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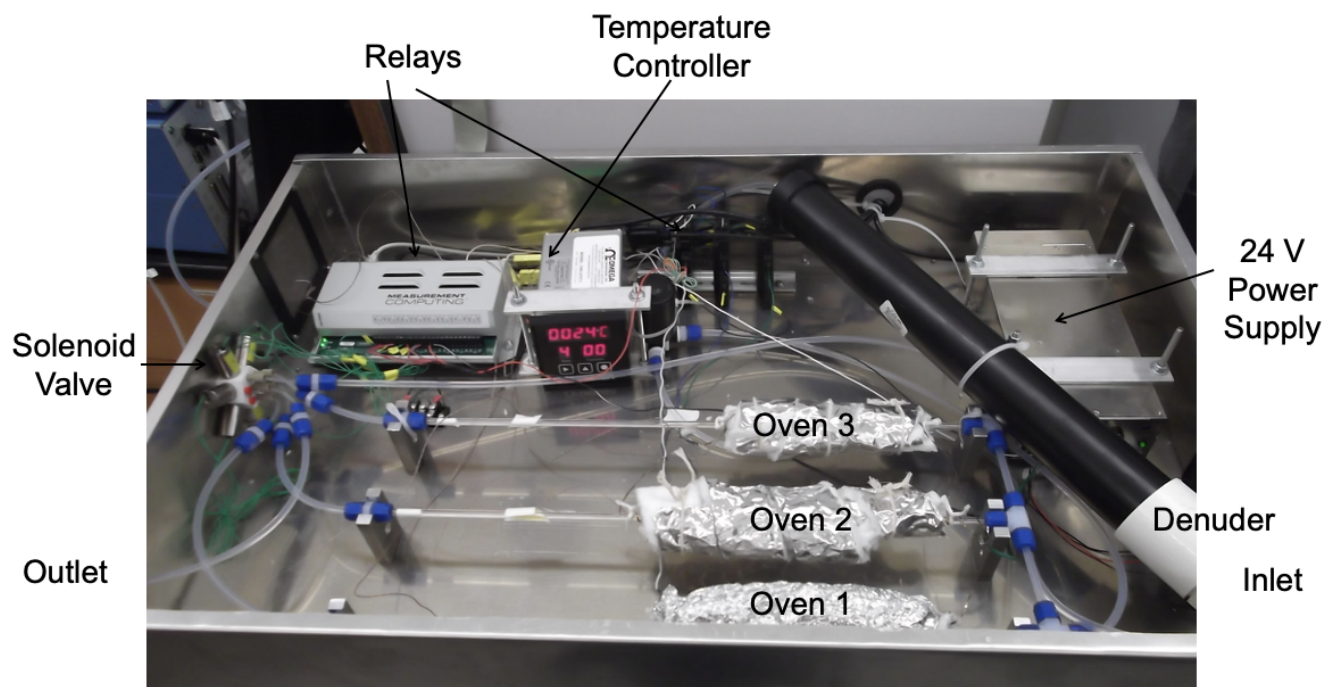
Supplement of

A thermal-dissociation–cavity ring-down spectrometer (TD-CRDS) for the detection of organic nitrates in gas and particle phases

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Figure S1. Oven inlet box.

