

## Supplementary Information

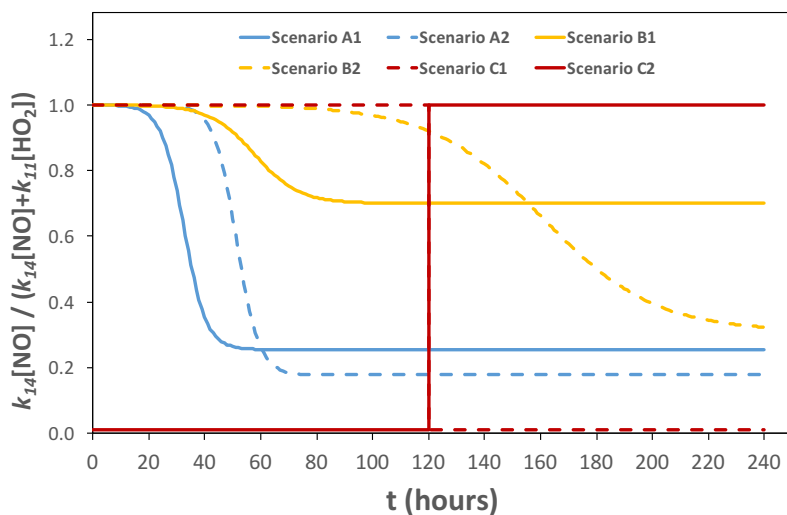
### Assumption of $\gamma$ as constant value

Changes to the ratio  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  at different times along the air mass trajectory will affect  $d[\text{RONO}_2]/dt$  at that time differently because  $d[\text{RONO}_2]/dt$  is also driven by  $[\text{RH}]$  which is a function of time. Hence the assumption of the mean value for this ratio,  $\gamma$ , being a constant is not mathematically valid. However, the errors introduced by the assumption of  $\gamma$  as a constant on  $[\text{RONO}_2]/[\text{RH}]$  calculated at time = 10 days, are on the order of 5 % (Table S1), while the observed changes in  $[\text{RONO}_2]/[\text{RH}]$  in the fire are considerably larger, on the order of a factor of 3 – 5. Hence we consider the assumption of  $\gamma$  as a constant to be a reasonable assumption for the sake of making the problem tractable, and that the changes to  $\gamma$  or  $[\text{OH}]_t$  that we calculate in the paper are not an artefact of this assumption.

Using Equation E3 and allowing the ratio  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  to vary with time we can examine the magnitude of changes to [2-butyl nitrate]/[n-butane] in pairs of scenarios where  $\gamma$  (i.e. the mean  $(k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2]))$ ) is the same for each pair but the time evolution of the ratio  $(k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2]))$  is different. Figure S1 illustrates how the ratio  $(k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2]))$  varies over the 10 days for each of six hypothetical scenarios: A1, A2, B1, B2, C1, and C2.  $\gamma$  is the same for both A scenarios and likewise for both B scenarios and both C scenarios. The time evolution of  $[\text{RH}]$  is calculated as  $[\text{RH}]_t = [\text{RH}]_0 e^{-k[\text{OH}]_t}$ , and  $[\text{NO}]$  as  $[\text{NO}]_t = [\text{NO}]_0 e^{-t/\tau} + [\text{NO}]_{\text{bg}}$ , where  $\tau$  is the NOx lifetime (assumed to be 4 hours (e.g. Liu et al., 2016, ACP)) and  $[\text{NO}]_{\text{bg}}$  is the assumed  $[\text{NO}]$  in the background atmosphere, and  $[\text{NO}]_0 = 2.5 \times 10^{11} \text{ cm}^{-3}$ .

The results are presented in Table S1 where we show the percentage difference in  $[\text{RONO}_2]/[\text{RH}]$  at time  $t = 10$  days for each pair of scenarios A, B and C. Scenarios A and B represent ‘realistic’ scenarios, in that the  $(k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2]))$  at time  $t = 0$  is  $\sim 1$  and falls to some sort of background value during transport away from an NO source region. This is what can be expected in reality since RH sources are generally co-located with NOx sources (i.e. emissions from motor vehicles) and hence NO concentrations are high close to the RH source. Scenario C represents an extreme scenario, but unlikely case, in which  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  is 0 for the first half of the transport time and 1 for the second half, or, 1 for the first half of the transport time and 0 for the second half. I.e.  $\gamma = 0.5$  in both cases. Such a scenario is purely hypothetical and serves only to demonstrate the upper range of uncertainty that could arise from the assumption of an average  $(k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2]))$ . We also consider the results using a range of  $[\text{OH}]$  in Table S1.

