

Supporting Information

Multi-instrument comparison and compilation of non-methane organic gas emissions from biomass burning and implications for smoke-derived secondary organic aerosol precursors

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Methods

Sampling periods

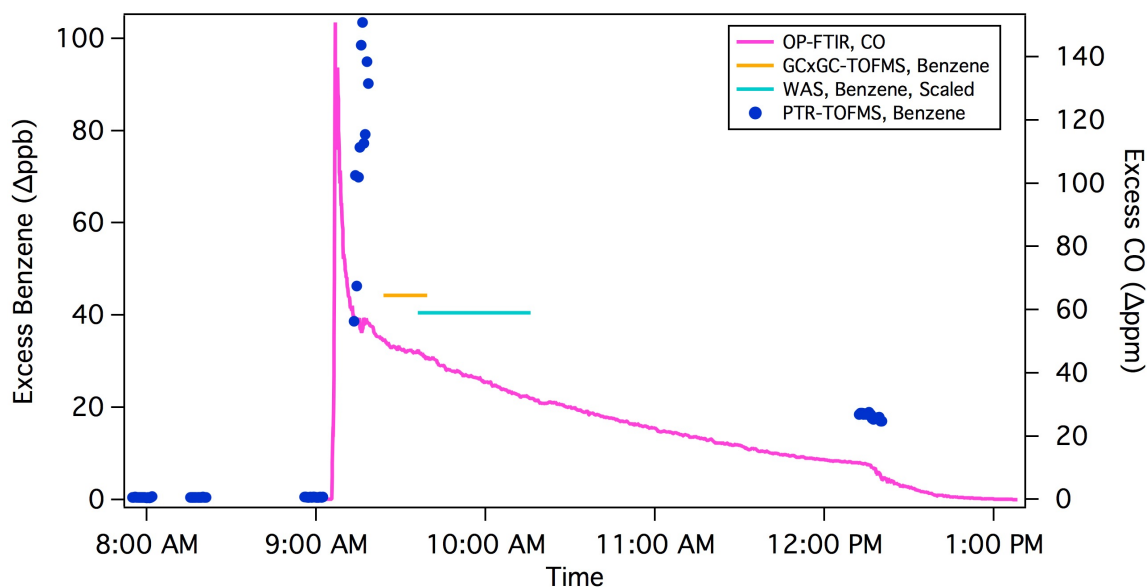


Figure S1. Sampling times for each instrument during the Chinese rice straw fire.

Figure S1 shows the relative sampling times for each instrument during the straw burn. Although the WAS canister was filled in under one minute, the sampling period corresponds to the approximate time that the smoke from the combustion chamber was injected into the smog chamber. For comparison to the room burn data, the WAS-measured benzene concentration was scaled by the smog chamber dilution ratio (~25), calculated as the ratio of the CO concentration measured by OP-FTIR in the combustion chamber averaged over the same period relative to the WAS-measured CO concentration in the smog chamber.

With the exception of the pine burn (for which the PTR-TOFMS sampled more frequently), all burns were similar to the Fig. S1 case, in which there was very little overlap between the PTR-TOFMS measurement period and GC×GC-TOFMS or WAS sampling periods. The GC×GC-TOFMS and WAS samples represent smoke that was well mixed. The PTR-TOFMS measured the initial rise in smoke concentration and briefly, the more well-mixed smoke at the end; in between, the PTR-TOFMS sampled from the smog chambers. The slight time difference between the peak concentrations measured by OP-FTIR and PTR-TOFMS demonstrates that there was a small time delay between the smoke reaching the OP-FTIR positioned on the platform and the instruments located in the control room (See section 2).

GC×GC-TOFMS Analysis

For the spruce smoke sample (burn 155), replicate samples were analyzed on two different column sets with two different GC methods: (1) a DB-VRX primary column (30 m, 0.25 mm I.D., 1.4 μm film, Agilent, Santa Clara, CA) and a Stabilwax secondary column (1.5 m, 0.25 mm I.D., 0.5 μm film, Restek, Bellefonte, PA). The primary oven temperature program was 45 °C for 5 min, 4 °C/min to 235 °C, 235 °C for 2.5 min; the secondary oven was set to 10 °C above the primary oven, which was 5 °C cooler than used in the analysis of samples from the other three fuels on this column set (Hatch et al., 2015). The injection split ratio was 10:1. (2) A Rxi-5ms primary column (30 m, 0.25 mm I.D., 0.25 μm film, Restek, Bellefonte, PA) with a Rxi-17Sil MS (1.5 m, 0.15 mm I.D., 0.15 μm film, Restek, Bellefonte, PA) secondary column. The primary oven was held at 45 °C for 5 min, ramped at 6 °C/min to 305 °C and held at 305 °C for 1 min; the secondary oven temperature was 15 °C above the primary oven temperature. The injection split ratio was 6:1. The same ~275 standard compounds were also analyzed under set #2, however with a 12:1 injection split ratio; therefore the analyte peak areas were scaled down by a factor of

2. Comparisons between the chromatograms resulting from each column set indicated that polar compounds in this sample (e.g., phenols) were underestimated by column set #1 due to the lower secondary oven temperature than was used in the standard analysis on column set #1. Calibration of hydrocarbons was assumed to be unaffected by the lower oven temperature, as supported by the agreement with other instruments. Because the chromatographic separation of light compounds was much better in set #1, data from set #2 were used for polar compounds only.

