

Supplement of Atmos. Chem. Phys., 18, 13457–13479, 2018
<https://doi.org/10.5194/acp-18-13457-2018-supplement>
© Author(s) 2018. This work is distributed under
the Creative Commons Attribution 4.0 License.



Supplement of

Insights into HO_x and RO_x chemistry in the boreal forest via measurement of peroxyacetic acid, peroxyacetic nitric anhydride (PAN) and hydrogen peroxide

J. N. Crowley et al.

Correspondence to: John N. Crowley (john.crowley@mpic.de)

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.

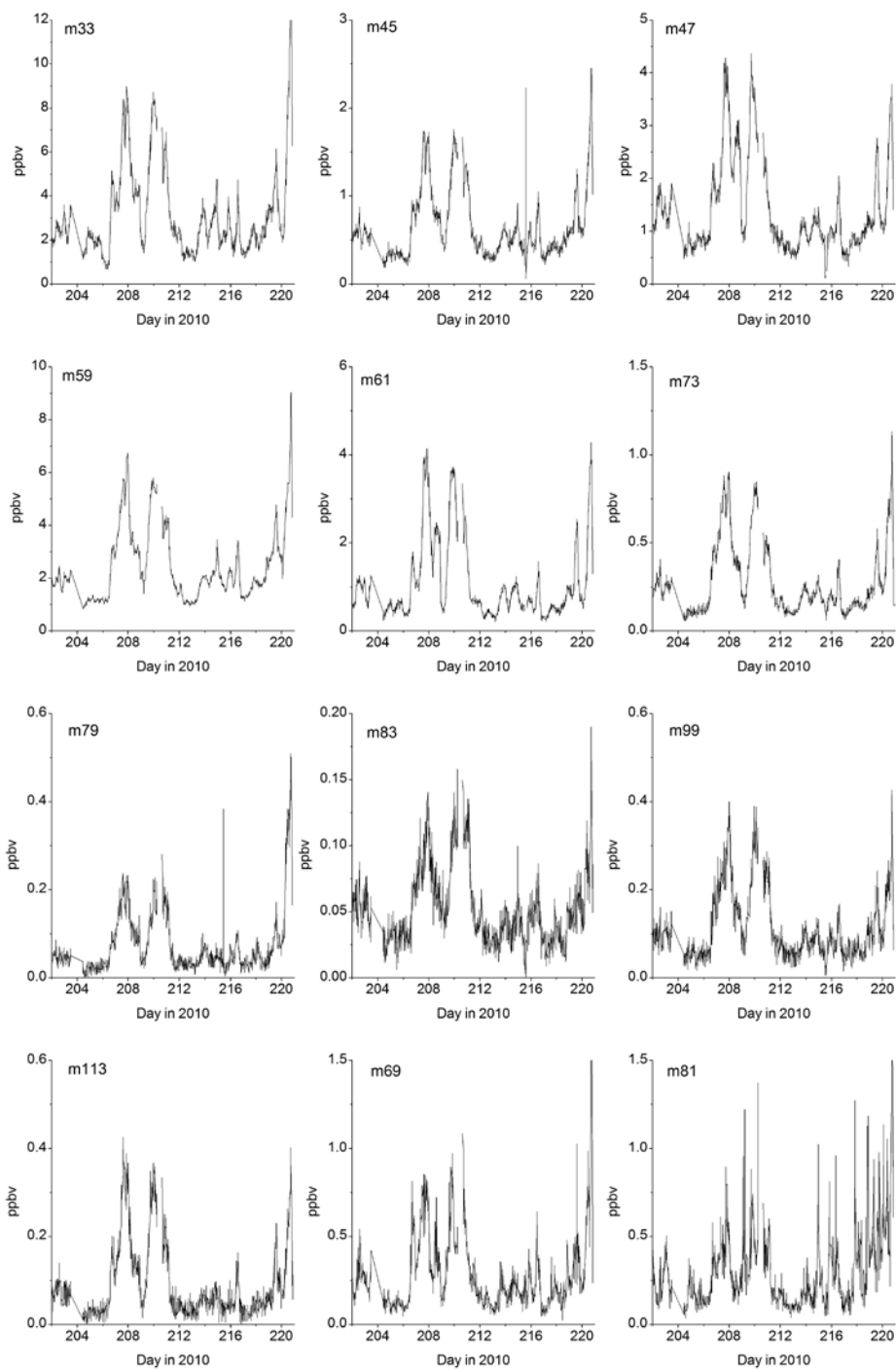


Figure S1. Selected PTRMS masses observed during the HUMPPA-COPEC campaign.

