SUPPLEMENTARY INFORMATION

1. Methods and materials

1.1. Nitrate ion CI-APi-TOF

The chemical ionization atmospheric-pressure-interface time-of-flight (CI-APi-TOF) mass spectrometer is built from three components:

1) Chemical ionization inlet (Airmodus A07) that utilizes coaxial sample and sheath flows. This is to minimize the sample loss to the walls.

2) Atmospheric-Pressure-interface that allows sampling from ambient pressure (~0.8 liter min^{-1}).

3) Time-of-Flight mass spectrometer (Tofwerk, Switzerland) that provides high resolution (>3000 Th/Th) mass-to-charge determination in high vacuum (10^{-6} mbar).

The CI-APi-TOF was run in the negative ion mode. Ionization is achieved using a ^{241}Am source and concentrated nitric acid (HNO_3) that acts as the reagent ion after ionization. The reagent ions produced, NO_3^-, $HNO_3NO_3^-$ and $(HNO_3)_2NO_3^-$, are guided into the ion reaction zone mixed with the sheath flow (20 liter min^{-1}). The sheath flow surrounds the sample flow (10 liter min^{-1}) which is taken from the middle of the carrier gas stream from the flow tube. This sample flow travels in the middle of the CI-inlet, minimizing sample losses to the walls. The reaction time in the inlet is ~200 ms. The original design of using coaxial flows is adapted from Eisele and Tanner (1). The inlet has been introduced in detail by e.g. Jokinen et al. (2) and Kurtén et al. (3) and the APi-TOF by Junninen et al. (4).

1.2. Calibration, ELVOC concentration and measurement uncertainty

The CI-APi-TOF is well known for sulfuric acid and its cluster detection from the gas phase with a high sensitivity and extremely low limit of detection (2). Thus, the calibration of the CI-APi-TOF was done using sulfuric acid (HSO_4^-, 96.9601 Th), and the calibration corresponded to a calibration coefficient (C) of $1.85 \bullet 10^9$ molec cm^{-3}. This coefficient was used for the calculation of the ELVOC concentrations (Eq. 1). The calibration factor includes the loss term from the ~10 cm sampling tube prior the CI-inlet ELVOC concentrations in this study are given in 2-minute averages.

$$[ELVOC] = \frac{ELVOC\ signal(s)}{\sum reagent\ ions} * C \qquad \text{(Eq. 1)}$$

The measurement uncertainty is estimated to be -50%/+100 %. This uncertainty arises from the calibration and from the possibility that the transmission at ELVOC-NO_3^- cluster differs somewhat from the transmission of H_2SO_4 used for calibration. The transmission curve was tuned as flat as possible so the transmission of ELVOC and sulfuric acid would similar to each other. The uncertainty estimate also includes the diffusional loss of ELVOC onto the flow tube walls. The wall loss of sulfuric acid is well determined (27 %) and it represents the maximum loss term. ELVOC are around three times bigger than a sulfuric acid molecule so the wall loss is thus estimated to be ~10 %.

2. Extremely Low Volatility Organic Compound (ELVOC)

2.1. Definition and yields

The charging of an oxidized organic compound took place via clustering with the nitrate ion monomer, so that NO_3^- and all ELVOC signals are detected as clusters. Since the vapor pressure of the detected compounds is not possible to determine experimentally, we classified ELVOC volatilities using three different but somewhat similar methods; SIMPOL (5), the Nannoollal method (6) and volatility estimation described in Donahue et al. (2011, 7). The borderline where ELVOC definition can be given to a certain compound was studied in details. We chose two reaction products from monoterpene oxidation, $C_{10}H_{16}O_6$ and $C_{10}H_{16}O_7$, and calculated their volatilities using two temperatures (Table S1)

In the case of detected monomers C_{10} compounds classified as ELVOC is $C_{10}H_{16}O_7$. Most identified ELVOC signals for all studied compounds are depicted in figure S1, where all detected highly oxygenated compounds are presented regardless if they are ELVOC or not. During ozonolysis of isoprene the signals arising from oxidation reactions were mostly so small that it was challenging to separate them from the background signal. Thus, some experiments were made using ^{13}C isotopically labelled isoprene ($^{13}C_1C_4H_8$) for positive identification of isoprene ELVOC.

In the case of monoterpenes, the total ELVOC concentration is calculated as the sum of signals in the mass-to-charge range of 280 – 620 Th that includes both monomers and dimers. In the case of myrcene the total ELVOC is a sum of 300 – 620 Th since the products with oxygen content than in $\leq C_{10}H_{16}O_6$ has been neglected from the total amount. The total isoprene ELVOC concentration is calculated from the sum of the signals in the range 240 – 300 Th. This range is carefully selected to fulfil the definition of an ELVOC (see the main text). The yield is calculated from the slope of the concentration of total ELVOC produced vs. concentration of reacted terpene (Eq. 3 and Eq. 4).

