

Supplement

**Characterization of gas-phase organics using proton transfer
reaction time-of-flight mass spectrometry: fresh and aged
residential wood combustion emissions**

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Potential fragmentation

In most cases, possible reactions of species relevant to wood combustion to produce ions other than $[M+H]^+$ in the PTR-ToF mass spectrometer are negligible, however, these reactions can be more considerable in the following cases (the nominal $[M+H]^+$ m/z is given in parentheses and only literature results obtained under the most similar instrumental conditions are discussed):

- *Ethanol (m/z 47)*: Reactions to produce ions in addition to $[M+H]^+$ are highly dependent on instrumental conditions and do not necessarily correlate with E/N . At an E/N of 142 Td, Baasandorj et al. (2015) found that ~80 to >95% of the signal undergoes dehydration to form m/z 29, whereas Blake et al. (2006) observed only 7% of the signal at m/z 29 at a higher E/N of 165 Td and Buhr et al. (2002) observed ~25% of the signal at m/z 45 and ~4% at m/z 65 at a lower E/N of ~120 Td.
- *Isomers of acetic acid/glycolaldehyde (m/z 61)*: At an E/N of 142 Td, Baasandorj et al. (2015) found that ~30-50% of acetic acid and ~45-60% of glycolaldehyde undergoes dehydration to form $[C_2H_3O]^+$ at m/z 43. At an E/N of 132 Td, Haase et al. (2012) also found that ~30-50% of acetic acid fragments to m/z 43. Reported emission factors for $[C_2H_4O_2+H]^+$ are thus lower limits and could increase by up to ~30% (assuming $[C_2H_3O]^+$ originates entirely from $[C_2H_4O_2+H]^+$).
- *Isomers of (E)-pent-2-ene/(Z)-pent-2-ene/2-methylbut-1-ene/2-methylbut-2-ene/pent-1-ene/3-methylbut-1-ene (m/z 71)*: Gueneron et al. (2015) found 46-48% of the signal at m/z 43 and ~10% of the signal at m/z 41 at an E/N of 120 Td.
- *Butane-2,3-dione (m/z 87)*: At an E/N of ~120 Td, Buhr et al. (2002) found ~7% of the signal at m/z 59 and 5% at m/z 88, whereas Karl et al. (2007) found 34% of the signal at m/z 59 and the remainder at $[M+H]^+$ at an E/N of ~120 Td.
- *Ethyl benzene (m/z 107)*: At an E/N of 145 Td, Jobson et al. (2010) found that 40% of ethylbenzene fragments to interfere with the benzene signal at m/z 79. Using this fragmentation pattern in the current experiments, if the entire signal at $[C_8H_{10}+H]^+$ arises from ethylbenzene, this would result in a negligible overestimate of the benzene signal of less than 1% in experiments 1 and 3-5 and ~2% in experiment 2.

