Supporting Information

Cyclic ion mobility spectrometry coupled to high-resolution time-of-flight mass spectrometry equipped with atmospheric solid analysis probe for the molecular characterization of combustion particulate matter

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Table S1. Information on the feed fuels for the combustion aerosol generation. * not measured, values according to EN590 fuel specification

	Unit	Spruce logwood	Lignite briquettes	Diesel fuel*
Heating value	MJ kg^{-1}	17.9	20.2	
Moisture	w%	6.9	14.4	<0.02
Ash	w%	0.6	5.9	<0.01
C	w%	47.6	54.5	
H	w%	5.7	4.1	
O	w%	39.1	20	
N	w%	0.09	0.58	
S	w%	0.014	0.6	<0.001

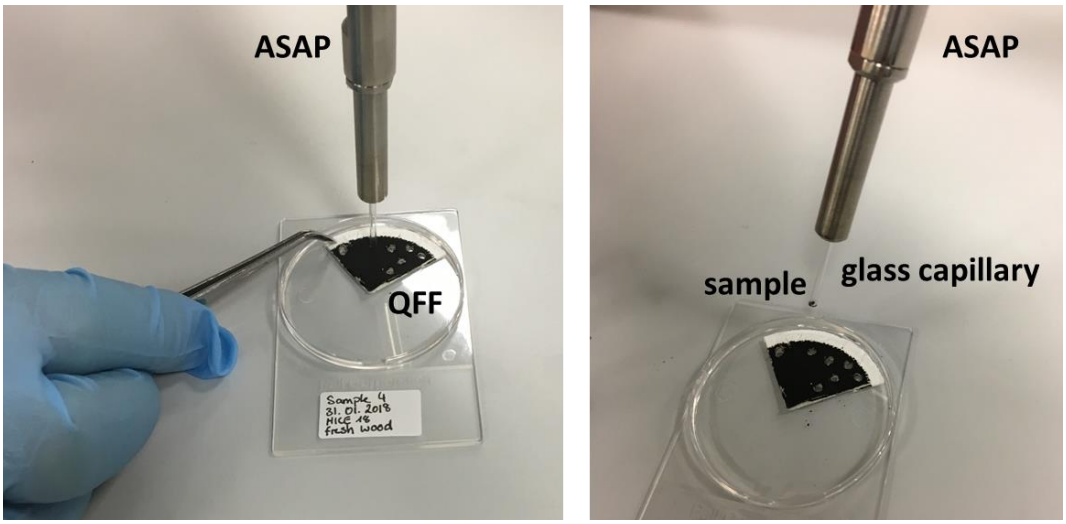

Figure S1: Photographic description of the particulate matter sampling from quartz-fiber filters for deploying to the atmospheric solid analysis probe. A tiny aliquot of the homogenously sampled aerosol is loaded to a pre-cleaned glass capillary and immediately transferred to the ASAP probe and into the ionization chamber, preventing contamination, at the same time starting data recording.

