Supporting information of

# *Volatile organic compounds from logwood combustion: Emissions and transformation under dark and photochemical aging conditions in a smog chamber*

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## Section S1. Experimental setup

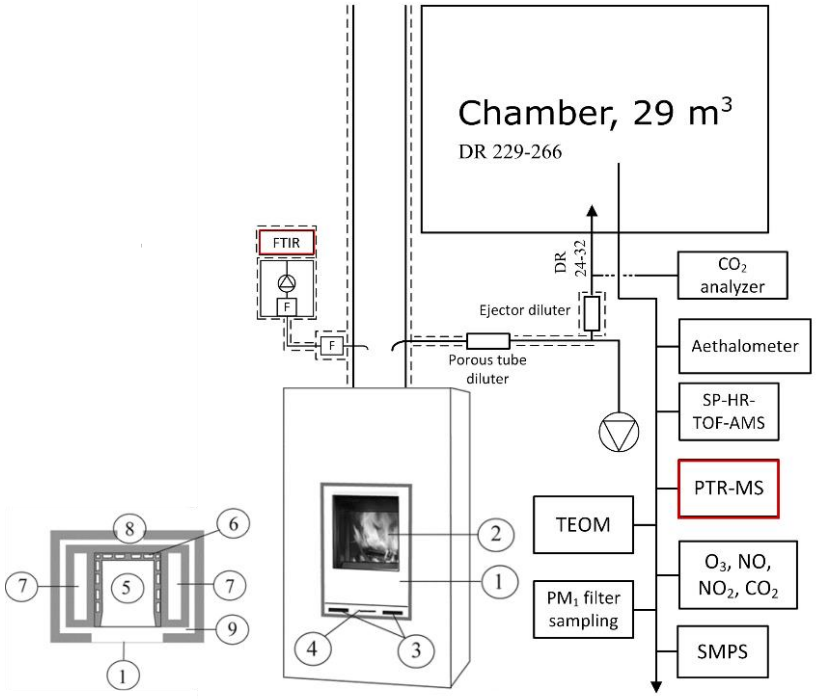


**Figure S1.** Experimental setup, with instruments measuring VOCs highlighted and the dilution ratio (DR) in the sampling line and chamber shown. The modern masonry heater is portrayed from both front and above: 1) door, 2) double glazed window; 3) air intakes; 4) adjusting of air; 5) firebox, primary air from the bottom (rift grate); 6) secondary air panels (ceramic elements); 7) flue gas ducts; 8) exhaust gas out; 9) insulated space.

The combustion cycle was divided into three parts based on the concentrations of $O_2$, and $CO_2$ (Figure S2), which were measured with FTIR from the raw exhaust in the stack.

1) ignition; from firing until the amount of oxygen is at its lower limit
2) 'stable' phase; From end of ignition until $CO_2 < 4\%$
3) burnout; from the end of stable phase to the end of combustion (35 min).

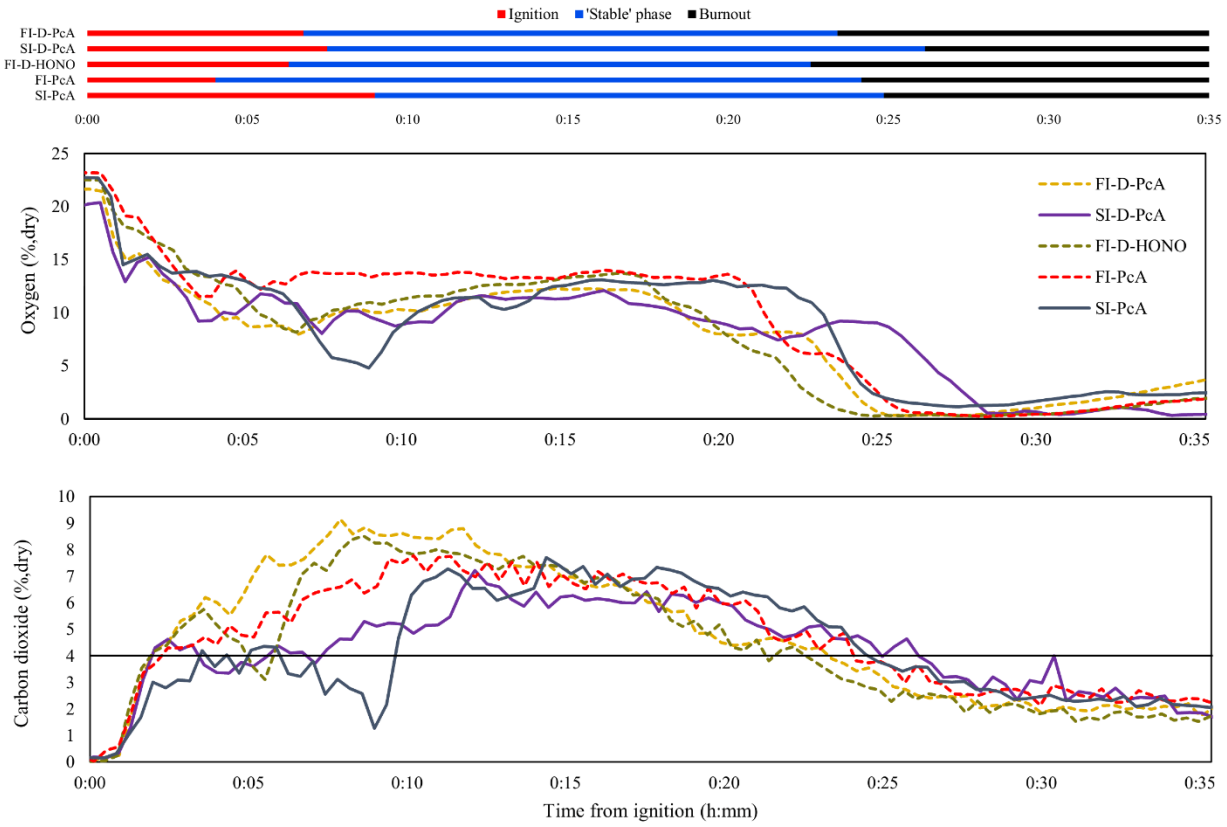


**Figure S2**. Progression of the combustion cycle and levels of oxygen and carbon dioxide, measured with FTIR from the flue gas in the stack. Burnout phase starts when $CO_2$ is below the 4% level.

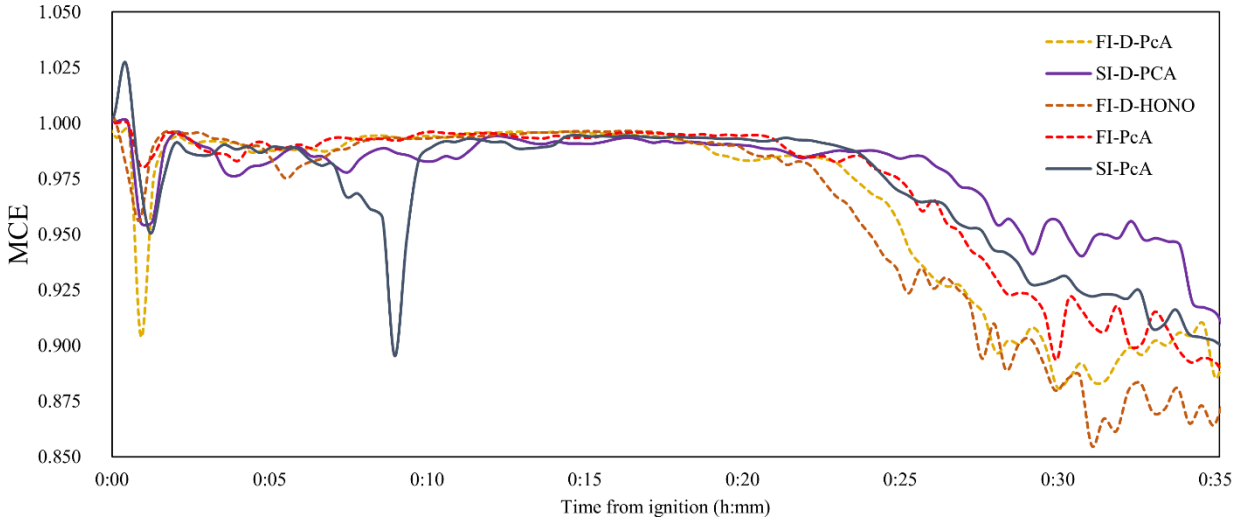


**Figure S3.** Modified combustion efficiency (MCE, $CO_2$ / ($CO_2$+CO), measured from the flue gas with FTIR) during combustion cycle.

# Section S2. PTR-MS measurements

## S2.1. Calibration

Transmission calibration of the PTR-MS was done using a mixture of eight VOCs (benzene, toluene, styrene, o-xylene, chlorobenzene, 1,3,5-trimethyl benzene, p-dichlorobenzene, 1,2,4-trichlorobenzene). The variety of the VOCs measured from combustion prevents calibration towards all of the measured VOCs, but the transmission curve enabled precise definition of the relative transmission efficiencies of $H_3O^+$ and $MH^+$-ions through the drift tube and the mass spectrometer.

The measurement error was examined based on the transmission gas and the benzene, toluene, styrene and xylenes in the exhaust: the transmission calibration provided ratios for the normalized counts per second (ncps) per ppb. Comparison to the transmission calibrated ncps $ppb^{-1}$ values revealed a 20-40% uncertainty in the measured concentrations. Reaction rates of compounds with $H_3O^+$ were based on the rates by Cappellin et al.[1] at E/N 120, while in our experiment the E/N was slightly higher (132 Td). The reaction rates may be slightly lower at higher E/N, which may correspondingly have led to underestimation of concentrations in our experiments.

Mass calibration was done using $H_3O^+$ (m/z 21.0226) and $NO^+$ (m/z 29.998). We compared the measured m/z to the calculated m/z of monoterpenes (m/z 137.129 to m/z 137.133) and nitrophenols (m/z 149.031 to m/z 140.035). The shift in m/z (~0.004) is minor, which ensures that the mass calibration was sufficient also for larger compounds.

## S2.2. Fragmentation

PTR is a soft ionization technique, and for most compounds (M) the protonation forms $MH^+$ ions. However, for some compounds fragmentation remains a possibility. $H_2O$-scission, i.e., dehydration, and dissociation during proton transfer reactions are sensitive to the E/N ratio, which in our experiments was high enough (132 Td) to enhance fragmentation. However, sufficiently high E/N was needed to prevent formation of water clusters in the PTR-MS drift tube, as the amount of water vapor was also high.[1]

Fragmentation complicates assessment of e.g. alkene concentrations, as many common fragment ions for long chain alkanes as well as dehydration products of alcohols and aldehydes are at m/z 41 ($C_3H_5^+$, otherwise allocated to propadiene), m/z 43 ($C_3H_7^+$, propene), and m/z 57 ($C_4H_{11}^+$, butane).[2, 3] Moreover, concentrations of benzene and toluene may be overestimated due to dissociative fragmentation of alkylbenzenes and monoaromatics: Jobson et al.[4] estimate that benzene may be

overestimated by 16%, mainly due to ethylbenzene fragmentation. This overestimation would, correspondingly, underestimate the total concentration of aromatic compounds.

Assessing fragmentation in the highly complicated mixture from combustion is problematic, especially as fragmentation patterns depend on instrument conditions. However, the effect of fragmentation is estimated to be minor, and accounting for unknown fragmentation patterns of the numerous ions is not within the scope of this work. Thus, corrections were applied only to monoterpenes, which fragment notably in a terpene-dependent pattern, primarily into m/z 81.[5] For this study, we used a correction factor of 2.1 for the monoterpene parent ion, m/z 137.12, based on previously assessed fragmentation of α-pinene in the instrument in use.

### S2.3. PTR-MS spectra

The PTR-MS measured the concentrations in the chamber throughout the experiments. To account for the background levels in the chamber, the PTR measurement was initiated before input of any exhaust or additional gases. Spectra (Fig. S3) and the presented emission factors and concentrations are background corrected, and the full list of observed ions is available in Table S4.