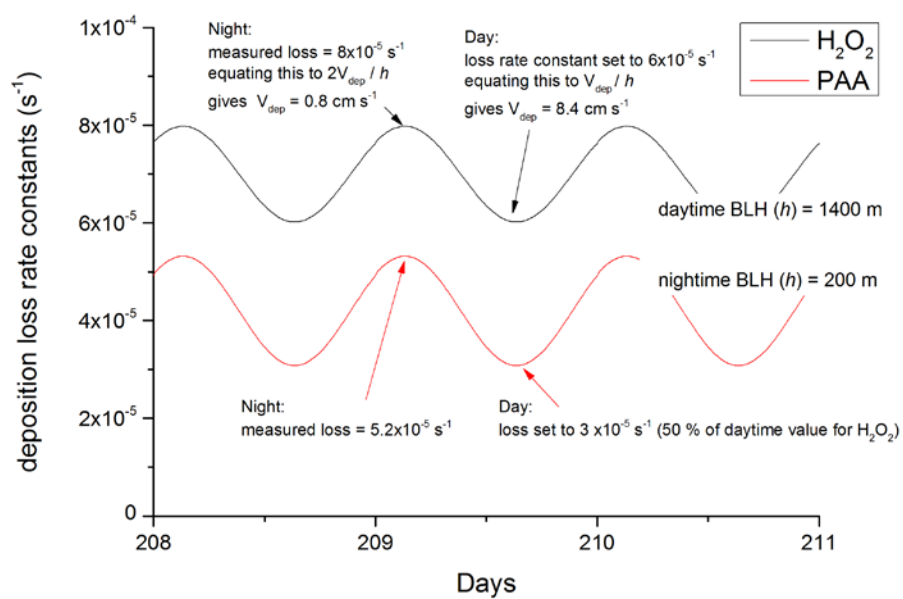


Figure S2. Campaign deposition velocities for PAA and H₂O₂.

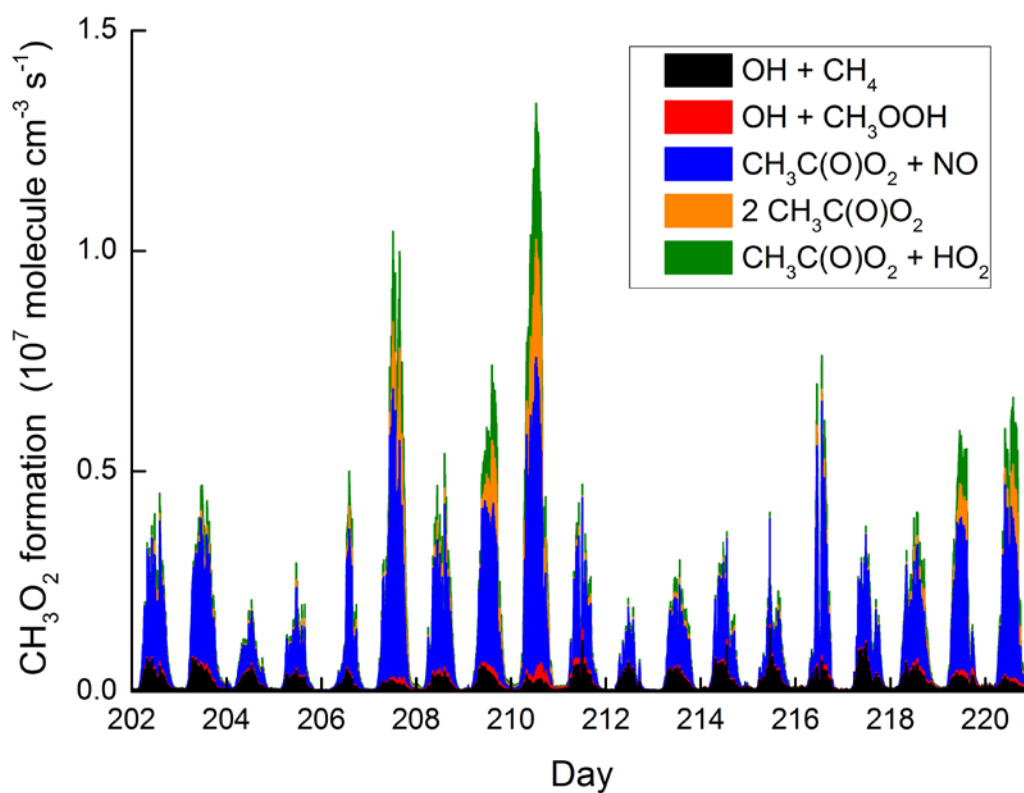


Figure S3. Modelled flux ($\text{molecule cm}^{-3} \text{ s}^{-1}$) through reactions that lead to CH_3O_2 formation.

Table S1. Reactions used in the box-model.

