Supplementary Information for "Gas-particle partitioning and SOA yields of organonitrate products from NO_3-initiated oxidation of isoprene under varied chemical regimes," Brownwood et al.

Table S1: Experimental parameters. Specified here are the reaction conditions for each experiment, and the chemical regime favored. The chamber reactant concentrations are listed as well other descriptors of the experiment. The total amount of isoprene consumed was modeled and predicted by Philip Carlsson (Forschungszentrum Jülich, IEK-8). The final alkyl nitrate concentration was measured by the TD-CRDS. Reactants were periodically reinjected throughout the experiment for a batch mode experiment. These injections tried to maintain a general concentration of NO_2 or O_3 in the chamber at all times and so the approximate maximum concentration of each injection is listed here. The total amount of isoprene injected by summing all additions is listed, alongside the calculated amount of isoprene consumed by NO_3, the latter of which is used to determine yields in this paper. Gas-phase experiments have white background; seeded have grey background.

Date	Favored Regime	Reactant Conc's in chamber (ppbv)	Expt Length (hours)	Chamber Conditions/ Description	RH (%)	Isoprene Consumed by NO_3 (ppbv)	Final Alkyl Nitrate Build Up (ppbv)	Maximum Wall Loss Correction %
3		O_3: 100 NO_2: 5 Isoprene: 11.1	6	humid	40	2.3	2.13	7
6	RO_2 enhanced	O_3: 100 NO_2: 5 Isoprene: 6	4 (before roof open)	Night-to-day, humid	30	4.0	Before roof open: 2.8 ± 0.1 After roof open: 1.39 ± 0.02	17
7	RO_2 isom	O_3: 50 NO_2: 5 Isoprene: 6	7	Slow RO_2, low humidity, HCl contam	10	4.2	1.9 ± 0.15	3
8	RO_2 enhanced	O_3: 100 NO_2: 25 Isoprene: 30	5	High NO_3, dry, HCl contam	0	14.4	11.1 ± 0.3	21
9	$RO_2 + HO_2$	O_3: 100 NO_2: 5 Isoprene: 7.5	5.5	120 ppm of CO, 100 ppb of propene, dry	0	3.2	3.3 ± 0.2	20
10	RO_2 isom	O_3: 50 NO_2: 5 Isoprene: 3.5	6.5	dry	0	2.5	1.75 ± 0.08	26
12	RO_2 enhanced	O_3: 100 NO_2: 5 Isoprene: 9.5	4.5	Night-to-day, 120ppm CO added when roof open, dry	0	4.8	Before roof open: 3.9 ± 0.2 After roof open: 2.5 ± 0.2	21

13	RO_2 enhanced	O_3: 100 NO_2: 25 Isoprene: 27	5.5	dry	0	11.6	10.5 ± 0.14	24

Date	**Favored Regime**	**Reactant Conc's in chamber* (ppbv)**	**Experiment Length (hours)**	**Chamber Conditions/ Description**	**RH (%)**	**Isoprene Consumed by NO_3 (ppbv)**	**Final Alkyl Nitrate Build Up (ppbv)**	**Maximum Wall Loss Correction %**
14 Aug 2018	RO_2 enhanced	O_3: 100 NO_2: 25 Isoprene: 20	4	High NO_3, dry, AS seed	0	10.3	9.23 ± 0.09	19
15	RO_2 enhanced	O_3: 100 NO_2: 25 Isoprene: 18	5	High NO_3 humid, AS seed	0 to 30	10.2	8.39 ± 0.09	25
16	isom enhanced	O_3: 100 NO_2: 5 Isoprene: 5	5	Photolysis (Night-to-day) humid, AS seed	30	4.2	2.7 ± 0.2	16
18	isom enhanced	O_3: 100 NO_2: 5 Isoprene: 7	4	AS seed with organic coating (β-caryophyllene + O_3), humid	60	4.0	2.1 ± 0.1	13

