Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Figure S1: WE-CAN research flight tracks colored by the total calculated OH reactivity (tOHR, s^{-1}) for free troposphere and aged smoke sampling periods. The maximum total OH reactivity is limited to the 95th percentile.

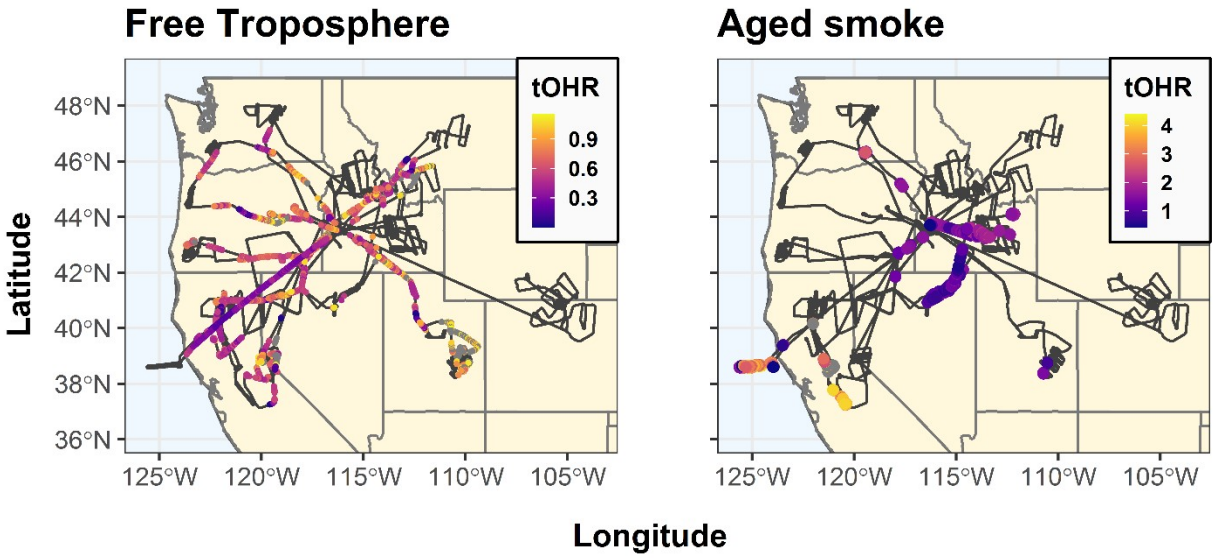

Figure S2. Total gas OH reactivity profiles for 24 fires reported in this work. Emission transects of the same fire completed more than 30 minutes apart are treated as separate fires and denoted with a, b, etc. Average total calculated OH reactivities (s^{-1}) are shown for each transect to the right of the bars.

