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Low levels of nitryl chloride at ground level: nocturnal nitrogen oxides in the Lower Fraser Valley of British Columbia

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Supplement of

Low levels of nitryl chloride at ground level: nocturnal nitrogen oxides in the Lower Fraser Valley of British Columbia

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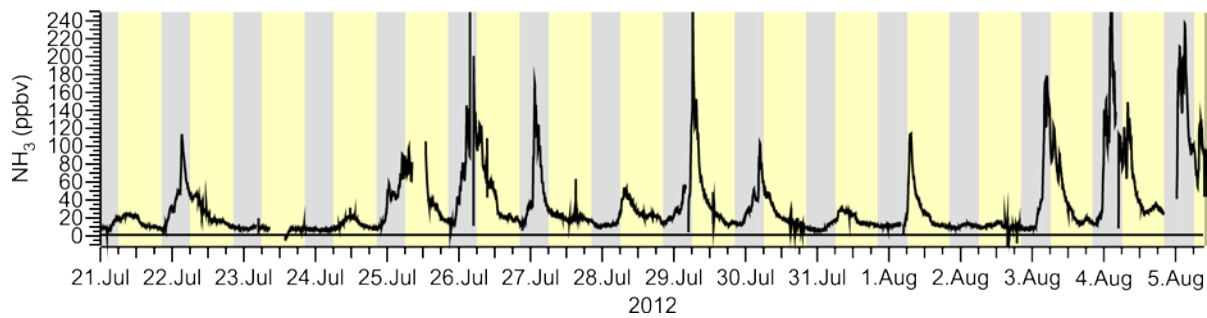
36 **Table S-1.** Volatile organic compounds quantified by GC-MS

Butane, 2-methyl-	Cyclohexane, methyl-	Benzene, 1,2,3-
1-Pentene	Pentane, 2,3,4-	trimethyl-
Pentane	trimethyl-	Benzene, 1,3-diethyl-
2-Pentene (Z) (cis)	Heptane, 2-methyl-	Benzene, 1,4-diethyl-
Isoprene (1,3-	Heptane, 3-methyl-	Undecane
Butadiene, 2-methyl-)	Toluene	Dodecane
2-Pentene (E) (trans)	Octane	Ethylene
Butane, 2,2-dimethyl-	Ethylbenzene	Acetylene
Cyclopentane	m & p-Xylene	Ethane
2,3-Dimethylbutane	Nonane	Propane
Pentane, 2-methyl-	Styrene	Propylene
Pentane, 3-methyl-	o-Xylene	Isobutane
1-Hexene	Isopropyl Benzene	1-Butene
Hexane	(Benzene, (1-methyleth	Butane
Cyclopentane, methyl-	Benzene, propyl-	2-Butene (trans)
Pentane, 2,4-dimethyl-	Benzene, 1-ethyl-3-	2-Butene (cis)
Cyclohexane	methyl-	Freon 11
Hexane, 2-methyl-	Benzene, 1-ethyl-4-	(Trichloromonofluorom
Benzene	methyl-	ethane)
2,3-Dimethylpentane	Benzene, 1,3,5-	Isopropyl Alcohol
Hexane, 3-methyl-	trimethyl-	Acetone
Pentane, 2,2,4-	Decane	Ethene, 1,1-dichloro-
trimethyl-	Benzene, 1-ethyl-2-	Methylene Chloride
Heptane	methyl-	Freon 113 (Ethane,
	Benzene, 1,2,4-	1,1,2-trichloro-1,2,2
	trimethyl-	

Carbon disulfide	Methyl Methacrylate	Benzene, 1,4-dichloro-
Ethene, 1,2-dichloro-, (E)-	1-Propene, 1,3- dichloro-, (Z)-	Benzene, 1,2-dichloro-
Methyl tertbutylether (Propane, 2-methox	Methyl Isobutyl Ketone	Benzene, 1,2,4- trichloro-
Ethane, 1,1-dichloro-	1-Propene, 1,3- dichloro-, (E)-	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-
Vinyl Acetate (Acetic acid ethenyl ester	Ethane, 1,1,2-trichloro-	Naphthalene
2-Butanone	2-Hexanone	Freon 12
Chloroform (Trichloromethane)	Methane, dibromochloro-	Chloromethane
Ethyl Acetate	Ethane, 1,2-dibromo-	Freon 114
Furan, tetrahydro-	Tetrachloroethylene	Vinyl chloride
Ethane, 1,2-dichloro-	Benzene, chloro-	1,3 Butadiene
Ethane, 1,1,1-trichloro-	Bromoform (Methane, tribromo-)	Bromomethane
Carbon Tetrachloride	Ethane, 1,1,2,2- tetrachloro-	Chloroethane
Trichloroethylene	Ethane, pentachloro-	Ethanol
Methane, bromodichloro-	Benzyl Chloride	1R-alpha-Pinene
1,4-Dioxane	Benzene, 1,3-dichloro-	Camphene
		beta-Pinene
		D-Limonene

