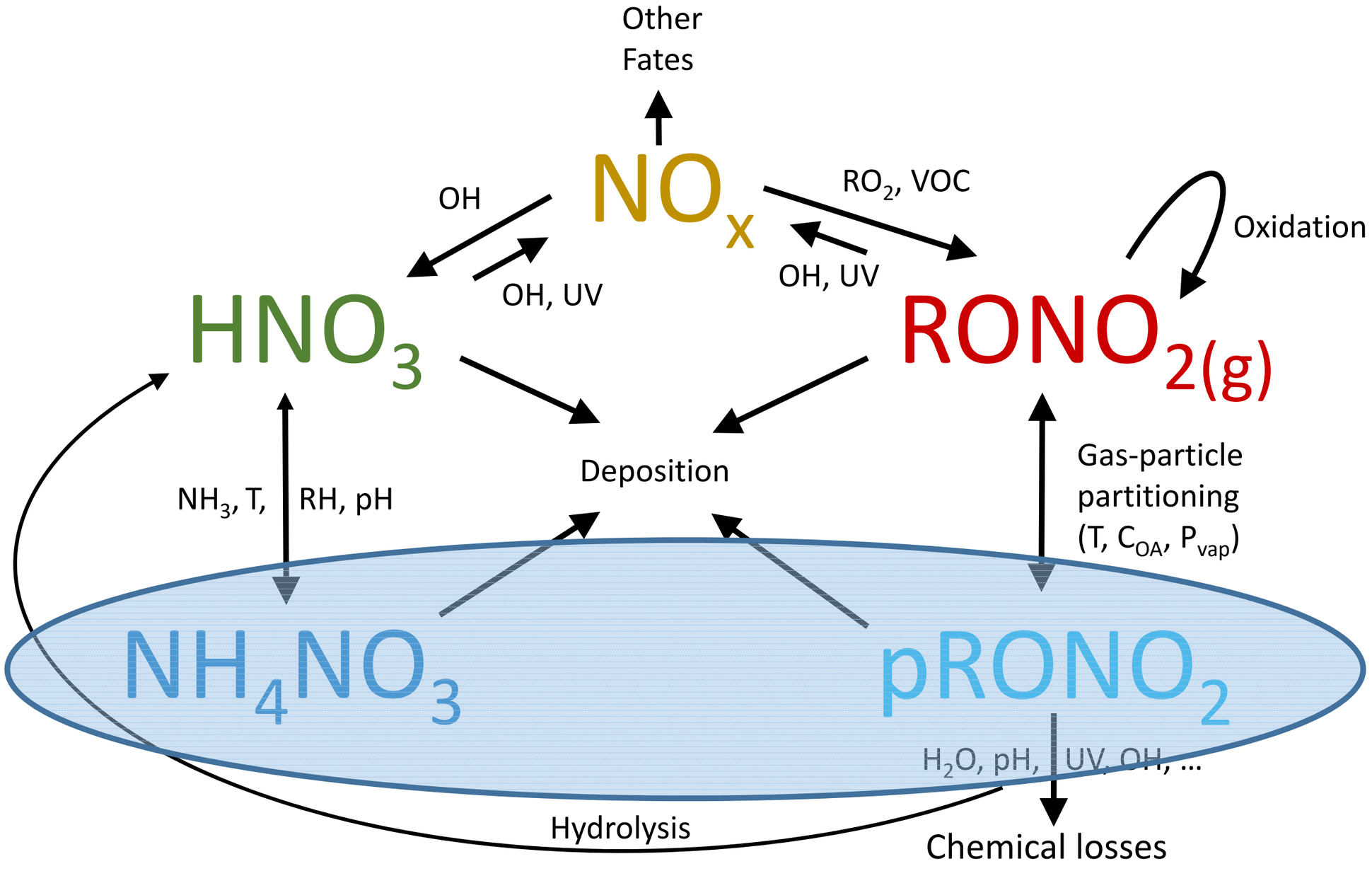
Organic Nitrates and Particle-phase Reactive Oxidized Nitrogen



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AMS Methods for $pRONO_2$ Quantification

- NO_2^+/NO^+ ion ratios (*Farmer et al., PNAS 2010; Fry et al. ACP 2013; Kiendler-Scharr, et al., GRL 2016*)
- ~~HNO_3^+/NO_x^+ ion ratios (*Farmer et al., PNAS 2010*)~~
- ~~$C_xH_yO_zN^+$ ions (*Farmer et al., PNAS 2010*)~~
- ~~Ammonium balance (*Aiken et al., ACP 2009; Farmer et al., PNAS 2010; Zaveri et al., JGR 2010; Docherty et al., ACP 2011; Häkkinen et al., ACP 2012*)~~
- Difference of total AMS nitrate and inorganic nitrate (*Farmer et al., PNAS 2010; Xu et al., PNAS 2015*)
- PMF including spectra of OA and nitrate ions (*Sun et al., ACP 2012; Hao et al., ACP 2014; Xu et al., ACP 2015*)

Day et al. (AMT, 2022) https://doi.org/10.5194/amt-15-459-2022

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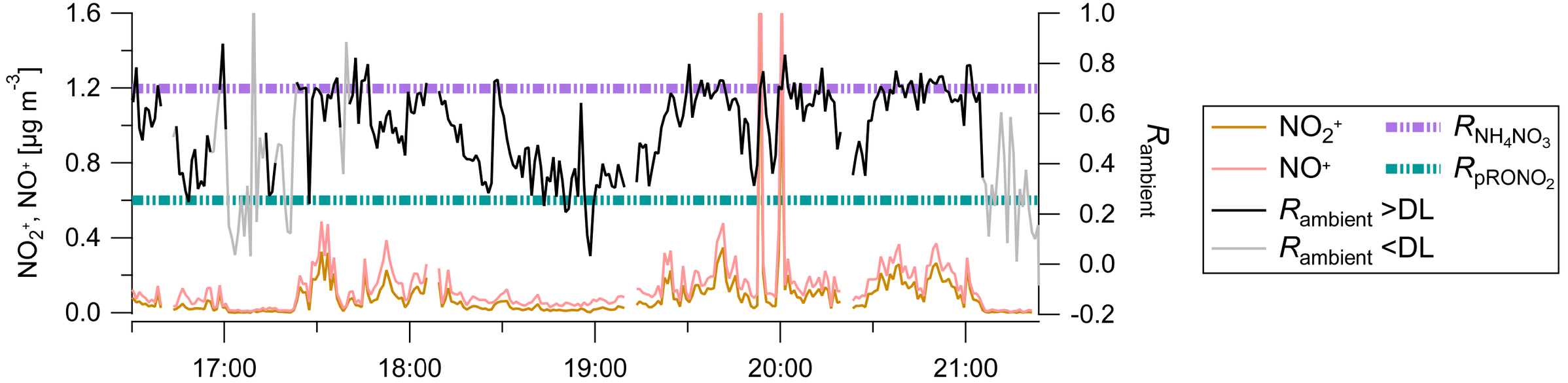
Nitrate Apportionment with NO_x^+ ions

- Organic nitrates and non-refractory inorganic nitrate produce different NO_2^+/NO^+ fragmentation ratios in AMS. (*Farmer et al., PNAS 2010*)

$R_{NH_4NO_3}$: NO_2^+/NO^+ ➔ ~0.2 - 1

R_{pRONO_2}: NO_2^+/NO^+ ➔ ~0.1 – 0.4

$R_{ambient}$: measured NO_2^+/NO^+ bounded by $R_{NH_4NO_3}$ and R_{pRONO_2}



Nitrate Apportionment with NO_x^+ ions

$$f_{pRONO_2} = \frac{pRONO_2}{pNO_3}$$

$$f_{NH_4NO_3} \frac{NH_4NO_3}{pNO_3}$$

$R_{NH_4NO_3}$: NO_2^+/NO^+ ➔ ~0.2 - 1

R_{pRONO_2}: NO_2^+/NO^+ ➔ ~0.1 – 0.4

$R_{ambient}$: measured NO_2^+/NO^+ bounded by $R_{NH_4NO_3}$ and R_{pRONO_2}

$$f_{pRONO_2} = \frac{(R_{ambient} - R_{NH_4NO_3})(1 + R_{pRONO_2})}{(R_{pRONO_2} - R_{NH_4NO_3})(1 + R_{ambient})}$$

Apportionment with NO_x^+ ions, *Ratio-of-Ratios*

- "Ratio-of-Ratios" (*RoR*) may be better metric to constrain R_{pRONO2} for ambient measurements
  (*Fry et al., ACP 2013; Day et al AMT 2022*)

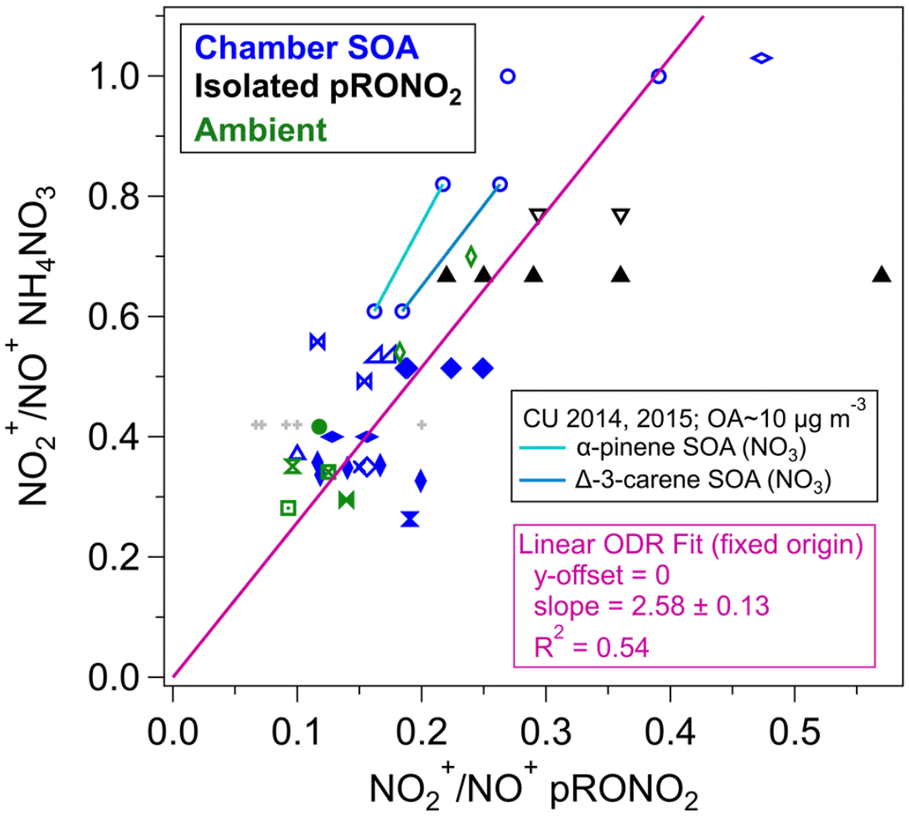
$$f_{pRONO_2} = \frac{(R_{ambient} - R_{NH_4NO_3})(1+R_{pRONO_2})}{(R_{pRONO_2} - R_{NH_4NO_3})(1+R_{ambient})}$$

