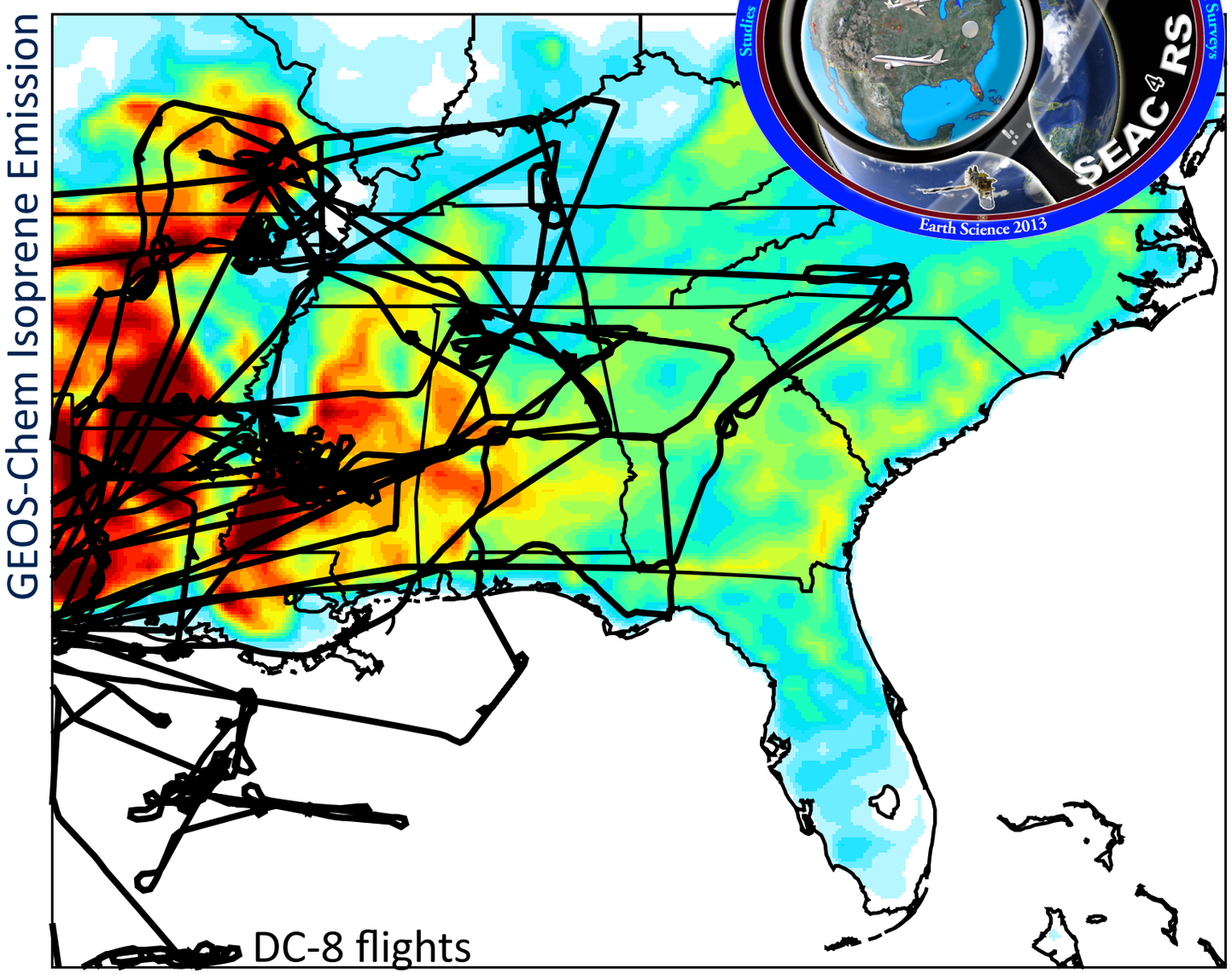
Organic nitrate chemistry in the Southeast US: implications for nitrogen and aerosol budgets



Jenny A. Fisher
University of Wollongong

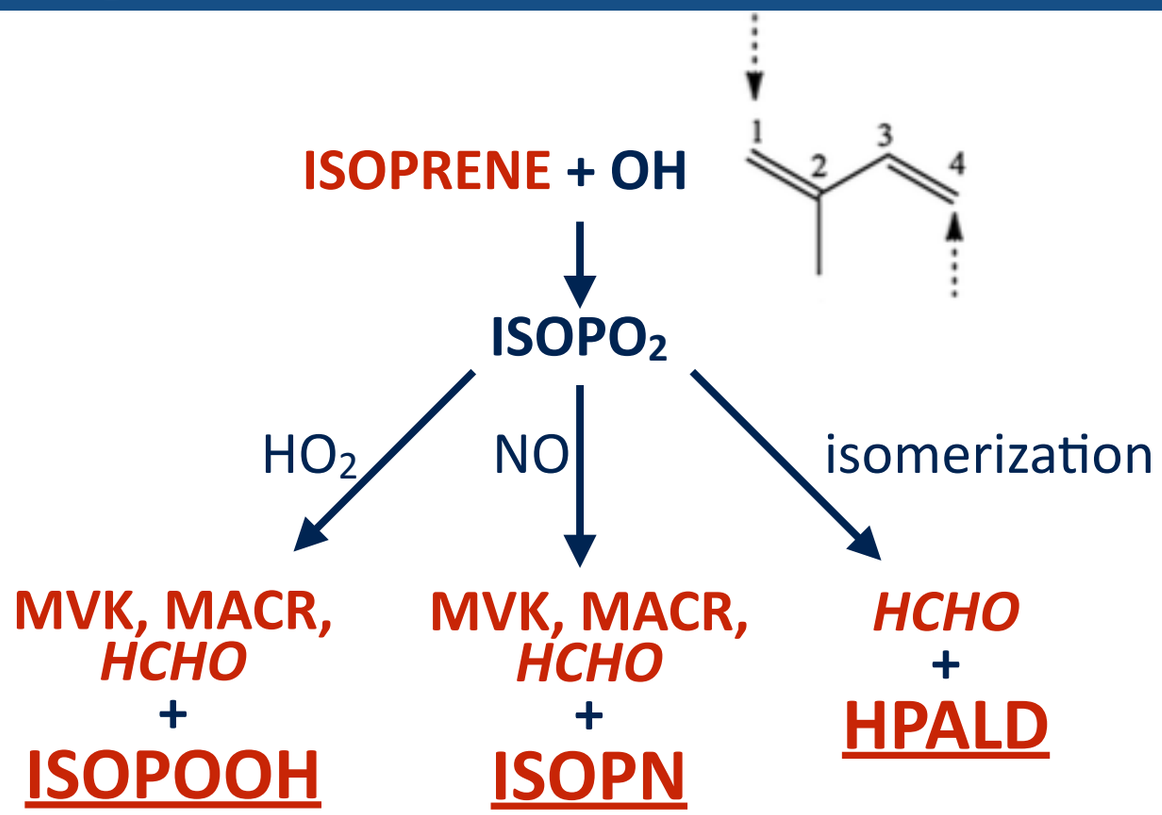
Daniel Jacob, Katherine Travis, Ronald Cohen, Alan Fried, Thomas Hanisco, Jingqiu Mao, Paul Wennberg, John Crounse, Jason St Clair, Alex Teng, Armin Wisthaler, Tomas Mikoviny, Jose Jimenez, Pedro Campuzano-Jost, Patrick Kim, Eloise Marais, Fabien Paulot, Karen Yu, Lei Zhu, Robert Yantosca, Melissa Payer Sulprizio

2015 SEAC4RS Science Team Meeting

Acknowledgements: NASA Tropospheric Chemistry Program, University of Wollongong Vice Chancellor's Fellowship

SEAC^{4}RS provides unprecedented dataset to evaluate biogenic VOC oxidation chemistry and impacts

Isoprene oxidation follows multiple pathways.



***species measured during SEAC^{4}RS by Wisthaler, *Hanisco, Fried*, Wennberg & Crounse groups**

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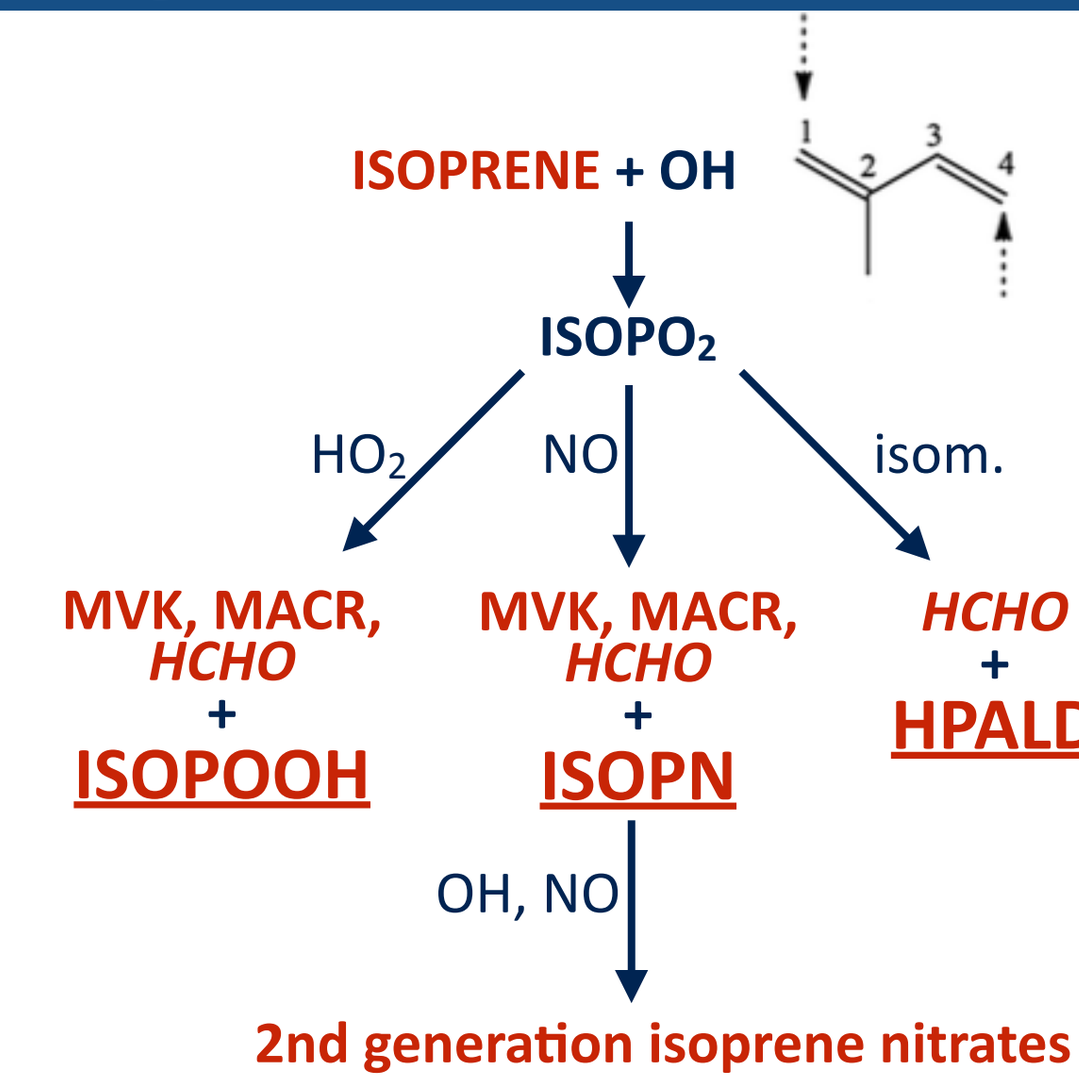

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Isoprene nitrates from $ISOPO_2$+NO can consume or store NO_X and produce organic nitrate aerosol.

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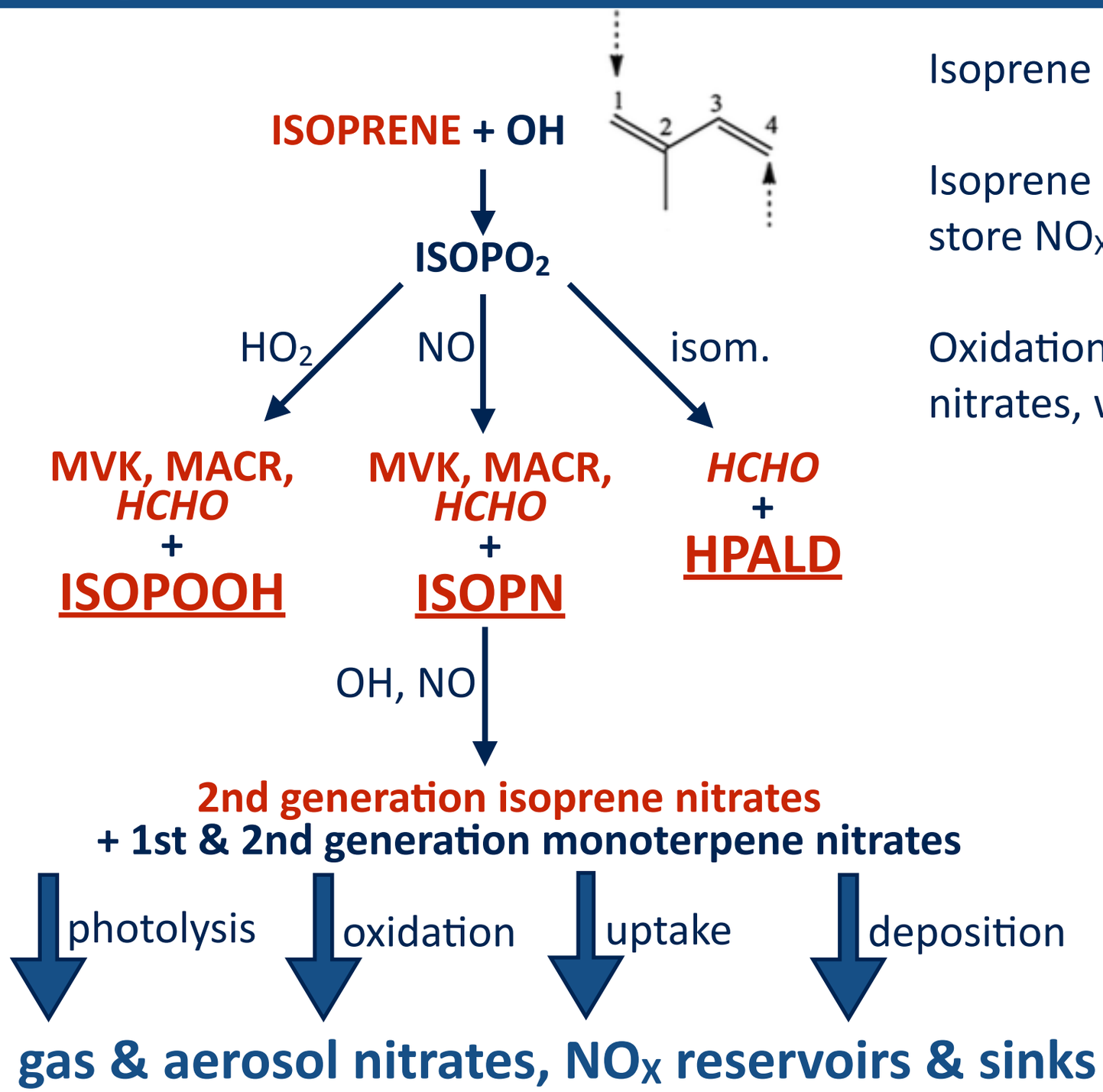

Isoprene oxidation follows multiple pathways.