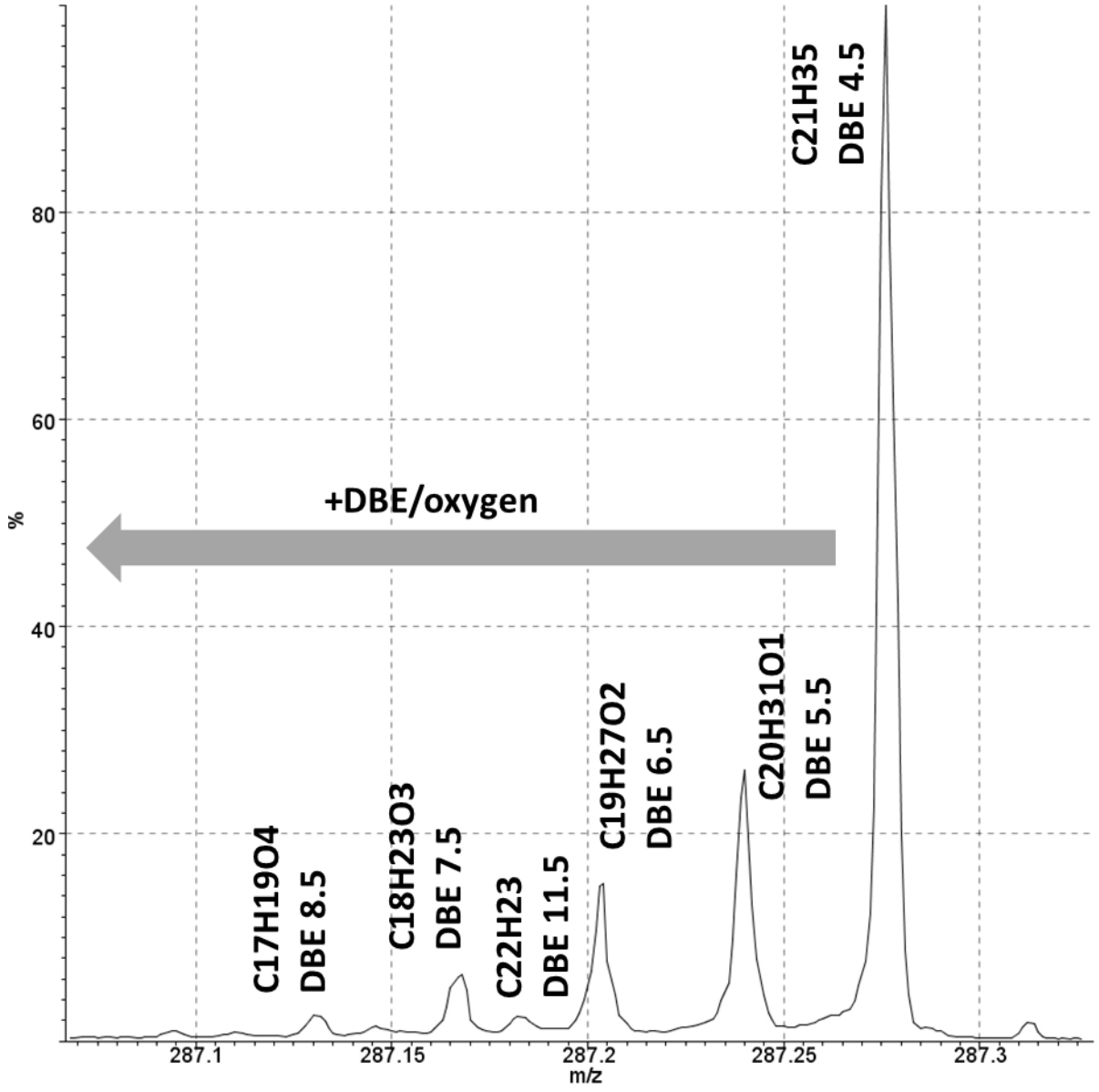

Figure S2: Zoom-in of the average atmospheric solid analysis probe high-resolution mass spectrum of the fresh diesel aerosol at nominal mass *m/z* 287 visualizing the isobaric complexity. The hydrocarbons and oxygenated series of the aromatic constituents can be resolved by the high-resolution time-of-flight mass analyzer.