Table S1. Applied reaction rates^{a,b}

| ion | species | reaction rate ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$) |
|--|--|---|
| [CH ₃ OH+H] ⁺ | methanol | 2.14 |
| [C ₂ H ₃ N+H] ⁺ | acetonitrile | 3.82 |
| [C ₂ H ₄ O+H] ⁺ | acetaldehyde | 3.02 |
| [C ₃ H ₆ +H] ⁺ | propene | 1.62 |
| [CH ₂ O ₂ +H] ⁺ | formic acid | 1.89 |
| [C ₂ H ₆ O+H] ⁺ | ethanol | 2.04 |
| [C ₄ H ₆ +H] ⁺ | buta-1,3-diene | 1.82 |
| [C ₃ H ₄ O+H] ⁺ | prop-2-enal | 3.43 |
| [C ₂ H ₂ O ₂ +H] ⁺ | oxaldehyde | 1.35 |
| [C ₃ H ₆ O+H] ⁺ | propan-2-one/propanal | 3.10 |
| [C ₂ H ₄ O ₂ +H] ⁺ | acetic acid/glycolaldehyde | 2.11 |
| [C ₄ H ₄ O+H] ⁺ | furan | 1.69 |
| [C ₅ H ₈ +H] ⁺ | isoprene/cyclopentene | 1.88 |
| [C ₄ H ₆ O+H] ⁺ | (<i>E</i>)-but-2-enal | 3.45 |
| | 3-buten-2-one | |
| | 2-methylprop-2-enal | |
| [C ₅ H ₁₀ +H] ⁺ | (<i>E</i>)-/(<i>Z</i>)-pent-2-ene | 1.91 |
| | 2-methylbut-1-ene | |
| | 2-methylbut-2-ene | |
| | pent-1-ene | |
| | 3-methylbut-1-ene | |
| [C ₄ H ₈ O+H] ⁺ | butan-2-one | 3.09 |
| | butanal | |
| | 2-methylpropanal | |
| [C ₃ H ₆ O ₂ +H] ⁺ | methyl acetate | 2.24 |
| [C ₆ H ₆ +H] ⁺ | benzene | 1.93 |
| [C ₆ H ₁₂ +H] ⁺ | (<i>E</i>)-hex-2-ene | 2.02 |
| | 2-methyl-pent-2-ene | |
| [C ₄ H ₆ O ₂ +H] ⁺ | butane-2,3-dione | 1.70 |
| [C ₄ H ₈ O ₂ +H] ⁺ | ethyl acetate | 4.15 |
| [C ₇ H ₈ +H] ⁺ | toluene | 2.08 |
| [C ₆ H ₆ O+H] ⁺ | phenol | 2.13 |
| [C ₅ H ₄ O ₂ +H] ⁺ | 2-furaldehyde | 3.88 |
| [C ₇ H ₁₄ +H] ⁺ | methylcyclohexane/hept-1-ene | 2.13 |
| [C ₆ H ₁₂ O+H] ⁺ | hexanal | 3.15 |
| [C ₈ H ₈ +H] ⁺ | styrene | 2.27 |
| [C ₇ H ₆ O+H] ⁺ | benzaldehyde | 3.63 |
| [C ₈ H ₁₀ +H] ⁺ | <i>m</i> -/ <i>o</i> -/ <i>p</i> -xylene | 2.26 |
| | ethylbenzene | |
| [C ₇ H ₈ O+H] ⁺ | <i>m</i> -/ <i>o</i> -/ <i>p</i> -cresol | 2.27 |
| [C ₇ H ₁₄ O+H] ⁺ | heptanal | 2.74 |
| [C ₉ H ₈ +H] ⁺ | 1 <i>H</i> -indene | 2.42 |
| [C ₈ H ₈ O+H] ⁺ | 1-phenylethanone | 3.23 |
| | 3-/4-methylbenzaldehyde | |
| [C ₉ H ₁₂ +H] ⁺ | <i>i</i> -propylbenzene | 2.39 |
| | <i>n</i> -propylbenzene | |
| | 1,3,5-trimethylbenzene | |
| [C ₁₀ H ₈ +H] ⁺ | naphthalene | 2.45 |
| [C ₁₁ H ₁₀ +H] ⁺ | 1-/2-methylnaphthalene | 2.71 |
| [C ₁₂ H ₈ +H] ⁺ | acenaphthylene | 2.86 |
| [C ₁₂ H ₁₀ +H] ⁺ | 1,1'-biphenyl | 2.81 |
| | 1,2-dihydroacenaphthylene | |
| [C ₁₃ H ₁₀ +H] ⁺ | fluorene | 2.88 |
| [C ₁₄ H ₁₀ +H] ⁺ | phenanthrene | 2.97 |
| | anthracene | |
| [C ₁₆ H ₁₀ +H] ⁺ | fluoranthene | 3.37 |
| | pyrene | |
| | acephenanthrylene | |

^aReaction rates taken from Cappellin et al. (2012) at a drift temperature of 90 °C and an *E/N* of 140 Td. A reaction rate of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is applied to all other ions.

^bIn the cases of isomers, an average of the available rate constants is applied.