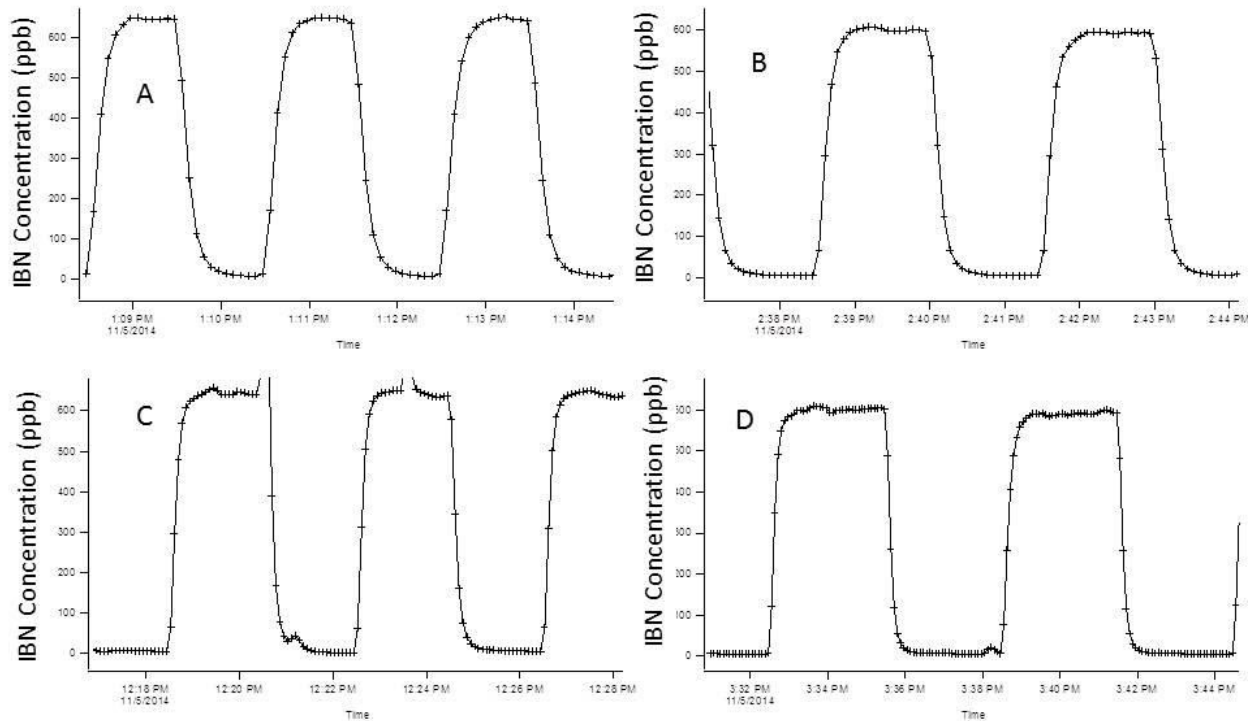


Figure S2. Channel switching frequency testing. Panel A shows 30 second sampling time, B 45 seconds, C 60 seconds, and 620 D 90 seconds.

