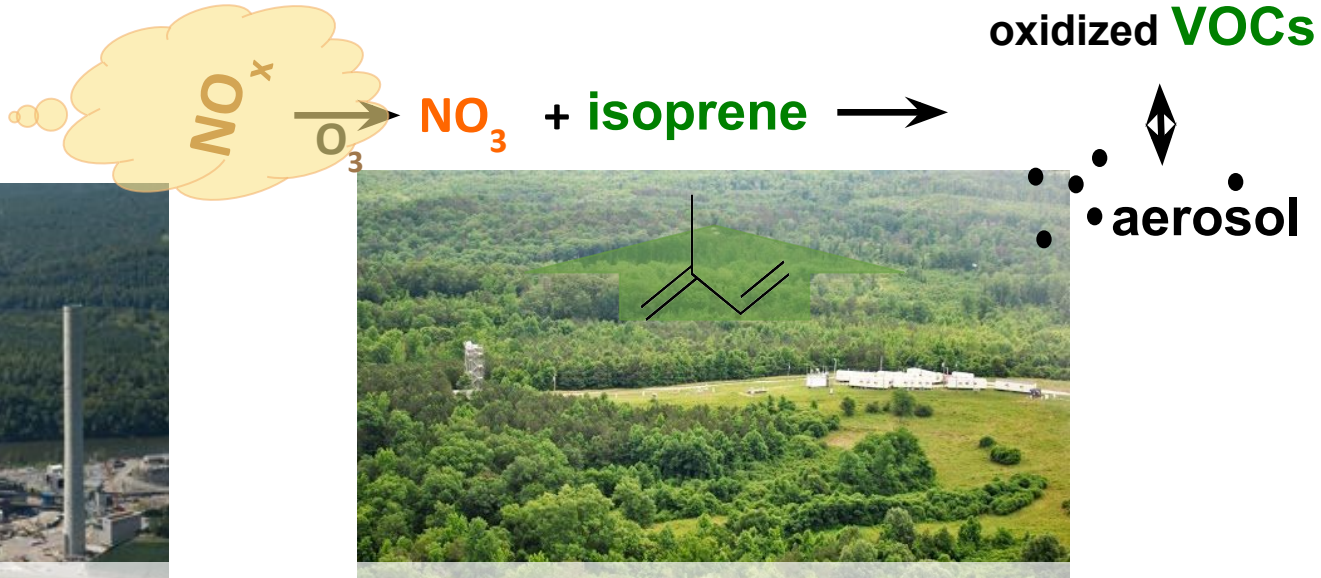


Aerosol formation from NO_3 + isoprene:

Field and laboratory studies on mechanism and yields

Juliane L. Fry, Associate Professor of Chemistry & Environmental Studies, Reed College, Portland, OR

American Chemical Society National Meeting @ San Diego, August 28, 2019

With a fantastic group of collaborators:

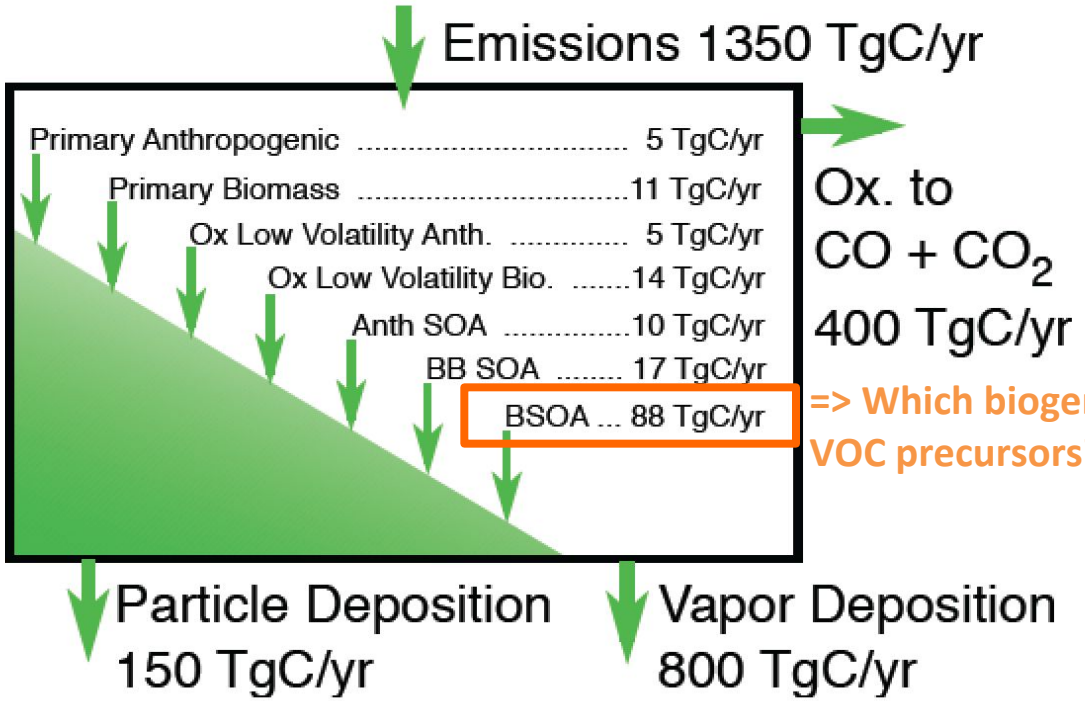
Pete Edwards [1], Steve Brown [2], Ann Middlebrook [2], Jose Jimenez [3], Doug Day [3], Bellamy Brownwood [4], Epameinondas Tsiligiannis [5], Mattias Hallquist [5], Avtandil Turdziladze [6], Thorsten Hohaus [6], Hendrik Fuchs [6], Anna Novelli [6], and the rest of the chamber measurement team of NO3ISOP 2018 @ SAPHIR

[1]Department of Chemistry, York University; [2]Chemical Sciences Division, NOAA Earth Systems Research Lab; [3]Department of Chemistry, University of Colorado at Boulder; [4]Chemistry and Environmental Studies, Reed College; [5]Department of Chemistry and Molecular Biology, University of Gothenburg; [6]Institute for Energy and Climate (IEK-8), Forschungszentrum Jülich

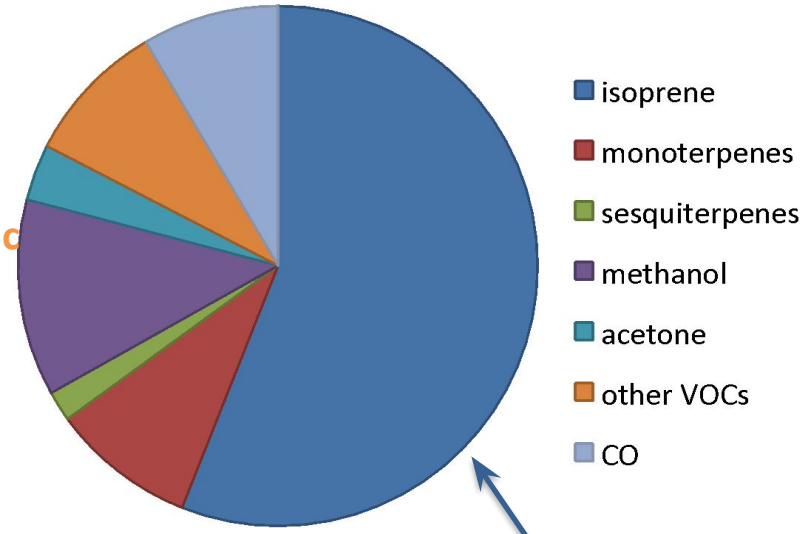
What's to come in this talk:

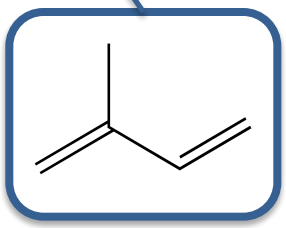
- Why do we think that **NO_3 + isoprene** may be an important contributor to atmospheric secondary organic aerosol (SOA)?
- **Field study**: Estimating SOA yields from NO_3 + isoprene based on nighttime aircraft power plant plume transects during SENEX 2013
- **Lab study**: Yields and gas/aerosol partitioning of organonitrate products from NO_3-initiated oxidation of isoprene under varied chemical regimes, measured at SAPHIR in Aug 2018

Global organic carbon budgets and biogenic secondary organic aerosol (SOA)



