Supplementary information

Identification of Criegee intermediates as potential oxidants in the troposphere

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Table SI-1. Average concentrations with 1σ standard deviation of measured unsaturated VOC during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, together with the rate coefficients of the reaction with ozone (IUPAC recommended values) (Atkinson et al., 2006).

Compound	**[molecules cm^{-3}]**		**Rate coefficient with O_3 [cm^3 $molecule^{-1}$ s^{-1}]**
	HUMPPA-COPEC 2010	**HOPE 2012**	
isoprene	$(1.8 \pm 1.8) \times 10^9$	$(2.2 \pm 2.2) \times 10^9$	1×10^{-14} exp(-1995/T)
α-pinene	$(2.7 \pm 3) \times 10^9$	$(1.5 \pm 1.5) \times 10^9$	8.1×10^{-16} exp(-640/T)
β-pinene	$(1.9 \pm 6.6) \times 10^8$	$(9 \pm 9) \times 10^8$	1.4×10^{-15} exp(-1270/T)
3-carene	$(1.7 \pm 2) \times 10^9$	$(5.6 \pm 4.7) \times 10^8$	$4.8 \times 10^{-17, b}$
myrcene	$(2.6 \pm 2.7) \times 10^8$	$(2.2 \pm 1.6) \times 10^8$	2.7×10^{-15} exp(-520/T)
limonene	n.a.	$(2.9 \pm 2.1) \times 10^8$	2.8×10^{-15} exp(-770/T)
sabinene	n.a.	$(9.2 \pm 9.6) \times 10^8$	$8.2 \times 10^{-17, b}$
γ-terpinene	n.a.	$(1 \pm 1) \times 10^8$	$1.5 \times 10^{-16, b}$
2-methylpropene	n.a.	$(4.2 \pm 2.5) \times 10^8$	2.7×10^{-15} exp(-1630/T)
but-1-ene	n.a.	$(1.4 \pm 4.2) \times 10^8$	$1.2 \times 10^{-17, a,b}$
propene	n.a.	$(4.7 \pm 3.7) \times 10^8$	5.5×10^{-15} exp(-1880/T)
cis-2-butene	n.a.	$(6.1 \pm 3.0) \times 10^7$	3.2×10^{-15} exp(-965/T)
ethene	n.a.	$(7.3 \pm 9.0) \times 10^9$	9.1×10^{-15} exp(-2580/T)

a, rate coefficient from Adeniji et al. (1981).
b, at 298 K

Table SI-2. Average concentrations with 1σ standard deviation of measured trace gas during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, with the rate coefficients of the reaction with OH (IUPAC recommended values) (Atkinson et al., 2006;Atkinson et al., 2004)

Compound	**[molecules cm^{-3}]**		**Rate coefficient with OH [cm^3 molecule^{-1} s^{-1}]**
	HUMPPA-COPEC 2010	**HOPE 2012**	
isoprene	(1.8 ± 1.8) x 10^{9}	(2.2 ± 2.0) x 10^{9}	2.7 x 10^{-11} exp(390/T)
α-pinene	(2.7 ± 3) x 10^{9}	(1.5 ± 1.5) x 10^{9}	1.2 x 10^{-11} exp(440/T)
β-pinene	(1.9 ± 6.6) x 10^{8}	(9 ± 9) x 10^{8}	7.4 x 10^{-11}, [a,b]
3-carene	(1.7 ± 2) x 10^{9}	(5.6 ± 4.7) x 10^{8}	8.8 x 10^{-11}, [a,b]
myrcene	(2.6 ± 2.7) x 10^{8}	(2.2 ± 1.6) x 10^{8}	3.3 x 10^{-10}, [b,c]
limonene	n.a.	(2.9 ± 2.1) x 10^{8}	3 x 10^{-11} exp(515/T),[d]
sabinene	n.a.	(9.2 ± 9.6) x 10^{8}	1.2 x 10^{-10}, [a,b]
γ-terpinene	n.a.	(1 ± 1) x 10^{8}	1.7 x 10^{-10}, [b]
MACR	(1.0± 0.9) x 10^{10}	(1.4 ± 0.9) x 10^{9}	8 x 10^{-12} exp(380/T)
ethanol	(3.6 ± 2.2) x 10^{10}	(1.8 ± 1.1) x 10^{10}	3.2 x 10^{-12} exp(20/T)
methanol	(1.0 ± 1.4) x 10^{11}	(9.0 ± 3.4) x 10^{10}	9 x 10^{-13}, [b]
ozone	(1.1 ± 0.2) x 10^{12}	(1.1 ± 0.3) x 10^{12}	1.7 x 10^{-12} exp(-940/T)
SO_2	(1.4 ± 1.7) x 10^{10}	(2.3 ± 2.2) x 10^{9}	2 x 10^{-12}, [b]
H_2O_2	(1.1 ± 1.0) x 10^{10}	n.a.	1.7 x 10^{-12}, [b]
HO_2	(9.0 ± 9.5) x 10^{8}	(1.4 ± 8.6) x 10^{8}	4.8 x 10^{-11} exp(250/T)
NO	(6.5 ± 7.0) x 10^{8}	(3.8 ± 5.0) x 10^{9}	1.3 x 10^{-11}, [b]
NO_2	(9.5 ± 5.0) x 10^{9}	(3.8 ± 2.4) x 10^{10}	1.1 x 10^{-11}, [b]
CO	(3.0 ± 1.2) x 10^{12}	(2.8 ± 0.4) x 10^{12}	2.1 x 10^{-13}, [b]