Table S2. Aged gas-phase emissions (mg kg⁻¹) measured using PTR-ToF-MS at an OH exposure of (4.5-5.5)×10⁷ molec cm⁻³ h^a

| species | monoisotopic <i>m/z</i> | structural assignment ^b | functional group | experiment | | | | | average ^c |
|--|----------------------------|---|-------------------------------|------------|------|------|------|------|----------------------|
| | | | | 1 | 2 | 3 | 4 | 5 | |
| NMOG | | | | 2600 | 9100 | 7100 | 2600 | 1600 | 5000±3000 |
| acid | | | | 990 | 4600 | 3500 | 960 | 570 | 2000±2000 |
| O-containing | | | | 680 | 2600 | 1900 | 620 | 390 | 1000±1000 |
| carbonyl | | | | 210 | 730 | 490 | 170 | 130 | 300±300 |
| oxygenated aromatic | | | | 34 | 56 | 55 | 35 | 26 | 40±10 |
| alcohol | | | | 140 | 590 | 350 | 100 | 65 | 200±200 |
| furan | | | | 24 | 72 | 51 | 20 | 14 | 40±20 |
| O- and N-containing | | | | 120 | 87 | 110 | 120 | 100 | 100±20 |
| C _x H _y | | | | 59 | 69 | 83 | 61 | 42 | 60±10 |
| aromatic hydrocarbon | | | | 180 | 81 | 270 | 380 | 140 | 200±100 |
| N-containing | | | | 31 | 46 | 42 | 28 | 24 | 34±9 |
| other | | | | 180 | 260 | 280 | 180 | 140 | 210±60 |
| [CH ₃ OH+H] ⁺ | 33.034 | methanol | alcohol | 110 | 590 | 340 | 92 | 56 | 200±200 |
| [C ₂ H ₃ N+H] ⁺ | 42.034 | acetonitrile | N-containing | 3.6 | 3.6 | 4.4 | 3.3 | 2.7 | 3.5±0.6 |
| [C ₃ H ₆ +H] ⁺ | 43.055 | propene | C _x H _y | 7.7 | 17 | 13 | 6.4 | 5.2 | 10±5 |
| [C ₂ H ₄ O+H] ⁺ | 45.034 | acetaldehyde | carbonyl | 50 | 130 | 94 | 42 | 30 | 70±40 |
| [CH ₂ O ₂ +H] ⁺ | 47.013 | formic acid | acid | 280 | 580 | 570 | 310 | 190 | 400±200 |
| [C ₂ H ₆ O+H] ⁺ | 47.050 | ethanol | alcohol | 33 | 1.1 | 6.8 | 8.9 | 9.1 | 10±10 |
| [C ₄ H ₆ +H] ⁺ | 55.055 | buta-1,3-diene | C _x H _y | 6.4 | 8.0 | 9.7 | 5.9 | 7.5 | 7±2 |
| [C ₃ H ₄ O+H] ⁺ | 57.034 | prop-2-enal | carbonyl | 6.9 | 39 | 27 | 7.4 | 1.8 | 20±20 |
| [C ₂ H ₂ O ₂ +H] ⁺ | 59.013 | oxaldehyde | carbonyl | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₃ H ₆ O+H] ⁺ | 59.050 | propan-2-one | carbonyl | 64 | 170 | 120 | 46 | 48 | 90±50 |
| [C ₂ H ₄ O ₂ +H] ⁺ | 61.029 | propanal | | | | | | | |
| | | acetic acid | acid | 710 | 4000 | 2900 | 650 | 370 | 2000±2000 |
| | | glycolaldehyde | | | | | | | |
| [C ₄ H ₄ O+H] ⁺ | 69.034 | furan | furan | 4.1 | 16 | 11 | 3.9 | 2.3 | 8±6 |
| [C ₅ H ₈ +H] ⁺ | 69.070 | isoprene | C _x H _y | 3.3 | 4.4 | 4.5 | 1.6 | 1.6 | 3±1 |
| | | cyclopentene | | | | | | | |
| [C ₄ H ₆ O+H] ⁺ | 71.050 | (<i>E</i>)-but-2-enal | carbonyl | 4.3 | 16 | 11 | 3.7 | 2.1 | 7±6 |
| | | 3-buten-2-one | | | | | | | |
| [C ₅ H ₁₀ +H] ⁺ | 71.086 | 2-methylprop-2-enal | | | | | | | |