Reaction / Process	Rate constant ^a	Reference / comment
Formation of OH and HO₂		
O ₃ → 2 OH	J-O(¹ D)	b
HONO → OH + NO	J-NO ₂ × 0.165	
HCHO → 2 HO ₂	J-HCHO	c
HC(O)CHO + hν → 2 HO ₂	J-NO ₂ × 0.0076	
HO ₂ + NO → NO ₂ + OH	3.45×10 ⁻¹² exp(270/T)	
HO ₂ + O ₃ → OH	2.03×10 ⁻¹⁶ (T/300) ^{4.57} exp(693/T)	
O ₃ + terpenes → OH	2.0×10 ⁻¹⁶ × 0.8	
OH + CO → HO ₂	1.44×10 ⁻¹³ (1+M/4.2× 10 ¹⁹)	
OH + HCHO → HO ₂	5.4×10 ⁻¹² exp(135/T)	
OH + O ₃ → HO ₂	1.7×10 ⁻¹² exp(-940/T)	
OH + CH ₄ + O ₂ → CH ₃ O ₂	1.85×10 ⁻¹² exp(-1690/T)	
CH ₃ O ₂ + NO → HO ₂ + NO ₂ + HCHO	2.3×10 ⁻¹² exp(360/T)	
RO ₂ + NO → HO ₂	1×10 ⁻¹¹	
RO ₂ + HO ₂ → ROOH	8×10 ⁻¹²	
RO ₂ + HO ₂ → OH	2×10 ⁻¹²	
RO ₂ + RO ₂ → 2 HO ₂	1×10 ⁻¹²	
Formation of CH₃C(O)O₂ and RO₂		
OH + CH ₃ CHO → CH ₃ C(O)O ₂	4.7×10 ⁻¹² exp(345/T)	
CH ₃ C(O)CHO + hν → CH ₃ C(O)O ₂ + HO ₂	J-NO ₂ × 0.019	
CH ₃ C(O)C(O)CH ₃ + hν → 2 CH ₃ C(O)O ₂	J-NO ₂ × 0.208	
CH ₃ C(O)C(O)OH + hν → CH ₃ C(O)O ₂ + HO ₂	J-NO ₂ × 0.033	
OH + OVOC + O ₂ → RO ₂ + H ₂ O	1×10 ⁻¹¹	
OH + terpenes (O ₂) → RO ₂	7×10 ⁻¹¹	
Formation of PAN, PAA and H₂O₂		
O ₃ + terpenes → H ₂ O ₂	2.0×10 ⁻¹⁶ × 0.17	
CH ₃ C(O)O ₂ + NO ₂ → PAN	T and P dependent	
CH ₃ C(O)O ₂ + HO ₂ → PAA + O ₂	3.14×10 ⁻¹² exp(580/T) × 0.37	
CH ₃ C(O)O ₂ + HO ₂ → CH ₃ C(O)OH + O ₃	3.14×10 ⁻¹² exp(580/T) × 0.13	
CH ₃ C(O)O ₂ + HO ₂ → OH	3.14×10 ⁻¹² exp(580/T) × 0.50	
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	(T, P, H ₂ O) dependent	
Loss of PAN and PAA and H₂O₂		
OH + PAA → CH ₃ C(O)O ₂ + H ₂ O	1×10 ⁻¹¹	
PAN → CH ₃ C(O)O ₂ + NO ₂	T and P dependent	
CH ₃ C(O)O ₂ + NO → NO ₂ + CH ₃ O ₂ + CO ₂	7.5×10 ⁻¹² exp(290/T)	
H ₂ O ₂ + OH → HO ₂ + H ₂ O	2.9×10 ⁻¹² exp(-160/T)	
H ₂ O ₂ + hν → OH + OH	J-H ₂ O ₂	
Other reactions		
NO ₂ → NO + O ₃	J-NO ₂	d
NO + O ₃ → NO ₂	3.0×10 ⁻¹² exp(-1500/T)	d
OH + NO ₂ → HNO ₃	T and P dependent	
CH ₃ O ₂ + HO ₂ → CH ₃ OOH	3.8×10 ⁻¹³ exp(780/T)	
OH + CH ₃ OOH → CH ₃ O ₂ + H ₂ O	0.6×5.3×10 ⁻¹² exp(190/T)	
OH + CH ₃ OOH → HCHO + OH + H ₂ O	0.4×5.3×10 ⁻¹² exp(190/T)	
OH + ROOH → RO ₂ + H ₂ O	1.0×10 ⁻¹¹	
Night-time radical formation		
NO ₂ + O ₃ → NO ₃ + O ₂	1.4×10 ⁻¹³ exp(-2470/T)	
NO ₃ + NO → 2 NO ₂	2.07×10 ⁻¹² exp(-1400/T)	
NO ₃ + hν → NO ₂ + O	J-NO ₂ × 20.8	
NO ₃ + hν → NO + O ₂	J-NO ₂ × 2.55	
NO ₂ + NO ₃ + M → N ₂ O ₅ + M	T and P dependent	

$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	T and P dependent	
$\text{NO}_3 + \text{terpenes} \rightarrow \text{products}$	1×10^{-11}	
$\text{CH}_3\text{C(O)O}_2 + \text{CH}_3\text{C(O)O}_2 \rightarrow 2 \text{CH}_3\text{O}_2$	$2.9 \times 10^{-12} \exp(500/T)$	
$\text{CH}_3\text{C(O)O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{O}_2 + \text{HCHO} + \text{CO}_2$	$0.9 \times 2.0 \times 10^{-12} \exp(500/T)$	
$\text{CH}_3\text{C(O)O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{C(O)OH} + \text{HCHO}$	$0.1 \times 2.0 \times 10^{-12} \exp(500/T)$	

^a Rate coefficient taken from the IUPAC evaluation. ^bJ-O(¹D) was modified using water vapour concentrations to take into account relative rates of quenching of O(¹D) by air and reaction with H₂O to form 2 OH. ^cRadical channel only (forming H + CHO) ^dAs NO, O₃ and NO₂ are all constrained, this reaction has no effect in the model. Parameters constrained by observations were the temperature and pressure as well as mixing ratios of O₃, NO, NO₂, HONO, CO, HCHO, CH₃CHO, terpenes, CH₄ (set to 1.86 ppmv) and dicarbonyls (proportional to HCHO and CH₃CHO). J-values for O₃, HCHO, NO₃, H₂O₂, and the di-carbonyls were based on filter-radiometer measurements.

Box-Model Development

In the following, we describe the stepwise development of the model chemistry (Model 1 to Model 3) and input parameters required to reach the goal of modelling both PAA and H₂O₂. Different simulations within each model are given, for example as M1-S2 (Model 1, Simulation 2). The table below summarises radical production in each model, detailed text concerning each model run is given below.