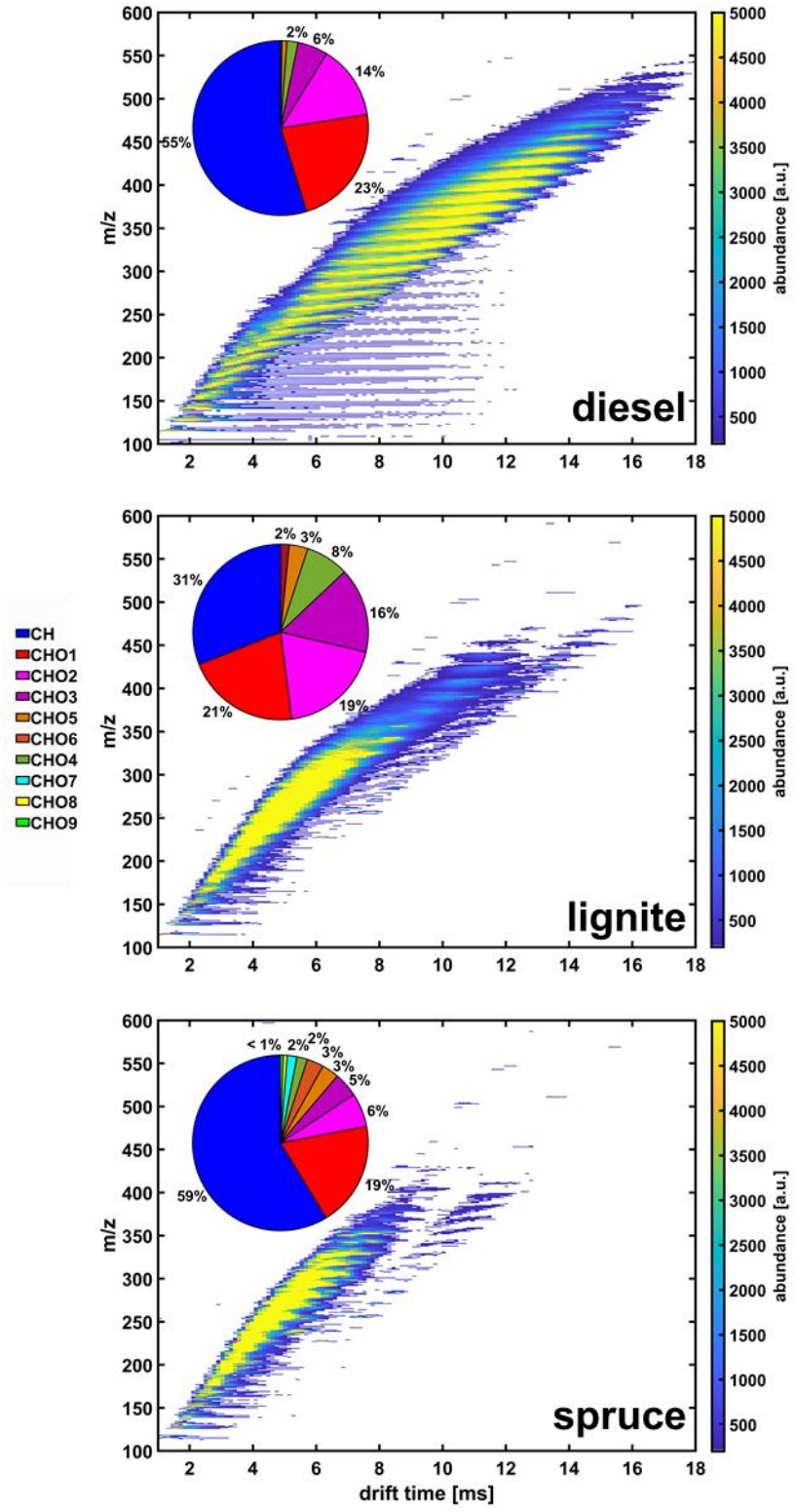

Figure S3: Survey of the ion mobility (drift time) and mass spectrometric (*m/z*) response for the three different non-aged aerosol emissions diesel, lignite and spruce combustion, color-coded according to abundance. The compound class distribution (percentages as a proportion from total attributed ion count) is given as inset.