Isoprene nitrates from $ISOPO_2$+NO can consume or store NO_X and produce organic nitrate aerosol.

Oxidation of monoterpenes can form monoterpene nitrates, with similar effects

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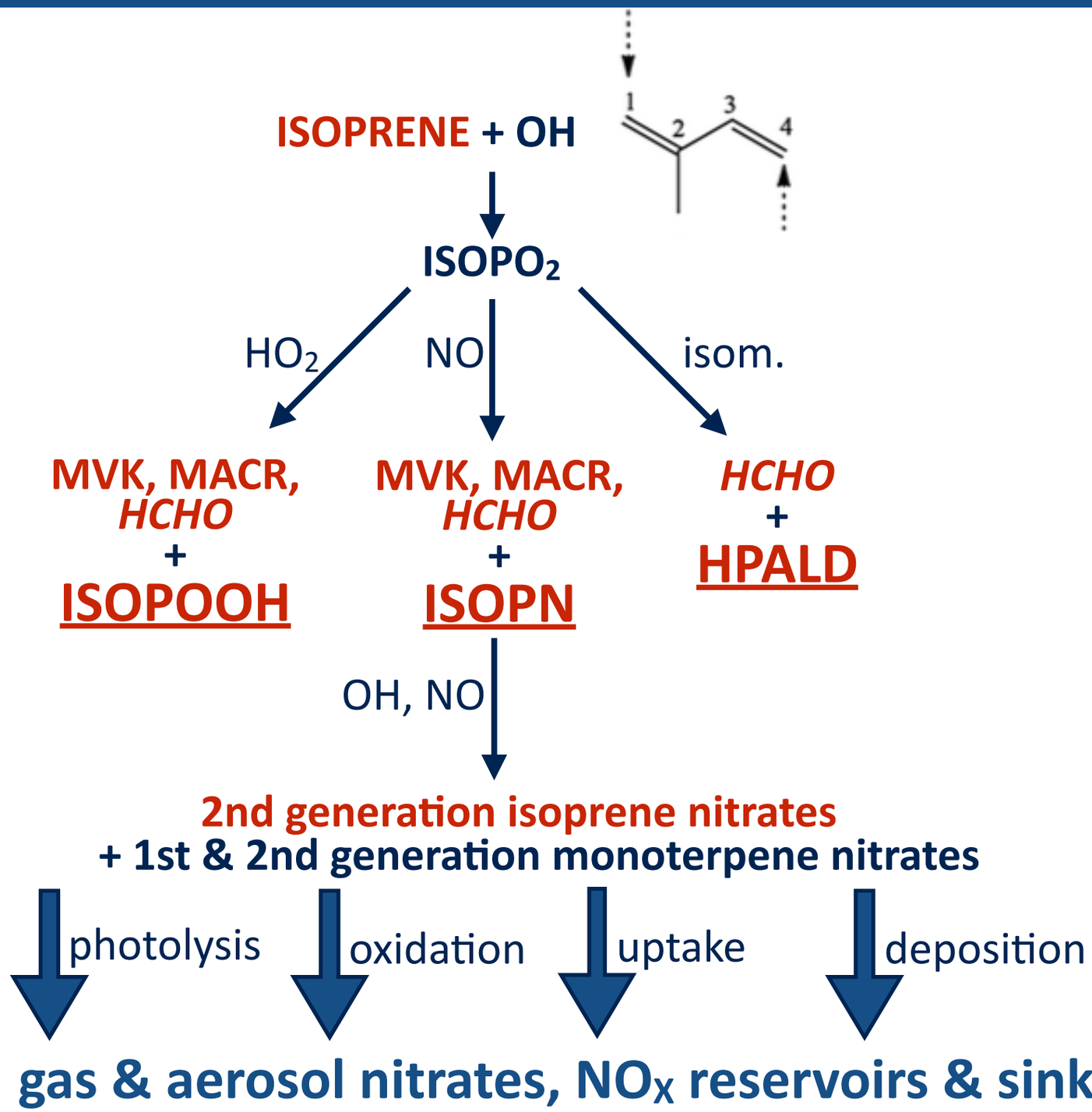
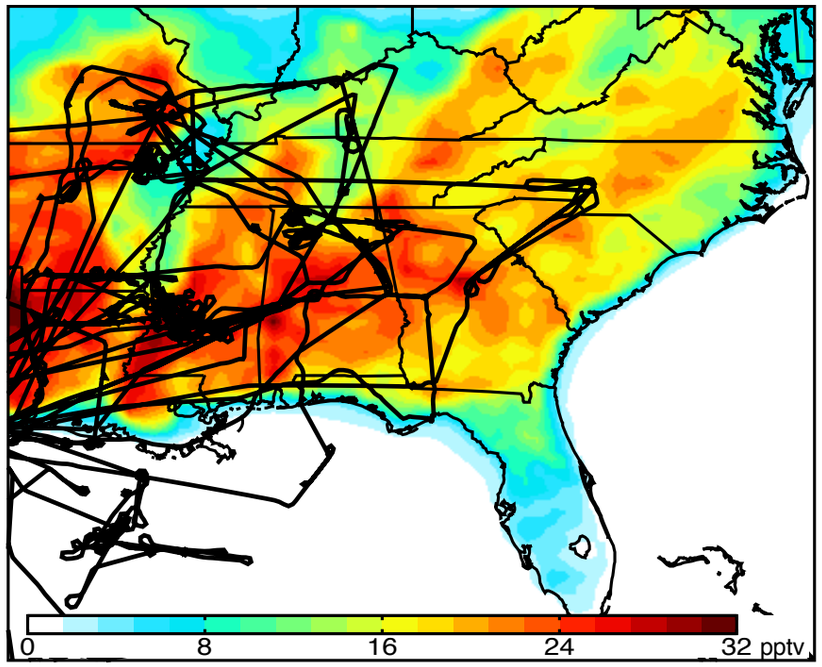


Aug-Sep 2013 SEAC^{4}RS flights over simulated surface ISOPN



SEAC^{4}RS provides a rich dataset to constrain chemistry & test impacts.

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High-resolution GEOS-Chem simulation provides framework for testing oxidation mechanisms

GEOS-Chem CTM driven by GEOS-FP meteorology at **0.25° x 0.3125°** horizontal resolution over N. America.

Biogenic emissions from MEGANv2.1, with isoprene reduced by 15% to match satellite HCHO (*L. Zhu*) and monoterpenes doubled to match PTRMS data

Isoprene chemistry modified from *Mao et al. (2013)*:

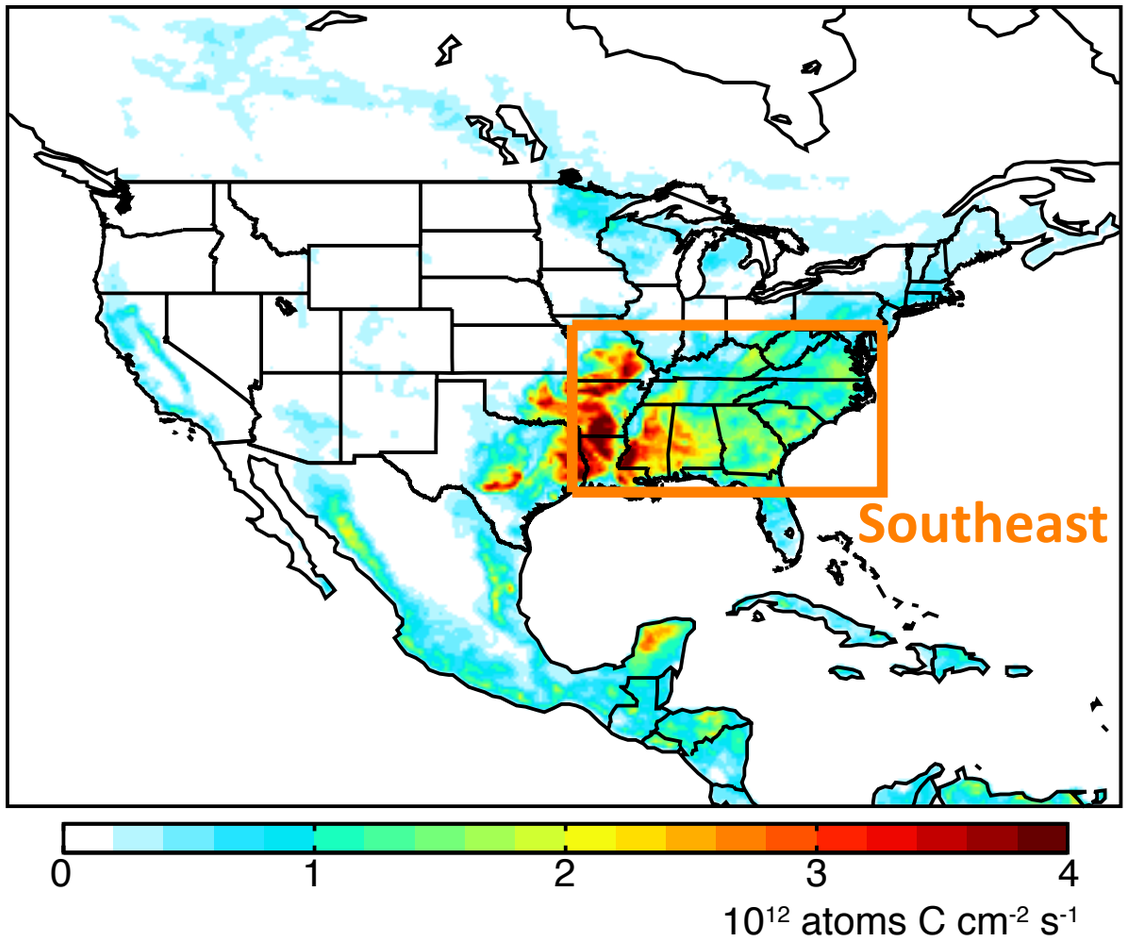
- **fast photolysis** of carbonyl nitrates (*Müller et al., 2014*)
- **updated kinetics & products** from lab studies for $ISOPO_2$+NO and $ISOPO_2$+HO_2 pathways (e.g., *Lee et al., 2014; Jacobs et al., 2014; Bates et al., 2014; …*)

Monoterpene chemistry based on *Browne et al. (2014)*

Enhanced deposition of isoprene oxidation products (*Nguyen et al., 2015*)

Aerosol uptake & subsequent hydrolysis of isoprene and monoterpene nitrates

August-September 2013 isoprene emissions



Jenny A. Fisher
jennyf@uow.edu.au

Take-home messages from this work (so far…):

1. **>50% of the observed alkyl nitrates** can be attributed to **isoprene nitrates (INs)** — but not all!

2. **Monoterpene nitrates (MTNs)** can explain another **~25%**, although this chemistry remains poorly constrained.

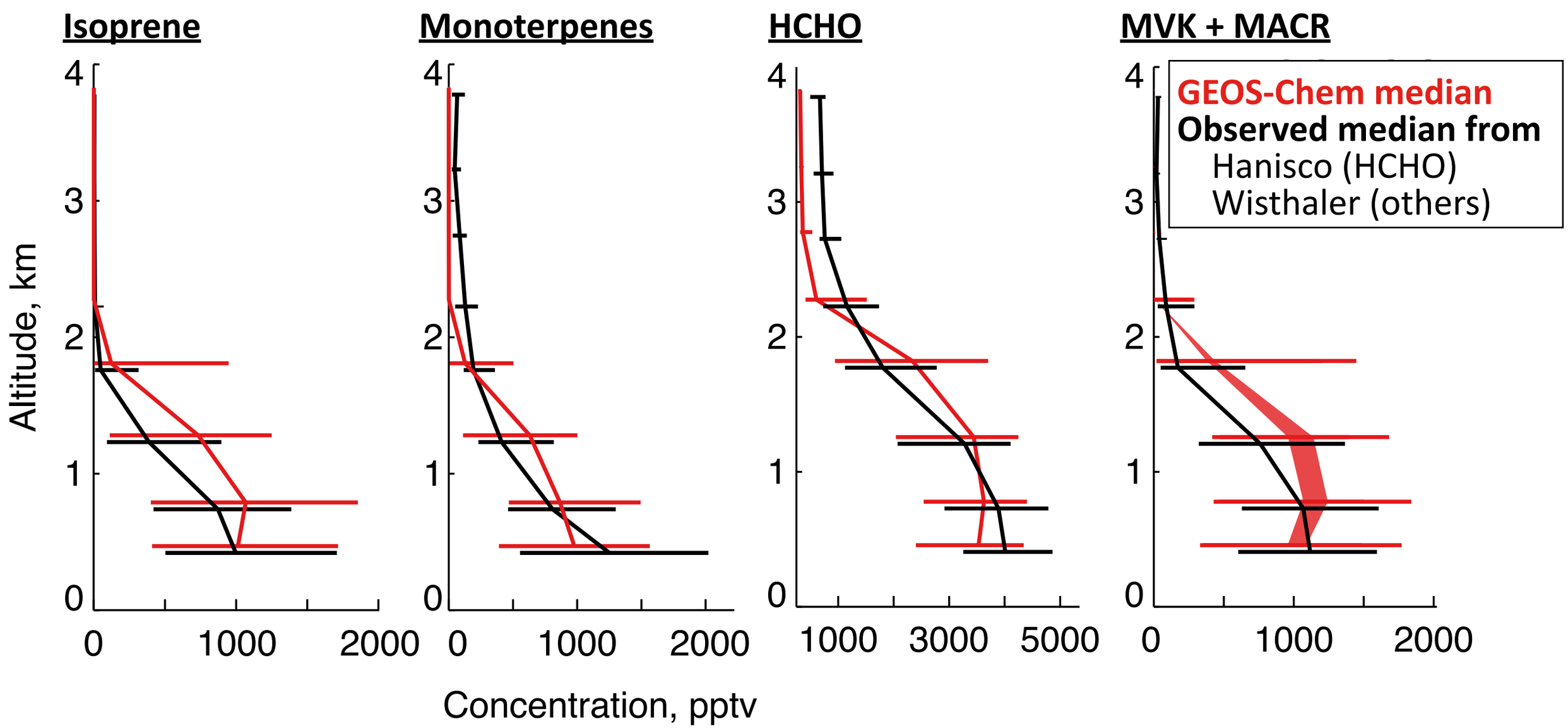
3. We simulate that **~10% of INs and MTNs** are in the **particle phase** at the surface — but overestimate particulate organic nitrate and underestimate total alkyl nitrates, both at the surface and aloft.

4. During SEAC4RS, **INs and MTNs** are responsible for **~10% of N deposition** over the Southeast US.

5. **Formation of INs and MTNs** can be responsible for **up to 70% of the terminal NO_X sink** in low-NO_X, high-VOC regions.