The results in Table S1 show that even though the time evolution of the ratio  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  varies, if the average value, i.e.  $\gamma$ , is the same, there is only a small percentage difference between the resulting values for  $[\text{RONO}_2]/[\text{RH}]$ . The differences increase with increasing assumed  $[\text{OH}]$ , but even for the largest value of  $[\text{OH}]$  for Scenarios A and B the greatest difference in  $[\text{RONO}_2]/[\text{RH}]$  at time  $t = 10$  days is  $< 6\%$ . For the extreme Scenario C, the difference is up to 35%. However, it is noted that the scenario, in which  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  is 0 for the first half of transport and 1 for the second half must be considered extremely unlikely.



**Figure S1** Six hypothetical scenarios with different time evolution of the  $k_{14}[\text{NO}]/(k_{14}[\text{NO}]+k_{11}[\text{HO}_2])$  ratio but where  $\gamma$  is the same for both A scenarios and likewise the same for both B and C scenarios.

**Table S1** Percentage difference in  $[\text{RONO}_2]/[\text{RH}]$  after 10 days between the scenarios within each pair shown in Figure S1 for  $[\text{OH}] = 2, 4, 6$  and  $12 \times 10^5 \text{ cm}^{-3}$ .  $[\text{RONO}_2]/[\text{RH}]$  calculated using Equation E3.  $[\text{RH}]$  calculated as  $[\text{RH}]_t = [\text{RH}]_0 e^{-k[\text{OH}]t}$ .

$[\text{OH}] / \text{cm}^{-3}$	$2 \times 10^5$	$4 \times 10^5$	$6 \times 10^5$	$1.2 \times 10^6$
<b>Scenarios A</b> ( $\gamma=0.36$ )	0.3	0.7	1.8	4.1
<b>Scenarios B</b> ( $\gamma=0.77$ )	2.1	2.9	3.5	5.9
<b>Scenarios C</b> ( $\gamma=0.50$ )	7.5	13.5	19.4	34.3

## Kinetic Data used in Calculations

**Table S2** Rate Constants and branching ratios used in calculations. All rate constants and branching ratios are taken from the MCMv3.3.1 (mcm.leeds.ac.uk; Jenkin et al., 1997)

	Rate Constants / molecules cm <sup>-3</sup> s <sup>-1</sup>			Branching Ratios	
	OH	NO	HO <sub>2</sub>	$\alpha_{13}$	$\alpha_{14}$
n-butane	$9.8 \times 10^{-12} e^{(-425/T)}$				
n-pentane	$2.44 \times 10^{-17} T^2 e^{(183/T)}$				
iso-pentane	$3.70 \times 10^{-12}$				
2-butyl peroxy		$2.7 \times 10^{-12} e^{(360/T)}$	$2.91 \times 10^{-13} e^{(1300/T)*0.625}$	0.873	0.090
2+3-pentyl peroxy		$2.7 \times 10^{-12} e^{(360/T)}$	$2.91 \times 10^{-13} e^{(1300/T)*0.706}$	0.568+0.349 <sup>a</sup>	0.130 <sup>b</sup>
3-methyl-2-butyl peroxy		$2.7 \times 10^{-12} e^{(360/T)}$	$2.91 \times 10^{-13} e^{(1300/T)*0.706}$	0.297	0.141
2-butyl nitrate	$8.6 \times 10^{-13}$				
2+3-pentyl nitrate	$1.49 \times 10^{-12} c$				
3-methyl-2-butyl nitrate	$1.70 \times 10^{-12}$				

a Sum of formation of 2-pentyl and 3-pentyl peroxy radicals

b Average of 2-pentyl peroxy (0.129) and 3-pentyl peroxy (0.131).