| | | (<i>E</i>)-/(<i>Z</i>)-pent-2-ene | C _x H _y | BDL | BDL | 1.1 | BDL | BDL | 0.2±0.5 |
| | | 2-methylbut-1-ene | | | | | | | |
| | | 2-methylbut-2-ene | | | | | | | |
| | | pent-1-ene | | | | | | | |
| | | 3-methylbut-1-ene | | | | | | | |
| [C ₃ H ₄ O ₂ +H] ⁺ | 73.029 | 2-oxopropanal | carbonyl | 18 | 60 | 48 | 17 | 11 | 30±20 |
| [C ₄ H ₈ O+H] ⁺ | 73.065 | butan-2-one | carbonyl | 9.7 | 39 | 24 | 6.7 | 7.0 | 20±10 |
| | | butanal | | | | | | | |
| | | 2-methylpropanal | | | | | | | |
| [C ₃ H ₆ O ₂ +H] ⁺ | 75.045 | methyl acetate | O-containing | 59 | 350 | 220 | 46 | 30 | 100±100 |
| [C ₆ H ₆ +H] ⁺ | 79.055 | benzene | aromatic hydrocarbon | 170 | 65 | 240 | 350 | 130 | 200±100 |
| [C ₅ H ₆ O+H] ⁺ | 83.050 | 2-methylfuran | furan | 2.1 | 9.0 | 5.9 | 2.1 | 1.4 | 4±3 |
| [C ₃ H ₈ O+H] ⁺ | 85.065 | 3-methyl-3-buten-2-one | carbonyl | 3.0 | 14 | 8.9 | 2.7 | 2.1 | 6±5 |
| [C ₆ H ₁₂ +H] ⁺ | 85.102 | (<i>E</i>)-hex-2-ene | C _x H _y | BDL | BDL | BDL | BDL | BDL | BDL |
| | | 2-methyl-pent-2-ene | | | | | | | |
| [C ₄ H ₆ O ₂ +H] ⁺ | 87.045 | butane-2,3-dione | carbonyl | 48 | 250 | 150 | 39 | 24 | 100±100 |
| [C ₇ H ₈ +H] ⁺ | 93.070 | toluene | aromatic hydrocarbon | 11 | 7.4 | 15 | 17 | 6.6 | 11±5 |
| [C ₆ H ₆ O+H] ⁺ | 95.050 | phenol | oxygenated aromatic | 2.3 | 3.5 | 6.4 | 6.1 | 4.0 | 4±2 |
| [C ₅ H ₄ O ₂ +H] ⁺ | 97.029 | furan-2-carbaldehyde | furan | 11 | 23 | 19 | 8.4 | 5.8 | 13±7 |
| [C ₆ H ₈ O+H] ⁺ | 97.065 | 2,4-/2,5-dimethylfuran | furan | 0.99 | 3.5 | 2.6 | 1.2 | 0.82 | 2±1 |
| [C ₄ H ₂ O ₃ +H] ⁺ | 99.008 | maleic anhydride ^d | O-containing | 110 | 260 | 200 | 92 | 74 | 140±80 |
| [C ₈ H ₈ +H] ⁺ | 105.070 | styrene | aromatic hydrocarbon | 0.88 | 1.5 | 1.5 | 1.3 | 0.61 | 1.2±0.4 |
| [C ₇ H ₆ O+H] ⁺ | 107.050 | benzaldehyde | oxygenated aromatic | 5.8 | 4.0 | 6.6 | 7.4 | 4.0 | 6±2 |
| [C ₈ H ₁₀ +H] ⁺ | 107.086 | <i>m</i> -/ <i>o</i> -/ <i>p</i> -xylene | aromatic hydrocarbon | 0.95 | BDL | 1.5 | 1.5 | BDL | 0.8±0.8 |
| [C ₇ H ₈ O+H] ⁺ | 109.065 | ethylbenzene | hydrocarbon | | | | | | |
| | | <i>m</i> -/ <i>o</i> -/ <i>p</i> -cresol | oxygenated aromatic | BDL | 0.96 | 1.1 | 0.94 | 0.48 | 0.7±0.4 |
| [C ₆ H ₆ O ₂ +H] ⁺ | 111.045 | <i>m</i> -/ <i>o</i> -/ <i>p</i> -benzenediol | oxygenated aromatic | 6.8 | 18 | 13 | 5.0 | 3.8 | 9±6 |
| [C ₉ H ₈ +H] ⁺ | 117.070 | 2-methylfuraldehyde | aromatic hydrocarbon | BDL | BDL | 0.80 | 0.79 | BDL | 0.3±0.4 |
| | | 1 <i>H</i> -indene | aromatic hydrocarbon | | | | | | |
| [C ₉ H ₁₀ +H] ⁺ | 119.086 | 2,3-dihydro-1 <i>H</i> -indene | aromatic hydrocarbon | BDL | BDL | BDL | BDL | BDL | BDL |