BVOCs and oxidation products over the Southeast US

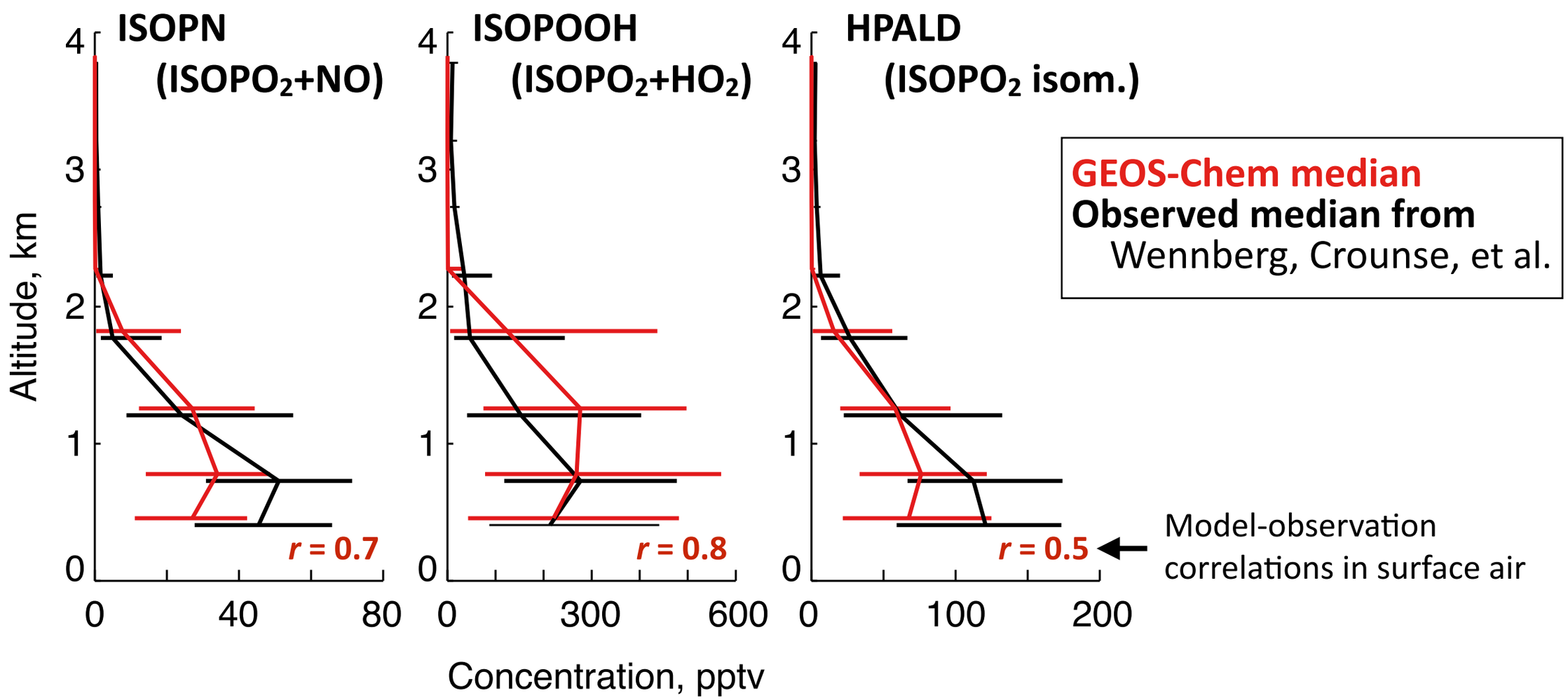
Isoprene, monoterpenes, and major oxidation products show expected boundary layer enhancement (reproduced by GEOS-Chem).



jennyf@uow.edu.au

Isoprene oxidation products over the Southeast US

Unique first generation products of isoprene oxidation pathways accurately partitioned in GEOS-Chem, although with some surface biases.



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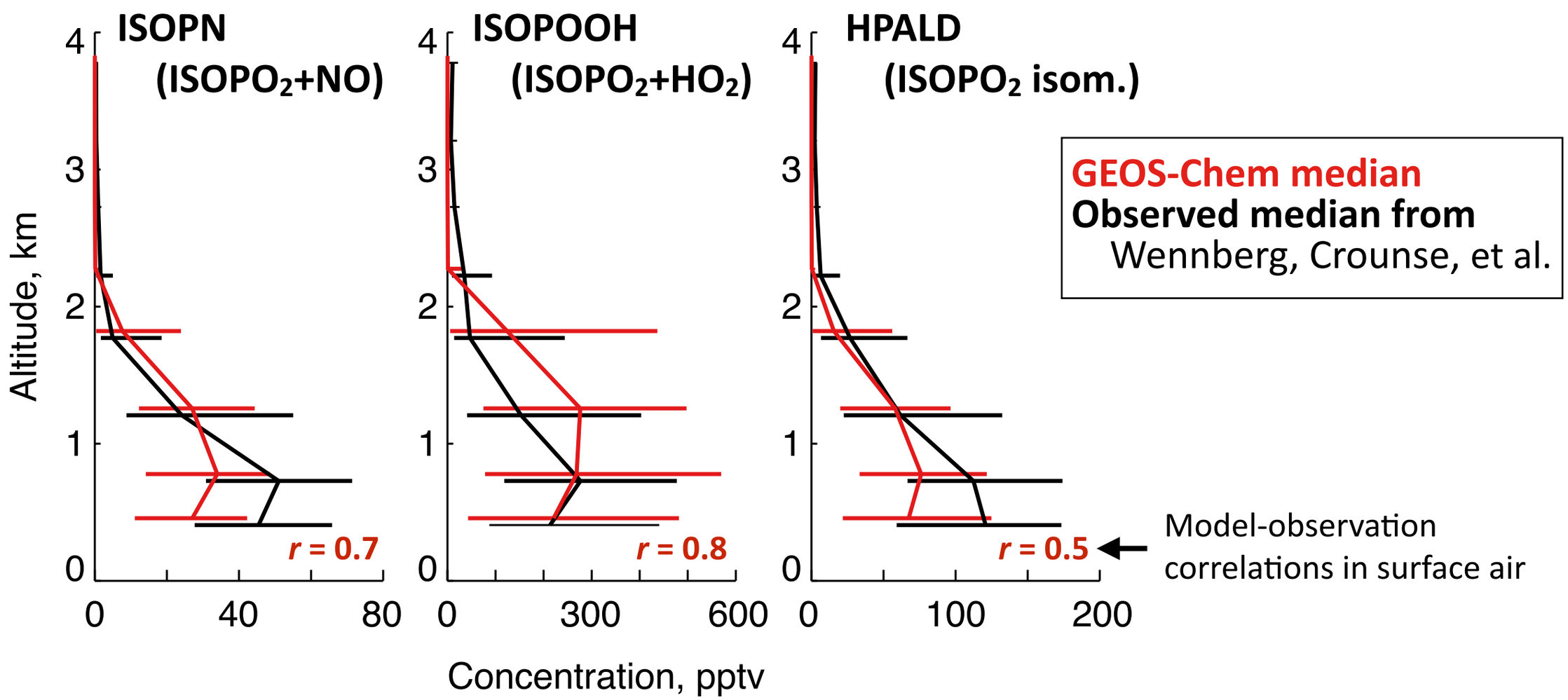
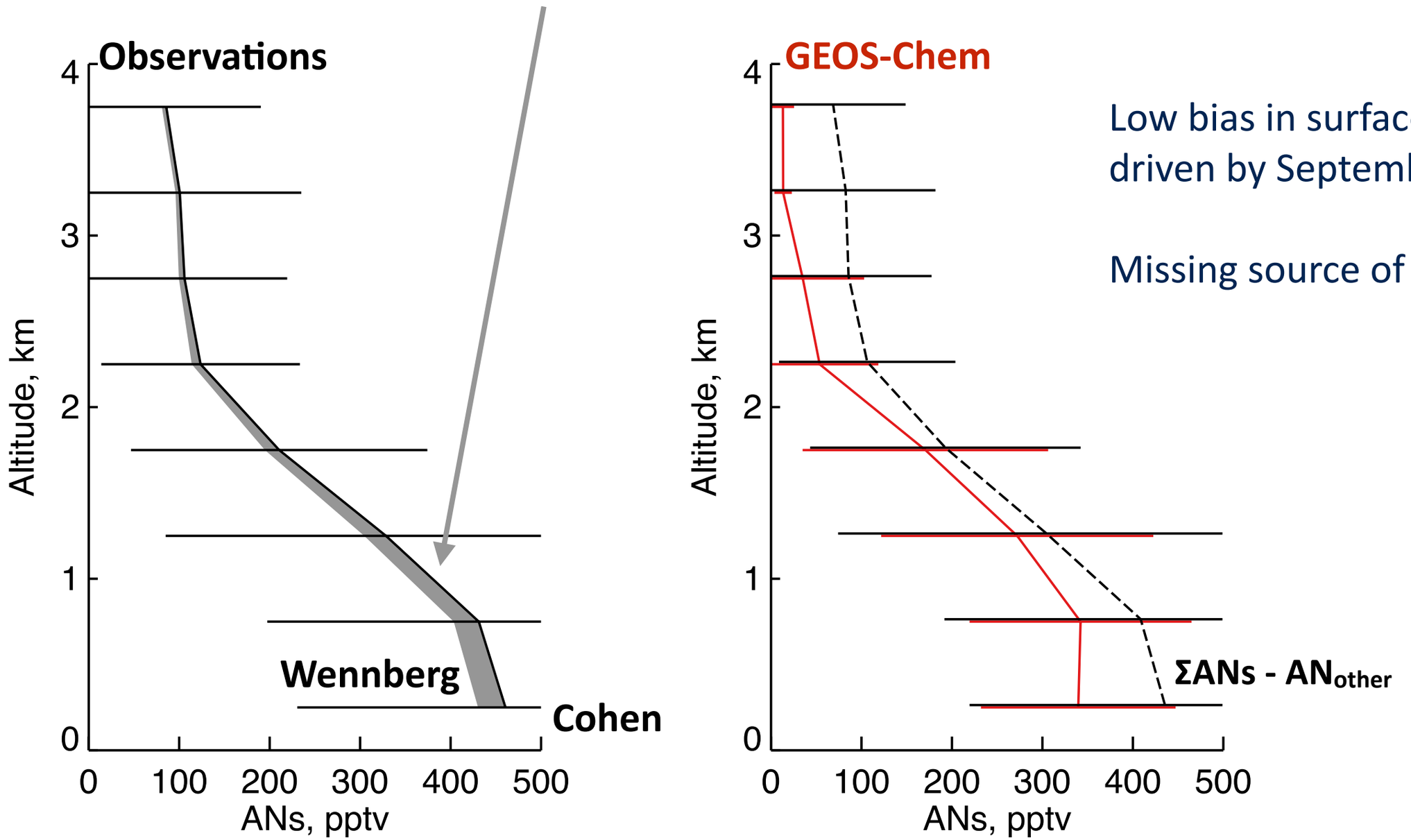


Reaction with NO is dominant fate for $ISOPO_2$ radicals during $SEAC^4RS$—How important is this pathway for atmospheric nitrogen cycling?

Constraints on alkyl nitrates from observations & model

AN_{other} = ANs not simulated in GEOS-Chem (NIEPOX, butene-hn, propene-hn, ethene-hn)

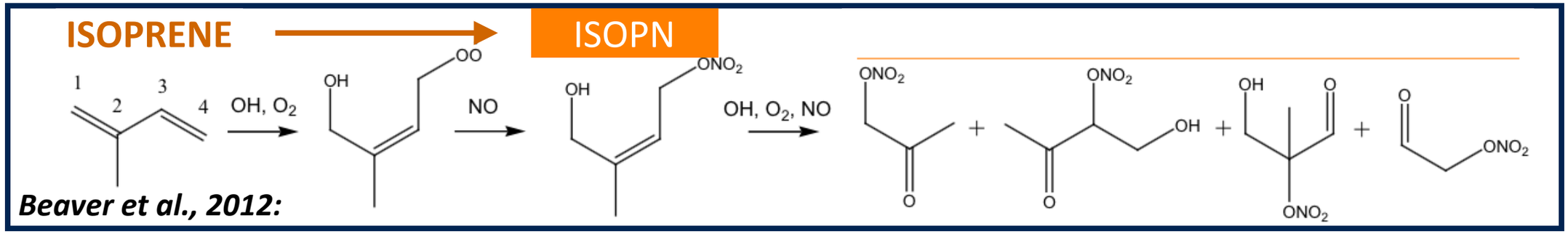


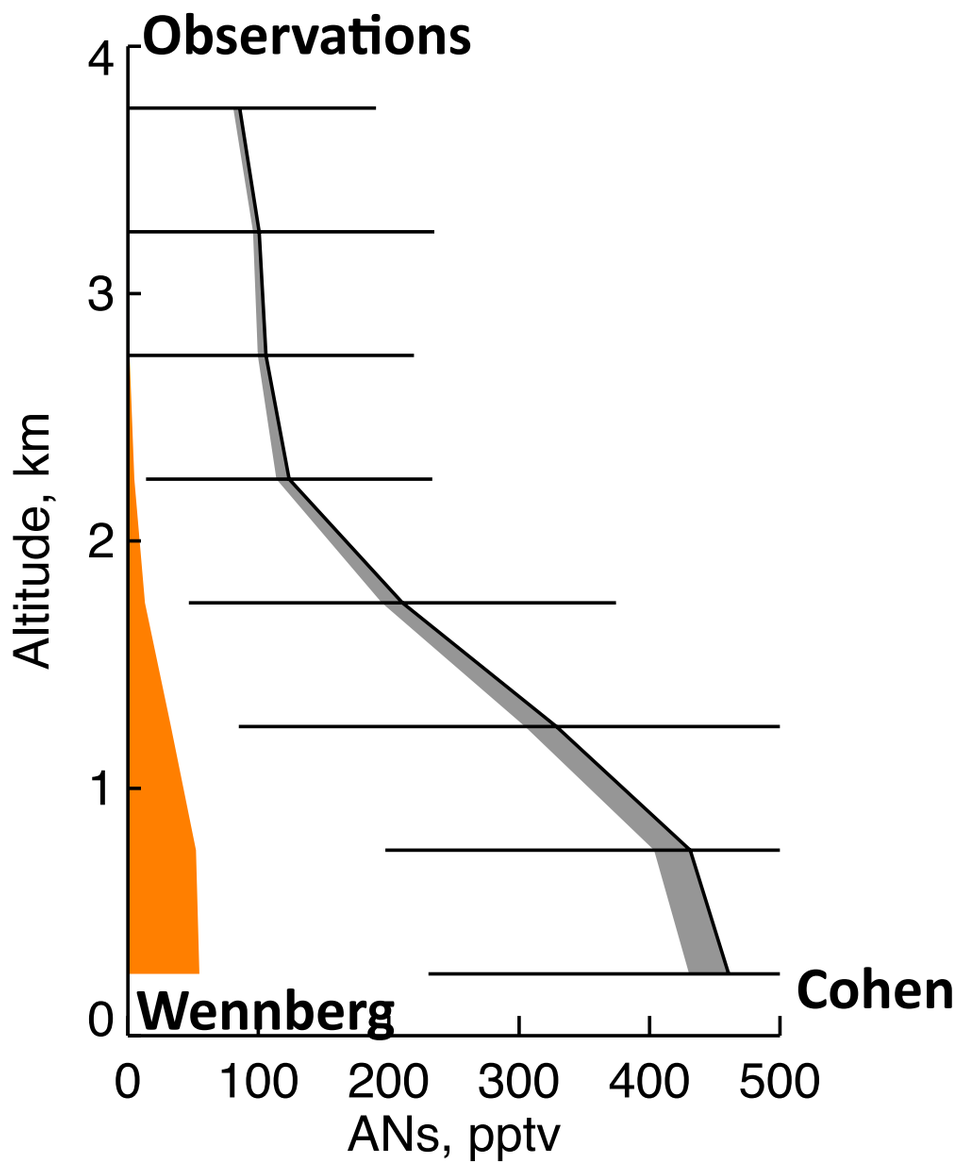
Low bias in surface ΣANs of ~20%, driven by September flights