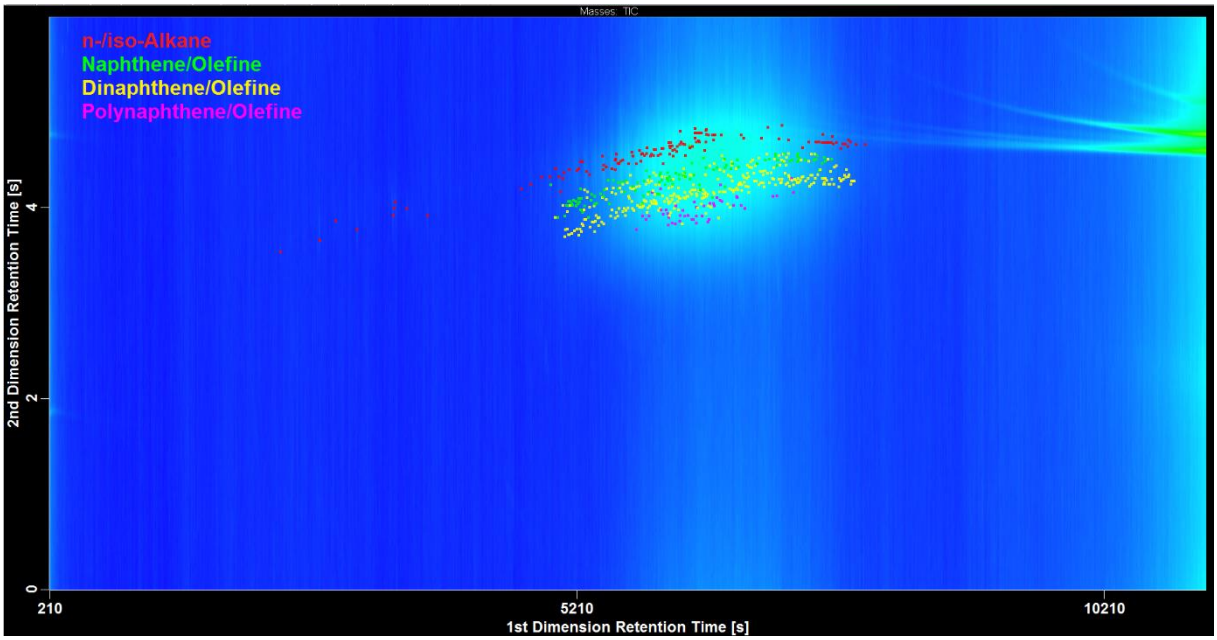

Figure S4: Screening of the lubrication oil used for running the diesel engine by comprehensive two-dimensional gas chromatography mass spectrometry (GCxGC-MS) performed by ASG Analytik-Service Gesellschaft mbH (Neusäss, Germany). Aside from alkanes, naphthenic constituents dominate the spectrum.