$$RoR = \frac{R_{NH_4NO_3}}{R_{pRONO_2}}$$

Substituting $\frac{R_{NH_4NO_3}}{RoR}$ for R_{pRONO_2}

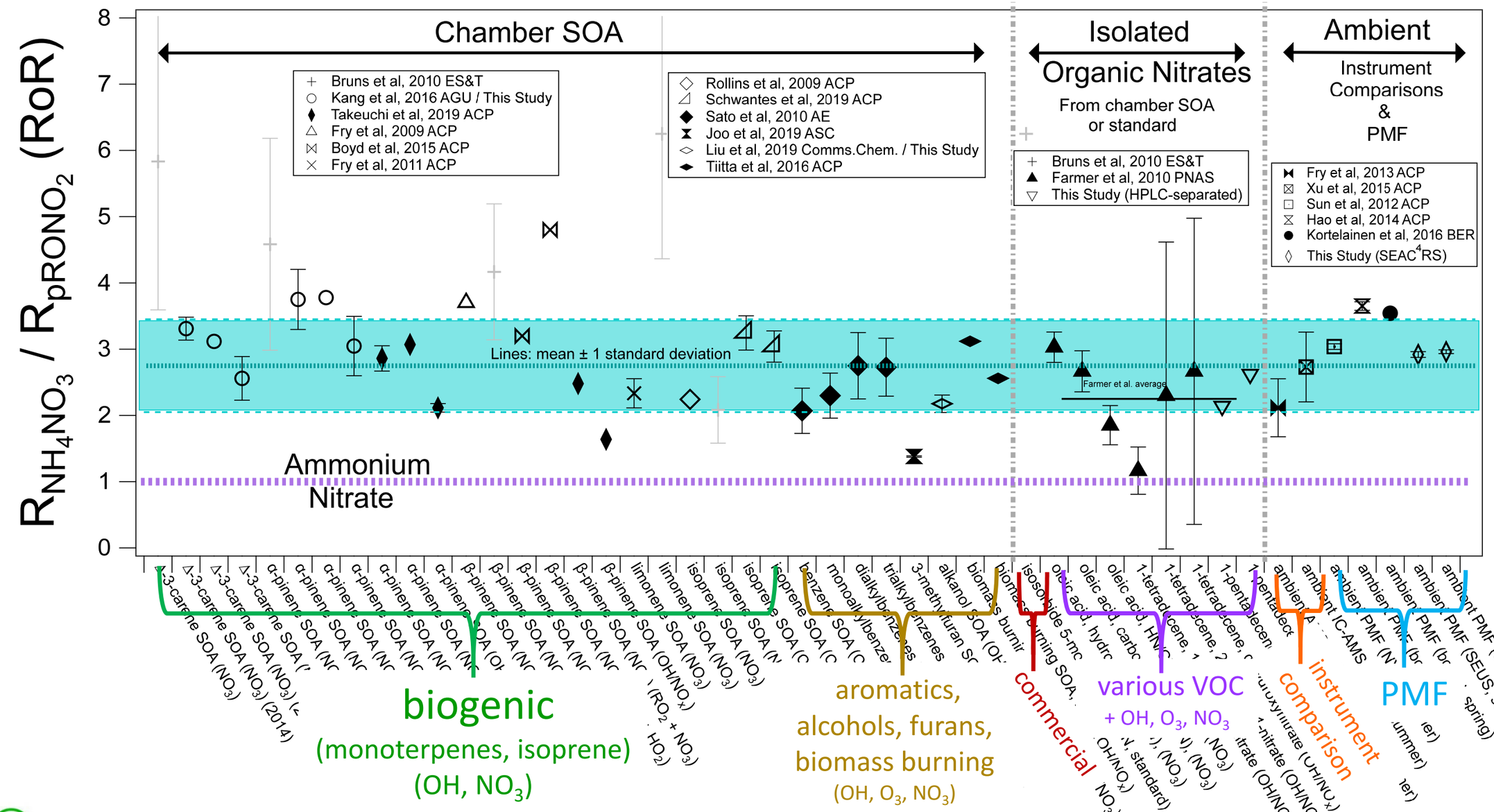
$$f_{pRONO_2} = \frac{(R_{ambient} - R_{NH_4NO_3})(1+\frac{R_{NH_4NO_3}}{RoR})}{(\frac{R_{NH_4NO_3}}{RoR} - R_{NH_4NO_3})(1+R_{ambient})}$$

$R_{NH_4NO_3}$ *vs* R_{pRONO_2}



Day et al. (AMT, 2022) https://doi.org/10.5194/amt-15-459-2022

Survey of $pRONO_2$ NO_x^+ ratios (as Ratio-of-Ratios)



Mean: 2.75
Standard. Deviation
±0.70 (25%)
Standard Error:
±0.11 (n=41; 4.0%)

Day et al. (AMT, 2022) https://doi.org/10.5194/amt-15-459-2022

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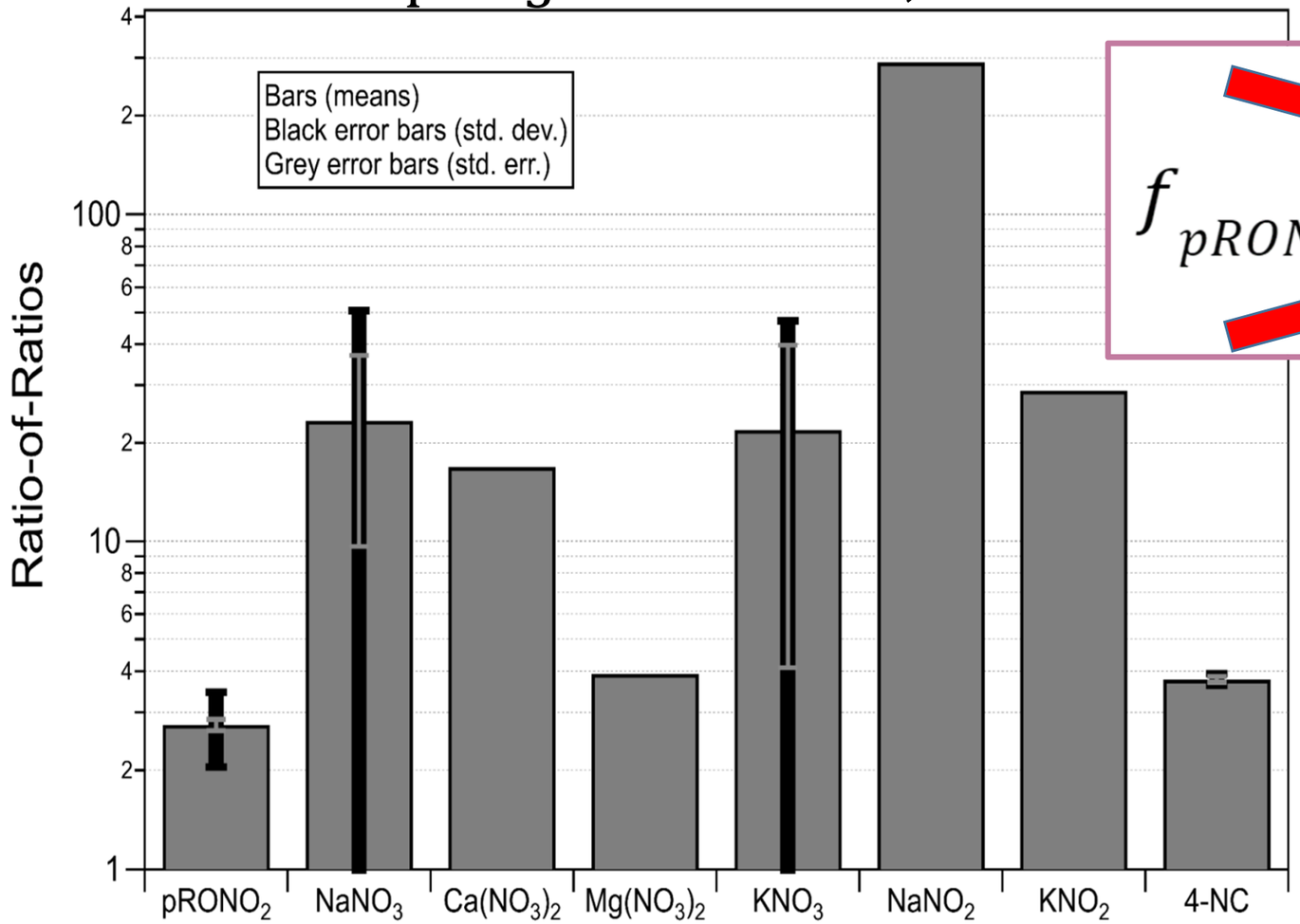
Not applicable under strong influence of nitrite or refractory nitrate

$(R_{NH_4NO_3}/R_{nitrate,nitrite})$

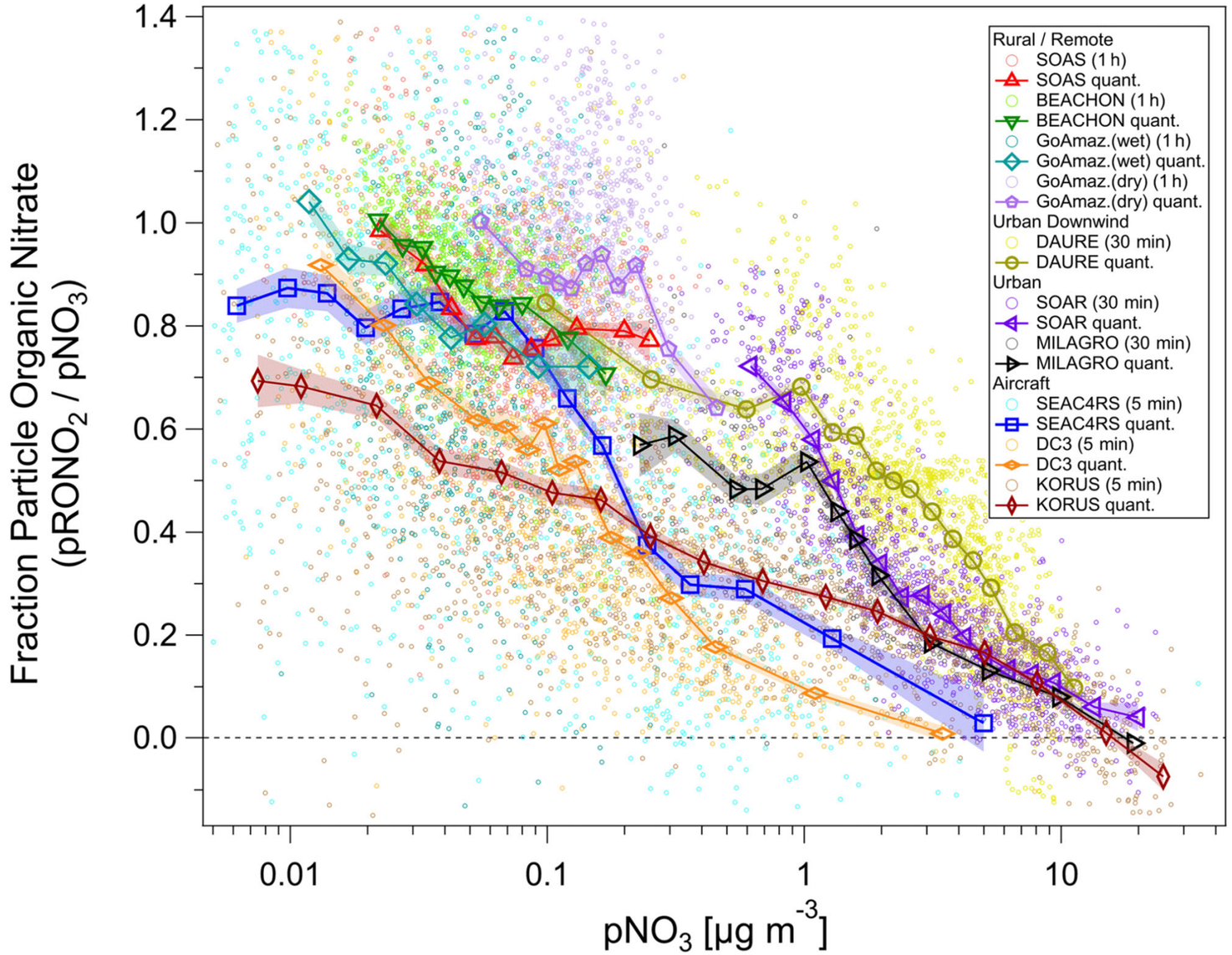


$$f_{pRONO_2} = \frac{(R_{ambient} - R_{NH_4NO_3})(1 + \frac{R_{NH_4NO_3}}{RoR})}{(\frac{R_{NH_4NO_3}}{RoR} - R_{NH_4NO_3})(1 + R_{ambient})}$$