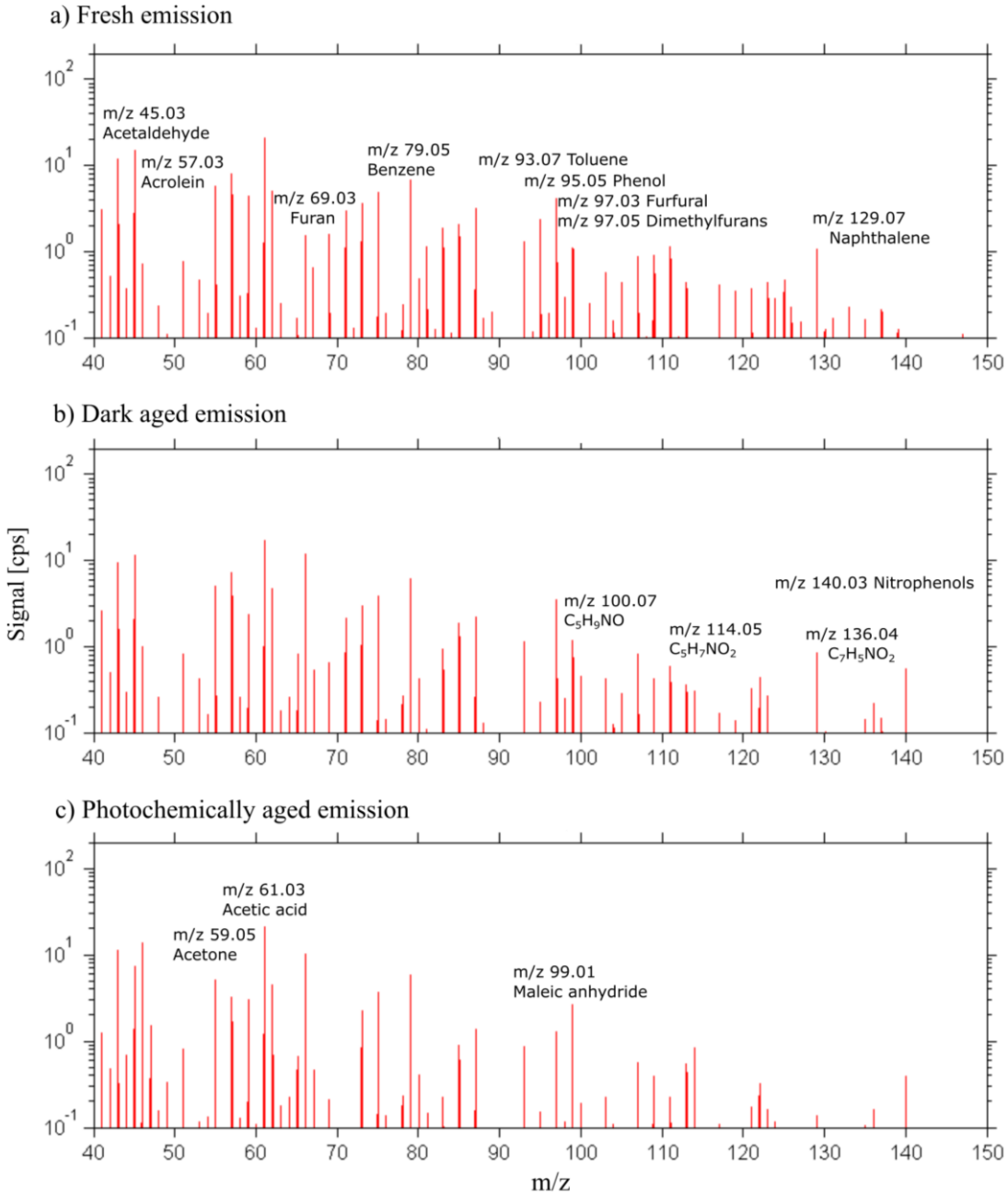


**Figure S4**. Background-corrected PTR-MS spectra from SI-D-PcA a) for fresh emission after stabilization, b) during 4th hour of dark aging, and c) during 3rd hour of photochemical aging.

## Section S3. Estimating SOA yields

The two-product model, presented by Odum et al.[6], estimates the formation of SOA based on the initial concentration of seed particles ($M_0$) and partitioning of the products (produced in portions $\alpha_1$ and $\alpha_2$) between gaseous and particulate phases (eq. S1).

$$Y = \frac{\Delta M_0}{\Delta VOCs} = M_0 * \left(\frac{\propto_1 K_1}{1+K_1 M_0} + \frac{\propto_2 K_2}{1+K_2 M_0}\right) \quad \text{(S1)}$$

The two-product parameters used for achieving SOA yields in the experimental conditions in the chamber are presented in Table S1. The yield estimate for monoterpenes is based on the distribution of isotopes in spruce combustion.[7] The yields in Table S2 were utilized for seven isotopes; for the remaining ~26% of monoterpenes a yield of 20% was used in dark conditions, based on the lower limit by Ng et al.[8] In photochemical aging conditions the yield used for other monoterpenes was 37%, the average of the yields in Lee et al.[9]

**Table S1.** Two-product parameters used for SOA yield estimations.

| Precursor | $\alpha_1$ | $K_1$ | $\alpha_2$ | $K_2$ | Reference |
|---|---|---|---|---|---|
| Benzene | 0.072 | 3.315 | 0.888 | 0.009 | Ng et al.[10] |
| Naphthalene | 0.144 | 2.9 | 30 | 0.226 | Barsanti et al.[11] |
| Biomass POA | 0.228 | 1.6 | 69 | 0.473 | Barsanti et al.[11] |

**Table S2.** The SOA yields applied for monoterpenes under dark conditions ($NO_3$ yield) and photochemical conditions (OH yield).

| | | $NO_3$ yield | | Ref. | OH yield[9] |
|---|---|---|---|---|---|
| Compound | Portion* | FI-D-HONO | SI-D-PcA | | |
| α-Pinene | 10% | 7% | 7% | Hallquist et al.[12] | 32% |
| Camphene | 27% | 20% | 20% | Ng et al.[8] | 37% |
| Sabinene | 1% | 35% | 35% | Fry et al.[13] | 37% |
| β-Pinene | 5% | 53% | 53% | Nah et al.[14] | 37% |
| β-Myrcene | 8% | 20% | 20% | Ng et al.[8] | 43% |
| 3-Carene | 8% | 63% | 63% | Fry et al.[13] | 38% |
| Limonene | 14% | 51% | 51% | Hallquist et al.[12] | 58% |

*Isotopes portion of the monoterpenes emitted from spruce combustion.[7]

## Section S4. FTIR measurements

The Fourier Transform Infrared Spectrometer (FTIR, Gasmet Technologies Inc.) measured the compounds specified in Table S3 directly from the fresh exhaust gas. The time series of the emission of non-methane organic gases, i.e., compounds 14-40 of Table S3, are shown in Figure S5 and their emission factors in Figure S6.

**Table S3.** Gaseous compounds measured with FTIR.

| | APP-153 Calibrations | 1/1/2005 | | | | | |
|---|---|---|---|---|---|---|---|
| | *Gas* | *Formula* | *CAS* | *Range 1* | *Unit* | *Range 2* | *Unit* |
| 1 | Water vapour | H2O | 7732-18-5 | 30 | % | | |
| 2 | Carbon dioxide | CO2 | 124-38-9 | 25 | % | | |
| 3 | Carbon monoxide | CO | 630-08-0 | 5000 | ppm | 2 | % |
| 4 | Nitrous oxide | N2O | 10024-97-2 | 200 | ppm | | |
| 5 | Nitrogen monoxide | NO | 10102-43-9 | 1000 | ppm | | |
| 6 | Nitrogen dioxide | NO2 | 10102-44-0 | 200 | ppm | | |
| 7 | Sulphur dioxide | SO2 | 7446-09-5 | 1000 | ppm | | |
| 8 | Carbonyl sulfide | COS | 463-58-1 | 100 | ppm | | |
| 9 | Ammonia | NH3 | 7664-41-7 | 500 | ppm | | |
| 10 | Hydrogen chloride | HCl | 7647-01-0 | 200 | ppm | | |
| 11 | Hydrogen cyanide | HCN | 74-90-8 | 100 | ppm | | |
| 12 | Hydrogen fluoride | HF | 7664-39-3 | 100 | ppm | | |
| 13 | Methane | CH4 | 74-82-8 | 1000 | ppm | | |
| 14 | Ethane | C2H6 | 74-84-0 | 200 | ppm | | |
| 15 | Propane | C3H8 | 74-98-6 | 200 | ppm | | |
| 16 | Butane | C4H10 | 106-97-8 | 200 | ppm | | |
| 17 | Pentane | C5H12 | 109-66-0 | 200 | ppm | | |
| 18 | Hexane | C6H14 | 110-54-3 | 200 | ppm | | |
| 19 | Heptane | C7H16 | 142-82-5 | 200 | ppm | | |
| 20 | Octane | C8H18 | 111-65-9 | 200 | ppm | | |
| 21 | Acetylene | C2H2 | 74-86-2 | 200 | ppm | | |
| 22 | Ethylene | C2H4 | 74-85-1 | 200 | ppm | | |
| 23 | Propene | C3H6 | 115-07-1 | 200 | ppm | | |
| 24 | 1,3-Butadiene | C4H6 | 106-99-0 | 200 | ppm | | |
| 25 | Benzene | C6H6 | 71-43-2 | 200 | ppm | | |
| 26 | Toluene | C7H8 | 108-88-3 | 200 | ppm | | |
| 27 | m-Xylene | C8H10 | 108-38-3 | 200 | ppm | | |
| 28 | o-Xylene | C8H10 | 95-47-6 | 200 | ppm | | |
| 29 | p-Xylene | C8H10 | 106-42-3 | 200 | ppm | | |
| 30 | 1,2,3-Trimethylbenzene | C9H12 | 526-73-8 | 200 | ppm | | |
| 31 | 1,2,4-Trimethylbenzene | C9H12 | 95-63-6 | 200 | ppm | | |
| 32 | 1,3,5-Trimethylbenzene (Mesitylene) | C9H12 | 108-67-8 | 200 | ppm | | |
| 33 | Formic acid | CH2O | 64-18-6 | 200 | ppm | | |
| 34 | Acetic acid | C2H4O2 | 64-19-7 | 200 | ppm | | |
| 35 | Formaldehyde | CH2O | 50-00-0 | 200 | ppm | | |
| 36 | Acetaldehyde | C2H4O | 75-07-0 | 200 | ppm | | |
| 37 | Methanol | CH3OH | 67-56-1 | 500 | ppm | | |
| 38 | Ethanol | C2H5OH | 64-17-5 | 500 | ppm | | |
| 39 | Propanol | C3H7OH | 71-23-8 | 500 | ppm | | |
| 40 | Methyl tertiary butyl ether (MTBE,tert-Butyl methyl ether) | C5H12O | 1634-04-4 | 200 | ppm | | |

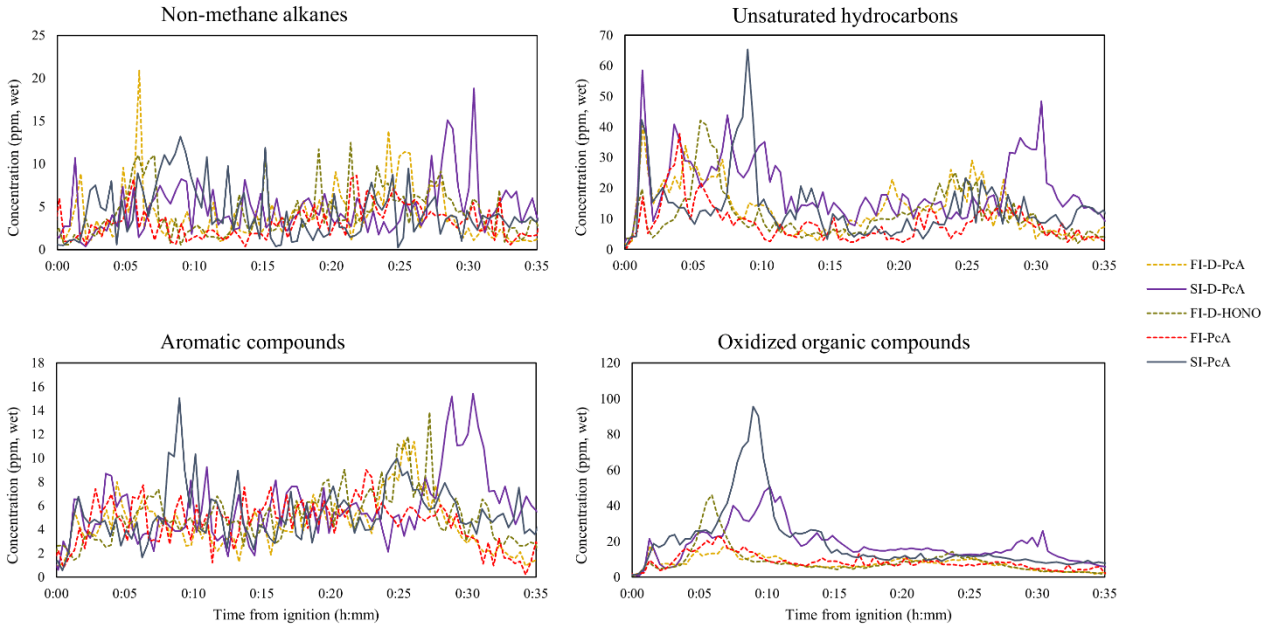


**Figure S5.** Emissions of volatile organic compounds measured with FTIR from the stack during combustion of a spruce batch, from cold start to burnout. Slow ignition experiments are marked with continuous lines, fast ignition experiments with dotted lines.

