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Supporting Information for

Detection of Ship Emissions from Distillate Fuel Operation via Single-Particle Profiling of Polycyclic Aromatic Hydrocarbons

by L. Anders, J. Schade, E.-I. Rosewig, T. Kröger-Badge, R. Irsig, S. Jeong, J. Bendl, M. Reza Saraji-Bozorgzad , J.-H. Huan, F.-Y. Zhang, C. Wang, T. Adam, M Sklorz, U. Etzien, B. Buchholz, T. Streibel, J. Passig and R. Zimmermann*

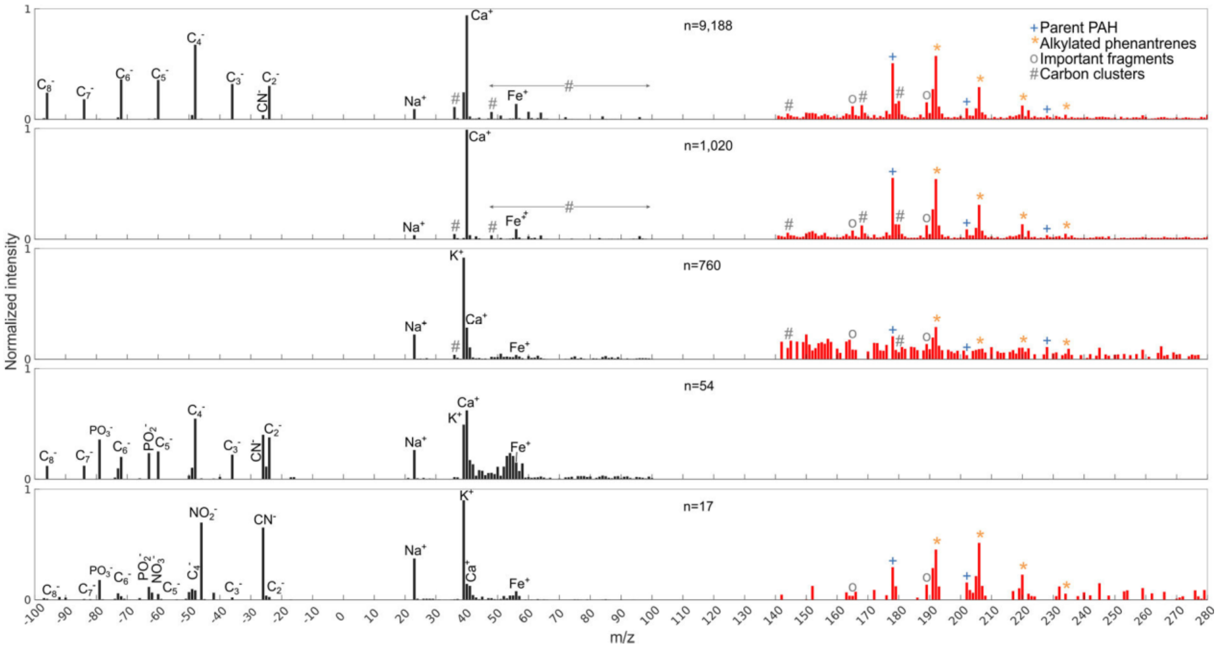

Figure S1. Mass spectra of the five main particle classes from ART2a-clustering of bipolar LDI mass spectra (black, n=11,039) recorded in free-running mode for 60 kW (75%) load of the research ship engine. Within this smaller particle ensemble (see Figure 3(a) in the manuscript), the most abundant particle classes also show the intense series of alkylated phenanthrenes. Clusters 3 and 4 have only weak PAH contributions. Cluster 5 shows strong signals of nitrate and phosphate, a slight shift in the peak intensity distributions of PAHs and a further row of unknown origin, beginning at m/z=232. However, it contains only 17 particles.

