

1 Tables and figures

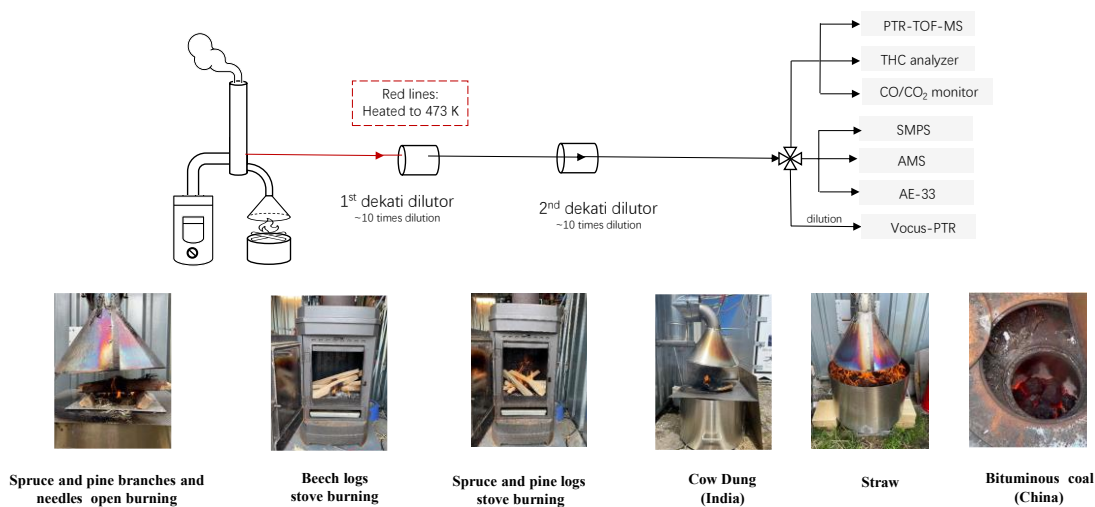


Figure S1. Schematic diagram of experimental setup.

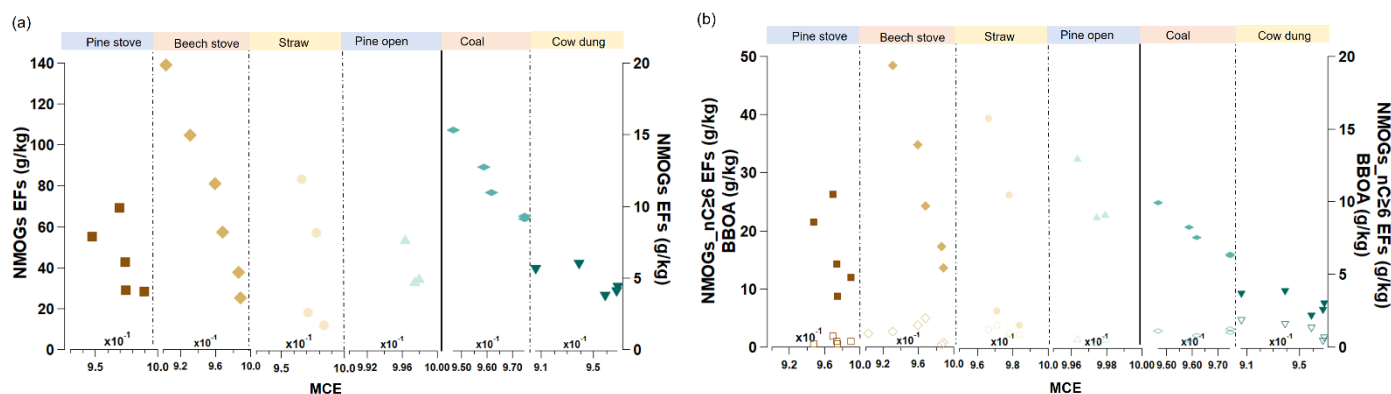


Figure S2. Scatter plot for (a) total NMOGs and (b) NMOGs with carbon number (nC) ≥ 6 (solid), primary biomass-burning organic aerosol (BBOA, hollow) emissions emission factors (EFs) and average modified combustion efficiency (MCE).

