Supplement of

A solid-state IR laser for two-step desorption/ionization processes in single-particle mass spectrometry

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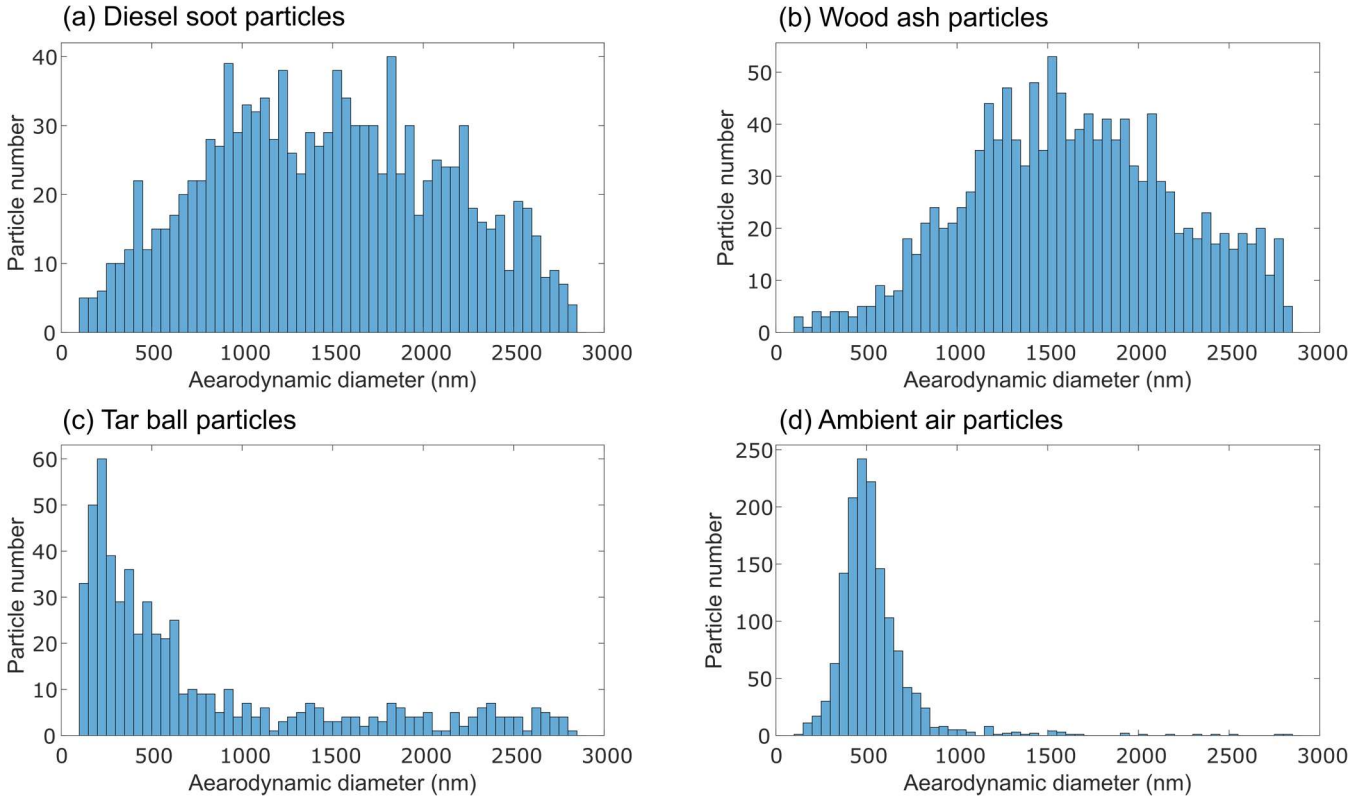


Figure S1 Particle size distributions, each n = 1200, of the laboratory and ambient air particles measured using the optical sizing unit of the SPMS: **(a)** Diesel soot particles; **(b)** Wood ash particles; **(c)** Tar ball particles; and **(d)** Ambient air particles.