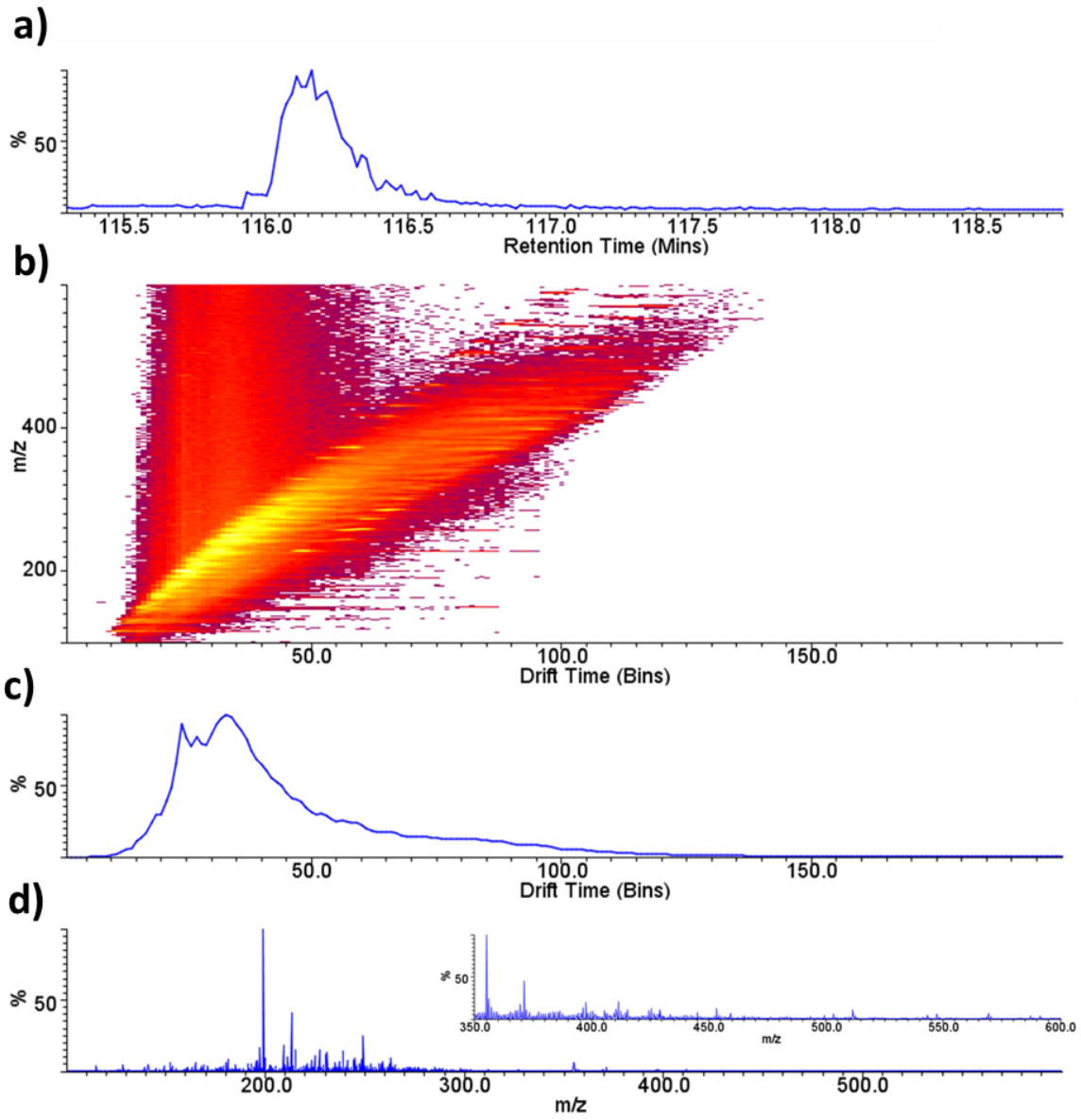

Figure S5: Aged lignite emission. The aging was conducted utilizing the PEAR with an unrealistic high Ozone-concentration of several hundred ppb. a) Time-resolved total ion count, b) Survey diagram (mass spectrometric response [m/z] versus drift time profile [drift time, bins]), c) Total ion count drift time profile of the average ASAP time-profile, d) Average mass spectrometric response with a zoom into larger m/z.