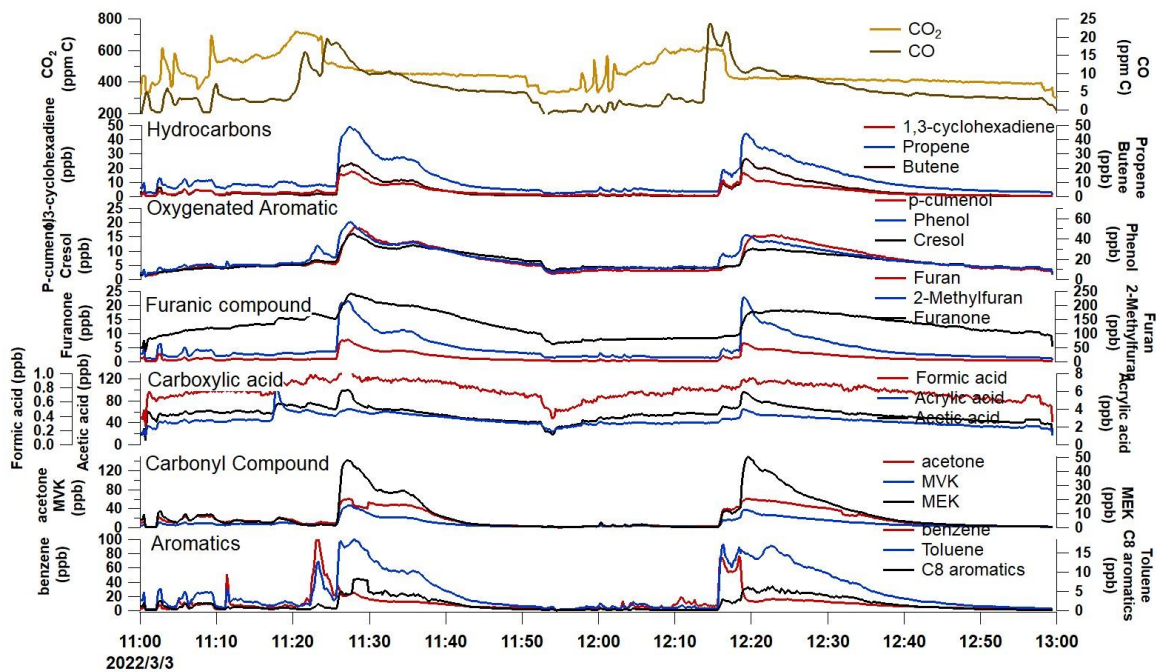


Figure S3. Time series of various primary organic gases for a burn of beech logs.