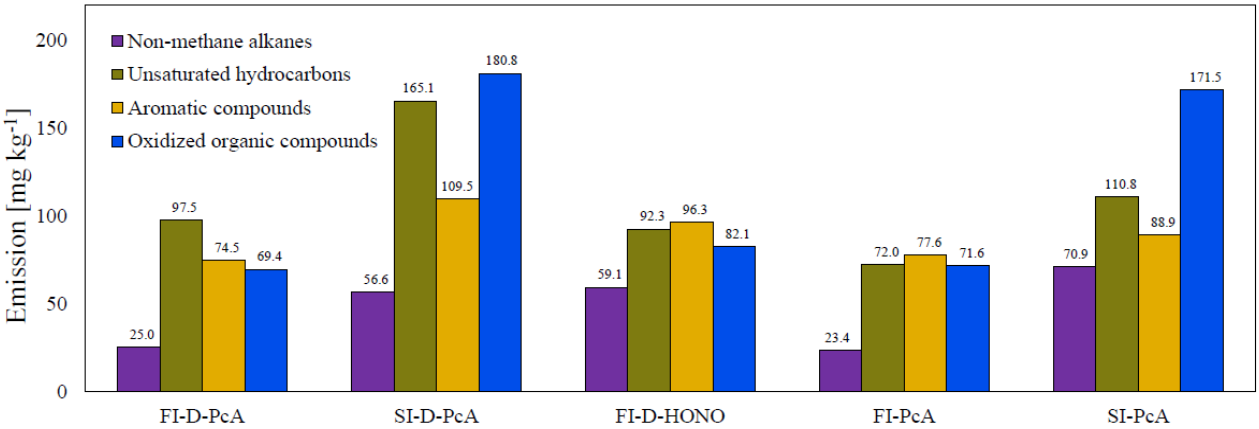


**Figure S6.** Average non-methane VOC emission factors of a full batch, as measured with FTIR from the stack during the 35-minute combustion period.

## Section S5. Conditions in the chamber during experiments

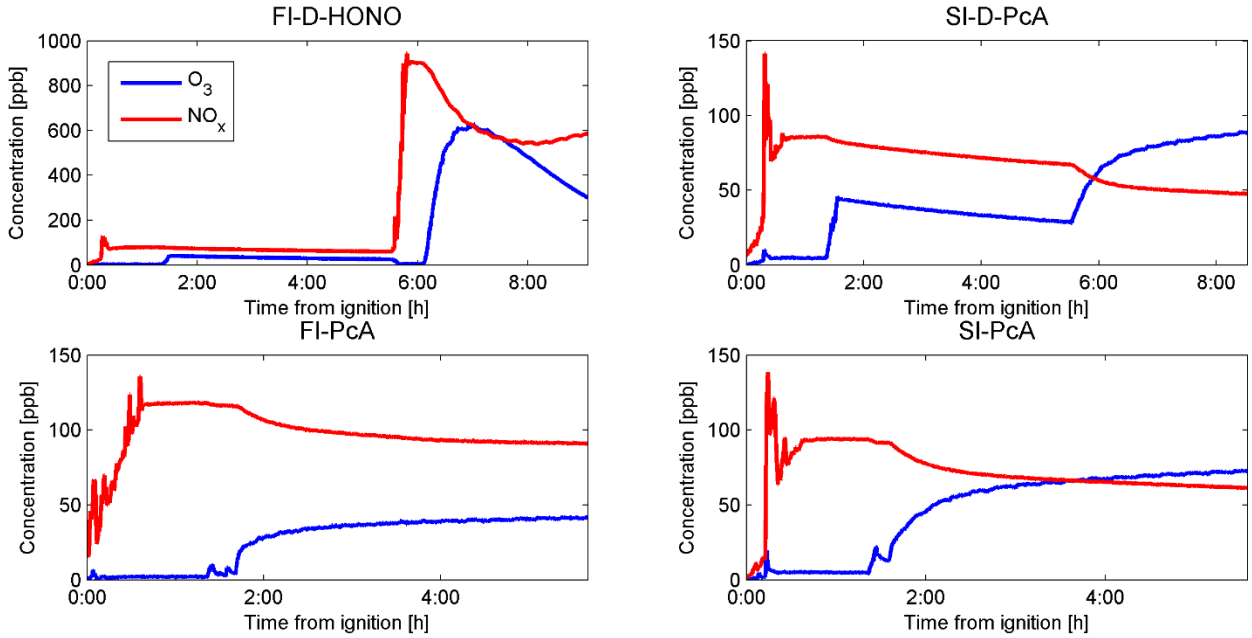


**Figure S7.** Levels of $NO_x$ and $O_3$ in the chamber during experiments.

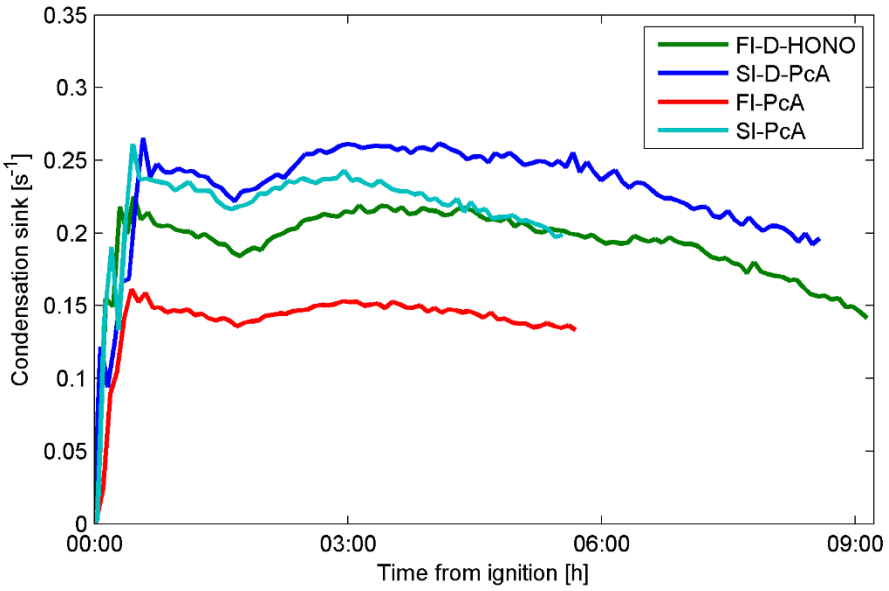


**Figure S8.** Condensation sink in the chamber during experiments.

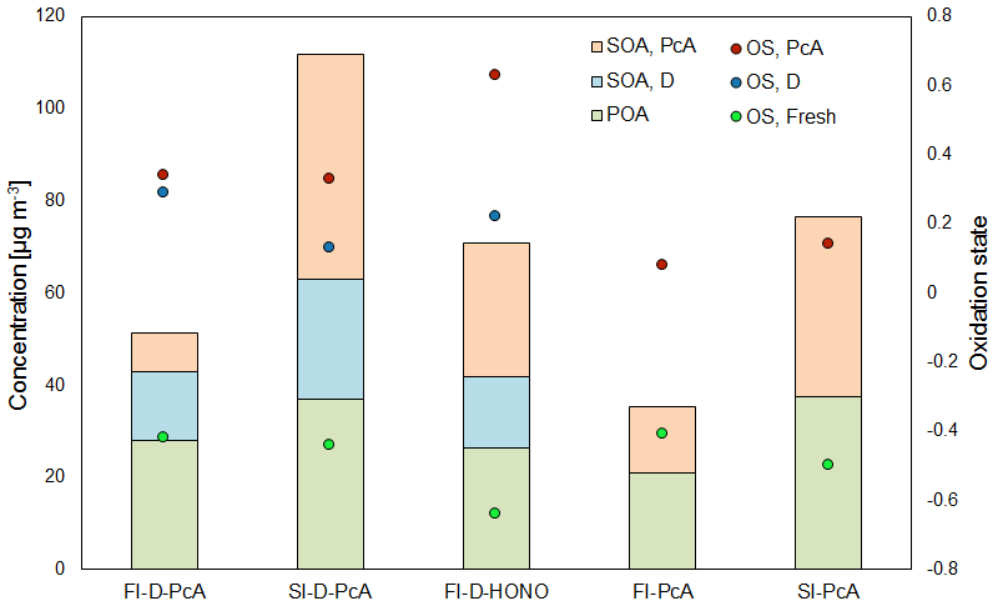


**Figure S9.** Concentrations of POA and SOA formed during dark (D) and photochemical (PcA) aging in the chamber (based on average concentrations of the last hour of exposure), and the oxidation states (OS) of OA at the end of each aging period. The results are based on AMS data, which have been previously published and discussed in depth by Tiitta et al.[15]

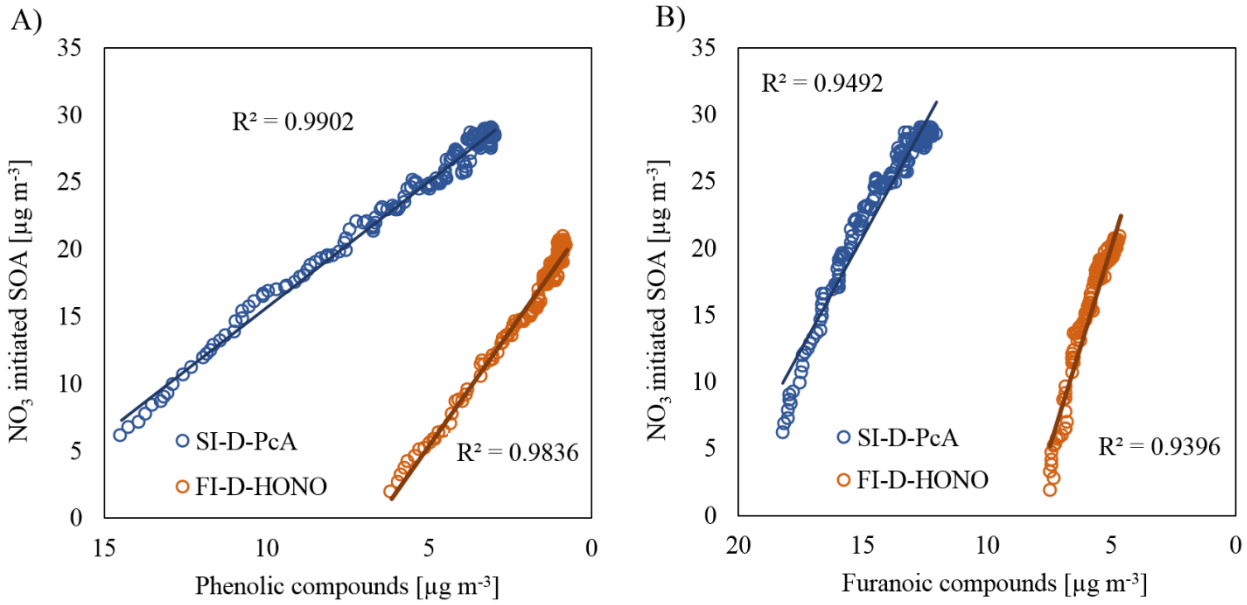


**Figure S10.** Correlation between the decaying concentrations of A) phenolic and B) furanoic compounds and the SOA assessed to be formed via $NO_3$ radical driven reactions during dark aging by Tiitta et al.[15]

## Section S6. Calculating the emission factors

The emission factors, i.e., the amount of emissions produced by a kilogram of fuel, were calculated by the procedure fully explained in e.g. Reda et al.[16] In short, the emission factors depend on

- the concentration of species in the flue gases ($c_n$)
- the air-to-fuel ratio ($\lambda$, eq. (S2)) during the combustion process

$$\lambda = \frac{20.9}{20.9 - O_2} \quad \text{(S2)}$$

- the fuel moisture factor (k), attained by eq. (S3), where the net heating value of dry fuel ($H_u$; 18.64 MJ kg$^{-1}$ for the dry spruce logs in use) is compared to the amount of energy consumed in evaporation of moisture of the fuel ($H_w$).

$$k = \frac{H_u}{H_u - H_w} \quad \text{(S3)}$$

$H_w$ depends on the mass ratio of water and dry matter in the fuel ($w_w$) and the evaporation heat of water ($l_w$ = 2.50 MJ kg$^{-1}$).

$$H_w = w_w * l_w \quad \text{(S4)}$$

- the dry volume of the flue gas produced in combustion of dry fuel ($Q_s$). For solid fuels, $Q_s$ = 0.25 m$^3$ MJ$^{-1}$

The total emission conversion factor used in converting the emissions from µg m$^{-3}$ to mg kg$^{-1}$ is

$$ECF = \lambda * k * Q_s\left(\frac{m^3}{MJ}\right) * H_u\left(\frac{MJ}{kg}\right) \quad \text{(S5)}$$

The emission factors are achieved with equation (S6).

$$EF\ (kg\ dry\ fuel^{-1}) = c_n(m^{-3}) * ECF(m^3\ kg^{-1}) \quad \text{(S6)}$$

## Section S7. Compound identification and changes during experiments

**Table S4.** Emission factors of the VOCs observed with PTR-MS during experiments, and the reaction rate (k-rate, in $10^{-9}$ cm $s^{-1}$) applied for each ion. Emission factors (mg $kg^{-1}$, see Section S6 for calculation procedure) are based on the background corrected initial concentrations measured from the chamber.