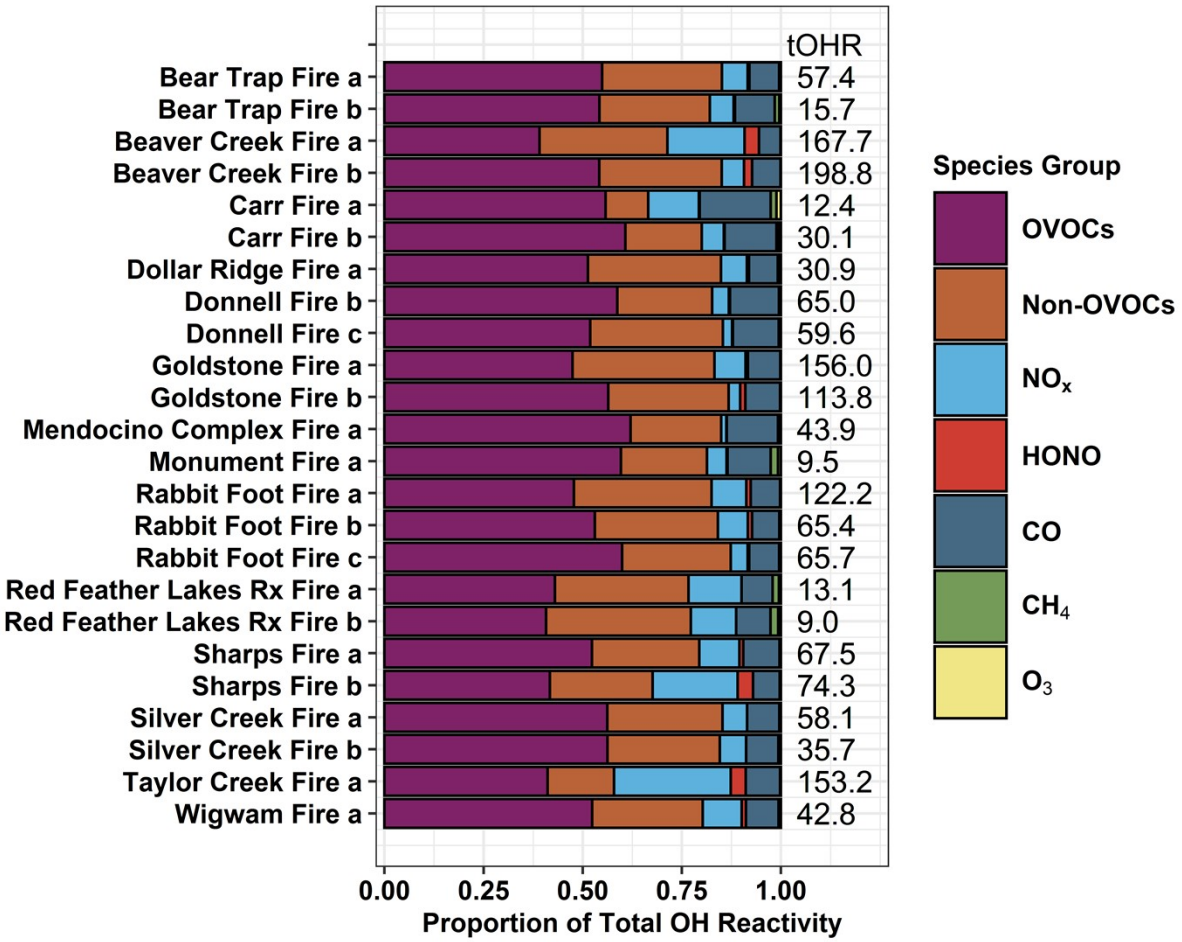

Figure S3. The proportion of VOC groups comprising the non-implemented VOC OHR fraction shown in Figure 4c. These groups represent those species that were measured during WE-CAN but are not implemented for biomass burning in the GEOS-Chem CTM.

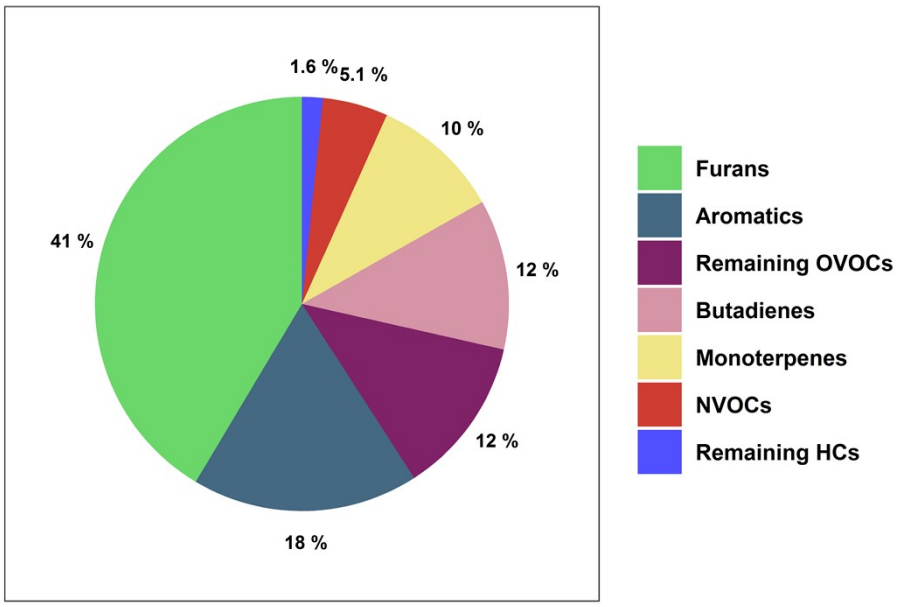

Table S1. VOC species used in this work, including the instrument each species was measured by, the isomeric fractional contributions to the PTR-ToF-MS measured ion, measurement uncertainty, and weighted rate constants for the reaction with the OH radical. [1,2]