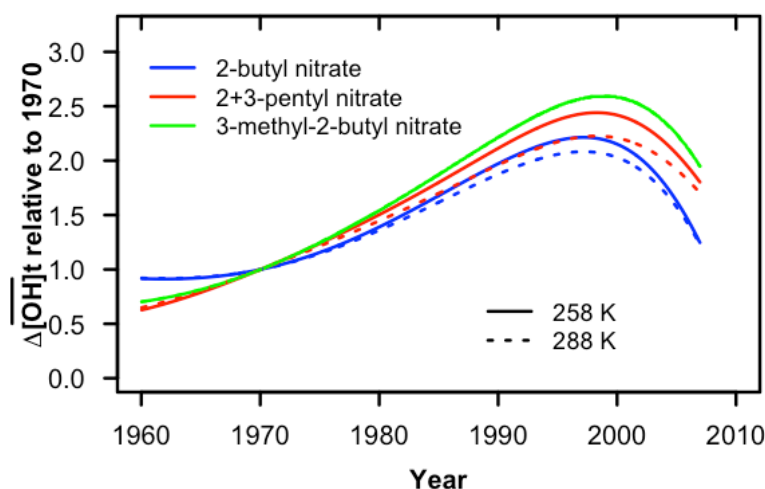
c Average of 2-pentyl nitrate ( $1.85 \times 10^{-12} \text{ cm}^{-3} \text{ s}^{-1}$ ) and 3-pentyl nitrate ( $1.12 \times 10^{-12} \text{ cm}^{-3} \text{ s}^{-1}$ )

## Sensitivity of calculations of $\overline{[\text{OH}]}t$ trend to temperature

A constant temperature of 273 K is assumed in all calculations. Changing the temperature (but keeping it as a constant) has no effect on the relative trend in  $\gamma$  (i.e. Figure 4 remains unchanged). Reducing the constant T by 15 K to 258 K, increases the calculated peak relative change in  $\overline{[\text{OH}]}t$  (i.e. the results in Figure 7) from a factor of 2.15 to 2.22 for 2-butyl nitrate, and from 2.33 to 2.44 for 2+3-pentyl nitrate (the  $\overline{[\text{OH}]}t$  calculated from 3-methyl-2-butyl nitrate is unchanged because the iso-pentane+OH rate constant from MCMv3.3.1 is not T dependent). Increasing the constant T by 15 K to 288 K, decreases the  $\overline{[\text{OH}]}t$  peak from 2.15 to 2.09 for 2-butyl nitrate and from 2.33 to 2.23 for 2+3-pentyl nitrate. These effects are shown in Figure S2.

Mean winter-time NH temperatures increased by  $\sim 1$  K between the beginning and end of the time period of study. Though temperatures may have changed by more in the Arctic, processing is basically finished by the time the air mass reaches the Arctic because there is no sunlight and hence no photochemistry.

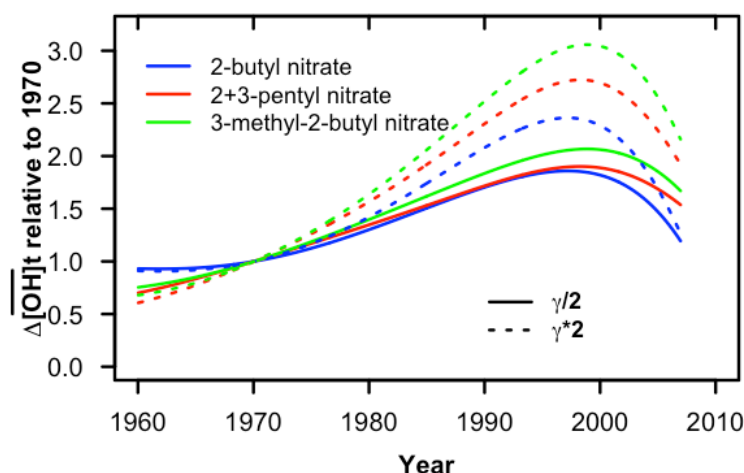
Changing source regions (and hence transport time) or atmospheric transport patterns would also change the temperature profile to which the air mass was exposed. However, as shown in Figure S2, changing temperature has a small effect on the calculations and the main effect on the alkyl nitrate/alkane ratio would be the change to processing time rather than any change in temperature.



**Figure S2** Effect on calculated temporal trend in  $\overline{[\text{OH}]}t$  of changing constant temperature used in Equation E7 from 273 K (see Figure 7) by 15 K to 258 K (solid lines) or 288 K (dashed lines).

### Sensitivity of calculated $\overline{[\text{OH}]}_t$ trend to $\gamma$

The value for  $\gamma$  used in Equation E7 for each alkyl nitrate is the mean value from the temporal trend shown in Figure 4 (0.31 for 2-butyl nitrate, 0.34 for 2+3-pentyl nitrate, 0.17 for 3-methyl-2-butyl nitrate). Figure S3 shows the temporal trends of  $\overline{[\text{OH}]}_t$  calculated when doubling or halving the  $\gamma$  values used in Figure 7.



**Figure S3** Effect on calculated temporal trend in  $\overline{[\text{OH}]}_t$  of doubling (dashed lines)/halving (solid lines) constant value for  $\gamma$  used in Equation E7, Figure 7.