Results & Discussion

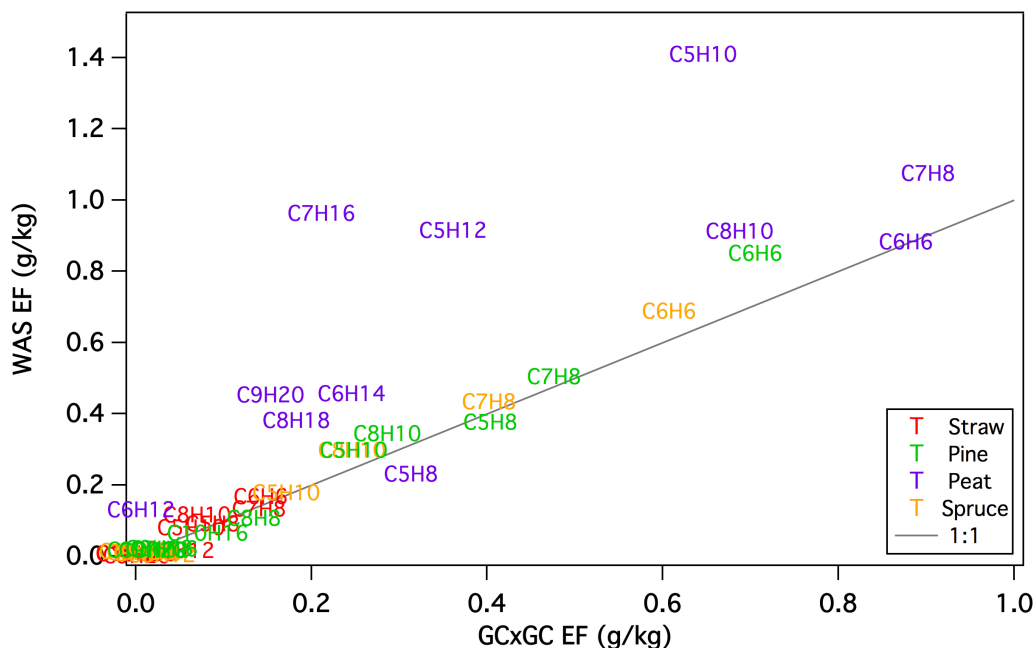


Figure S2. Comparison of WAS and GC×GC-TOFMS emission factors. EFs were summed over overlapping isomers only.

Emission factors measured by WAS and GC×GC-TOFMS agree well for all burns except peat (Fig. S2). In the peat burn, the largest deviations occurred for alkanes (i.e., C_5H_{12} , C_7H_{16} , C_9H_{20} , C_6H_{14} , C_8H_{18}) and pentene isomers (C_5H_{10}). Although both techniques measured monoterpenes during the peat burn, none of the measured isomers overlapped and thus no comparison is included.