$R_{nitrate}$ ➔ NO_2^+/NO^+

Day et al. (AMT, 2022) https://doi.org/10.5194/amt-15-459-2022

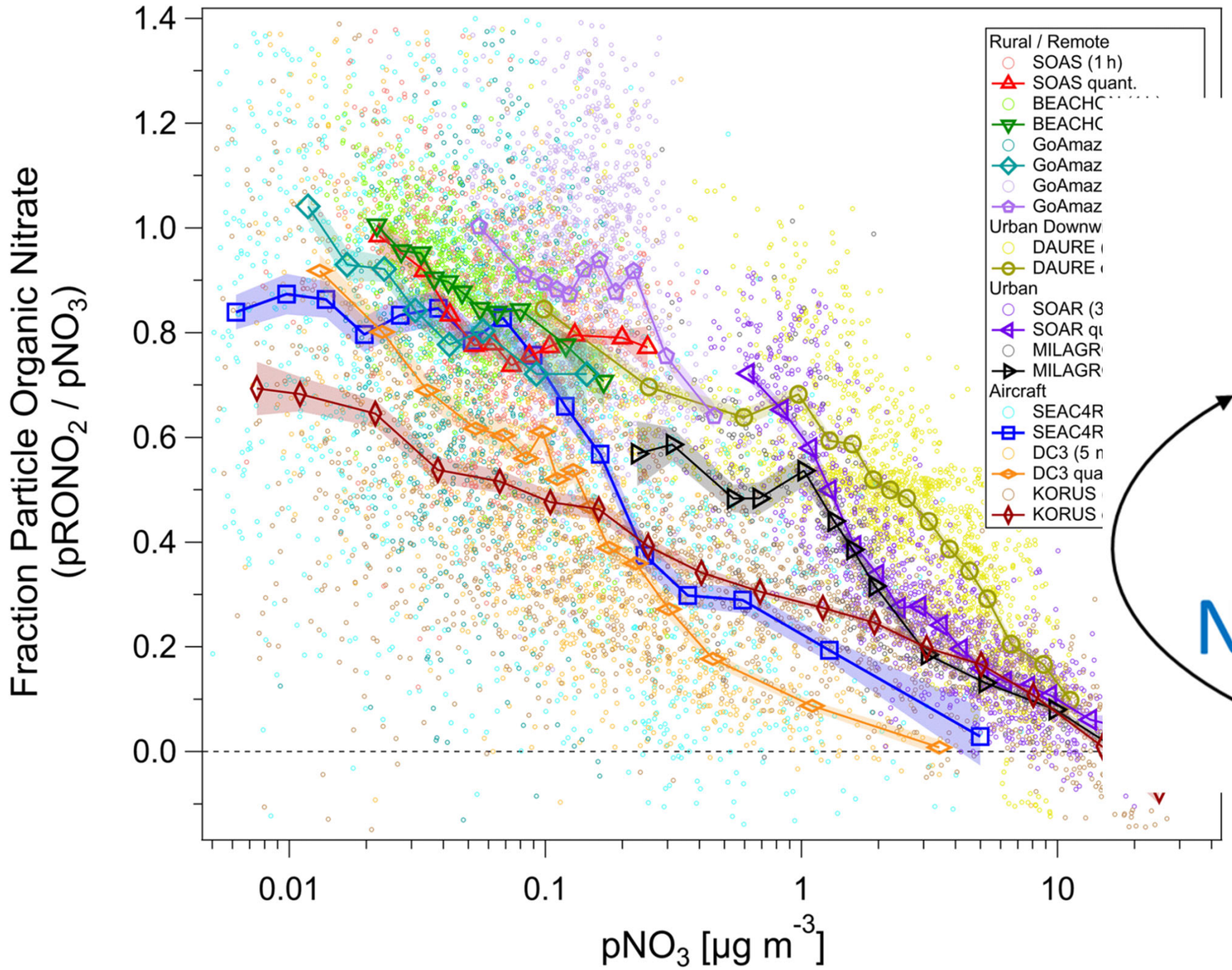
Application and Further Support (Organic vs. Inorganic Nitrate)

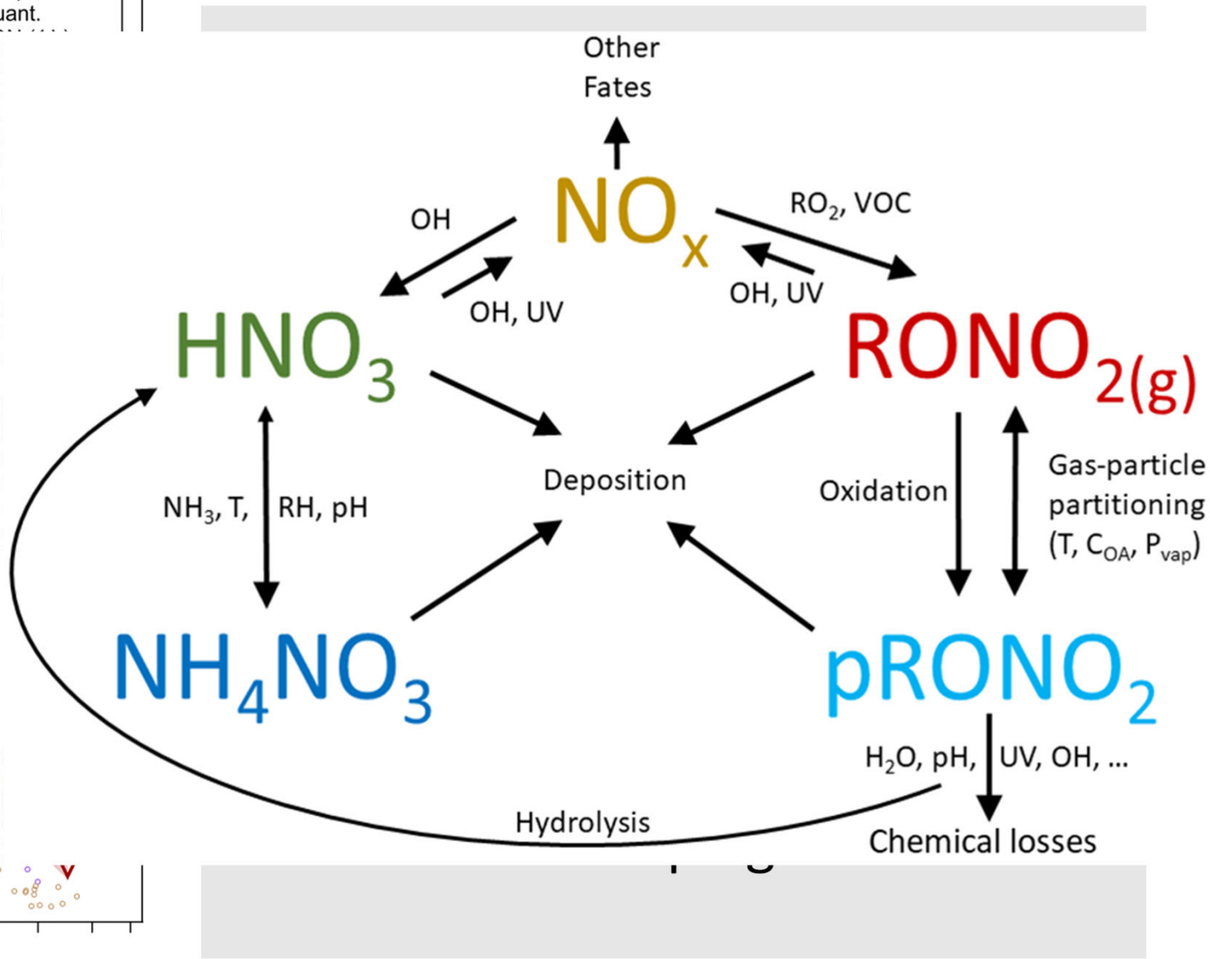


- 10 Campaigns
- Ground, Aircraft
- Remote, Rural, Urban, Mixed
- Warm seasons
- Overall trend: $fpRONO_2$ decrease with pNO_3 increase
- Substantial differences for aircraft campaigns

Day et al. (AMT, 2022) https://doi.org/10.5194/amt-15-459-2022

Application and Further Support (Organic vs. Inorganic Nitrate)





Day et al. (AMT, 2022) https://doi.org/10.5194/amt-15-459-2022

Uncertainties Systematically Explored

$R_{nitrate,mix}$: NO_2^+/NO^+

$$RoR = \frac{R_{NH_4NO_3}}{R_{pRONO_2}}$$

$$f_{pRONO_2} = \frac{(R_{ambient} - R_{NH_4NO_3})(1 + \frac{R_{NH_4NO_3}}{RoR})}{(\frac{R_{NH_4NO_3}}{RoR} - R_{NH_4NO_3})(1 - R_{ambient})}$$

$$pRONO_2 = f_{pRONO_2} \times pNO_3$$

$$NH_4NO_3 = f_{NH_4NO_3} \times pNO_3$$

$\sigma_{R_{ambient}}$: composition, concentration, instrument

$\sigma_{R_{NH_4NO_3}}: \pm 5\%$

$\sigma_{RoR}: \pm 15\%$

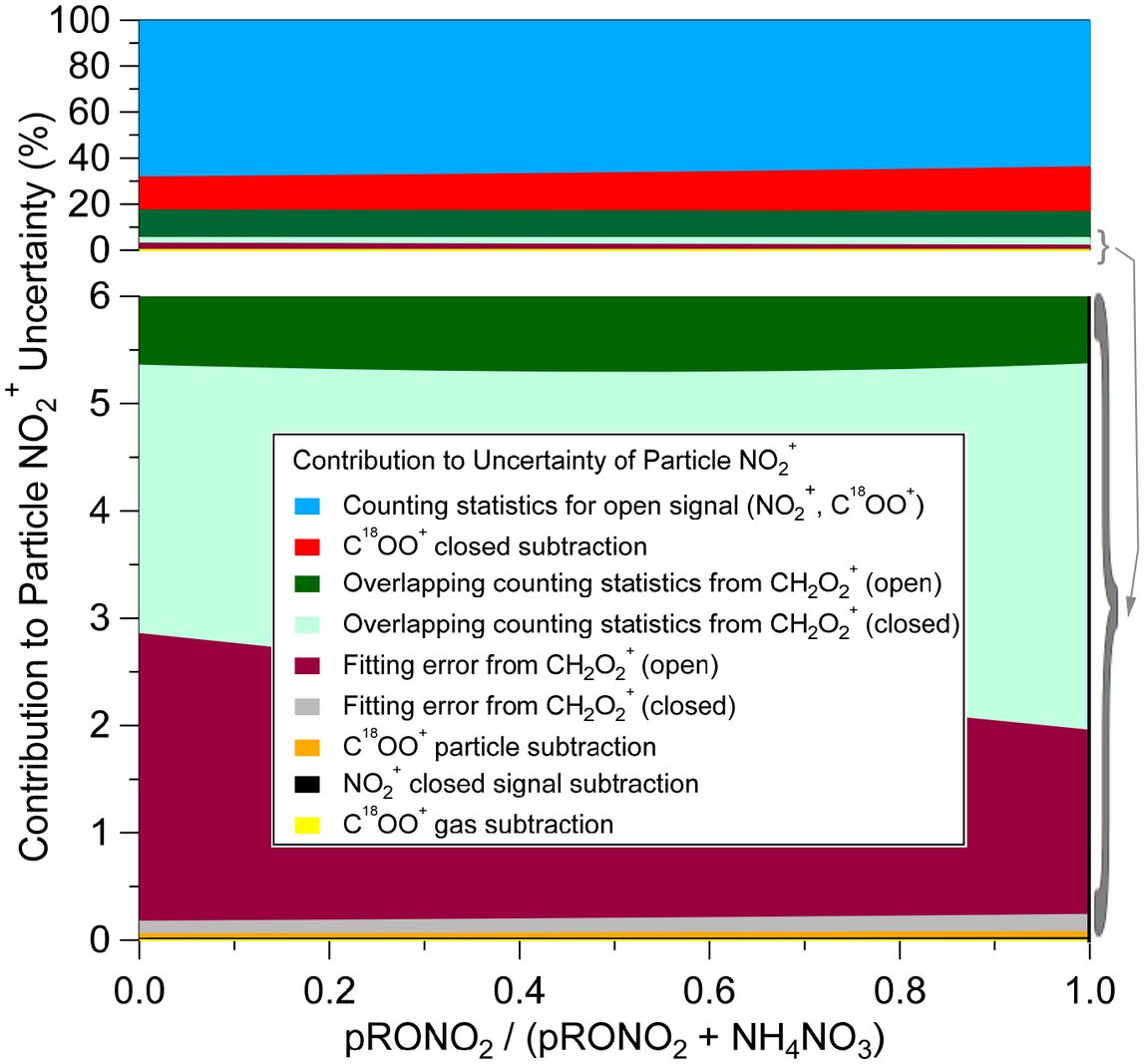
(Day et al., AMT 2022)

$\sigma_{[pNO_3]}: \pm 16.5\%$

(Bahreini et al., AMT 2009)