In Figure S3 it is seen that the chosen value of  $\gamma$  has a significant effect on the calculated value of  $\overline{[\text{OH}]}_t$ , with higher values of  $\gamma$  leading to greater peak values for the  $\overline{[\text{OH}]}_t$  change relative to 1970.

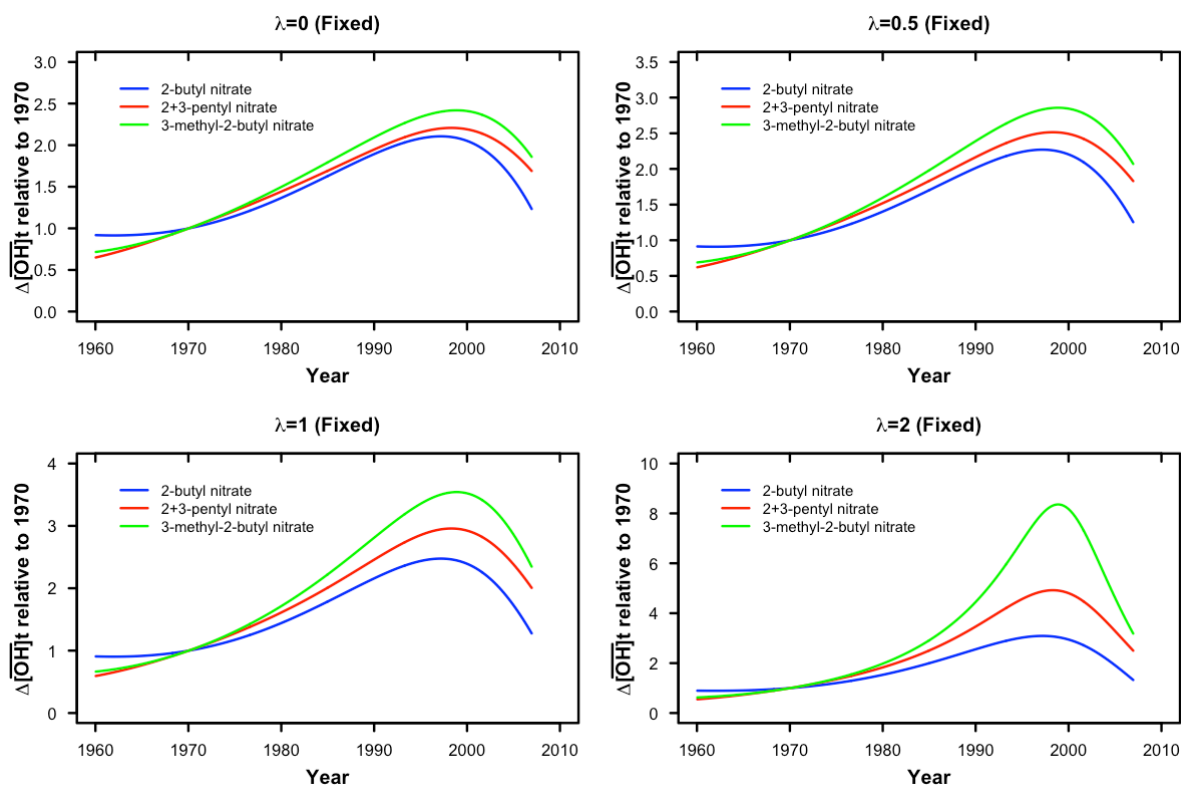
### Sensitivity of calculated $\overline{[\text{OH}]}_t$ trend to photolysis rate

In Figure 4, the photolysis loss rate for the alkyl nitrates,  $j_{16}$ , is set at a constant value of  $j_{16}=k_{15}[\text{OH}]$ , i.e. equal to the loss to OH (i.e.  $\lambda=1$ ). Changing this constant value has no effect on the calculated relative trend in  $\gamma$  presented in Figure 4.

In Equation E7, used to generate the  $\overline{[\text{OH}]}_t$  temporal trend presented in Figure 7,  $\lambda$  is assumed to vary with  $\overline{[\text{OH}]}$ . I.e, when the relative  $\overline{[\text{OH}]}_t$  in Figure 7 has doubled,  $\lambda$  has halved.  $\lambda$  is set to 1 in 1970.