Formula	Dominant isotopologue mass (da)	VOC contributor	Instrument	Fractional contribution to PTR-ToF-MS ion signal	Uncertainty (%)	k_{OH} (10^{-12} cm^3 molecule^{-1} s^{-1})
C_2H_2	26.0157	Ethyne	AWAS		10	1
HCN	27.0109	Hydrogen cyanide	CIMS		30	0
C_2H_4	28.0313	Ethene	AWAS		10	7.8
CH_2O	30.0106	Formaldehyde	PTR	1	40	8.5
C_2H_6	30.0470	Ethane	AWAS		10	0.24
CH_4O	32.0262	Methanol	PTR	1	15	0.8
C_2H_3N	41.0265	Acetonitrile	PTR	1	15	0
C_3H_6	42.0470	Propene	PTR	0.62	50	30
C_3H_6	42.0470	Fragments	PTR	0.38		
HNCO	43.0058	Isocyanic acid	PTR	1	50	0
C_2H_5N	43.0422	Ethenamine	PTR	1	50	0.2
C_2H_4O	44.0262	Acetaldehyde	PTR	1	15	15
C_3H_8	44.0626	Propane	TOGA		30	1.09
CH_3NO	45.0215	Formamide	PTR	1	50	1.5
CH_2O_2	46.0055	Formic acid	CIMS		30	0.4
C_2H_6O	46.0419	Ethanol	TOGA		30	3.2
HONO	47.0007	HONO	CIMS		30	6
C_4H_4	52.0313	1-Buten-3-yne	PTR	0.87	50	20
C_4H_4		Fragments	PTR	0.13		
C_3H_3N	53.0265	Acrylonitrile	PTR	1	50	4
C_3H_2O	54.0106	2-Propynal	PTR	1	50	20
C_4H_6	54.0470	1,3-Butadiene	PTR	0.82	50	58.8
C_4H_6	54.0470	1,2-Butadiene	PTR	0.01	50	58.8
C_4H_7		Fragments	PTR	0.17		
C_3H_5N	55.0422	Propanenitrile	PTR	1	50	0.3
C_3H_4O	56.0262	Acrolein	TOGA		30	20
C_4H_8	56.0626	Butenes	PTR	0.59	15	31.8
C_4H_9		Fragments	PTR	0.41		
C_2H_3NO	57.0215	Methyl isocyanate	PTR	0.5	50	0.1
C_2H_3NO	57.0215	Hydroxyacetonitrile	PTR	0.5	50	0.1
C_3H_7N	57.0578	Propene amine	PTR	1	50	15
$C_2H_2O_2$	58.0055	Glyoxal	PTR	1	50	11
C_3H_6O	58.0419	Acetone	PTR	0.83	20	0.2
C_3H_6O	58.0419	Propanal	PTR	0.17	20	0.2
C_4H_{10}	58.0783	Isobutane	TOGA		15	2.3