37

39



40

41 **Figure S-1.** Time series of gas-phase ammonia data reported by Metro Vancouver. Data were
42 not quality-assured and are non-quantitative.

43

44 **Box model to rationalize O_x loss by dry deposition**

45 A box model was set up to simulate the median nocturnal decays of O₃ and O_x. These
46 simulations are intended as back-of-the-envelope type estimates of major processes only since
47 an accurate description of the nocturnal boundary layer chemistry would require modeling of
48 horizontal and vertical transport, i.e., altitude-resolved information (Geyer and Stutz, 2004).
49 Such information was not available in this work.

50 The reactions used in this model are summarized in Table S-2. The mechanism consists of O₃
51 and NO₂ dry deposition, titration of NO with O₃ (R8) and chemical loss of O₃ to a generic
52 biogenic hydrocarbon. For dry deposition, the velocities of $v_d(\text{O}_3) = 0.2 \text{ cm s}^{-1}$ and $v_d(\text{NO}_2) =$
53 $\alpha \times v_d(\text{O}_3)$ with $\alpha=0.65$ from Lin et al. (2010) were used. The rate constants for reaction with
54 the generic biogenic hydrocarbon was set to that of α -pinene with O₃ ($5 \times 10^{-11} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$,
55 (Seinfeld and Pandis, 2006)).

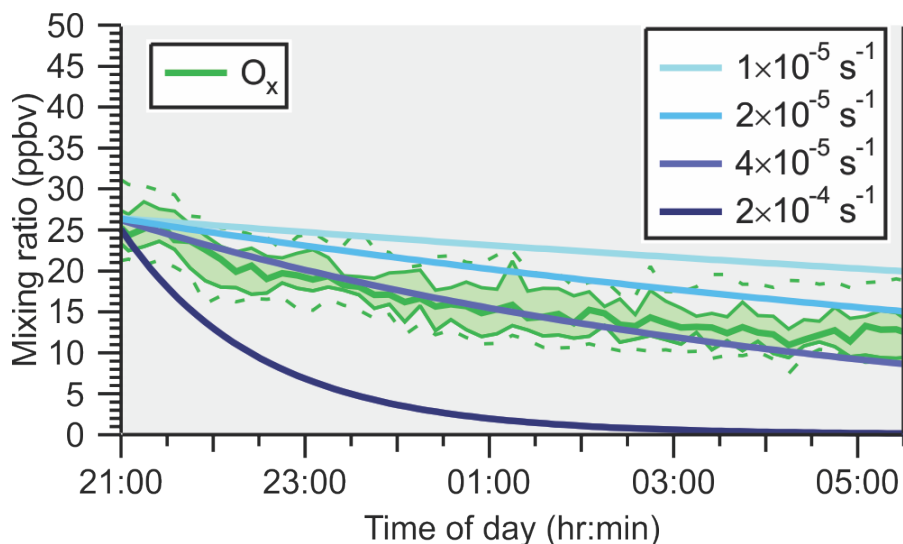
56 Model simulations were carried out using a custom differential equation integrator macro in the
57 software package Igor Pro (Wavemetrics) and were initiated with the campaign median NO₂
58 and O₃ concentrations observed at sunset.