Table S2. Summary of Models and Simulations

Model	Radical generation and loss	PAA *	H ₂ O ₂ *	HO ₂ ^{*a}	OH *	ROOH *
M1S1	OH reacts only with trace gases constrained by measurement. HO₂ : HCHO + <i>hν</i> , OH + CO, OH + HCHO, OH + H ₂ O ₂ OH : O ₃ + <i>hν</i> , H ₂ O ₂ + <i>hν</i> , HO ₂ + NO, CH ₃ C(O)O ₂ + HO ₂ , terpenes + O ₃ CH₃C(O)O₂ : PAN, OH + CH ₃ CHO, OH + PAA NO₃ : formation in NO ₃ + O ₃ and loss by photolysis, reaction with NO, HO ₂ and terpenes.	0.20	0.62	0.44	3.4	0.32
M2S1	OH loss rate enhanced OH + OVOC → RO ₂ RO ₂ + NO → HO ₂	0.19	0.47	0.30	0.75	0.25
M2S2	HO _x recycling (RO ₂ + HO ₂ → OH)	0.22	0.61	0.36	0.99	0.30
M3S1	CH₃C(O)O₂ production increased PAN decomposition rate coefficient increased by factor 5	1.37	0.74	0.43	0.94	2.23
M3S2	CH₃C(O)O₂ production rate increased: CH ₃ C(O)O ₂ from OH + VOC	0.26	0.42	0.30	0.65	0.35
M3S3	CH₃C(O)O₂ and HO₂ from di-carbonyls CH ₃ C(O)CHO + <i>hν</i> → CH ₃ C(O)O ₂ + HO ₂ BIAC + <i>hν</i> → 2 CH ₃ C(O)O ₂ HC(O)CHO + <i>hν</i> → 2 HO ₂ CH ₃ C(O)C(O)OH + <i>hν</i> → CH ₃ C(O)O ₂ + HO ₂	0.86	1.03	0.49	1.11	1.25

The box-model was constrained by measurements of temperature, O₃, HCHO, CO, NO₂, PAN, CH₃CHO and J-values. PAA, and H₂O₂ as well as HO_x were formed photochemically. *Slope of least-squares, linear fit to modelled versus measured mixing ratios. ^aThe HO₂ measurements (LIF-HO₂) were heavily biased by detection of RO₂ as described in the manuscript.

M1-S1

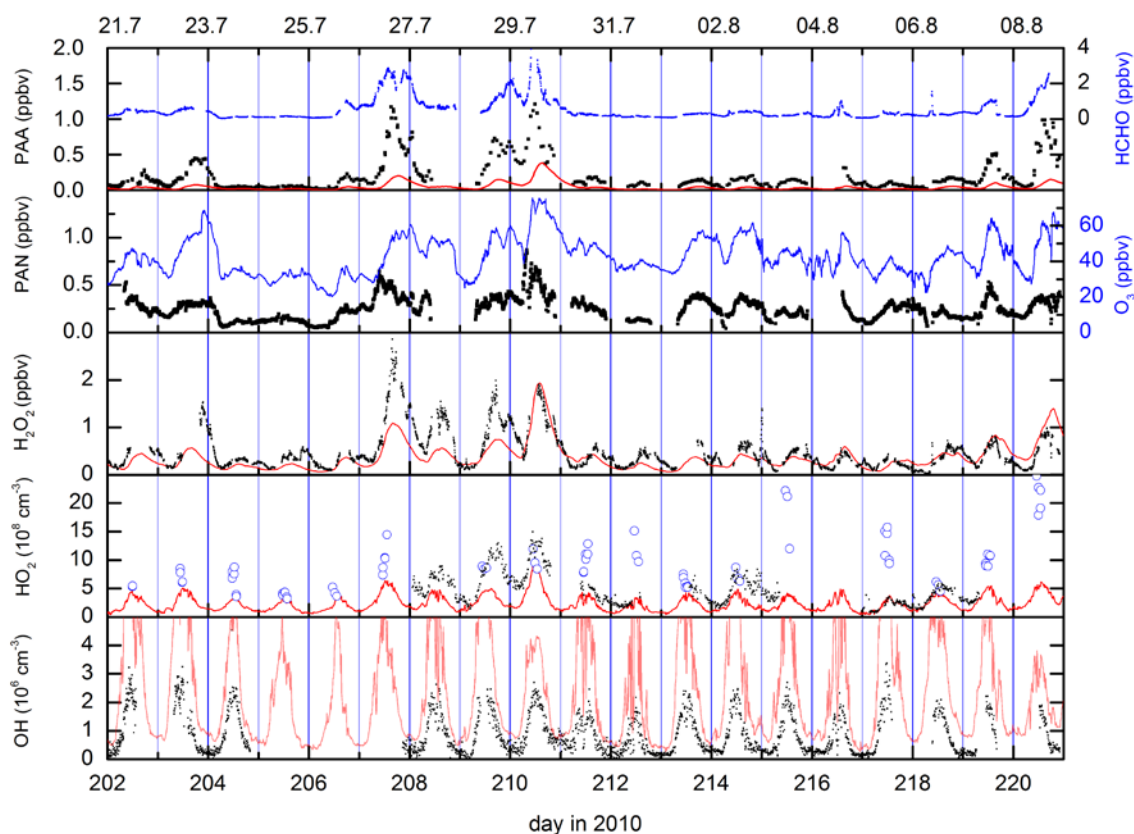
In M1-S1, OH production was limited to the photolysis of O₃, HONO and H₂O₂ and the reactions of HO₂ with NO, O₃ and CH₃C(O)O₂. HO₂ formation was via photolysis of HCHO and the reactions of OH with CO, HCHO, and H₂O₂ as well as via the reaction of CH₃O (from methane degradation) with O₂. CH₃C(O)O₂ was formed from PAN decomposition and in the reactions of OH with CH₃CHO and PAA.