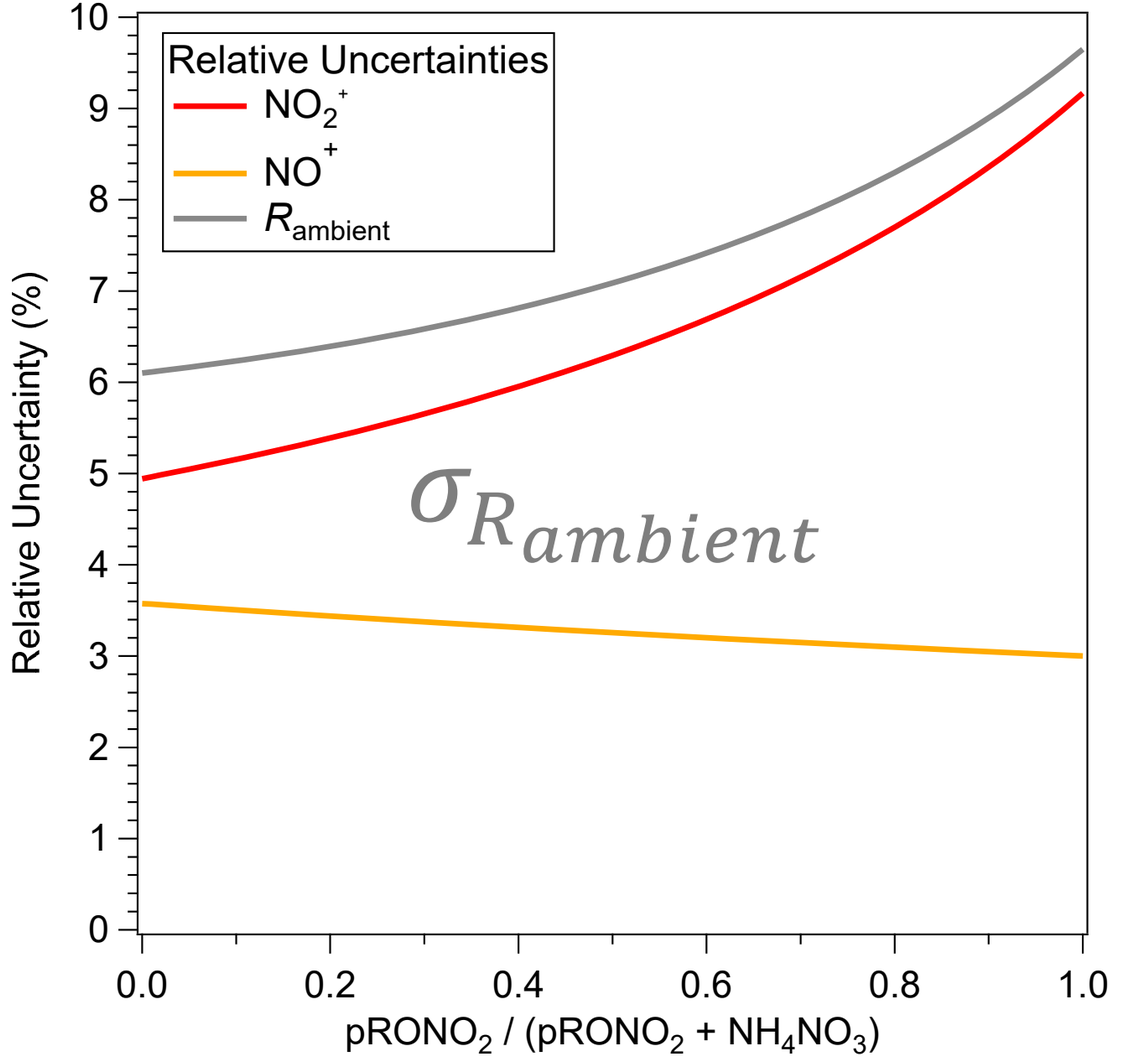
Contributions to particle NO_x^+, $R_{ambient}$ uncertainty

Particle NO_2^+ Uncertainty Contribution



NH_4NO_3 ⟷ $pRONO_2$

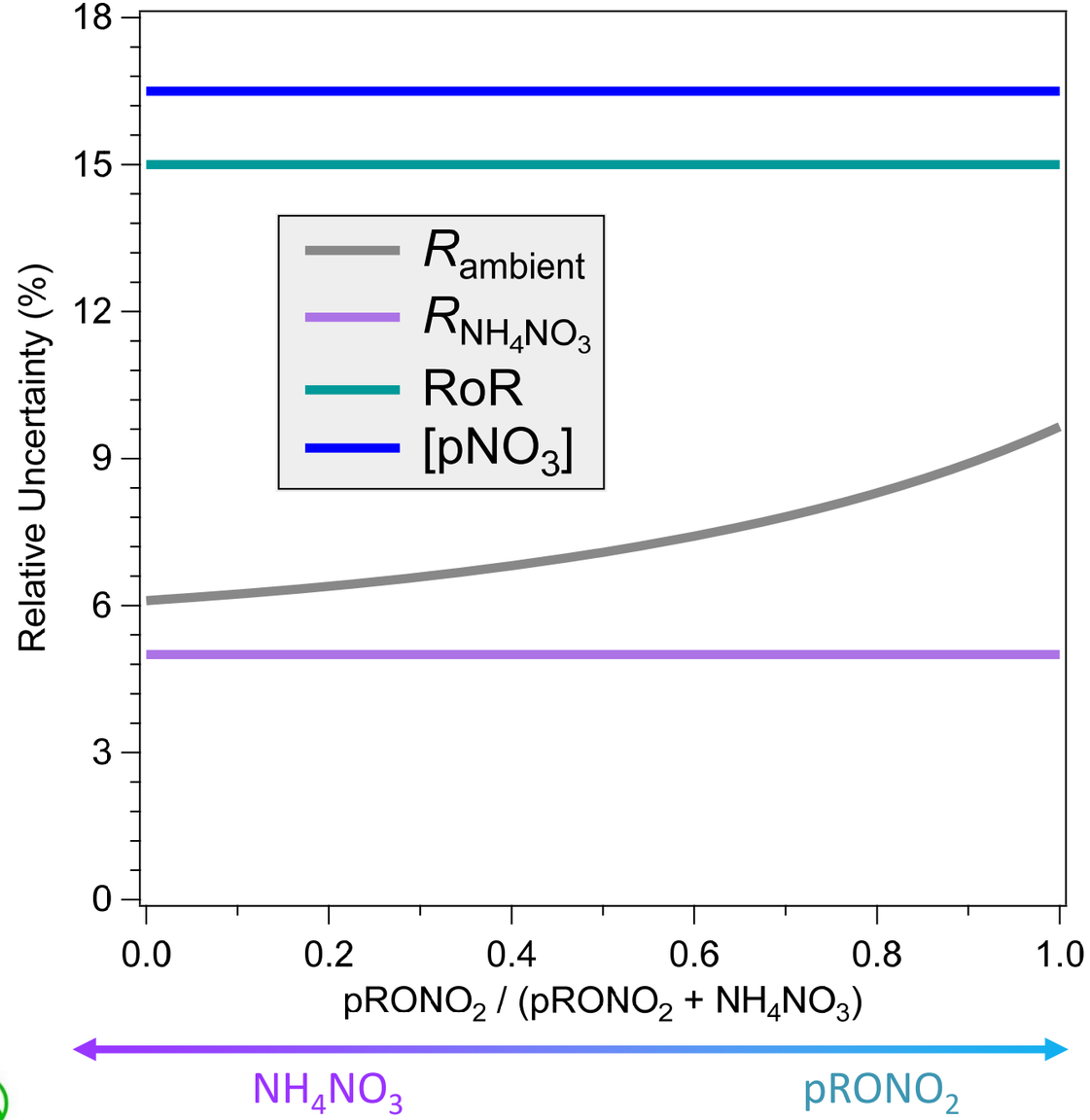
NO_2^+, NO^+, $R_{ambient}$ uncertainty



NH_4NO_3 ⟷ $pRONO_2$

Overall Uncertainties

Input Terms (as Rel. Uncert)



$$\sigma_{R_{ambient}}$$

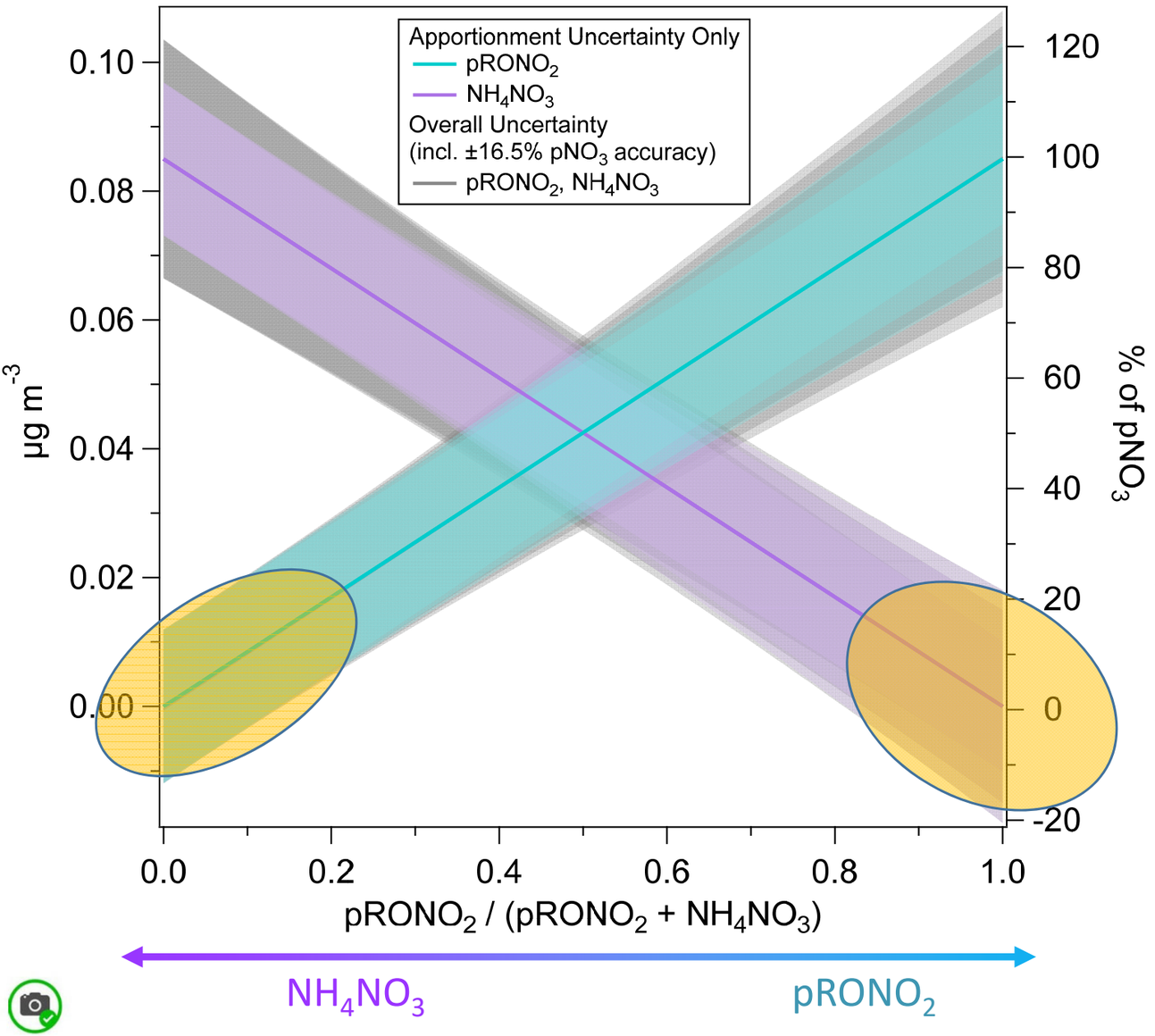
$$\sigma_{R_{NH_4NO_3}}: \pm 5\%$$

$$\sigma_{RoR}: \pm 15\%$$

$$\sigma_{[pNO_3]}: \pm 16.5\%$$

Overall Uncertainties

Absolute Uncertainties



Monte Carlo Simulations

$$f_{pRONO_2} = \frac{(R_{ambient} - R_{NH_4NO_3})(1 + \frac{R_{NH_4NO_3}}{RoR})}{(\frac{R_{NH_4NO_3}}{RoR} - R_{NH_4NO_3})(1 + R_{ambient})}$$