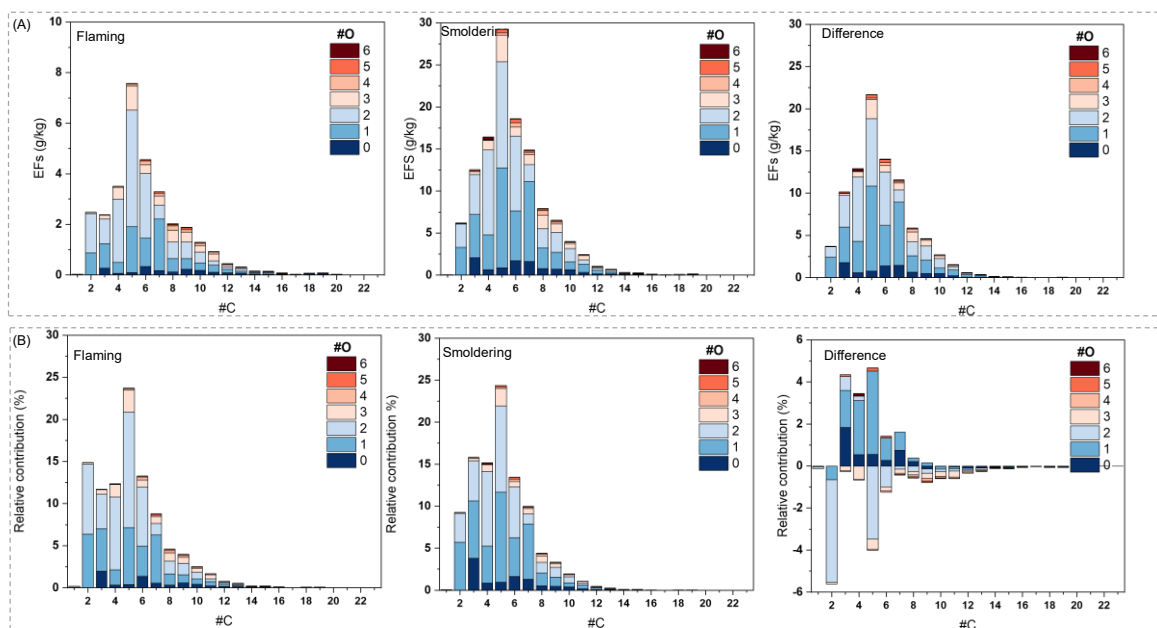
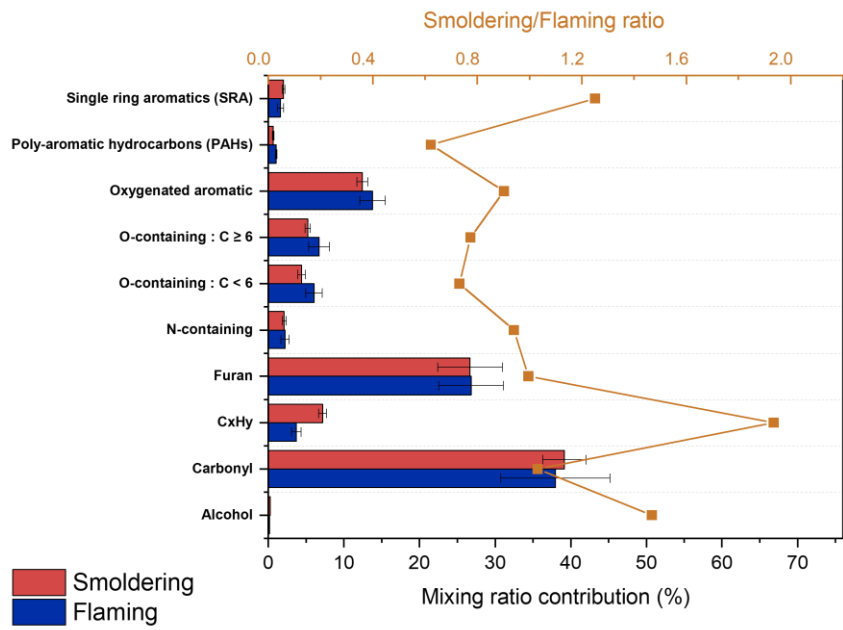


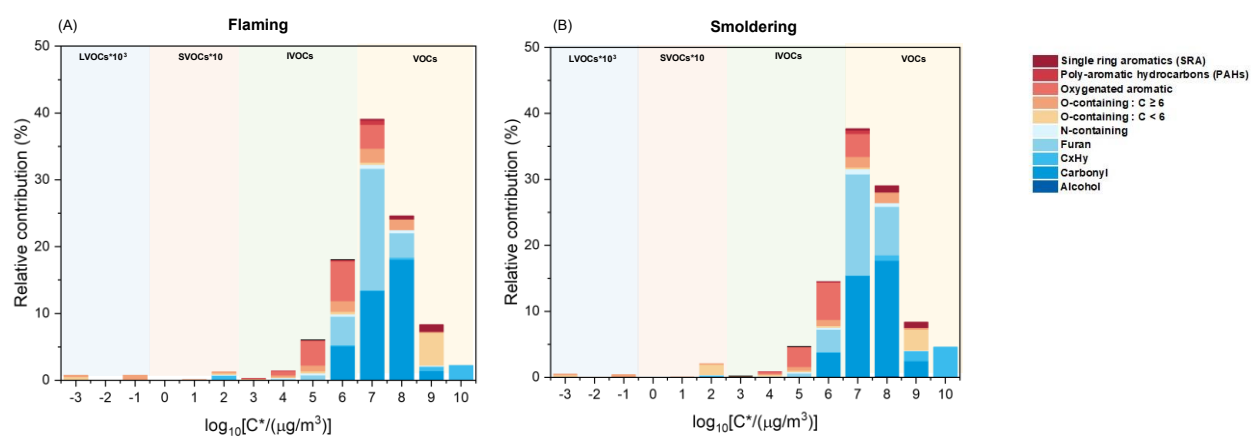
Figure S4. The average carbon and oxygen distribution for the flaming, smoldering phase and the difference between these two phases are colored by oxygen number in panel (A) absolute emission factors panel (B) relative contribution.