MEGAN model estimates 760 TgC yr^{-1} global BVOC emissions, of which >60% is isoprene:



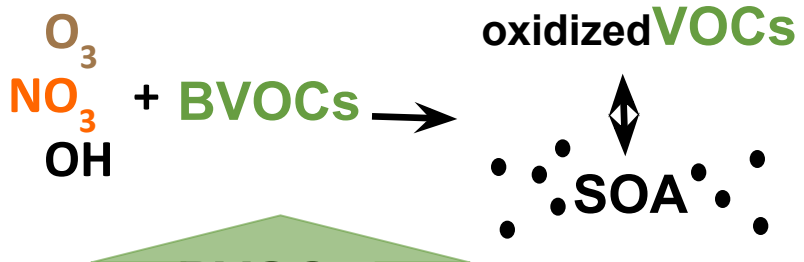


isoprene

Hallquist et al., ACP 2009

Sindelarova et al., ACP 2014

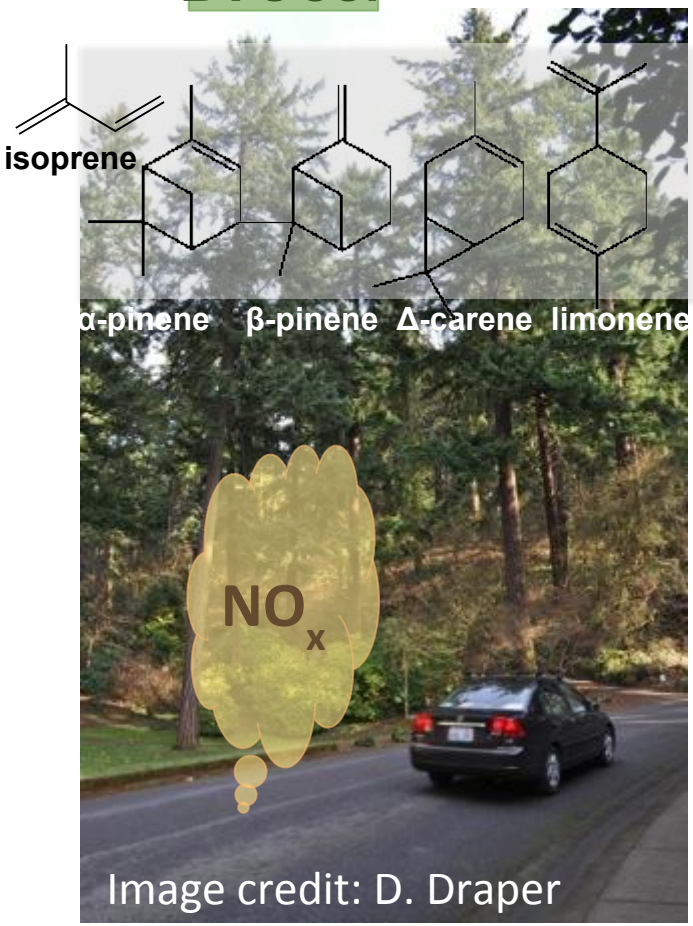
Isoprene oxidation by NO_3 is ***fast***



$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$

*NO_3 is rapidly photolyzed and thus active primarily at night

BVOCs:



BVOC lifetimes w.r.t. each oxidant

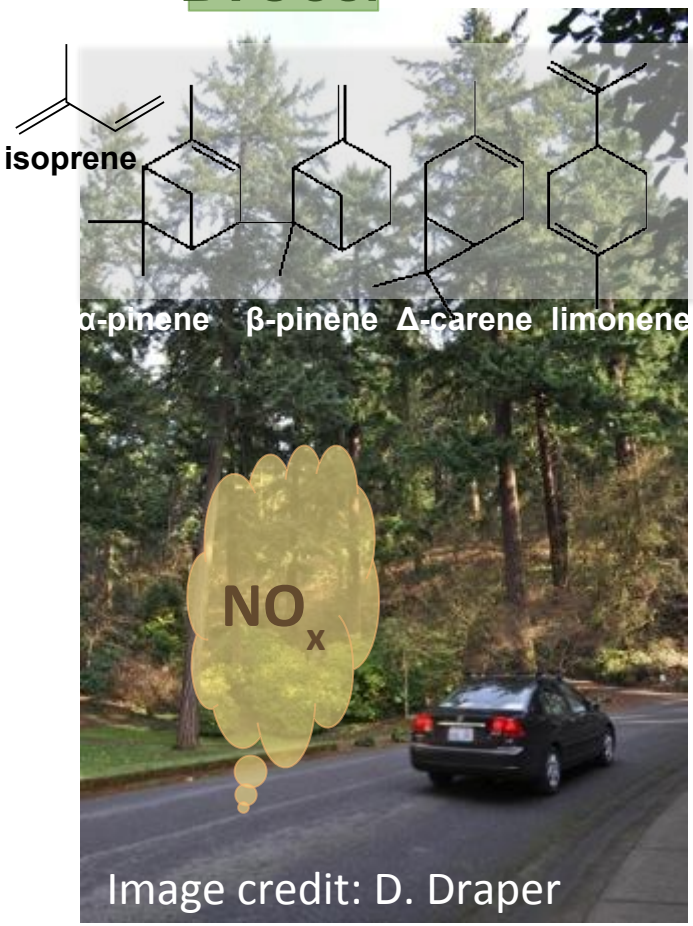
BVOC	OH	O_3	NO_3
isoprene	*1.4 hr*	*1.3 day*	*48 min*
α-pinene	2.7 hr	4.7 hr	5.4 min
β-pinene	1.9 hr	1.1 day	13 min
Δ-carene	1.6 hr	11 hr	3.7 min
limonene	51 min	1.9 hr	2.7 min

@ "typical" conc's: 12-h daytime avg [OH]: $2x10^6$ #/cm^3; 24 h avg [O_3]: $7x10^{11}$ #/cm^3; 12 h nighttime avg [NO_3]: $5x10^8$ #/cm^3 = 20 ppt (Atkinson & Arey, 2003)

Isoprene oxidation by NO_3 is ***fast*** … *but not* ***too*** *fast*

O_3, NO_3, OH + BVOCs → oxidized VOCs ↔ SOA

BVOCs:



$$\left[\begin{array}{l} NO_2 + h\nu \rightarrow NO + O \\ O + O_2 + M \rightarrow O_3 + M \end{array}\right]$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + h\nu \rightarrow NO_2 + O$$

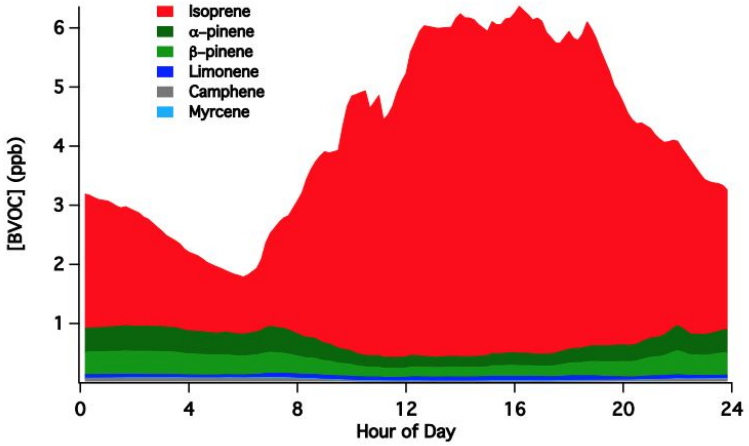
*NO_3 is rapidly photolyzed and thus active primarily at night