$$pRONO_2 = f_{pRONO_2} \times pNO_3$$

(propagated in simple quadrature)

$$\sigma_{pRONO_2} = \sqrt{\sigma_{f_{pRONO_2}}{}^2 + \sigma_{[pNO_3]}{}^2}$$

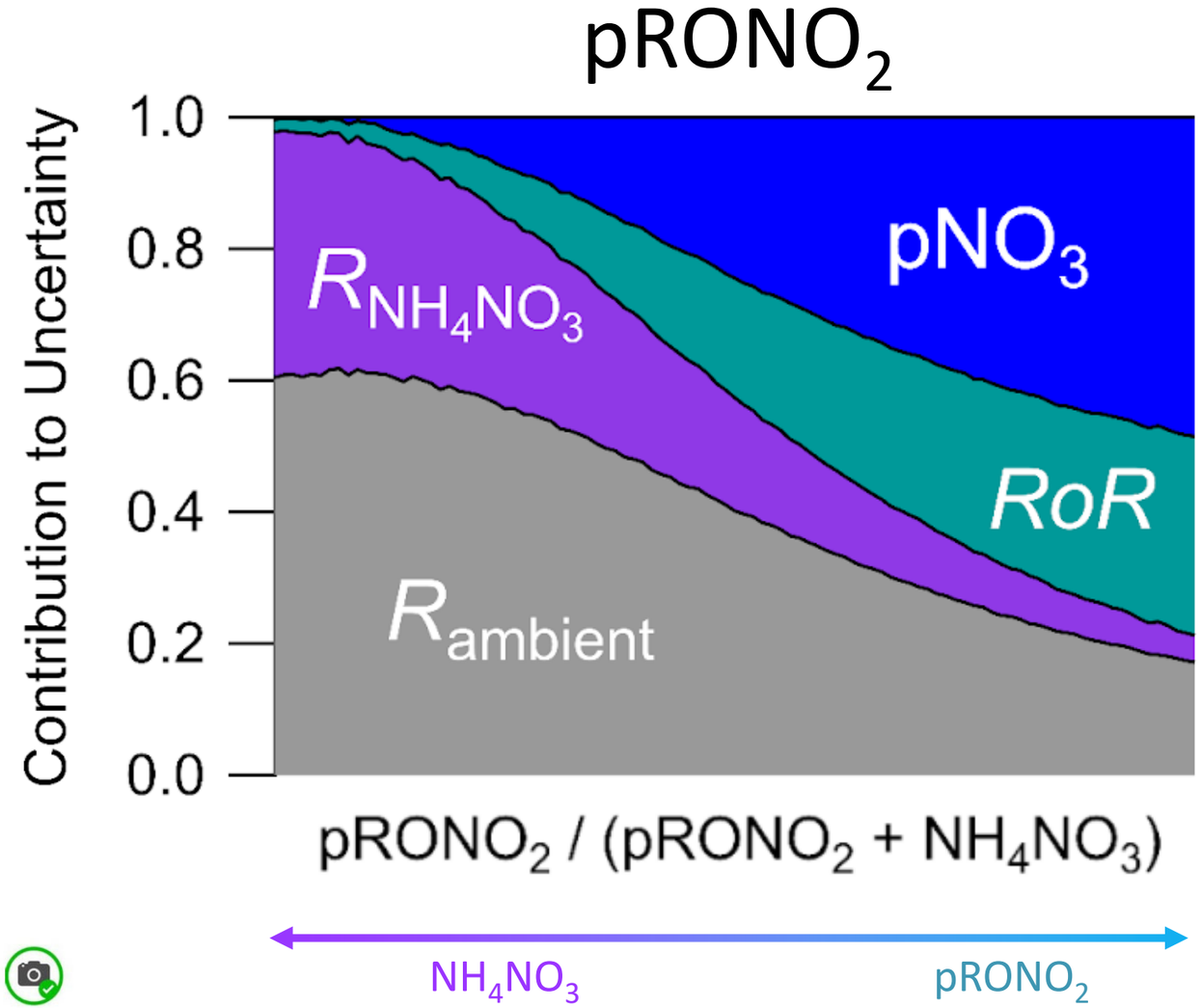
Contributions to Overall Uncertainties

$\sigma_{R_{ambient}}$ (composition-dependent)