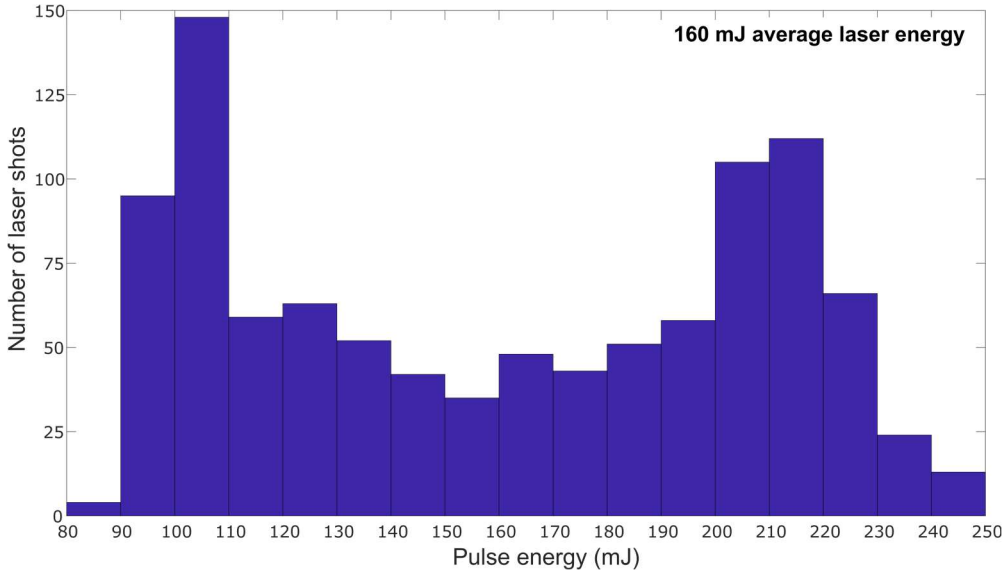


Figure S2 Pulse energies of 1022 laser pulses from the Er:YAG laser. The observed high fluctuation is attributed to the random nature of particle events inducing thermal lensing effects in the laser resonator; the average pulse energy was determined to be 160 mJ.