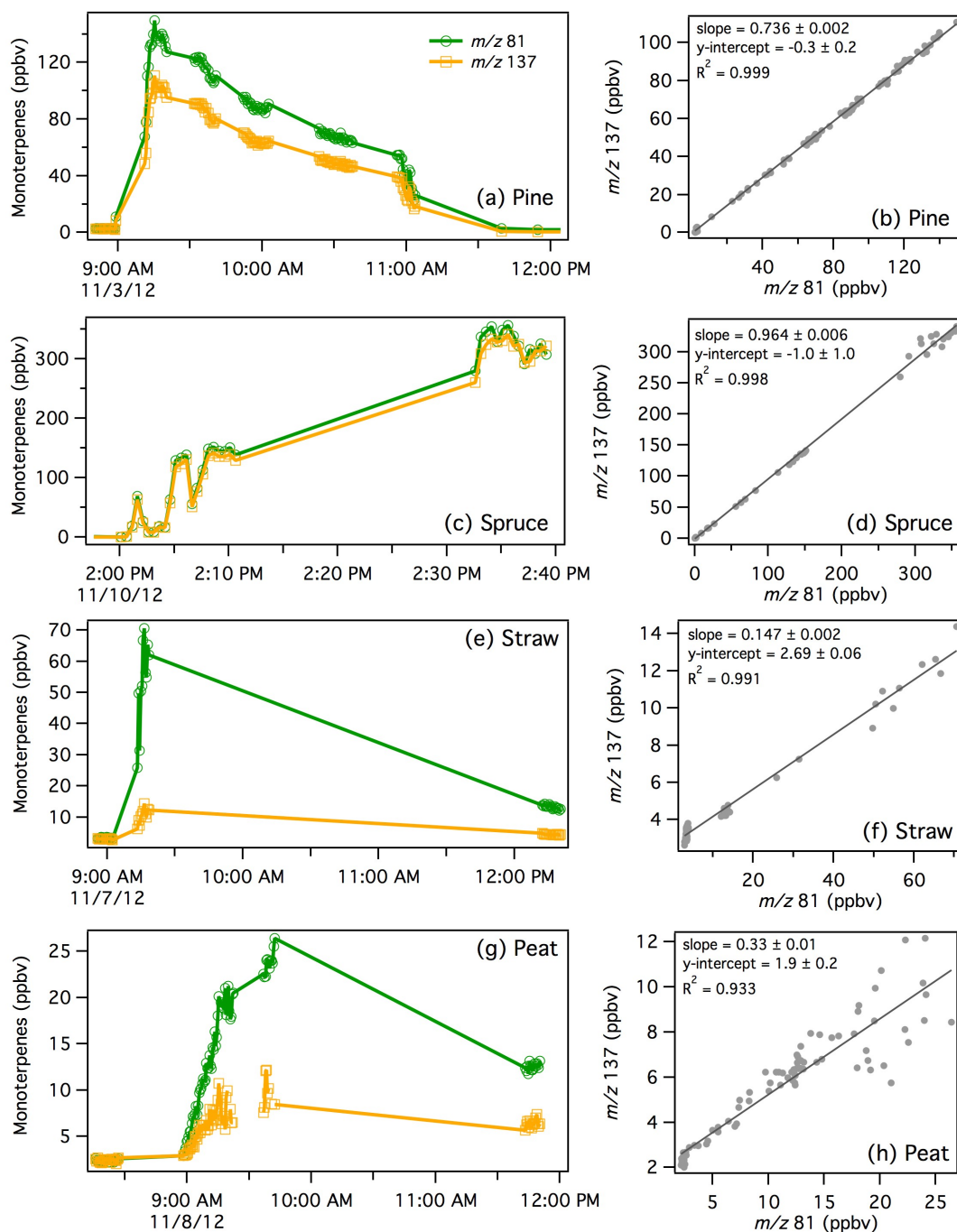


Figure S3. Comparison of the monoterpene ions, m/z 137 and m/z 81, measured by PTR-TOFMS. The time series for each ion is shown the left column. Correlation plots between m/z 137 and m/z 81 for each fuel are given in the right column.

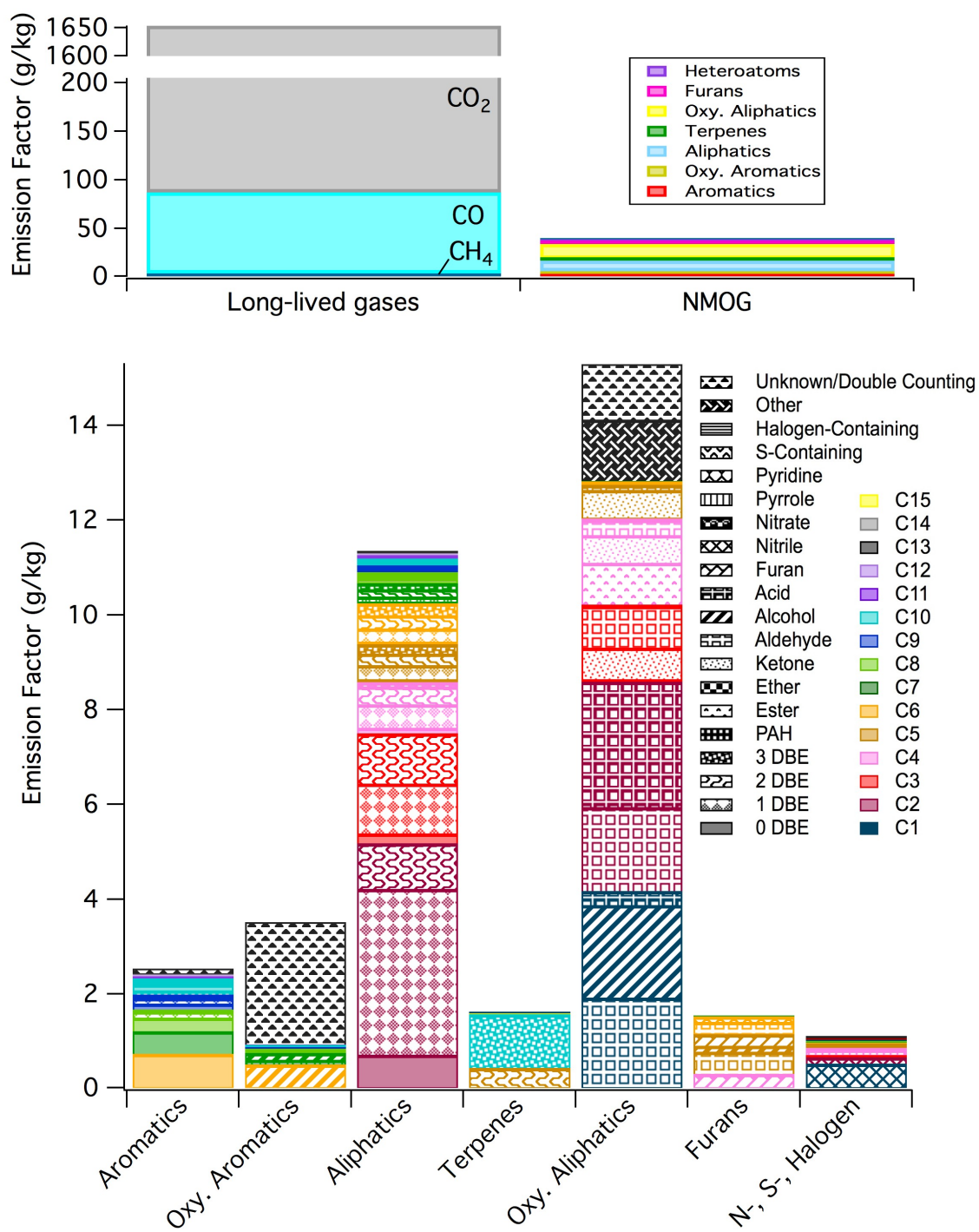


Figure S4. Gas-phase emission factors from a ponderosa pine fire. Top panel: long-lived gases compared to NMOG. Bottom panel: Speciation of NMOG; colors represent carbon number and patterns indicate functionality.