19	RO_2 enhanced, no O_3	O_3: -- NO_2: -- Isoprene: 9.5	4	N_2O_5 source, later MVK addition, dry	0	3.0	6.04 ± 0.06	~0
20	RO_2 enhanced	O_3:120 NO_2: 5 Isoprene: 9	5.5	AS seed with organic coating (β-caryophyllene + O_3), humid	60	5.5	3.55 ± 0.08	24
21	$RO_2 + HO_2$	O_3: 100 NO_2: 5 Isoprene: 9	6	Plant emissions (propene addition), humid	60	3.6	4.3 ± 0.2	22

Table S2: Key instruments used for the alkyl nitrate and aerosol analysis herein.

Instrument	Relevant species measured for this study	Inlet description	Time resolution	Section where described
TD-CRDS (custom thermal dissociation + NO_2 cavity ringdown)	gas-phase total alkyl nitrates (ΣANs)	5 meter long ¼" Teflon inlet line	8 minutes	3.2
3 independent NO_2 monitors	NO_2	4-6 meter long ¼" Teflon inlet line	1 minute	3.2
HR-ToF-AMS, Aerodyne Research Inc., USA	Aerosol-phase OA, total NO_3, and $OrgNO_3$	4 meter long ¼" stainless steel inlet line	4 minutes	3.4
VOCUS	isoprene	2 meter long ¼" Teflon inlet line	1 minute	3.3
SMPS	total particle volume concentration (size range between 10nm to 450 nm)	4-6 meter long ¼" stainless steel inlet line	7 minutes	3.5
FIGAERO HR-ToF-CIMS (I- ionization), Aerodyne Research Inc.	Gas and particle-phase speciated alkyl nitrates and organics	Gas inlet 4m long ¼" PFA. Particle inlet 4m long ½" stainless steel	1 second	4.1
HR-ToF-CIMS (Br− ionization), Aerodyne Research Inc.	gas-phase organonitrates	no external inlet	2 seconds	4.1

Table S3: Breakdown of the reactive fate of the initially formed nitrate peroxy radicals by day for four exemplary days, nomenclature and mechanism following Vereecken *et al.,* 2021 (ref. 46). Relative weight of 1-nitrate to 4-nitrate addition sites are modeled as 87/13. The equilibrium ratio of the site specific peroxy radicals was calculated to be 8% Z-ISOP1N4OO, 18% E-ISOP1N4OO, 74% ISOP1N2OO and 20% Z-ISOP1OO4N, 40% E-ISOP1OO4N, 40% ISOP3OO4N, respectively. Only the Z-conformers have contributing unimolecular decomposition pathways.

09 August "HO_2"	unimolecular loss /%	reaction with HO_2 /%	reaction with NO_3 /%	reaction with RO_2 /%
Z-ISOP1N4OO	37	54	1	8
E-ISOP1N4OO	-	86	2	12
ISOP1N2OO	-	98	2	0
all 1-nitrate RO2	**3**	**92**	**2**	**3**
Z-ISOP1OO4N	63	32	1	5
E-ISOP1OO4N	-	86	2	12
ISOP3OO4N	-	94	2	4
all 4-nitrate RO2	**13**	**78**	**1**	**8**
all nitrate RO2	**4**	**91**	**2**	**4**

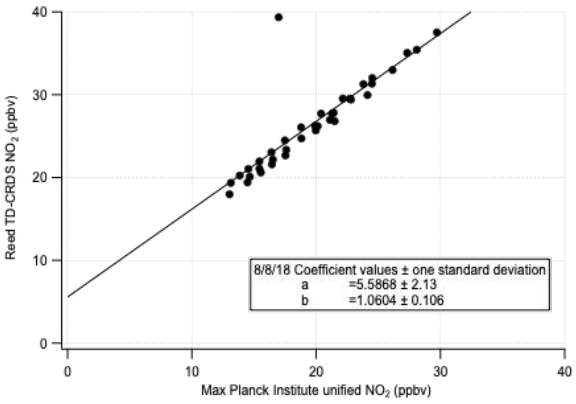
10 August "isom enhanced"	unimolecular loss /%	reaction with HO_2 /%	reaction with NO_3 /%	reaction with RO_2 /%
Z-ISOP1N4OO	78	9	5	8
E-ISOP1N4OO	-	40	22	38
ISOP1N2OO	-	64	36	0
all 1-nitrate RO2	**6**	**55**	**31**	**8**
Z-ISOP1OO4N	91	4	2	3
E-ISOP1OO4N	-	41	26	33
ISOP3OO4N	-	54	34	13
all 4-nitrate RO2	**18**	**39**	**24**	**19**

