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Alkyl nitrates in the boreal forest: formation via the NO_3-, OH- and O_3-induced oxidation of biogenic volatile organic compounds and ambient lifetimes

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Table S1: Rate coefficients and branching ratios used for the calculations of $P_{\sum AN}$

VOC	$k(NO_3)$ at 298 K (molecules cm^{-3} s^{-1})	α^{NO_3}	$k(OH)$ at 298 K (molecules cm^{-3} s^{-1})	α^{RO_2}	$k(O_3)$ at 298 K (molecules cm^{-3} s^{-1})	α^{O_3}
α-pinene	6.2×10^{-12} [1]	0.15 [2,5]	5.3×10^{-11} [1]	0.18 [6]	9.6×10^{-17} [1]	0.80 [1]
β-pinene	2.5×10^{-12} [1]	0.40 [2,3]	7.6×10^{-11} [1]	0.24 [2]	1.9×10^{-17} [1]	0.30 [1]
Δ-carene	9.1×10^{-12} [1]	0.77 [3]	8.8×10^{-11} [2]	0.23 [2]	4.9×10^{-17} [1]	0.86 [1]
d-limonene	1.2×10^{-11} [1]	0.67 [2,5]	1.7×10^{-10} [1]	0.23 [2]	2.2×10^{-16} [1]	0.75 [1]
isoprene	6.5×10^{-13} [1]	0.70 [1]	1.0×10^{-10} [1]	0.07 [4]	1.28×10^{-17} [1]	1.00 [1]
unattributed	-	0.70	-	-	-	-

α^{NO3}: yield of AN in the reaction of the BVOC with NO_3 in air.

α^{RO2}: yield of AN in the reaction of the peroxy radical (formed in OH + BVOC + O_2) with NO.

α^{O3} is the yield of peroxy radicals formed in the reaction of each BVOC with O_3 in air

[1]Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J. http://iupac.pole-ether.fr/index.html., 2019.

[2]Perring, A. E., Pusede, S. E., and Cohen, R. C.: An observational perspective on the atmospheric impacts of alkyl and multifunctional nitrates on ozone and secondary organic aerosol, Chemical Reviews, 113, 5848-5870, doi:10.1021/cr300520x, 2013.

[3]Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkler, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO3 Oxidation of Biogenic Hydrocarbons, Environmental Science & Technology, 48, 11944-11953, 10.1021/es502204x, 2014.

[4]Lockwood, A. L., Shepson, P. B., Fiddler, M. N., and Alaghmand, M.: Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry, Atmos. Chem. Phys., 10, 6169-6178, https://doi.org/10.5194/acp-10-6169-2010, 2010.

[5]Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., Wirtz, K.: Reactions of NO_3 radicals with limonene and α-pinene: Product and SOA formation, Atmospheric Environment, 40, S116, https://doi.org/10.1016/j.atmosenv.2005.09.093, 2006.

[6]Nozière, B., Barnes, I., and Becker, K.-H.: Product study and mechanisms of the reactions of α-pinene and of pinonaldehyde with OH radicals, Journal of Geophysical Research: Atmospheres, 104, 23645-23656, doi:10.1029/1999JD900778, 1999.

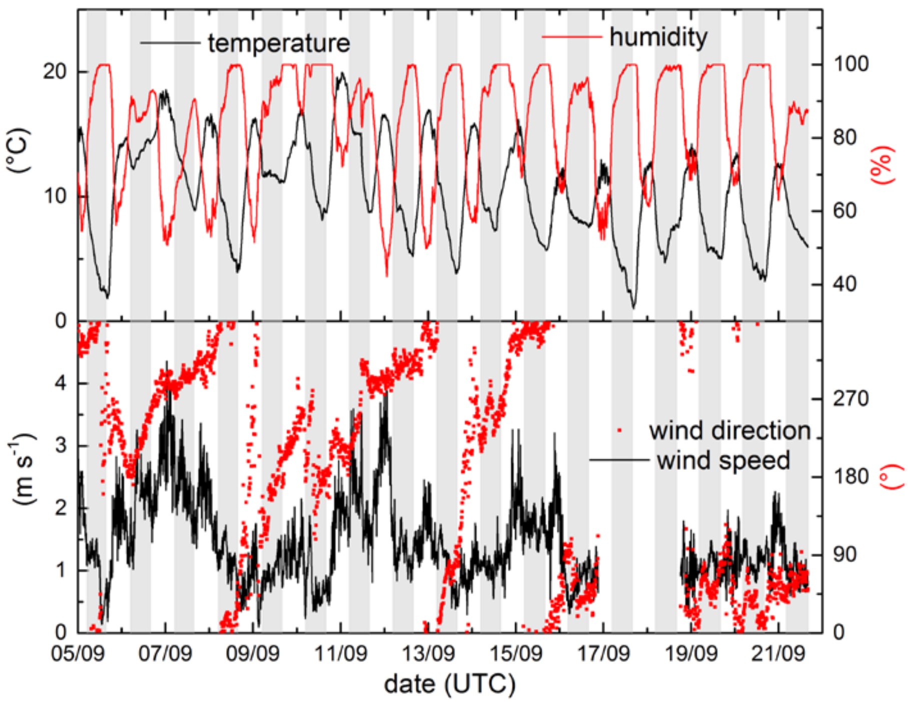

Figure S1: Overview of meteorological measurements during IBAIRN. The grey shaded regions represent night-time.