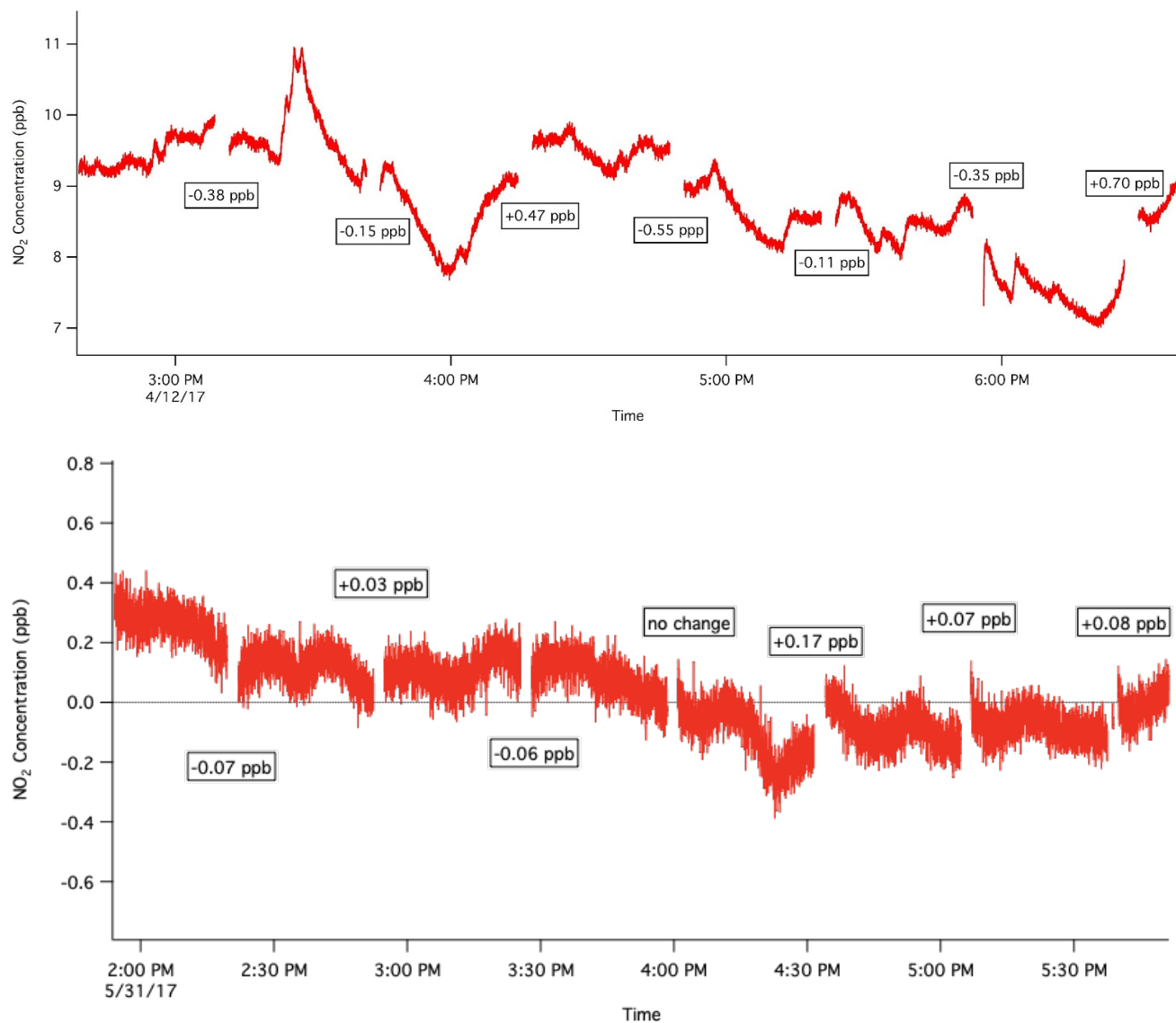


Figure S3. CRDS running for 4 hours on room air (upper panel) or zero air (lower panel). Seven instrument zeroes are visible across each timeseries to show the typical changes in signal. For the detection limit analysis included in the manuscript, the standard deviation of the zero signal measured over the full length of the lower panel was calculated, and found to be $\sigma_{\text{zero}} = 0.16$ ppb.

Table S1. Rate constants for different species used in kinetics model.

Dissociation / Recombination Reactions	Dissociation rate parameters (Day et al., 2002, Table 1)				Recombination parameters (“JPL Data Evaluation” 2015, Table 2-1)			
	k_0^a	a^a	k_h^b	b^b	$k_0^{300,c}$	n^c	$k_\infty^{300,d}$	m^d
PN ↔ NO ₂ + CH ₃ C(O)OO	4.9x10 ⁻³	12100	4x10 ¹⁶	13600	9.7x10 ⁻²⁹	5.6	9.3x10 ⁻¹²	1.5
AN ↔ NO ₂ + C ₂ H ₅ CO or C ₃ H ₇ O	-	-	3.16x10 ¹⁶	20129	2x10 ⁻²⁷	4	2.8x10 ⁻¹¹	1
HNO ₃ ↔ NO ₂ + OH	(1.82x10 ⁻⁴)(T/298) ^{-1.98}	24004	2x10 ¹⁵	24658	1.8x10 ⁻³⁰	3	2.8x10 ⁻¹¹	0
Loss Reaction	Rate constant							
OH → walls ^e	46 s ⁻¹							
n-C ₄ H ₉ O + O ₂ → products ^f	(8.9x10 ⁻¹⁴)(e ^{-550/T}) cm ³ molecule ⁻¹ s ⁻¹							

- 630 a. Low pressure limit $k_0(T) = k_0 \exp(-a/T)$, where T is temperature in Kelvin, cm³ molecule⁻¹ s⁻¹
- b. High pressure limit $k_h(T) = k_h \exp(-b/T)$, where T is temperature in Kelvin, cm³ molecule⁻¹ s⁻¹
- c. Low pressure limit $k_0(T) = k_0^{300} (T/300)^{-n}$, where T is temperature in Kelvin, cm³ molecule⁻¹ s⁻¹
- d. High pressure limit $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$, where T is temperature in Kelvin, cm³ molecule⁻¹ s⁻¹
- e. Knopf, Pöschl, and Shiraiwa 2015
- 635 f. IUPAC evaluation, reaction RO_5, <http://iupac.pole-ether.fr/>