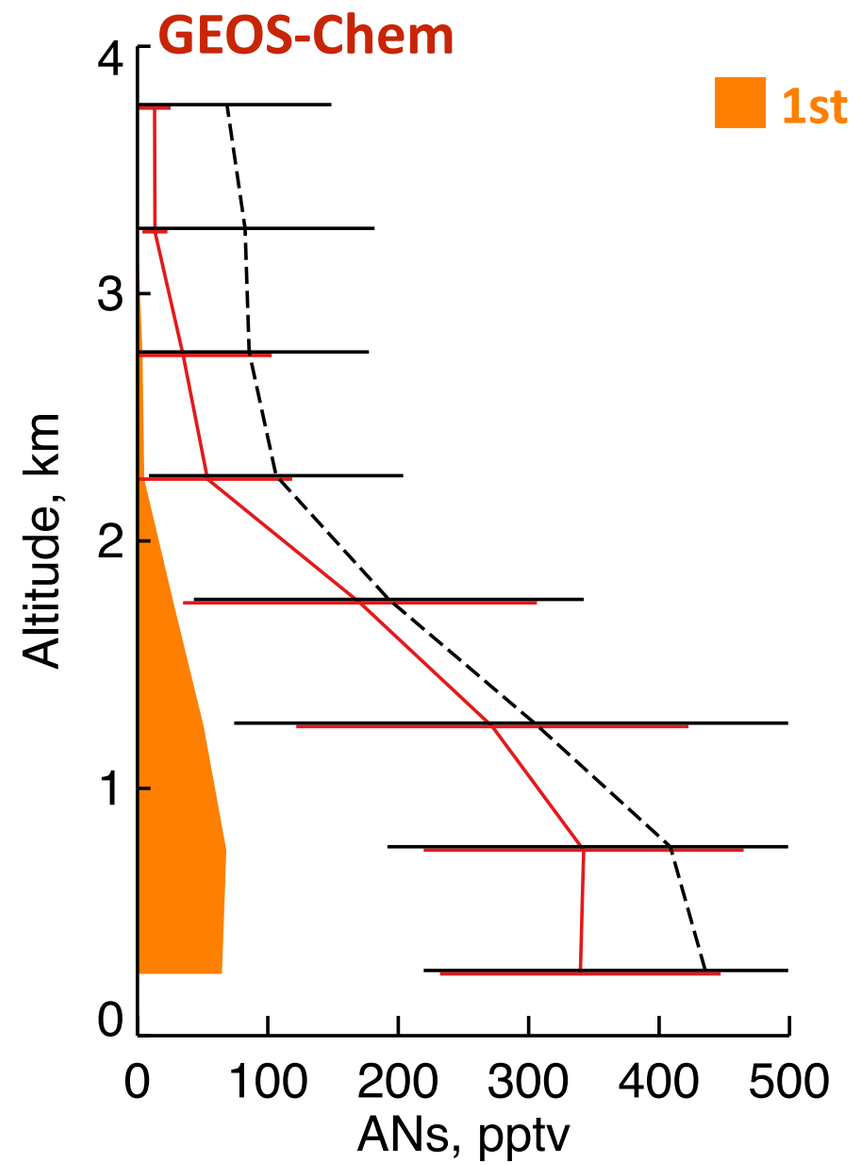
Missing source of ΣANs aloft

jennyf@uow.edu.au

Diverse species contribute to SEAC^{4}RS ΣANs: isoprene nitrates (INs) and monoterpene nitrates (MTNs)







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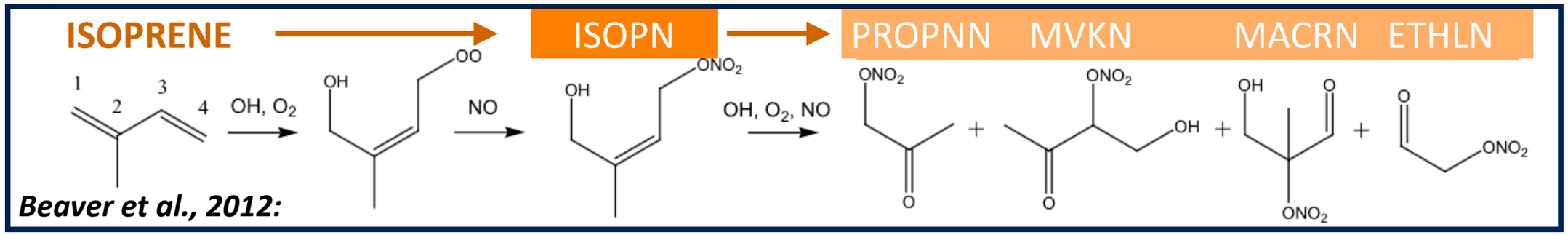

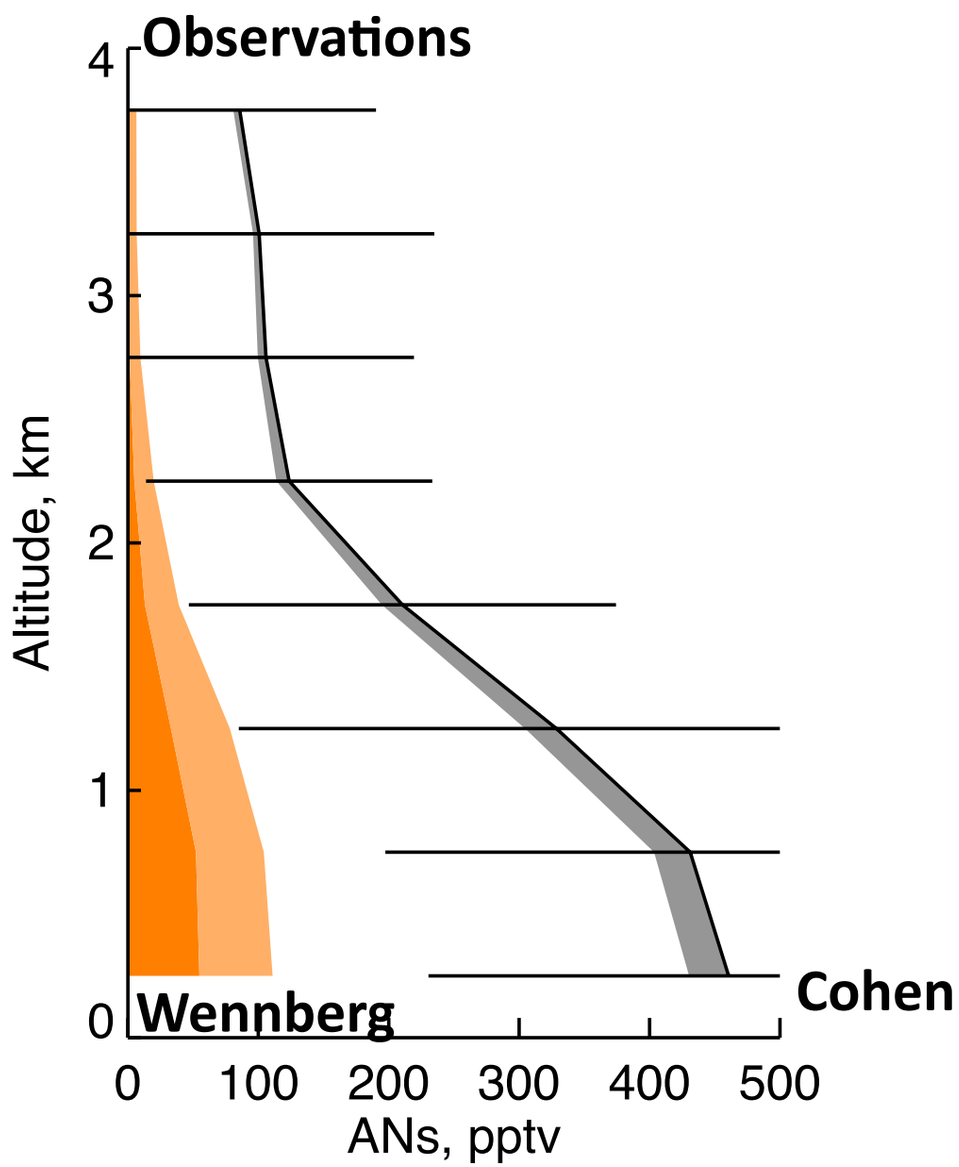

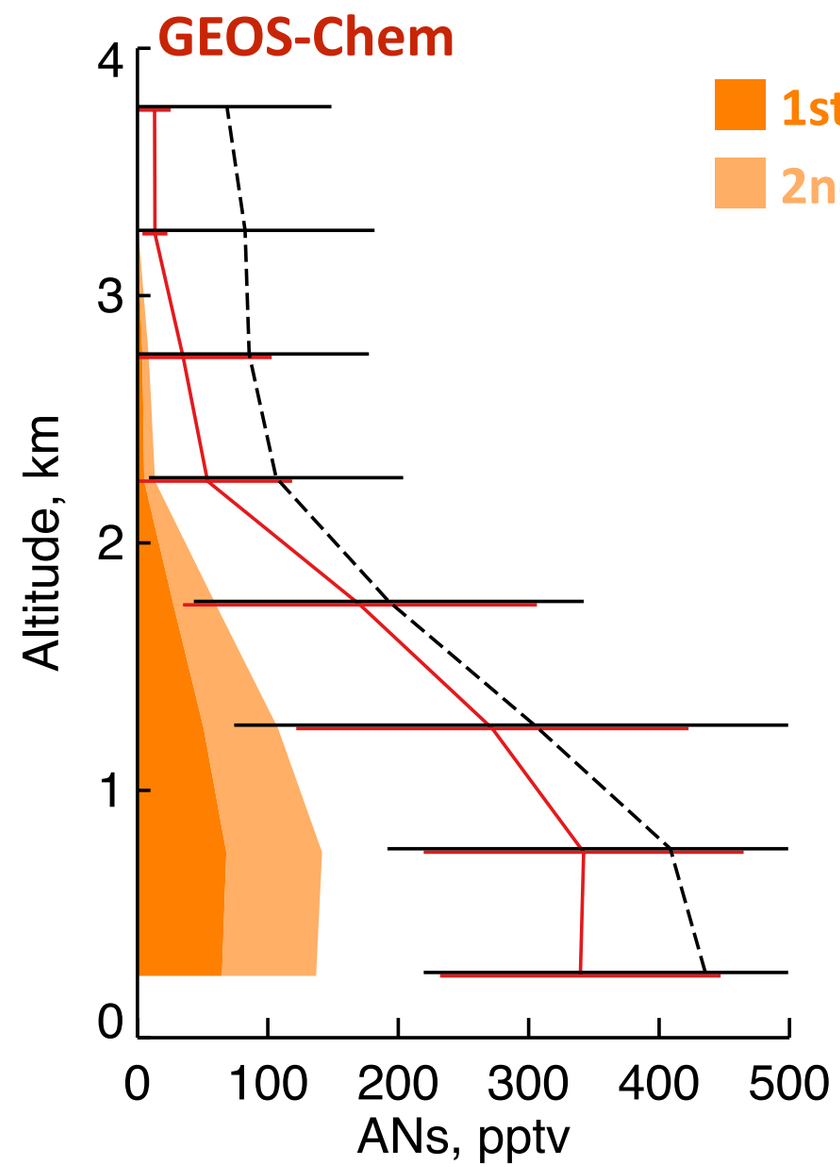

1st generation INs

2nd generation INs (PROPNN+MVKN+MACRN+ETHLN)

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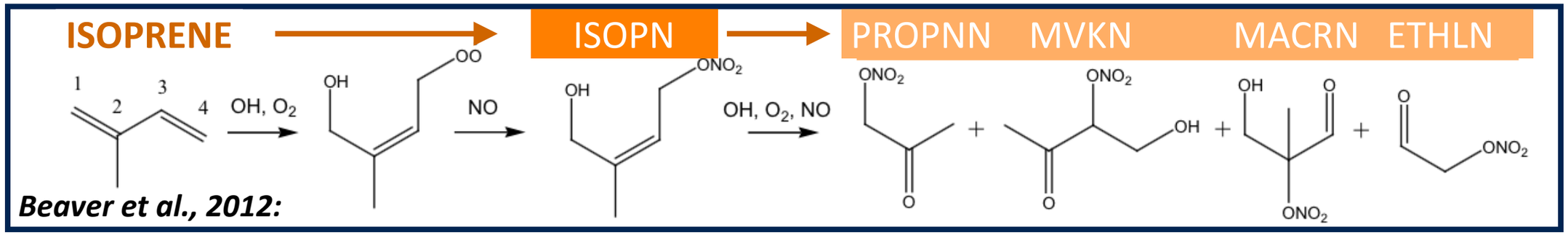