HONO	$(3.4 \pm 3.1) \times 10^{9}$	n.a.	6.0×10^{-12}, [b]
propanal	n.a.	$(5.8 \pm 3.0) \times 10^{9}$	$4.9 \times 10^{-12} \exp(405/T)$
acetaldehyde	$(1.8 \pm 1.0) \times 10^{10}$	$(2.9 \pm 1.4) \times 10^{10}$	1.5×10^{-11}, [b]
formaldehyde	$(1.4 \pm 1.6) \times 10^{10}$	$(2.1 \pm 0.4) \times 10^{10}$	8.5×10^{-12}, [b]
acetone	$(8.2 \pm 3.8) \times 10^{10}$	$(6.0 \pm 2.2) \times 10^{10}$	1.8×10^{-13}, [b]
CH_4	$(4.4 \pm 0.07) \times 10^{13}$	$(4.3 \pm 0.1) \times 10^{13}$	6.4×10^{-15}, [b]
2-methylpropene	n.a.	$(4.2 \pm 2.5) \times 10^{8}$	6.1×10^{-11}, [a,b]
but-1-ene	n.a.	$(1.4 \pm 4.2) \times 10^{8}$	3.1×10^{-11}, [a,b]
propene	n.a.	$(4.7 \pm 3.7) \times 10^{8}$	2.9×10^{-11}, [b]
cis-2-butene	n.a.	$(6.1 \pm 3.0) \times 10^{7}$	6.4×10^{-11}, [b]
ethene	n.a.	$(7.3 \pm 9.0) \times 10^{9}$	7.8×10^{-12}, [b]
p-xylene	n.a.	$(7.2 \pm 5.2) \times 10^{8}$	2.0×10^{-11}, [a,b]
benzene	$(2.1 \pm 1.9) \times 10^{9}$	$(8.0 \pm 4.0) \times 10^{8}$	1.2×10^{-12}, [a,b]
ethylbenzene	n.a.	$(2.3 \pm 2.1) \times 10^{8}$	7.0×10^{-12}, [a,b]
Toluene	$(6.1 \pm 3.0) \times 10^{9}$	$(1.2 \pm 0.7) \times 10^{9}$	5.6×10^{-12}, [a,b]
ethane	n.a.	$(1.8 \pm 0.3) \times 10^{10}$	$4.8 \times 10^{-11} \exp(250/T)$, [a]
propane	n.a.	$(5.6 \pm 3.6) \times 10^{9}$	1.1×10^{-12}, [a,b]
methylpropane	$(1.8 \pm 2.3) \times 10^{9}$	$(1.4 \pm 0.9) \times 10^{9}$	2.1×10^{-12}, [a,b]
butane	$(1.8 \pm 1.6) \times 10^{9}$	$(2.0 \pm 1.2) \times 10^{9}$	2.3×10^{-12}, [a,b]
2-methylbutane	$(1.6 \pm 1.2) \times 10^{9}$	n.a.	3.6×10^{-12}, [a,b]
n-pentane	$(1.0 \pm 0.9) \times 10^{9}$	$(5.6 \pm 5.0) \times 10^{9}$	3.8×10^{-12}, [a,b]

a, rate coefficient from (Atkinson and Arey, 2003).
b, at 298 K.
c, rate coefficient from (Hites and Turner, 2009)
d, rate coefficient from (Braure et al., 2014)