C_4H_{10}	58.0783	n-Butane	TOGA		15	2.4
C_2H_5NO	59.0371	Acetamide	PTR	1	50	8.6
C_3H_9N	59.0735	Trimethylamine	PTR	1	50	60
$C_2H_4O_2$	60.0211	Acetic acid	PTR	0.67	40	3.7
$C_2H_4O_2$	60.0211	Glycolaldehyde (=hydroxyacetaldehyde)	PTR	0.33	40	3.7
C_3H_8O	60.0575	Isopropanol	TOGA		30	5.7
CH_3NO_2	61.0164	Nitromethane	PTR	1	50	0
C_2H_6S	62.0190	Dimethyl sulfide	AWAS		10	6
C_4H_3N	65.0265	Cyanoallene isomers	PTR	1	50	4
C_5H_6	66.0470	1,3-Cyclopentadiene	PTR	0.22	50	92
C_5H_7		Fragments	PTR	0.78		
C_4H_5N	67.0422	Pyrrole	PTR	0.57	50	111.4
C_4H_5N	67.0422	Butene nitrile isomers	PTR	0.43	50	111.4
C_3O_2	67.9898	Carbon suboxide	PTR	1	50	1.5
C_4H_4O	68.0262	Furan	TOGA		40	40
C_5H_8	68.0626	Isoprene	PTR	0.63	20	100
C_4H_7N	69.0578	Butane nitrile	PTR	0.61	50	7.7
C_4H_7N	69.0578	Dihydropyrrole	PTR	0.39	50	7.7
$C_3H_2O_2$	70.0055	Propiolic acid	PTR	1	50	26
C_4H_6O	70.0419	Methyl vinyl ketone	PTR	0.6	20	24.8
C_4H_6O	70.0419	Methacrolein	PTR	0.28	20	24.8
C_4H_6O	70.0419	2-Butenal (=crotonaldehyde)	PTR	0.13	20	24.8
C_5H_{10}	70.0783	Pentene, Methylbutenes	PTR	0.69	50	57.2
C_5H_{11}		Fragments	PTR	0.31		
C_4H_9N	71.0735	Buteneamines, Tetrahydropyrole	PTR	1	50	25
$C_3H_4O_2$	72.0211	Pyruvaldehyde (=methyl glyoxal)	PTR	0.5	50	21.1
$C_3H_4O_2$	72.0211	Acrylic acid	PTR	0.5	50	21.1
C_4H_8O	72.0575	Methyl ethyl ketone	PTR	0.85	20	5.5
C_4H_8O	72.0575	2-Methyl propanal	PTR	0.14	20	5.5
C_4H_8O	72.0575	Butanal	PTR	0.01	20	5.5
C_5H_{12}	72.0939	n-Pentane	TOGA		15	3.9
C_5H_{12}	72.0939	Isopentane	TOGA		15	3.9
$C_2H_3NO_2$	73.0164	Nitroethene	PTR	1	50	1.2
$C_3H_6O_2$	74.0368	Hydroxyacetone	PTR	0.5	50	2.2
$C_3H_6O_2$	74.0368	Methyl acetate	PTR	0.35	50	2.2
$C_3H_6O_2$	74.0368	Ethyl formate	PTR	0.14	50	2.2
$C_2H_5NO_2$	75.0320	Nitroethane, Ethyl nitrite	PTR	1	50	0.1
CS_2	75.9441	Carbon disulfide	TOGA		50	1.98
C_6H_6	78.0470	Benzene	PTR	0.95	15	1.2
C_6H_6		Fragments	PTR	0.05		
C_5H_5N	79.0422	Pentadienenitriles	PTR	0.56	50	5.6