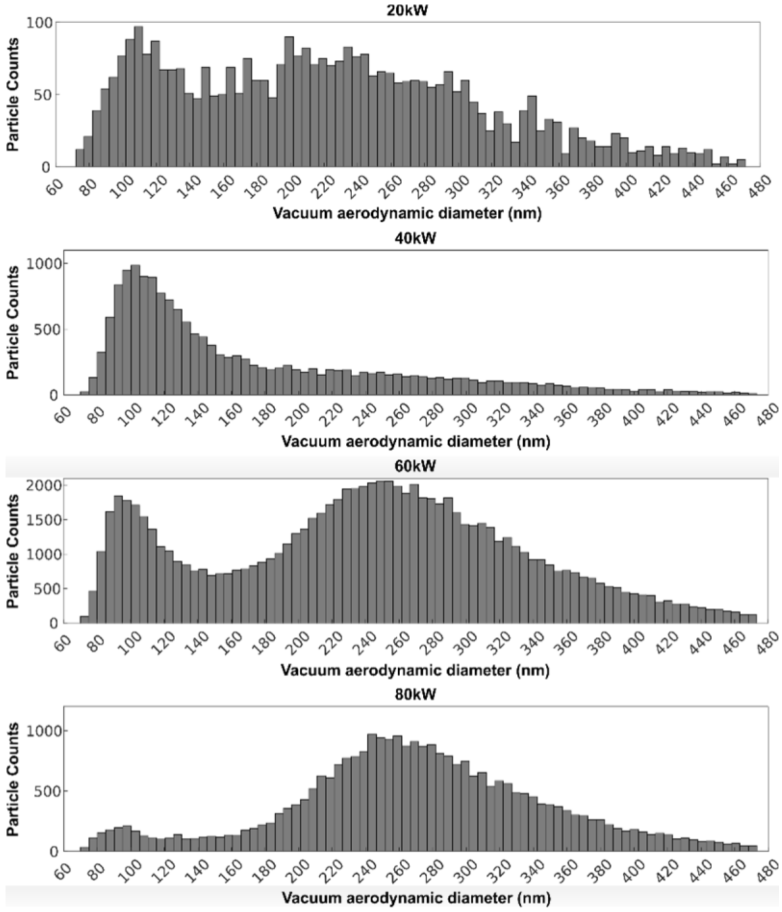

Figure S2. Particle size distribution for different engine loads. For higher loads, a second mode of larger particles appears. Note that the detection efficiency of the optical sizing unit drops rapidly below 200 nm and reaches its maximum towards 500 nm. An exemplary size distribution for 60 kW load, measured with SMPS, is shown in the manuscript, Figure 3(a).