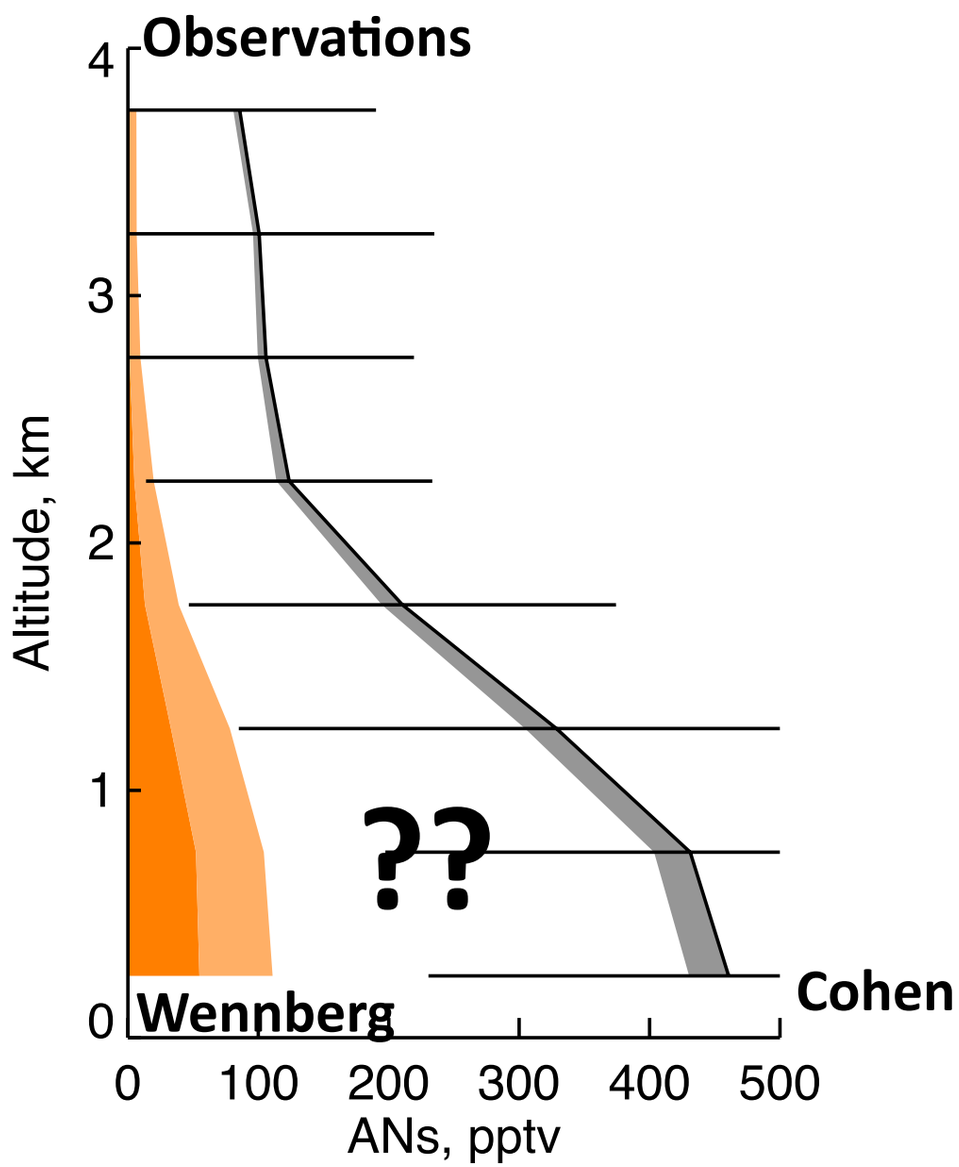

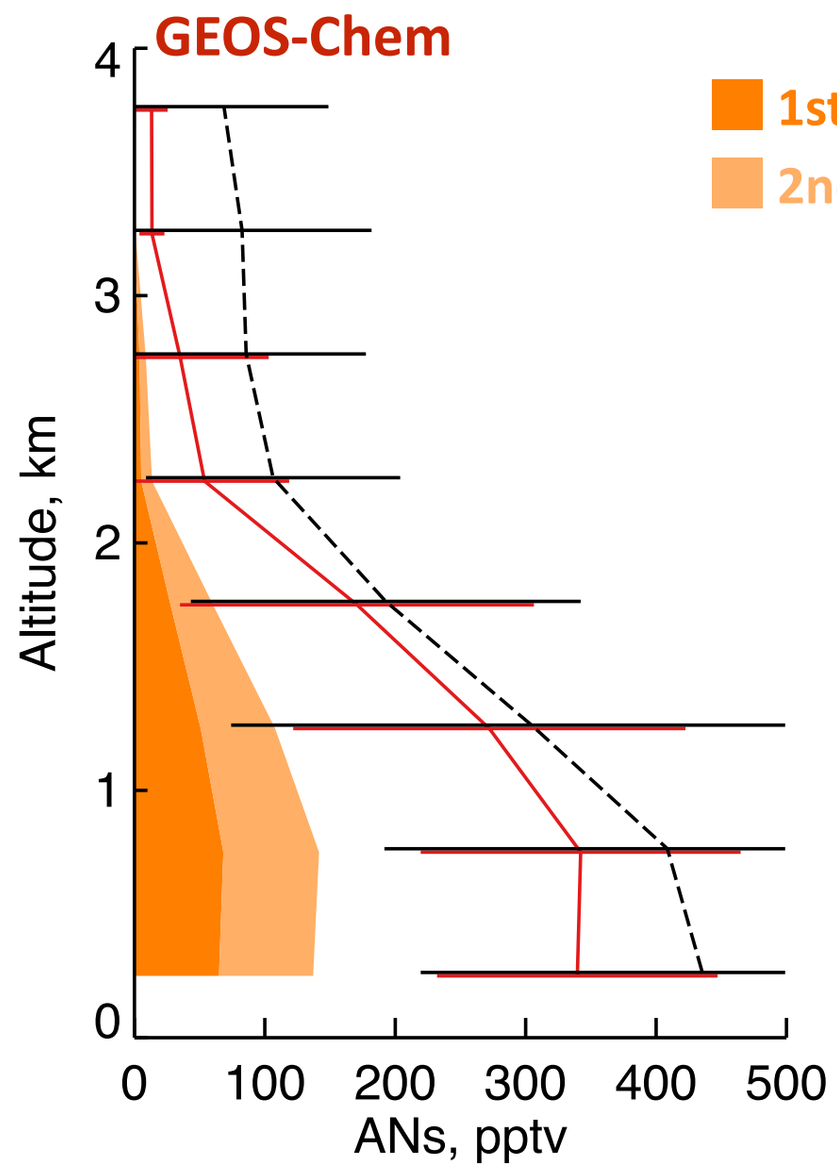

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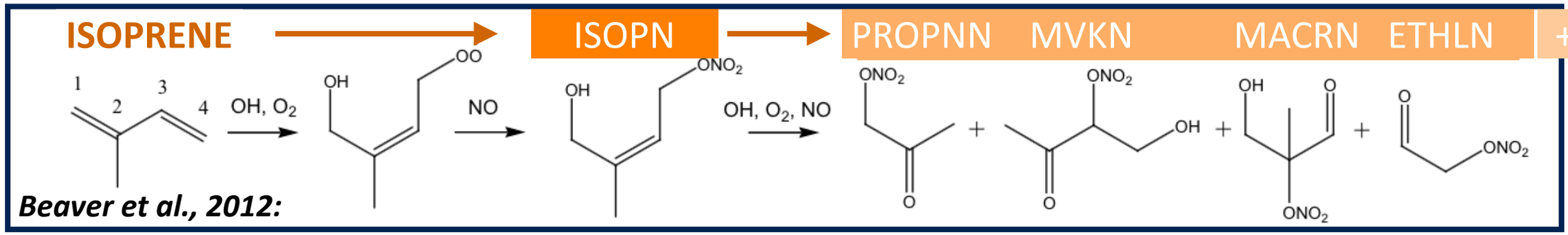

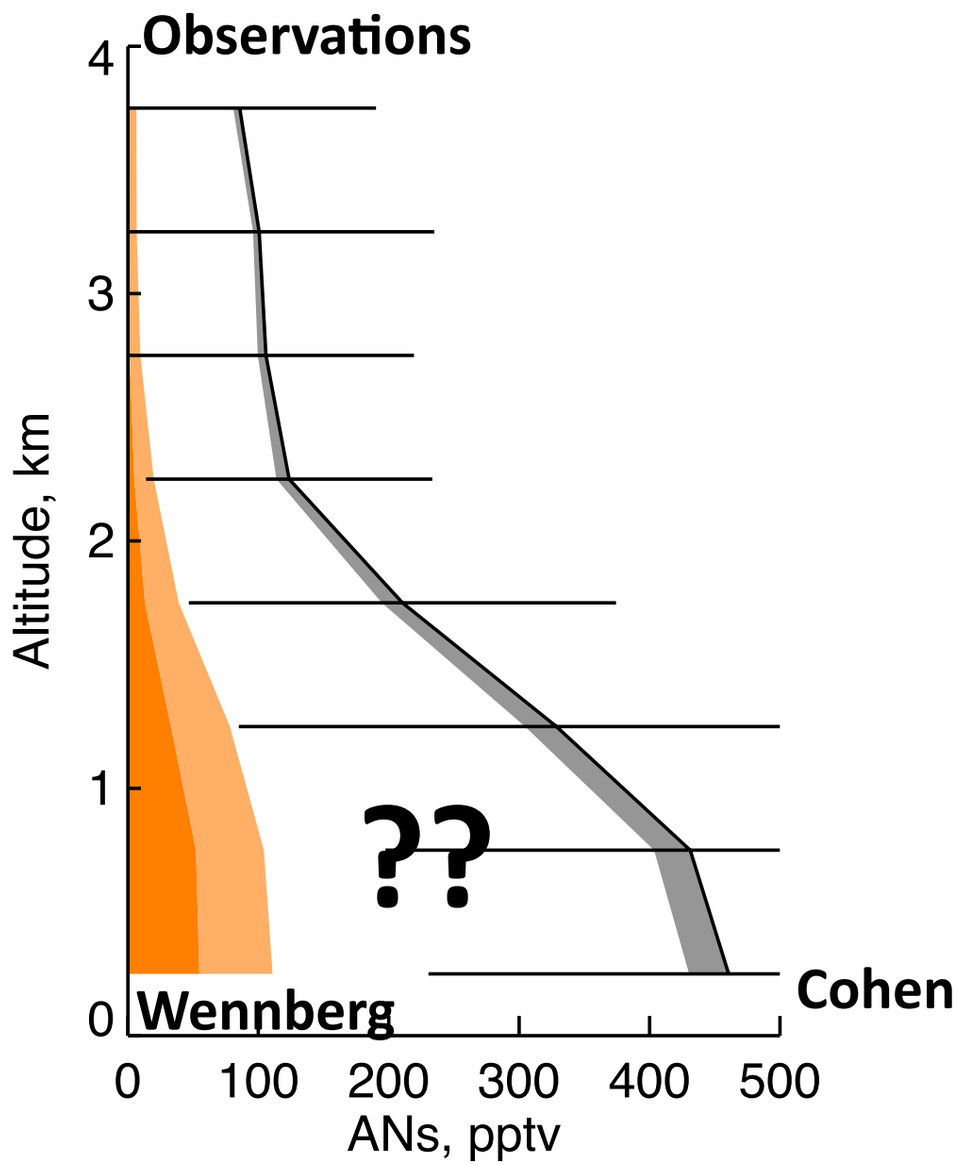

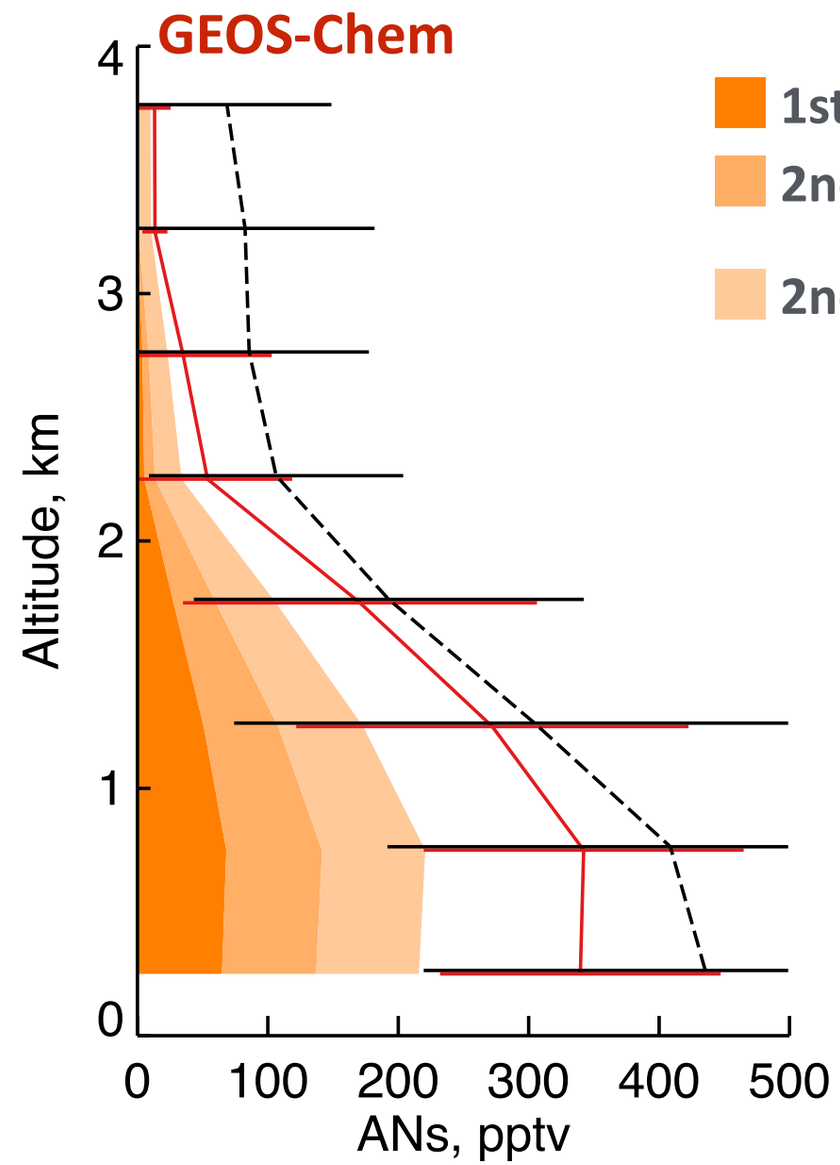

1st generation INs

2nd generation INs (PROPNN+MVKN+MACRN+ETHLN)