| | | | | Emission factors [mg $kg^{-1}$] | | | |
|---|---|---|---|---|---|---|---|
| m/z | Ion formula | Compound | k-rate | FI-D-HONO | FI-PcA | SI-D-PcA | SI-PcA |
| *Aromatic hydrocarbons* | | | | | | | |
| 79.05 | C6H6-H+ | Benzene | 1.93 | 14.3 | 10.5 | 22.3 | 14.6 |
| 93.07 | C7H8-H+ | Toluene | 2.00 | 2.7 | 2.0 | 5.0 | 3.5 |
| 105.07 | C8H8-H+ | Styrene | 2.27 | 0.9 | 0.7 | 1.7 | 1.3 |
| 107.08 | C8H10-H+ | Xylene or ethylbenzene | 2.26 | 0.6 | 0.5 | 1.3 | 1.0 |
| 129.07 | C10H8-H+ | Naphthalene | 2.45 | 3.2 | 2.4 | 5.5 | 4.3 |
| 131.06 | C10H10-H+ | Naphthalene dihydro-, 2-methylindene | 2.00 | 0.9 | 0.7 | 1.5 | 1.6 |
| 167.09 | C13H10-H+ | Fluorene | 2.00 | <0.5 | <0.4 | <0.5 | 0.5 |
| *Furanoic compounds* | | | | | | | |
| 69.03 | C4H4O-H+ | Furan | 1.70 | 2.0 | 1.4 | 4.9 | 5.1 |
| 83.05 | C5H6O-H+ | Methylfurans | 2.00 | 2.6 | 1.8 | 6.1 | 6.1 |
| 97.03 | C5H4O2-H+ | Furfural | 4.02 | 3.9 | 3.2 | 8.5 | 10.3 |
| 97.06 | C6H8O-H+ | Dimethyl- & ethyl furan | 2.00 | 1.1 | 0.9 | 2.5 | 2.9 |
| 99.04 | C5H6O2-H+ | Furfuryl alcohol | 2.00 | 2.1 | 1.8 | 4.1 | 5.3 |
| 125.02 | C6H4O3-H+ | 2,5-Furandicarboxaldehyde | 2.00 | 0.5 | 0.4 | 1.0 | 1.2 |
| 127.04 | C6H6O3-H+ | 5-Hydroxymethylfurfural | 2.00 | <0.5 | <0.4 | 0.7 | 0.9 |
| 119.05 | C8H6O-H+ | Benzofuran | 2.00 | 1.1 | 0.7 | 1.8 | 1.2 |
| *Phenolic compounds* | | | | | | | |
| 95.05 | C6H6O-H+ | Phenol | 2.18 | 5.2 | 3.7 | 9.3 | 6.4 |
| 109.06 | C7H8O-H+ | Cresols | 1.99 | 1.8 | 1.2 | 3.8 | 2.9 |
| 111.04 | C6H6O2-H+ | Benzenediols | 2.00 | 2.5 | 2.1 | 5.5 | 5.6 |
| 123.08 | C8H10O-H+ | Dimethylphenol | 2.00 | 0.6 | 0.4 | 1.4 | 1.3 |
| 125.06 | C7H8O2-H+ | Guaiacol | 2.00 | 0.9 | 0.8 | 2.5 | 2.9 |
| 139.07 | C8H10O2-H+ | Creosol, tyrosol | 2.00 | <0.4 | <0.3 | 0.9 | 1.3 |
| 153.05 | C8H8O3-H+ | e.g. Methoxy-benzoic acid | 2.00 | 0.4 | 0.4 | 0.9 | 0.9 |
| *Other oxygen containing aromatic compounds* | | | | | | | |
| 107.05 | C7H6O-H+ | Benzaldehyde | 3.82 | 1.1 | 0.9 | 2.0 | 1.3 |
| 109.03 | C6H4O2-H+ | Benzoquinone | 2.30 | 1.1 | 1.0 | 1.9 | 1.5 |
| 121.06 | C8H8O-H+ | Acetophenone | 3.48 | 0.6 | 0.5 | 1.1 | 0.9 |
| 123.04 | C7H6O2-H+ | Benzoic acid | 2.75 | 1.1 | 1.0 | 1.7 | 1.7 |
| 135.04 | C8H6O2-H+ | e.g. Isophthalaldehyde, phenylglyoxal | 2.00 | 0.5 | 0.5 | 0.9 | 0.8 |
| 137.06 | C8H8O2-H+ | e.g. Benzeneacetic acid , methyl-benzoic acid | 2.00 | 0.6 | 0.6 | 1.3 | 1.2 |
| *Carbonyls-A* | | | | | | | |
| 45.03 | C2H4O-H+ | Acetaldehyde | 3.12 | 8.1 | <28.4 | 17.3 | 18.6 |
| 57.03 | C3H4O-H+ | Acrolein | 3.55 | 4.5 | 3.6 | 9.4 | 8.6 |
| 71.02 | C3H2O2-H+ | Propiolic acid | 2.00 | <0.3 | 0.2 | 0.5 | 0.6 |
| 71.05 | C4H6O-H+ | Methyl vinyl ketone, methacrolein | 3.60 | 2.2 | 1.9 | 4.6 | 4.5 |
| 73.03 | C3H4O2-H+ | 2-Propenoic acid | 2.67 | 2.9 | 2.0 | 7.4 | 6.9 |
| 75.04 | C3H6O2-H+ | Hydroxy-2-propanone | 2.41 | 4.1 | <7.4 | 11.5 | 15.4 |
| 83.01 | C4H2O2-H+ | 3-Cyclobutene-1,2-dione | 2.00 | <0.3 | <0.2 | 0.4 | 0.4 |
| 85.06 | C5H8O-H+ | e.g. Pentenal | 2.00 | 1.3 | 1.0 | 2.4 | 3.2 |
| 87.04 | C4H6O2-H+ | e.g. 2,3- butadione | 1.70 | 6.1 | 5.1 | 13.5 | 18.9 |
| 101.06 | C5H8O2-H+ | e.g. 2,3-pentanedione | 2.00 | <1.0 | <0.8 | <1.6 | 3.2 |
| 103.04 | C4H6O3-H+ | Acetic anhydride | 2.00 | 1.1 | 0.9 | 2.6 | 3.1 |
| 103.07 | C5H10O2-H+ | e.g. Methyl-butanoic acid or pentanoic acid | 2.00 | <0.4 | <0.4 | <0.4 | 0.3 |
| 117.05 | C5H8O3-H+ | e.g. Acetyloxypropanone | 2.00 | 0.9 | 0.7 | 2.2 | 2.3 |

Table S4 - continued

| m/z | Ion formula | Compound | k-rate | Emission factors [mg kg$^{-1}$] FI-D-HONO | FI-PcA | SI-D-PcA | SI-PcA |
|---|---|---|---|---|---|---|---|
| *Carbonyls-B* | | | | | | | |
| 59.05 | C3H6O-H+ | Acetone | 3.21 | 3.5 | <6.3 | 6.9 | 8.2 |
| 61.03 | C2H4O2-H+ | Acetic acid, glycolaldehyde | 2.32 | 19.6 | 21.4 | 41.5 | 47.6 |
| 73.06 | C4H8O-H+ | 2-butanone and 2-methylpropanal | 3.23 | <0.7 | <0.5 | <0.8 | 1.4 |
| 77.02 | C2H4O3-H+ | Acetic acid, hydroxy- | 2.00 | <0.2 | <0.2 | <0.3 | <0.1 |
| 89.06 | C4H8O2-H+ | Acetoin | 4.30 | <0.3 | <0.3 | 0.4 | 0.9 |
| 91.04 | C3H6O3-H+ | e.g. lactic acid | 2.00 | <0.1 | <0.3 | 0.2 | 0.2 |
| 99.01 | C4H2O3-H+ | Maleic anhydride | 2.00 | 2.4 | 3.1 | 4.3 | 4.1 |
| 101.02 | C4H4O3-H+ | Succinic anhydride | 2.00 | <1.4 | <1.0 | <2.3 | <0.7 |
| 105.03 | C4H8O3-H+ | e.g. Acetic acid, methoxy- | 2.00 | <0.3 | <0.3 | <0.5 | 0.2 |
| *CHN* | | | | | | | |
| 42.03 | C2H3N-H+ | Acetonitrile | 2.00 | 0.6 | 0.6 | 0.8 | 0.6 |
| 54.03 | C3H3N-H+ | Propenenitrile | 2.00 | 0.3 | 0.3 | 0.4 | 0.3 |
| 104.04 | C7H5N-H+ | Benzonitrile | 2.00 | 0.5 | 0.5 | 0.7 | 0.7 |
| 133.06 | C8H8N2-H+ | n.i. | 2.00 | 0.8 | 0.5 | 1.3 | 1.0 |
| *CHNO, m/z < 100* | | | | | | | |
| 44.01 | HCNO-H+ | Isocyanic acid | 2.00 | 0.7 | 0.8 | 0.6 | 0.8 |
| 58.04 | C2H3NO-H+ | Methyl isocyanate | 2.00 | 0.3 | 0.3 | 0.7 | 0.7 |
| 60.05 | C2H5NO-H+ | e.g. Acetamide | 2.00 | <0.6 | <0.8 | <0.6 | 0.4 |
| 62.02 | CH3NO2-H+ | e.g. Methyl nitrite | 2.00 | 7.7 | 9.3 | 11.9 | 10.6 |
| 72.05 | C3H5NO-H+ | Methoxyacetonitrile or acrylamide | 2.00 | <0.2 | <0.2 | 0.4 | 0.4 |
| 76.05 | C2H5NO2-H+ | e.g. Nitroethane | 2.00 | 0.2 | <0.5 | 0.5 | 0.7 |
| 88.04 | C2H5N3O-H+ | or C3H5NO2-H+ | 2.00 | <0.3 | <0.3 | 0.6 | 0.8 |
| 96.05 | C5H5NO-H+ | Pyridine-N-oxide | 2.00 | 0.4 | 0.3 | 0.7 | 0.6 |
| 98.03 | C3H3N3O-H+ | 1H-Pyrazole, 4-nitro-1 | 2.00 | 0.5 | 0.5 | 1.1 | 1.4 |
| *CHNO, m/z > 100* | | | | | | | |
| 100.01 | C3HNO3-H+ | n.i. | 2.00 | <0.2 | <0.2 | <0.3 | 0.2 |
| 100.07 | C5H9NO-H+ | n.i. | 2.00 | <0.9 | <0.7 | <0.4 | <0.4 |
| 114.05 | C5H7NO2-H+ | n.i. | 2.00 | <1.6 | <1.2 | <0.9 | <0.6 |
| 122.02 | C6H3NO2-H+ | e.g. Oxo-furan-2-acetonitrile | 2.00 | 0.3 | 0.4 | 0.4 | 0.3 |
| 136.04 | C7H5NO2-H+ | e.g. 2-Furoylacetonitrile | 2.00 | 0.5 | 0.5 | 0.7 | 0.6 |
| 140.03 | C6H5NO3-H+ | Nitrophenols, Oxiniacic acid | 2.00 | 0.7 | 0.5 | 0.5 | 0.4 |
| 150.02 | C7H3NO3-H+ | e.g. 2,3-Pyridinedicarboxylic anhydride | 2.00 | <0.5 | <0.4 | <0.6 | 0.3 |
| 154.05 | C7H7NO3-H+ | e.g. Aminosalicylic Acid or 5-Nitro-o-cresol | 2.00 | 0.6 | 0.6 | 0.7 | 0.8 |
| *CHO* | | | | | | | |
| 33.03 | CH3OH-H+ | Methanol | 2.22 | 15.1 | 12.4 | 31.1 | 46.9 |
| 49.03 | CH4O2-H+ | Methyl peroxide or methanediol | 2.00 | <0.2 | <0.2 | 0.2 | 0.2 |
| 63.04 | C2H6O2-H+ | n.i. | 2.00 | <0.2 | <0.3 | 0.3 | 0.3 |
| 77.05 | C3H8O2-H+ | e.g. Ethanol 2-methoxy- | 2.00 | <0.1 | <0.2 | <0.3 | 0.1 |
| 81.03 | C5H4O-H+ | 2,4-Cyclopentadiene-1-one | 2.00 | 1.6 | 1.1 | 3.7 | 3.5 |
| 85.03 | C4H4O2-H+ | Furanone | 2.00 | 2.9 | 3.0 | 6.7 | 6.3 |
| 111.08 | C7H10O-H+ | e.g. Heptenedial or trimethylfuran | 2.00 | <0.4 | <0.4 | 0.7 | 1.3 |
| 113.02 | C5H4O3-H+ | e.g. 2-furoic acid | 2.00 | 0.9 | 1.1 | 2.1 | 1.8 |
| 113.06 | C6H8O2-H+ | eg. Methylcyclohexanone | 2.00 | 0.7 | 0.6 | 1.2 | 2.2 |
| 115.04 | C5H6O3-H+ | e.g. Hydroxymethylfuranone | 2.00 | <0.9 | <0.7 | <1.1 | 0.7 |
| 149.02 | C8H4O3-H+ | Phthalic anhydride | 2.00 | <1.9 | <1.3 | <2.8 | <0.3 |
| *Aliphatic hydrocarbons* | | | | | | | |
| 53.04 | C4H4-H+ | Butenyne | 2.00 | 0.4 | 0.3 | 0.9 | 0.7 |
| 67.05 | C5H6-H+ | 1,3-cyclopentadiene | 2.00 | 0.7 | 0.6 | 1.6 | 1.3 |
| 69.07 | C5H8-H+ | Isoprene | 1.96 | <0.5 | <0.3 | <0.6 | 1.0 |
| 81.07 | C6H8-H+ | e.g. Cyclohexa-1,3-diene; fragments | 2.00 | 0.4 | 0.3 | 1.1 | 1.6 |
| 137.13 | C10H16-H+ | Monoterpenes | 2.42 | 0.7 | 0.6 | 2.0 | 3.4 |