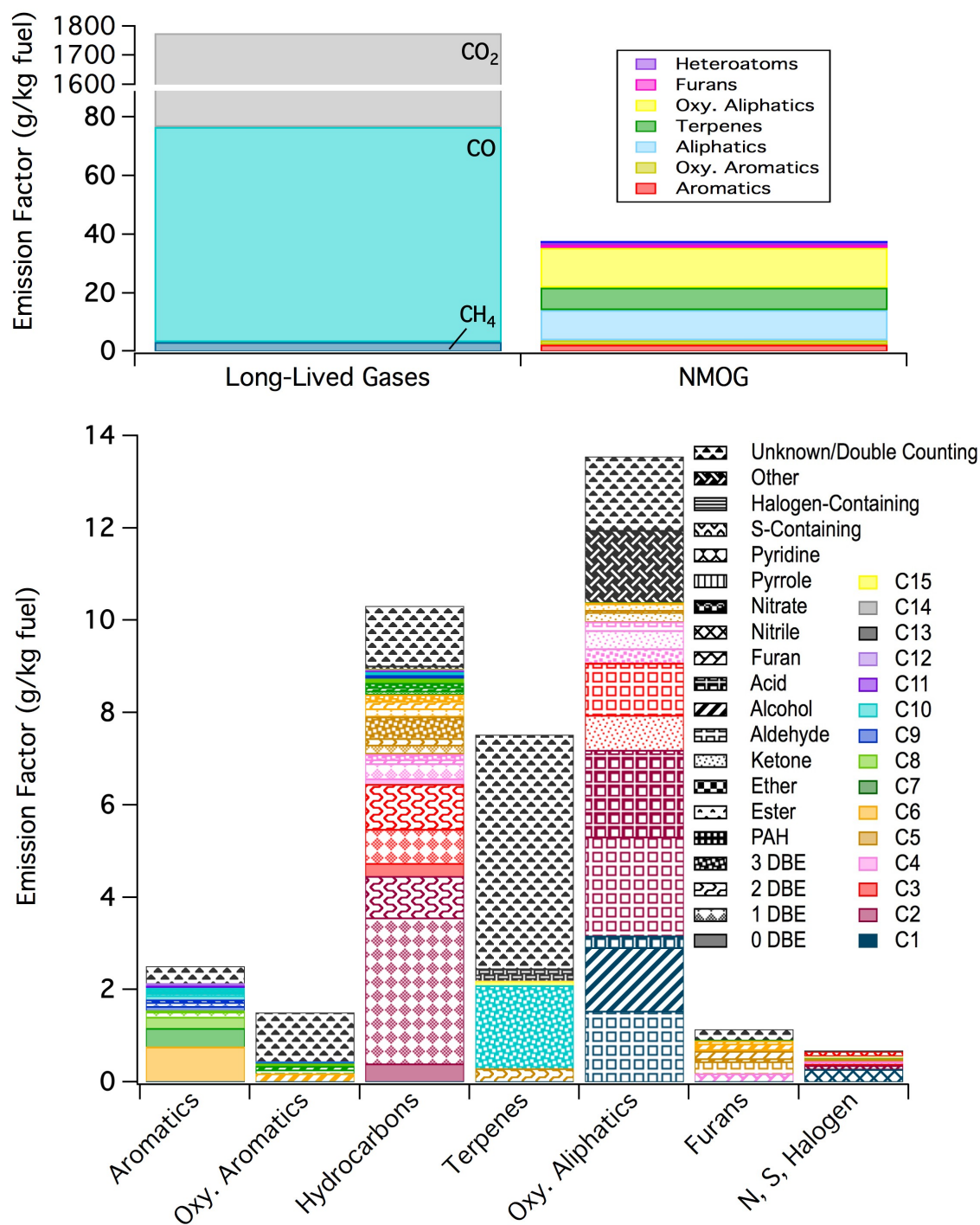


Figure S5. As in Fig. S3, for a black spruce fire.