3. Low O_2 and OH scavenger experiments
   Runs with and without the OH scavenger allows distinguishing between ELVOC produced via ozonolysis or OH radical reaction, see Figure S3 for α-pinene, β-pinene and isoprene experiments. The OH scavengers used in this study, propane and H_2, acted similarly and equally effectively during OH scavenging experiments.

Reacted [terpene] with O_3: $$k(O_3 + terpene) \cdot [terpene] \cdot [O_3] \cdot \tau \quad \text{(Eq.3)}$$

Reacted [terpene] with OH: $$k(O_3 + terpene) \cdot [terpene] \cdot [O_3] \cdot \tau \cdot (OHyield) \quad \text{(Eq. 4)}$$

Values of *k* and OH yields are listed in Table S2. Lifetime τ is the residence time in the flow tube, 40 s.

References

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Table S1: Estimated volatilities for $C_{10}H_{16}O_6$ and $C_{10}H_{16}O_7$ in 298 and 273 K using SIMPOL and Nannoolal method. The volatilities (Pa) are also calculated to fit Donahue et al. (2012) vapor pressure estimation method (log10Coi) and the classification in colors is also adapted from Donahue et al. (2012).

	$C_{10}H_{16}O_6$		$C_{10}H_{16}O_7$	
	298 K	273 K	298 K	273 K
SIMPOL (Pa)	2,46E-04	5,67E-06	1,61E-06	2,02E-08
Pa → log10Coi(ug/m3)	1.3626	-0,2367	-0.7926	-2.6560
Nannoolal et al. 2008 (Pa)	6,41E-05	6,70E-07	6,41E-08	1,88E-10
Pa → log10Coi(ug/m3)	0.7785	-1.1643	-2.1926	-4.6872

Classification based on Donahue et al. (2012):

IVOC	SVOC	LVOC	ELVOC

Table S2: Experimental conditions during each oxidation reaction experiment. References for reaction rate constants and OH yields are in brackets and superscripted.

	Limonene	α-Pinene	Myrcene	β-Pinene	Isoprene
[alkene], molec.cm^{-3}	(1 - 10000) $\cdot 10^{9}$	(2.3 - 4300) $\cdot 10^{9}$	(4.5 - 24500) $\cdot 10^{8}$	(9.0 - 900) $\cdot 10^{11}$	(4.0 - 40) $\cdot 10^{12}$
[O_3], molec.cm^{-3}	(6.1 - 6.9) $\cdot 10^{11}$	(5.9 - 6.3) $\cdot 10^{11}$	$6.2 \cdot 10^{11}$	$6.3 \cdot 10^{11}$	$6.2 \cdot 10^{11}$
k(O_3+alkene), cm^{3} s^{-1}	$2.5 \cdot 10^{-16}$ (8)	$1.1 \cdot 10^{-16}$ (8)	$4.8 \cdot 10^{-16}$ (8)	$2.24 \cdot 10^{-17}$ (9)	$1.34 \cdot 10^{-17}$ (9)
OH yield, %	86 (10)	85 (10)	100 (10)	35 (10)	25 (11)
ELVOC from O_3, %	87	90	31	38	57
ELVOC from OH, %	13	10	69	62	43

Table S3. SOA precursor reaction rates according to IUPAC.

	O_3	OH	NO_3
Monoterpenes	$6.3\times10^{-16} \exp(-580/T)$	$1.2\times10^{-11} \exp(440/T)$	$1.2\times10^{-12} \exp(490/T)$
Isoprene	$1.03\times10^{-14}\exp(-1995/T)$	$2.7\times10^{-11} \exp(390/T)$	$3.15\times10^{-12}\exp(-450/T)$

Table S4. Global and regional SOA, CN, CCN, growth rate (GR) and condensation sink (CS) budgets. Global values are annual averages, while regional values correspond to respective summer period (JJA for North America and Siberia, DJF for South America and Australia). Total SOA production (Tg) is given for each experiment, and ELVOC fraction of total SOA formation is given in parenthesis. Absolute values for CN, CCN(1.0%) and CCN(0.2%) concentrations as well as growth rate and condensation sink are given for CTRL experiment, while differences to CTRL simulation are given for the four additional simulations NOSOA, NOISOP and NOELVOC.