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Figure S5. The average relative contribution of the primary gas-phase species of different functional groups during the flaming and smoldering phase, respectively. Error bars correspond to the sample geometric standard deviation of the replicates. The square represents the mixing ratio between smoldering and flaming.



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Figure S6. Volatility distribution of primary emissions for beech logs stove burning in flaming and smoldering phase as a function of binned saturation vapor concentration. Columns are color-coded by each functional group. Shaded areas indicate the volatility ranges with units of $\mu\text{g m}^{-3}$: VOCs (yellow) as $\log_{10}(C^*) > 6.5$, IVOCs (blue) as $\log_{10}(C^*)$ between 6.5 to 2.5, semi-VOCs (SVOCs, green) as $\log_{10}(C^*)$ between 2.5 to - 0.5 and low-VOCs (LVOCs, orange) as $\log_{10}(C^*) < - 0.5$. The relative contribution of LVOCs and SVOCs are multiplied by a factor of 1000 and 10, respectively.

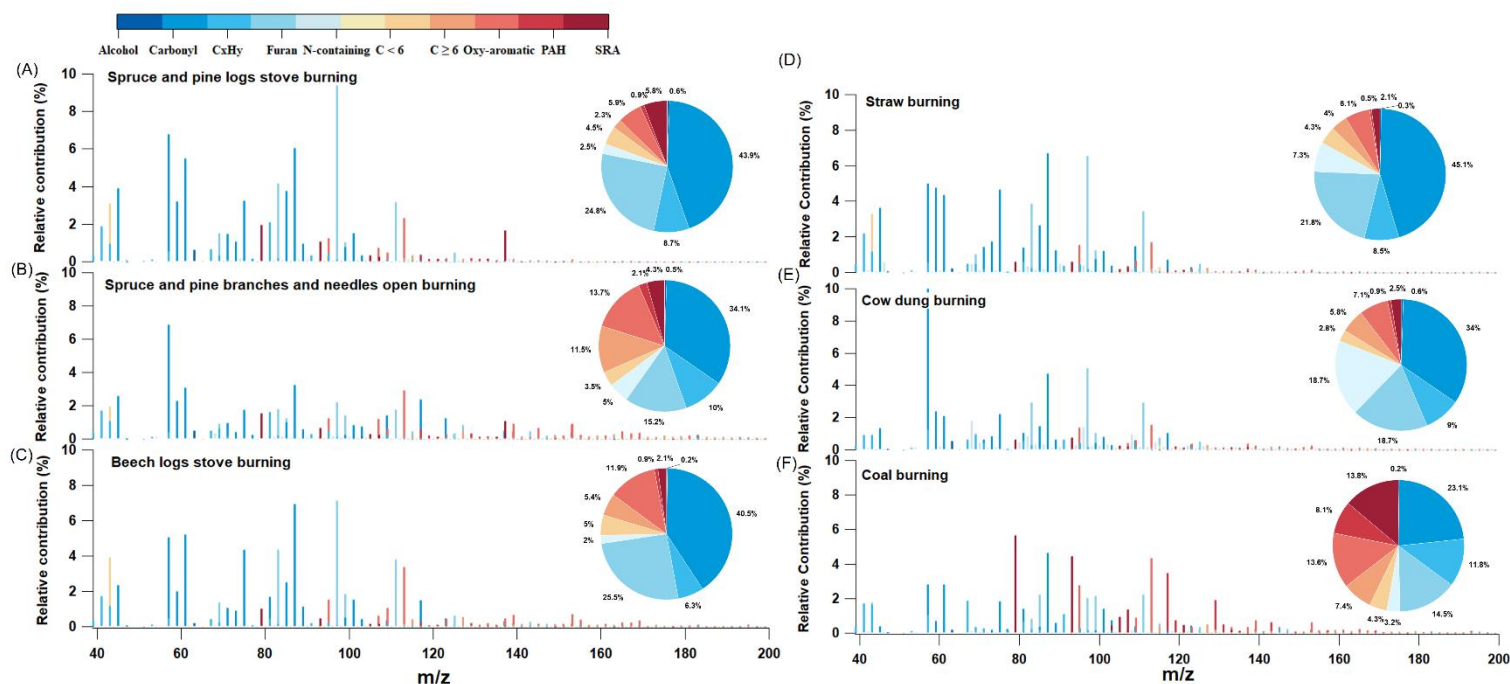


Figure S7. Average mass spectra of primary NMOG emissions for each burn colored by functional group. The pie chart shows the average fractional contribution of each functional group to the total mixing ratio for each experiment.