59

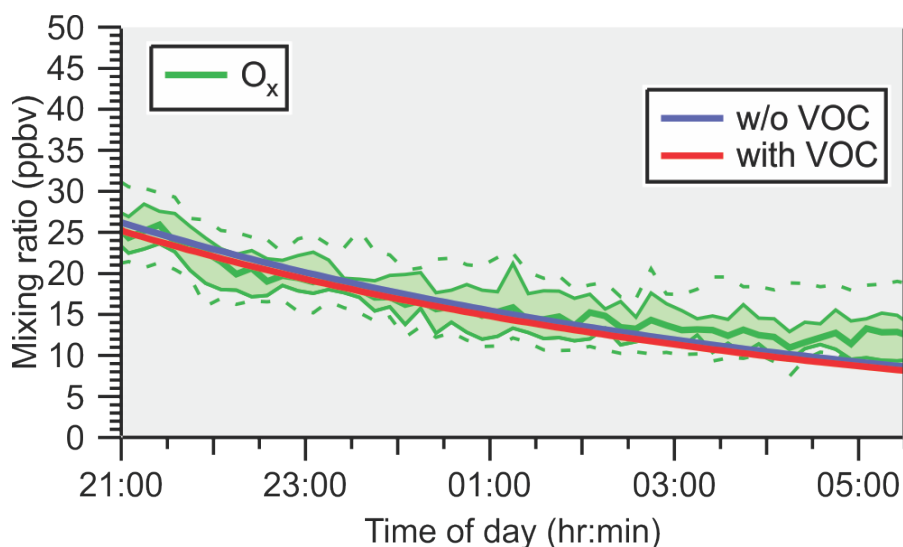
60 **Table S-2.** Reactions included in box model to estimate dry deposition velocities

Reaction	Rate constant
O ₃ → products	$k_{\text{dep}}(\text{O}_3)$
NO ₂ → products	$k_{\text{dep}}(\text{NO}_2)$
O ₃ + NO → NO ₂ + O ₂	$4.8 \times 10^{-4} \text{ ppbv}^{-1} \text{ s}^{-1}$
O ₃ + VOC → products	$1.25 \text{ ppbv}^{-1} \text{ s}^{-1}$

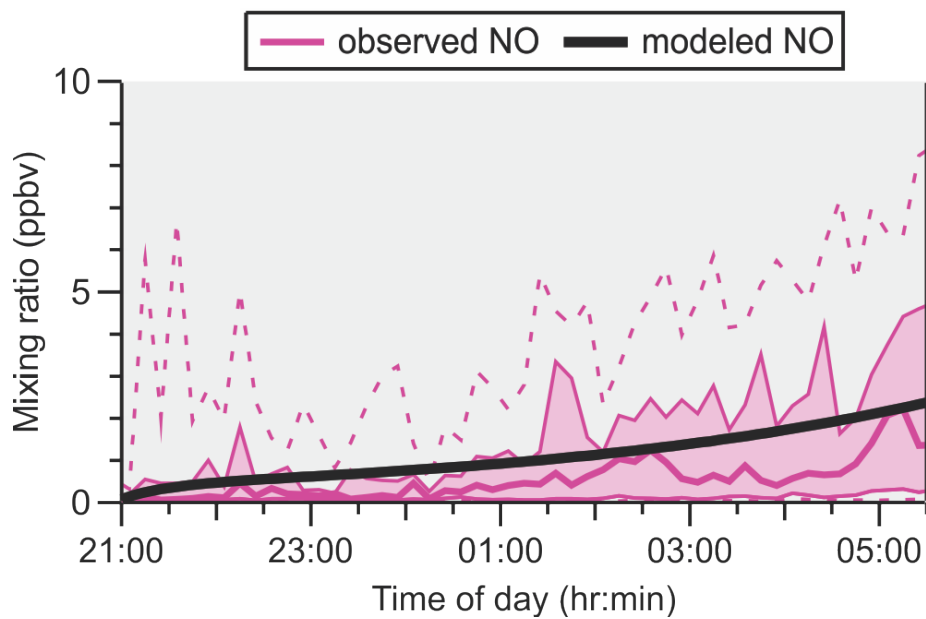
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62
 63 **Figure S-2.** Observed and simulated O_x loss in the NBL at Abbotsford assuming O_3 dry
 64 deposition rates of $2 \times 10^{-4} \text{ s}^{-1}$, $4 \times 10^{-5} \text{ s}^{-1}$, $2 \times 10^{-5} \text{ s}^{-1}$ and $1 \times 10^{-5} \text{ s}^{-1}$, corresponding to approximate
 65 mixing heights of 10 m, 50 m, 100 m, and 200 m.