BVOC lifetimes w.r.t. each oxidant

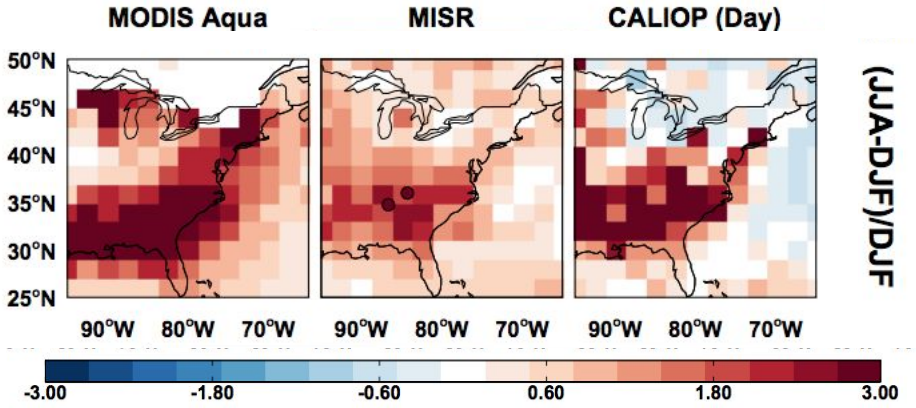
	BVOC	OH	O_3	NO_3
C_5H_8	*isoprene*	*1.4 hr*	*1.3 day*	***48 min***
$C_{10}H_{16}$	α-pinene	2.7 hr	4.7 hr	**5.4 min**
$C_{10}H_{16}$	β-pinene	1.9 hr	1.1 day	**13 min**
$C_{10}H_{16}$	Δ-carene	1.6 hr	11 hr	**3.7 min**
$C_{10}H_{16}$	limonene	51 min	1.9 hr	**2.7 min**

@ "typical" conc's: 12-h daytime avg [OH]: $2x10^6$ #/cm^3; 24 h avg [O_3]: $7x10^{11}$ #/cm^3; 12 h nighttime avg [NO_3]: $5x10^8$ #/cm^3 = 20 ppt (Atkinson & Arey, 2003)

Isoprene dominates BVOC mix in summertime SEUS, coincident with aerosol optical depth (AOD) summer enhancement

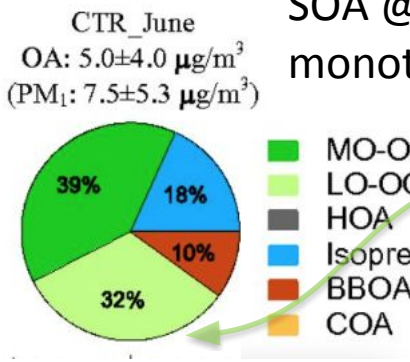


Surface measurements @ SOAS 2013
Ayres et al., ACP 2015



Observed **3x** enhancements in summer AOD
Ford & Heald, ACP 2013
But surface enhancements are only 25-55%

Carlton et al., BAMS 2019: NO_3 SOA @ SOAS is mostly from monoterpenes (high SOA yields).



LO-OOA: NO_3+ terpenes, $^1/_3$ of SOA in SEUS!
Xu et al., PNAS 2015.

BVOC lifetimes w.r.t. each oxidant

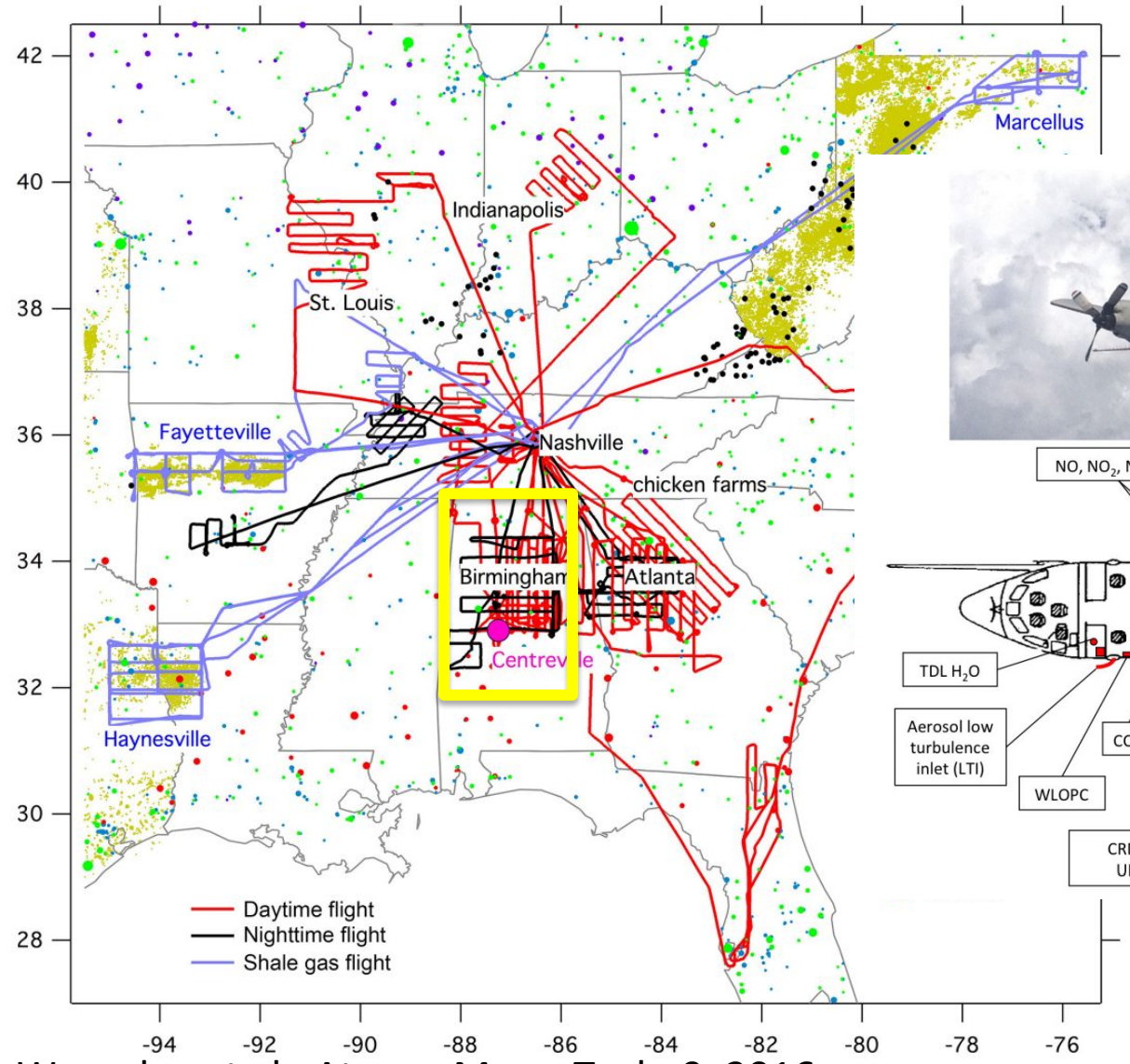
BVOC	OH	O_3	NO_3
isoprene	*1.4 hr*	*1.3 day*	***48 min***
			5.4 min
			13 min
			3.7 min
			2.7 min

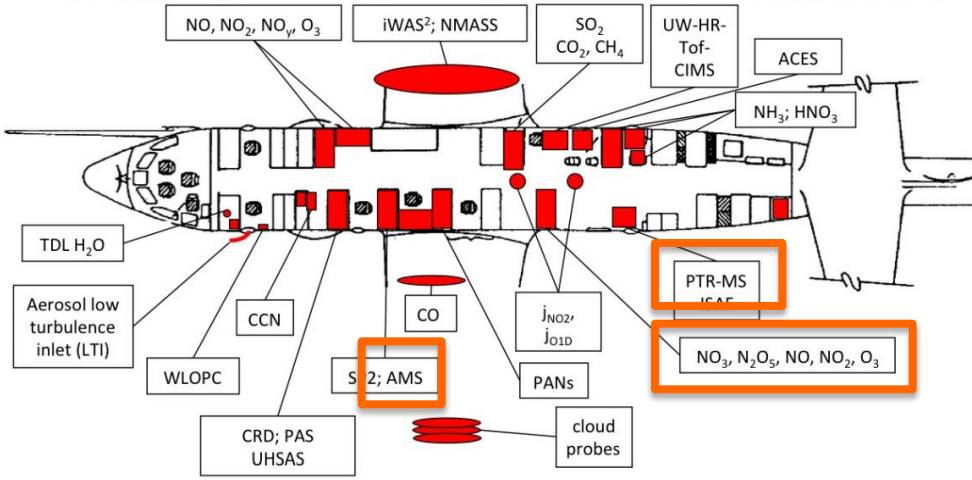
=> Could its longer NO_3 lifetime mean [isoprene] is higher aloft, producing more SOA in the residual layer?