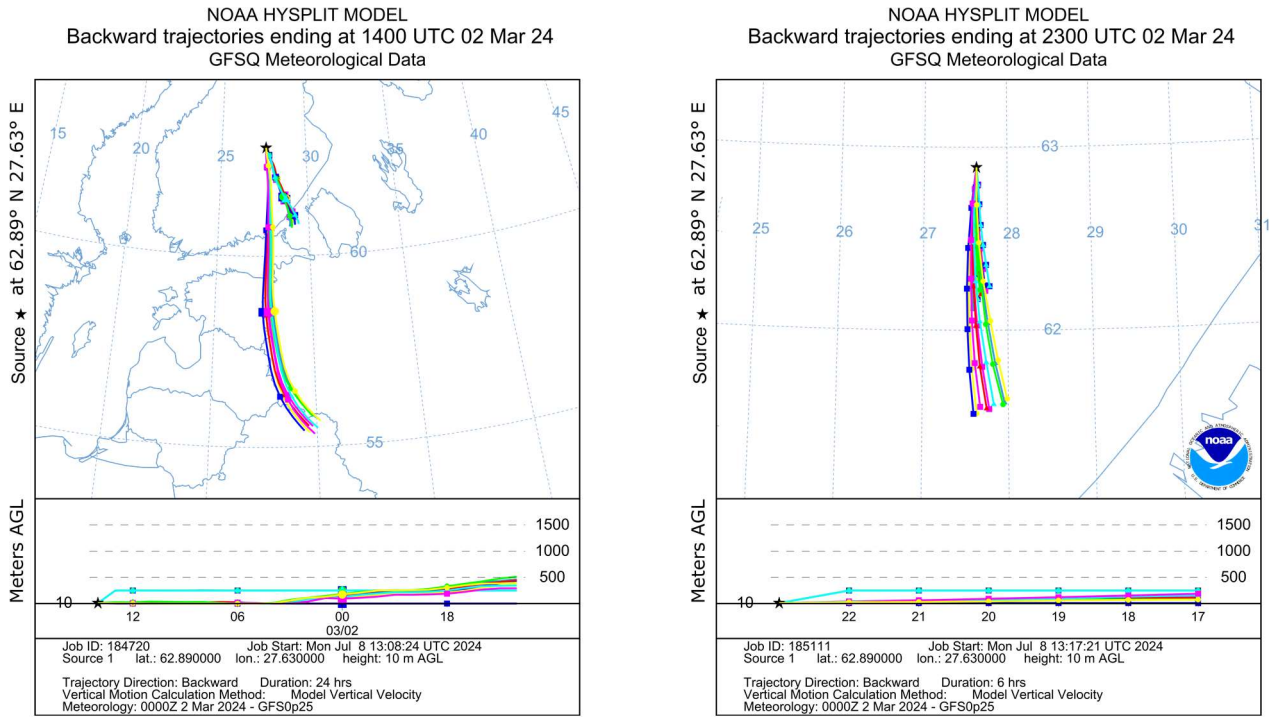


Figure S3 HYSPLIT backward trajectories for 24 h run time (left) for the ambient air experiments with the LD-REMPI approach and with 6 h run time for the subsequent experiments with the combined LD-REMPI/LDI approach (right), both ending at the measurement location.