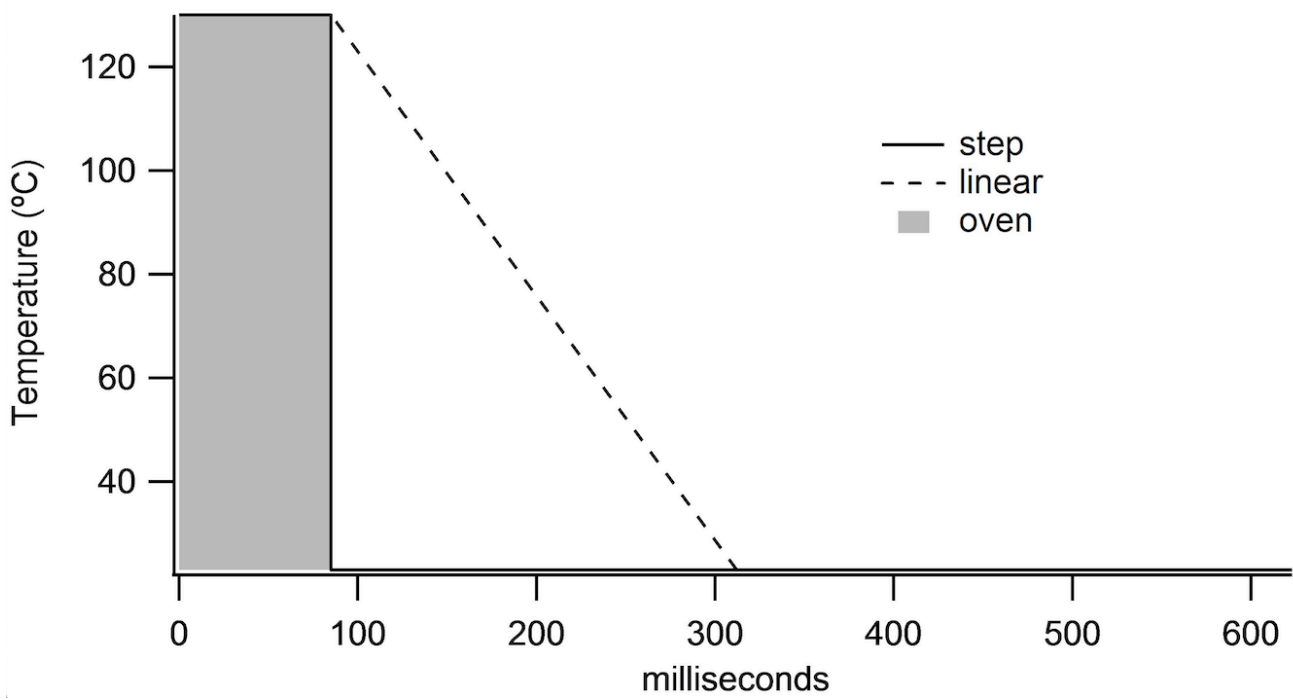
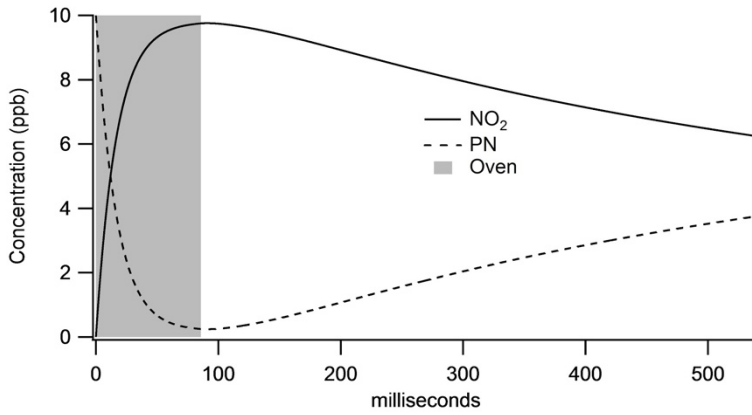
