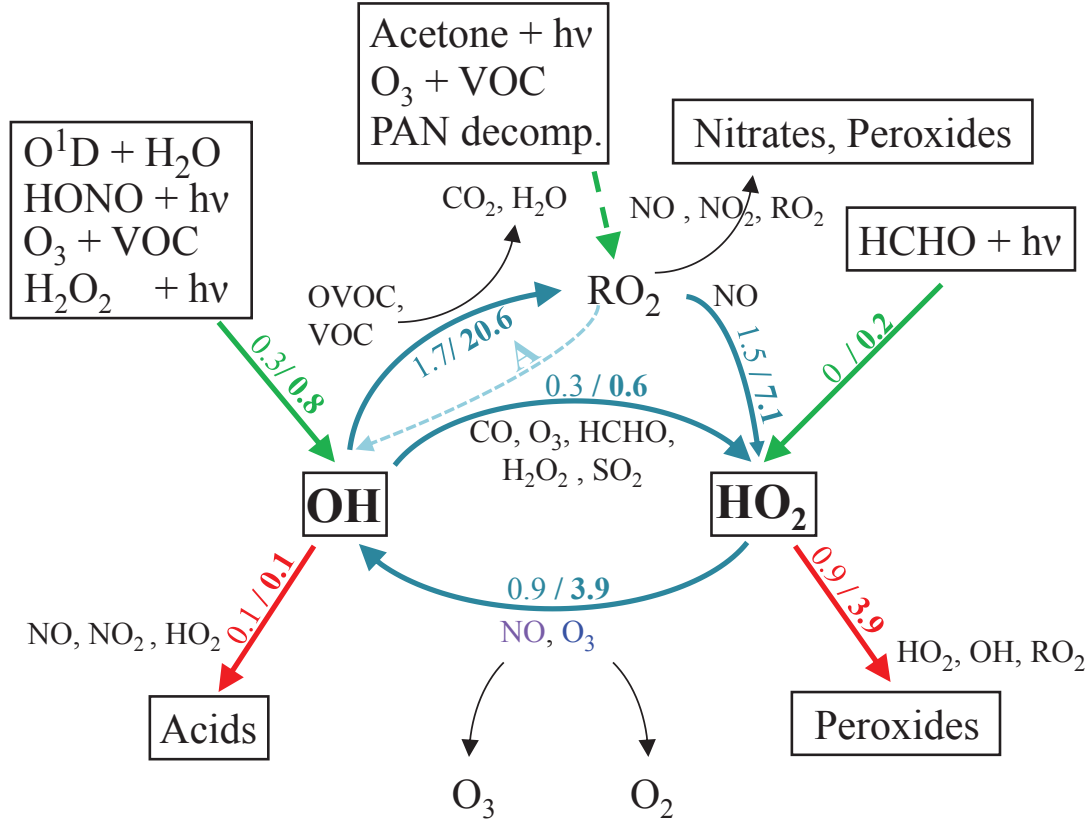


**HO_x recycling pathways under different conditions of observed
radiation and total OH reactivity during HUMPPA-COPEC
2010**

This document is part of the electronic supplement to our article
“Observation and modelling of HO_x radicals in a boreal forest”
in ACP (2014), available at:
<http://www.atmospheric-chemistry-and-physics.net>

Table S1: HO_x budget under different conditions of observed total OH reactivity (moderate/**high**) at low radiation ($J_{O(^1D)} \leq 3 \times 10^{-6} \text{ s}^{-1}$). Radical production (green), recycling (blue), and loss (red) pathways are indicated by bold arrows. All rates are given in $10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$.



$k'_{OH} \leq 15 \text{ s}^{-1}$	$k'_{OH} > 15 \text{ s}^{-1}$
<ul style="list-style-type: none"> • $P_{OH}^{total} = (2.1 \pm 0.8) \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$ • $HO_2 + NO/O_3$ is inhibited ($P_{OH, HO_2+NO/O_3} \approx 1 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$) • $\sim 40\%$ of P_{OH}^{total} is unknown ($P_{OH}^{missing} \approx 1 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$) • Potential OH sources: <ul style="list-style-type: none"> - Ozonolysis of unmeasured VOCs - could be related to NO_3 ($P_{NO_3} \approx 1 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$) 	<ul style="list-style-type: none"> • $P_{OH}^{total} = (21.3 \pm 7.2) \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$ • $\sim 80\%$ of P_{OH}^{total} is unknown ($P_{OH}^{missing} \approx 17 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$) • about 16% of P_{OH}^{total} by $HO_2 + NO/O_3$ ($P_{OH, HO_2+NO/O_3} \approx 4 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$) • $\sim 60\%$ of the RO_2 production rate imply unknown loss processes that could lead to direct OH recycling <p style="text-align: center;">• RO_2 sink is missing \rightarrow potential OH source</p> <p>\Rightarrow alkylperoxy radicals + HO_2 (Thornton et al., 2002; Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008) and H-shifts (Peeters et al., 2009) are likely</p>

Table S2: Median levels and variability of relevant trace gases under different conditions of observed radiation and total OH reactivity.