		SOA	ELVOCs	Isoprene
Global	CTRL	(CTRL-NOSOA)	(CTRL-NOELVOC)	(CTRL-NOISOP)
SOA prod. (ELVOC %) (Tg yr^{-1})	27 (3.2%)	0 (0.0%)	27 (0.0%)	7 (12.0%)
CN	1003	-0.70	3.32	-3.43
CCN(1.0%)	357	-2.66	0.63	-2.31
CCN(0.2%)	134	1.62	0.27	0.75
GR (nm h^{-1})	0.36	26.46	29.73	-1.36
CS (10^{3} s^{-1})	1.57	3.92	0.70	2.14
Siberia				
SOA prod. (ELVOC %) (Tg JJA^{-1})	0.3 (5.6%)	0 (0.0%)	0.3 (0.0%)	0.14 (12.0%)
CN	913	14.63	29.76	-9.47
CCN(1.0%)	249	-0.81	5.29	-3.28
CCN(0.2%)	73	7.22	0.94	2.30
GR (nm h^{-1})	0.40	242.48	269.23	-0.73
CS (10^{3} s^{-1})	1.34	16.65	5.10	4.45
Australia				
SOA prod. (ELVOC %) (Tg DJF^{-1})	1.1 (1.6%)	0 (0.0%)	1.1 (0.0%)	0.18 (9.8%)
CN	1141	-7.92	8.54	-12.54
CCN(1.0%)	409	-12.76	1.68	-10.21
CCN(0.2%)	117	8.84	0.74	4.41
GR (nm h^{-1})	0.41	14.55	26.97	-5.98
CS (10^{3} s^{-1})	1.49	12.01	1.59	7.29
NAM				
SOA prod. (ELVOC %) (Tg JJA^{-1})	0.69 (2.7%)	0 (0.0%)	0.69 (0.0%)	0.17 (11.1%)
CN	3743	-8.20	3.27	-8.08
CCN(1.0%)	1174	-12.24	0.84	-8.48
CCN(0.2%)	405	2.37	0.78	0.65
GR (nm h^{-1})	1.25	25.29	33.32	-3.26
CS (10^{3} s^{-1})	3.48	7.62	1.16	4.76
SAM				
SOA prod. (ELVOC %) (Tg DJF^{-1})	1.9 (4.4%)	0 (0.0%)	1.9 (0.0%)	0.6 (13.7%)
CN	1083	24.72	43.39	-16.04
CCN(1.0%)	287	2.36	6.48	-2.75
CCN(0.2%)	103	4.24	0.73	2.13
GR (nm h^{-1})	1.04	488.44	541.15	-0.90
CS (10^{3} s^{-1})	1.62	23.34	6.69	7.81