Field study: Assess **NO_3 + isoprene SOA yield** from aircraft measurements in regions of rapid NO_3 oxidation of isoprene: power plant plumes

Gorgas steam plant, Parrish, Alabama

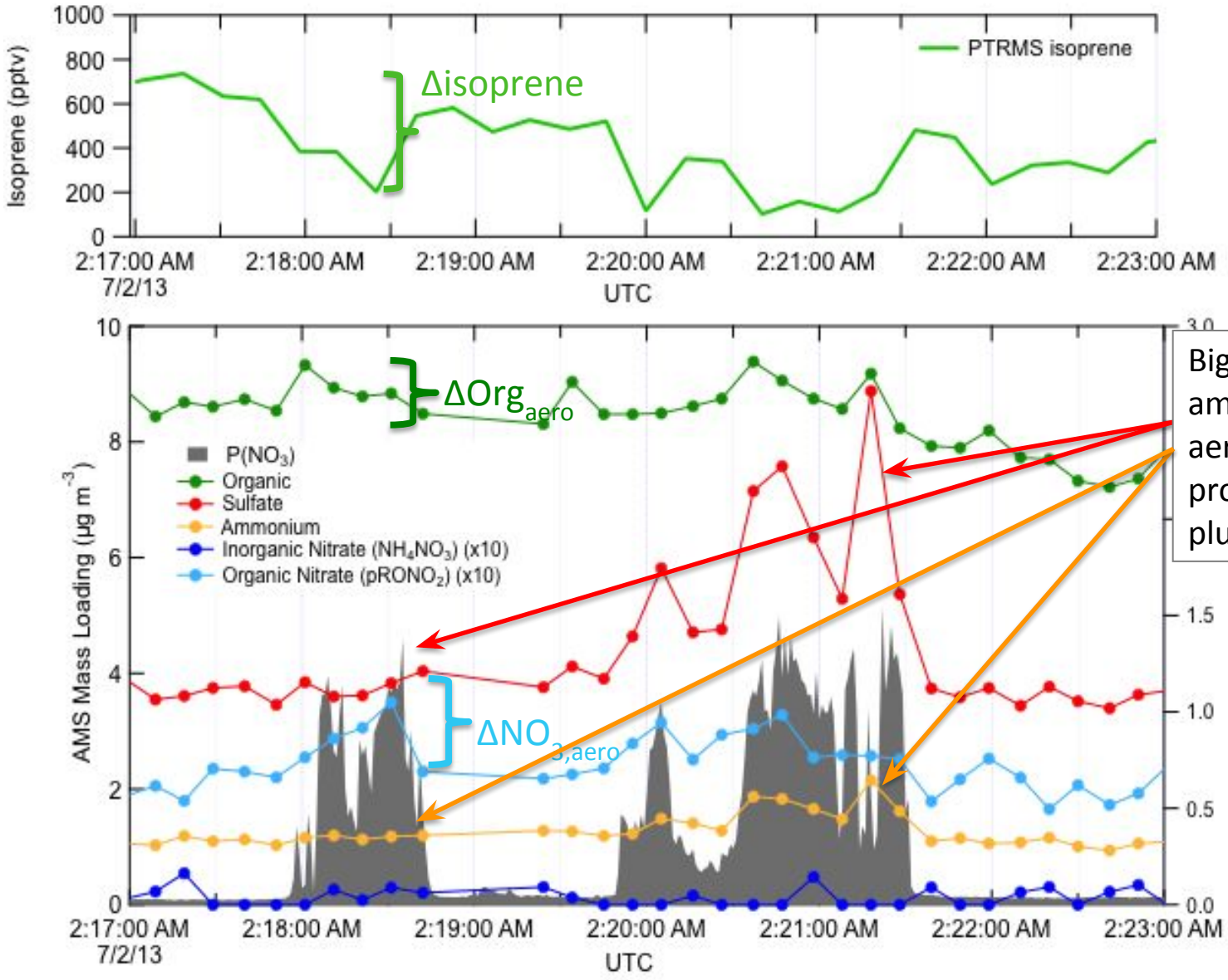
SENEX 2013: 21 research flights





Warneke, et al., Atmos. Meas. Tech. 9, 2016.

Aircraft power plant plume transects



Big differences in ammonium and sulfate aerosol emitted/ produced in different plumes.

Can we use this data to determine an SOA yield? Verify that aerosol increases were produced only by NO_3 + isoprene

(1) is all of the **NO_3 reactivity** in plumes due to reaction with isoprene?

✔ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in **aerosol nitrate mass concentration** due to NO_3 + isoprene reactions?

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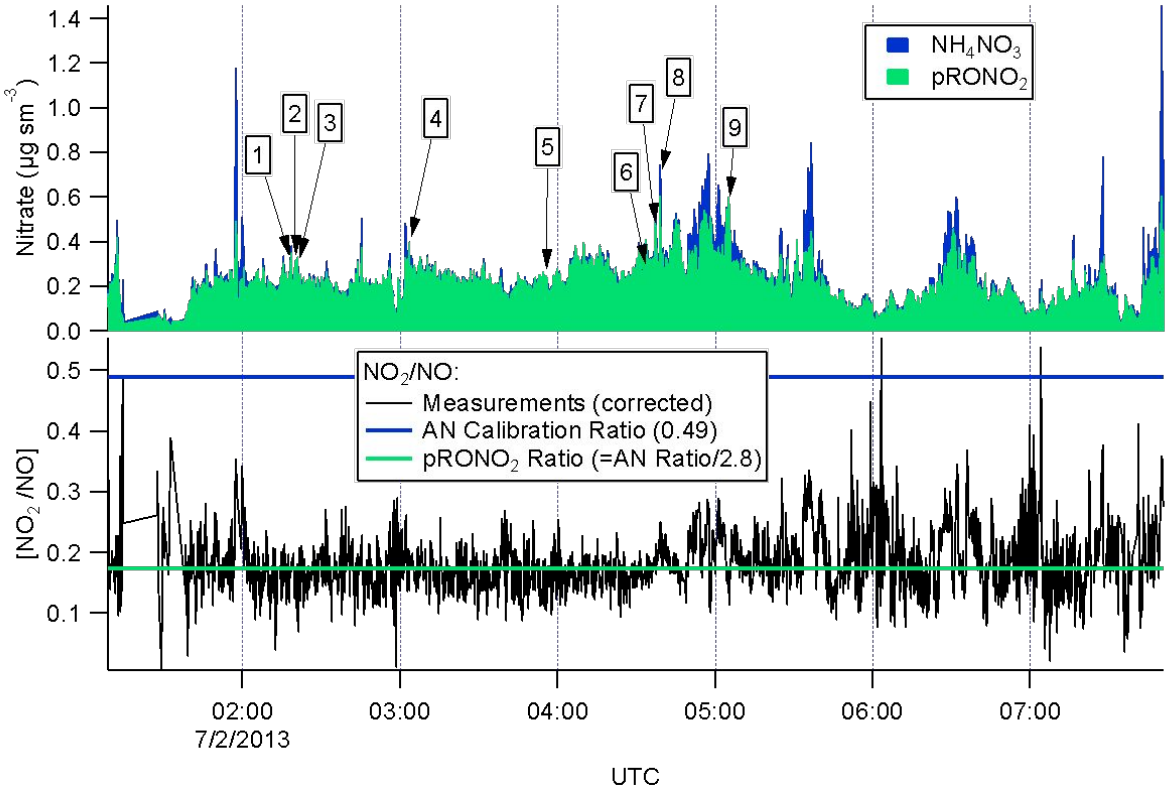


Previous studies report NO_2^+:NO^+ ratios for organic nitrates typically 2–3 times lower than for NH_4NO_3 (Fry et al., 2009, 2011; Bruns et al., 2010; Farmer et al., 2010; Liu et al., 2012); this can be used to apportion organic (pRONO2) vs. inorganic (NH_4NO_3) nitrate. **Conclusion: no sign of signficant inorganic nitrate interference in plumes.**

Can we use this data to determine an SOA yield? **YES!** Verify that aerosol increases were produced only by NO_3 + isoprene

(1) is all of the **NO_3 reactivity** in plumes due to reaction with isoprene?

✔ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in **aerosol nitrate mass concentration** due to NO_3 + isoprene reactions?

