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

Supplement

Polycyclic Aromatic Hydrocarbons as Fuel Markers in Ship Engine Emissions using Single-Particle Mass Spectrometry

Lukas Anders[a,b], Julian Schade[a,b,c], Ellen Iva Rosewig[a,b], Marco Schmidt[a,b], Robert Irsig[d], Seongho Jeong[a,b,c], Uwe Käfer[a,f], Thomas Gröger[a], Jan Bendl[a,c], Mohammad Reza Saraji-Bozorgzad[a,c,d], Thomas Adam[a,c], Uwe Etzien[e], Hendryk Czech[a], Bert Buchholz[e], Thorsten Streibel[a,b], Johannes Passig[a,b] and Ralf Zimmermann[a,b]*

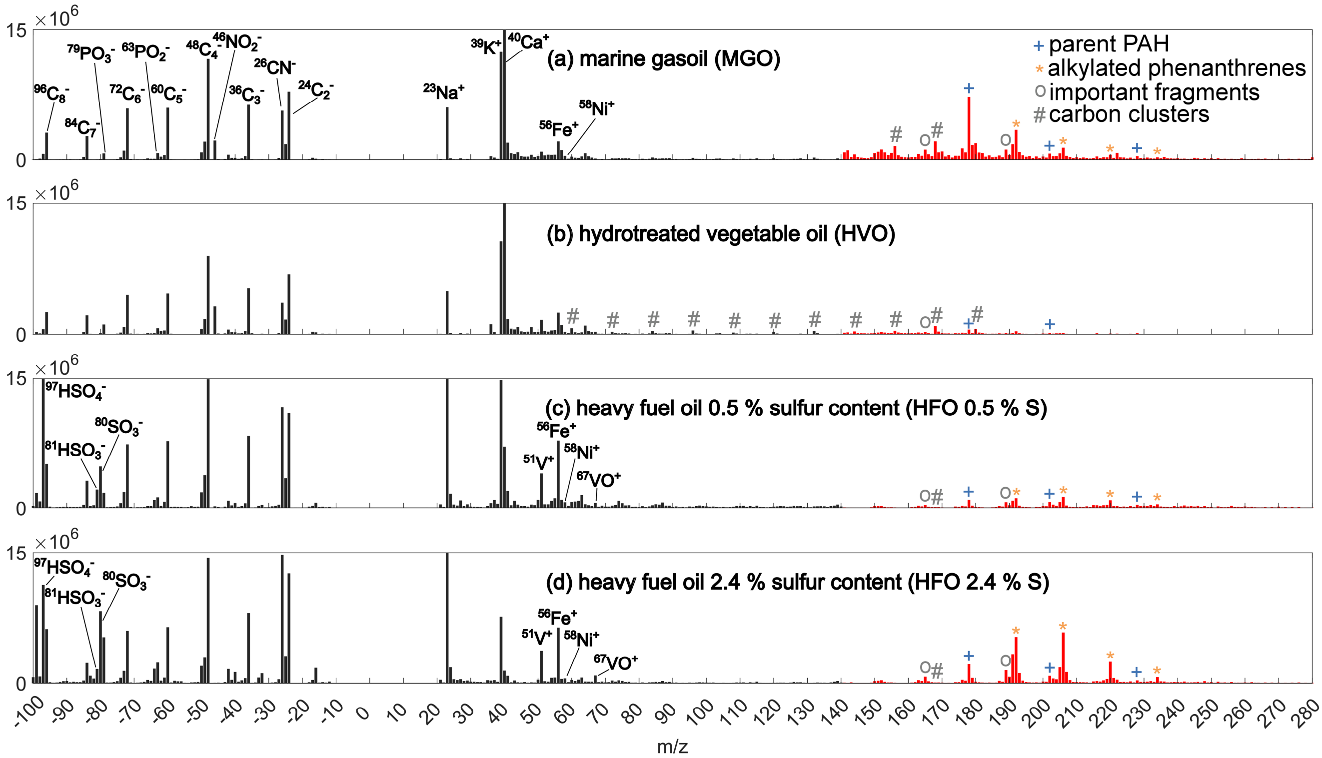

Figure S1. Sum mass spectra of particles from the four shipping fuels as in Fig. 1. Each spectrum shows the sum signal of 10,000 particles without normalization.