	$J_{\text{O}(^1\text{D})} > 3 \times 10^{-6} \text{ s}^{-1}$	$J_{\text{O}(^1\text{D})} \leq 3 \times 10^{-6} \text{ s}^{-1}$
$k'_{\text{OH}} \leq 15 \text{ s}^{-1}$	<p>OH $\approx (1.0 \pm 0.8) \times 10^6 \text{ molec. cm}^{-3}$</p> <p>HO₂ $\approx (10 \pm 1) \text{ ppt}_V$</p> <p>O₃ $\approx (33 \pm 2) \text{ ppb}_V$</p> <p>NO $\approx (46 \pm 16) \text{ ppt}_V$</p> <p>NO₂ $\approx (280 \pm 40) \text{ ppt}_V$</p> <p>CO $\approx (85 \pm 1) \text{ ppb}_V$</p> <p>C₅H₈ $\approx (145 \pm 30) \text{ ppt}_V$</p> <p>$\alpha$-pinene $\approx (63 \pm 15) \text{ ppt}_V$</p> <p>$\beta$-pinene $\approx (16 \pm 4) \text{ ppt}_V$</p> <p>$\beta$-myrcene $\approx (5 \pm 1) \text{ ppt}_V$</p> <p>$\Delta^3$-carene $\approx (30 \pm 8) \text{ ppt}_V$</p>	<p>OH $\approx (3.8 \pm 3.0) \times 10^5 \text{ molec. cm}^{-3}$</p> <p>HO₂ $\approx (10 \pm 6) \text{ ppt}_V$</p> <p>O₃ $\approx (35 \pm 7) \text{ ppb}_V$</p> <p>NO $\approx (3 \pm 39) \text{ ppt}_V$</p> <p>NO₂ $\approx (570 \pm 210) \text{ ppt}_V$</p> <p>CO $\approx (96 \pm 5) \text{ ppb}_V$</p> <p>C₅H₈ $\approx (62 \pm 65) \text{ ppt}_V$</p> <p>$\alpha$-pinene $\approx (68 \pm 67) \text{ ppt}_V$</p> <p>$\beta$-pinene $\approx (20 \pm 17) \text{ ppt}_V$</p> <p>$\beta$-myrcene $\approx (5 \pm 4) \text{ ppt}_V$</p> <p>$\Delta^3$-carene $\approx (44 \pm 44) \text{ ppt}_V$</p>
$k'_{\text{OH}} > 15 \text{ s}^{-1}$	<p>OH $\approx (6.4 \pm 5.6) \times 10^5 \text{ molec. cm}^{-3}$</p> <p>HO₂ $\approx (27 \pm 2) \text{ ppt}_V$</p> <p>O₃ $\approx (51 \pm 1) \text{ ppb}_V$</p> <p>NO $\approx (28 \pm 7) \text{ ppt}_V$</p> <p>NO₂ $\approx (320 \pm 20) \text{ ppt}_V$</p> <p>CO $\approx (93 \pm 1) \text{ ppb}_V$</p> <p>C₅H₈ $\approx (112 \pm 13) \text{ ppt}_V$</p> <p>$\alpha$-pinene $\approx (80 \pm 4) \text{ ppt}_V$</p> <p>$\beta$-pinene $\approx (17 \pm 1) \text{ ppt}_V$</p> <p>$\beta$-myrcene $\approx (5.0 \pm 0.3) \text{ ppt}_V$</p> <p>$\Delta^3$-carene $\approx (38 \pm 2) \text{ ppt}_V$</p>	<p>OH $\approx (6.3 \pm 2.0) \times 10^5 \text{ molec. cm}^{-3}$</p> <p>HO₂ $\approx (22 \pm 4) \text{ ppt}_V$</p> <p>O₃ $\approx (51.0 \pm 0.3) \text{ ppb}_V$</p> <p>NO $\approx (17 \pm 5) \text{ ppt}_V$</p> <p>NO₂ $\approx (290 \pm 30) \text{ ppt}_V$</p> <p>CO $\approx (92 \pm 1) \text{ ppb}_V$</p> <p>C₅H₈ $\approx (110 \pm 5) \text{ ppt}_V$</p> <p>$\alpha$-pinene $\approx (61 \pm 8) \text{ ppt}_V$</p> <p>$\beta$-pinene $\approx (14 \pm 1) \text{ ppt}_V$</p> <p>$\beta$-myrcene $\approx (4.0 \pm 0.5) \text{ ppt}_V$</p> <p>$\Delta^3$-carene $\approx (27 \pm 5) \text{ ppt}_V$</p>