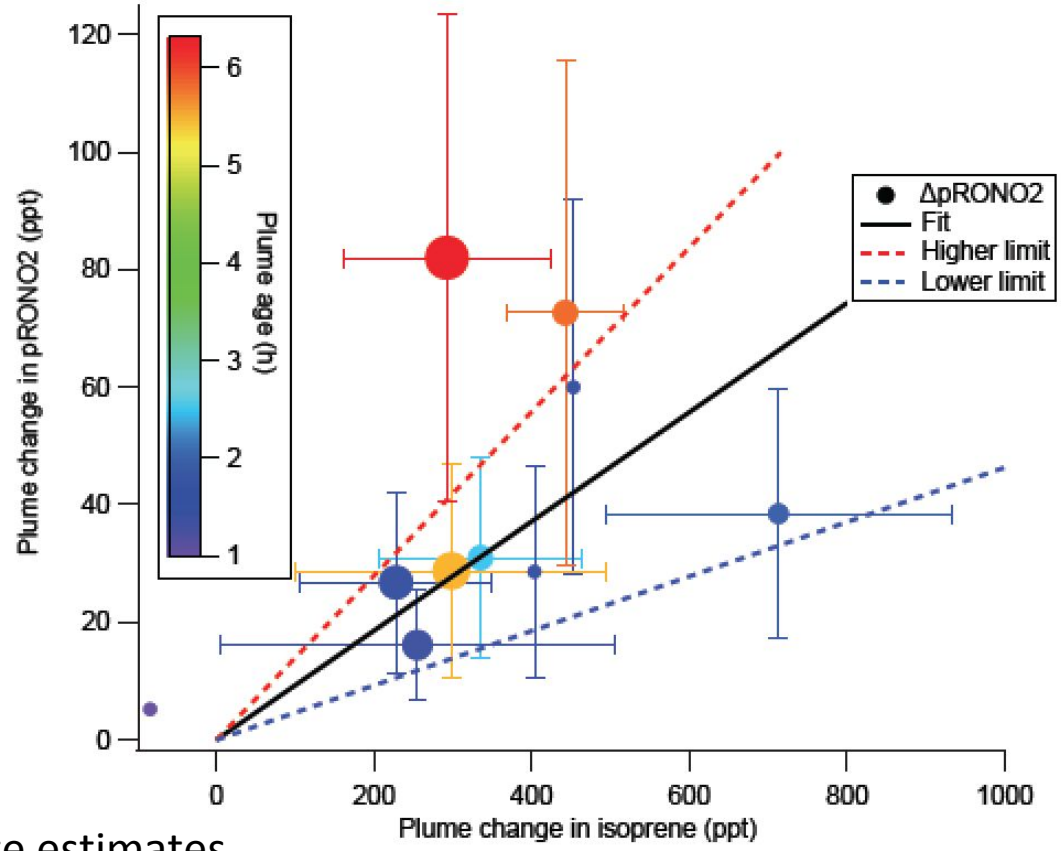
✔ Based on NO^+:NO_2^+ ratios, all increase is organic nitrate (& $pRONO_2$ is separable)

So, we will calculate SOA mass yields as:

$$Y_{SOA,mass} = \frac{(pRONO2_{plume} \pm SD_{pRONO2plume}) - (pRONO2_{bkg} \pm SD_{pRONO2bkg})}{-[(isop_{plume} \pm SD_{isopplume}) - (isop_{bkg} \pm SD_{isopbkg})]} \times 3 \times \frac{329ppt}{\mu g\ m^{-3}}$$

3: nitrate mass + associated organics, assumed to be approximately double the nitrate mass. Requires ~4 additional oxygens: e.g. a tri-hydroperoxynitrate

Observed SOA yields are large; higher at longest plume ages



SOA mass yield from these data:
27% +/- 14%

Previous chamber-based SOA mass yields:
12-14%
(Ng et al., 2008; Rollins et al., 2009)

Plume age estimates based on O_3/NO_2 ratio clock and model

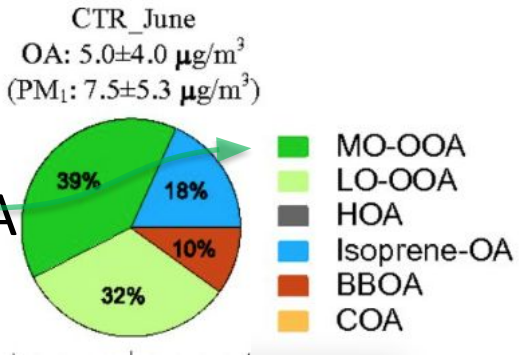
Fry et al., ACP 2018

=> Why more SOA in older plumes? Why more than previous chamber studies?

Conclusions about field-based NO_3 + isoprene SOA yields

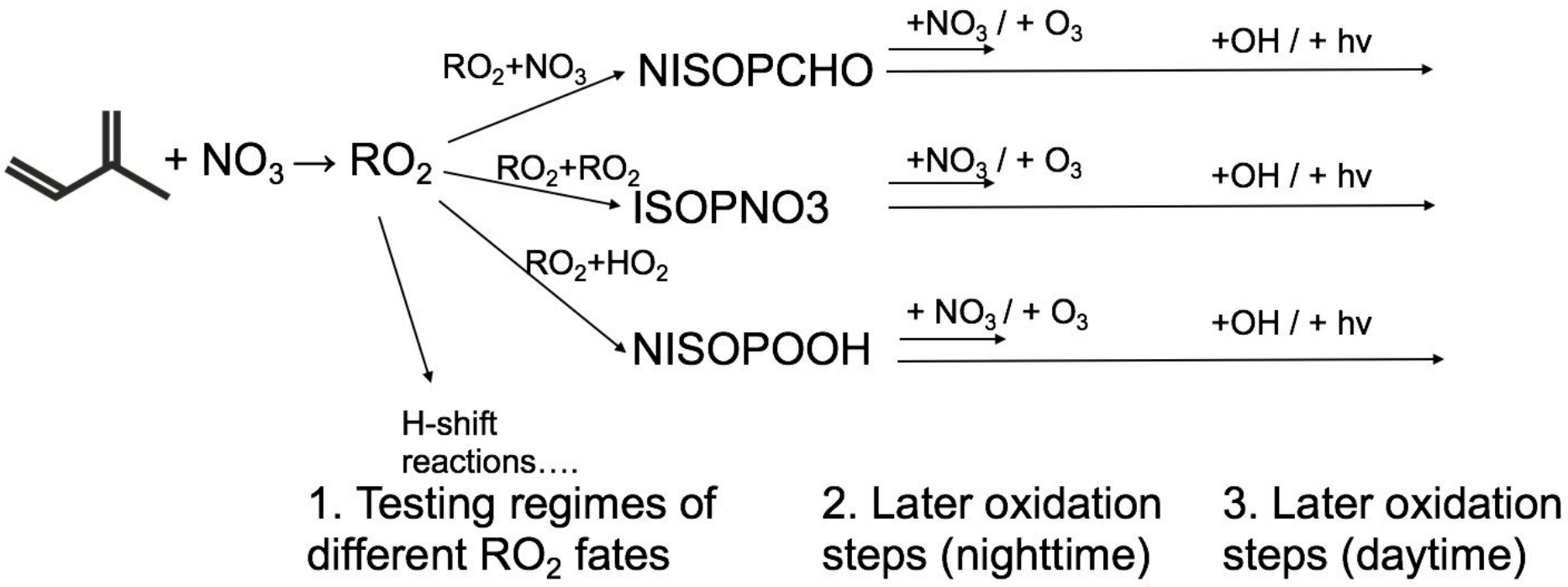
- NO_3 + isoprene yields assessed from aircraft measurements increased with plume age, on average ~ **3x** the previously chamber-measured yields, which are used in models

- NO_3 + isoprene products may contribute substantially to another organic aerosol factor (MO-OOA) comprising 40% of total OA at the surface: more oxidized, day and night peaks



- **Question: why haven't previous chamber studies observed these larger SOA yields for NO_3 + isoprene?**

Laboratory study: To the SAPHIR chamber, seeking the chemical regime that enables these larger SOA yields