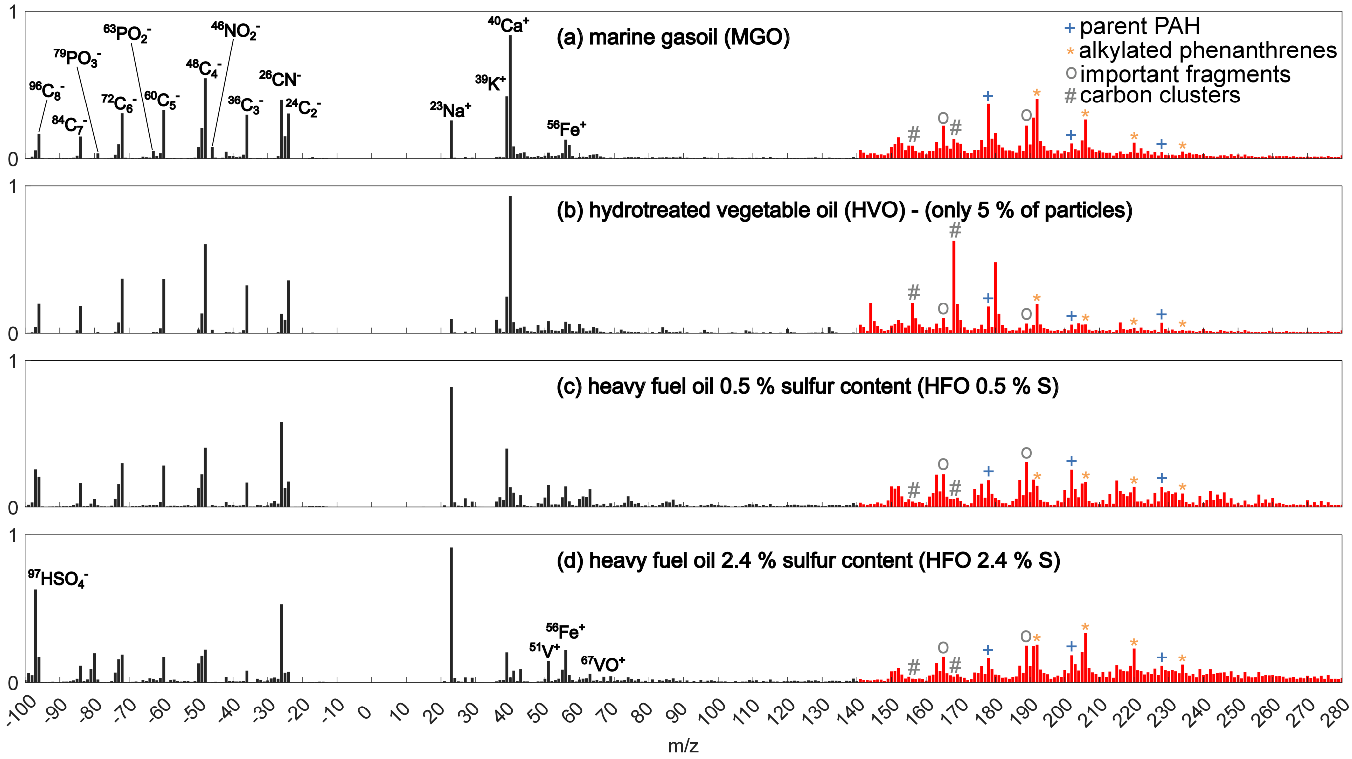

Figure S2. Sum mass spectra of four shipping fuels (a) marine gas oil (MGO), (b) hydrotreated vegetable oil (HVO), (c) heavy fuel oil 0.5 % S (HFO) and (d) heavy fuel oil 2.4 % S. LDI mass spectra (black) and REMPI spectra (red) for 20 kW (25 %) load of the research ship engine. Each spectrum shows 10,000 particles with individually normalized LDI and REMPI signals.