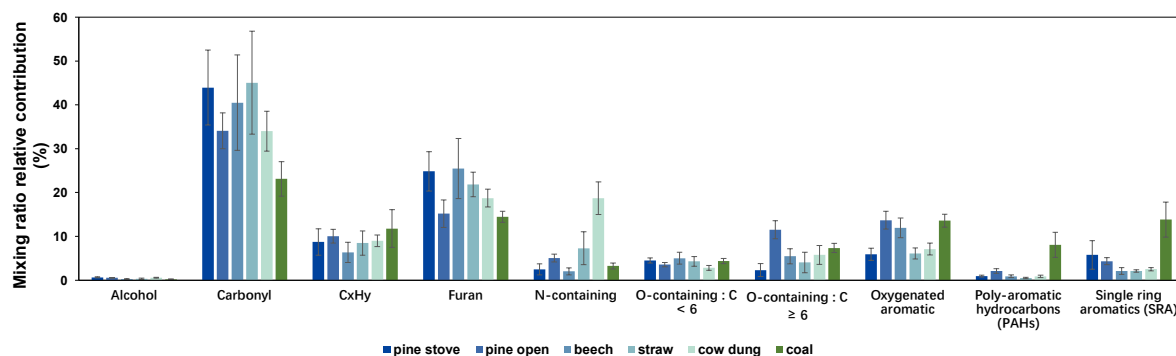


Figure S8. The average relative fractional contribution of each category to the total primary organic gases. Error bars correspond to one standard deviation of the replicates. Error bars correspond to one sample one standard deviation of the replicates.

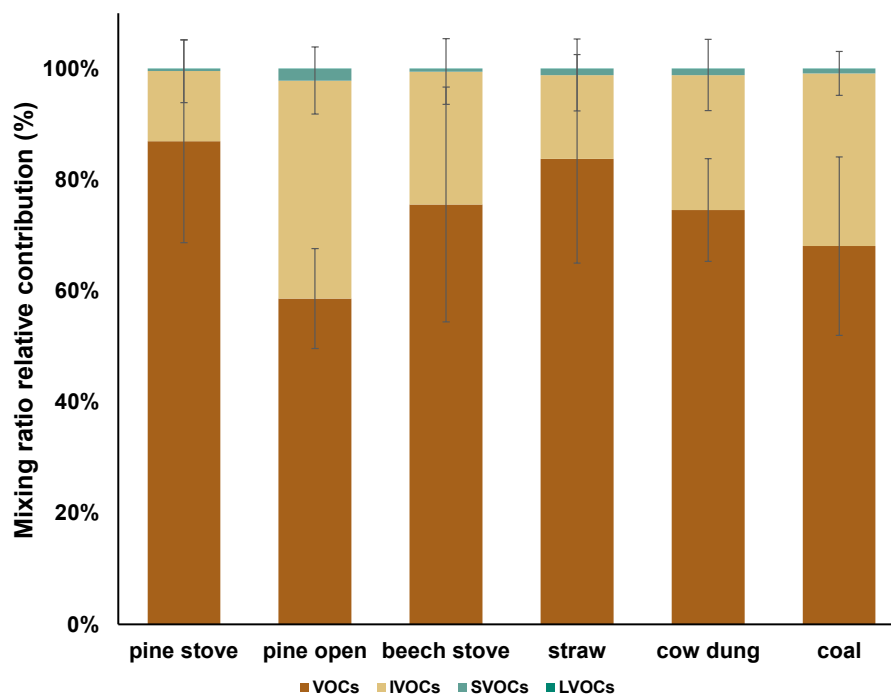


Figure S9. The average relative contribution of the primary organic gases sorted by volatility. Error bars correspond to one sample one standard deviation of the replicates.