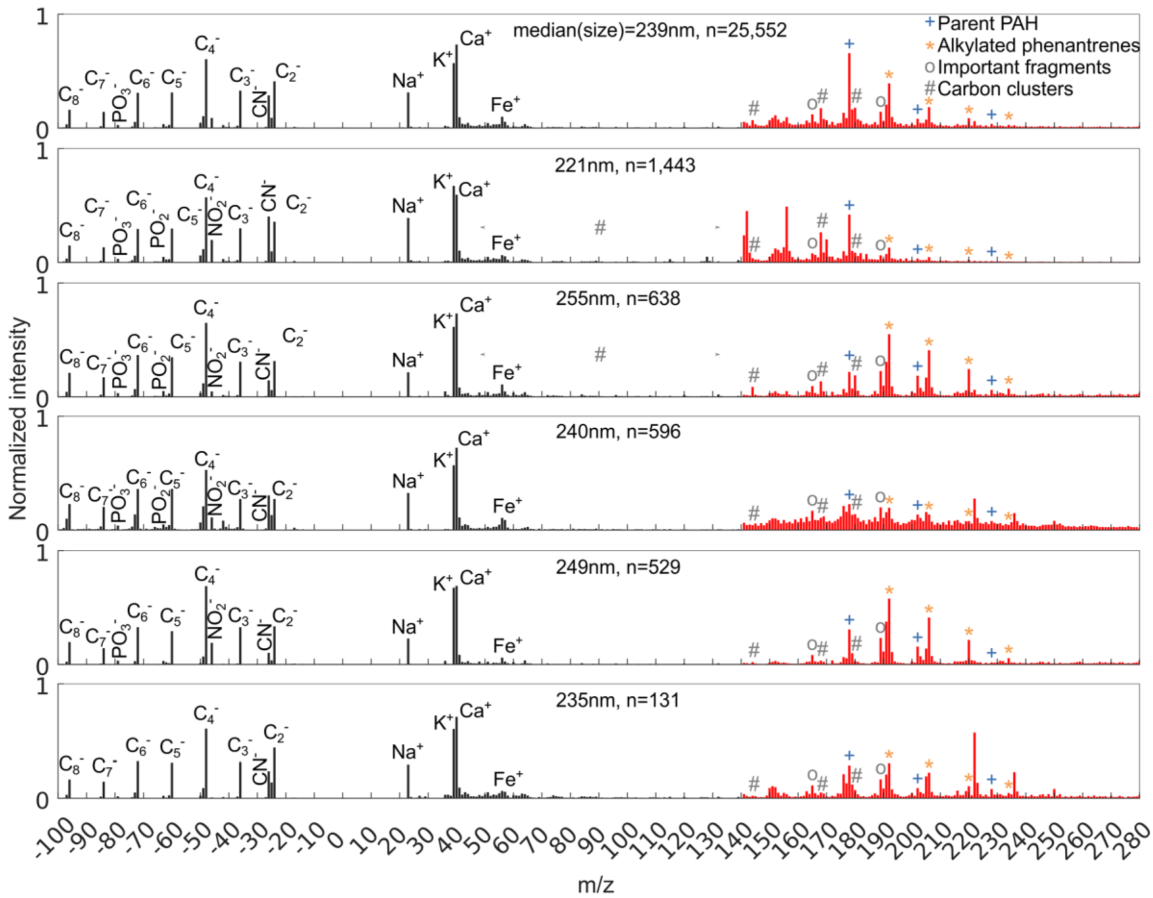

Figure S3. Mass spectra of the six main particle classes from ART2a-clustering of PAH mass spectra (red, n=28,889) recorded for 60 kW (75%) load of the research ship engine. The majority (88 %) belongs to the first cluster, but together with clusters 3 and 5, 92% of the PAH-containing particles show the typical strong row of alkylated phenanthrenes. In cluster 2, the row of C1- to C3-naphthalenes (m/z 142, 156 and 170) are increased, without clear correlations with the signals from the inorganic composition. In clusters 4 and 6, the unknown row beginning at m/z=222 appears.

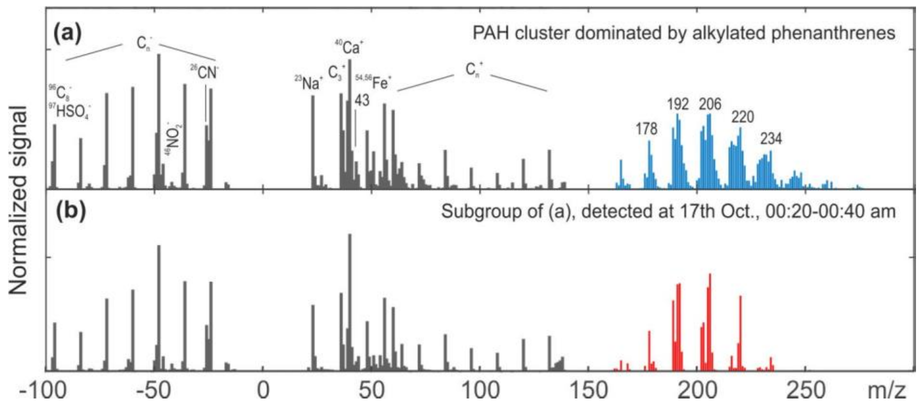

Figure S4. (a) Average mass spectra from an ART-2a-derived particle class with pronounced signals from alkylated phenanthrenes measured in ambient air at the Swedish coast (see Passig et al., 2022)[1]. The mass spectrum from LDI (black) indicates a low degree of ageing (small peaks from $^{-46}NO_2^-$ and the oxygen-containing fragment $C_2H_3O^+$ at m/z=+43). The particle detection times are depicted in Fig. 6 in the manuscript and show a correlation with onshore wind at low wind speed, pointing on ship emissions. (b) A particle subclass of (a), detected at the same time (circled in Fig. 6(c)), indicating a single source. Their small size (see Fig. 6) and even smaller ageing markers compared to (a) suggest a local source. Wind analysis and ship transponder data revealed a ferry as particle source, passing the measurement site in about 15-20 km distance.