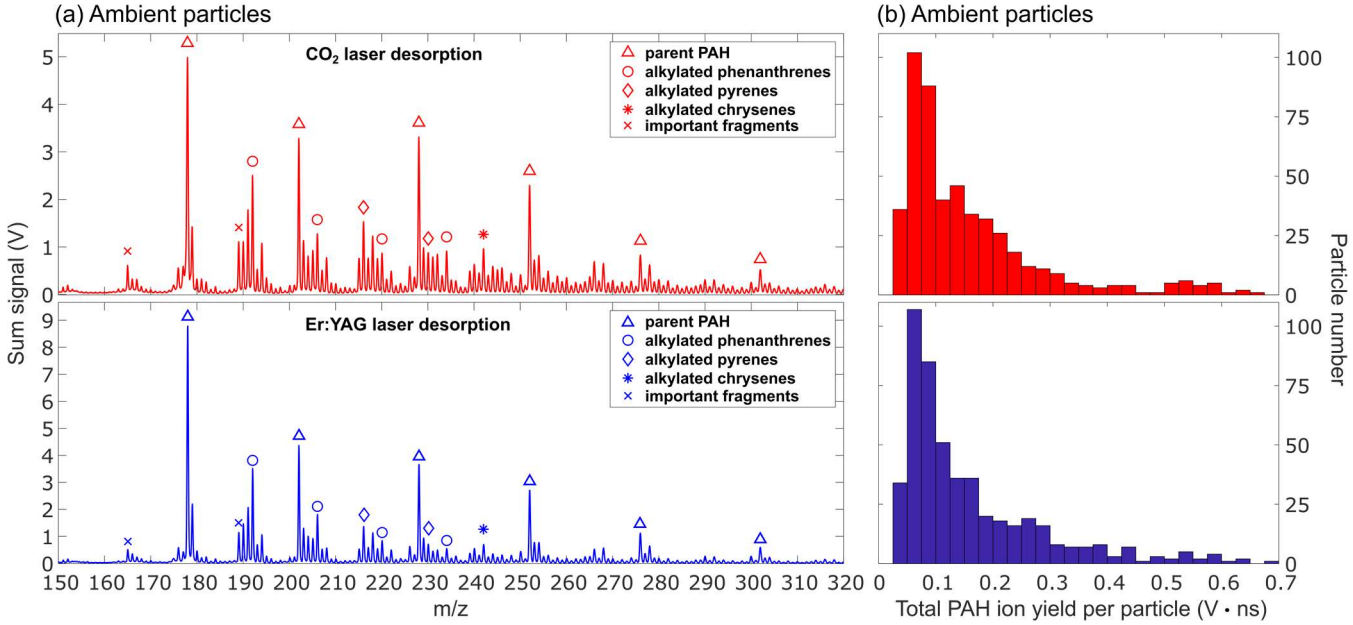
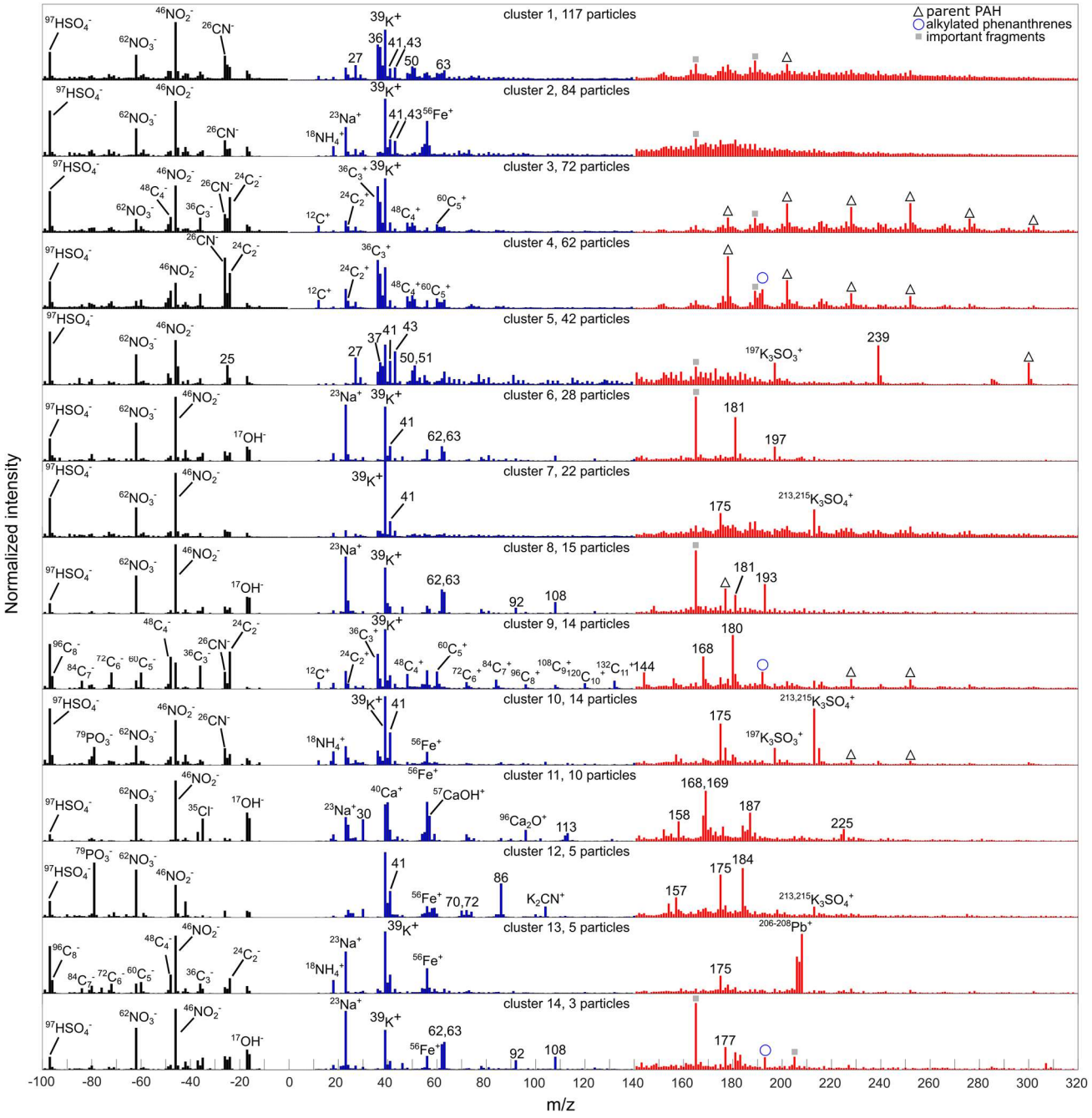