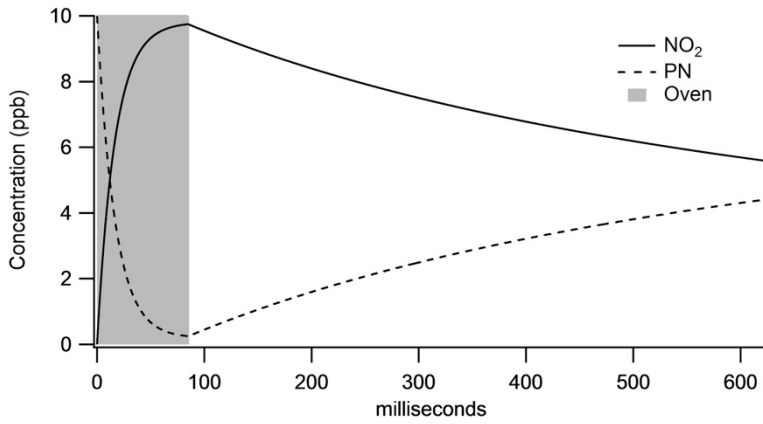
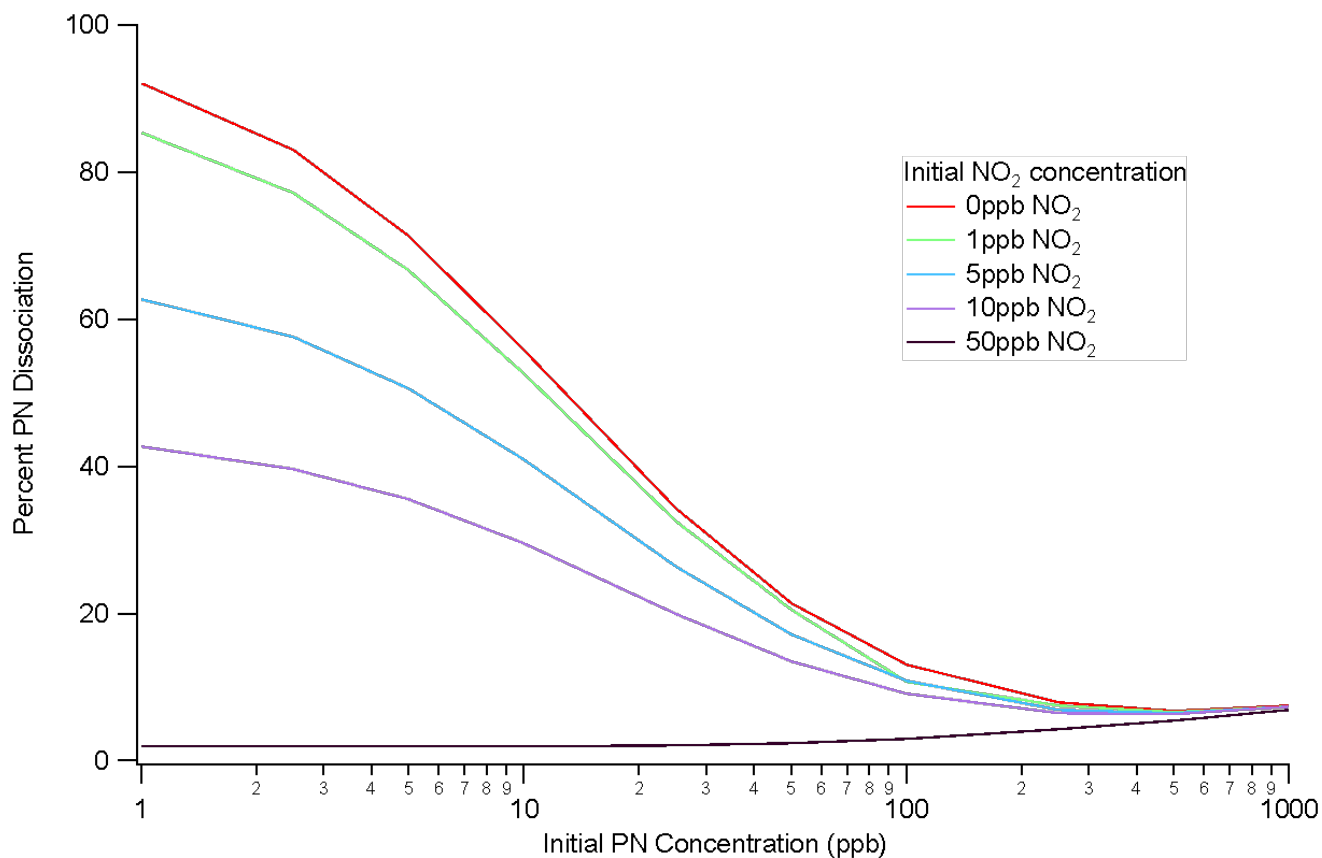