2nd generation INs - other

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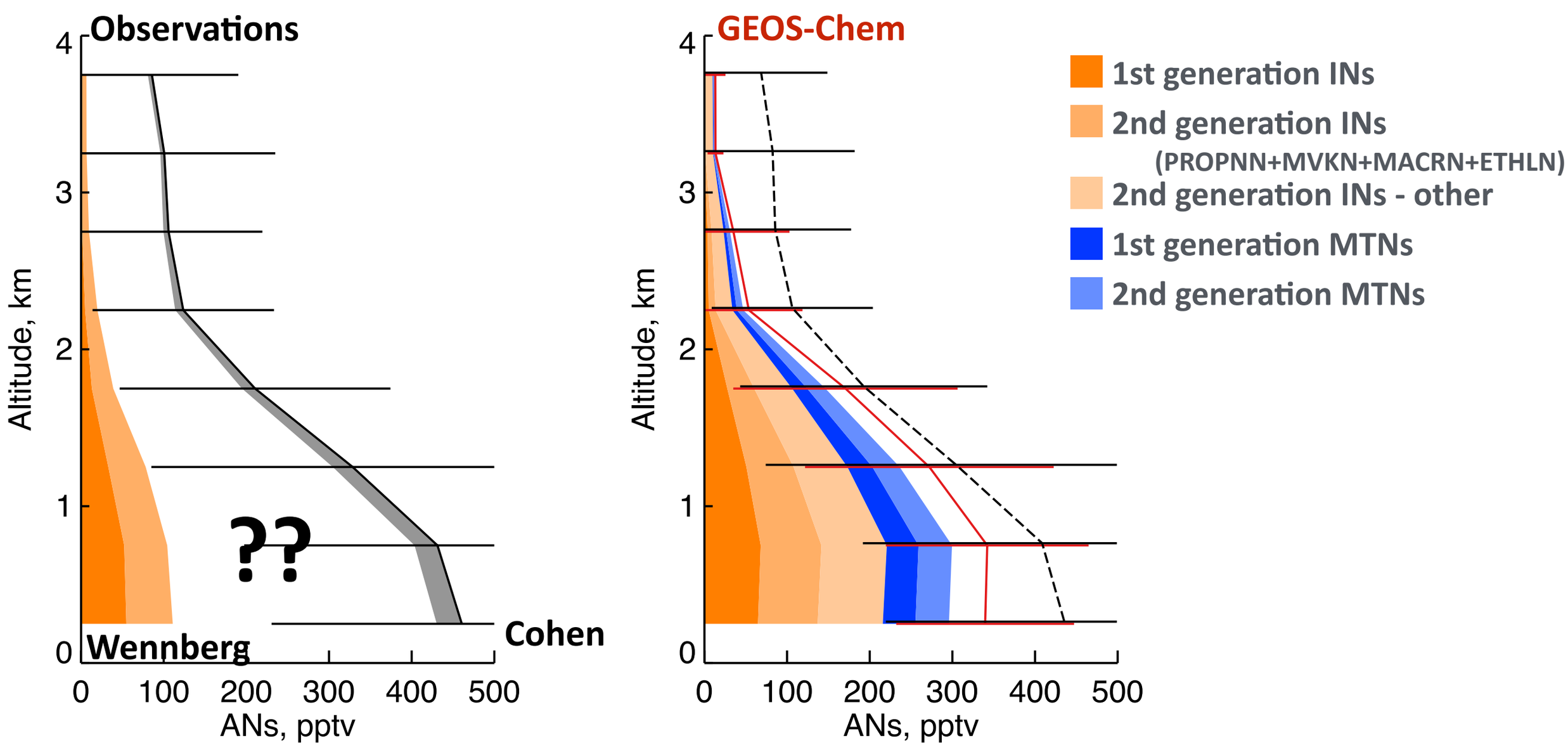
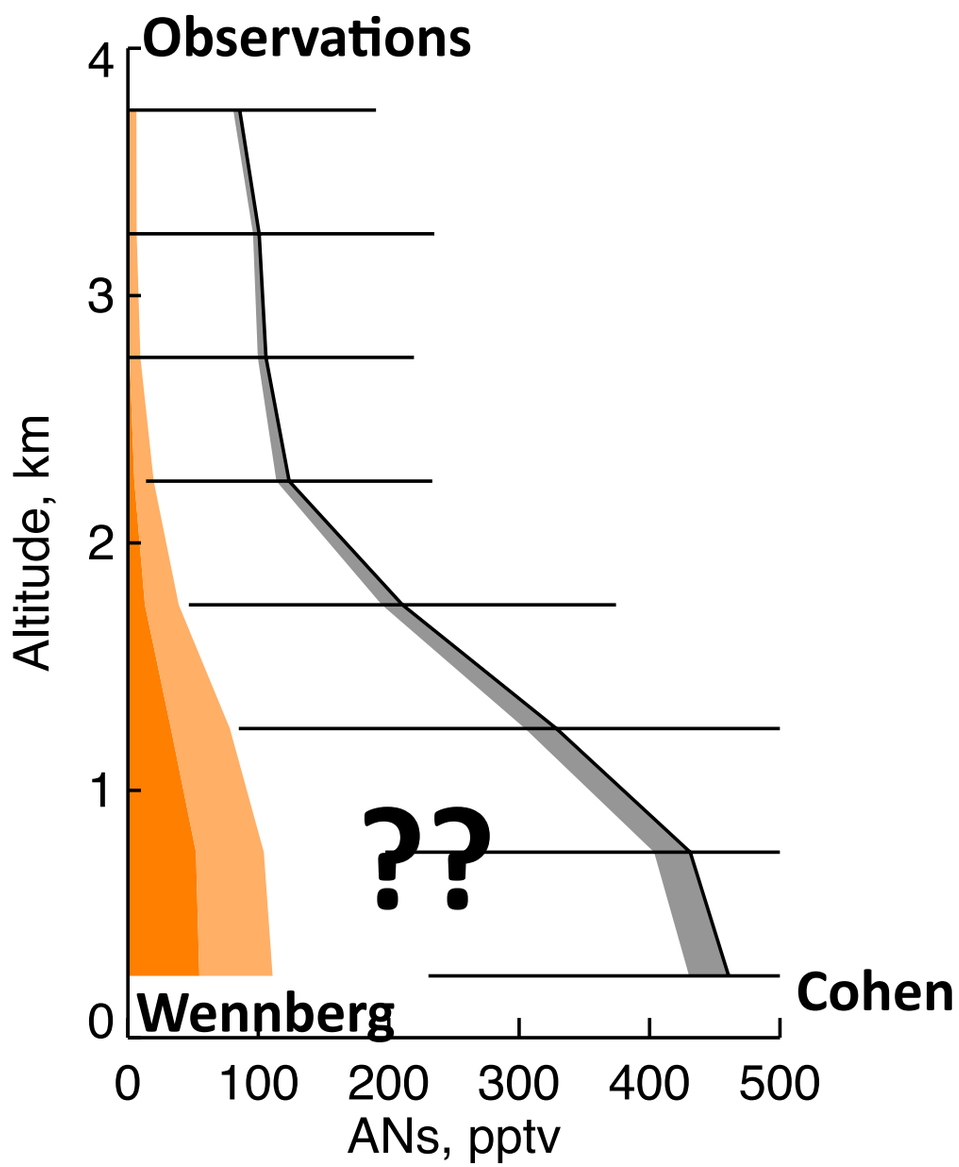
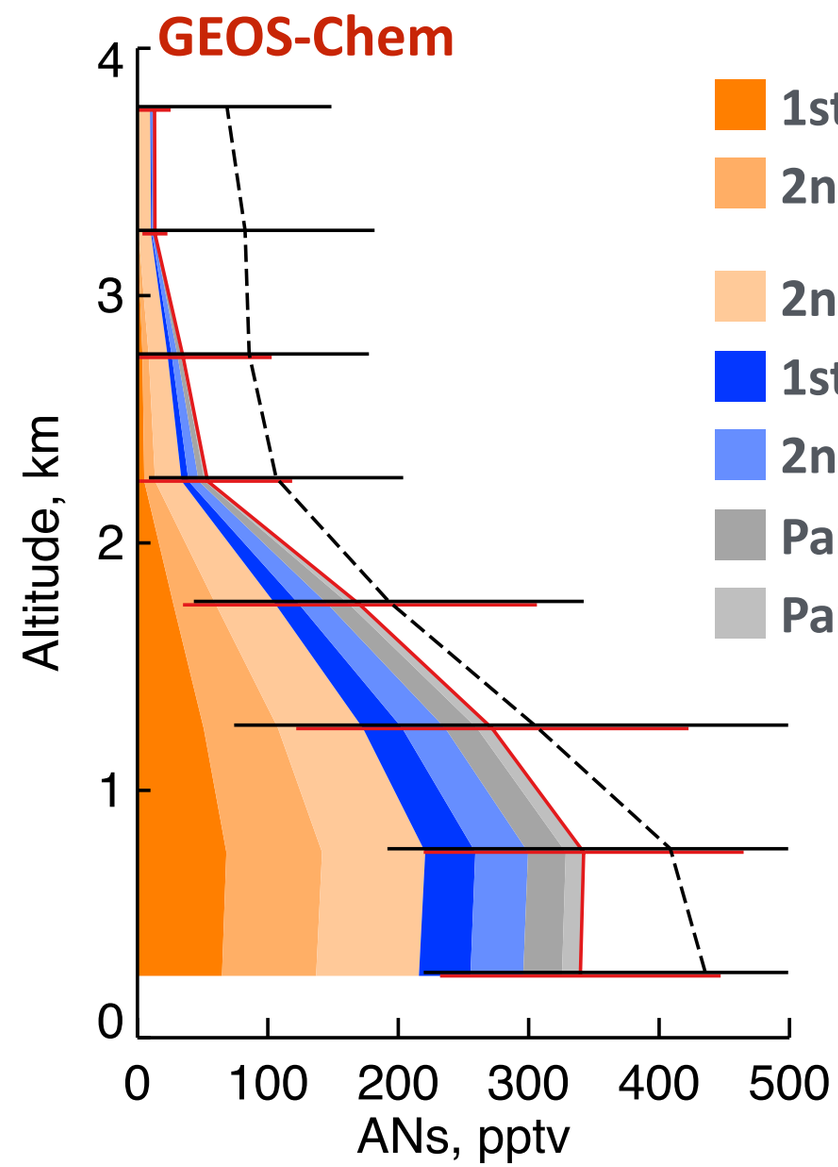


Diverse species contribute to SEAC^{4}RS ΣANs: isoprene nitrates (INs) and monoterpene nitrates (MTNs)

ISOPRENE → ISOPN → 2nd generation isoprene nitrates

MONOTERPENES → MTN → 2nd generation monoterpene nitrates

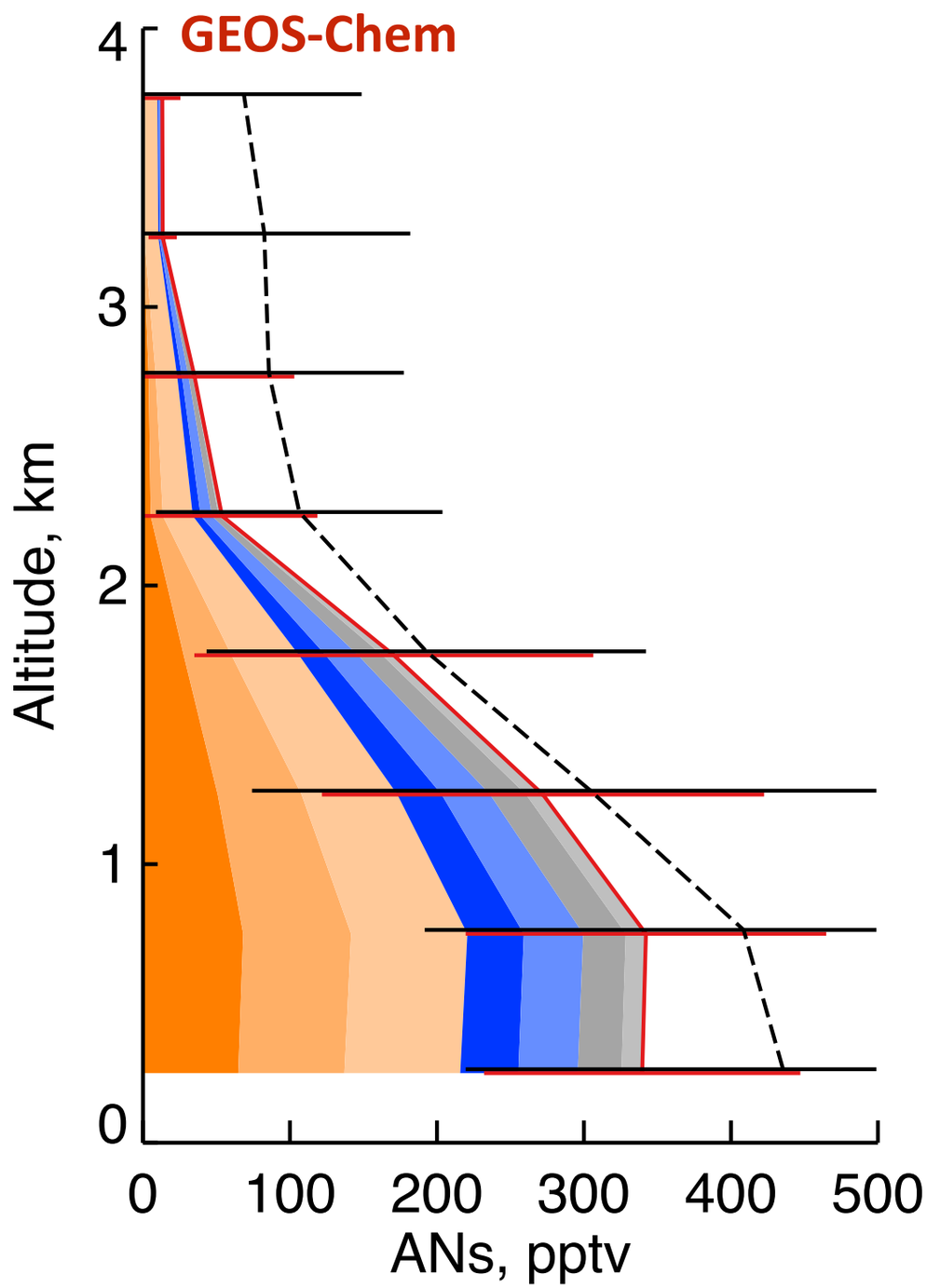




- 1st generation INs
- 2nd generation INs (PROPNN+MVKN+MACRN+ETHLN)
- 2nd generation INs - other
- 1st generation MTNs
- 2nd generation MTNs
- Particle-phase INs
- Particle-phase MTNs

Jenny A. Fisher jennyf@uow.edu.au

Diverse species contribute to SEAC^{4}RS ΣANs: isoprene nitrates (INs) and monoterpene nitrates (MTNs)



At the surface, 87% of GEOS-Chem ΣANs are in the gas phase, comprised of 63% isoprene nitrates and 24% monoterpene nitrates.

This implies surface air organic nitrate aerosol concentrations of 0.1 μg/m^3, higher than measured by the AMS —> a work in progress!