C_5H_5N	79.0422	Pyridine	PTR	0.44	50	5.6
C_5H_4O	80.0262	2,4-Cyclopentadiene-1-one	PTR	0.42	50	20
C_5H_4O		Fragments	PTR	0.58		
C_5H_7N	81.0578	Pentenenitriles	PTR	0.67	50	62.7
C_5H_7N	81.0578	Methylpyrroles	PTR	0.33	50	62.7
C_5H_6O	82.0419	2-Methylfuran	TOGA		20	100
C_5H_6O	82.0419	3-Methyl furan	TOGA		20	100
C_6H_{10}	82.0783	2,2-Dimethylbutane	AWAS		10	5.95
C_5H_9N	83.0735	Pentanenitriles	PTR	1	50	0.5
$C_4H_4O_2$	84.0211	2(3H)-Furanone	PTR	0.81	50	44.5
C_5H_8O	84.0575	3-Methyl-3-buten-2-one	PTR	0.37	50	11.5
C_5H_8O	84.0575	Cyclopentanone	PTR	0.18	50	11.5
C_5H_8O		Fragments	PTR	0.45		
C_6H_{12}	84.0939	Cyclohexane	AWAS		10	7.2
$C_4H_6O_2$	86.0368	2,3-Butanedione	PTR	0.87	50	0.8
$C_4H_6O_2$	86.0368	Methyl acrylate	PTR	0.05	50	0.8
$C_4H_6O_2$		Fragments	PTR	0.08		
$C_5H_{10}O$	86.0732	3-Methyl-2-butanone	PTR	0.43	50	7.9
$C_5H_{10}O$	86.0732	2-Pentanone	PTR	0.32	50	7.9
$C_5H_{10}O$	86.0732	3-Pentanone	PTR	0.21	50	7.9
$C_5H_{10}O$	86.0732	2-Methylbutanal, 3-Methylbutanal	PTR	0.04	50	7.9
C_6H_{14}	86.1096	n-Hexane	AWAS		10	5.4
C_6H_{14}	86.1096	3-Methylpentane	AWAS		10	5.45
$C_3H_4O_3$	88.0160	Pyruvic acid	PTR	1	50	0.1
$C_4H_8O_2$	88.0524	Methyl propanoate	PTR	1	50	0.9
$C_3H_7NO_2$	89.0477	Nitropropanes	PTR	1	50	1.2
C_7H_{16}	90.0470	2,4-Dimethylpentane	AWAS		10	6.89
C_6H_5N	91.0422	Ethylnylpyrrole	PTR	1	50	145
C_7H_8	92.0626	Toluene	PTR	1	15	5.6
C_5H_3NO	93.0215	3-Furancarbonitrile	PTR	0.7	50	40
C_5H_3NO	93.0215	2-Furancarbonitrile	PTR	0.3	50	40
C_6H_7N	93.0578	2-Methylpyridine	PTR	0.93	50	2.6
C_6H_7N	93.0578	3-Methylpyridine	PTR	0.07	50	2.6
C_6H_6O	94.0419	Phenol	CIMS		30	28
$C_5H_4O_2$	96.0211	2-Furfural (=furaldehyde)	PTR	0.84	20	35.6
$C_5H_4O_2$	96.0211	3-Furfural	PTR	0.04	20	35.6
$C_5H_4O_2$		Fragments	PTR	0.11		
C_6H_8O	96.0575	C2-Substituted furan isomers	PTR	0.46	50	132
C_6H_8O	96.0575	2,5-Dimethylfuran	PTR	0.44	50	132
C_6H_8O	96.0575	2-Ethylfuran	PTR	0.1	50	132
$C_6H_{11}N$	97.0891	4-Methylpentanenitrile	PTR	1	50	5