Figure S4. Two considered models of cooling rates in the quartz tubing after the PN oven.

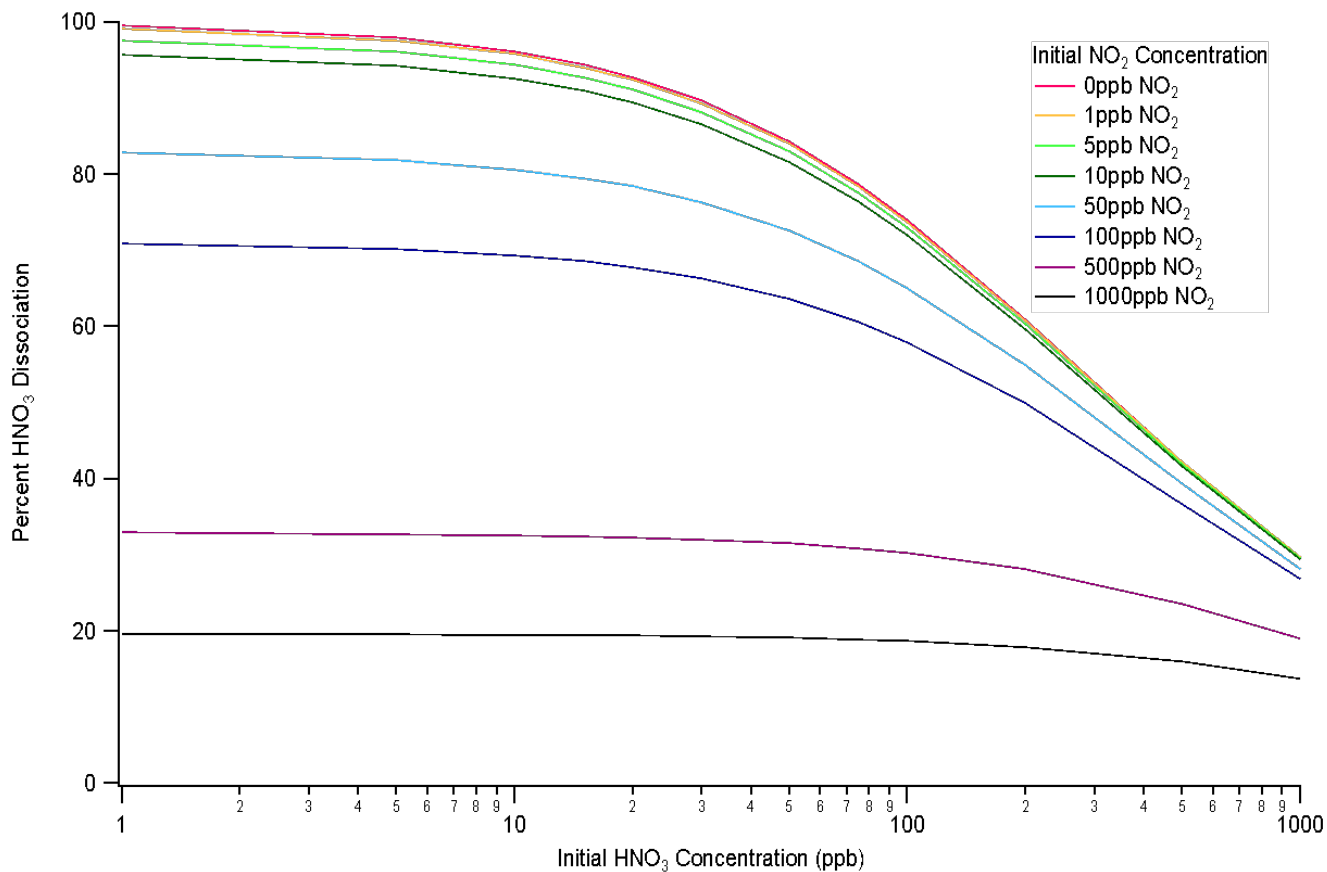


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Figure S5. Model of PN dissociation through an oven at 120°C, using both step function (top) and linear temperature decay (bottom). Shaded region is the heated portion of the oven.