$\sigma_{R_{NH_4NO_3}}$: ±5%

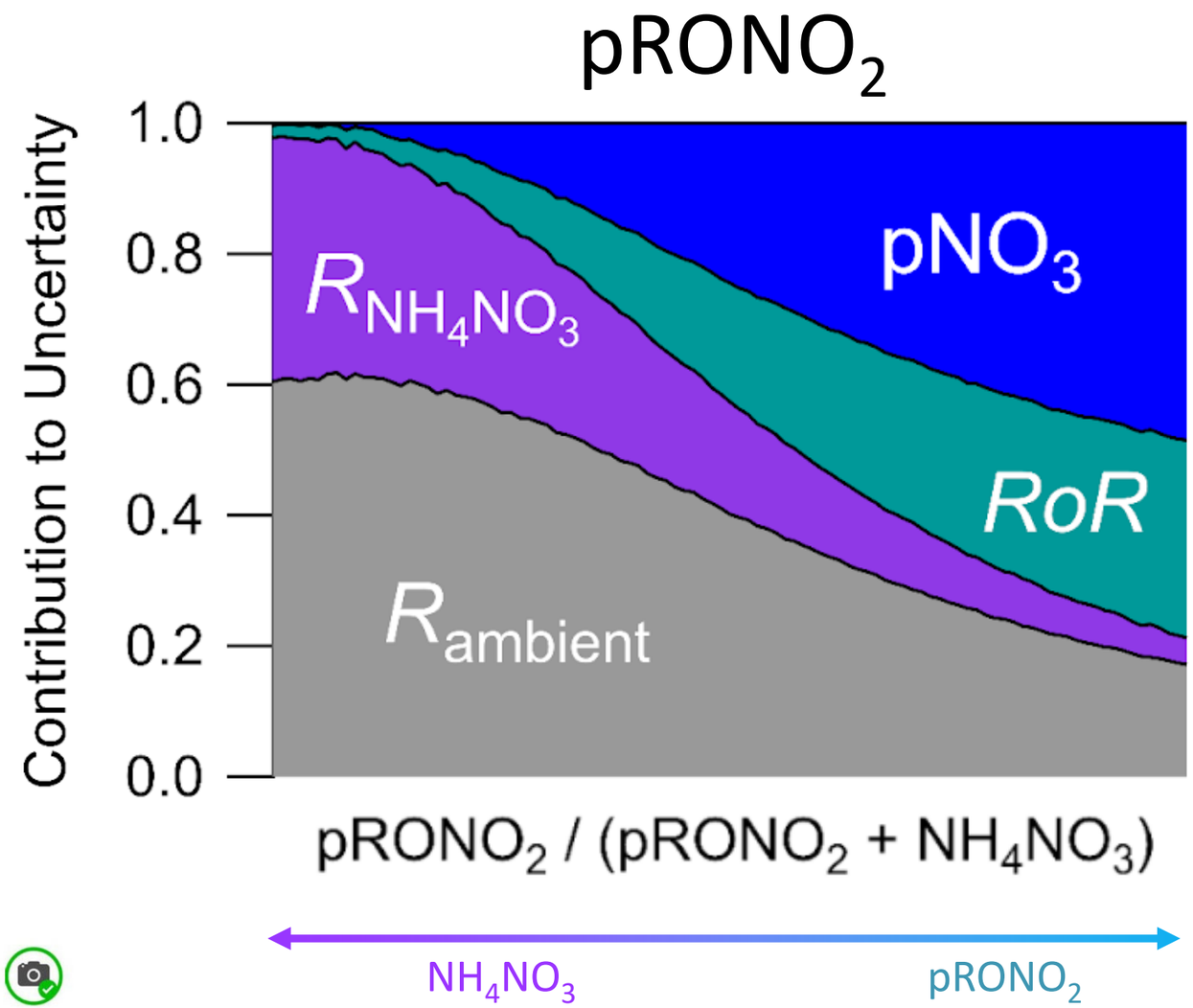
σ_{RoR}: ±15%

$\sigma_{[pNO_3]}$: ±16.5%

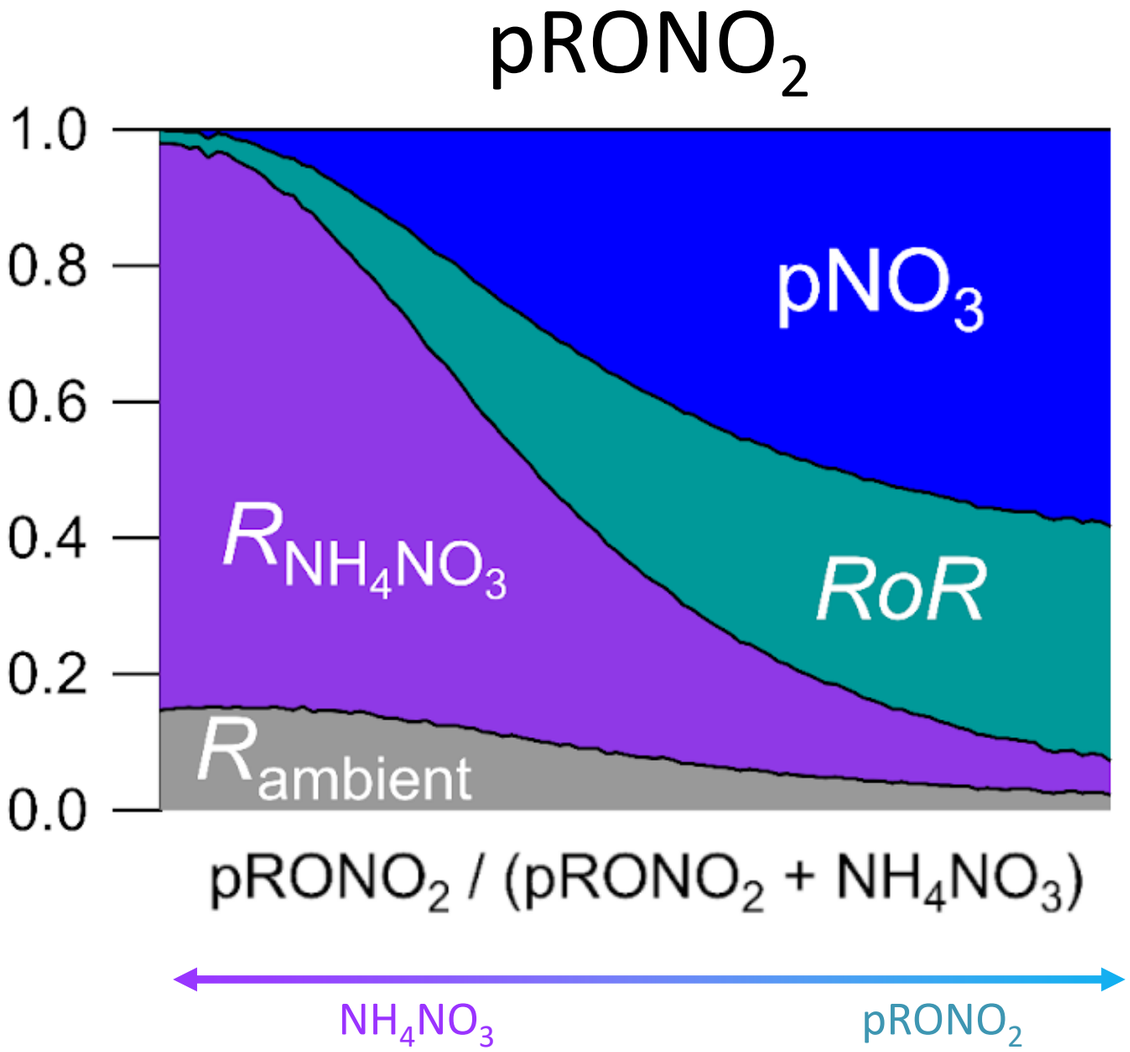


Contributions to Overall Uncertainties

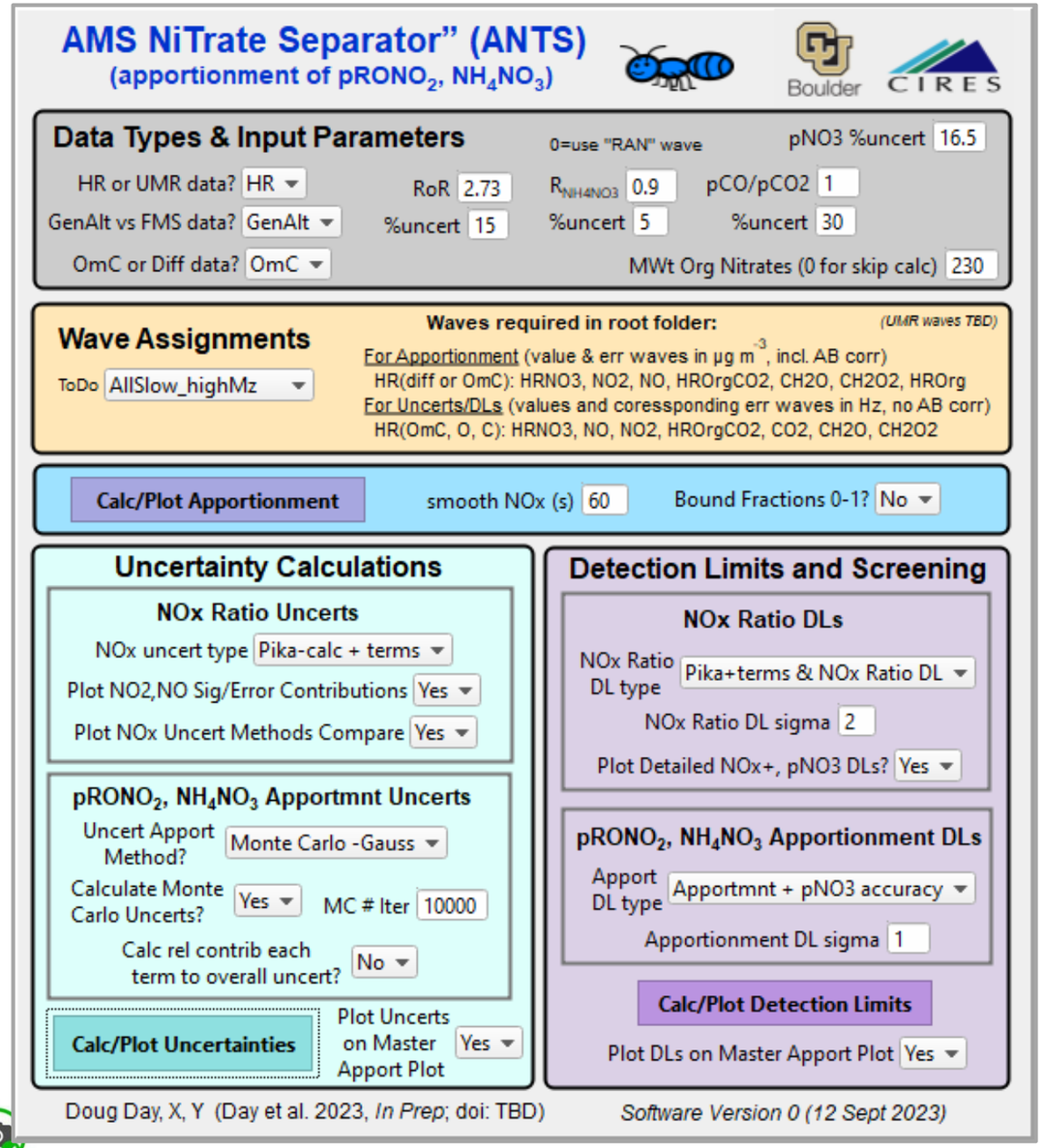
Base Case (1-min average)



10-min averaging

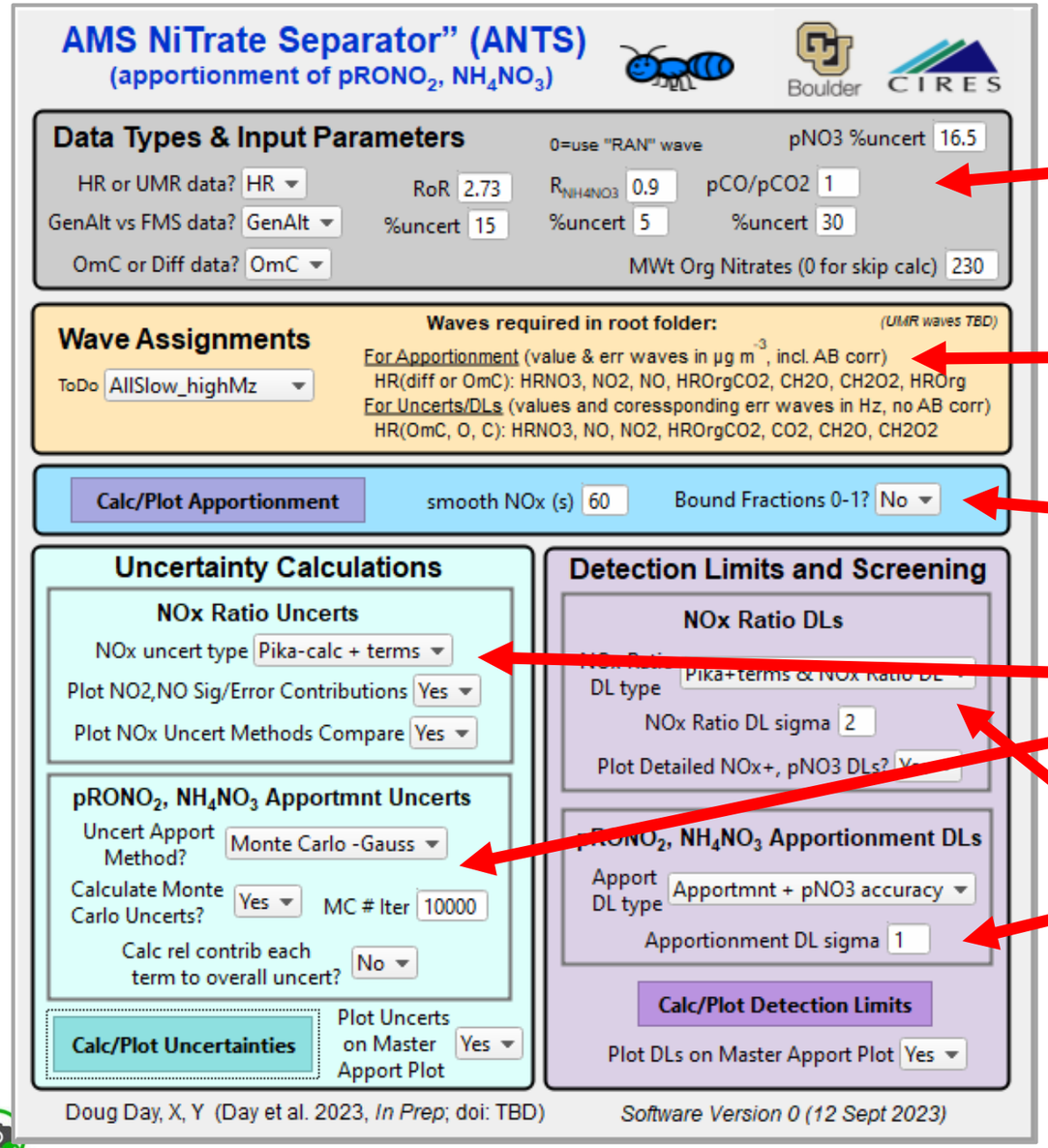


ANTS software (AMS NiTrate Separator)



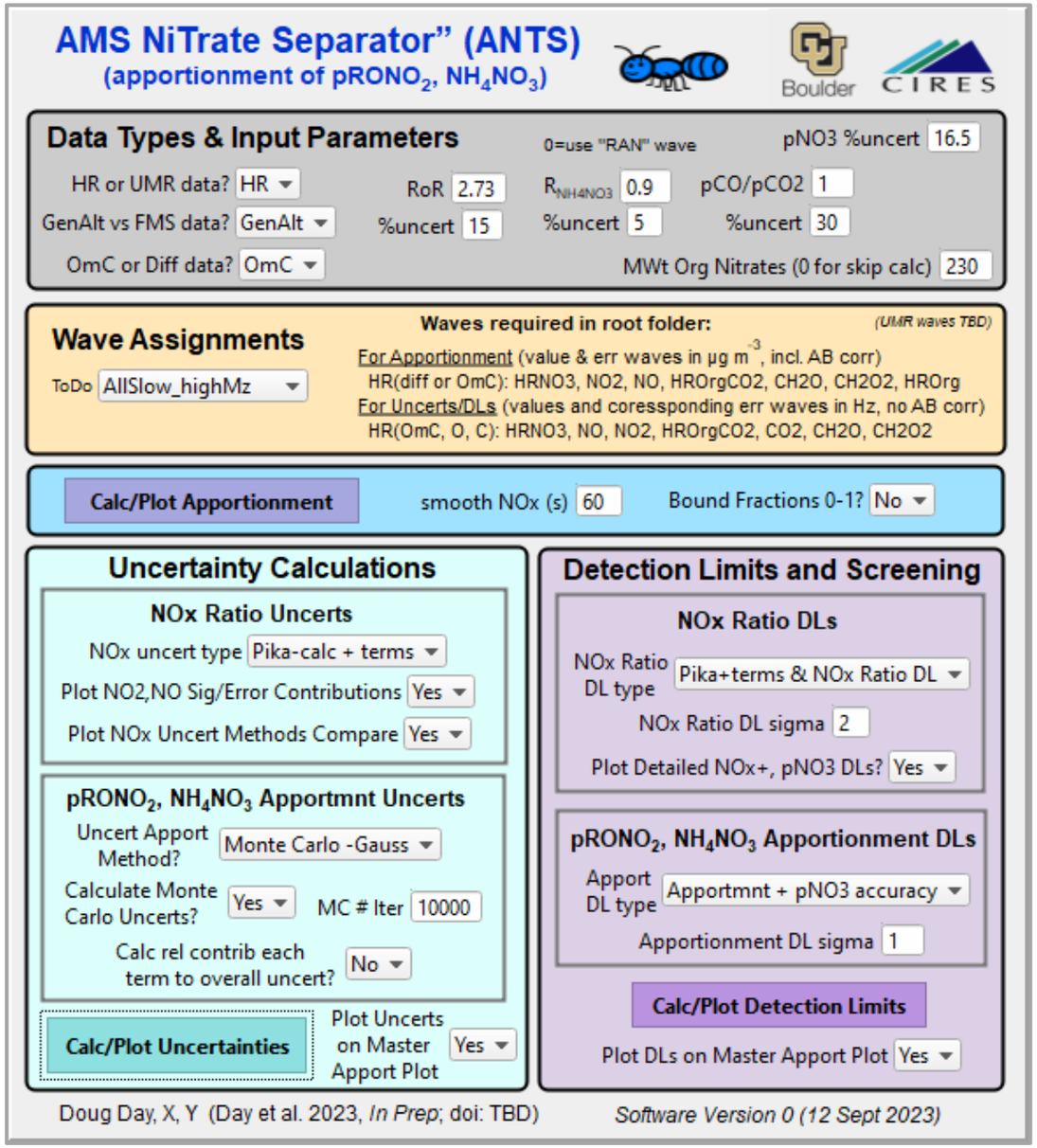
- Publically-available open-source
- Beta version complete. Further testing on ambient datasets.
- UMR apportionment & uncertainties to be added.

ANTS software (AMS NiTrate Separator)



- User selectable input: e.g. type of data, parameters, uncertainties
- Runs in AMS analysis software (Sq/Pika) Generates all required waves
- Computes/plots apportionment
- Computes/plots uncertainties.
- Computes/plots detection limits.