In accord with the observations, the model predicts enhanced PAA and H₂O₂ mixing ratios in the periods impacted by biomass burning, which is related to the increased rate of production of HO₂ (via HCHO photolysis) and CH₃C(O)O₂ (via higher levels of CH₃CHO and PAN).

M1-S1 under-predicts PAA on average by a factor of ≈ 5 over the whole campaign. Similarly H₂O₂ is also significantly under-predicted, (on average by a factor of 1.7) though, as for PAA its day-to-day and diel variability are captured reasonably well.

The results of the model calculations are summarised in Table 1. During the campaign, OH was measured (by LIF-FAGE) just above canopy height and at the same height as the PAA/PAN inlets and also at ground level by CIMS). Only the CIMS data set was continuous throughout the campaign as the LIF-FAGE instrument was moved from the ground to the tower following an inter-comparison with the CIMS. Details of the OH measurements are given in Hens et al. (2014) who also show that the higher levels of OH above the canopy are related to a higher actinic flux. On average, the ratio of J-O(¹D) above and below the canopy was ≈ 1.9 . From Hens et al. (2014), the incremental change in OH (in molecule cm⁻³) per change in J-O(¹D) (in s⁻¹) is roughly given by 1.5×10^{11} OH cm⁻³ s. The difference in measured j-O(¹D) above and below the canopy was then used to correct each data-point from the ground-based dataset. The campaign average ratio of OH above to below canopy was 1.55.

Clearly, in M1-S1, the modelled OH concentration, with maximum daytime values as large as 1×10^7 molecule cm^{-3} is significantly larger than observed. The overestimation of OH (on average by a factor of 3.4) and the underestimation of HO_2 (and H_2O_2) are due to reactions that convert OH to HO_2 which are not accounted for in M1-S1. Indeed, the model loss rate of OH, obtained by summing over all loss reactions included varies from about 1 to 4 s^{-1} , with a campaign average of $1.3 \pm 0.5 \text{ s}^{-1}$, which is much lower than the observed average value of \approx

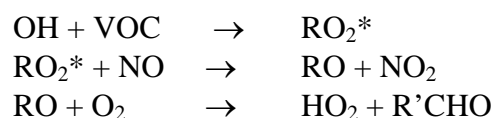


Simulations (in red) from MIS1

12 s^{-1} with a peak reactivity of $> 50 \text{ s}^{-1}$, mainly due to reaction with organic trace gases. The difference between model and observation in M1-S1 is expected as the only reactions of OH with organics taken into account are with terpenes, PAA, CH_4 and CH_3CHO .

M2-S1,2

The deviation between modelled and observed OH reactivity was addressed in M2-S1 by adding a generic reaction of OH with oxidised volatile organic trace gases (OVOC) leading to peroxy radicals (RO_2^* other than CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$) which are treated explicitly) and the subsequent formation of HO_2 via their reaction with NO and formation of alkoxy radicals (RO):