1. Testing regimes of different RO_2 fates

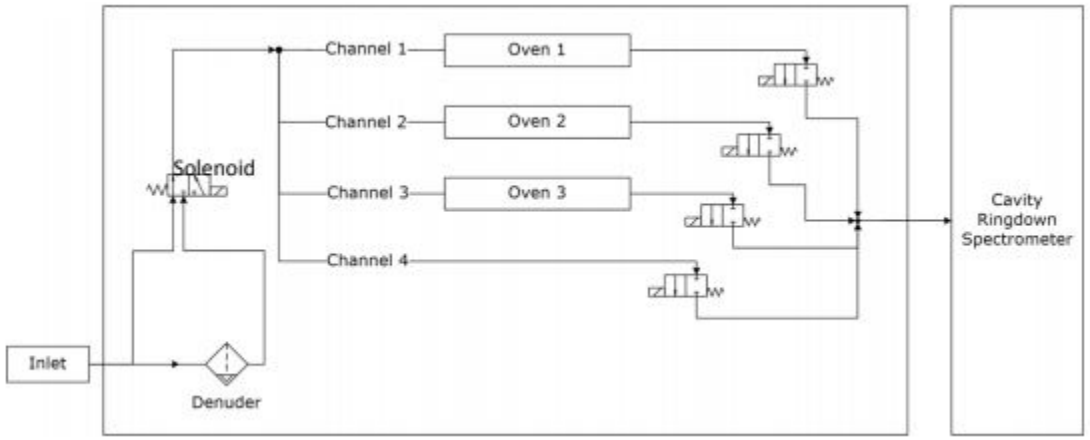
2. Later oxidation steps (nighttime)

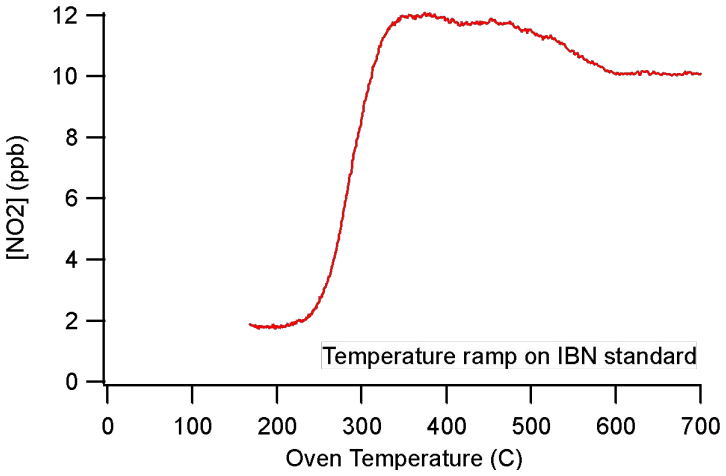
3. Later oxidation steps (daytime)

Preliminary results **from the August 2018 NO3ISOP campaign at Forschungszentrum Jülich**

EUROCHAMP 2020

Thermal dissociation – Cavity Ringdown Spectroscopy (TD-CRDS) detection of organic nitrates





Species that dissociate in each oven:

Oven 1 (700 C): NO_2 + ∑PANs + ∑ANs + HNO_3

Oven 2 (385 C): NO_2 + ∑PANs + ∑ANs

Oven 3 (130 C): NO_2 + ∑PANs

"Oven" 4 (21 C): NO_2

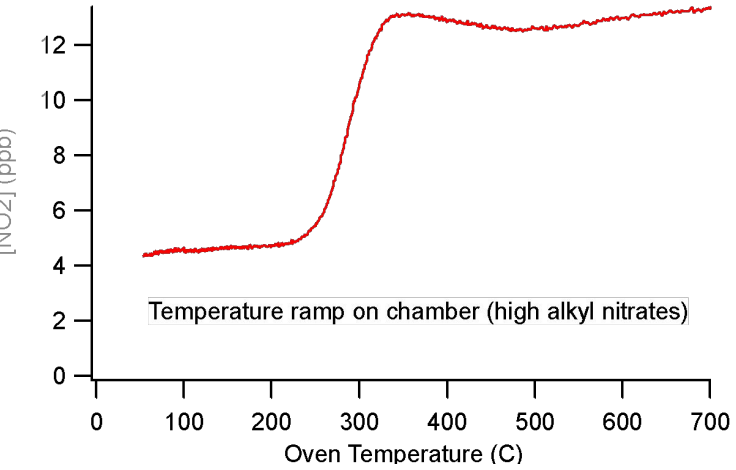
Concentrations calculations:

HNO_3 = Oven 1 - Oven 2

∑ANs = Oven 2 - Oven 3

∑PANs = Oven 3 - Oven 4

NO_2 = Oven 4



NOTE: ammonium nitrate would also appear in the 700 C channel

4 weeks of chamber expts, Aug 2018

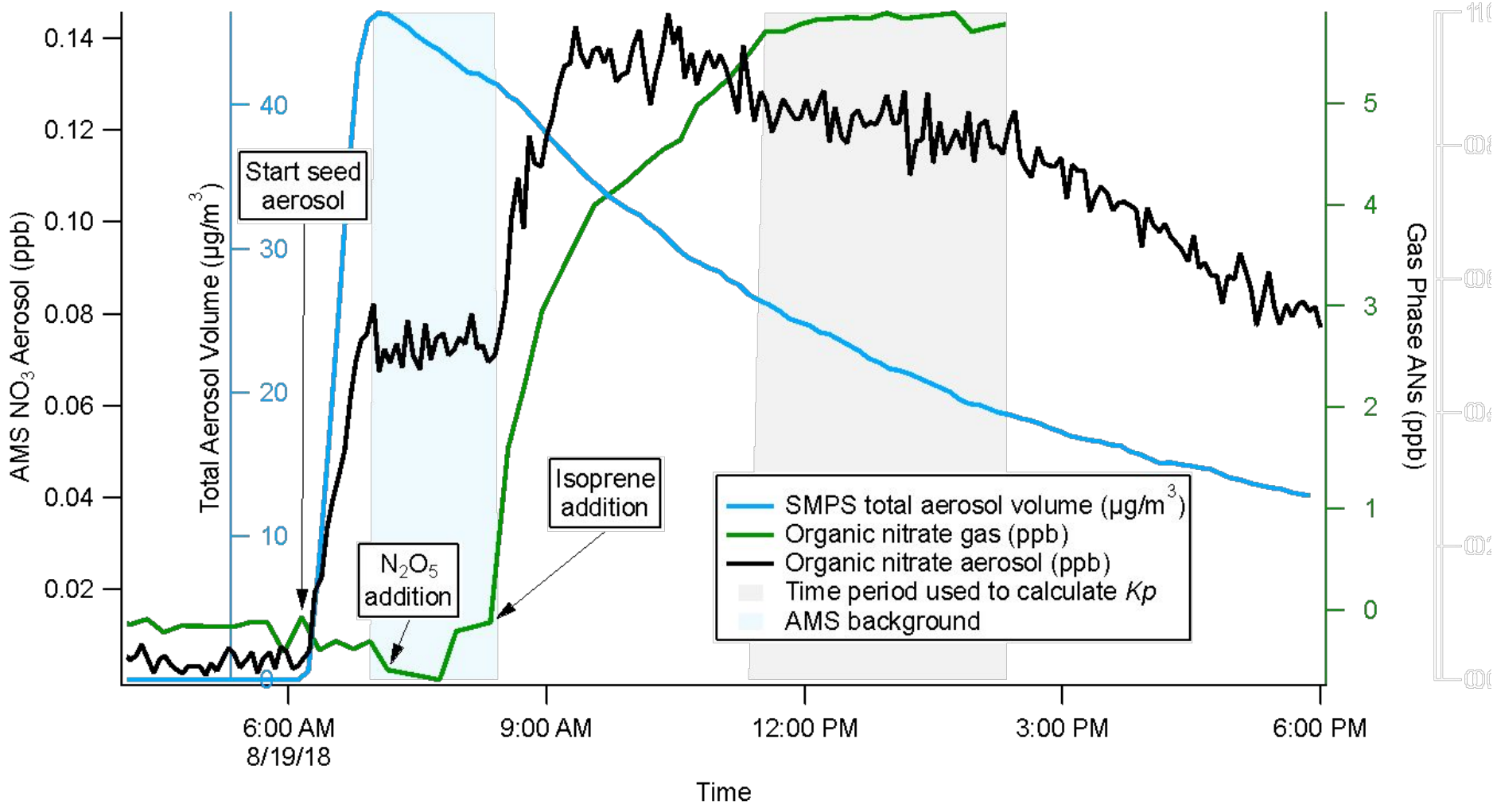
Unseeded

- 31.07. NO3 from 5ppb NO2 and 100ppb O3, dry air
- 01.08. NO3 from 5ppb NO2 and 100ppb O3, after 3 hours 3ppb isoprene, dry air
- 02.08. NO3 from 5ppb NO2 and 100ppb O3, after 3 hours 3ppb isoprene, dry air
- 03.08. Humid Daytime low Nox Isoprene + nighttime NO3 isoprene 100pbbv/5ppb
- 06.08. Humid nighttime NO3 isoprene 100pbbv/5ppb Daytime low Nox
- 07.08. lower O3 NO3+ISOP +NO3 second product (humidity 20%)
- 08.08. High Ro2 production 2x isoprene + NO3 + second oxidation products
- 09.08. NO3 isoprene + ethene: HO2+RO2
- 10.08. Repeat lower O3 NO3+ISOP +NO3 second product (dry)
- 12.08. Dry nighttime NO3 isoprene 100pbbv/5ppb + Daytime low Nox + CO
- 13.08. Repeat High Ro2 production 2x isoprene + NO3 + second oxidation products