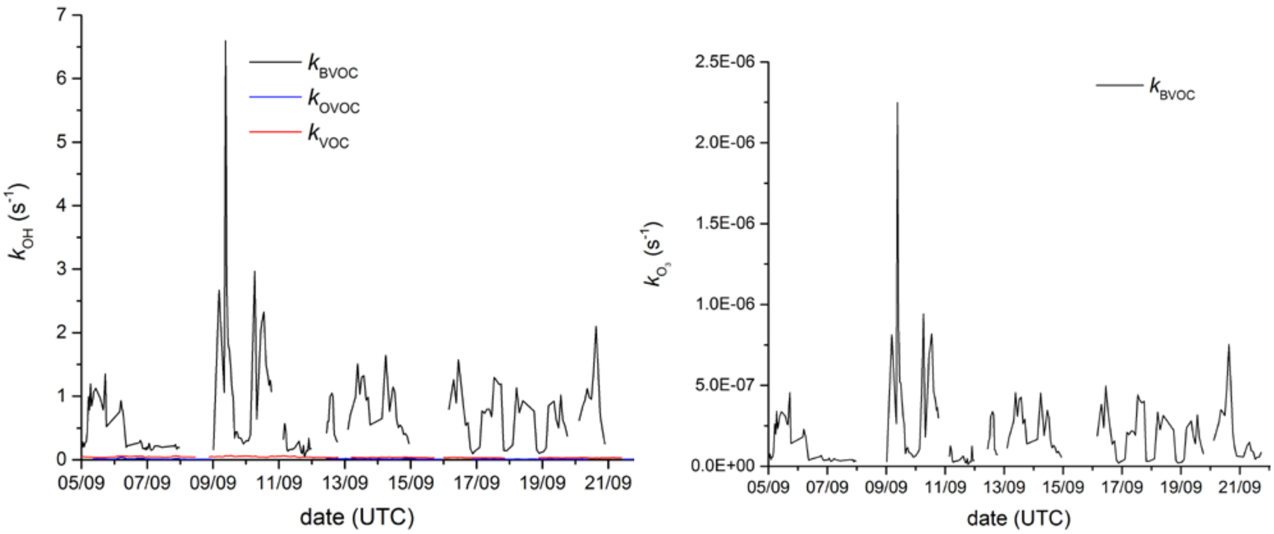

Figure S2: Calculated OH reactivity (k_{OH}) and O_3 reactivity (k_{O3}) from VOC measurements.

k_{BVOC} (biogenic VOCs) consists of α-pinene, β-pinene, Δ-carene, *d*-Limonene, isoprene, and camphene.

k_{OVOC} (oxidised VOCs) consists of propanoic acid, butanoic acid, isopentanoic acid, pentanoic acid, hexanoic acid, 1-pentanol, 1-penten-3-ol, cis-3-hexen-1-ol, 1-hexanol.

k_{VOC} (remaining VOCs) consists of benzene, toluene, p/m-xylene, styrene, o-xylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, hexane, pentanal, hexanal, methacrolein, 4-acetyl-1-methylcyclohexene, nopinone, heptanal, octanal, nonanal, decanal, ethane and propane.

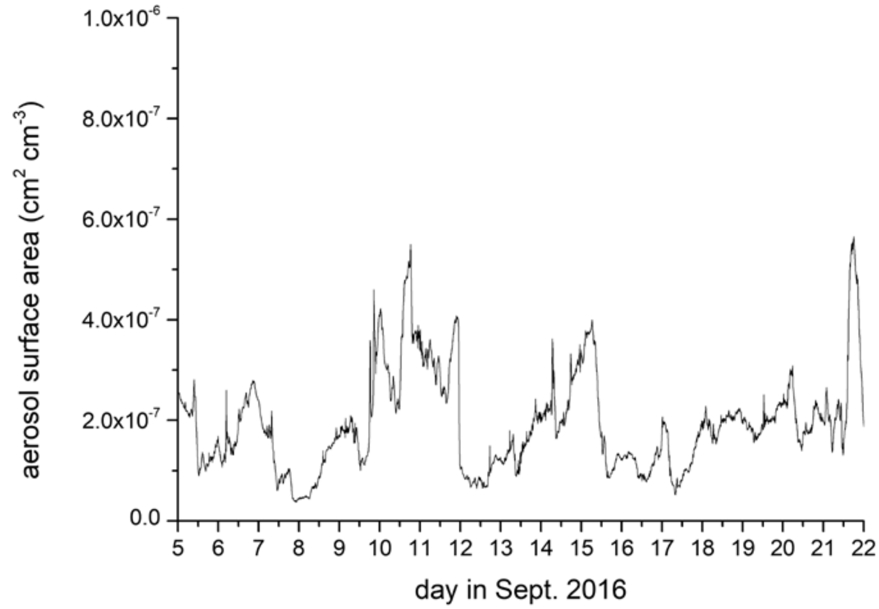

Figure S3: Aerosol surface area during IBAIRN.