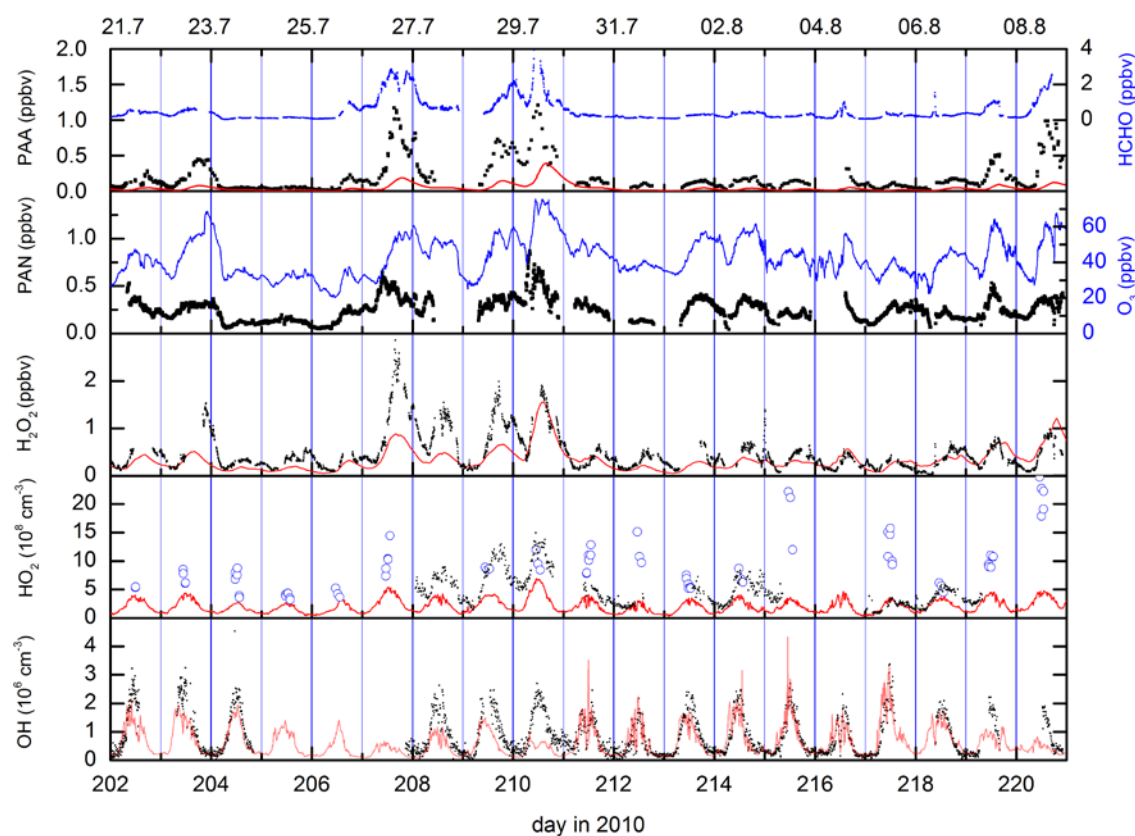


In order to account for the observation that the periods of highest OH reactivity were associated with the biomass burning influenced periods, the modelled concentration of OVOC was tied to that of HCHO and CH₃CHO. Use of any other short-lived, oxidised organic from the PTRMS dataset would provide a similar variation in OH reactivity (and thus peroxy radical production rates) during the campaign. This is intuitive, as OH reactivity should be correlated with the production of HCHO, an end organic product of the photochemical degradation of many biogenic and anthropogenic trace gases.

Model RO₂* also reacted with HO₂ to form generic, organic peroxides, ROOH.



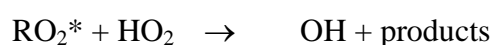
In order to simulate the diel variation of the measured OH loss rates, the concentration of OVOC was set to ~30 times the HCHO or CH₃CHO concentrations with the rate constant for reaction with OH with VOC set to 1×10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The choice of rate coefficient and relative concentration is arbitrary, i.e. a factor 5 lower relative concentration combined with a factor five higher rate coefficient gives the same result.



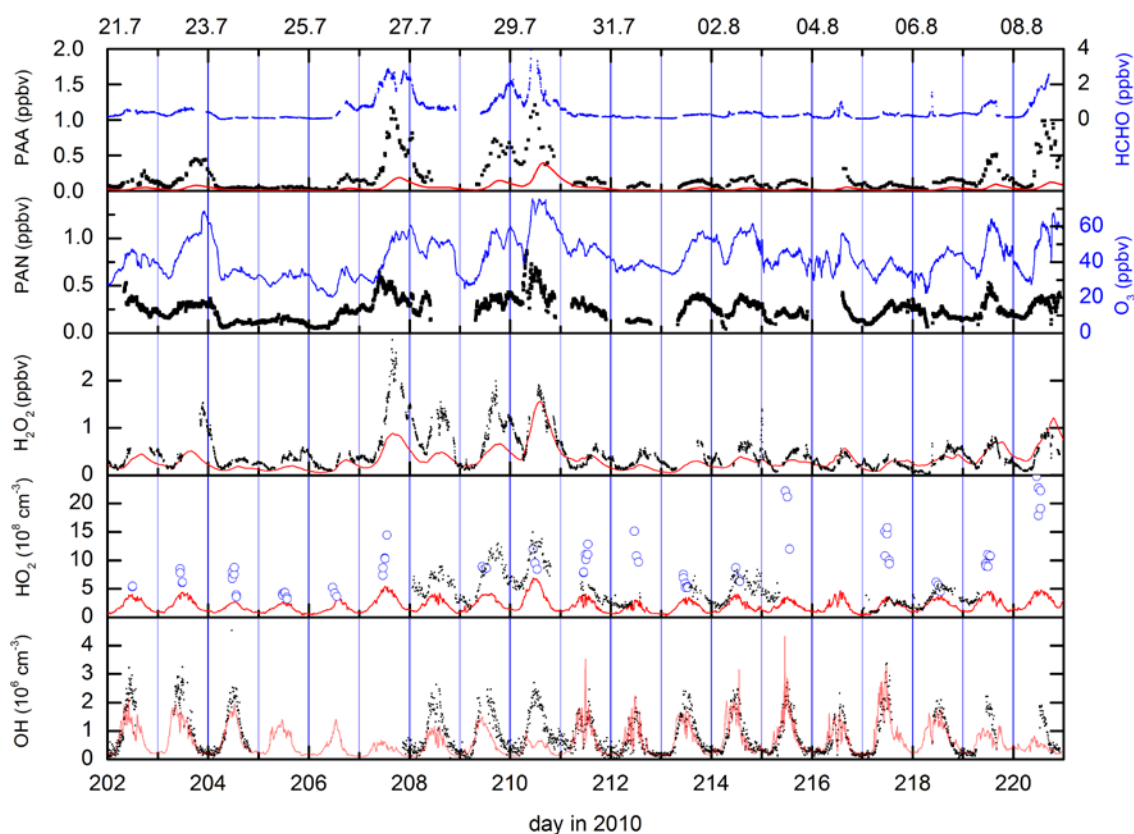
Simulations (in red) from M2S1

This simulation, fails to reproduce the measured PAA, which is underestimated, on average, by a factor ~ 5 . H_2O_2 is also underestimated, though by a smaller amount (on average by a factor ≈ 2). The model underestimates OH slightly (on average by a factor 1.3) but by a factor 2-3 during the biomass-burning influenced episodes. Modelled HO_2 , is on average a factor three too low. The model shortcomings are seen most clearly in the biomass-burning episodes, during which the elevated levels of HOx and both PAA and H_2O_2 are not reproduced.