Fuel Samples: GCxGC-HRTOFMS Method

All GCxGC-HRTOFMS experiments were carried out on a Pegasus 4D HRT 6000 series mass spectrometer platform (Leco, St. Joseph, MI, USA) with an Agilent Technologies 7890A gas chromatograph (Palo Alto, CA, USA) and OPTIC 4 programmed temperature vaporizing injector. For GCxGC capabilities, the system is equipped with a secondary oven and a cryogenic dual-stage liquid nitrogen modulator. All fuels were diluted in dichloromethane (10 % m/m) to reduce viscosity before injection. Data processing and visualization was conducted using ChromaTOF HRT (Leco, St. Joseph, MI, USA) similar to previously published approaches[1,2]. Briefly described, obtained raw spectra were post calibrated before deconvolution and peak picking. Peaks were assigned to chemical groups according to specific electron ionization fragments and retention time windows.

Aromatic Compounds measured by GCxGC-HRTOFMS in Fuel Samples

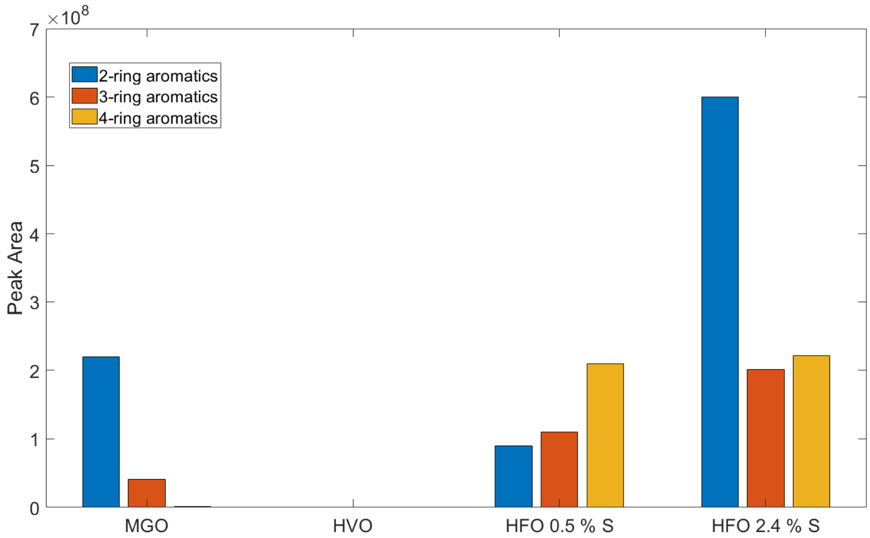

Figure S3. GCxGC-MS data showing 2-ring aromatics, 3-ring aromatics and 4-ring aromatics in marine gas oil (MGO), hydrotreated vegetable oil (HVO), heavy fuel oil (HFO) 0.5 % S and HFO 2.4 % S. It shows that most of these aromatics are present in the heavy fuel oils, while not detected in HVO.