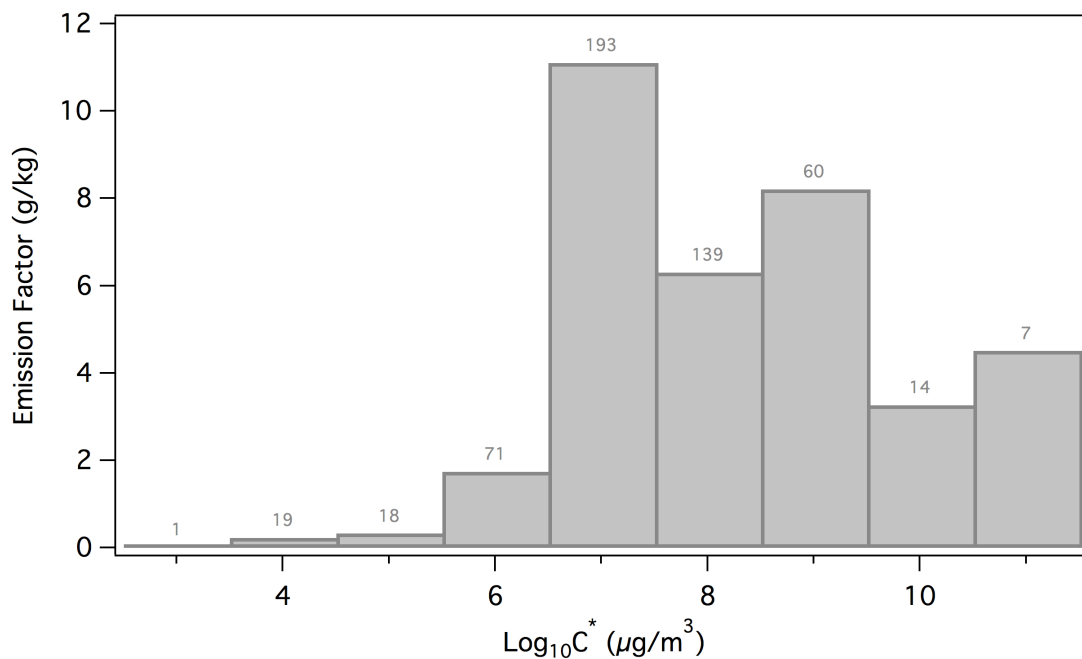


Figure S6. Emission factors of NMOG determined in black spruce smoke, as a function of volatility. The number of compounds included in each bin is indicated above the bars.

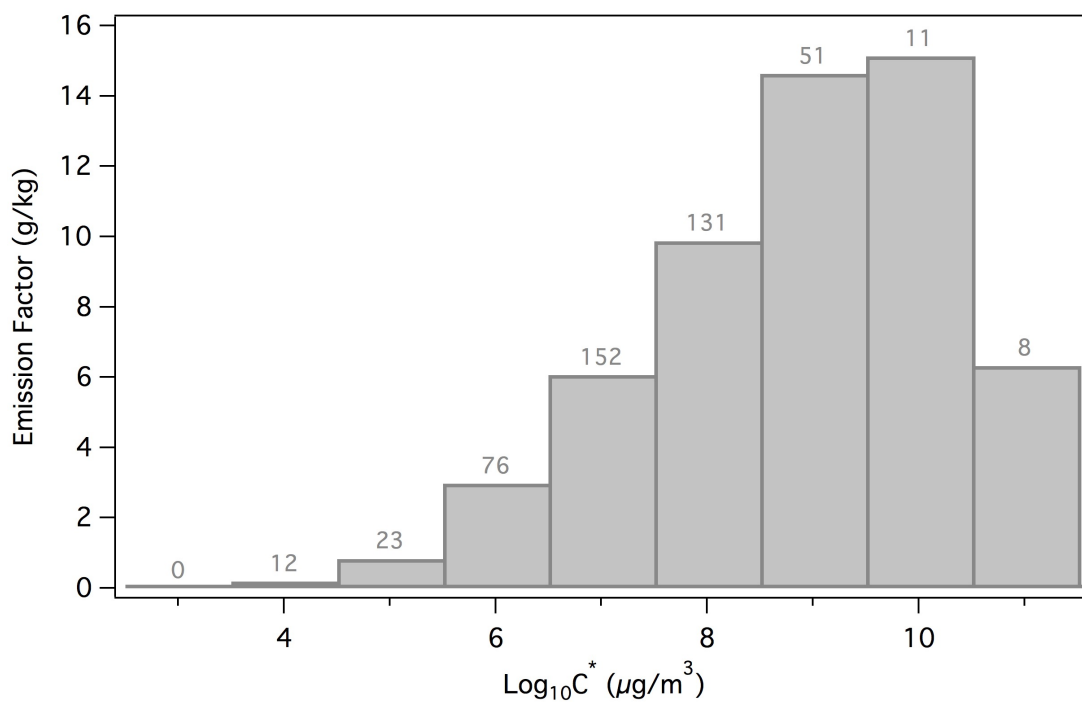


Figure S7. As in Fig. S5, for an Indonesian peat fire.