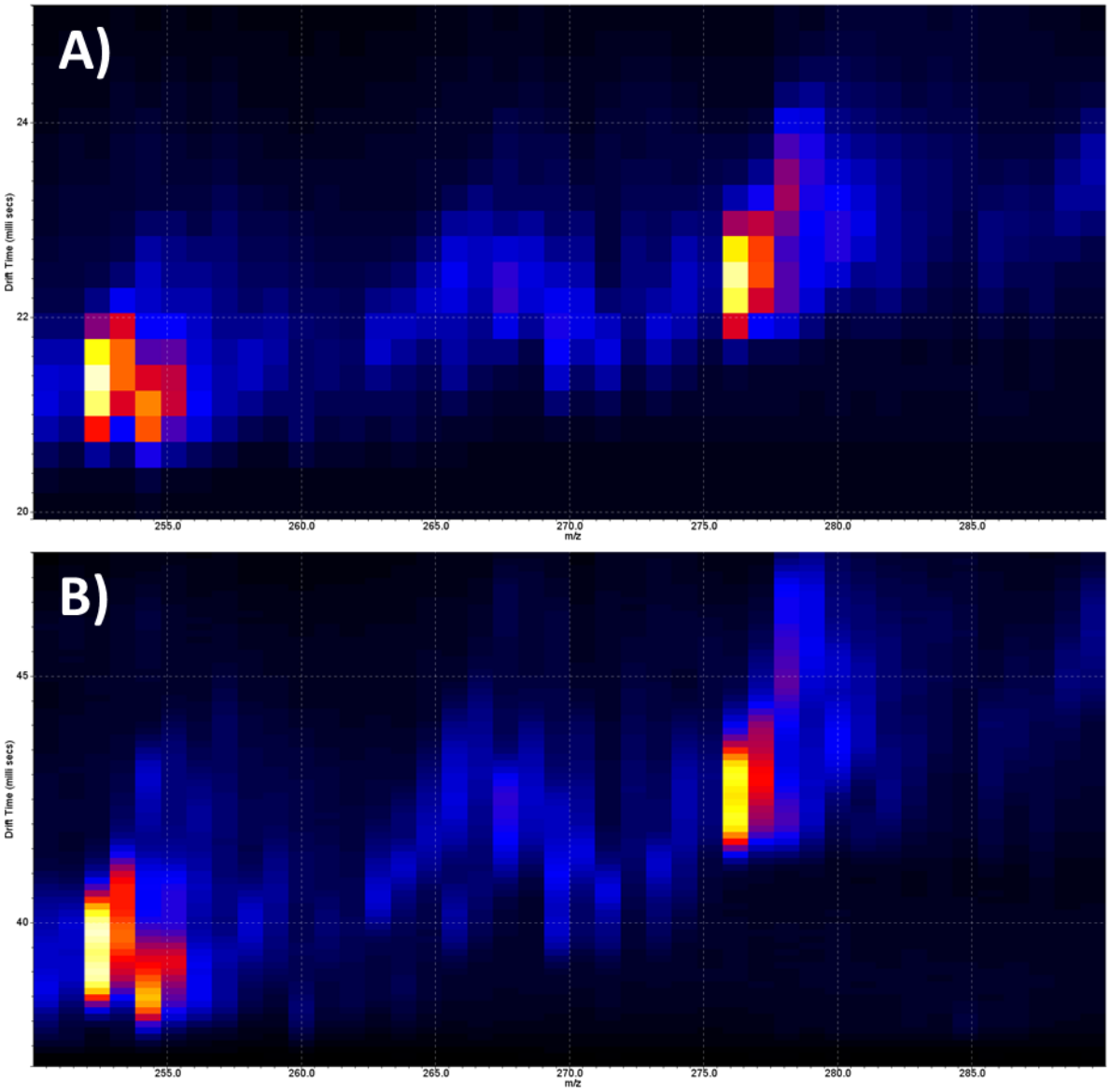

Figure S6: Direct comparison of the ion mobility versus mass spectrometric survey data received after one pass (A) and three passes (B) for ASAP cIMS HRMS of a fresh spruce emission sample. Please note the drastically higher number of data points (bins) per drift time peak aside of enabling a higher resolving power a better description of the peak apex position and FWHM.

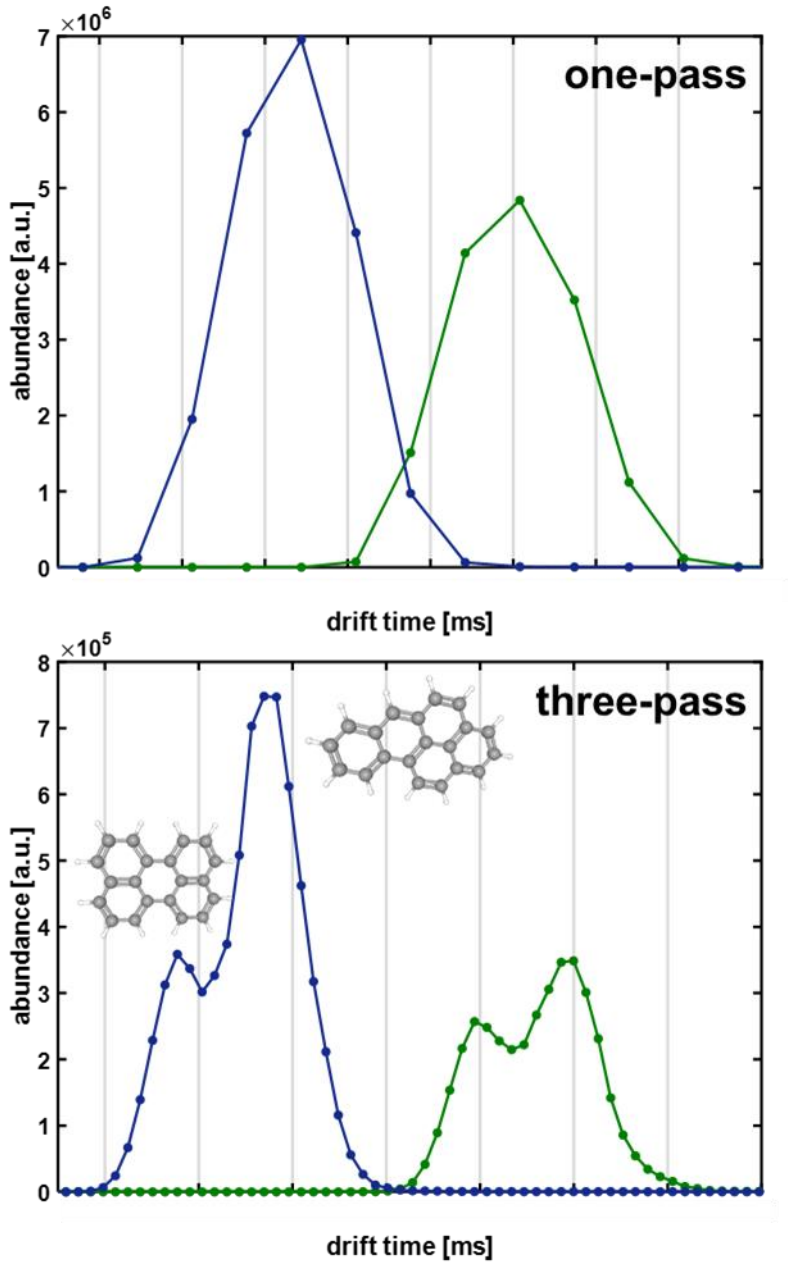

Figure S7: Direct comparison of the drift time profile for the extracted ion mobilogram of $C_{20}H_{12}$ (blue-left) and $C_{22}H_{12}$ (green-right). With one pass, the peaks are described by 6-8 bins, whereas three passes increase the bin number per drift time peak above 20.