all nitrate RO2	**8**	**53**	**30**	**9**

12 August "RO_2 enhanced" (slower RO_2 production)	**unimolecular loss /%**	**reaction with HO_2 /%**	**reaction with NO_3 /%**	**reaction with RO_2 /%**
Z-ISOP1N4OO	65	14	9	13
E-ISOP1N4OO	-	38	24	38
ISOP1N2OO	-	61	38	0
all 1-nitrate RO2	**5**	**53**	**33**	**8**
Z-ISOP1OO4N	85	6	4	5
E-ISOP1OO4N	-	40	26	34
ISOP3OO4N	-	52	35	13
all 4-nitrate RO2	**17**	**38**	**25**	**20**
all nitrate RO2	**7**	**51**	**32**	**10**

13 August "RO_2 enhanced" (faster RO_2 production)	**unimolecular loss /%**	**reaction with HO_2 /%**	**reaction with NO_3 /%**	**reaction with RO_2 /%**
Z-ISOP1N4OO	45	20	11	24
E-ISOP1N4OO	-	34	19	47
ISOP1N2OO	-	64	36	1
all 1-nitrate RO2	**4**	**55**	**31**	**11**
Z-ISOP1OO4N	74	11	7	8
E-ISOP1OO4N	-	38	22	40
ISOP3OO4N	-	53	31	17
all 4-nitrate RO2	**15**	**38**	**22**	**25**