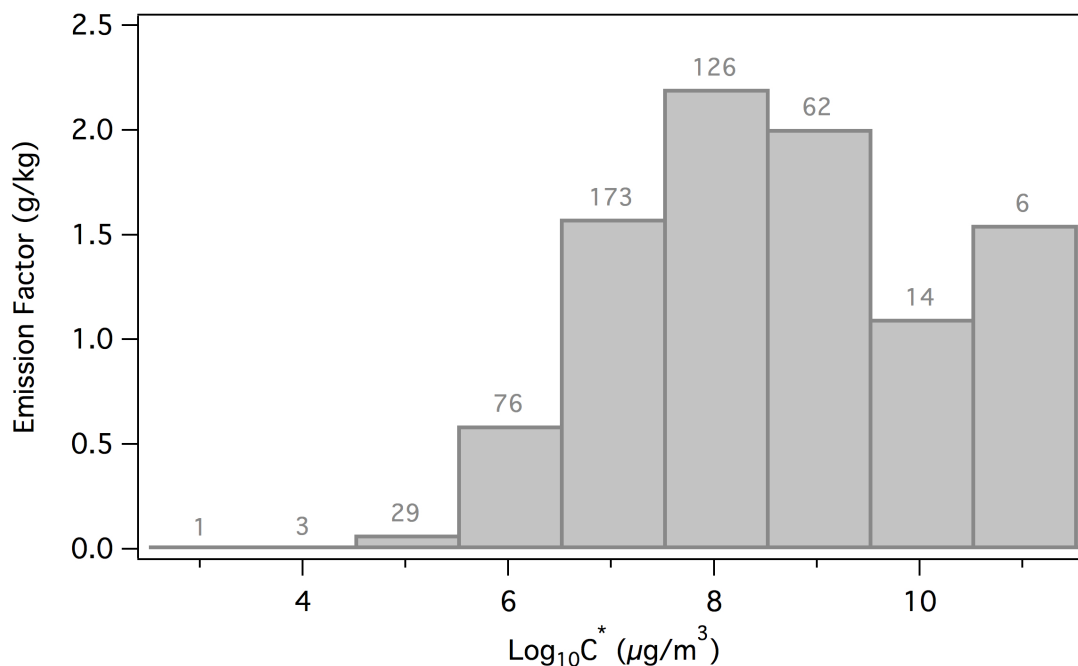


Figure S8. As in Fig. S5, for a Chinese rice straw fire.

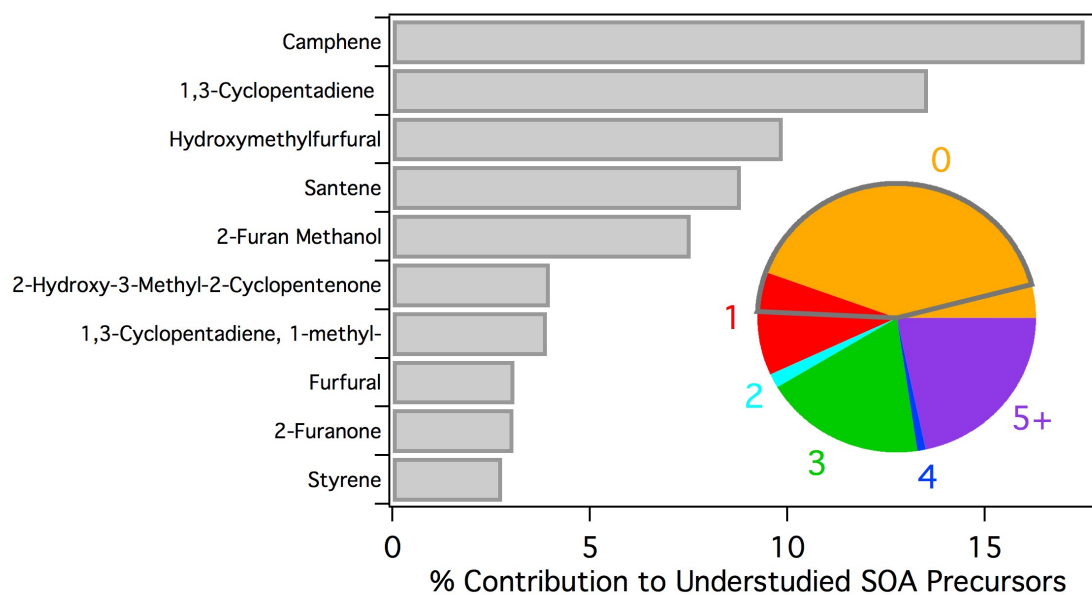


Figure S9. Assessment of SOA yields for compounds observed in the black spruce fire. Pie chart: Classification of reactive carbon (see Section 3.3.2 of main text) by the number of publications reporting an SOA yield following hydroxyl radical oxidation. The gray-outlined wedge represents the understudied compounds with the most potential to form SOA. Bar chart: Percent contribution of the top 10 compounds included in the gray wedge.