Table SI-3. Average sum of concentrations with 1σ standard deviation of BVOC (isoprene, α-pinene, β-pinene, 3-carene, myrcene, limonene, sabinene, γ-terpinene) and temperature for the entire HOPE 2012 field campaign excluding the period between 26th to 28th of July 2012.

	Σ[VOC] [molecules cm^{-3}]	Temperature [°C]
HOPE 2012 campaign	$(5 \pm 4) \times 10^{9}$	16 ± 3
26th to 28th of July 2012	$(1.3 \pm 0.9) \times 10^{10}$	22 ± 3

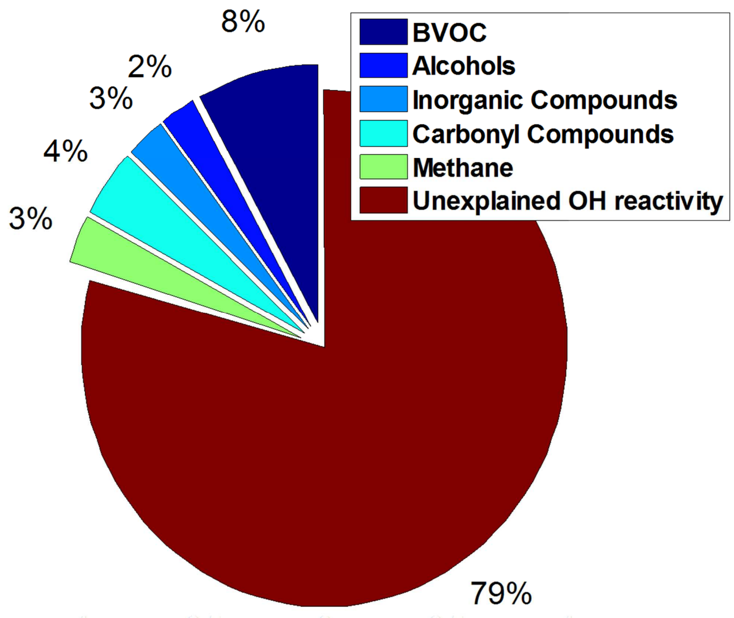

Figure SI-1. Contributions of measured trace gases to the measured OH reactivity during the HUMPPA-COPEC 2010.