67
 68 **Figure S-3.** Effect of biogenic VOC emissions on O_x . The observed and simulated O_x loss in
 69 the NBL at Abbotsford assuming an O_3 dry deposition rate of $4 \times 10^{-5} \text{ s}^{-1}$ are shown as green
 70 and blue traces, respectively. The red trace shows the effect of adding 1 ppbv of reactive
 71 biogenic VOC at sunset and continuous biogenic VOC emissions of $3 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$
 72 throughout the night.



74

75 **Figure S-4.** Comparison of observed and simulated NO mixing ratios after constant emissions
 76 of 2.9×10^{-4} ppbv s^{-1} (~ 1.05 ppbv hr^{-1}) of NO and 3×10^{-5} ppbv s^{-1} (~ 0.05 ppbv hr^{-1}) of NO₂ were
 77 added.

78

79 **Box model to determine the time necessary for NO₃ and N₂O₅ to achieve a steady state**
80 **with respect to production and loss**

81 The validity of the steady state assumption was evaluated in a similar fashion as described by
82 Brown et al. (2003) using a simple box model. Reactions and rate coefficients included in these
83 simulations are listed in Table S-3. Model simulations were carried out using a custom
84 differential equation integrator macro in the software package Igor Pro (Wavemetrics). Rate
85 coefficients were calculated for a temperature of 286 K, which is the median nocturnal
86 temperature of this study (Figure 8B). Simulations were initiated with the median nocturnal
87 NO₂ and O₃ mixing ratios of 7.5 ppbv (1.92×10¹¹ molecules cm⁻³) and of either 18 ppbv
88 (4.5×10¹¹ molecules cm⁻³) or 5.0 ppbv (1.3×10¹¹ molecules cm⁻³), respectively. The simulations
89 assume pseudo-first order N₂O₅ and NO₃ loss with frequencies of 1×10⁻³ s⁻¹ and between
90 1×10⁻² s⁻¹ and 0 s⁻¹, respectively.

91 Simulated temporal profiles of NO₃ and N₂O₅ are show in Figure S-5 (left axis) and those of O₃
92 and NO₂ on the right axis. The subpanels A, B, and C are simulations with k_{NO₃} = 0 s⁻¹, 1×10⁻³
93 s⁻¹ or 1×10⁻² s⁻¹, respectively. In each case, the rate of change of [N₂O₅] with respect to time,
94 d[N₂O₅]/dt, approaches zero after a period of ~70 min, or less, indicating the time to approach
95 steady state. The simulations also show that the amount of O₃ and NO₂ removed through
96 chemical reactions of NO₃ and N₂O₅ are ~1 ppbv and between ~1.9 and ~1.6 ppbv over a period
97 of 4 hours. These are upper limits as in this study much of the NO₃ was titrated by NO. In any
98 case, loss of O₃ through nocturnal gas-phase is predicted to be rather small compared to the
99 total O₃ loss observed (~26 ppbv over 9 hours, see section 3.1.3 and Figure 4C in the main text).
100 Brown et al. (2003) show that in these scenarios, NO₃, N₂O₅, and NO₂ remain in equilibrium
101 almost throughout; for completeness, the corresponding plot for these simulations is shown in
102 Figure S-6.