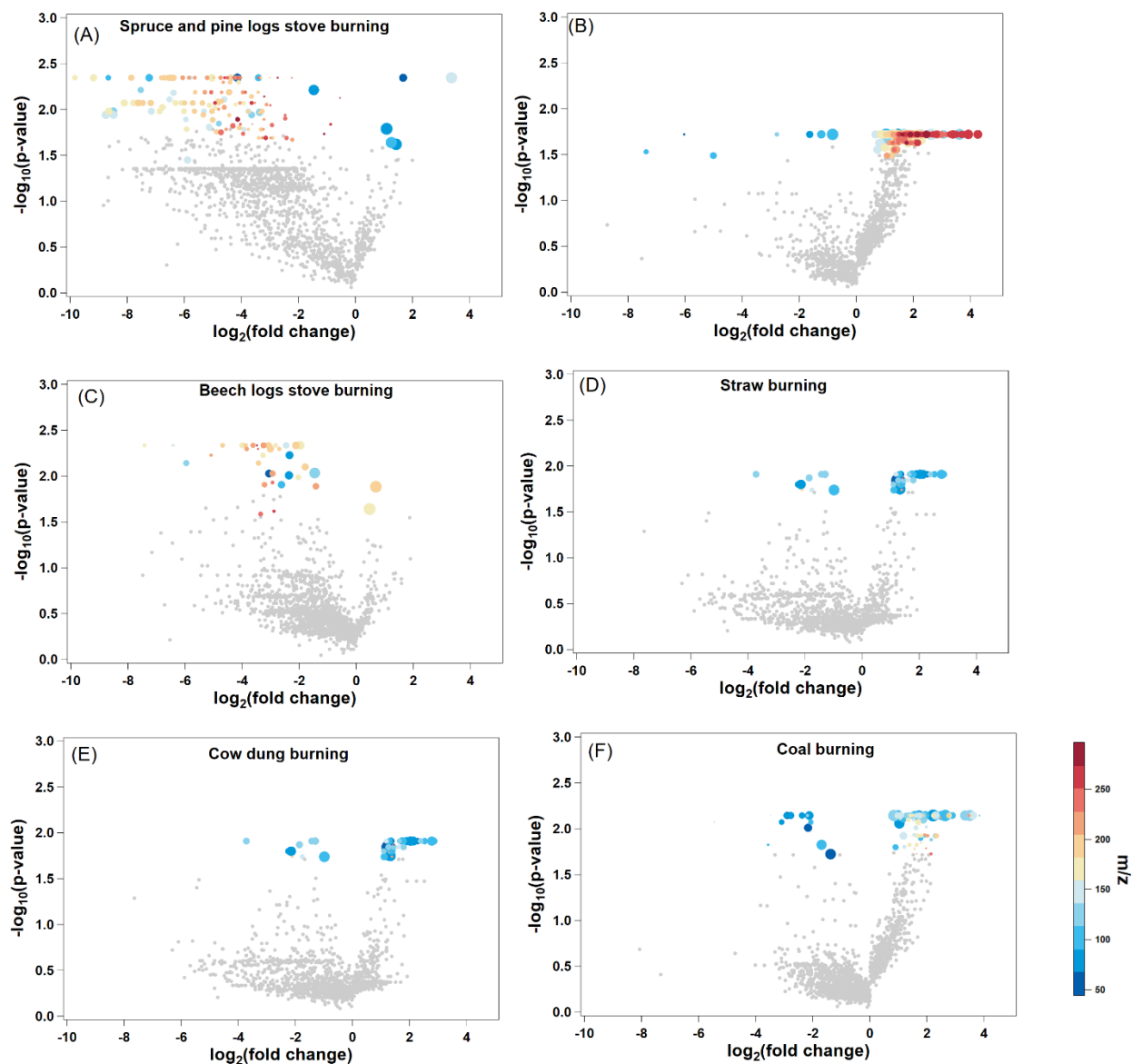


Figure S10. The static p-value vs. fold change. They are sized by the logarithm of fractional contribution and colored by the mass to charge.