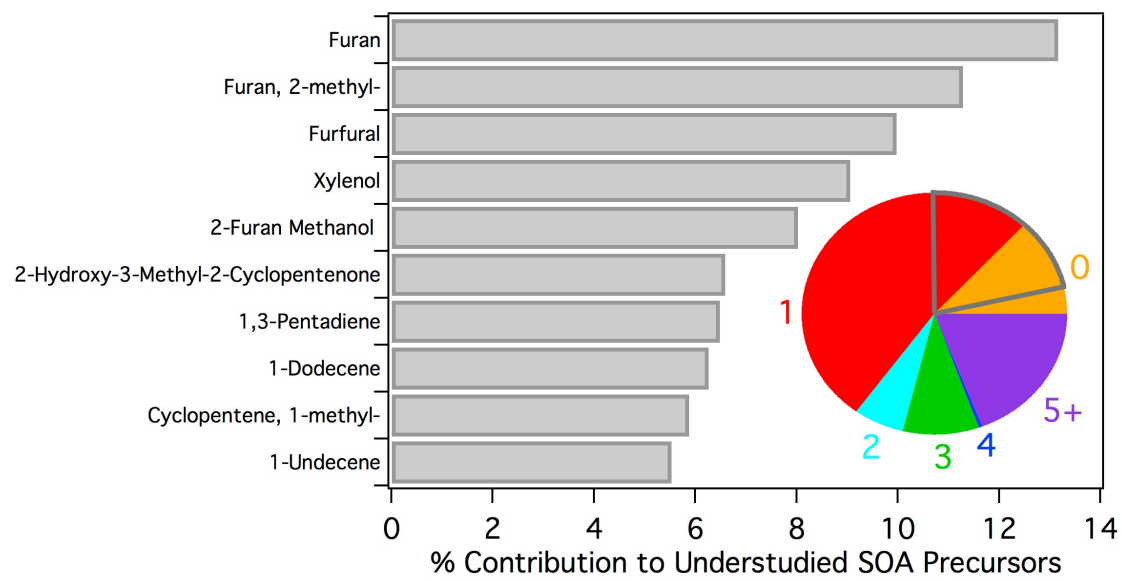


Figure S10. As in Fig. S8, for an Indonesian peat fire.

Table S2. References and classifications used in the SOA yield assessment

# of Pubs.	Compound	Potential Precursor? ^a	SOA Yield References
<i>Well-studied Compounds</i>			
≥5	Isoprene		(Bregonzio-Rozier et al., 2015; Chan et al., 2010; Chen and Jang, 2012; Chhabra et al., 2010; Kleindienst et al., 2006; Kroll et al., 2006; Lambe et al., 2015; Lee et al., 2006; Nguyen et al., 2011; Pandis et al., 1991; Sato et al., 2011; Surratt et al., 2007)
	Limonene		(Griffin et al., 1999; Hoffmann et al., 1997; Jaoui et al., 2006; Lee et al., 2006; Mutzel et al., 2016; Zhao et al., 2015)
	α-Pinene		(Bruns et al., 2015; Eddingsaas et al., 2012; Hoffmann et al., 1997; Kleindienst et al., 2006; Lambe et al., 2015; Lee et al., 2006; Mutzel et al., 2016; Ng et al., 2007a; Odum et al., 1996; Takekawa et al., 2003; Yu et al., 2008; Zhao et al., 2015)
	β-Pinene		(Griffin et al., 1999; Hoffmann et al., 1997; Lee et al., 2006; Mutzel et al., 2016; Pandis et al., 1991; Zhao et al., 2015)
	Benzene		(Borras and Tortajada-Genaro, 2012; Li et al., 2016; Martin-Reviejo and Wirtz, 2005; Nakao et al., 2011; Ng et al., 2007b)
	Toluene		(Chhabra et al., 2010; Hildebrandt et al., 2009; Kamens et al., 2011; Li et al., 2016; Nakao et al., 2011; Ng et al., 2007b; Odum et al., 1997; Ruiz et al., 2015; Takekawa et al., 2003; Wang et al., 1992; Zhou et al., 2011)
	<i>m</i> - & <i>p</i> -Xylene		(Chhabra et al., 2010; Li et al., 2016; Nakao et al., 2011; Ng et al., 2007b; Odum et al., 1996; Odum et al., 1997; Takekawa et al., 2003; Zhou et al., 2011)
	Naphthalene		(Chan et al., 2009; Chen et al., 2016; Chhabra et al., 2010; Kleindienst et al., 2012; Shakya and Griffin, 2010)
4	Methyl Naphthalenes		(Chan et al., 2009; Chen et al., 2016; Kleindienst et al., 2012; Shakya and Griffin, 2010)
	Decane		(Hunter et al., 2014; Lambe et al., 2012; Lim and Ziemann, 2009; Presto et al., 2010)
3	β-Myrcene		(Boge et al., 2013; Griffin et al., 1999; Lee et al., 2006)
	3-Carene		(Griffin et al., 1999; Hoffmann et al., 1997; Lee et al., 2006)
	1,3-Butadiene		(Angove et al., 2006; Jaoui et al.,