$C_4H_2O_3$	98.0004	Maleic anhydride	PTR	1	50	1.4
$C_5H_6O_2$	98.0368	2-Furanmethanol	PTR	0.34	50	13.6
$C_5H_6O_2$		Fragments	PTR	0.66		
$C_6H_{10}O$	98.0732	C6H10O Ketones	PTR	0.74	50	6.4
$C_6H_{10}O$	98.0732	Methylcyclopentanone, Cyclohexanone	PTR	0.26	50	6.4
C_7H_{14}	98.1096	Methylcyclohexane	AWAS		10	11
$C_4H_4O_3$	100.0160	Dihydrofurandione (=succinic anhydride)	PTR	1	50	20
$C_5H_8O_2$	100.0524	Methyl methacrylate	PTR	0.69	50	30.3
$C_5H_8O_2$		Fragments	PTR	0.31		
$C_6H_{12}O$	100.0888	Hexanones	PTR	0.53	30	18.6
$C_6H_{12}O$	100.0888	Hexanal	PTR	0.47	30	18.6
C_7H_{16}	100.1252	n-Heptane	AWAS		10	7.11
C_7H_{16}	100.1252	2-Methylhexane	AWAS		10	6.7
C_7H_{16}	100.1252	3-Methylhexane	AWAS		10	6.3
C_7H_{16}	100.1252	2,3-Dimethylpentane	AWAS		10	6.89
$C_4H_6O_3$	102.0317	Acetic anhydride	PTR	1	50	43
C_7H_5N	103.0422	Benzonitrile	PTR	1	50	1
C_8H_8	104.0626	Styrene	TOGA		40	58
$C_3H_7NO_3$	105.0426	Isopropyl nitrate	TOGA		15	0.42
$C_3H_7NO_3$	105.0426	n-Propyl nitrate	TOGA		15	0.73
C_7H_7N	105.0578	Vinylpyridine	PTR	1	50	57
C_7H_6O	106.0419	Benzaldehyde	PTR	1	50	12
C_8H_{10}	106.0783	*(m,p)*-Xylenes	PTR	0.46	20	13.2
C_8H_{10}	106.0783	Ethylbenzene	PTR	0.36	20	13.2
C_8H_{10}	106.0783	*o*-Xylene	PTR	0.18	20	13.2
$C_6H_4O_2$	108.0211	Quinone (=*p*-benzoquinone)	PTR	1	50	4.6
C_7H_8O	108.0575	2-Methylphenol (=o-cresol)	PTR	0.5	50	26.2
C_7H_8O	108.0575	Anisol	PTR	0.5	50	26.2
$C_6H_6O_2$	110.0368	5-Methyl furfural	PTR	0.5	30	80.1
$C_6H_6O_2$	110.0368	Benzene diols (=catechol, resorcinol)	PTR	0.5	30	80.1
$C_7H_{10}O$	110.0732	C3 Furans	PTR	0.55	50	23.3
$C_7H_{10}O$		Fragments	PTR	0.45		
$C_5H_5NO_2$	111.0320	Dihydroxy pyridine	PTR	0.5	50	10.3
$C_5H_5NO_2$	111.0320	Methyl maleimide	PTR	0.5	50	10.3
$C_5H_4O_3$	112.0160	5-Hydroxy 2-furfural/2-furoic acid	PTR	1	50	49
$C_6H_8O_2$	112.0524	2-Hydroxy-3-methyl-2-cyclopenten-1-one	PTR	1	50	57
$C_7H_{12}O$	112.0888	Ethylcyclopentanone	PTR	1	50	10
$C_4H_3NO_3$	113.0113	Nitrofuran	PTR	1	50	40
$C_5H_6O_3$	114.0317	5-Hydroxymethyl-2[3H]-furanone	PTR	0.5	50	100
$C_6H_{10}O_2$	114.0681	C6 1-DBE esters	PTR	0.54	50	20