all nitrate RO2	5	53	30	13


Reed TD-CRDS NO2 (ppbv)
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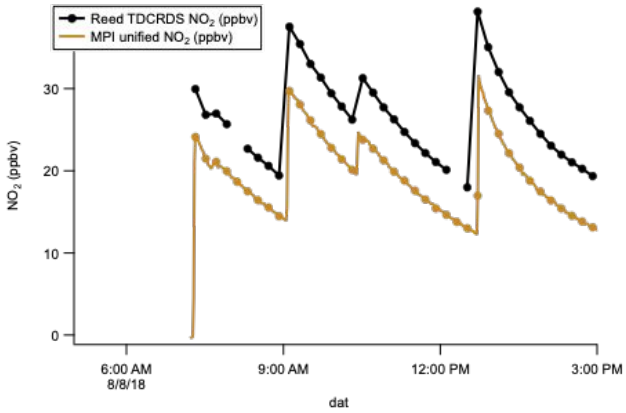
b =1.0604 ± 0.106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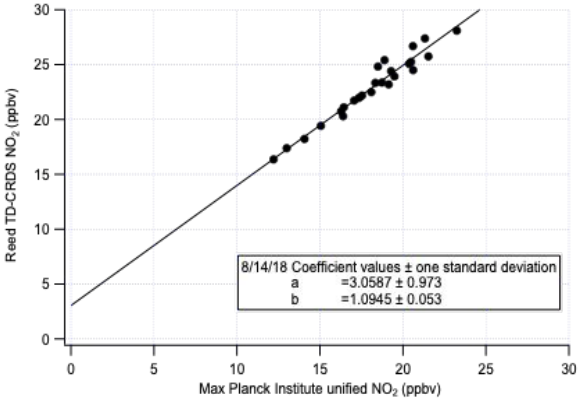
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8/14/18 Coefficient values ± one standard deviation
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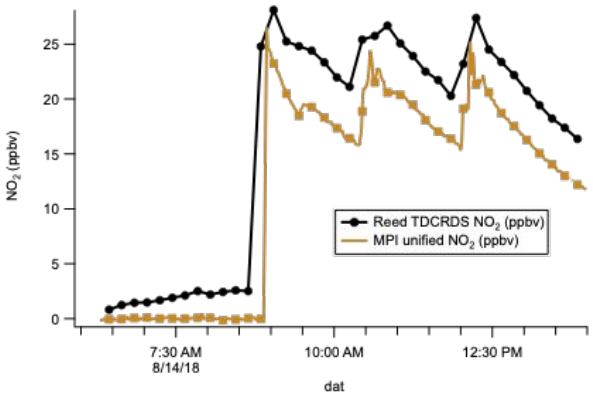
b =1.0945 ± 0.053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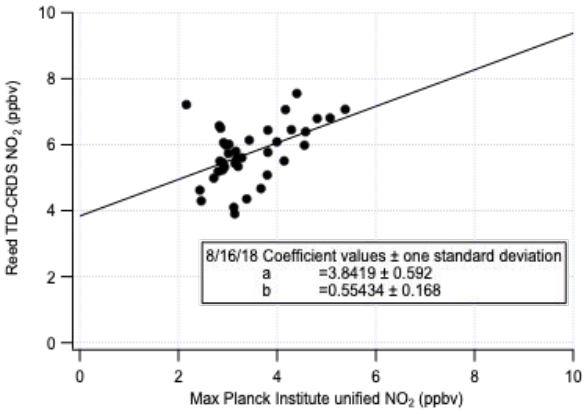
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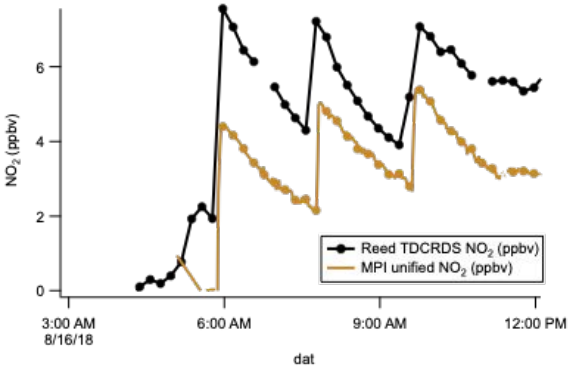
b =0.55434 ± 0.168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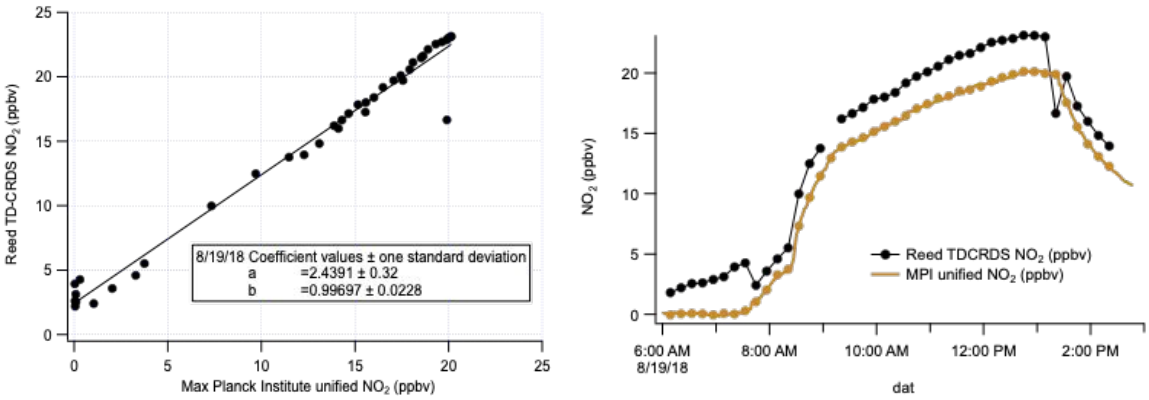

Figure S1. Scatterplot NO_2 comparisons from Figure 2 alongside corresponding timeseries comparisons.