103 As shown in equation (2) of the manuscript, the steady state lifetime is approximately equal to:

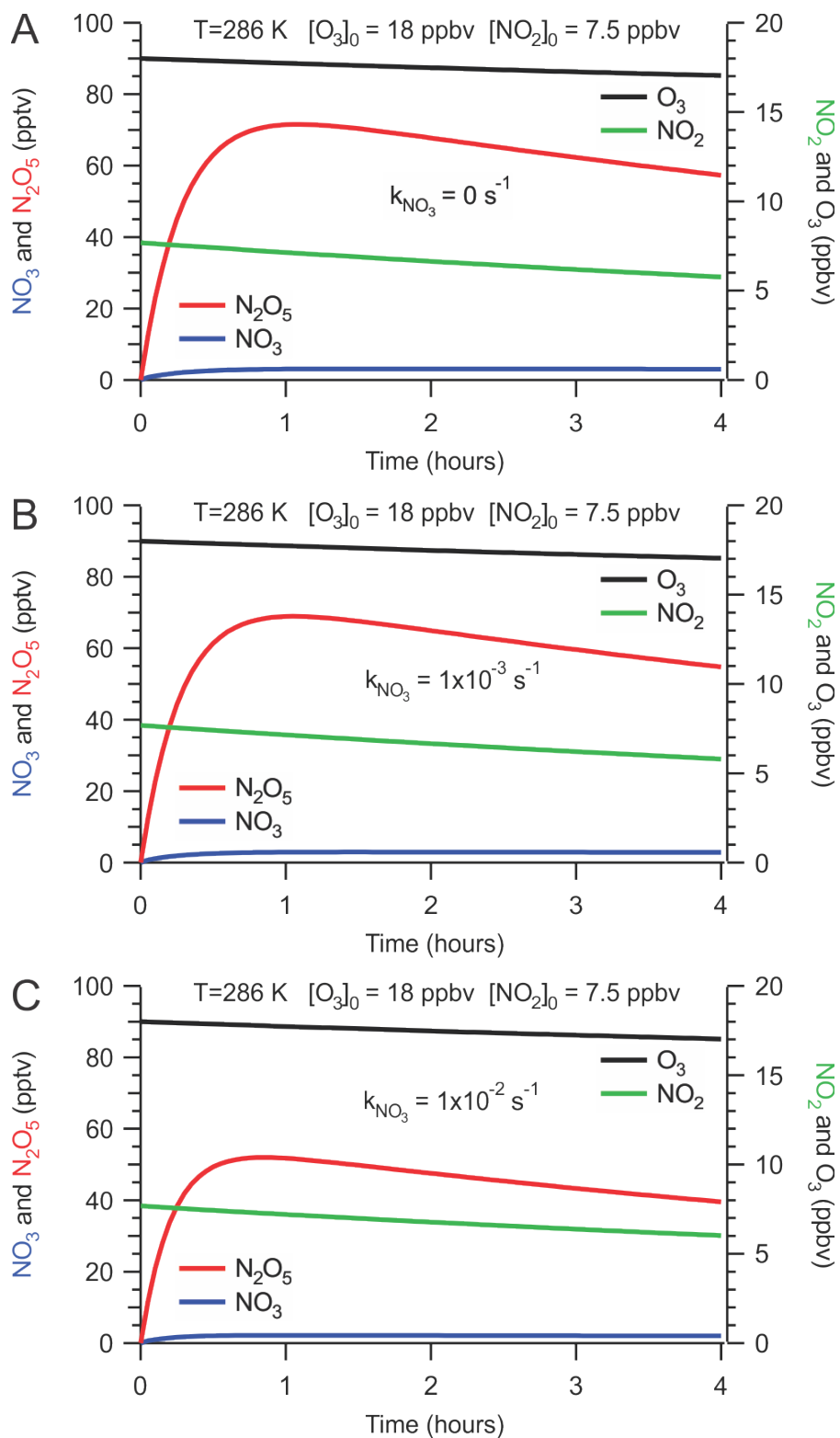
104
$$\frac{[N_2O_5]}{k_1[NO_2][O_3]} \approx \left(k_{N_2O_5} + \frac{k_{NO_3}}{K_2[NO_2]} \right)^{-1} \quad (2)$$

105 A comparison of these two expressions is shown in Figure S-7. The time when these two
106 expressions are equal is equal to the time to steady state.