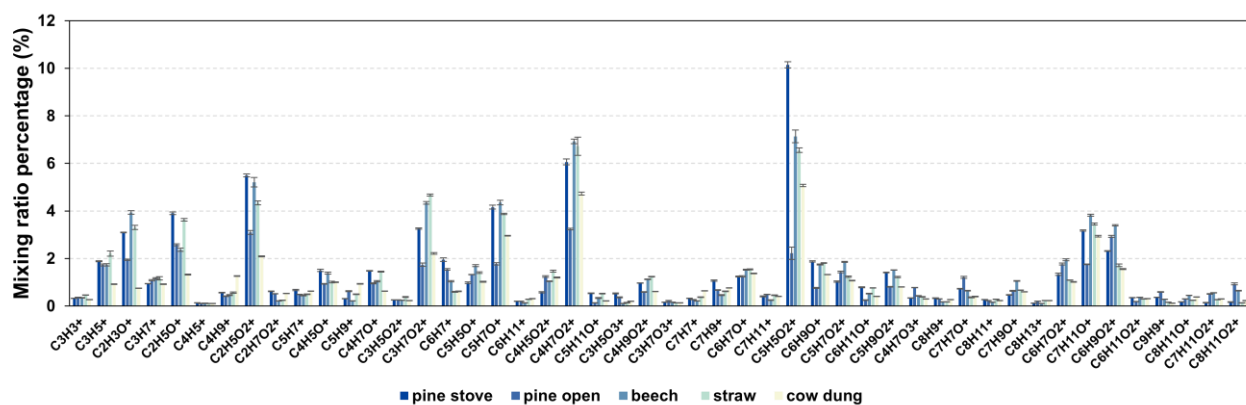


Figure S11. Mixing ratio percentage of the several dominant compounds measured by the Vocus in biomass (except coal) burning, where the bar colors denote the different experiments. Error bars correspond to one sample one standard error of the replicates.

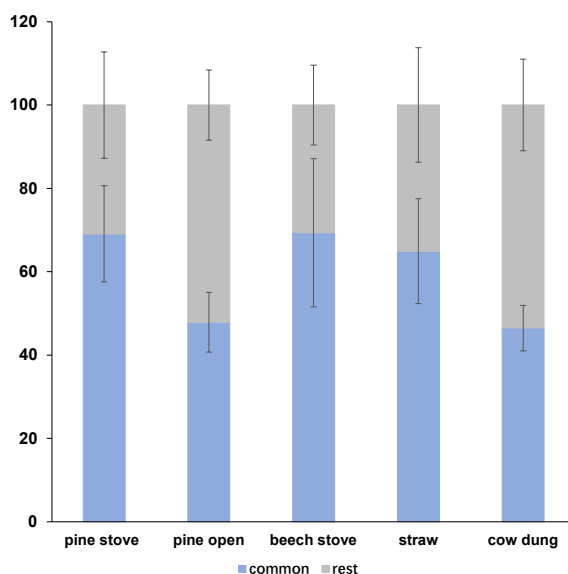


Figure S12. Mixing ratio percentage of the several dominant compounds for biomass fuels and rest primary organic gases measured by the Vocus in biomass (except coal) burning, where the bar colors denote the different experiments.

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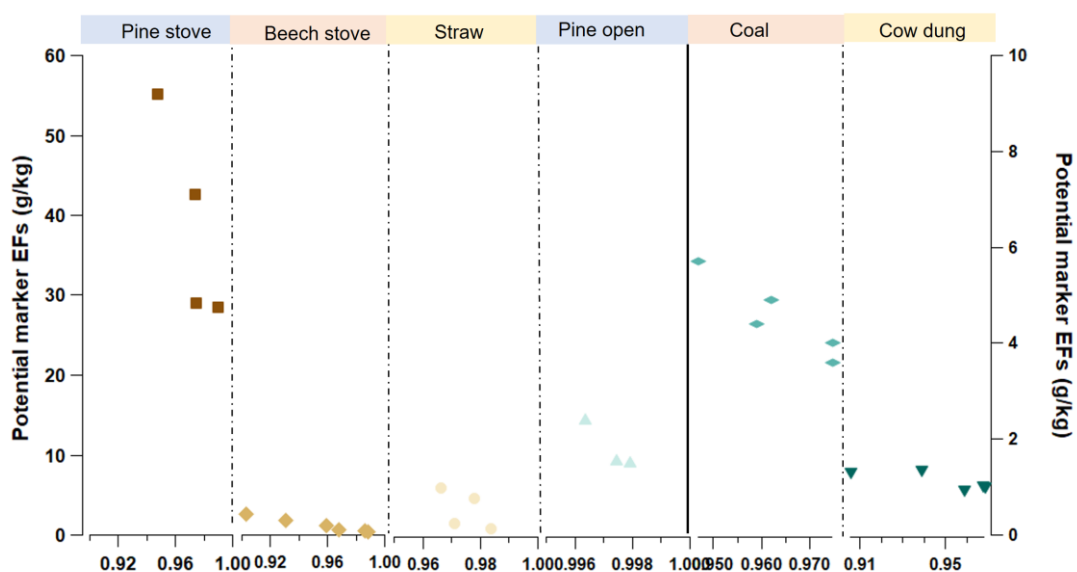