| | | | | | | | | | |
|--|---------|---|-------------------------------------|------|-----|------|------|------|----------|
| [C ₈ H ₈ O+H] ⁺ | 121.065 | 1-phenylethanone | oxygenated | 3.0 | 2.8 | 3.3 | 2.7 | 1.8 | 2.7±0.6 |
| [C ₉ H ₁₂ +H] ⁺ | 121.102 | 3-/4-methylbenzaldehyde <i>i</i> -propylbenzene <i>n</i> -propylbenzene | aromatic aromatic hydrocarbon | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₈ H ₁₀ O+H] ⁺ | 123.081 | 1,3,5-trimethylbenzene 2,4-/2,6-/3,5-dimethylphenol | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₇ H ₈ O ₂ +H] ⁺ | 125.060 | 2-methoxyphenol methylbenzenediols | oxygenated aromatic | BDL | 5.5 | 3.7 | 0.94 | BDL | 2±2 |
| [C ₈ H ₆ O ₃ +H] ⁺ | 127.040 | 5-(hydroxymethyl)furan-2-carbaldehyde | furan | 6.1 | 21 | 13 | 4.4 | 3.4 | 9±7 |
| [C ₁₀ H ₈ +H] ⁺ | 129.070 | naphthalene | aromatic hydrocarbon | BDL | BDL | 4.6 | 4.6 | 0.84 | 2±2 |
| [C ₈ H ₁₀ O ₂ +H] ⁺ | 139.076 | 2-methoxy-4-methylphenol 4-(2-hydroxyethyl)phenol | oxygenated aromatic | BDL | 2.9 | 2.1 | 0.71 | BDL | 1±1 |
| [C ₁₁ H ₁₀ +H] ⁺ | 143.086 | 1-/2-methylnaphthalene | aromatic hydrocarbon | BDL | BDL | BDL | BDL | 0.4 | 0.07±0.2 |
| [C ₉ H ₆ O ₂ +H] ⁺ | 147.045 | 2,3-dihydroinden-1-one | oxygenated aromatic | 3.8 | 3.6 | 4.8 | 3.8 | 2.5 | 3.7±0.8 |
| [C ₈ H ₄ O ₃ +H] ⁺ | 149.024 | phthalic anhydride ^d | O-containing | 55 | 71 | 74 | 59 | 55 | 63±9 |
| [C ₈ H ₈ O ₃ +H] ⁺ | 153.055 | 4-hydroxy-3-methoxybenzaldehyde | oxygenated aromatic | 1.2 | 3.3 | 2.6 | 1.4 | BDL | 2±1 |
| [C ₁₂ H ₈ +H] ⁺ | 153.070 | acenaphthylene | aromatic hydrocarbon | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₉ H ₁₂ O ₂ +H] ⁺ | 153.092 | 4-ethyl-2-methoxyphenol 1,2-dimethoxy-4-methylbenzene | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₈ H ₁₀ O ₃ +H] ⁺ | 155.071 | 2,6-dimethoxyphenol | oxygenated aromatic | BDL | BDL | BDL | BDL | 0.5 | 0.1±0.2 |
| [C ₁₂ H ₁₀ +H] ⁺ | 155.086 | 1,1'-biphenyl | aromatic hydrocarbon | BDL | BDL | BDL | 1.2 | BDL | 0.2±0.5 |
| [C ₁₂ H ₁₂ +H] ⁺ | 157.102 | 1,2-dihydroacenaphthylene dimethylnaphthalene | aromatic hydrocarbon | BDL | 1.7 | 1.4 | BDL | BDL | 0.6±0.9 |
| [C ₁₀ H ₁₂ O ₂ +H] ⁺ | 165.092 | 2-methoxy-4-[(<i>E</i>)-prop-1-enyl]phenol 2-methoxy-4-prop-2-enylphenol 2-methoxy-4-[(<i>Z</i>)-prop-1-enyl]phenol | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₉ H ₁₀ O ₃ +H] ⁺ | 167.071 | 1-(4-hydroxy-3-methoxyphenyl)ethanone 2,5-dimethylbenzaldehyde 3,4-dimethoxybenzaldehyde | oxygenated aromatic | 1.4 | 1.9 | 1.9 | 0.96 | BDL | 1.2±0.8 |
| [C ₁₃ H ₁₀ +H] ⁺ | 167.086 | fluorene | aromatic hydrocarbon | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₁₀ H ₁₄ O ₂ +H] ⁺ | 167.107 | 2-methoxy-4-propylphenol | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₉ H ₁₂ O ₃ +H] ⁺ | 169.086 | 2,6-dimethoxy-4-methylphenol | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₁₄ H ₁₀ +H] ⁺ | 179.086 | phenanthrene anthracene | aromatic hydrocarbon | 2.8 | 2.1 | 1.9 | 1.6 | 3.9 | 2.5±0.9 |
| [C ₁₃ H ₈ O+H] ⁺ | 181.065 | fluoren-9-one phenalen-1-one | aromatic aromatic | 4.2 | 4.1 | 3.7 | 2.5 | 4.2 | 3.7±0.7 |
| [C ₁₀ H ₁₂ O ₃ +H] ⁺ | 181.086 | 1-(4-hydroxy-3-methoxyphenyl)propan-2-one | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₉ H ₁₀ O ₄ +H] ⁺ | 183.066 | 3,4-dimethoxybenzoic acid | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₁₀ H ₁₄ O ₃ +H] ⁺ | 183.102 | 4-hydroxy-3,5-dimethoxybenzaldehyde 4-ethyl-2,6-dimethoxyphenol | oxygenated aromatic | BDL | BDL | BDL | BDL | BDL | BDL |
| [C ₁₅ H ₁₂ +H] ⁺ | 193.102 | 1-/2-/3-/9-methylphenanthrene 2-methylanthracene | aromatic hydrocarbon | 0.71 | BDL | 0.60 | BDL | 0.77 | 0.4±0.4 |
| [C ₁₁ H ₁₄ O ₃ +H] ⁺ | 195.102 | 1,3-dimethoxy-2-prop-2-enoxybenzene 2,6-dimethoxy-4-[(<i>Z</i>)-prop-1-enyl]phenol | oxygenated aromatic | BDL | BDL | BDL | BDL | 0.43 | 0.09±0.2 |
| [C ₁₆ H ₁₀ +H] ⁺ | 203.086 | fluoranthene pyrene acephenanthrylene | aromatic hydrocarbon | BDL | BDL | BDL | BDL | 0.45 | 0.09±0.2 |