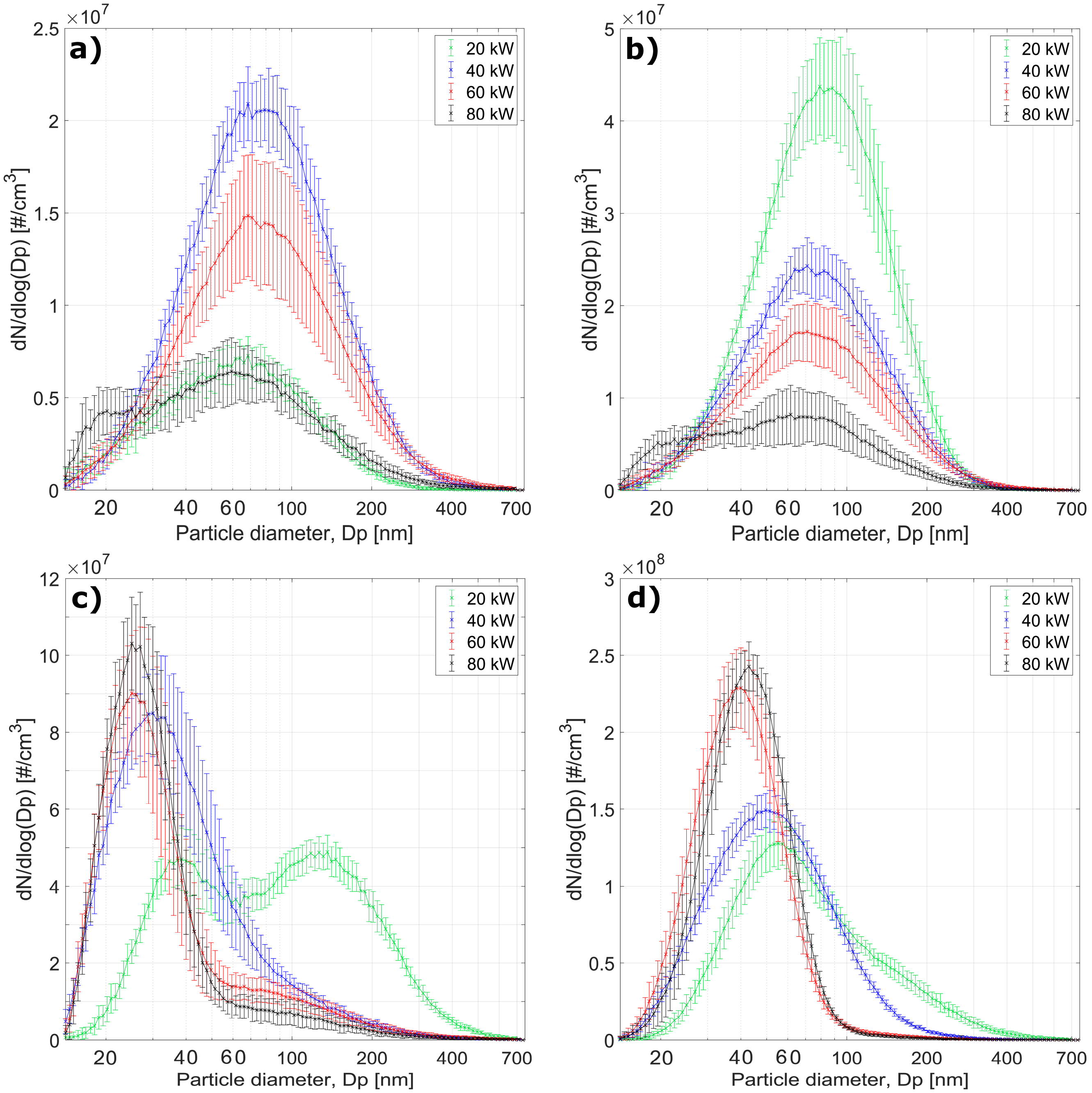

Figure S4. Particle size distributions, measured using the scanning mobility particle sizer for different shipping fuels: a) MGO, b) HVO, c) HFO 0.5 % S, d) HFO 2.4 % S.