Table S4 - continued

| m/z | Ion formula | Compound | k-rate | Emission factors [mg kg$^{-1}$] FI-D-HONO | FI-PcA | SI-D-PcA | SI-PcA |
|---|---|---|---|---|---|---|---|
| *Other compounds* | | | | | | | |
| 31.02 | CH2O-H+ | Formaldehyde (unquantifiable) | 2.00 | 5.1 | 5.7 | 9.1 | 9.2 |
| 41.04 | C3H4-H+ | Propadiene, fragments | 2.00 | 3.0 | <1.9 | 6.2 | 5.4 |
| 42.01 | C2H2O+? | n.i. | 2.00 | 0.3 | 0.3 | 0.6 | 0.5 |
| 42.05 | C3H6+ | Fragments | 2.00 | <0.1 | <0.1 | 0.2 | 0.2 |
| 43.02 | C2H2O-H+ | Hexyl acetate; propanol fragment | 2.00 | 9.4 | 9.9 | 19.1 | 21.9 |
| 43.06 | C3H6-H+ | Propene; fragments | 2.00 | 2.1 | <2.2 | 3.6 | 3.3 |
| 44.02 | HN3+? | | 2.00 | <0.2 | <0.2 | 0.4 | 0.5 |
| 48.01 | | n.i. | 2.00 | <0.2 | 0.5 | 0.4 | 0.5 |
| 49.06 | | n.i.; product of photochemical aging | 2.00 | <0.1 | <0.1 | <0.1 | <0.1 |
| 51.04 | CO2H7+ | n.i.; proposed fragment | 2.00 | 0.7 | 0.6 | 1.4 | 2.2 |
| 57.07 | C4H8-H+ | Butene; fragments | 2.00 | <1.4 | <1.3 | <1.5 | 1.6 |
| 62.10 | | n.i.; product of photochemical aging | 2.00 | <0.1 | <0.1 | <0.1 | <0.1 |
| 65.09 | C2H10NO-H+ | n.i.; product of photochemical aging | 2.00 | <0.1 | <0.1 | <0.1 | <0.1 |
| 69.00 | C3O2-H+ | Carbon suboxide | 2.00 | <0.3 | <0.2 | <0.3 | 0.5 |
| 78.04 | C6H6+ | n.i.; proposed fragment | 2.00 | 0.6 | 0.4 | 0.8 | 0.5 |
| 80.06 | C6H8+ | n.i.; proposed fragment | 2.00 | 0.6 | 0.5 | 1.0 | 0.7 |
| 83.08 | C6H10-H+ | Fragment and e.g. fragmented hexenol (C6H12O-H2O) | 2.00 | <0.3 | <0.2 | <0.3 | 0.8 |
| 120.05 | | n.i. | 2.00 | 0.1 | 0.1 | 0.2 | 0.1 |

**Table S5.** Concentrations [ng m$^{-3}$] of nitrophenols in particulate phase in the chamber, measured from offline filter samples collected from fresh emission and at the end of dark (D) and photochemical aging (PcA). They were analyzed with in situ derivatization thermal desorption gas chromatography and time-of-flight mass spectrometry, with 4-nitrophenol d4 as the internal standard. RSD = relative standard deviation for each procedure.

| | | **FI-D-PcA** | | | **SI-D-PcA** | | | **FI-D-HONO** | | | **FI-PcA** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | RSD | Fresh | D | PcA | Fresh | D | PcA | Fresh | D | PcA | Fresh | PcA |
| 4-Nitrophenol | 9 % | < 71.6 | 10040 | 3650 | 822 | 5140 | 6190 | 2430 | 18090 | 3230 | 984 | 736 |
| 4-Nitrocresol | 10 % | < 217 | < 127 | < 81 | < 139 | < 127 | < 130 | < 217 | < 253 | < 127 | < 217 | < 127 |
| 2-Methoxy-4-nitrophenol | 9 % | 15390 | 13150 | < 26.7 | 1330 | 8920 | 31150 | 629 | 3170 | 411 | 1590 | 244 |
| 4-Nitrocatechol | 12 % | < 227 | < 133 | 1970 | < 146 | < 133 | < 136 | < 227 | < 265 | < 133 | < 227 | < 133 |
| 2,6-Dimethoxy-4-nitrophenol | 9 % | < 71.6 | < 41.8 | < 26.7 | < 45.8 | < 41.8 | < 42.8 | < 71.6 | < 83.5 | < 41.8 | < 71.6 | < 41.8 |

**Table S6.** Background concentrations in the chamber prior to the experiments, and the background corrected mass concentrations [μg $m^{-3}$] of compounds measured from PTR-MS in initial emissions, at the last hour of dark aging (D), and the last hour of photochemical aging (PcA)