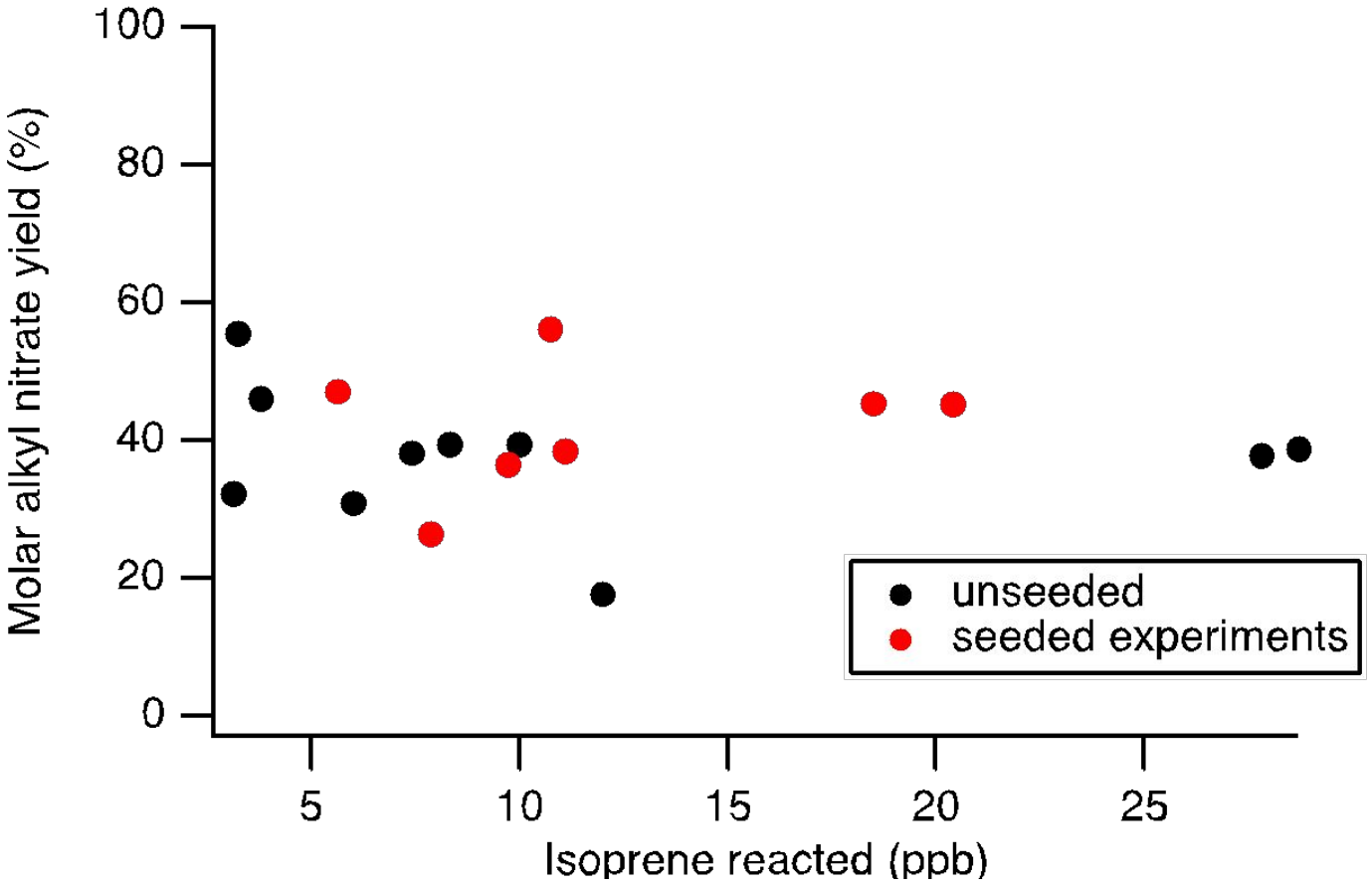
Seeded

- 14.08. Seed aerosol, dry High isoprene + NO3 + second oxidation products
- 15.08. Seed aerosol humid High isoprene + NO3 + second oxidation products
- 16.08. Seed aerosol humid medium isoprene + NO3 + daytime
- 17.08. NO2+O3, nitrate injection dry and NO2+O3 humid: HNO3 production, nitrate injection
- 18.08. Seed aerosol ozonolysis beta-carophyllene + humid medium isoprene + NO3 + daytime
- 19.08. NO3 from frozen N2O5 + medium ISOP; seed + 2nd injection ISOP
- 20.08. Seed aerosol humid ozonolysis or NO3 beta-carophyllene + isoprene + NO3 + second oxidation products
- 21.08. Seed aerosol humid medium isoprene + NO3 + second oxidation products + propene
- Later bisulfate aerosol
- 22.08. Plant chamber (oak isoprene emitter) + medium NO3, maybe later seed aerosol
- 23.08. Seed aerosol? Reference: Isop Ozonolysis 100ppb, later high isoprene NO3
- 24.08. NO2+O3, Seed aerosol humid low isoprene + NO3 + second oxidation products

Example NO_3+isoprene chamber data used for $RONO_2$ yield & gas/aerosol partitioning



Molar $RONO_2$ yield is ~40%*, largely independent of [isoprene], seed state, RO_2 regime



* Based on preliminary isoprene reacted numbers, subject to update.

$K_p = C_{aero}/(C_{gas} * M_t)$ derived from seeded experiments

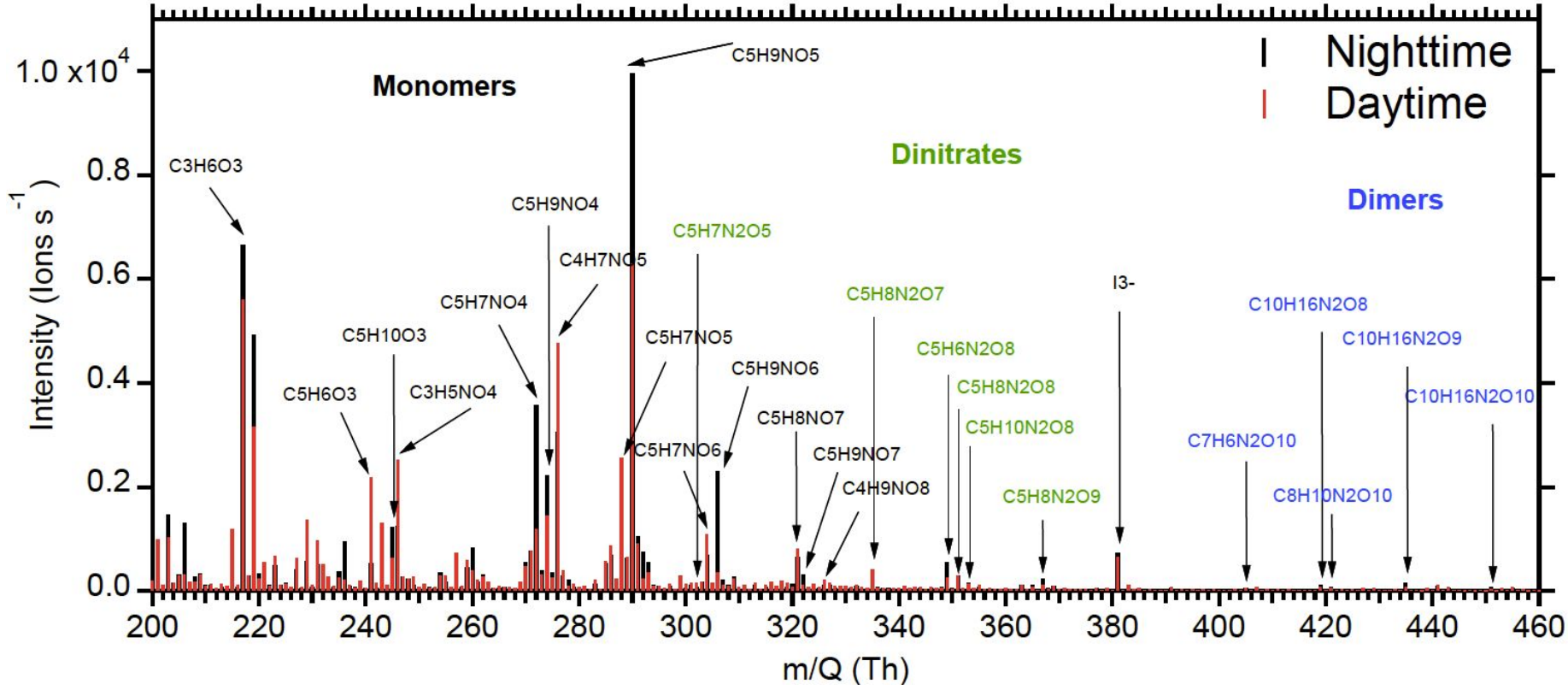
c_{aero}: AMS; c_{gas}: TD-CRDS, bkg M_t: SMPS