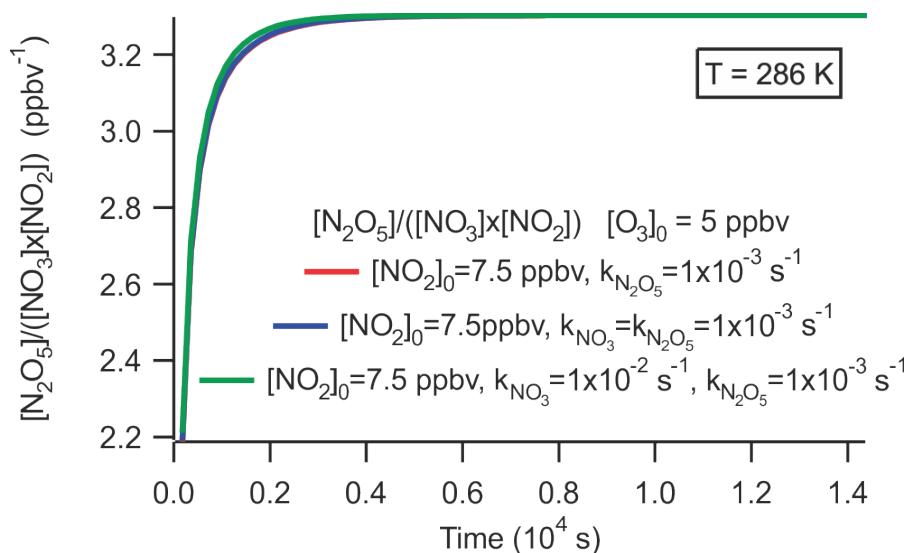
107 **Table S-3.** Reactions included in the box model to estimate the time for NO₃ and N₂O₅ to
 108 achieve steady state with respect to their production and loss
 109

#	Reaction	Rate coefficient
R1	NO ₂ + O ₃ → NO ₃ + O ₂	2.28×10 ⁻¹⁷ cm ³ molecule ⁻¹ s ⁻¹
R2 _f	NO ₃ + NO ₂ → N ₂ O ₅	1.35×10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹
R2 _r	N ₂ O ₅ → NO ₃ + NO ₂	0.00923 s ⁻¹
(R7)	NO ₃ → products	k _x = k _{NO3} = 0 s ⁻¹ , 1×10 ⁻³ s ⁻¹ or 1×10 ⁻² s ⁻¹
(R5)	N ₂ O ₅ → products	k _y = k _{N2O5} = 1×10 ⁻³ s ⁻¹

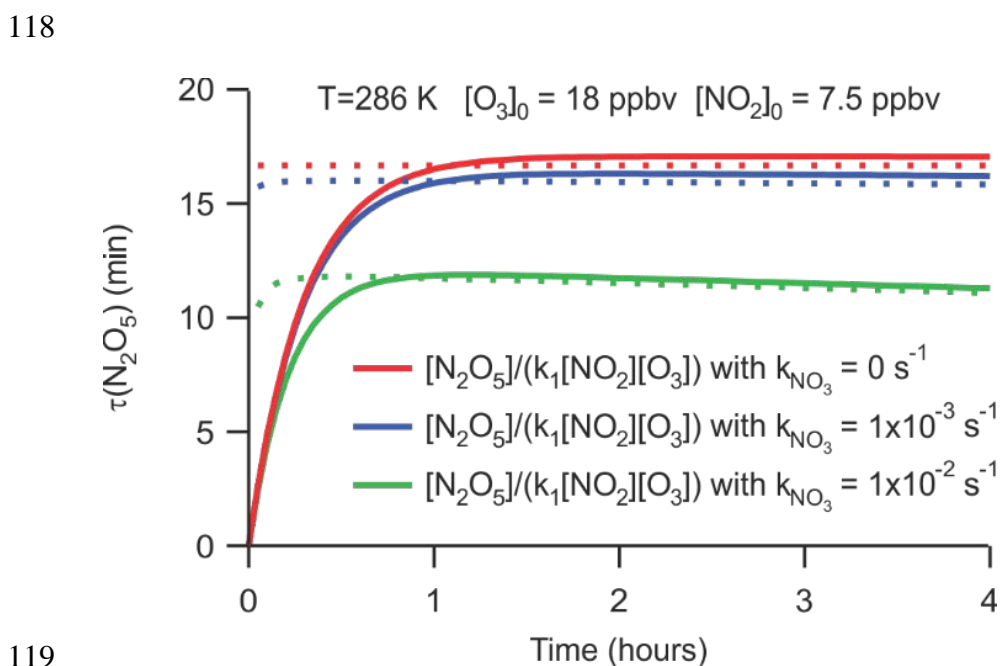
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111
 112 **Figure S-5.** Simulated temporal profiles of NO_3 and N_2O_5 (left axis) and O_3 and NO_2 (right
 113 axis). The subpanels A, B, and C are simulations with $k_{\text{NO}_3} = 0\text{ s}^{-1}$, $1 \times 10^{-3}\text{ s}^{-1}$ or $1 \times 10^{-2}\text{ s}^{-1}$,
 114 respectively.