$C_6H_{10}O_2$	114.0681	C6 Diones	PTR	0.46	50	20
$C_7H_{14}O$	114.1045	Heptanal	PTR	0.63	50	21.4
$C_7H_{14}O$	114.1045	2,4-Dimethyl-3-pentanone	PTR	0.24	50	21.4
$C_7H_{14}O$	114.1045	Heptanone	PTR	0.13	50	21.4
C_8H_{18}	114.1409	2,2,4-Trimethylpentane	TOGA		15	5.4
C_8H_{18}	114.1409	n-Octane	AWAS		10	8.11
C_8H_{18}	114.1409	2-Methylheptane	AWAS		10	12.2
C_8H_{18}	114.1409	2,3,4-Trimethylpentane	AWAS		10	6.5
C_8H_{18}	114.1409	3-Methylheptane	AWAS		10	14
$C_5H_8O_3$	116.0473	5-Hydroxymethyl tetrahydro 2-furanone, 5-Hydroxy tetrahydro 2-furfural	PTR	1	50	5
$C_6H_{12}O_2$	116.0837	C6 Esters	PTR	1	50	6
C_8H_7N	117.0578	Benzeneacetonitrile	PTR	1	50	1.2
C_8H_6O	118.0419	Benzofuran	PTR	1	50	37
C_9H_{10}	118.0783	Methyl styrenes	PTR	0.84	50	50.4
C_9H_{10}	118.0783	Indane	PTR	0.13	50	50.4
C_9H_{10}	118.0783	Propenyl benzenes	PTR	0.03	50	50.4
C_8H_8O	120.0575	Tolualdehyde	PTR	1	50	16
C_9H_{12}	120.0939	C9 Aromatics	PTR	1	15	22
$C_7H_6O_2$	122.0368	2-Hydroxybenzaldehyde	PTR	1	50	38
$C_8H_{10}O$	122.0732	C2 Phenols	PTR	0.5	50	46.6
$C_8H_{10}O$	122.0732	Methyl anisol	PTR	0.5	50	46.6
$C_6H_4O_3$	124.0160	Hydroxy benzoquinone	PTR	1	50	4.6
$C_7H_8O_2$	124.0524	Guaiacol (=2-methoxyphenol)	PTR	1	50	75
$C_6H_6O_3$	126.0317	5-(Hydroxymethyl)-2-furfural	PTR	1	50	100
C_9H_{20}	128.1565	n-Nonane	AWAS		10	9.7
C_9H_8O	132.0575	Methylbenzofuran	PTR	1	50	37
$C_{10}H_{12}$	132.0939	Ethyl styrene	PTR	0.5	50	33
$C_{10}H_{12}$	132.0939	Methylpropenylbenzenes, Butenylbenzenes	PTR	0.5	50	33
$C_9H_{10}O$	134.0732	3-Methylacetophenone	PTR	1	50	4.5
$C_{10}H_{14}$	134.1096	C10 Aromatics	PTR	0.92	15	9.5
$C_{10}H_{15}$		Fragments	PTR	0.8		
$C_8H_8O_2$	136.0524	Methyl benzoic acid	PTR	1	50	12
$C_{10}H_{16}$	136.1252	Camphene	PTR	0.38	40	162.8
$C_{10}H_{16}$	136.1252	α-Pinene	PTR	0.33	40	162.8
$C_{10}H_{16}$	136.1252	β-Pinene, Myrcene	PTR	0.21	40	162.8
$C_{10}H_{16}$	136.1252	Tricyclene	PTR	0.07	40	162.8
$C_7H_7NO_2$	137.0477	Nitrotoluene	PTR	1	50	0.1
$C_8H_{10}O_2$	138.0681	2-Methoxy-4-methylphenol (=creosol)	PTR	1	50	100
$C_{11}H_{10}$	142.0783	Methylnaphthalene	PTR	1	50	50
$C_6H_8O_4$	144.0423	Product of levoglucosan dehydration (pyrolysis)	PTR	1	50	4.6

$C_{10}H_{10}O$	146.0732	Dimethylbenzofuran	PTR	1	50	37
$C_{10}H_{12}O$	148.0888	Methyl chavicol (=estragole)	PTR	1	50	50
$C_{11}H_{16}$	148.1252	C11 Aromatics	PTR	1	50	50
$C_9H_{10}O_2$	150.0681	Vinyl guaiacol	PTR	1	50	100
$C_8H_8O_3$	152.0473	Vanillin	PTR	1	50	85
$C_{10}H_{16}O$	152.1201	Oxygenated monoterpenes	PTR	0.7	50	4.3
$C_{10}H_{16}O$	152.1201	Camphor	PTR	0.3	50	4.3
$C_8H_{10}O_3$	154.0630	Syringol	PTR	1	50	100
$C_{10}H_{18}O$	154.1358	Cineole	PTR	1	50	25
$C_{10}H_{18}O$	154.1358	Other oxygenated monoterpenes	PTR	0	50	25
$C_{12}H_{12}$	156.0939	1,3-Dimethylnaphthalene	PTR	1	50	60
$C_{10}H_{20}O$	156.1514	Decanal	PTR	1	50	13
$C_{12}H_{18}$	162.1409	C12 aromatics	PTR	1	50	113
$C_{10}H_{12}O_2$	164.0837	Eugenol, Isoeugenol	PTR	1	50	100
$C_{13}H_{20}$	176.1565	C13 aromatics	PTR	1	50	113
$C_{15}H_{24}$	204.1878	Sesquiterpenes	PTR	1	50	300

Table S2. Global Fire Assimilation System version 1.2 (GFAS) emission inventory estimates for the 21 biomass burning VOC species and CO implemented in GEOS-Chem version 13.3.2. GFAS emissions were retrieved for July–September 2018 over the western U.S. domain (36° N-127° W, 49.5° N-105° W). Note that GFAS ERs for lumped aldehydes, MEK, formic acid, and acetic acid were updated based on Permar et al. (2021)