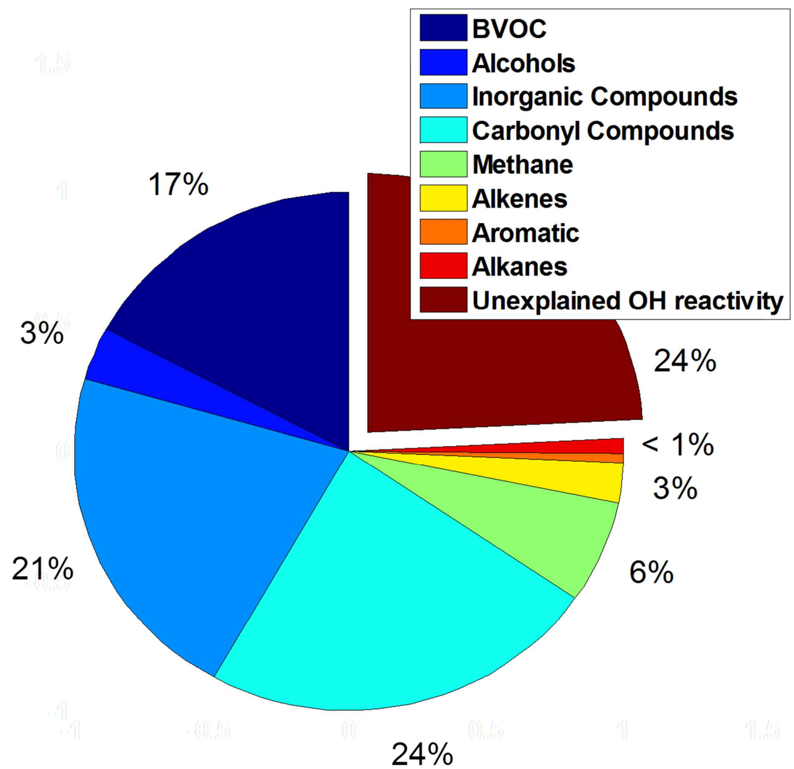

Figure SI-2. Contributions of measured trace gases to the measured OH reactivity during the HOPE 2012.

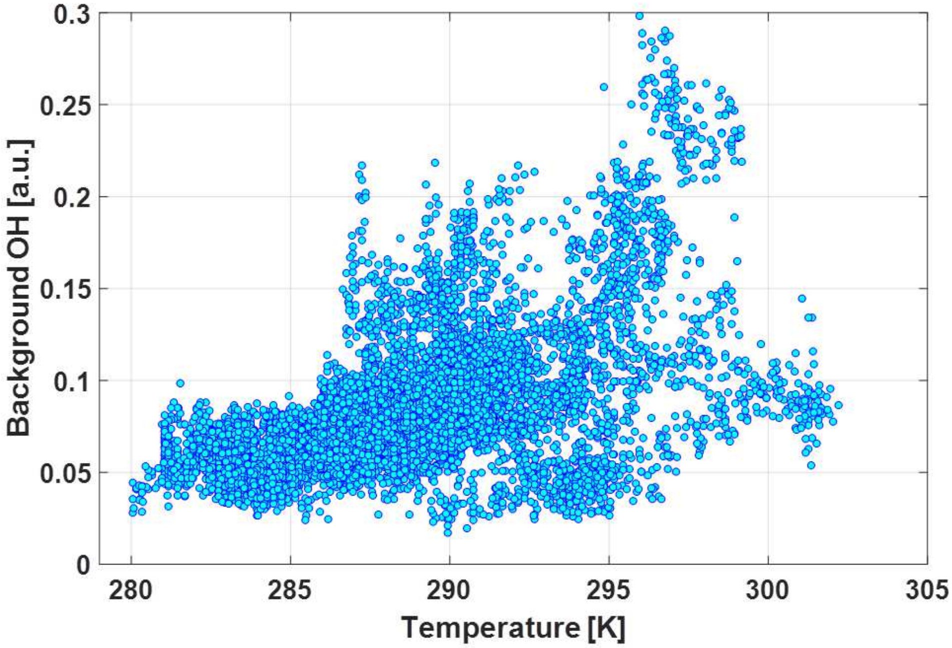

Figure SI-3. Background OH as a function of temperature during the HOPE 2012 campaign.