ANTS output


AMS NiTrate Separator" (ANTS)
(apportionment of pRONO2, NH4NO3)
Boulder
CIRES
Data Types & Input Parameters
0=use "RAN" wave
pNO3 %uncert 16.5
HR or UMR data? HR
RoR 2.73
R NH4NO3 0.9
pCO/pCO2 1
GenAlt vs FMS data? GenAlt
%uncert 15
%uncert 5
%uncert 30
OmC or Diff data? OmC
MWt Org Nitrates (0 for skip calc) 230
Wave Assignments
(UMR waves TBD)
Waves required in root folder:
For Apportionment (value & err waves in µg m-3, incl. AB corr)
HR(diff or OmC): HRNO3, NO2, NO, HROrgCO2, CH2O, CH2O2, HROrg
For Uncerts/DLs (values and coressponding err waves in Hz, no AB corr)
HR(OmC, O, C): HRNO3, NO, NO2, HROrgCO2, CO2, CH2O, CH2O2
ToDo AllSlow_highMz
Calc/Plot Apportionment
smooth NOx (s) 60
Bound Fractions 0-1? No
Uncertainty Calculations
NOx Ratio Uncerts
NOx uncert type Pika-calc + terms
Plot NO2,NO Sig/Error Contributions Yes
Plot NOx Uncert Methods Compare Yes
pRONO2, NH4NO3 Apportmnt Uncerts
Uncert Apport Method? Monte Carlo -Gauss
Calculate Monte Carlo Uncerts? Yes
MC # Iter 10000
Calc rel contrib each term to overall uncert? No
Calc/Plot Uncertainties
Plot Uncerts on Master Apport Plot Yes
Detection Limits and Screening
NOx Ratio DLs
NOx Ratio DL type Pika+terms & NOx Ratio DL
NOx Ratio DL sigma 2
Plot Detailed NOx+, pNO3 DLs? Yes
pRONO2, NH4NO3 Apportionment DLs
Apport DL type Apportmnt + pNO3 accuracy
Apportionment DL sigma 1
Calc/Plot Detection Limits
Plot DLs on Master Apport Plot Yes
Doug Day, X, Y (Day et al. 2023, In Prep; doi: TBD)
Software Version 0 (12 Sept 2023)

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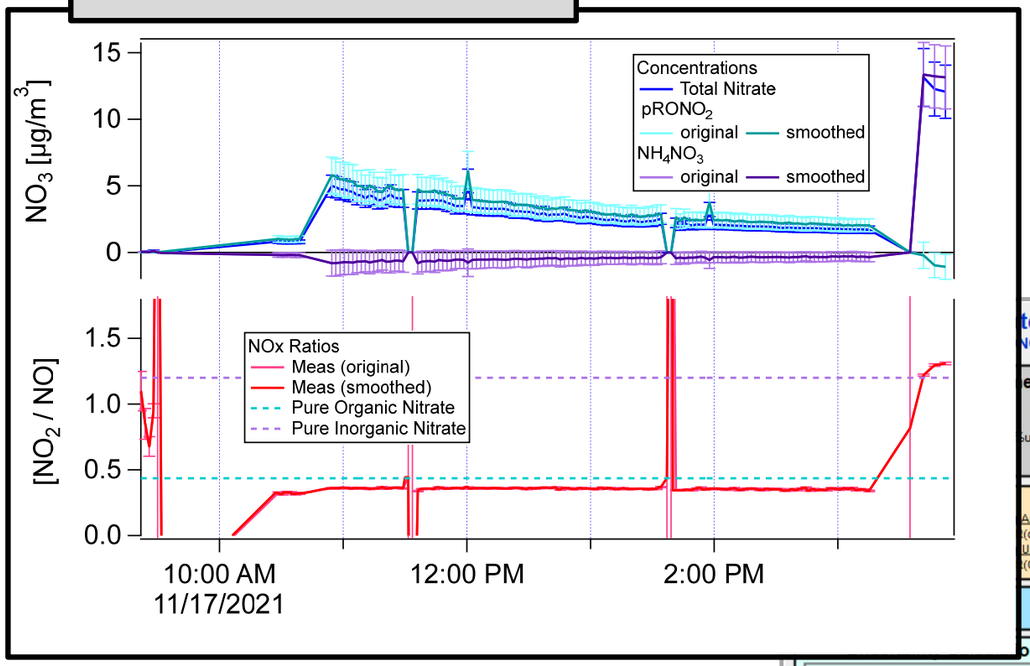
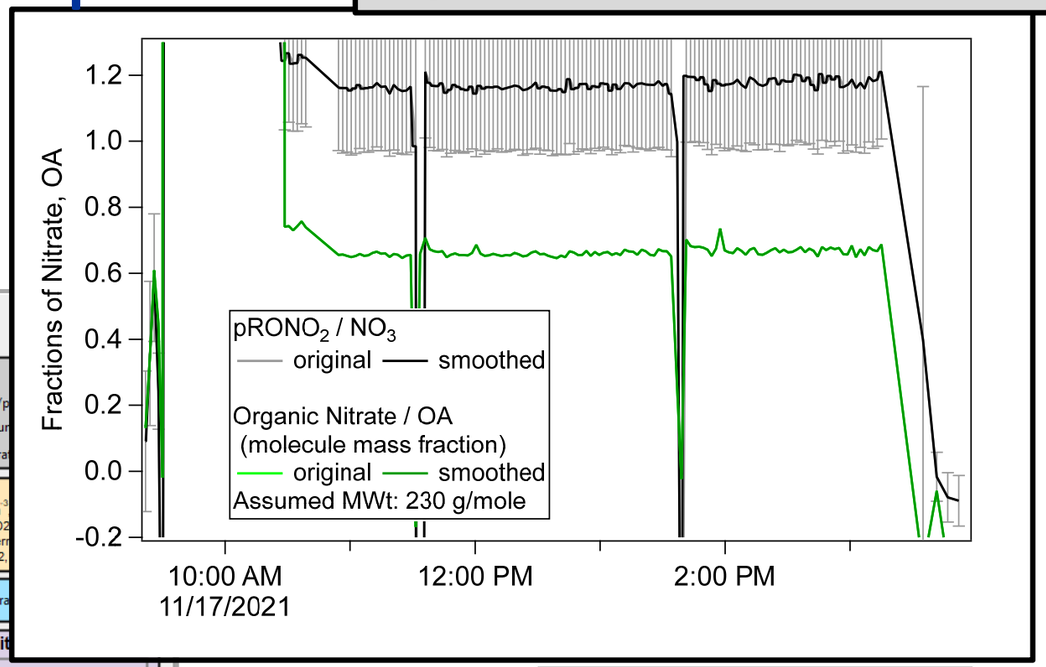
ANTS output

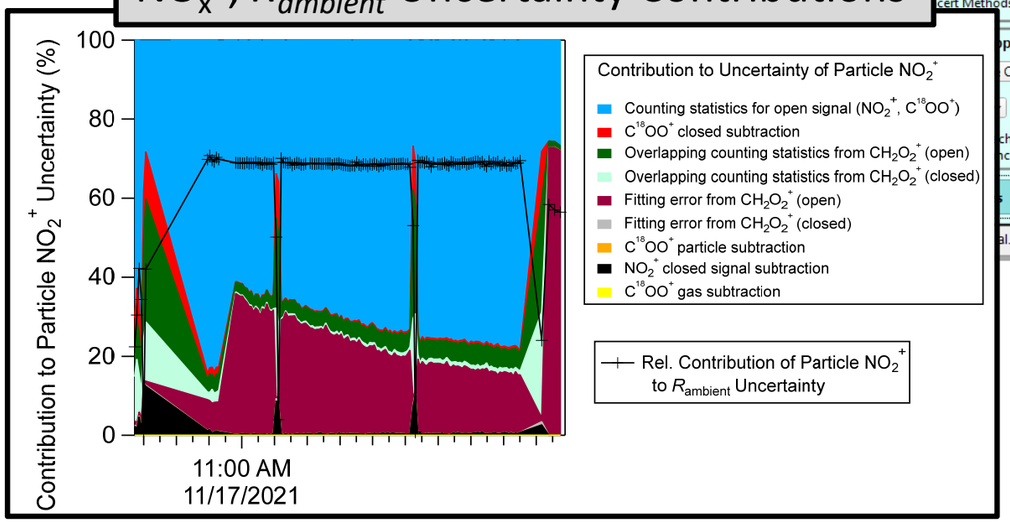
Nitrate Apportionment + Uncertainties + DLs



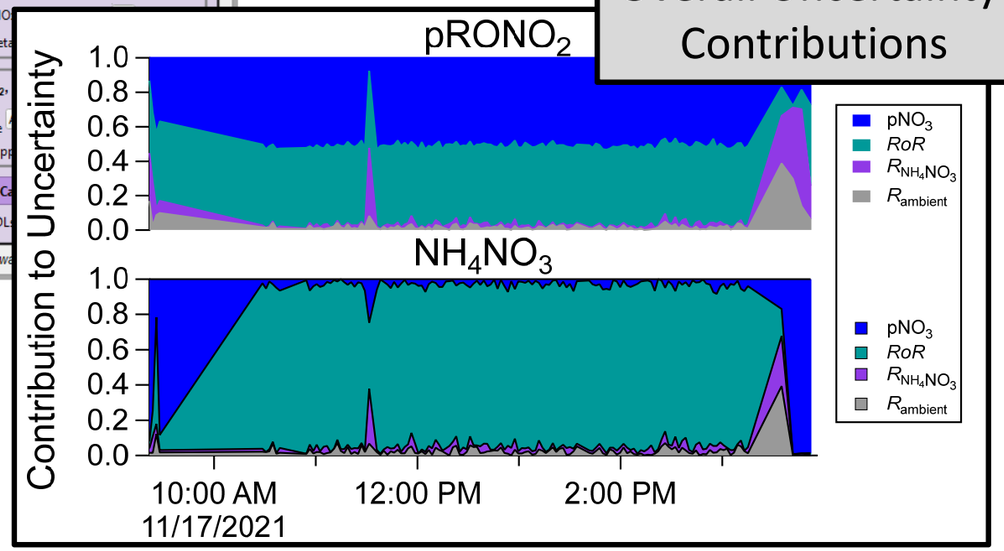
Organic Nitrate Contributions to OA



NO_x^+, $R_{ambient}$ Uncertainty Contributions



Overall Uncertainty Contributions



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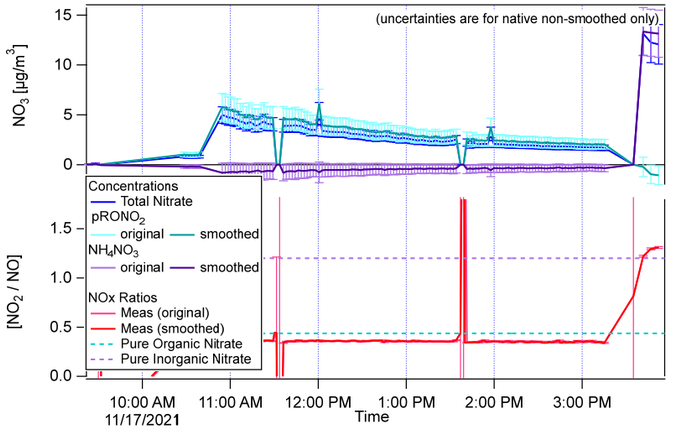
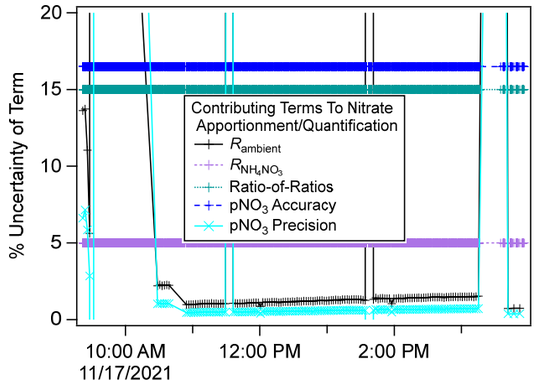
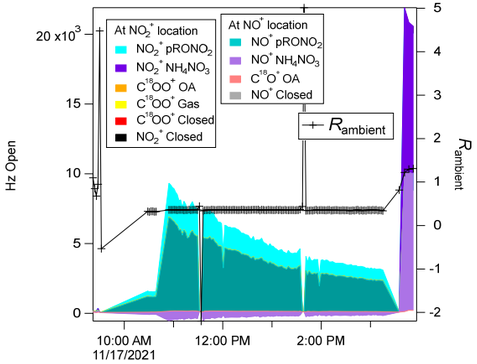
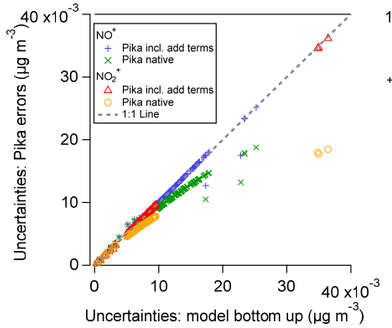
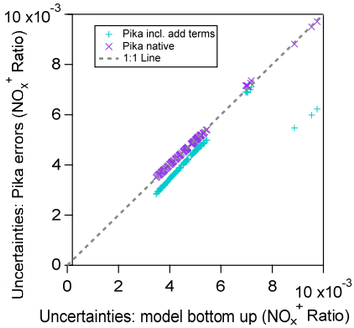
ANTS output