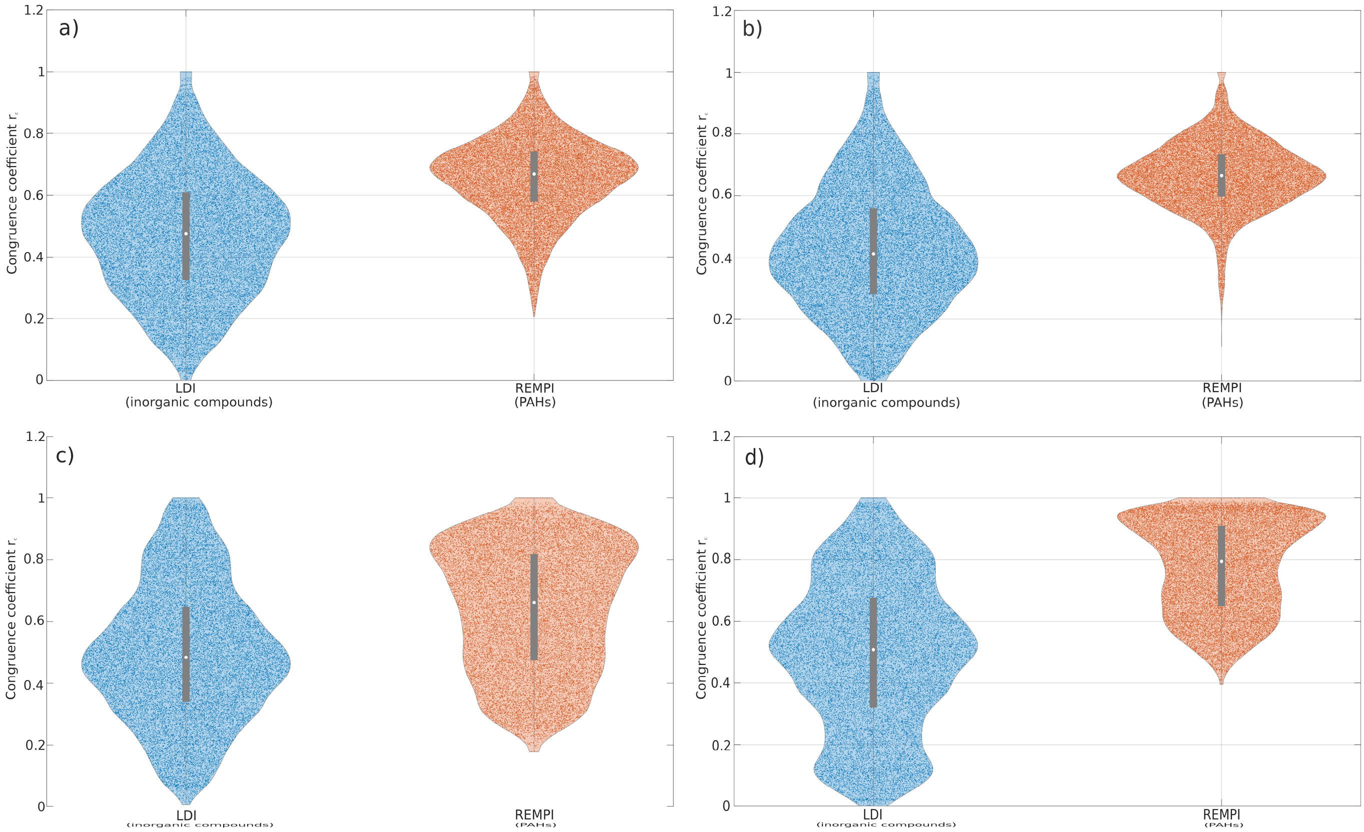

Figure S5. Violin plots of the congruence coefficients r_c between single-particle mass spectra from four different fuels, measured at an engine load of 20 kW: a) marine gasoil b) hydrotreated vegetable oil c) heavy fuel oil 0.5 % S d) heavy fuel oil 2.4 % S. The plot shows the congruence analysis of each fuel with the corresponding interquartile ranges for LDI and REMPI derived particles. For all fuels, there is a difference in the interquartile range between LDI and REMPI, supporting a higher variability in the inorganic particle composition and more uniform, fuel-dependent PAH signatures. For example, particles from the REMPI process have a consistently higher interquartile radius than those from the LDI process.