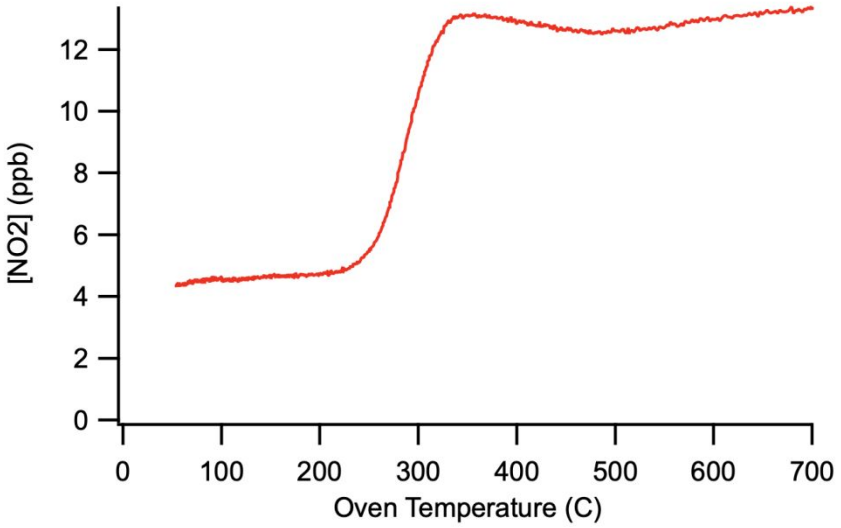

Figure S2. Thermogram (oven temperature ramp) on a chamber mix of isoprene + NO_3 products. This supports the selection of 385 as the over temperature to measure alkyl nitrates. Collected on the SAPHIR chamber on 17. August 2018.

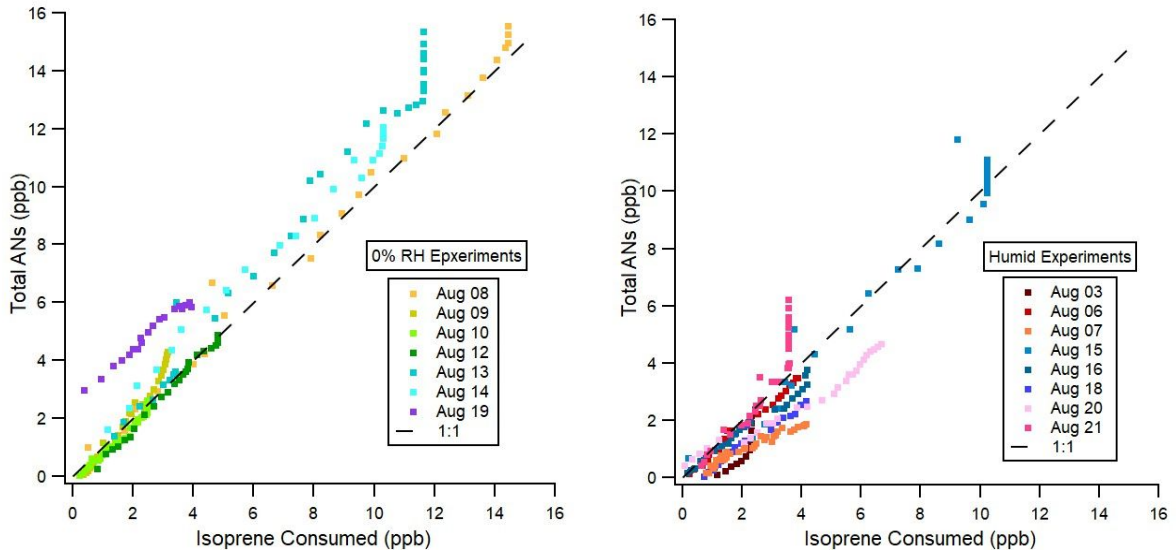

Figure S3. Total alkyl nitrate yield plots split out by humidity.