115
 116 **Figure S-6.** Equilibrium constants for reaction (2) calculated for the three scenarios shown in
 117 Figure S-5.



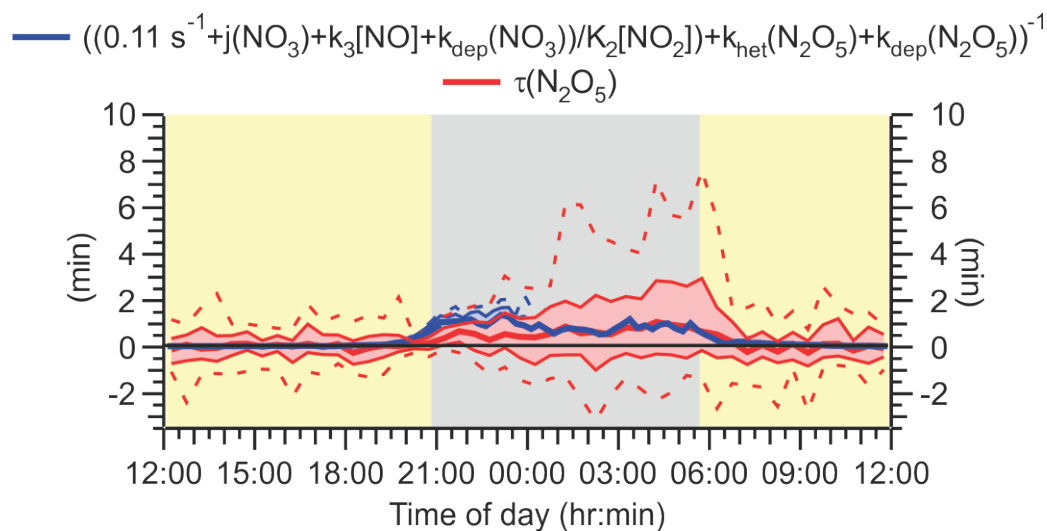
119
 120 **Figure S-7.** Comparison of $\tau(\text{N}_2\text{O}_5)$ calculated using equation (2) of the main manuscript, with
 121 the dashed lines calculated using equation (11) of Brown et al. (2003).
 122

123 **Estimates of how loss of NO₃ to VOCs would affect the lifetime of N₂O₅**

124 The steady state lifetime calculation presented in Figure 8C of the main manuscript neglects
 125 losses of NO₃ to VOCs due to poor data coverage, i.e., presents a scenario where
 126 $\Sigma k_{\text{NO}_3+\text{VOC},i}[\text{VOC}]_i$ is assumed to be zero, which is, of course, unrealistic.

127 We used all available VOC data and calculated a time series of $\Sigma k_{\text{NO}_3+\text{VOC},i}[\text{VOC}]_i$. The average
 128 ($\pm 1 \sigma$) value at night is $(0.038 \pm 0.026) \text{ s}^{-1}$. The N₂O₅ loss frequency, calculated by dividing this
 129 value with the N₂O₅:NO₃ ratio, is $(1.1 \pm 0.9) \times 10^{-5} \text{ s}^{-1}$, corresponding to a lifetime of ~2.5 hours,
 130 which is negligible.

131 However, as stated in the main manuscript, the VOC data coverage is sparse and did not include
 132 measurements of all hydrocarbons towards which NO₃ is reactive. Recently, Liebmann et al.
 133 (2018) reported an average of nocturnal NO₃ loss frequency of 0.11 s^{-1} in the boreal forest of
 134 Finland. This value likely included loss of NO₃ to NO and a variety of hydrocarbons such as
 135 sesqui- and diterpenes, which are likely present in higher concentration in a boreal forest than
 136 at Abbotsford and hence represents an upper limit Taking this value and dividing it by the
 137 N₂O₅:NO₃ ratio, the average nocturnal N₂O₅ loss frequency via NO₃-VOC reactions is
 138 calculated to $(5.6 \pm 1.3) \times 10^{-3} \text{ s}^{-1}$. Figure S-8 shows the result of including this value in the
 139 calculation of N₂O₅ lifetime.



140
 141 **Figure S-8.** Same as Figure 8c but including an assumed NO₃ loss frequency to VOCs of 0.11
 142 s⁻¹.

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