| | | | Background concentrations [μg $m^{-3}$] | | | | FI-D-HONO Concentration [μg $m^{-3}$] | | | FI-PcA Concentration [μg $m^{-3}$] | | SI-D-PcA Concentration [μg $m^{-3}$] | | | SI-PcA Concentration [μg $m^{-3}$] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m/z | Ion formula | Compound | FI-D-HONO | FI-PcA | SI-D-PcA | SI-PcA | Initial | D | +HONO | Initial | PcA | Initial | D | PcA | Initial | PcA |
| *Aromatic hydrocarbons* | | | | | | | | | | | | | | | | |
| 79.05 | C6H6-H+ | Benzene | 0.3 | 0.2 | 0.3 | 0.2 | 8.8 | 8.0 | 9.3 | 6.9 | 6.2 | 15.1 | 14.0 | 13.4 | 11.0 | 9.8 |
| 93.07 | C7H8-H+ | Toluene | <0.1 | <0.1 | <0.1 | <0.1 | 1.6 | 1.4 | 1.3 | 1.3 | 1.0 | 3.4 | 3.1 | 2.3 | 2.6 | 1.8 |
| 105.07 | C8H8-H+ | Styrene | <0.1 | <0.1 | <0.1 | <0.1 | 0.5 | 0.4 | 0.1 | 0.5 | 0.1 | 1.2 | 0.8 | 0.1 | 0.9 | 0.1 |
| 107.08 | C8H10-H+ | Xylene or ethylbenzene | <0.1 | <0.1 | <0.1 | <0.1 | 0.4 | 0.3 | 0.3 | 0.3 | 0.2 | 0.9 | 0.8 | 0.4 | 0.8 | 0.4 |
| 129.07 | C10H8-H+ | Naphthalene | 1.3 | 1.0 | 2.5 | 0.7 | 2.0 | 1.3 | 1.1 | 1.6 | <0.4 | 3.7 | 2.5 | <0.6 | 3.3 | 1.2 |
| 131.06 | C10H10-H+ | Naphthalene dihydro-, 2-methylindene | 0.3 | 0.4 | 0.7 | 0.2 | 0.6 | <0.3 | 0.4 | 0.4 | <0.3 | 1.0 | <0.4 | <0.4 | 1.2 | 0.4 |
| 167.09 | C13H10-H+ | Fluorene | 0.4 | 0.3 | 0.5 | 0.3 | <0.3 | <0.3 | 1.6 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 0.4 | <0.2 |
| *Furanoic compounds* | | | | | | | | | | | | | | | | |
| 69.03 | C4H4O-H+ | Furan | 0.2 | 0.2 | 0.4 | 6.8 | 1.2 | 0.4 | 0.5 | 0.9 | 0.3 | 3.3 | 1.4 | 0.5 | 3.8 | 1.1 |
| 83.05 | C5H6O-H+ | Methylfurans | 0.3 | 0.2 | 0.6 | <0.1 | 1.6 | 0.9 | 0.6 | 1.2 | 0.3 | 4.1 | 2.2 | 0.5 | 4.6 | 0.9 |
| 97.03 | C5H4O2-H+ | Furfural | 0.4 | 0.4 | 0.4 | 1.1 | 2.4 | 1.9 | 1.0 | 2.1 | 0.9 | 5.8 | 5.0 | 1.8 | 7.8 | 2.6 |
| 97.06 | C6H8O-H+ | Dimethyl- & ethyl furan | 0.3 | <0.2 | 0.7 | 0.5 | 0.7 | 0.3 | <0.2 | 0.6 | <0.2 | 1.7 | 0.8 | <0.4 | 2.2 | 0.2 |
| 99.04 | C5H6O2-H+ | Furfuryl alcohol | 1.0 | 0.7 | 2.4 | <0.3 | 1.3 | 1.0 | <0.5 | 1.2 | <0.4 | 2.8 | 2.2 | <0.7 | 4.0 | 1.2 |
| 125.02 | C6H4O3-H+ | 2,5-Furandicarboxaldehyde | <0.1 | 0.3 | 0.5 | <0.1 | 0.3 | <0.3 | 0.3 | 0.3 | <0.3 | 0.7 | <0.4 | <0.4 | 0.9 | 0.3 |
| 127.04 | C6H6O3-H+ | 5-Hydroxymethylfurfural | 0.3 | 0.3 | 0.7 | <0.2 | <0.3 | <0.3 | 0.4 | <0.3 | <0.3 | 0.5 | <0.4 | <0.4 | 0.7 | 0.7 |
| 119.05 | C8H6O-H+ | Benzofuran | 0.3 | <0.1 | <0.1 | 0.2 | 0.7 | 0.2 | 0.2 | 0.5 | 0.1 | 1.2 | 0.5 | 0.1 | 0.9 | 0.2 |
| *Phenolic compounds* | | | | | | | | | | | | | | | | |
| 95.05 | C6H6O-H+ | Phenol | 0.9 | <0.9 | 0.9 | 0.5 | 3.2 | <0.8 | <0.8 | 0.8 | <0.9 | 6.3 | <0.8 | <0.8 | 4.8 | 0.9 |
| 109.06 | C7H8O-H+ | Cresols | <0.2 | <0.1 | <0.1 | <0.1 | 1.1 | <0.2 | <0.2 | 1.4 | 0.5 | 2.6 | 0.2 | <0.1 | 2.2 | 0.1 |
| 111.04 | C6H6O2-H+ | Benzenediols | 0.5 | 0.4 | 0.7 | 0.3 | 1.5 | 0.7 | 0.5 | 0.3 | <0.2 | 3.7 | 1.9 | 0.7 | 4.2 | 1.1 |
| 123.08 | C8H10O-H+ | Dimethylphenol | <0.2 | <0.2 | <0.3 | <0.1 | 0.4 | <0.2 | <0.2 | 0.5 | <0.2 | 0.9 | <0.3 | <0.3 | 1.0 | <0.1 |
| 125.06 | C7H8O2-H+ | Guaiacol | <0.3 | <0.2 | 0.4 | <0.2 | 0.5 | <0.3 | <0.3 | <0.2 | <0.2 | 1.7 | 0.3 | <0.3 | 2.2 | 0.3 |
| 139.07 | C8H10O2-H | Creosol, tyrosol | <0.3 | <0.2 | <0.4 | <0.1 | <0.3 | <0.3 | <0.3 | 0.3 | <0.2 | 0.6 | <0.4 | <0.4 | 1.0 | <0.1 |
| 153.05 | C8H8O3-H+ | e.g. Methoxy-benzoic acid | <0.2 | <0.2 | <0.3 | <0.1 | 0.3 | <0.2 | <0.2 | 2.4 | <0.2 | 0.6 | <0.3 | <0.3 | 0.7 | <0.1 |
| *Other oxygen containing aromatic compounds* | | | | | | | | | | | | | | | | |
| 107.05 | C7H6O-H+ | Benzaldehyde | <0.1 | <0.1 | <0.1 | <0.1 | 0.7 | 0.7 | 0.7 | 0.6 | 0.5 | 1.3 | 1.3 | 0.9 | 1.0 | 0.8 |
| 109.03 | C6H4O2-H+ | Benzoquinone | <0.2 | <0.2 | <0.3 | <0.1 | 0.7 | 0.6 | 1.0 | 0.7 | 0.6 | 1.3 | 1.1 | 1.0 | 1.1 | 0.8 |
| 121.06 | C8H8O-H+ | Acetophenone | <0.1 | <0.1 | <0.1 | <0.1 | 0.4 | 0.3 | 0.4 | 0.3 | 0.2 | 0.8 | 0.7 | 0.4 | 0.7 | 0.4 |
| 123.04 | C7H6O2-H+ | Benzoic acid | 0.4 | 0.3 | 0.9 | 0.2 | 0.7 | 0.5 | 1.3 | 0.7 | 0.5 | 1.1 | 0.8 | 0.5 | 1.3 | 1.1 |
| 135.04 | C8H6O2-H+ | e.g. Isophthalaldehyde, phenylglyoxal | 0.3 | <0.3 | <0.2 | <0.2 | 0.3 | <0.2 | <0.2 | 0.3 | <0.3 | 0.6 | 0.6 | 0.4 | 0.6 | 0.3 |
| 137.06 | C8H8O2-H+ | e.g. Benzeneacetic acid | <0.2 | <0.2 | <0.2 | <0.1 | 0.4 | 0.3 | 0.3 | 0.4 | <0.2 | 0.9 | 0.7 | 0.3 | 0.9 | 0.4 |
| *Carbonyls-A* | | | | | | | | | | | | | | | | |
| 45.03 | C2H4O-H+ | Acetaldehyde | 5.4 | <18.7 | 10.7 | 2.3 | 5.0 | 4.0 | 3292.1 | <18.7 | <18.7 | 11.7 | 9.8 | 6.5 | 14.0 | 13.0 |
| 57.03 | C3H4O-H+ | Acrolein | 0.6 | 0.8 | 1.3 | 0.3 | 2.8 | 2.5 | 51.5 | 2.4 | 1.3 | 6.3 | 5.9 | 2.7 | 6.5 | 3.9 |
| 71.02 | C3H2O2-H+ | Propiolic acid | <0.2 | 0.1 | 0.4 | <0.1 | <0.2 | <0.2 | 0.3 | 0.2 | <0.1 | 0.3 | <0.2 | <0.2 | 0.4 | 0.2 |
| 71.05 | C4H6O-H+ | Methyl vinyl ketone, methacrolein | 0.7 | 0.4 | 1.6 | 0.3 | 1.4 | 1.1 | 0.6 | 1.3 | 0.5 | 3.1 | 2.4 | <0.4 | 3.4 | 1.3 |
| 73.03 | C3H4O2-H+ | 2-Propenoic acid | 1.8 | 2.5 | 3.4 | 0.9 | 1.8 | 1.5 | 28.6 | 1.3 | <0.7 | 5.0 | 4.5 | 3.4 | 5.2 | 4.6 |
| 75.04 | C3H6O2-H+ | Hydroxy-2-propanone | 1.8 | 6.4 | 2.8 | 1.1 | 2.5 | 2.0 | 370.0 | <4.9 | <4.9 | 7.8 | 6.6 | 6.4 | 11.6 | 10.7 |
| 83.01 | C4H2O2-H+ | 3-Cyclobutene-1,2-dione | <0.2 | <0.1 | <0.2 | <0.1 | <0.2 | <0.2 | 0.4 | <0.1 | <0.1 | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 |
| 85.06 | C5H8O-H+ | e.g. Pentenal | 0.8 | 0.5 | 2.1 | 0.4 | 0.8 | <0.5 | <0.5 | 0.7 | <0.4 | 1.6 | 0.7 | <0.7 | 2.4 | 0.7 |
| 87.04 | C4H6O2-H+ | e.g. 2,3- butadione | 2.9 | 1.9 | 6.2 | 1.3 | 3.8 | 2.8 | 6.7 | 3.4 | 2.4 | 9.2 | 7.0 | 4.6 | 14.2 | 10.0 |
| 101.06 | C5H8O2-H+ | e.g. 2,3-pentanedione | 1.4 | 1.1 | 3.5 | 0.7 | <0.6 | <0.6 | 0.9 | <0.5 | <0.5 | <1.1 | <1.1 | <1.1 | 2.4 | 1.2 |
| 103.04 | C4H6O3-H+ | Acetic anhydride | 0.4 | 0.5 | 0.9 | 0.2 | 0.7 | 0.6 | 2.8 | 0.6 | 0.4 | 1.8 | 1.4 | 0.7 | 2.4 | 1.5 |
| 103.07 | C5H10O2-H | e.g. Methyl-butanoic acid | <0.2 | <0.3 | 0.4 | <0.2 | <0.2 | <0.2 | 0.5 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 0.2 | 0.3 |
| 117.05 | C5H8O3-H+ | e.g. Acetyloxypropanone | <0.3 | <0.3 | 0.5 | <0.2 | 0.6 | <0.3 | 0.9 | 0.5 | <0.3 | 1.5 | 0.6 | 0.4 | 1.7 | 1.0 |
| *Carbonyls-B* | | | | | | | | | | | | | | | | |
| 59.05 | C3H6O-H+ | Acetone | 3.6 | 5.6 | 7.0 | 1.7 | 2.1 | <1.6 | 127.0 | <4.1 | <4.1 | 4.6 | 3.1 | 3.6 | 6.2 | 7.4 |
| 61.03 | C2H4O2-H+ | Acetic acid, glycolaldehyde | 10.0 | 8.9 | 19.5 | 6.0 | 12.1 | 10.2 | 195.6 | 14.1 | 16.8 | 28.1 | 24.5 | 29.8 | 35.8 | 41.2 |
| 73.06 | C4H8O-H+ | 2-butanone and 2-methylpropanal | 1.2 | 0.6 | 2.9 | 0.3 | <0.4 | <0.4 | <0.4 | <0.3 | <0.3 | <0.5 | <0.5 | <0.5 | 1.1 | 1.2 |
| 77.02 | C2H4O3-H+ | Acetic acid, hydroxy- | <0.1 | <0.1 | <0.2 | <0.1 | <0.1 | <0.1 | 16.6 | <0.1 | <0.1 | <0.2 | <0.2 | <0.2 | <0.1 | 0.2 |
| 89.06 | C4H8O2-H+ | Acetoin | 0.3 | 0.2 | 0.6 | 0.1 | <0.2 | <0.2 | 0.5 | <0.1 | 0.1 | 0.2 | <0.2 | <0.2 | 0.7 | 0.7 |
| 91.04 | C3H6O3-H+ | e.g. lactic acid | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 2.0 | <0.1 | <0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 |
| 99.01 | C4H2O3-H+ | Maleic anhydride | 1.1 | 0.8 | 1.5 | 0.5 | 1.5 | 1.6 | 4.8 | 2.0 | 3.7 | 2.9 | 3.3 | 7.5 | 3.1 | 8.7 |
| 101.02 | C4H4O3-H+ | Succinic anhydride | 2.8 | 2.1 | 6.1 | 1.4 | <0.9 | <0.9 | 3.2 | <0.7 | <0.7 | <1.5 | <1.5 | <1.5 | <0.5 | 1.4 |
| 105.03 | C4H8O3-H+ | e.g. Acetic acid, methoxy- | 0.2 | 0.2 | 0.6 | <0.1 | <0.2 | <0.2 | 0.8 | <0.2 | <0.2 | <0.3 | <0.3 | <0.3 | 0.1 | 0.2 |
| *CHN* | | | | | | | | | | | | | | | | |
| 42.03 | C2H3N-H+ | Acetonitrile | <0.3 | <0.3 | <0.2 | 0.1 | 0.4 | 0.3 | 3.8 | 0.4 | 0.4 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 54.03 | C3H3N-H+ | Propenenitrile | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | 0.1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.2 | 0.2 | 0.3 | 0.2 |
| 104.04 | C7H5N-H+ | Benzonitrile | <0.1 | <0.1 | <0.1 | <0.1 | 0.3 | 0.2 | 5.8 | 0.4 | 0.3 | 0.5 | 0.4 | 0.4 | 0.5 | 0.4 |
| 133.06 | C8H8N2-H+ | n.i. | <0.1 | <0.1 | <0.1 | <0.1 | 0.5 | <0.1 | <0.1 | 0.4 | <0.1 | 0.9 | 0.3 | <0.1 | 0.8 | 0.1 |
| *CHNO, m/z < 100* | | | | | | | | | | | | | | | | |
| 44.01 | HCNO-H+ | Isocyanic acid | 0.6 | 0.5 | 1.0 | 0.5 | 0.4 | 0.4 | 4.7 | 0.5 | 1.1 | 0.4 | <0.4 | 0.8 | 0.6 | 1.3 |
| 58.04 | C2H3NO-H+ | Methyl isocyanate | 0.1 | 0.1 | 0.3 | 0.1 | 0.2 | 0.2 | 4.5 | 0.2 | 0.2 | 0.4 | 0.4 | 0.2 | 0.5 | 0.4 |
| 60.05 | C2H5NO-H+ | e.g. Acetamide | 0.5 | 0.7 | 1.0 | 0.5 | <0.4 | <0.4 | 8.0 | <0.5 | <0.5 | <0.4 | <0.4 | <0.4 | 0.3 | 0.5 |
| 62.02 | CH3NO2-H+ | e.g. nitromethane, methyl nitrite | 0.4 | 0.3 | 0.6 | 0.2 | 4.8 | 4.4 | 8.8 | 6.1 | 5.4 | 8.0 | 7.6 | 7.2 | 8.0 | 7.1 |
| 72.05 | C3H5NO-H+ | Methoxyacetonitrile or acrylamide | 0.2 | <0.1 | 0.3 | 0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.3 | 0.2 | <0.2 | 0.3 | 0.1 |
| 76.05 | C2H5NO2-H | e.g. Nitroethane | <0.1 | 0.3 | 0.2 | <0.1 | 0.1 | <0.1 | 16.5 | <0.3 | <0.3 | 0.4 | 0.3 | 0.3 | 0.5 | 0.5 |
| 88.04 | C2H5N3O-H+ | or C3H5NO2-H+ | 0.2 | 0.2 | 0.4 | 0.2 | <0.2 | <0.2 | 0.4 | <0.2 | <0.2 | 0.4 | 0.3 | <0.3 | 0.6 | 0.4 |
| 96.05 | C5H5NO-H+ | Pyridine-N-oxide | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | <0.1 | <0.1 | 0.2 | <0.1 | 0.5 | <0.1 | <0.1 | 0.4 | 0.1 |
| 98.03 | C3H3N3O-H | 1H-Pyrazole, 4-nitro-1 | <0.2 | <0.1 | <0.2 | <0.1 | 0.3 | 0.3 | 0.2 | 0.3 | 0.2 | 0.8 | 0.7 | 0.3 | 1.0 | 0.4 |