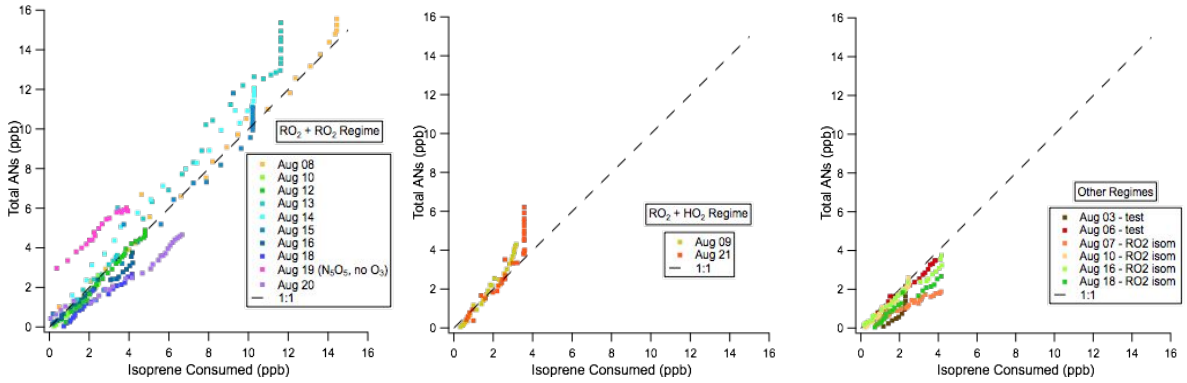

Figure S4. Total alkyl nitrate yield plots split out by RO_2 fate / reaction regime. The most common $RO_2 + RO_2$ enhanced regime has significant scatter, but $RO_2 + HO_2$ enhanced hints at higher yield and RO_2 isomerization at lower yields.