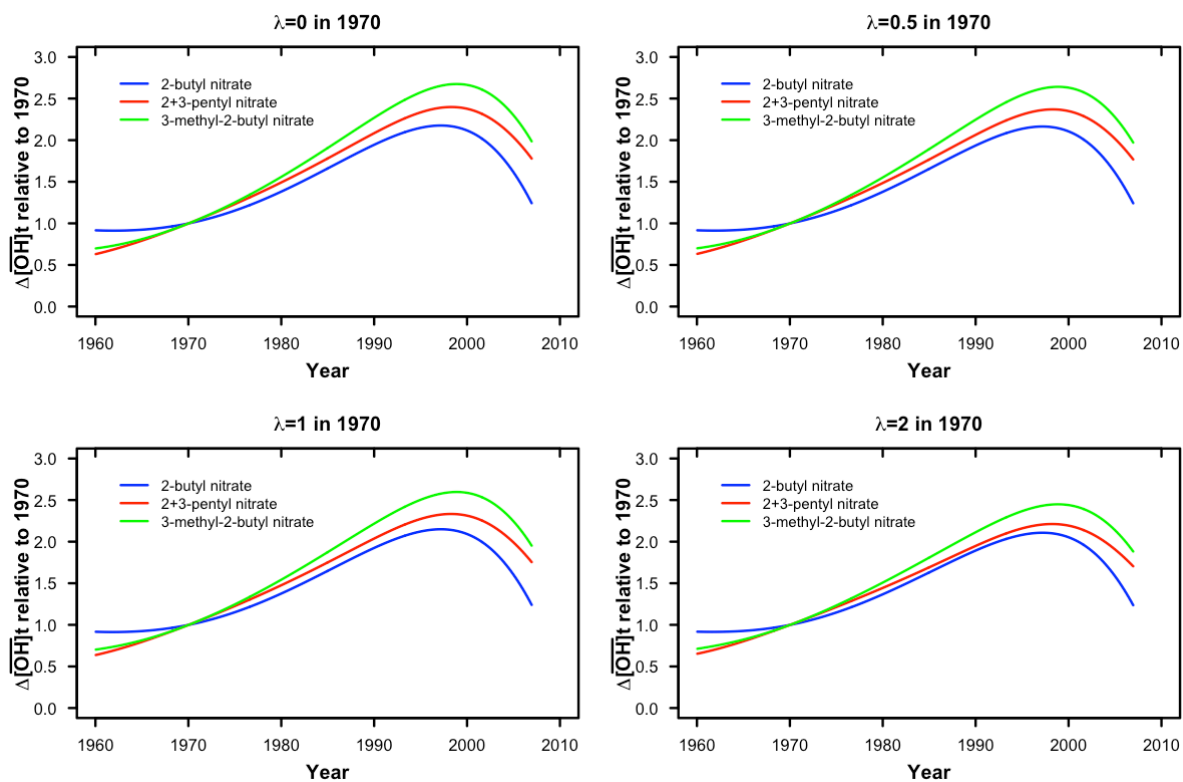
Figure S4 shows the temporal trend of  $\overline{[\text{OH}]}_t$  calculated if  $\lambda$  is assumed to remain constant in Equation E7 at 0, 0.5, 1 or 2.

Figure S5 shows the temporal trend of  $\overline{[\text{OH}]}_t$  calculated if  $\lambda$  varies, as in Figure 7, but the value which  $\lambda$  is set to in 1970 is 0, 0.5, 1 or 2.



**Figure S4** Effect of changing the value of  $\lambda$ , ( $j_{16}/k_{15}[\text{OH}]$ ) on the trend in  $\overline{[\text{OH}]}t$  calculated using Equation E7 assuming a fixed value of  $\lambda$ .

In Figure S4 it is seen that as the constant value of  $\lambda$  is increased, the calculated change in  $[\text{OH}]t$  between 1970 and the peak increases. This difference becomes very large at  $\lambda=2$ . However, this effect is not seen in Figure S5, when  $\lambda$  is allowed to vary with changing  $[\text{OH}]$  (assuming the change in  $\overline{[\text{OH}]}t$  to be caused by changes to  $\overline{[\text{OH}]}$  rather than  $t$ .) as it does in Figure 7.



**Figure S5** Effect of changing the value of  $\lambda$  in 1970, on the trend in  $\overline{[\text{OH}]}_t$  calculated using Equation E7.

In Figure S5 it is seen that there is very little variation between the trends derived when assuming  $\lambda$  in 1970 = 0, 0.5 or 1. For  $\lambda$  in 1970 = 2, the peaks are reduced by 2 % for 2-butyl nitrate and 5 % for the pentyl nitrates.