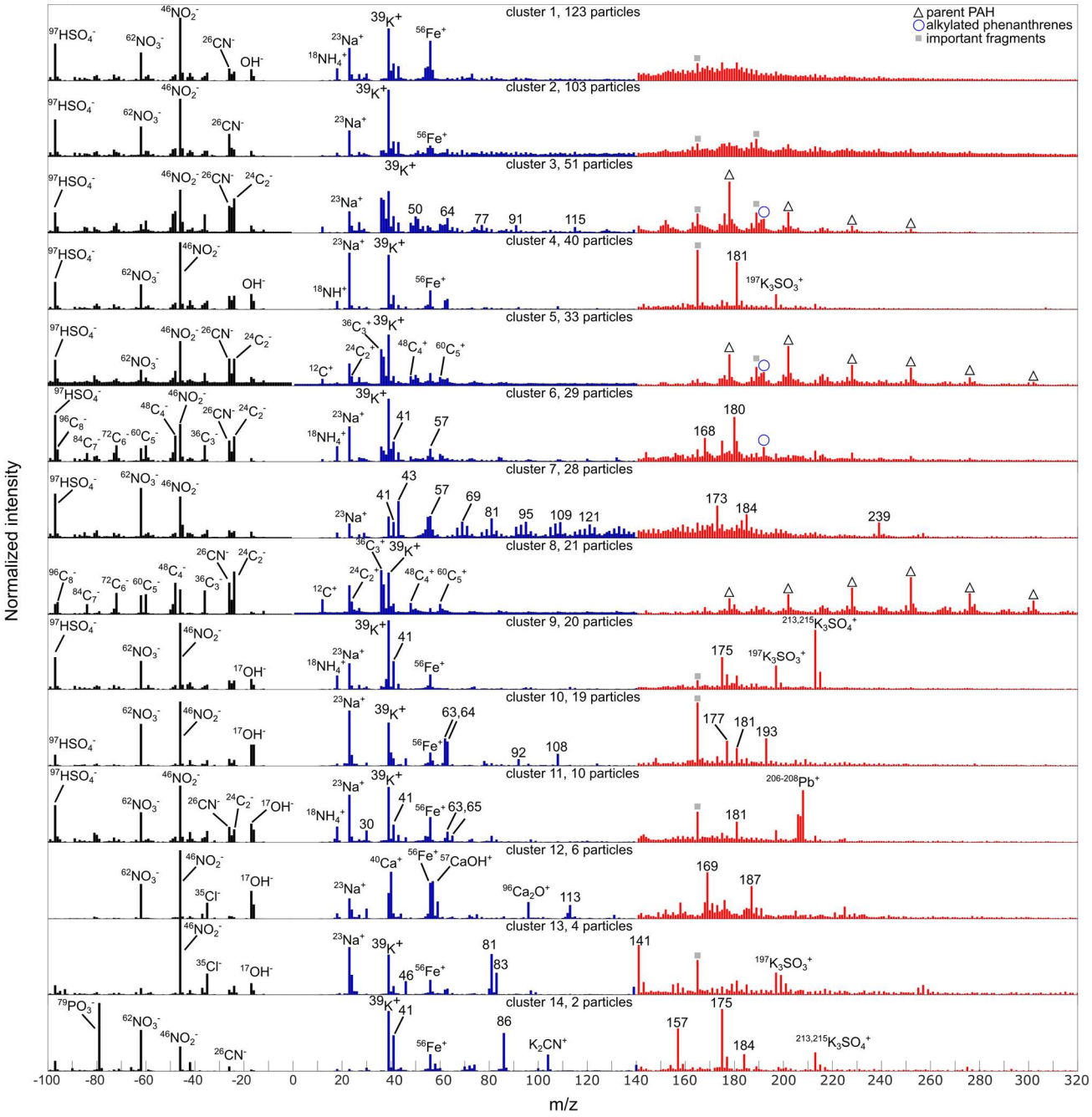