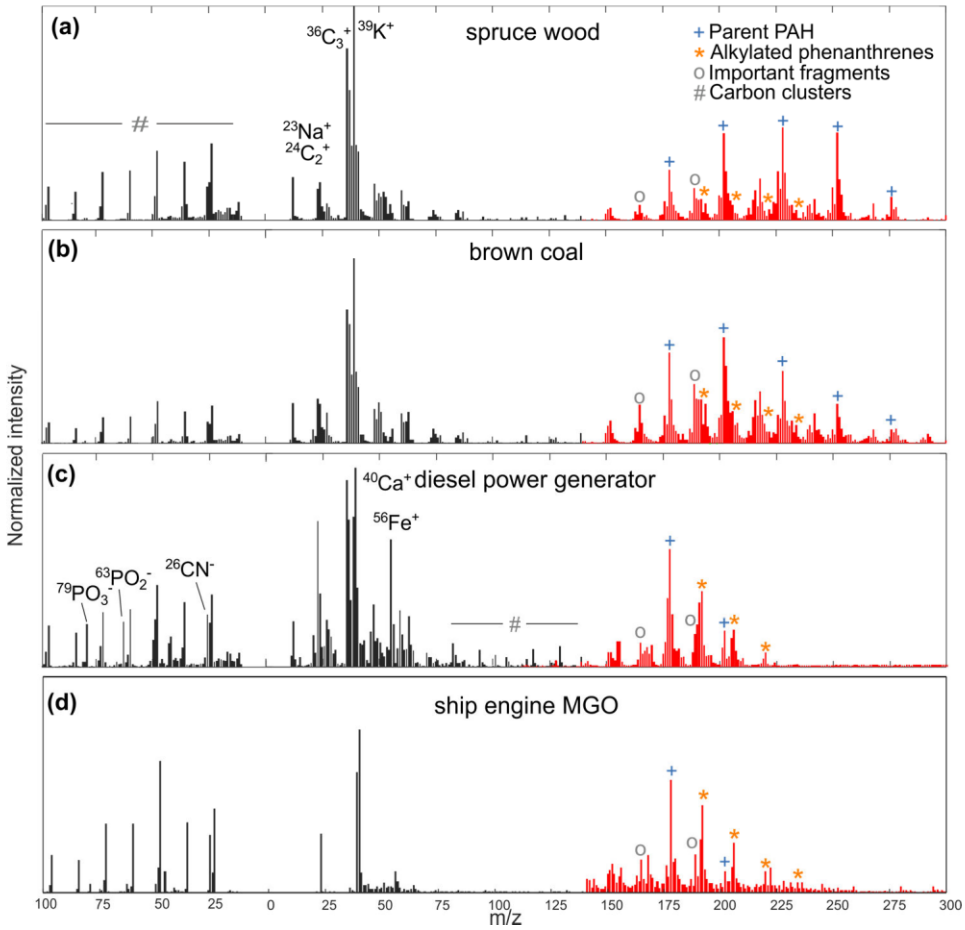

Figure S5. Average mass spectra from different combustion sources measured with the same instrument and settings (unpublished data). The PAH profiles of (a) wood and (b) coal combustion in a stove are very different and show stronger signals from parent PAHs, also at higher masses. (c) The PAH signature from a small diesel power generator (5.7 kW single cylinder, Kipor KDE6500e_230V) resembles the profile from the ship engine running on MGO described in this paper (d). For details of the combustion sources and sampling, see Miersch et al.[2]

References

1 J. Passig, J. Schade, R. Irsig, T. Kröger-Badge, H. Czech, T. Adam, H. Fallgren, J. Moldanova, M. Sklorz, T. Streibel and R. Zimmermann, Single-particle characterization of polycyclic aromatic hydrocarbons in background air in northern Europe, *Atmos. Chem. Phys.*, 2022, **22**, 1495–1514.

2 T. Miersch, H. Czech, A. Hartikainen, M. Ihalainen, J. Orasche, G. Abbaszade, J. Tissari, T. Streibel, J. Jokiniemi, O. Sippula and R. Zimmermann, Impact of photochemical ageing on Polycyclic Aromatic Hydrocarbons (PAH) and oxygenated PAH (Oxy-PAH/OH-PAH) in logwood stove emissions, *The Science of the total environment*, 2019, **686**, 382–392.