Figure S13. Scatter plot for the average modified combustion efficiency (MCE).

Table S1. Composition classes and the values for saturation mass concentration parameterizations.

Classes	n_c^0	b_c	b_o	b_{co}	b_N
CH	23.8	0.4681			
CHO	22.66	0.4481	1.656	-0.7790	
CHN	24.59	0.4066			0.9619
CHON	24.13	0.3667	0.7732	-0.0779	1.114

82 **Table S2** Average emission factors of CO, CO₂, Organic gases and PM, BC, OC as well as MCE for 6 types of
83 solid fuels

Exp. No.	Solid fuel type	MCE	Emission factor (g/kg)					
			CO	CO ₂	Organic vapors	PM	OC	BC
BS1	beech stove	0.96	31.2	1469.3	57.4	5	4.45	0.26
BS2	beech stove	0.95	37.7	1394.5	81.1	3.8	3.14	0.41
BS3	beech stove (flaming)	0.98	14.4	1568.4	37.7	0.5	0.31	0.40
BS4	beech stove (smoldering)	0.92	60.8	1284.4	104.7	2.7	2.3	0.15
BS5	beech stove (flaming)	0.99	11.9	1603.2	25.1	0.8	0.46	0.5
BS6	beech stove (smoldering)	0.87	76.5	1136.2	139.1	2.3	2.0	0.14
SPS1	spruce stove	0.99	10.8	1591.7	28.5	1	0.91	0.13
SPS2	spruce stove	0.97	25.9	1559.9	29	0.5	0.22	0.33
SPS3	spruce stove	0.97	25.9	1523.6	42.6	1	0.66	0.47
SPS4	spruce stove	0.95	50.6	1436	55.1	0.5	0.4	0.1
SPS5	spruce stove	0.97	29.2	1447.3	69.3	1.9	1.6	0.26
SPO1	spruce + pine open	0.99	3.6	1545.2	52.9	1.2	0.99	0.46
SPO2	spruce + pine open	0.99	2.1	1593.4	34.1	1.1	0.91	0.49
SPO3	spruce + pine open	0.99	2.6	1599.2	32.4	0.5	0.35	0.34
SO1	straw open	0.98	16.7	1579.2	11.7	2.1	2.27	0.53
SO2	straw open	0.97	29.1	1533	18.2	3.8	3.6	0.92
SO3	straw open	0.97	30.7	1379.3	83.3	3	3.32	0.3
SO4	straw open	0.98	21	1462.4	57	2.3	2.51	0.39
CDO1	cow dung open	0.89	97.2	1463.2	5.7	1.9	2.1	0.1
CDO2	cow dung open	0.94	63.3	1521.2	6	1.6	1.8	0.02
CDO3	cow dung open	0.97	32.7	1580.7	4.4	0.7	0.67	0.12
CDO4	cow dung open	0.96	42.6	1563.6	3.8	1.3	1.6	0.01
CDO5	cow dung open	0.97	33.7	1580.5	4.1	0.43	0.48	0.02
CS1	coal stove	0.95	58.3	1632.7	15.3	1.1	1.26	0.03
CS2	coal stove	0.96	45.6	1668.6	12.7	0.42	0.49	0.02

CS3	coal stove	0.96	42.4	1677.7	11	0.81	0.62	0.41
CS4	coal stove	0.97	28.4	1711.7	9.1	1.01	0.87	0.25
CS5	coal stove	0.97	28.4	1710.3	9.3	1.25	1.44	0.01