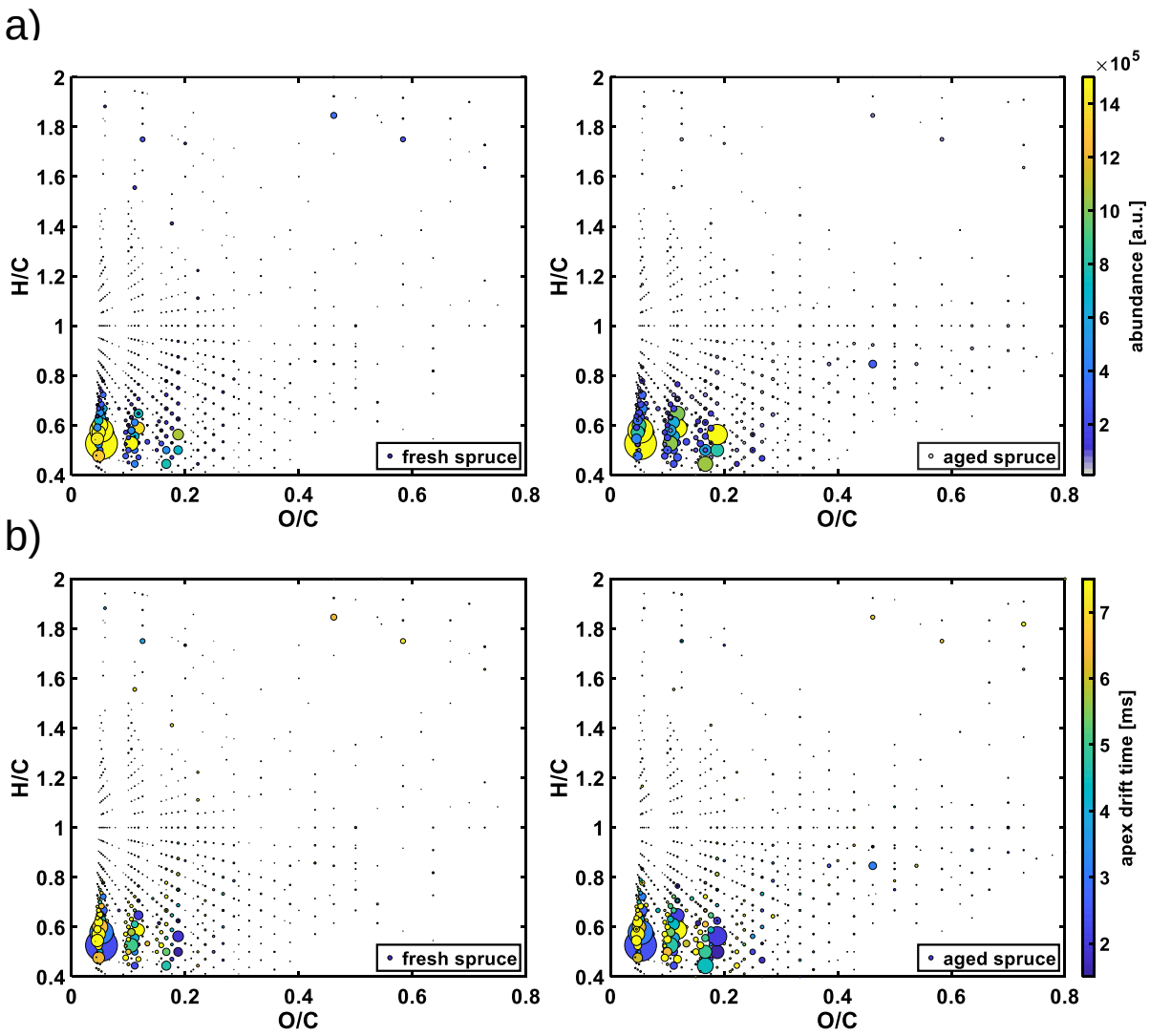

Figure S8: Van Krevelen diagram of the mass spectra of fresh (left) and aged (right) spruce emission particles based on average value for the elemental composition attributions found in all three replicates. Higher oxygenated species with increased abundance can be found. a) Classical van Krevelen diagram color-coded based on the abundance [a.u.]. b) Van Krevelen diagram color-coded based on the apex of the drift time profile [ms] – for non mono-modal ion mobility profiles, the drift time of the highest signal was taken. A shift towards higher oxidized species can be observed.