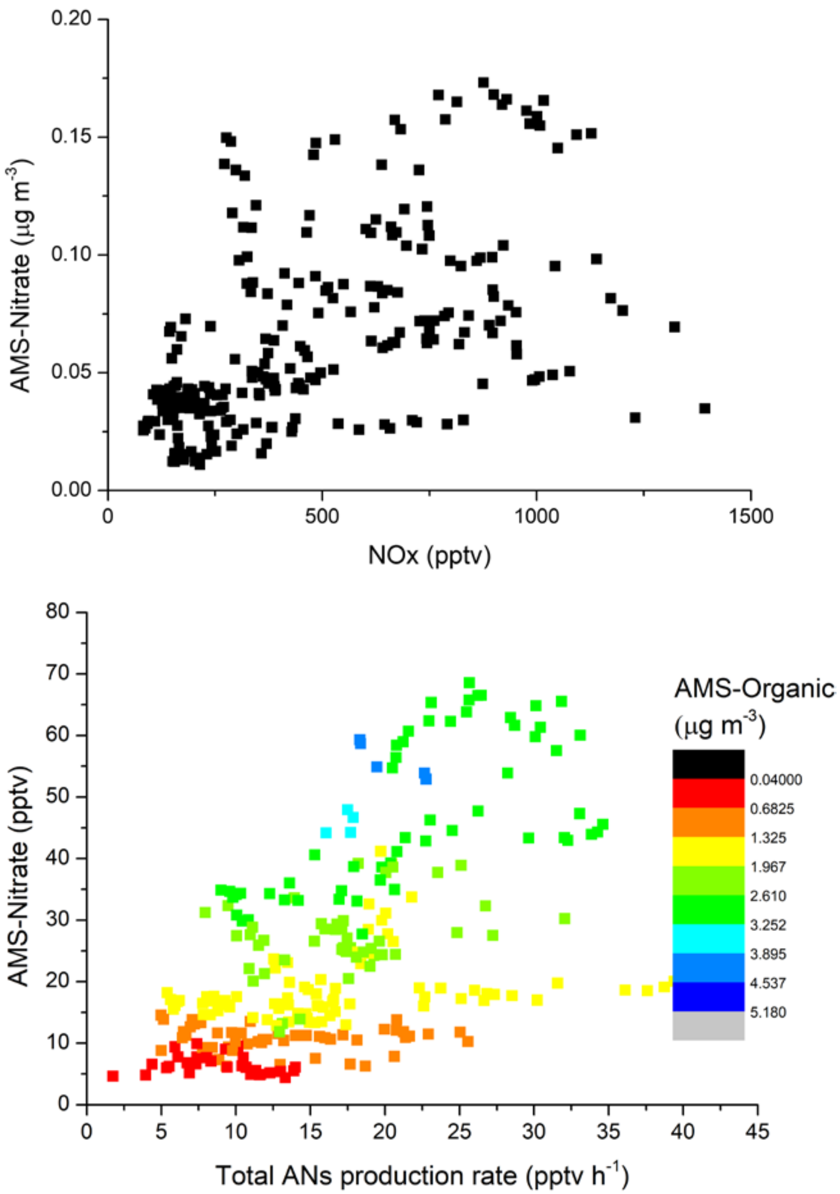

Figure S4: Upper: AMS-nitrate versus NO_X (5^{th}-22^{nd} Sept 2016).
Lower: AMS-nitrate versus the total ANs production rate colour-coded with AMS-organic mass.

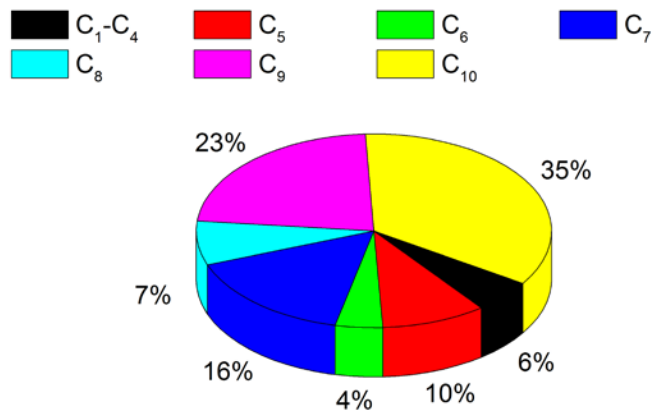

Figure S5: Campaign averaged relative contribution of the measured organic nitrates as measured by the I-CIMS (assuming equal sensitivity across the mass-range).