Characterization of organic low-, semi-, intermediate- and volatile organic compounds from four-stroke ship engine emissions: implications for atmospheric processing.

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Ship engines typically combust low-grade fuels and emit significant amounts of harmful particulate matter (PM) as well as reactive gases, such as NO_x, SO_2 and hydrocarbons (HC). Recently measures to reduce SO_2 emissions have been implemented, by limiting the fuel sulfur content in vulnerable environments. Reduction of primary PM and NOx emissions are being targeted as well. Little attention has been payed to the assessment of the gaseous HC fraction instead, such as the speciation of low-, semi-, intermediate- and volatile organic compounds (L-/S-/I-/VOCs). Neither has the potential of those emissions to form secondary organic aerosols (SOA) been addressed.

SOA is formed when organic gaseous material is reacted in the atmosphere into lower volatility compounds that condenses on preexisting particles or forms new particles. In order to implement efficient emissions reduction strategy, the SOA contribution to the total PM burden needs to be assessed.

We operated a 4-stroke ship diesel engine with heavy fuel oil (2.3% S) and marine gas oil (0.08% S). Both fuels are globally used in maritime transport. Characterization of gaseous organic compounds was performed using online HR-ToF-PTR-MS. This was complemented by analysis of gas and particle-phase samples on quartz fiber filters and Tenax sorbents, using a gas chromatography-mass spectrometry (GC-MS) approach by Zhao et al. The retrieved fractional contribution of organic mass attributed to alkane bins is converted into volatility distributions (logC* bins) using SIMPOL.1 (Pankow et Asher, 2008). The response of the organic PM to heat was further studied using a thermodenuder, coupled with an HR-ToF-AMS, SMPS for size-distribution, a DMA-APM for effective density measurements, and an SP2 for black carbon mass to derive additional information on the partitioning behavior between gas- and particle phase of the primary emissions.

The gaseous pollutants emitted by HFO combustion contain a significant fraction of aromatic HC (Fig. 1a). Those have a distinct profile from other emission sources, such as modern gasoline and diesel vehicles. The HFO composition is shifted towards multi-ring aromatics. MGO, a distillate fuel, is comparatively similar to diesel emissions, containing lighter aromatic HC and relatively more oxygenated species (Fig. 1b).

The shift towards a molecular composition with lower vapor pressure for HFO is also reflected in our results from the GC-MS analysis of lower volatility material. A higher proportion of material is found in the bins -4 to 3 compared to 4-7 for HFO vs. MGO emissions (Fig. 1c).

The implementation of representative volatility distributions of shipping emissions in chemical transport models is crucial when assessing the burden of ship emissions to the atmosphere. Therefore, we will compare the derived distributions to the current implementations for shipping emissions in chemical transport models, and assess on the implications for SOA formation.
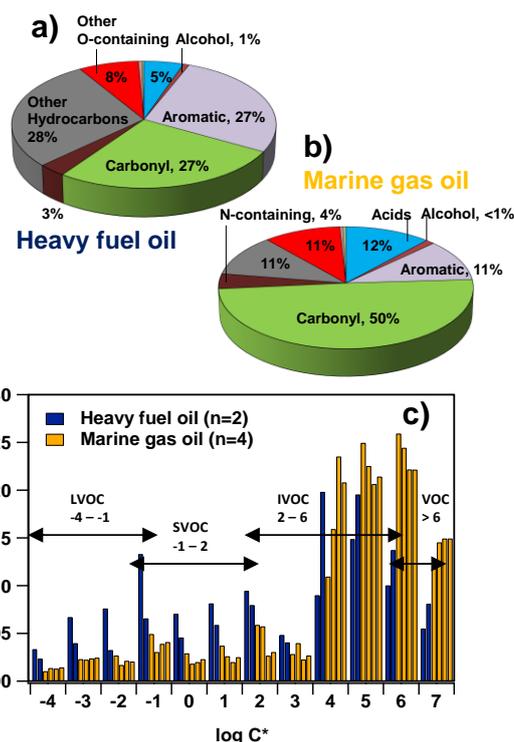
Figure 1. Chemical characterization of gaseous emissions from a) HFO and b) MGO combustion (HR-PTR-ToF-MS). c) GC-MS derived volatility distribution from filter and sorbent tubes.

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Pankow et Asher (2008) ACP, 8, 2773-2796
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