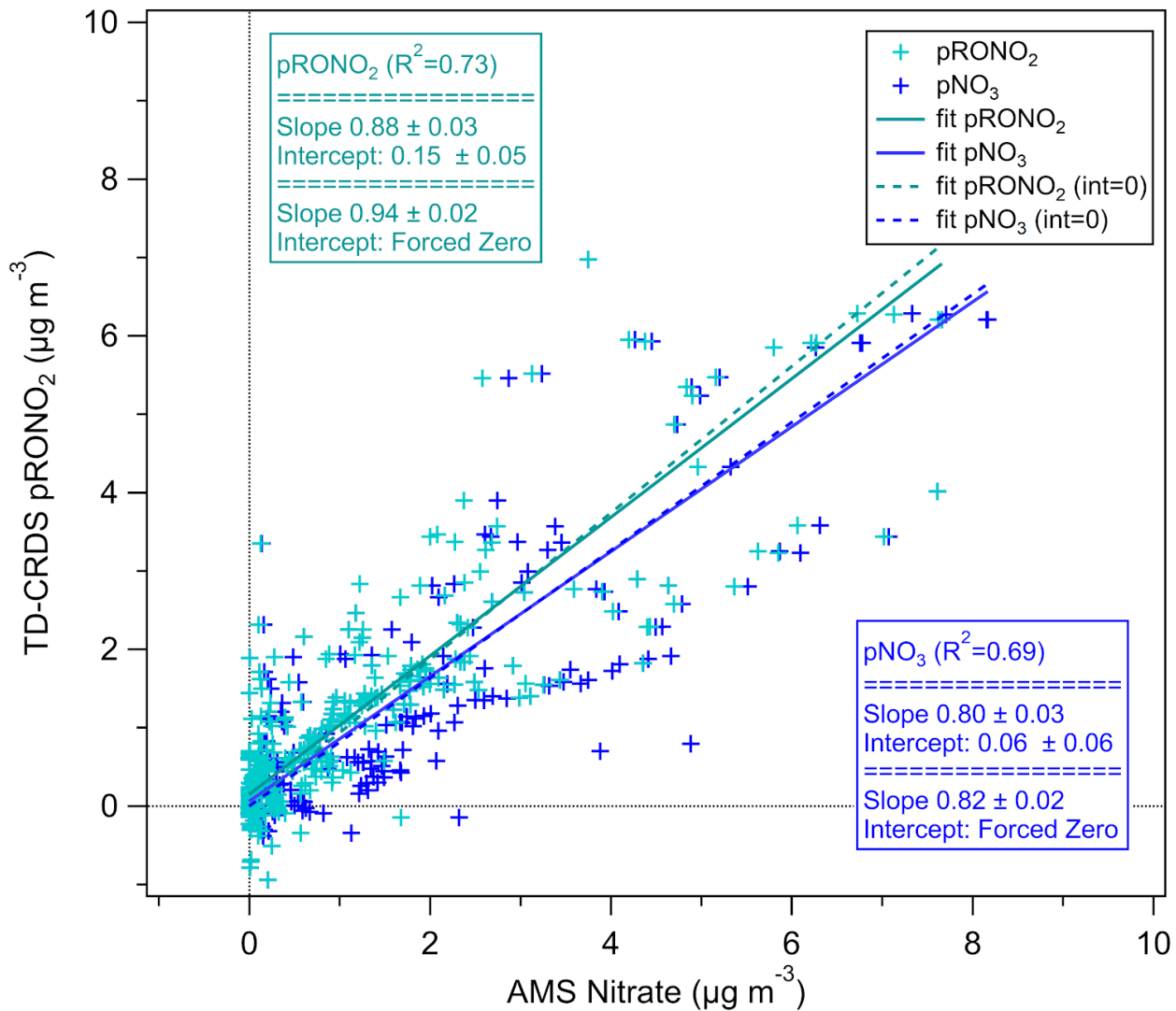


645 **Figure S6.** Percent PNs detected at CRDS at different initial concentrations of PNs and NO₂. Most work is done in the lower concentration range of both PNs and NO₂, where the percent of PNs that remain dissociated to the detector is relatively higher; however we note the recombination effect here is larger than for ANs or HNO₃ (see Figure S7). Percent dissociated is equivalent to percent detected.



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Figure S7. Percent HNO₃ detected at CRDS at different initial concentrations of nitric acid and NO₂. Most work is done in the lower concentration range of both HNO₃ and NO₂, where the percent HNO₃ that remains dissociated to the detector is high. Percent dissociated is equivalent to percent detected.



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Figure S8. TD-CRDS organic nitrate vs AMS total nitrate (pNO₃) and apportioned organic nitrate fraction (pRONO₂).