Date	Experiment	Regime	K_p ($m^3 \mu g^{-1}$) Total NO3 (upper limit)	K_p ($m^3 \mu g^{-1}$) OrgNO3 (lower limit)
14 Aug 2018	High NO_3	$RO_2 + RO_2$	$1.6 \pm 0.2 \times 10^{-3}$	$1.0 \pm 0.1 \times 10^{-3}$
15 Aug 2018	High NO_3	$RO_2 + RO_2$	$1.3 \pm 0.1 \times 10^{-3}$	$6.0 \pm 0.9 \times 10^{-4}$
16 Aug 2018	Inorganic seed & photolysis	$RO_2 + RO_2$	Roof closed: 2.85×10^{-3} Roof opened: $2.5 \pm 0.3 \times 10^{-3}$	Roof closed: 1.08×10^{-3} Roof opened: $1.7 \pm 0.2 \times 10^{-3}$
18 Aug 2018	O &			sed: 2.02×10^{-3} ed: $2.5 \pm 0.3 \times 10^{-3}$
19 Aug 2018	N_2O_5			$\pm 1 \times 10^{-4}$
20 Aug 2018	Organic seed & NO_3		$2.9 \pm 0.3 \times 10^{-3}$	$2.2 \pm 0.2 \times 10^{-3}$
21 Aug 2018	NO_3 & HO_x	$RO_2 + HO_2$	$1.0 \pm 0.2 \times 10^{-3}$	$4.4 \pm 0.7 \times 10^{-4}$
22 Aug 2018	Plant emissions	Isomerization, then $RO_2 + RO_2$	$8.5 \pm 1.2 \times 10^{-4}$	$7.65 \pm 1.1 \times 10^{-4}$
23 Aug 2018	Isop+O_3 seed		$3.3 \pm 0.7 \times 10^{-3}$	$1.4 \pm 0.3 \times 10^{-3}$

Bulk $K_p \sim 4 \times 10^{-4}$ -- 2×10^{-3} m^3 μg^{-1}

[$C^* \sim 500 - 2500$ μg m^{-3}]

I- CIMS measurement of individual nitrates

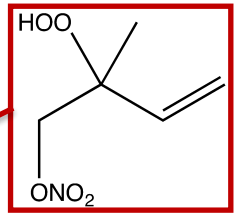


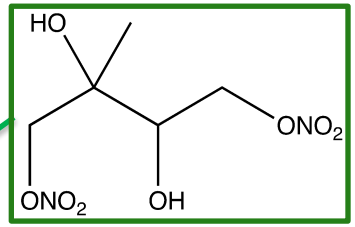
Monomers: C_5 fragments **Dinitrates**: C_5 with 2 NO_3 groups **Dimers**: C_{10} fragments

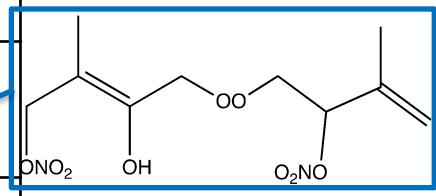
Predicted K_p's from absorptive partitioning theory

$$K_{p,i}(\text{theoretical}) = \frac{760 RT f_{om}}{MW_{om} 10^6 \zeta_i p^\circ_{L,i}}$$

Number of Functional Groups						Product, MW (amu)	Theoretical K_p ($m^3\ \mu g^{-1}$)
C	NO_3	OH	C=O	OOH	R-O-O-R		
5	1	--	1	--		ICN, 145[a]	5.26×10^{-7}
5	1	1	--	--		IHN, 147[a]	9.85×10^{-6}
5	1	2	--	--		IDHN, 161[a]	1.47×10^{-3}
5	1	1	1	--		IHCN, 163[a]	7.68×10^{-5}
5	**1**	**--**	**--**	**1**		**INP, $C_5H_9NO_5$, 163[a]**	**1.60×10^{-5}**
5	1	1	--	1		IHPN, 179[a]	2.38×10^{-3}
5	1	2	1	--		179	1.14×10^{-2}
5	1	1	1	1		195	1.88×10^{-2}
5	**2**	**2**	**--**	**--**		**IDHDN, $C_5H_{10}N_2O_8$, 226[b]**	**1.71×10^{-1}**
10	**2**	**1**	**--**	**--**	**1**	**$C_{10}H_{16}N_2O_9$, 308**	**2.67×10^{-1}**







[a]Schwantes et al (2015), [b]Rollins et al (2009).

P_{vap}s from Pankow & Asher 2008.

Are speciated nitrates consistent with observed bulk partitioning?

If we assume equal sensitivity to all species, the rough relative amount of the 3 types of nitrates from the I- CIMS are (summed signal) :

10 mononitrate : 0.7 dinitrate : 0.2 dimer

Taking as representative of their class the theoretical Kp's of the major observed **mononitrate ($C_5H_9NO_5$: 1.60×10^{-5})** , **dinitrate ($C_5H_6N_2O_8$: 1.71×10^{-1}),** and **dimer ($C_{10}H_{16}N_2O_9$: 2.67×10^{-1})**, we would obtain a weighted average "bulk" K_p of:

$K_p = (10 \times 1.60\times10^{-5} + 0.7 \times 1.71\times10^{-1} + 0.2 \times 2.67\times10^{-1})/10.9 =$ **5.4×10^{-2} m^3 μg^{-1}**

$C^* = 20$ µg m^{-3}

I- CIMS speciated

c.f. observed range of bulk ~~4×10^{-4} - 2×10^{-3} m^3 μg^{-1}~~

$C^* = 500$ - 2500 µg m^{-3}

=> Bulk gas/aerosol partitioning suggests much more volatile nitrates than speciated measurements.

Conclusions *so far* from chamber studies of NO_3 + isoprene

- Organic nitrate molar yield is ~40%, independent of RO_2 regime, seed, and [isoprene]
- Bulk gas-aerosol partitioning of nitrates is consistent with a species with volatility between $C_5H_9NO_5$ and $C_5H_{10}N_2O_8$ / $C_{10}H_{16}N_2O_9$
- Photolysis reduces the average volatility of the organonitrate mix slightly
- More detailed yields and SOA analysis is pending final data from the chamber campaign

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Want to talk more?
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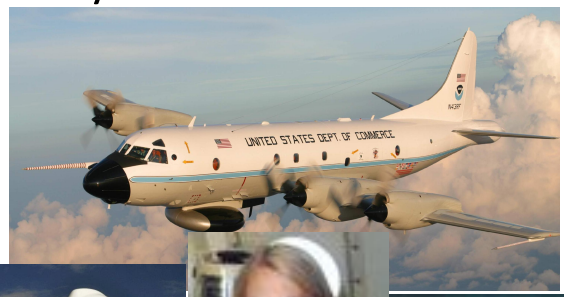


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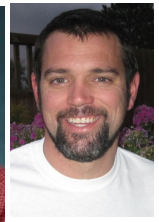
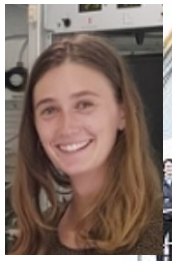

Doug Day


Bella Brownwood

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