Figure S4 (a) Sum PAH mass spectra from ambient air particles (n = 500) measured in the LD-REMPI ionization approach. In direct comparison, the mass spectral signatures are similar between the CO_2 laser and the Er:YAG laser for LD. The Er:YAG produces slightly higher signal intensities for parent PAH, especially for m/z = 178, as discussed before. **(b)** The single-particle signal intensities of PAHs are also comparable for both lasers.

(a) Cluster analysis of LD/LDI mass spectra with CO_2 laser



(b) Cluster analysis of LD/LDI mass spectra with Er:YAG laser



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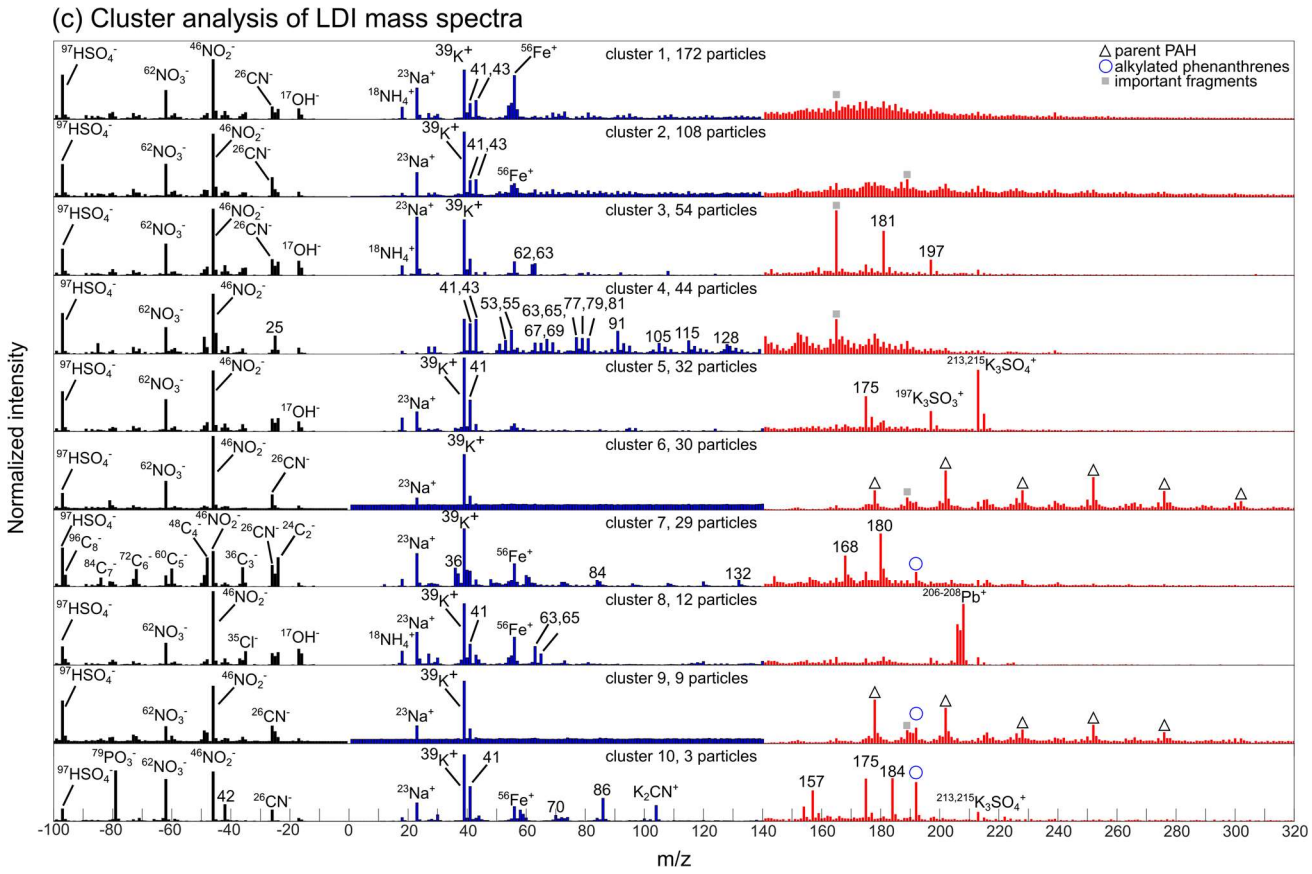

Figure S5 Results of the ART-2a cluster analyses, each including 500 PAH mass spectra from the respective ionization scheme. The combined LD-REMPI/LDI scheme yields comparable cluster centers and numbers of particles in each cluster for **(a)** using the CO2 laser and **(b)** using the Er:YAG laser for the LD step. **(c)** The single-step LDI scheme yields fewer clusters due to its higher fragmentation and lower sensitivity. The most abundant clusters are dominated by unidentified fragment signals. Only 39 out of 500 particles show clear PAH signatures for LDI.