As both organic radicals and HO_2 are removed in their mutual reaction (to make ROOH), this reaction was modified (in M2-S2) to force complete radical recycling by generating only OH.



Whilst, this is known to take place with $\sim 50\text{-}60\%$ efficiency (see above) in the reaction of acetyl peroxy with HO_2 , and possibly in reactions of isoprene peroxy radicals with HO_2 , in many reactions of organic peroxy radicals with HO_2 , the peroxide product dominates (Dillon 2008) so that this represents an upper limit to recycling via this mechanism.



Simulations (in red) from M2S2

Incorporating this reaction in M2-S2 enhanced HO_x levels only slightly, suggesting that recycling of HO₂ via reaction with NO is in any case dominant. For subsequent model runs, the OH yield from RO₂* + HO₂ was set at 20 %. (i.e. in M3 simulations as discussed below). The disagreement between modelled and measured H₂O₂ and PAA can have several sources including inaccuracy in the PAA or H₂O₂ measurement, a missing production term for the HO₂ and CH₃C(O)O₂ radicals or an overestimation of the deposition velocities. The uncertainty associated with the measurement is estimated at ≈ 30 % (Phillips et al., 2013), which cannot explain the much larger model underestimation. Whilst reduction of the H₂O₂ and PAA deposition velocity has the desired effect of increasing their modelled maximum concentrations it also broadens the diel cycle and modelled H₂O₂ and PAA no longer return to low values at night-time as observed. We therefore turn to extra chemical sources of radicals to explain the high levels of H₂O₂ and PAA observed compared to the model.

So far, CH₃C(O)O₂ production is considered to be via PAN decomposition and reaction of OH with CH₃CHO only. An increase in the PAN decomposition rate would help to increase the concentration of CH₃C(O)O₂ and thus, for a given HO₂ level, the PAA formation rate.

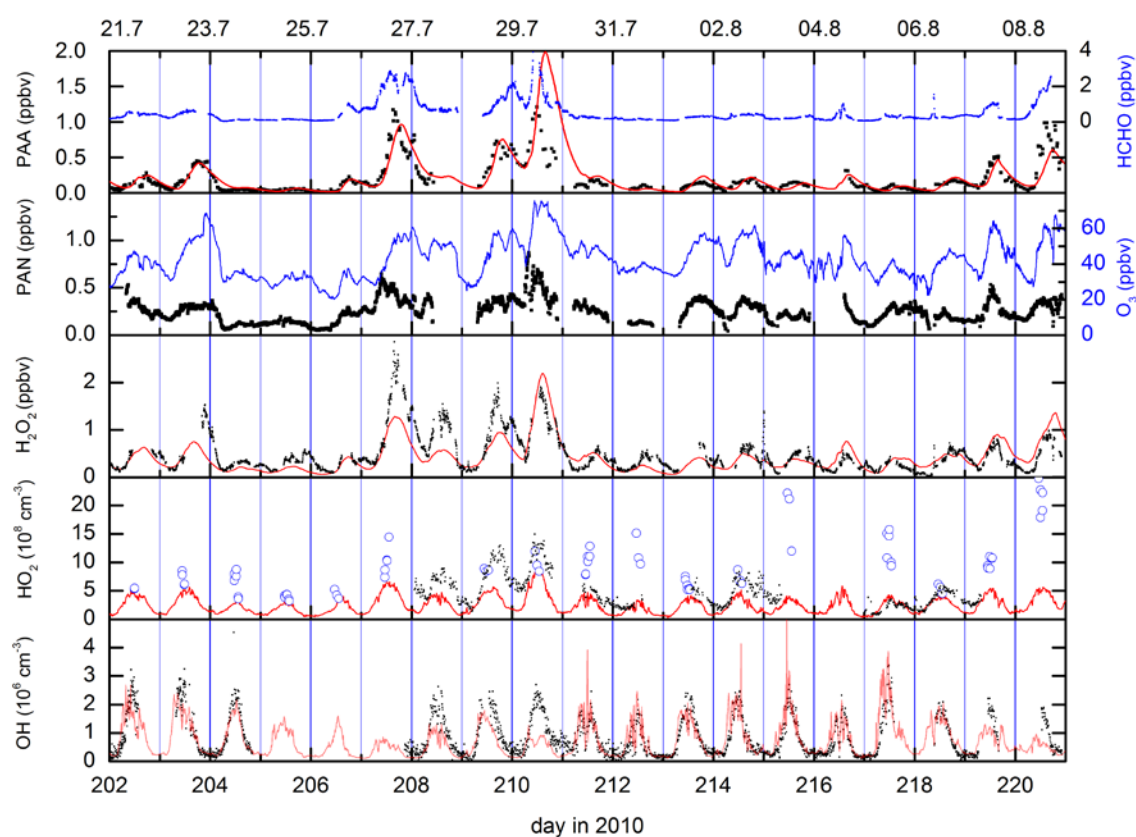
M3-S1,2,3

Scenarios in which rates of CH₃C(O)O₂ formation were enhanced were tested in M3. Model CH₃C(O)O₂ formation can be enhanced by increasing the rate coefficient for PAN decomposition compared to that preferred by the IUPAC and NASA data evaluation panels. In M3-S1, a factor of 5 increase in this parameter was found to result in improved agreement between modelled and measured PAA (slope of 1.37). It also has the desired effect of increasing HO₂ and thus H₂O₂ toward the measured values (slope of 0.74), which stems from reactions of CH₃C(O)O₂ with HO₂ and NO forming OH and CH₃O₂, both of which result in enhanced HO_x production rates. A factor 5 in the PAN decomposition rate constant is however unreasonably large as this parameter is expected to be well determined for the mid-latitude boundary temperatures where most laboratory experimental work on PAN has been conducted. Likewise, increasing the PAN concentration in the model would increase CH₃C(O)O₂ production rates, yet the factor required (three-to-five) lie beyond the reported experimental uncertainty for the PAN measurement.