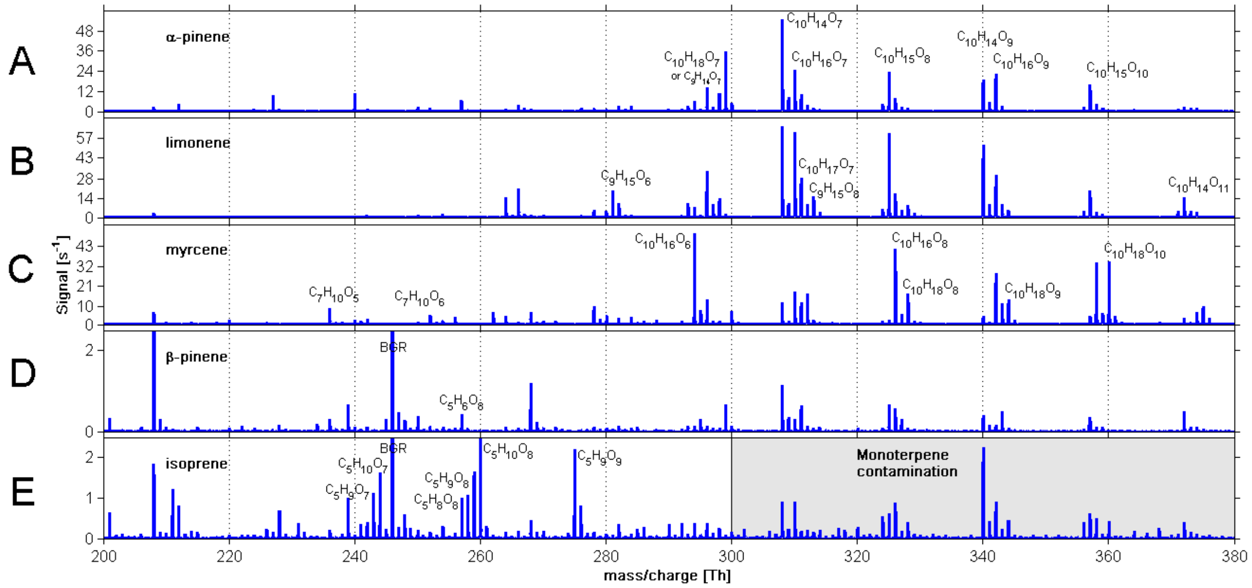

Figure S1. Monomer spectral “fingerprints” for the studied monoterpenes, A) α-pinene, B) limonene, C) myrcene, D) β-pinene and E) for isoprene, showing the most important reaction products during ozonolysis. Composition is marked only once, e.g. >300 Th peaks for b-pinene have the same elemental composition as the peaks in upper panels. In the case of isoprene, most peaks in the dimer area (mass-to-charge >300 Th) were found to be contamination from previous monoterpene ($C_{10}H_{16}$) experiments.

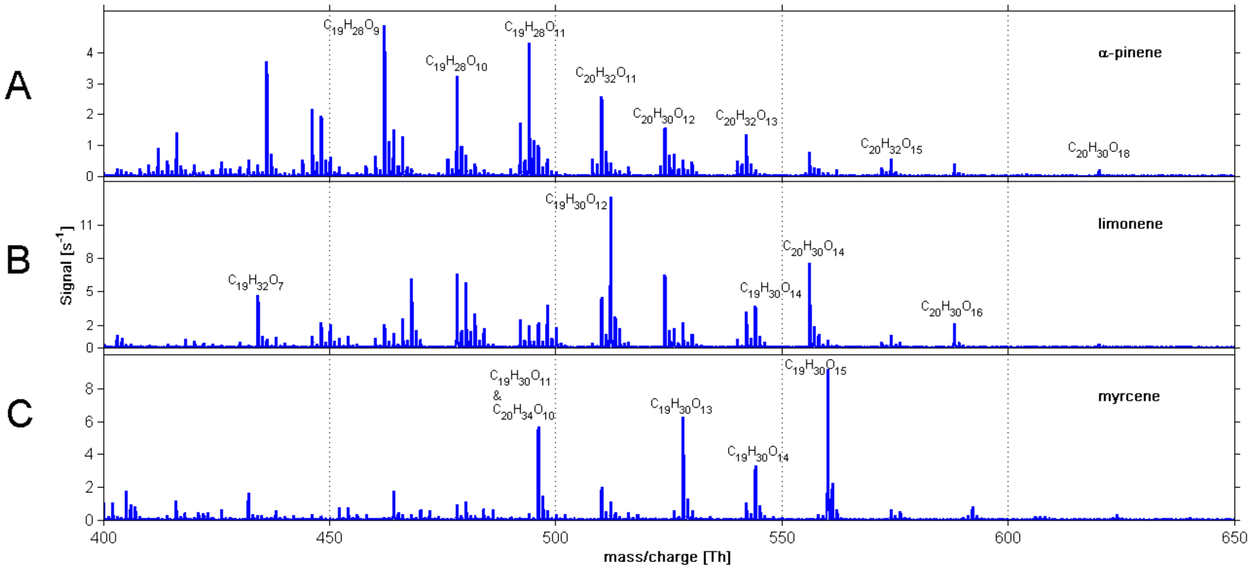

Figure S2. Dimer (~C_{20}) spectral “fingerprints” for the studied monoterpenes, A) α-pinene, B) limonene and C) myrcene. β-pinene is not shown in this figure because of the low intensities of mass spectrum peaks. Isoprene dimer region is shown in figure S1E.