^aBDL indicates value is below the detection limit, the determination of which is described in the text.

^bMultiple structural assignments for a given ion correspond to possible isomers.

^cUncertainties correspond to one sample standard deviation of the replicates.

^dStructural assignment based on known products produced during oxidation of aromatics (Bandow et al., 1985; Chan et al., 2009; Praplan et al., 2014).

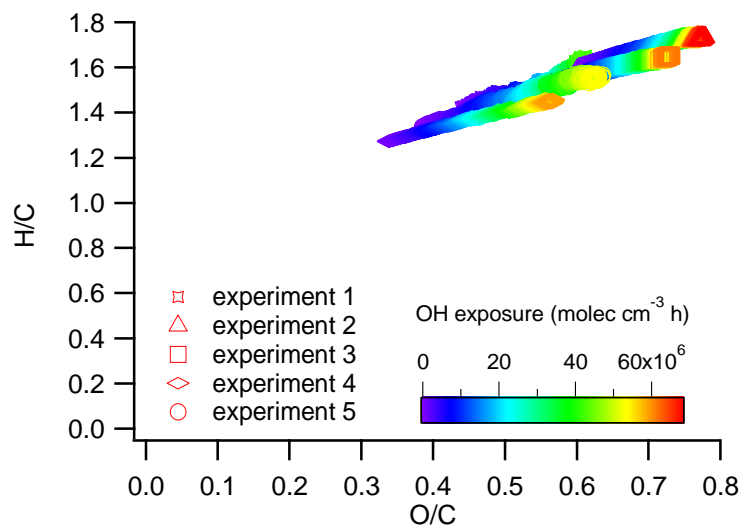


Figure S1. Elemental composition of the speciated NMOG bulk as a function of OH exposure for all experiments.