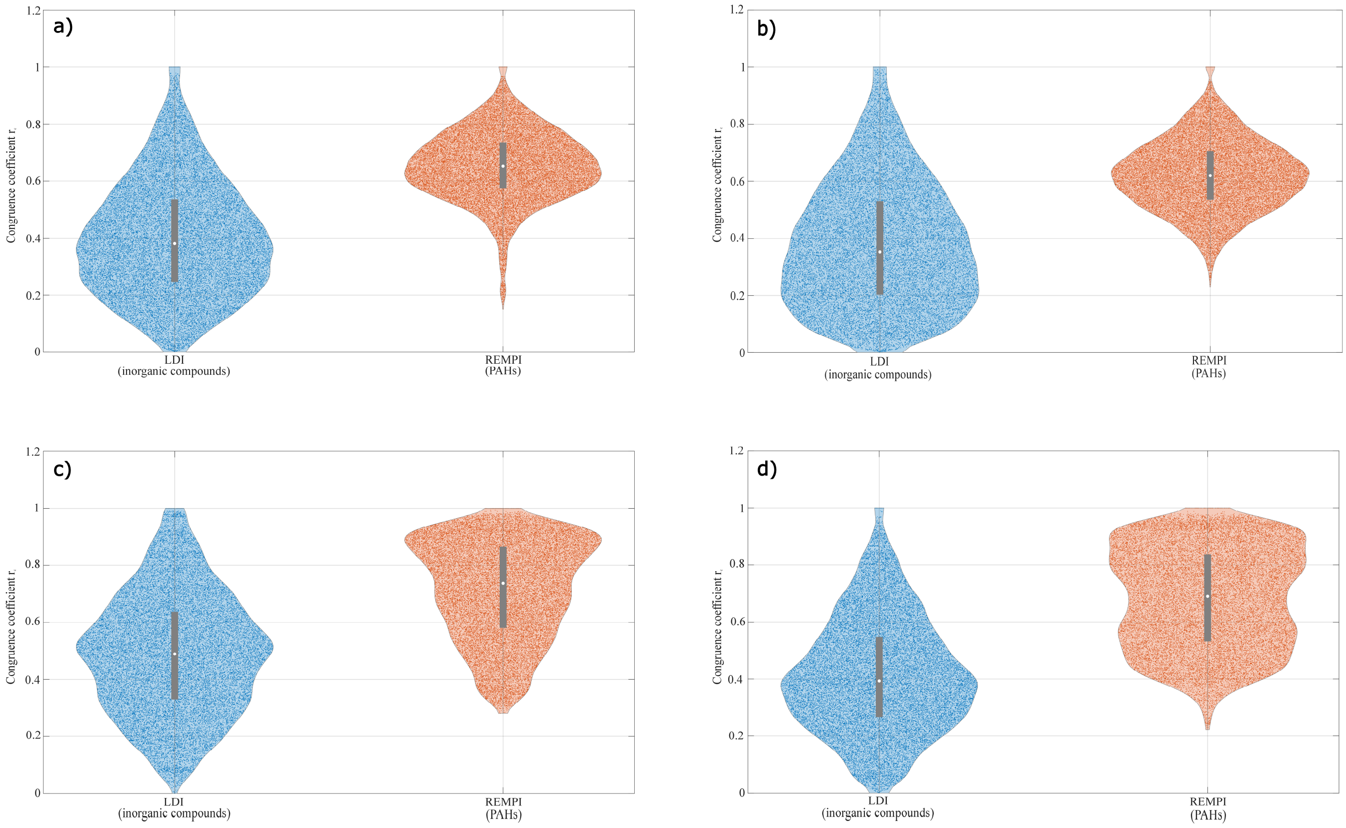

Figure S6. Violin plots of four different fuels at a load of 60 kW of the research engine: a) marine gasoil b) hydrotreated vegetable oil c) heavy fuel oil 0.5 % S d) heavy fuel oil 2.4 % S. Similar results can be observed for the low engine load (Fig. S5) and the higher load here.

References

1 U. Käfer, T. Gröger, C. J. Rohbogner, D. Struckmeier, M. R. Saraji-Bozorgzad, T. Wilharm and R. Zimmermann, Detailed Chemical Characterization of Bunker Fuels by High-Resolution Time-of-Flight Mass Spectrometry Hyphenated to GC × GC and Thermal Analysis, *Energy Fuels*, 2019, **33**, 10745–10755.

2 A. Neumann, U. Käfer, T. Gröger, T. Wilharm, R. Zimmermann and C. P. Rüger, Investigation of Aging Processes in Bitumen at the Molecular Level with High-Resolution Fourier-Transform Ion Cyclotron Mass Spectrometry and Two-Dimensional Gas Chromatography Mass Spectrometry, *Energy Fuels*, 2020, **34**, 10641–10654.