			2014; Sato et al., 2011)
	1-Octene		(Forstner et al., 1997; Matsunaga et al., 2009; Wang et al., 1992)
	Dodecane		(Lim and Ziemann, 2009; Loza et al., 2014; Presto et al., 2010)
	<i>o</i> -Xylene		(Odum et al., 1997; Vivanco et al., 2011; Zhou et al., 2011)
	Methacrolein		(Bregonzio-Rozier et al., 2015; Chan et al., 2010; Zhang et al., 2012)
	Phenol		(Borras and Tortajada-Genaro, 2012; Nakao et al., 2011; Yee et al., 2013)
2	Ethylbenzene		(Odum et al., 1997; Stern et al., 1987)
	1-Decene		(Forstner et al., 1997; Matsunaga et al., 2009)
	Undecane		(Lim and Ziemann, 2009; Takekawa et al., 2003)
	Phenol, 2-methyl		(Henry et al., 2008; Nakao et al., 2011)
	<i>o</i> -Guaiacol		(Lauraguais et al., 2014; Yee et al., 2013)
	Catechol		(Borras and Tortajada-Genaro, 2012; Nakao et al., 2011)
<i>Understudied Compounds</i>			
1	Styrene	Y	(Jia and Xu, 2010)
	Benzene, 1,2,4-Trimethyl	Y	(Takekawa et al., 2003)
	1-Undecene	Y	(Matsunaga et al., 2009)
	1-Dodecene	Y	(Matsunaga et al., 2009)
	Furan	Y	(Gómez Alvarez et al., 2009)
	Furan, 2-methyl	Y	(Gómez Alvarez et al., 2009)
	Xylenol	Y	(Nakao et al., 2011)
	Ethane		(Lim and Ziemann, 2009) ^b
	Propane		(Lim and Ziemann, 2009) ^b
	<i>n</i> -Butane		(Lim and Ziemann, 2009) ^b
	<i>n</i> -Pentane		(Lim and Ziemann, 2009) ^b
	Hexane		(Lim and Ziemann, 2009)
	2,3-Dimethyl Butane		(Lim and Ziemann, 2009) ^b
	2-Methyl Pentane		(Lim and Ziemann, 2009) ^b
	Heptane		(Lim and Ziemann, 2009)
	2-Methyl Hexane		(Lim and Ziemann, 2009) ^b
	3-Methyl Hexane		(Lim and Ziemann, 2009) ^b
	Octane		(Lim and Ziemann, 2009) ^b
	Ethene		(Matsunaga et al., 2009) ^b
	Propene		(Matsunaga et al., 2009) ^b
	1-Butene		(Matsunaga et al., 2009) ^b
	<i>i</i> -Butene		(Matsunaga et al., 2009) ^b
	<i>trans</i> -2-Butene		(Matsunaga et al., 2009) ^b
	<i>cis</i> -2-Butene		(Matsunaga et al., 2009) ^b
	1-Pentene		(Matsunaga et al., 2009) ^b
	2-Pentene, (<i>Z</i>)-		(Matsunaga et al., 2009) ^b
	2-Pentene, (<i>E</i>)-		(Matsunaga et al., 2009) ^b
	2-Methyl-2-Butene		(Matsunaga et al., 2009) ^b
	2-Methyl-1-Butene		(Matsunaga et al., 2009) ^b
	3-Methyl-1-Butene		(Matsunaga et al., 2009) ^b
	1-Hexene		(Matsunaga et al., 2009) ^b
	1-Heptene		(Matsunaga et al., 2009) ^b

	1-Nonene	(Matsunaga et al., 2009)
	Acetylene	(Volkamer et al., 2009)
	2-Butenal	(Chan et al., 2010)
	Acrolein	(Chan et al., 2010)
0	Cyclopentene	Y
	1,4-Pentadiene	Y
	1,3-Pentadiene, (E)	Y
	1,3-Cyclopentadiene	Y
	Cyclopentene, 1-Methyl	Y
	1,3-Cyclopentadiene, 1-methyl	Y
	1,3-Cyclopentadiene, 5-methyl-	Y
	1,3-Cyclohexadiene	Y
	1,3-Pentadiene, 2-methyl-, (Z)	Y
	Benzene, 1-ethenyl-3-methyl-	Y
	<i>p</i> -Cymene	Y
	Indene	Y
	Santene	Y
	Camphene	Y
	Tricyclene	Y
	Hydroxymethylfurfural	Y
	2-Furanone	Y
	Furfural	Y
	5-Methyl Furfural	Y
	2-Furfuryl alcohol	Y
	Furan, 2,5-dimethyl	Y
	Furan, 2-Acetyl	Y
	Benzofuran	Y
	Cyclopentanone	Y
	2-Cyclopenten-1-one	Y
	2,4-Cyclopentadiene-1-one	Y
	2-Cyclopenten-1-one, 2-Methyl	Y
	2-Hydroxy-3-Methyl-2-	Y
	Cyclopentenone	Y
	Benzaldehyde	Y
	Vinylphenol	Y
	Salicylaldehyde	Y
	Bornyl Acetate	Y
	Pyrrole	Y
	Pyridine	Y
	Benzonitrile	Y
	Propyne	
	Butenyne	
	Cyclopentane	
	Formaldehyde	
	Acetaldehyde	
	Propanal	
	Propanal, 2-Methyl	
	Butanal	
	Butanal, 2-Methyl	
	Butanal, 3-Methyl	
	Ethyl Acetate	
	Methylglyoxal	
	2-Propynal	
	Glycolaldehyde	
	Methanol	

Methyl vinyl ketone
3-Buten-2-one, 3-methyl-
Acetone
2-Butanone
2,3-Butanedione
2-Pentanone
2,3-Pentanedione
Hydroxyacetone
Butyrolactone
Formic acid
Acetic Acid
Acetic Acid, Methyl Ester
Hydrogen Cyanide
Acetonitrile
Methyl chloride
Carbonyl Sulfide

^aAssessed only for understudied compounds (0-1 publication)

^bReported trends of SOA yield vs. carbon number were assumed to extend to compounds lighter than those tested in the cited publication.

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