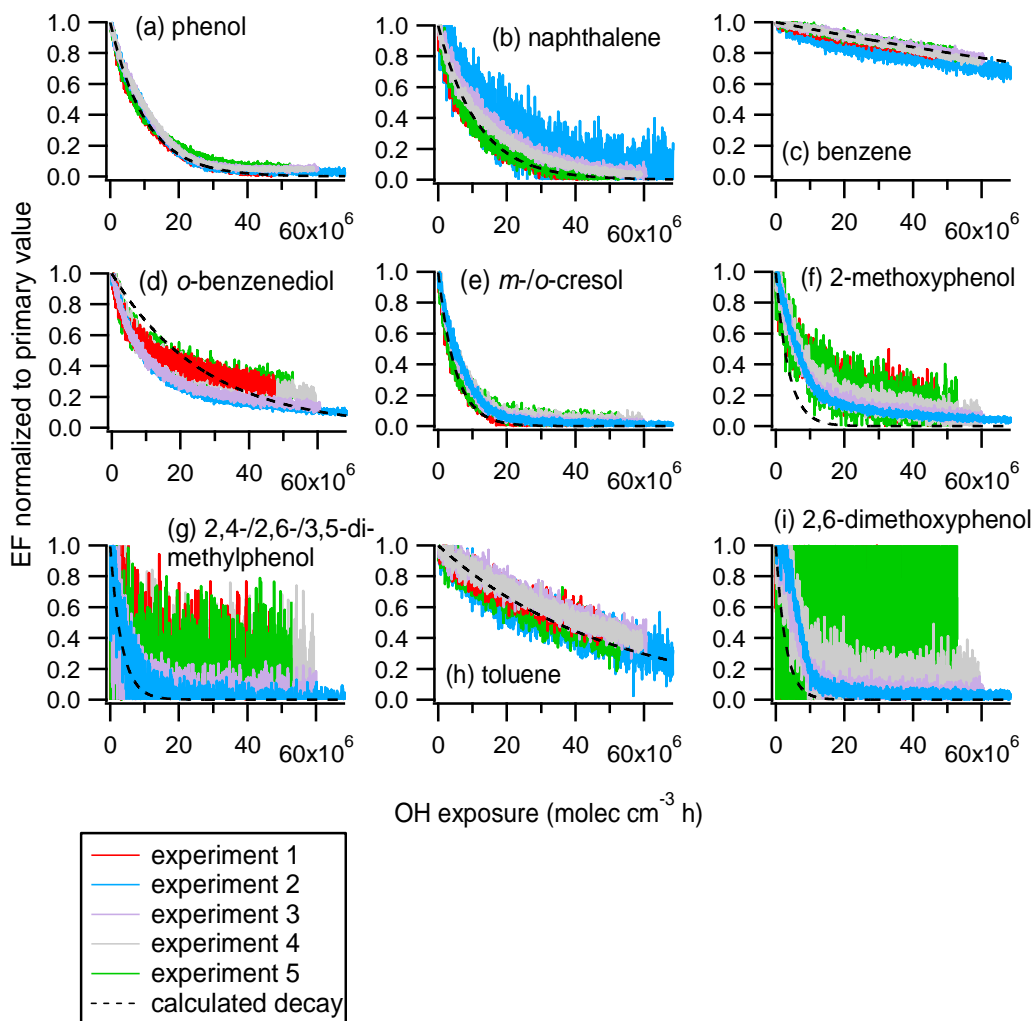


Figure S2. (a-i) Behavior with aging of individual compounds contributing the most to SOA formation for experiments 1-5. The black, dashed line in each panel is the expected decay rate of each species based on the OH concentration and reaction rate with OH.

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