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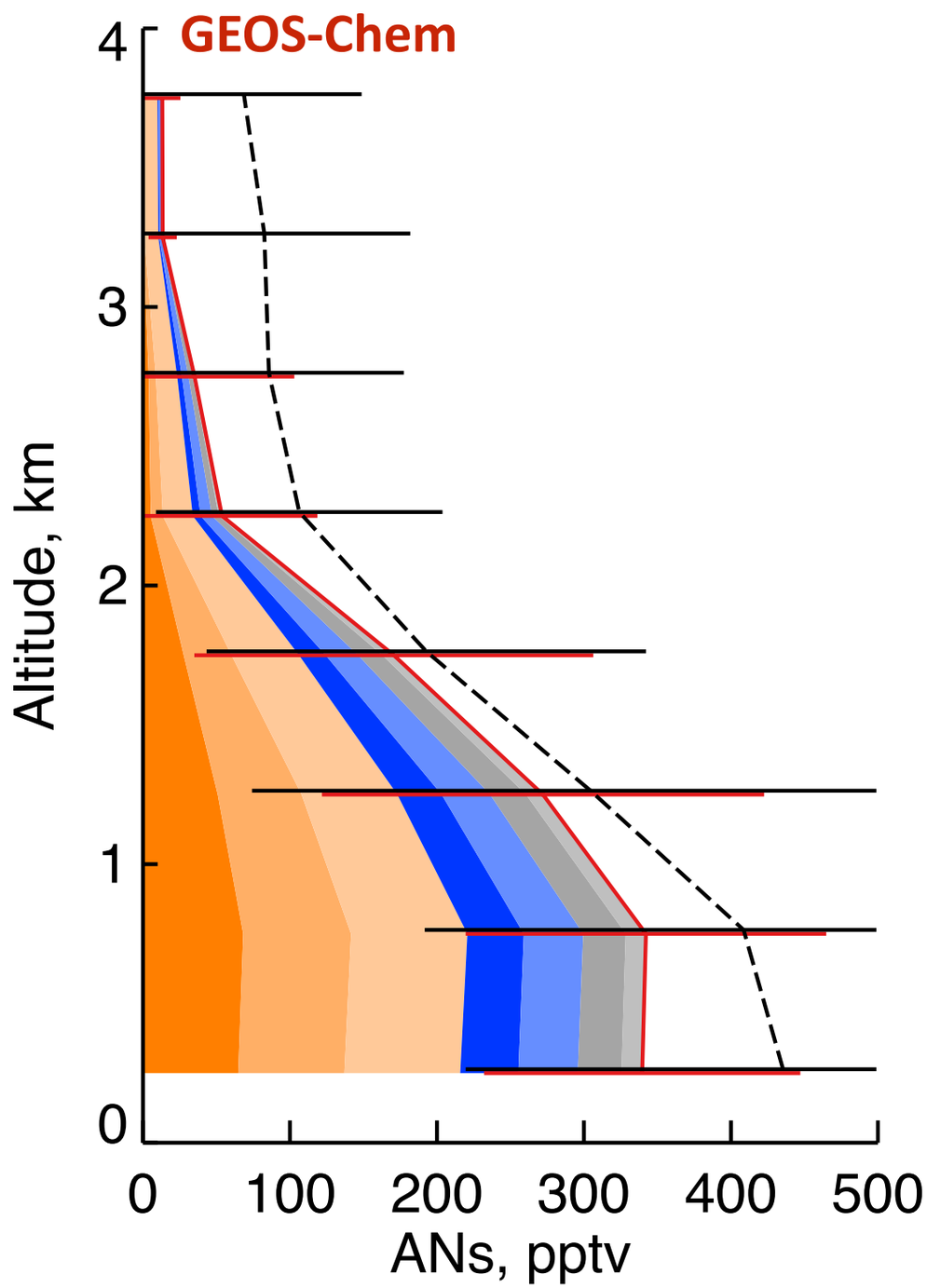

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We cannot reconcile observed & simulated ΣANs with gas-phase isoprene nitrates alone.

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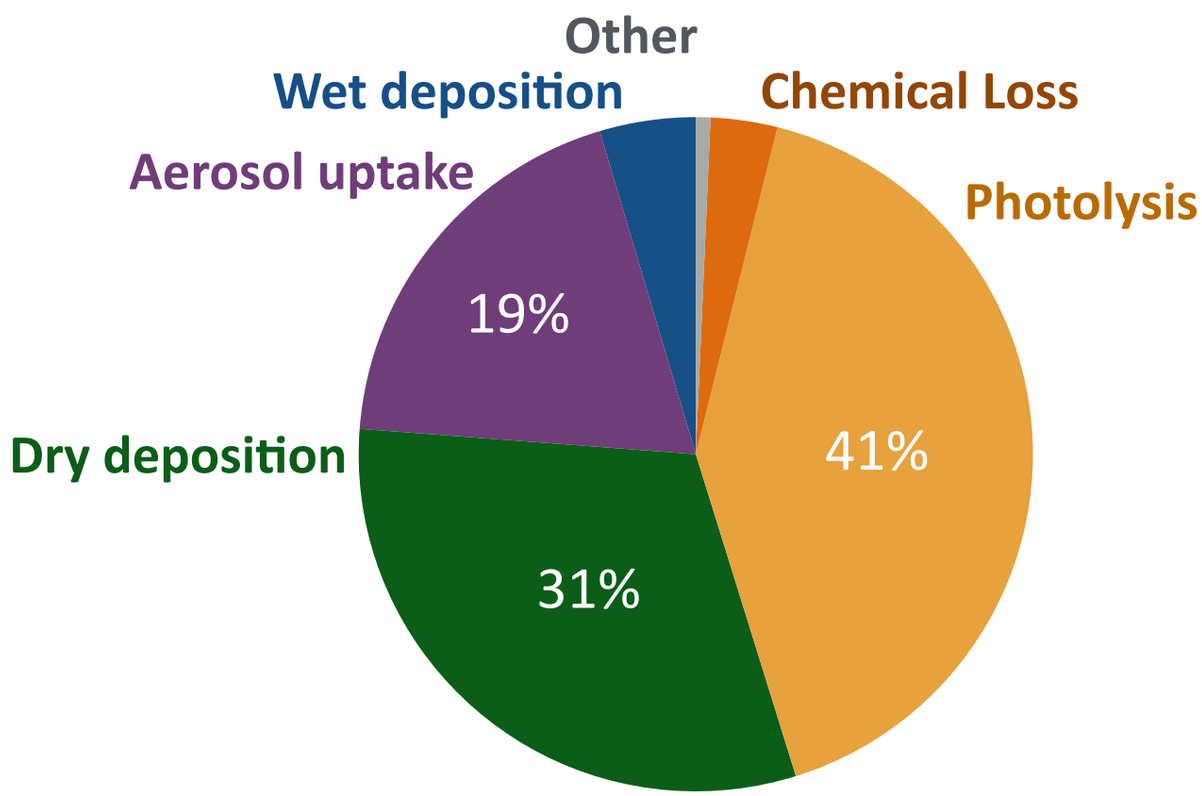
ΣANs budget in the Southeast US boundary layer: implications for nitrogen budgets

Simulated ΣANs Loss Pathways*



** Excluding pathways that conserve ANs*

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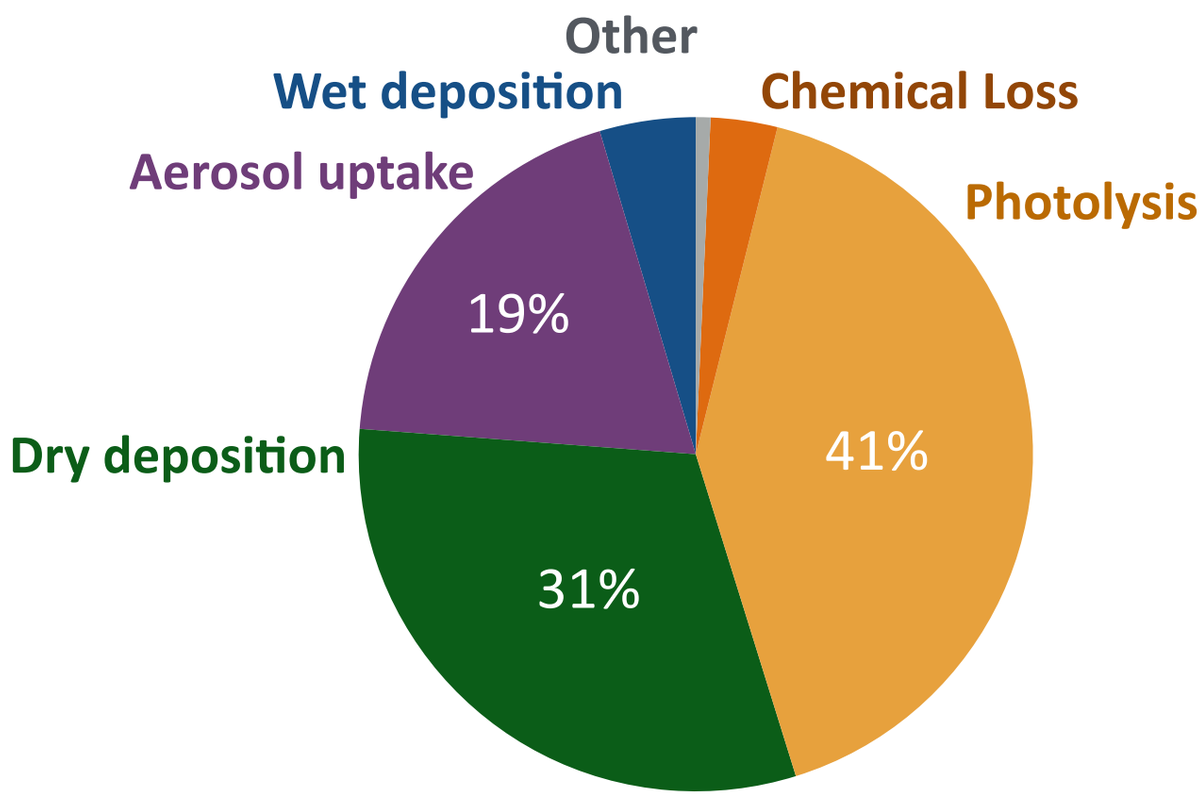
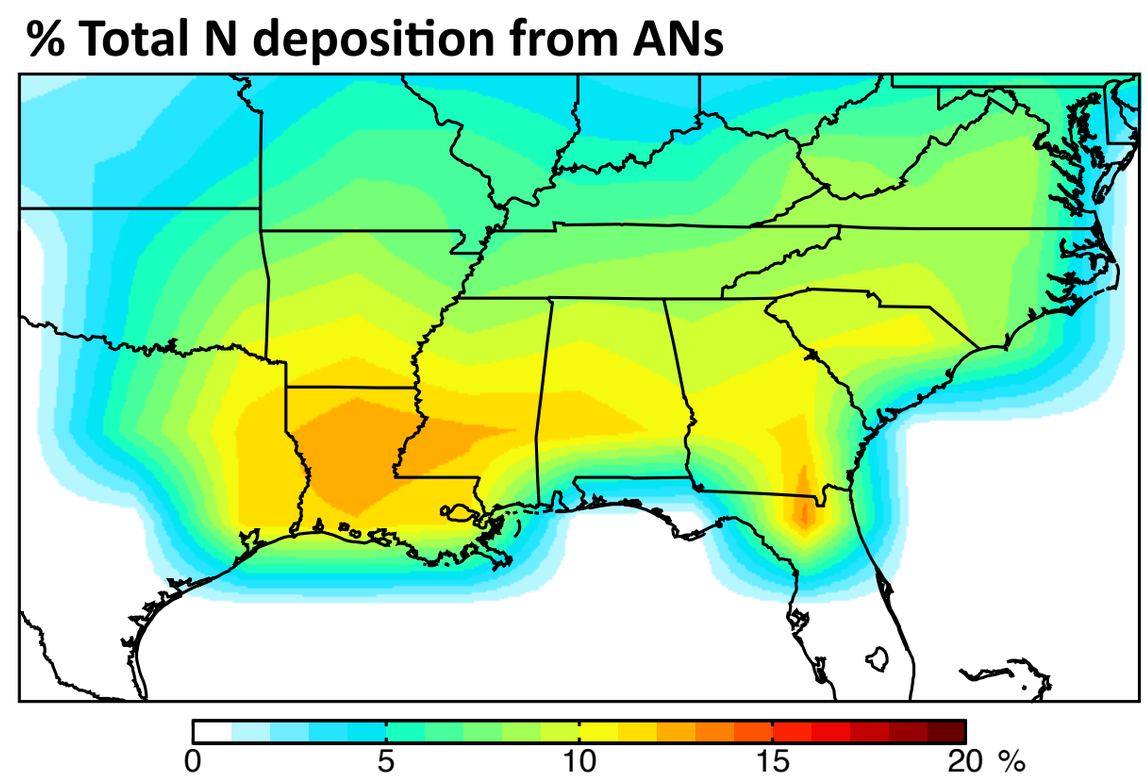


** Excluding pathways that conserve ANs*

Simulated nitrogen deposition



Over the SEAC^{4}RS period, ANs deposited ~20 Gg N over the Southeast US.

This is equivalent to 7-8% of total N deposition (up to 14% over Louisiana), comparable to results from Nguyen et al. (2015) at SOAS site.

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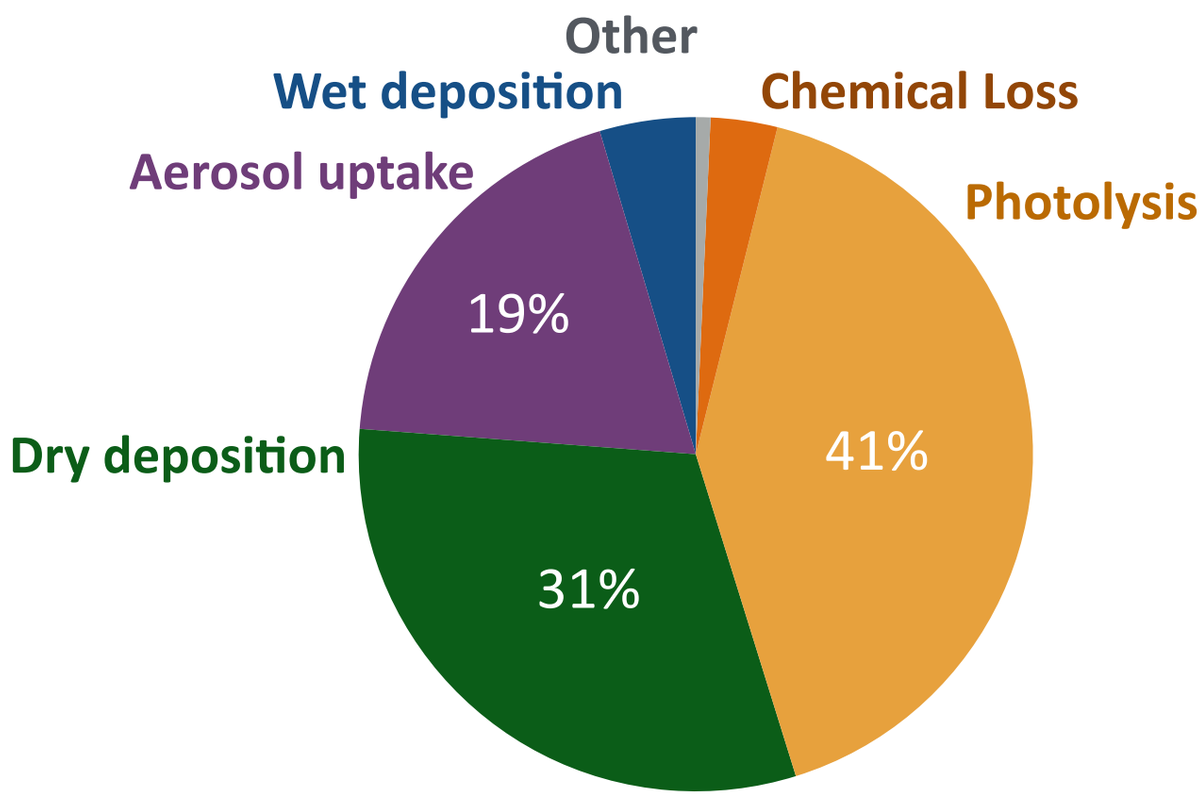