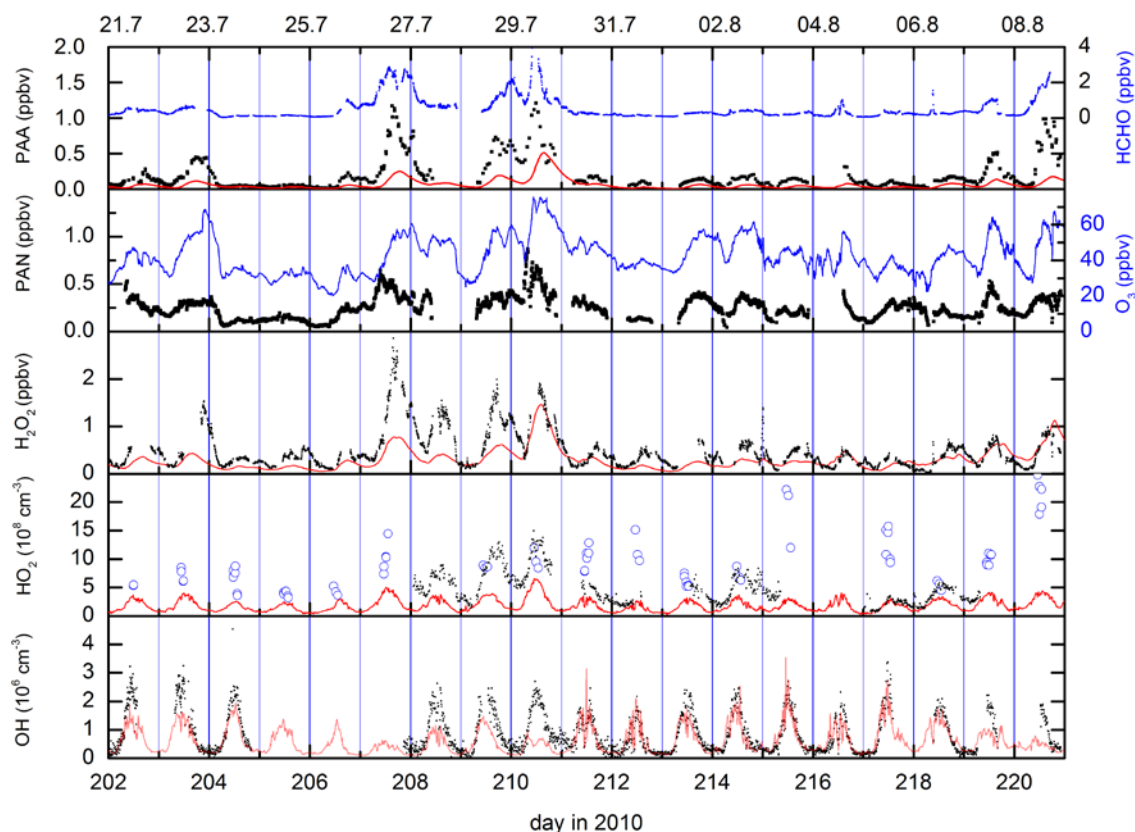
We also simulated (M3-S2) an extra source of CH₃C(O)O₂ by adding a fractional production (30 %) of CH₃C(O)O₂ formation in the reaction of OH with VOC. Even small increases (less than factor of two) in the modelled concentration of PAA could only be achieved at the cost

of lowering the OH, HO₂ and thus H₂O₂ concentrations significantly, which increases the model-measurement discrepancy.

This is readily understood as PAA is an effective sink of HO_x for this low NO_x environment. A further option to increase the PAA production rate is to introduce a CH₃C(O)O₂ production term that does not require initiation by reaction with OH, i.e. photolysis of a precursor trace gas, essentially an oxidised organic which results in CH₃CO release. This is described in detail in the main manuscript.



Simulations (in red) from M3S1



Simulations (in red) from M3S2

References

Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nolscher, A. C., Oswald, R., Paasonen, P., Petaja, T., Regelin, E., Sander, R., Sinha, V., Sipila, M., Taraborrelli, D., Ernest, C. T., Williams, J., Lelieveld, J., and Harder, H.: Observation and modelling of HOx radicals in a boreal forest, *Atmos. Chem. Phys.*, 14, 8723-8747, doi:10.5194/acp-14-8723-2014, 2014.

Phillips, G. J., Pouvesle, N., Thieser, J., Schuster, G., Axinte, R., Fischer, H., Williams, J., Lelieveld, J., and Crowley, J. N.: Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) measurements by iodide chemical ionisation mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes, *Atmos. Chem. Phys.*, 13, 1129-1139, doi:doi:10.5194/acp-13-1129-2013, 2013.