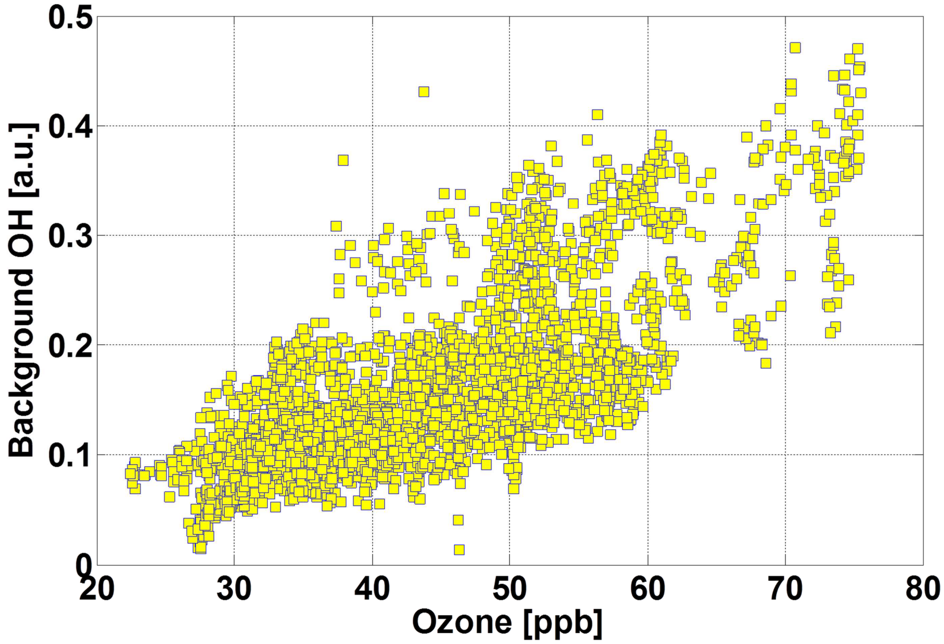

Figure SI-4. Background OH as a function of the ozone concentration during the HUMPPA-COPEC 2010 campaign.

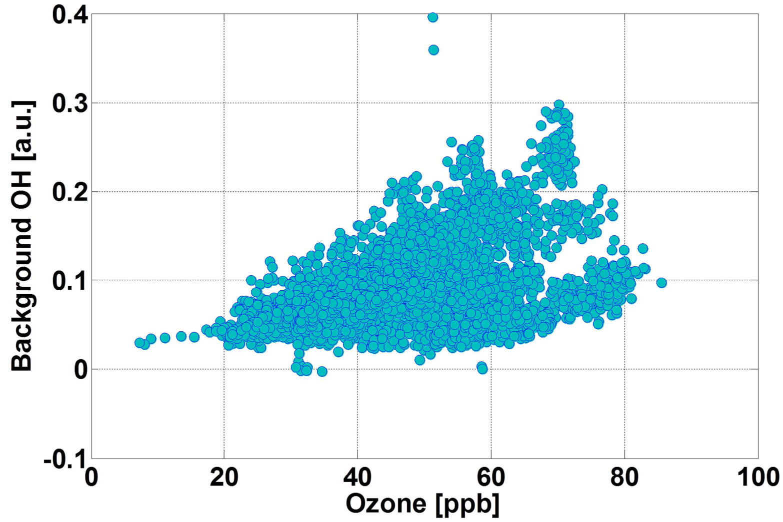

Figure SI-5. Background OH signal as a function of ozone concentration during the HOPE 2012 campaign.

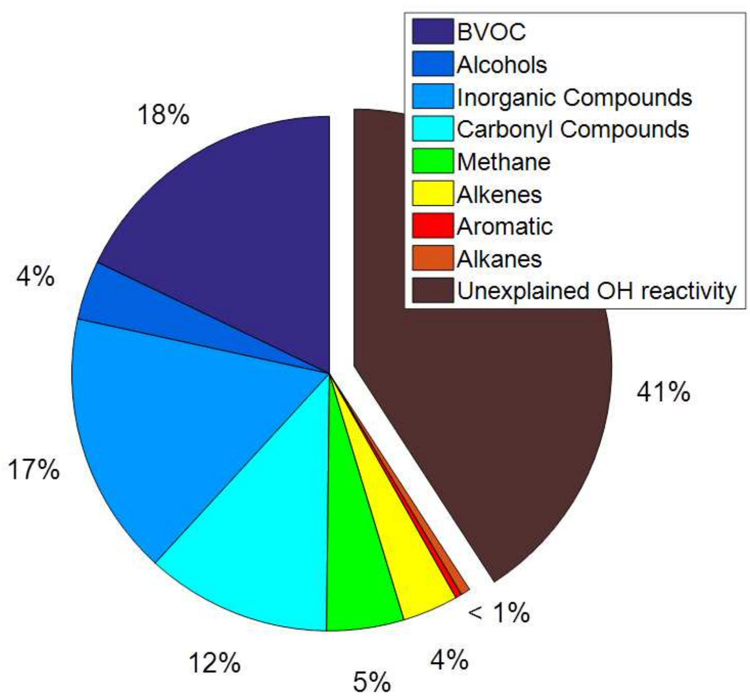

Figure SI-6. Contribution of measured trace gases to the measured OH reactivity during HOPE 2012 between the 1st and 3rd of August 2012.

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