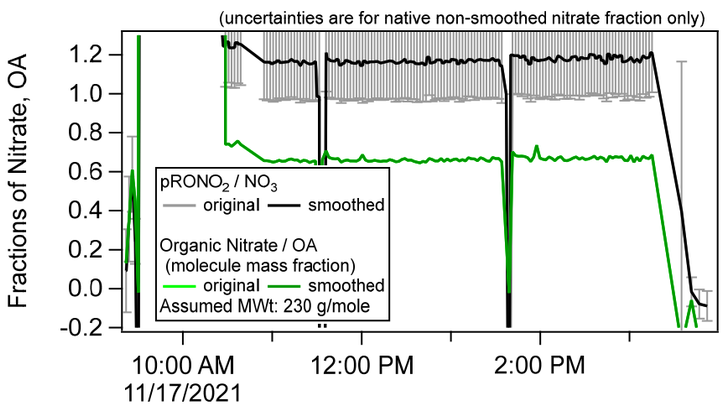


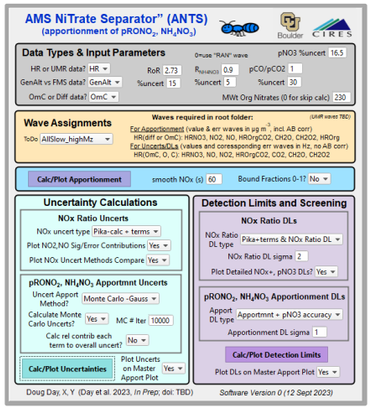


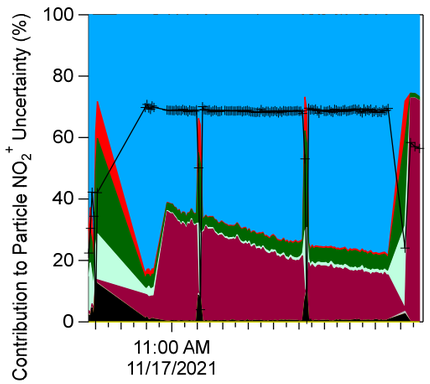


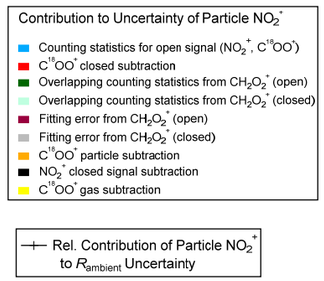


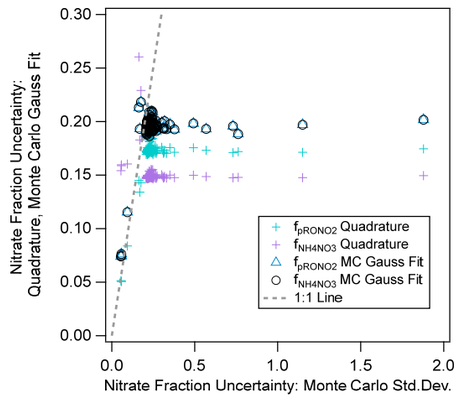


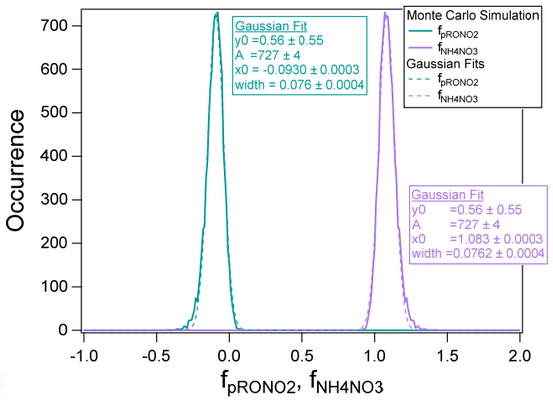


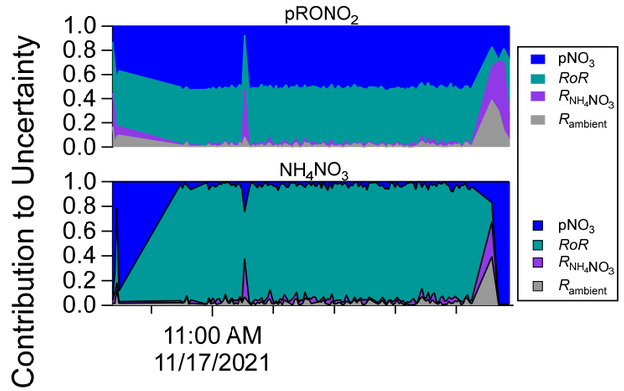


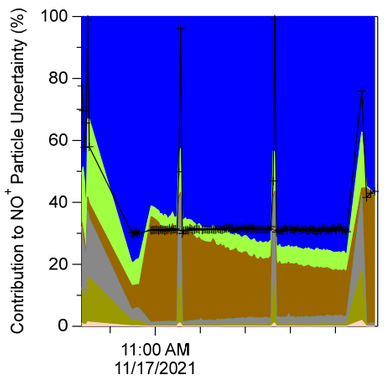


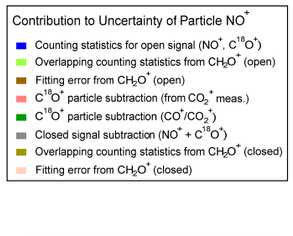


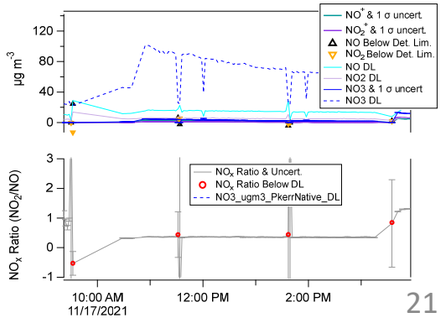












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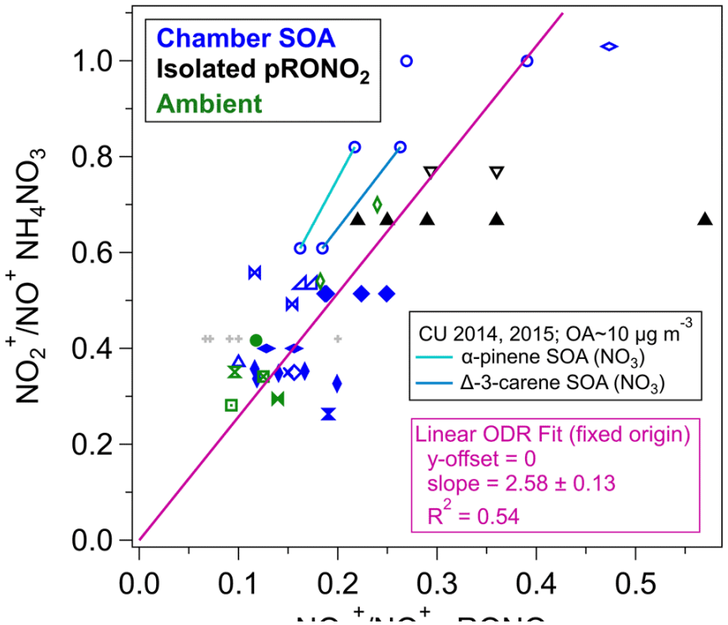
R_{pRONO_2} tracks $R_{NH_4NO_3}$ (NO_x^+ Ratio-of-Ratios, RoR)

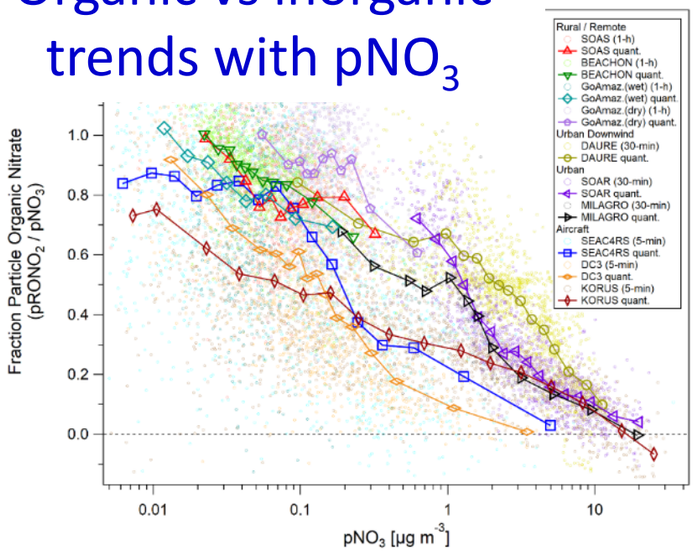


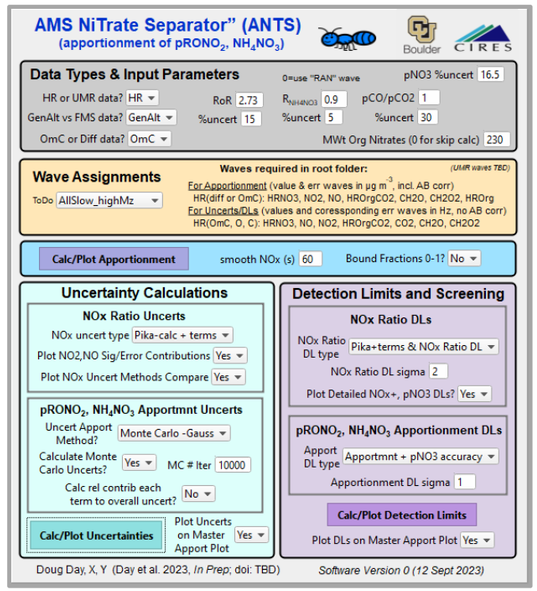
Strong dependencies of uncertainties & contributions to uncertainties with composition, averaging

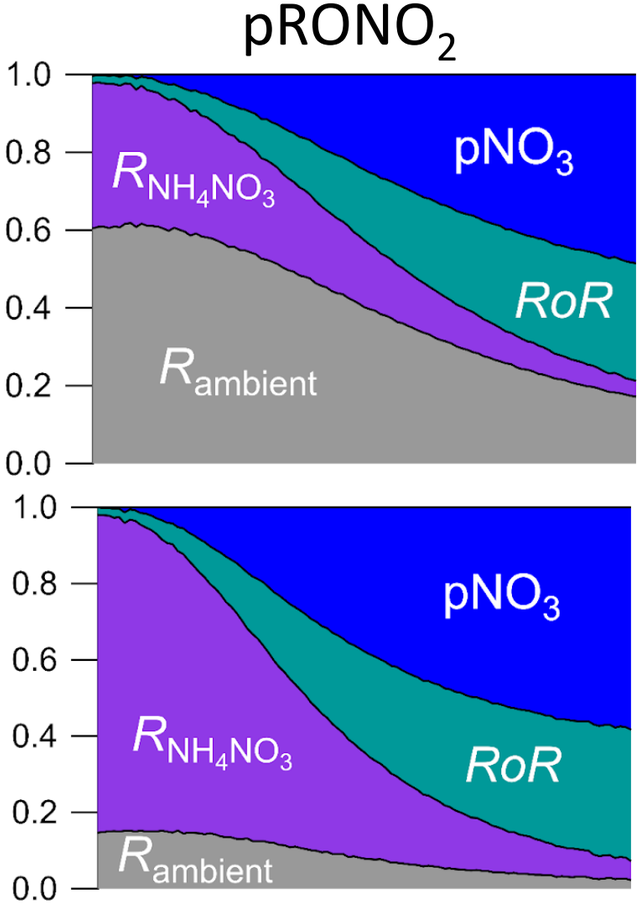
paper on uncertainties + software coming soon

Overview

Organic vs inorganic trends with pNO_3







Easy-to-use software tool for computing and exploring:

- apportionment
- uncertainties
- detection limits