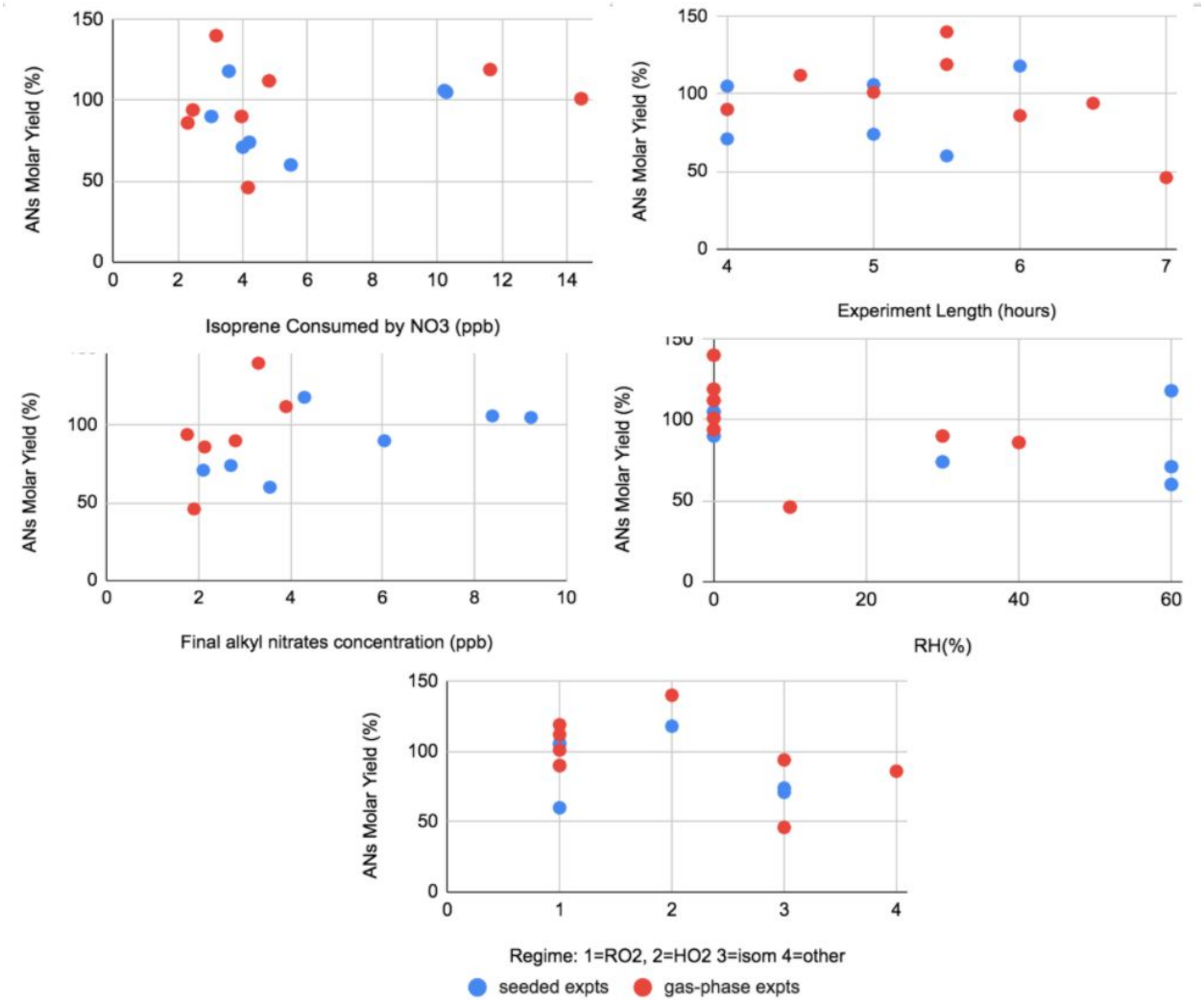

Figure S5. ANs yields plotted against several experimental variables in search of any dependencies. There are no clear dependences on isoprene consumed, alkyl nitrate formed, experiment length, %RH, or whether seeded. There is significant scatter within each chemical regime, but HO_2 regime experiments appear to have higher yields and isomerization experiments slightly lower yields.

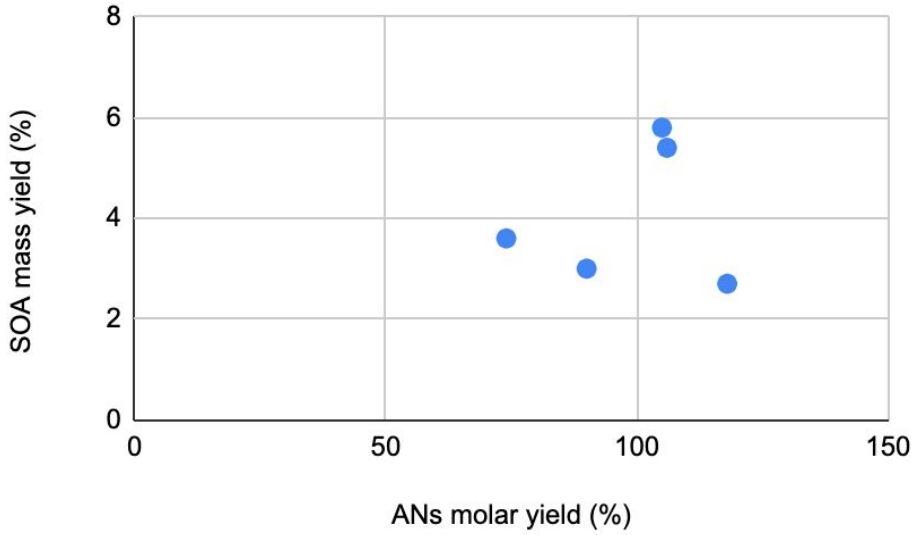

Figure S6. SOA mass yield measurements (using values from OrgNO3 with R = 0.19) scattered against alkyl nitrate yield, for all experiments for which both measures are available. No clear trend is observed.