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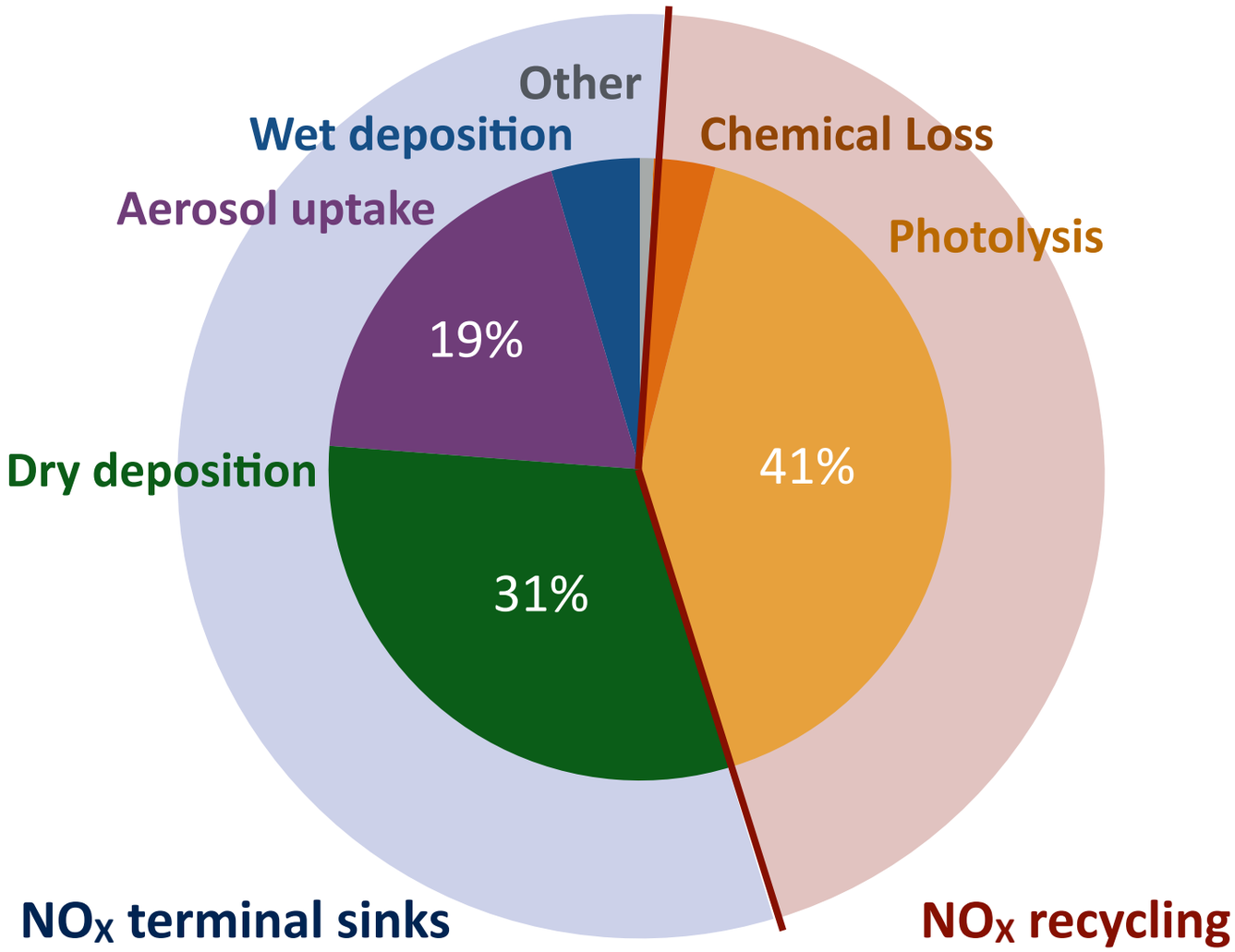

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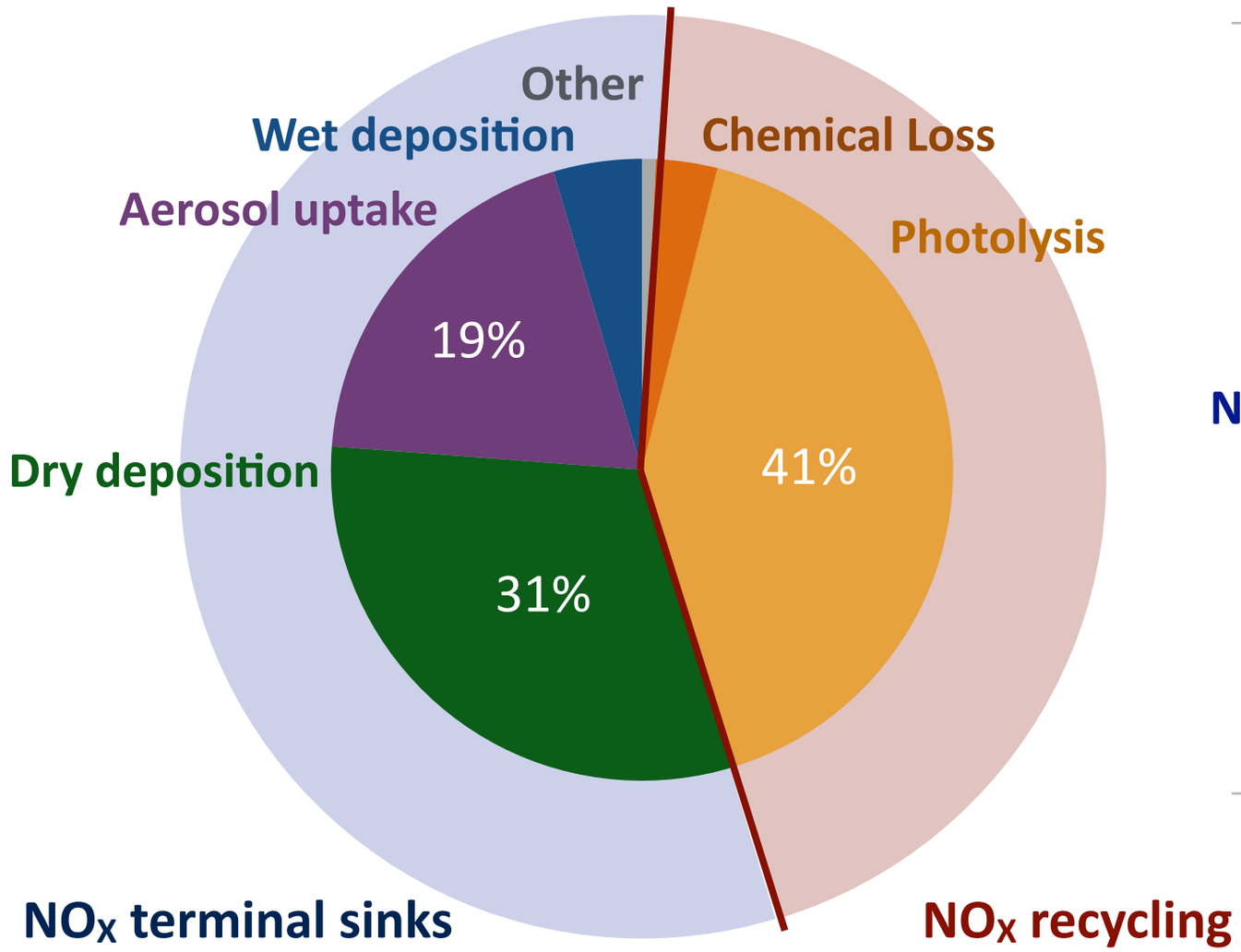
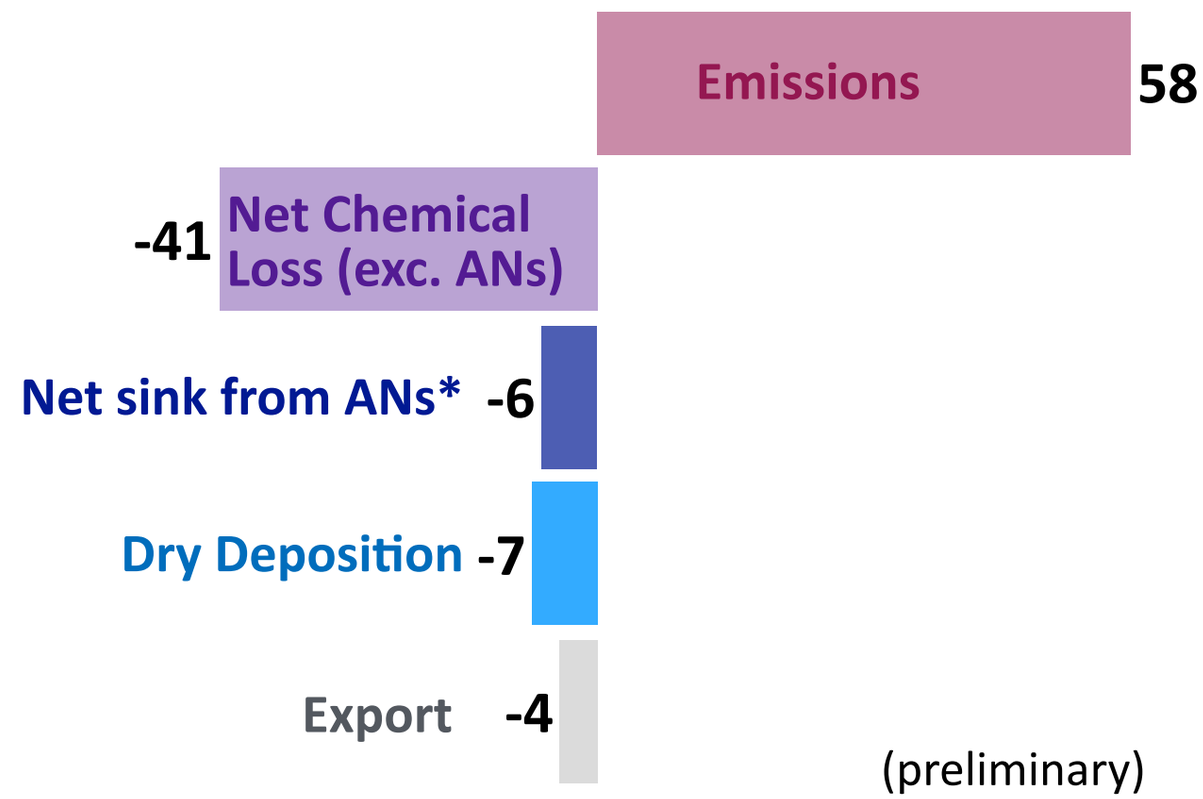


Simulated NO_X budget (Gg N month^{-1})



***11 Gg N lost to AN production, 5 Gg N recycled to NO_X (45%)**

** Excluding pathways that conserve ANs*

On average, ANs represent ~10% of NO_X sink

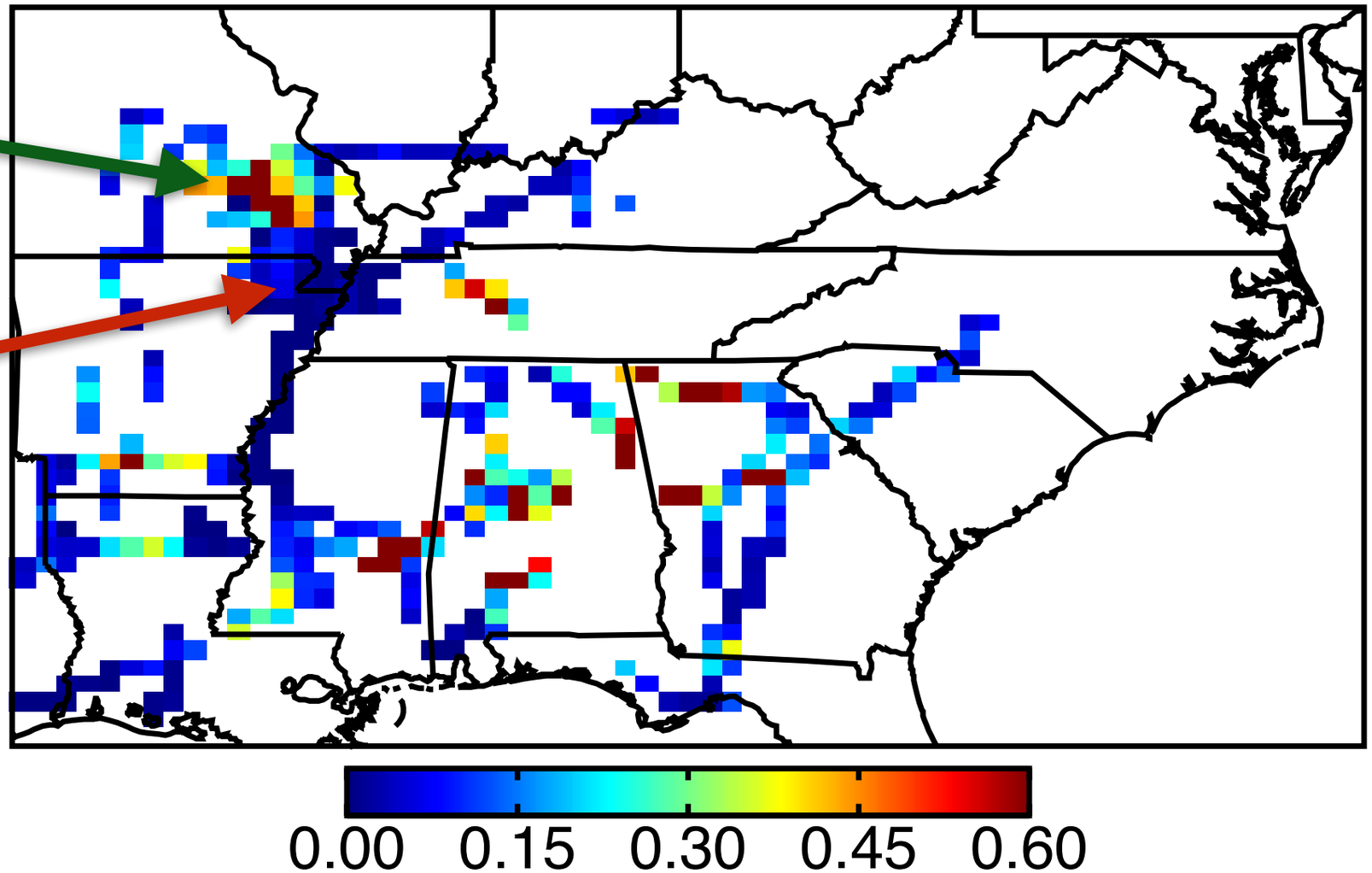
Jenny A. Fisher jennyf@uow.edu.au

Importance of ANs formation as a sink for NO_X depends on both NO_X & VOC emissions

Simulated fraction of NO_X sink due to ANs production (surface air)

Low-NO_X, high BVOC:
~70% NO_X sink from ANs

High-NO_X, low BVOC:
~2% NO_X sink from ANs



As NO_X emissions decrease across the Southeast US, ANs will become an increasingly important sink.

Take-home messages from this work (so far…):

1. **>50% of the observed alkyl nitrates** can be attributed to **isoprene nitrates (INs)** — but not all!

2. **Monoterpene nitrates (MTNs)** can explain another **~25%**, although this chemistry remains poorly constrained.

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4. During SEAC4RS, **INs and MTNs** are responsible for **~10% of N deposition** over the Southeast US.

5. **Formation of INs and MTNs** can be responsible for **up to 70% of the terminal NO_X sink** in low-NO_X, high-VOC regions.