Table 6- continued

| m/z | Ion formula | Compound | Background concentrations [µg m$^{-3}$] FI-D-HONO | FI-PcA | SI-D-PcA | SI-PcA | FI-D-HONO Concentration [µg m$^{-3}$] Initial | D | +HONO | FI-PcA Concentration [µg m$^{-3}$] Initial | PcA | SI-D-PcA Concentration [µg m$^{-3}$] Initial | D | PcA | SI-PcA Concentration [µg m$^{-3}$] Initial | PcA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *CHNO, m/z > 100* | | | | | | | | | | | | | | | | |
| 100.01 | C3HNO3-H+ | n.i. | <0.2 | <0.1 | <0.2 | <0.1 | <0.2 | <0.2 | 0.3 | <0.1 | 0.2 | <0.2 | 0.2 | 0.4 | 0.1 | 0.5 |
| 100.07 | C5H9N3-H+ | n.i. | 0.7 | 0.6 | <0.3 | <0.3 | <0.5 | 0.9 | <0.5 | <0.5 | 0.5 | <0.3 | 1.3 | 0.6 | <0.3 | 0.9 |
| 114.05 | C5H7NO2-H | n.i. | 1.2 | 1.1 | 1.0 | 0.8 | <1.0 | <1.0 | 4.5 | <0.8 | 2.4 | <0.6 | 1.2 | 3.0 | <0.4 | 3.1 |
| 122.02 | C6H3NO2-H | e.g. Oxo-furan-2-acetonitrile | <0.1 | <0.2 | <0.2 | <0.1 | 0.2 | 0.8 | 41.8 | 0.3 | 0.4 | 0.3 | 1.8 | 1.5 | 0.2 | 0.8 |
| 136.04 | C7H5NO2-H | e.g. Furoylacetonitrile | <0.2 | 0.1 | <0.1 | <0.1 | 0.3 | 0.6 | 0.7 | 0.3 | 0.2 | 0.4 | 1.0 | 0.8 | 0.5 | 0.5 |
| 140.03 | C6H5NO3-H | Nitrophenols, Oxiniacic acid | <0.2 | <0.2 | <0.2 | <0.1 | 0.4 | 1.6 | 1.4 | 0.4 | 0.3 | 0.3 | 2.5 | 1.8 | 0.3 | 0.6 |
| 150.02 | C7H3NO3-H | e.g. Pyridinedicarboxylic anhydride | 0.4 | 0.3 | 1.1 | 0.2 | <0.3 | <0.3 | 0.7 | <0.2 | <0.2 | <0.4 | <0.4 | <0.4 | 0.2 | 0.3 |
| 154.05 | C7H7NO3-H | e.g. Nitrocresol | <0.2 | 0.2 | <0.2 | <0.1 | 0.4 | 0.6 | 0.7 | 0.4 | 0.2 | 0.5 | 1.2 | 0.8 | 0.6 | 0.5 |
| *CHO* | | | | | | | | | | | | | | | | |
| 33.03 | CH3OH-H+ | Methanol | 1.3 | 1.6 | 1.4 | 1.0 | 9.3 | 13.0* | 101.5 | 8.2 | 10.9* | 21.1 | 24.2* | 23.8 | 35.3 | 37.5* |
| 49.03 | CH4O2-H+ | Methyl peroxide or methanediol | <0.1 | <0.1 | 0.2 | <0.1 | <0.1 | <0.1 | 14.4 | <0.1 | <0.1 | 0.1 | <0.1 | 0.2 | 0.2 | 0.2 |
| 63.04 | C2H6O2-H+ | n.i. | <0.1 | <0.2 | <0.2 | <0.1 | <0.1 | <0.1 | 25.9 | <0.2 | <0.2 | 0.2 | <0.1 | <0.2 | 0.2 | 0.2 |
| 77.05 | C3H8O2-H+ | e.g. Ethanol 2-methoxy- | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 2.3 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.1 |
| 81.03 | C5H4O-H+ | 2,4-Cyclopentadiene-1-one | <0.2 | <0.2 | <0.2 | <0.2 | 1.0 | <0.2 | <0.2 | 0.7 | <0.2 | 2.5 | 0.2 | <0.2 | 2.7 | 0.1 |
| 85.03 | C4H4O2-H+ | Furanone | 0.7 | 0.5 | 1.2 | 0.3 | 1.8 | 1.7 | 1.4 | 2.0 | 1.2 | 4.5 | 4.4 | 2.2 | 4.7 | 3.0 |
| 111.08 | C7H10O-H+ | e.g. Heptenedial or trimethylfuran | 0.2 | <0.2 | 0.5 | <0.1 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | 0.5 | <0.4 | <0.4 | 1.0 | <0.1 |
| 113.02 | C5H4O3-H+ | e.g. 2-furoic acid | 0.8 | 0.6 | 1.2 | 0.3 | 0.6 | 0.6 | 1.9 | 0.7 | 1.1 | 1.4 | 1.3 | 2.0 | 1.4 | 2.7 |
| 113.06 | C6H8O2-H+ | eg. Methylcyclohexanone | 0.6 | 0.5 | 1.4 | 0.4 | 0.4 | <0.4 | <0.4 | 0.4 | <0.3 | 0.8 | <0.6 | <0.6 | 1.7 | 0.5 |
| 115.04 | C5H6O3-H+ | e.g. Hydroxymethylfuranone | 0.8 | 0.7 | 1.9 | 0.4 | <0.6 | <0.6 | 0.6 | <0.4 | <0.4 | <0.7 | <0.7 | <0.7 | 0.5 | 0.7 |
| 149.02 | C8H4O3-H+ | Phthalic anhydride | 3.7 | 2.4 | 10.8 | 1.8 | <1.2 | <1.2 | 3.5 | <0.9 | 1.1 | <1.9 | <1.9 | <1.9 | <0.3 | 1.7 |
| *Aliphatic hydrocarbons* | | | | | | | | | | | | | | | | |
| 53.04 | C4H4-H+ | Butenyne | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.6 | 0.6 | 0.2 | 0.5 | 0.2 |
| 67.05 | C5H6-H+ | 1,3-cyclopentadiene | <0.1 | <0.1 | 0.1 | <0.1 | 0.4 | <0.1 | 0.3 | 0.4 | <0.1 | 1.1 | 0.1 | <0.1 | 1.0 | <0.1 |
| 69.07 | C5H8-H+ | Isoprene | 0.7 | 0.4 | 1.0 | 0.3 | <0.3 | <0.3 | <0.3 | <0.2 | <0.2 | <0.4 | <0.4 | <0.4 | 0.8 | <0.2 |
| 81.07 | C6H8-H+ | e.g. Cyclohexa-1,3-diene; fragments | 0.1 | <0.1 | 0.2 | <0.1 | 0.2 | <0.1 | <0.1 | 0.2 | <0.13 | 0.7 | <0.2 | <0.2 | 1.2 | <0.1 |
| 137.13 | C10H16-H+ | Monoterpenes | <0.2 | <0.1 | <0.3 | <0.1 | 0.4 | <0.2 | <0.2 | 0.4 | <0.15 | 1.3 | <0.3 | <0.3 | 2.6 | <0.1 |
| *Other compounds* | | | | | | | | | | | | | | | | |
| 31.02 | CH2O-H+ | Formaldehyde (unquantifiable) | 1.5 | <2.5 | 3.4 | 0.7 | 3.2 | 3.0 | 481.6 | 3.8 | 4.1 | 6.1 | 5.8 | 7.1 | 6.9 | 8.1 |
| 41.04 | C3H4-H+ | Propadiene, fragments | 0.9 | <1.9 | 1.1 | 0.7 | 1.9 | 1.6 | 308.5 | <1.9 | <1.9 | 4.2 | 3.6 | 1.8 | 4.1 | 2.1 |
| 42.01 | C2H2O+? | n.i. | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 2.3 | 0.2 | 0.1 | 0.4 | 0.4 | 0.3 | 0.4 | 0.3 |
| 42.05 | C3H6+ | Fragments | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 19.7 | <0.1 | <0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 |
| 43.02 | C2H2O-H+ | Hexyl acetate; propanol fragment | 4.2 | 4.9 | 8.8 | 2.3 | 5.8 | 4.8 | 570.8 | 6.5 | 7.4 | 12.9 | 10.9 | 12.9 | 16.5 | 18.9 |
| 43.06 | C3H6-H+ | Propene; fragments | 0.4 | <2.2 | 0.8 | 0.2 | 1.3 | 1.1 | 550.1 | <2.2 | <2.2 | 2.4 | 2.0 | <0.3 | 2.5 | 0.9 |
| 44.02 | HN3+? | | <0.2 | 0.2 | 0.3 | 0.5 | <0.2 | <0.2 | 13.1 | <0.2 | <0.2 | 0.3 | 0.2 | 0.3 | 0.4 | 0.4 |
| 48.01 | | n.i. | <0.2 | <0.3 | <0.2 | <0.2 | <0.2 | 0.3 | 2.3 | 0.4 | <0.3 | 0.3 | 0.4 | <0.2 | 0.4 | <0.2 |
| 49.06 | | n.i.; product of photochemical aging | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.4 | <0.1 | <0.1 | 0.4 | <0.1 | 0.4 |
| 51.04 | CO2H7+ | n.i.; proposed fragment | <0.1 | <0.1 | <0.1 | <0.1 | 0.4 | 0.6 | 4.2 | 0.4 | 0.5 | 0.9 | 1.0 | 1.0 | 1.6 | 1.6 |
| 57.07 | C4H8-H+ | Butene; fragments | <1.4 | <1.3 | 1.6 | <0.4 | <1.4 | <1.4 | 2.5 | <1.3 | <1.3 | <1.5 | <1.5 | <1.5 | 1.2 | <0.4 |
| 62.10 | | n.i.; product of photochemical aging | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.7 | <0.1 | 0.9 | <0.1 | 0.1 | 1.0 | <0.1 | 1.0 |
| 65.09 | C2H10NO-H | n.i.; product of photochemical aging | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 | 0.6 | <0.1 | 0.1 | 0.7 | <0.1 | 0.7 |
| 69.00 | C3O2-H+ | Carbon suboxide | 0.4 | 0.3 | 0.6 | 0.2 | <0.3 | <0.3 | <0.3 | <0.2 | <0.2 | <0.3 | <0.3 | <0.3 | 0.3 | 0.2 |
| 78.04 | C6H6+ | n.i.; proposed fragment | <0.1 | <0.1 | <0.1 | <0.1 | 0.3 | 0.4 | 0.8 | 0.3 | 0.2 | 0.5 | 0.7 | 0.6 | 0.4 | 0.4 |
| 80.06 | C6H8+ | n.i.; proposed fragment | <0.1 | <0.1 | <0.1 | <0.1 | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.7 | 0.6 | 0.6 | 0.5 | 0.5 |
| 83.08 | C6H10-H+ | Fragment and e.g. fragmented hexenol | 0.4 | 0.3 | 0.5 | <0.1 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.3 | <0.3 | <0.3 | 0.6 | <0.1 |
| 120.05 | | n.i. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 12.6 | 0.1 | <0.1 | 0.1 | 0.1 | <0.1 | 0.1 | <0.1 |

*methanol increase during $O_3$ input; not from aging.

**Table S7.** Times where half of the change in ion concetration had taken place (t-50%s) during dark and photochemical aging. They were calculated for changes exceeding detection limit, and are presented as time in chamber (min), and for photochemical aging the corresponding time in atmospheric age (atm. h), assuming ambient OH concentration of 1E6 molec. $cm^{-3}$.