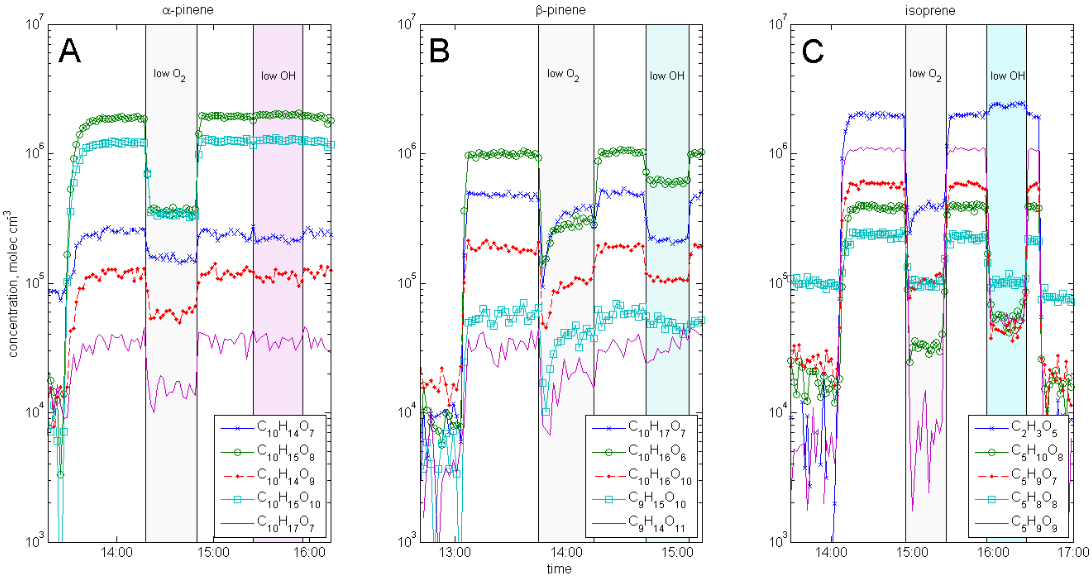

Figure S3. Effect of low oxygen level and OH scavenger (propane in pink or hydrogen in light blue) on ELVOC production during ozonolysis of A) α-pinene, B) β-pinene and C) isoprene. During low-oxygen experiments ELVOC formation is significantly suppressed as O_2 addition to the intermediate reaction products becomes slower, as also seen in figure 1 in the main text. During α-pinene oxidation only a few ELVOC species are affected by OH scavenging (light blue: propane, light red: hydrogen) illustrating that ozonolysis is the main pathway for ELVOC formation in our experiment. In the case of β-pinene and isoprene, a clear decrease in total ELVOC concentration was observed upon OH scavenging demonstrating the role of OH oxidation as the main ELVOC formation pathway.

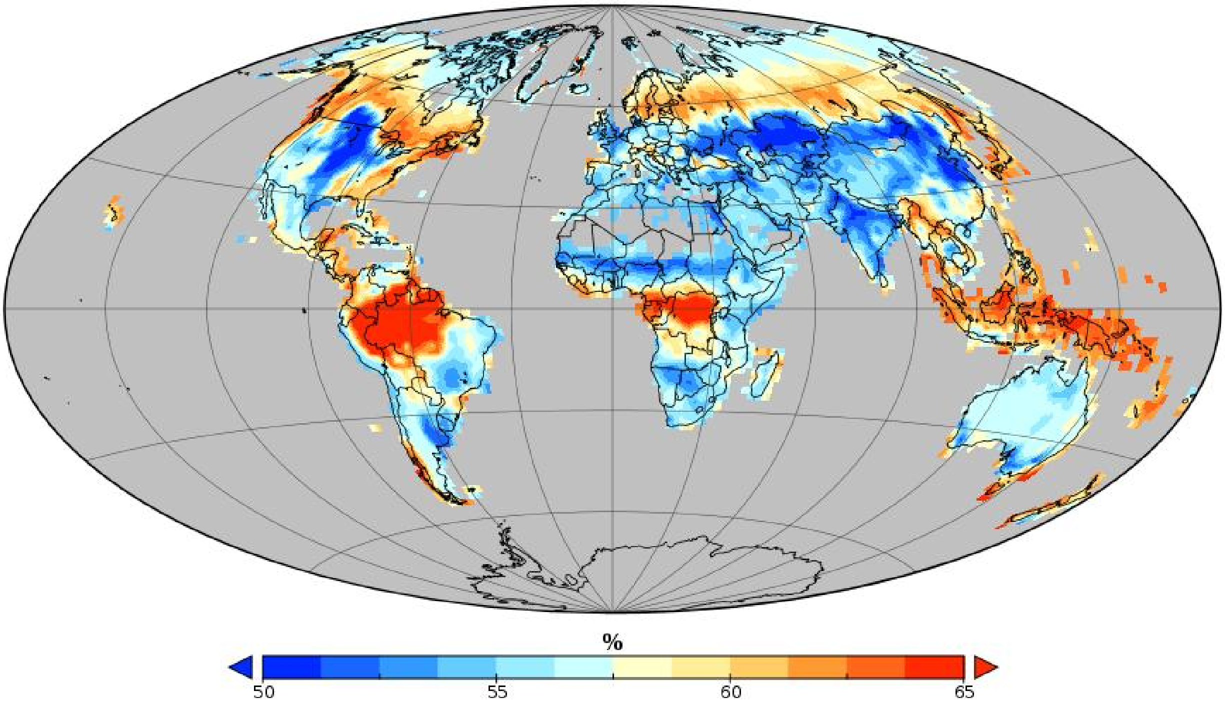

Figure S4. Fraction of endocyclic monoterpenes from total monoterpene emission averaged over June.