GEOS-Chem Species	**Formula**	k_{OH}	**Total emissions (Gg carbon)**
CO	CO	0.14	1690
Ethane	C_2H_6	0.25	19
Propane	C_3H_8	1.09	6.37
Lumped C≥4 alkanes	-	4.2	7.95
Ethene	C_2H_4	8.5	42
Lumped C≥3 alkenes	-	30.7	35
Methanol	CH_4O	0.9	34
Ethanol	C_2H_6O	3.2	0.47
Benzene	C_6H_6	1.22	17
Toluene	C_7H_8	5.6	12
Xylenes	C_8H_{10}	13.2	1.26
Isoprene	C_5H_8	100	2.46
Formaldehyde	CH_2O	8.95	25
Acetaldehyde	C_2H_4O	15	19
Lumped C≥3 aldehydes	-	18.7	4.82
Dimethyl sulfide	C_2H_6S	6	0.59
Acetone	C_3H_6O	0.2	17
Methyl Ethyl Ketone	C_4H_8O	1.2	4.65
Methacrolein	C_4H_6O	2.8	2.35
Glycolaldehyde	$C_2H_4O_2$	1.2	9.14
Formic acid	CH_2O_2	0.4	15.12
Acetic acid	$C_2H_4O_2$	3.7	29.18

Table S3. Initialization values used for the Framework for 0-D Atmospheric Modeling of the Taylor Creek Fire.

Compound	Formula	Taylor Creek Fire (ppb)
CO	CO	5670.68
NO	NO	6.76
NO_2	NO_2	58.86
HONO	HONO	64.49
Ozone	O_3	31.75
Furan	C_4H_4O	6.33
Benzene	C_6H_6	8.10
HNO_3	HNO_3	21.00
Guaiacol	$C_7H_8O_2$	1.05
PAN	$C_2H_3NO_5$	6.90
Isoprene	C_5H_8	1.19
Ethene	C_2H_4	82.53
Catechol	$C_6H_6O_2$	1.00
2-Methylfuran	C_5H_6O	1.56
Methylfurfural	$C_6H_6O_2$	1.00
Dimethylfuran	C_6H_8O	0.67
Syringol	$C_8H_{10}O_3$	0.07
3-Methylfuran	C_5H_6O	0.31
Formaldehye	CH_2O	126.05
Acetaldehyde	C_2H_4O	53.88
Acetone	C_3H_6O	14.34
Propanal	C_3H_6O	2.94
MVK	C_4H_6O	4.90
MACR	C_4H_6O	2.29
PPN	$C_3H_5NO_5$	0.84
Phenol	C_6H_6O	4.23
o-Xylene	C_8H_{10}	0.29
α-Pinene	$C_{10}H_{16}$	0.34
p-Xylene	C_8H_{10}	0.75
Cresol	C_7H_8O	1.81
1-Butene	C_4H_8	5.03
n-Butane	C_4H_{10}	0.90

Ethylbenzene	C_8H_{10}	0.59
1,2,3-Trimethylbenzene	C_9H_{12}	0.42
Styrene	C_8H_8	1.59
Benzaldehyde	C_7H_6O	1.07
n-Pentane	C_5H_{12}	1.05
n-Hexane	C_6H_{14}	0.22
n-Heptane	C_7H_{16}	0.18
n-Octane	C_8H_{18}	0.11
3-Methyl-1-butene	C_5H_{10}	0.27
1-Hexene	C_6H_{12}	1.69
β-Pinene	$C_{10}H_{16}$	0.22
Acrolein	C_3H_4O	5.50
2-Butenal	C_4H_6O	1.06
Butanal	C_4H_8O	0.27
Pentanal	$C_5H_{10}O$	0.38
Propene	C_3H_6	17.43
Butadiene	C_4H_6	7.27
Glyoxal	$C_2H_2O_2$	0.29
Sesquiterpenes	$C_{15}H_{24}$	0.02
Methylglyoxal	$C_3H_4O_2$	2.63
Biacetyl	$C_4H_6O_2$	2.43
Formic acid	CH_2O_2	51.1
Acetic acid	$C_2H_4O_2$	32.09
Acetol	$C_3H_6O_2$	2.91
Furfural (=furaldehyde)	$C_5H_4O_2$	7.34

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