| | | | Dark aging | | Photochemical aging | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | FI-D-HONO | SI-D-PcA | FI-D-HONO | | SI-D-PcA | | FI-PcA | | SI-PcA | |
| m/z | Ion formula | Compound | [min] | [min] | [min] | [atm. h] | [min] | [atm. h] | [min] | [atm. h] | [min] | [atm. h] |
| *Aromatic hydrocarbons* | | | | | | | | | | | | |
| 79.05 | C6H6-H+ | Benzene | 25 | 11 | 40 | 3.1 | 25 | 6.5 | 8 | 3.3 | 16 | 3.8 |
| 93.07 | C7H8-H+ | Toluene | 37 | 6 | 15 | 2.0 | 24 | 6.8 | 14 | 3.6 | 23 | 5.1 |
| 105.07 | C8H8-H+ | Styrene | 67 | 77 | 15 | 1.7 | 9 | 2.7 | 11 | 3.0 | 11 | 2.6 |
| 107.08 | C8H10-H+ | Xylene or ethylbenzene | — | 5 | 17 | 2.8 | 22 | 6.0 | 28 | 6.6 | 23 | 5.4 |
| 129.07 | C10H8-H+ | Naphthalene | 33 | 30 | 6 | 1.5 | 15 | 4.2 | 22 | 5.9 | 21 | 4.9 |
| 131.06 | C10H10-H+ | Naphthalene dihydro-, 2-methylindene | 26 | 29 | 83 | 2.9 | 13 | 3.3 | 13 | 3.5 | 9 | 2.6 |
| 167.09 | C13H10-H+ | Fluorene | — | — | 47 | 2.7 | 25 | 6.4 | — | — | 27 | 5.9 |
| *Furanoic compounds* | | | | | | | | | | | | |
| 69.03 | C4H4O-H+ | Furan | 69 | 93 | 21 | 2.4 | 14 | 3.5 | 19 | 4.9 | 17 | 3.7 |
| 83.05 | C5H6O-H+ | Methylfurans | 22 | 29 | 36 | 2.6 | 17 | 4.5 | 15 | 3.7 | 14 | 3.6 |
| 97.03 | C5H4O2-H+ | Furfural | 49 | 26 | 28 | 2.0 | 15 | 4.1 | 18 | 5.2 | 18 | 3.4 |
| 97.06 | C6H8O-H+ | Dimethyl- & ethyl furan | 17 | 19 | 12 | 2.3 | 14 | 3.8 | 14 | 3.6 | 11 | 2.5 |
| 99.04 | C5H6O2-H+ | Furfuryl alcohol | 83 | 106 | 8 | 1.7 | 16 | 4.5 | 20 | 5.3 | 22 | 4.5 |
| 125.02 | C6H4O3-H+ | 2,5-Furandicarboxaldehyde | 54 | 35 | 16 | 2.1 | — | — | 34 | 6.0 | 20 | 5.4 |
| 127.04 | C6H6O3-H+ | 5-Hydroxymethylfurfural | — | 72 | 23 | 2.2 | — | — | — | — | 151 | 12.7 |
| 119.05 | C8H6O-H+ | Benzofuran | 73 | 101 | 134 | 2.7 | 10 | 3.6 | 18 | 5.3 | 16 | 4.2 |
| *Phenolic compounds* | | | | | | | | | | | | |
| 95.05 | C6H6O-H+ | Phenol | 44 | 68 | — | — | — | — | 11 | 3.0 | 11 | 2.6 |
| 109.06 | C7H8O-H+ | Cresols | 29 | 42 | — | — | 19 | 5.2 | 14 | 3.5 | 14 | 3.8 |
| 111.04 | C6H6O2-H+ | Benzenediols | 50 | 65 | 68 | 3.6 | 14 | 3.7 | 12 | 3.0 | 8 | 2.3 |
| 123.08 | C8H10O-H+ | Dimethylphenol | 21 | 30 | — | — | — | — | 17 | 4.6 | 16 | 3.8 |
| 125.06 | C7H8O2-H+ | Guaiacol | 23 | 28 | — | — | 31 | 6.9 | — | — | 13 | 3.3 |
| 139.07 | C8H10O2-H+ | Creosol, tyrosol | — | 24 | — | — | — | — | 9 | 3.5 | 21 | 5.3 |
| 153.05 | C8H8O3-H+ | e.g. Methoxy-benzoic acid | 34 | 44 | — | — | — | — | 16 | 4.6 | 16 | 3.8 |
| *Other oxygen containing aromatic compounds* | | | | | | | | | | | | |
| 107.05 | C7H6O-H+ | Benzaldehyde | — | — | 83 | 2.6 | 44 | 7.7 | — | — | 104 | 11.2 |
| 109.03 | C6H4O2-H+ | Benzoquinone | 43 | 28 | 11 | 2.4 | 11 | 3.9 | 16 | 4.6 | 23 | 5.0 |
| 121.06 | C8H8O-H+ | Acetophenone | 18 | 10 | 127 | 3.2 | 21 | 5.3 | 13 | 3.2 | 17 | 3.5 |
| 123.04 | C7H6O2-H+ | Benzoic acid | 25 | 59 | 37 | 2.9 | 21 | 5.5 | 19 | 5.3 | 27 | 6.0 |
| 135.04 | C8H6O2-H+ | e.g. Isophthalaldehyde, phenylglyoxal | 10 | 10 | — | — | 99 | 12.0 | 74 | 9.2 | 78 | 10.0 |
| 137.06 | C8H8O2-H+ | e.g. Benzeneacetic acid | 9 | 18 | 85 | 3.1 | 24 | 7.0 | 36 | 6.3 | 31 | 6.0 |
| *Carbonyls-A* | | | | | | | | | | | | |
| 45.03 | C2H4O-H+ | Acetaldehyde | 88 | 79 | 28 | 1.9 | 34 | 7.5 | — | — | 119 | 11.7 |
| 57.03 | C3H4O-H+ | Acrolein | 35 | 18 | 33 | 1.8 | 25 | 6.5 | 28 | 6.6 | 34 | 7.2 |
| 71.02 | C3H2O2-H+ | Propiolic acid | — | 54 | 20 | 2.3 | — | — | 13 | 3.5 | 26 | 5.6 |
| 71.05 | C4H6O-H+ | Methyl vinyl ketone, methacrolein | 65 | 47 | 53 | 2.7 | 16 | 4.3 | 18 | 5.2 | 22 | 4.6 |
| 73.03 | C3H4O2-H+ | 2-Propenoic acid | 119 | 98 | 34 | 1.7 | 64 | 10.1 | 85 | 9.7 | 152 | 13.3 |
| 75.04 | C3H6O2-H+ | Hydroxy-2-propanone | 18 | 17 | 46 | 2.3 | 32 | 6.7 | — | — | 42 | 7.8 |
| 83.01 | C4H2O2-H+ | 3-Cyclobutene-1,2-dione | — | 118 | 23 | 2.2 | 46 | 9.0 | — | — | — | — |
| 85.06 | C5H8O-H+ | e.g. Pentenal | 44 | 50 | — | — | 12 | 3.7 | 14 | 3.5 | 15 | 4.4 |
| 87.04 | C4H6O2-H+ | e.g. 2,3- butadione | 59 | 54 | 43 | 3.1 | 30 | 6.5 | 40 | 6.7 | 59 | 9.0 |
| 101.06 | C5H8O2-H+ | e.g. 2,3-pentanedione | — | — | 52 | 3.5 | — | — | — | — | 19 | 4.4 |
| 103.04 | C4H6O3-H+ | Acetic anhydride | 46 | 52 | 46 | 2.2 | 26 | 6.4 | 51 | 7.2 | 27 | 6.1 |
| 103.07 | C5H10O2-H+ | e.g. Methyl-butanoic acid | — | — | 22 | 2.3 | — | — | — | — | 187 | 14.4 |
| 117.05 | C5H8O3-H+ | e.g. Acetyloxypropanone | 34 | 48 | 47 | 2.7 | 36 | 8.1 | 17 | 4.8 | 13 | 3.3 |
| *Carbonyls-B* | | | | | | | | | | | | |
| 59.05 | C3H6O-H+ | Acetone | 76 | 61 | 30 | 2.5 | 50 | 9.5 | — | — | 16 | 3.8 |
| 61.03 | C2H4O2-H+ | Acetic acid, glycolaldehyde | 73 | 50 | 49 | 2.9 | 20 | 5.4 | 41 | 6.9 | 25 | 5.9 |
| 73.06 | C4H8O-H+ | 2-butanone and 2-methylpropanal | — | — | — | — | — | — | — | — | 15 | 4.3 |
| 77.02 | C2H4O3-H+ | Acetic acid, hydroxy- | — | — | 57 | 2.5 | — | — | — | — | 36 | 7.2 |
| 89.06 | C4H8O2-H+ | Acetoin | 77 | 36 | 26 | 2.3 | — | — | 157 | 11.2 | — | — |
| 91.04 | C3H6O3-H+ | e.g. lactic acid | — | — | 53 | 2.6 | — | — | — | — | 106 | 10.7 |
| 99.01 | C4H2O3-H+ | Maleic anhydride | 20 | 64 | 16 | 2.1 | 19 | 5.4 | 31 | 6.5 | 27 | 5.8 |
| 101.02 | C4H4O3-H+ | Succinic anhydride | — | — | 22 | 2.3 | — | — | — | — | 45 | 7.7 |
| 105.03 | C4H8O3-H+ | e.g. Acetic acid, methoxy- | — | — | 40 | 3.1 | — | — | — | — | 84 | 10.6 |
| *CHN* | | | | | | | | | | | | |
| 42.03 | C2H3N-H+ | Acetonitrile | 145 | — | — | — | — | — | — | — | — | — |
| 54.03 | C3H3N-H+ | Propenenitrile | 77 | 4 | 102 | 3.5 | 14 | 3.7 | 14 | 3.5 | 22 | 4.6 |
| 104.04 | C7H5N-H+ | Benzonitrile | 75 | 30 | 34 | 2.4 | 15 | 4.5 | 12 | 3.0 | 15 | 5.9 |
| 133.06 | C8H8N2-H+ | n.i. | 29 | 47 | — | 2.1 | 12 | 4.2 | 12 | 3.1 | 12 | 4.2 |
| *CHNO, m/z < 100* | | | | | | | | | | | | |
| 44.01 | HCNO-H+ | Isocyanic acid | 105 | 103 | 43 | 3.1 | 65 | 3.8 | 106 | — | 96 | 4.3 |
| 58.04 | C2H3NO-H+ | Methyl isocyanate | 73 | — | 31 | 3.2 | 17 | 10.2 | 12 | 10.2 | 31 | 11.1 |
| 60.05 | C2H5NO-H+ | e.g. Acetamide | — | — | 30 | 2.4 | — | — | — | — | 37 | 6.9 |
| 62.02 | CH3NO2-H+ | e.g. nitromethane, methyl nitrite | 25 | 10 | 47 | 2.5 | 85 | 11.4 | 73 | 9.4 | 75 | 9.7 |
| 72.05 | C3H5NO-H+ | Methoxyacetonitrile or acrylamide | — | 92 | — | — | 11 | 3.9 | — | — | 22 | 4.5 |
| 76.05 | C2H5NO2-H+ | e.g. Nitroethane | 104 | 21 | 45 | 2.6 | — | — | — | — | 154 | 13.2 |
| 88.04 | C2H5N3O-H+ or C3H5NO2-H+ | | — | 24 | 35 | 2.4 | 39 | 8.8 | — | — | 41 | 8.0 |
| 96.05 | C5H5NO-H+ | Pyridine-N-oxide | 48 | 60 | — | — | — | — | 16 | 4.3 | 16 | 4.2 |
| 98.03 | C3H3N3O-H+ | 1H-Pyrazole, 4-nitro-1 | 38 | 25 | 106 | 3.5 | 19 | 5.4 | 17 | 4.6 | 15 | 4.3 |

Table 7 - continued

| m/z | Ion formula | Compound | Dark aging FI-D-HONO [min] | Dark aging SI-D-PcA [min] | Photochemical aging FI-D-HONO [min] | FI-D-HONO [atm. h] | SI-D-PcA [min] | SI-D-PcA [atm. h] | FI-PcA [min] | FI-PcA [atm. h] | SI-PcA [min] | SI-PcA [atm. h] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *CHNO, m/z > 100* | | | | | | | | | | | | |
| 100.01 | C3HNO3-H+ | n.i. | — | 51 | 23 | 2.2 | 21 | 5.3 | 32 | 6.3 | 29 | 6.6 |
| 100.07 | C5H9NO-H+ | n.i. | 44 | 42 | 65 | 2.7 | 56 | 9.9 | 13 | 3.6 | 11 | 2.6 |
| 114.05 | C5H7NO2-H+ | n.i. | — | 94 | 55 | 2.9 | 28 | 6.9 | 38 | 6.0 | 33 | 6.7 |
| 122.02 | C6H3NO2-H+ | e.g. Oxo-furan-2-acetonitrile | 46 | 72 | 57 | 2.3 | 106 | 12.7 | 13 | 3.3 | 28 | 6.5 |
| 136.04 | C7H5NO2-H+ | e.g. Furoylacetonitrile | 30 | 47 | 64 | 3.0 | 54 | 9.8 | 49 | 7.0 | 11 | 2.6 |
| 140.03 | C6H5NO3-H+ | Nitrophenols, Oxiniacic acid | 51 | 78 | 104 | 3.3 | 75 | 11.1 | 150 | 12.2 | 20 | 5.2 |
| 150.02 | C7H3NO3-H+ | e.g. Pyridinedicarboxylic anhydride | — | — | 29 | 2.3 | — | — | — | — | 121 | 11.6 |
| 154.05 | C7H7NO3-H+ | e.g. Nitrocresol | 38 | 50 | — | — | 43 | 7.8 | 24 | 4.8 | 26 | 5.6 |
| *CHO* | | | | | | | | | | | | |
| 33.03 | CH3OH-H+ | Methanol | — | — | 55 | 3.2 | 25 | 6.5 | — | — | — | — |
| 49.03 | CH4O2-H+ | Methyl peroxide or methanediol | — | 89 | 38 | 3.1 | 13 | 3.3 | — | — | 21 | 4.8 |
| 63.04 | C2H6O2-H+ | n.i. | — | 178 | 26 | 2.0 | — | — | — | — | — | — |
| 77.05 | C3H8O2-H+ | e.g. Ethanol 2-methoxy- | — | — | 37 | 2.7 | — | — | — | — | — | — |
| 81.03 | C5H4O-H+ | 2,4-Cyclopentadiene-1-one | 17 | 27 | — | — | 20 | 5.4 | 7 | 2.8 | 6 | 1.7 |
| 85.03 | C4H4O2-H+ | Furanone | 2 | 3 | 45 | 2.6 | 24 | 7.0 | 37 | 5.9 | 45 | 7.8 |
| 111.08 | C7H10O-H+ | e.g. Heptenedial or trimethylfuran | — | 16 | — | — | — | — | — | — | 11 | 2.5 |
| 113.02 | C5H4O3-H+ | e.g. 2-furoic acid | 161 | 167 | 16 | 2.1 | 21 | 5.4 | 25 | 4.8 | 20 | 5.4 |
| 113.06 | C6H8O2-H+ | eg. Methylcyclohexanone | 40 | — | — | — | — | — | 12 | 3.1 | 17 | 3.9 |
| 115.04 | C5H6O3-H+ | e.g. Hydroxymethylfuranone | — | — | 28 | 2.2 | — | — | — | — | 7 | 2.1 |
| 149.02 | C8H4O3-H+ | Phthalic anhydride | — | — | 25 | 2.1 | — | — | 62 | 8.8 | 65 | 8.9 |
| *Aliphatic hydrocarbons* | | | | | | | | | | | | |
| 53.04 | C4H4-H+ | Butenyne | 7 | 43 | 76 | 2.5 | 15 | 4.1 | 19 | 5.0 | 16 | 3.8 |
| 67.05 | C5H6-H+ | 1,3-cyclopentadiene | 12 | 14 | 50 | 3.6 | 10 | 3.1 | 5 | 1.9 | 4 | 0.8 |
| 69.07 | C5H8-H+ | Isoprene | 77 | — | — | — | — | — | — | — | 9 | 2.7 |
| 81.07 | C6H8-H+ | e.g. Cyclohexa-1,3-diene; fragments | 9 | 11 | — | — | 6 | 0.9 | 3 | 0.6 | 4 | 0.6 |
| 137.13 | C10H16-H+ | Monoterpenes | 17 | 28 | — | — | — | — | 5 | 1.7 | 6 | 1.6 |

**Table S8.** Reaction rates [$cm^3$ $molec.^{-1}$ $s^{-1}$] of selected gases with OH, $O_3$ and $NO_3$, based on previous research compiled in the NIST Chemical Kinetics Database.[17] Rates are recited at 291.15K, if not otherwise specified.

| | OH | | $O_3$ | | $NO_3$ | |
|---|---|---|---|---|---|---|
| *Aromatic hydrocarbons* | | | | | | |
| Benzene | 1.2E-12 | | 9.4E-23 * | | <3.0E-17 | 298K |
| Toluene | 6.3E-12 | 298K | 2.3E-22 * | | 6.8E-17 | 298K |
| Naphthalene | 2.2E-11 | 298K | <3.0E-19 | 295K | 2.0E-11 | 298K |
| *Furanoic compounds* | | | | | | |
| Furan | 4.2E-11 | | 2.4E-18 | 298K | 1.4E-12 | 295K |
| Furfural | 3.5E-11 | 300K | | | 1.2E-12 | 298K |
| *Phenolic compounds* | | | | | | |
| Phenol | 2.8E-11 | 296K | | | 3.6E-12 | 298K |
| m-cresol | 5.7E-11 | 300K | 1.9E-19 | | 1.2E-11 | 298K |
| Guaiacol | 7.4E-11 | 295K | 2.2E-19 | 294K | | |
| *Monoterpenes* | | | | | | |
| Camphene | 5.3E-11 | 296K | 9.0E-19 | 296K | 6.6E-13 | 296K |
| Limonene | 1.7E-10 | 294K | 2.1E-16 | 296K | 1.2E-11 | 298K |
| a-pinene | 5.3E-11 | 298K | 8.7E-17 | 296K | 6.4E-12 | |
| *Carbonyls* | | | | | | |
| Acetaldehyde | 1.7E-11 * | | <6.0E-21 | 296K | 2.1E-15 | |
| Acetone | 2.3E-13 | 300K | | | <8.5E-18 | |
| Acetic acid | 8.0E-13 | 298K | | | | |
| *Other compounds* | | | | | | |
| NO | 3.2E-11 | | 1.6E-14 | | 2.6E-11 | |
| $NO_2$ | 7.6E-11 | | 2.9E-17 | | 1.9E-12 | |
| Propene | 3.0E-11 | | 8.6E-18 | | 8.7E-15 | |
| Benzaldehyde | 1.3E-11 | 298K | <2.0E-19 | 299K | 2.0E-15 | 298K |
| Methanol | 8.5E-13 | | | | 1.1E-16 | |

*= value extrapolated to out of the temperature range of the original experiment.

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