Physical and chemical characterisation of PM emissions from in-operation ship engines

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Emissions of particulate matter (PM) from shipping contribute significantly to the anthropogenic burden of PM. The environmental effects of PM from shipping include negative impact on human health through increased concentrations of particles in many coastal areas and harbour cities and the climate impact. The chemical composition and physical properties of PM vary with type of fuel burned, type of engine and engine operation mode.

In this paper a number of parameters describing emission factors (EFs) of particulate matter from ship engines were investigated during 2 on-board measurement campaigns for 3 different engines and 3 different types of fuels. The measured EFs for PM mass were in the range 0.3 to 2.7 g/kg-fuel with lowest values for emissions from combustion of marine gas oil (MGO) and the highest for heavy fuel oil (HFO). The emission factors for particle numbers EF(PN) in the range 5×10^{15} - 1×10^{17} #/kg-fuel were found, the number concentration was dominated by particles in the ultrafine mode and c.a. 2/3 of particles were non-volatile. The PM mass was dominated by particles in accumulation mode.

Main metal elements in case of HFO exhaust PM were V, Ni, Fe, Ca and Zn, in case of MGO Ca, Zn and P. V and Ni were typical tracers of HFO while Ca, Zn and P are tracers of the lubricant oil. EC makes up 10-38% of the PM mass, there were not found large differences between HFO and MGO fuels. EC and ash elements make up 23-40% of the PM mass. Organic matter makes-up 25-60% of the PM. The measured EF(OC) were 0.59 ± 0.15 g/kg-fuel for HFO and 0.22 ± 0.01 g/kg-fuel for MGO. The measured EF(SO_4^{2-}) were low, c.a. 100-200 mg/kg-fuel for HFO with 1% FSC, 70-85 mg/kg-fuel for HFO with 0.5% FSC and 3-6 mg/kg-fuel for MGO. This corresponds to 0.2-0.7% and 0.01-0.02% of fuel S converted to PM sulphate for HFO and MGO, respectively.

The (scanning) transmission electron microscopy (TEM and STEM) images of the collected PM have shown different types of particles. The maps of elements obtained from STEM showed heterogeneous composition of primary soot particles with respect to the trace metals and sulphur. Composition of the char-mineral particles indicates that species like $CaSO_4$, CaO and/or $CaCO_3$, SiO_2 and/or Al_2SiO_5, V_2O_5 and Fe_3O_4 may be present; the last two were also confirmed by analyses of FTIR spectra of the PM samples. The Temperature Programmed Oxidation (TPO) of PM from the ship exhaust samples showed higher soot oxidation reactivity compared to automotive diesel soot, PM from the HFO exhaust is more reactive than PM from the MGO exhaust. This higher oxidation reactivity could be explained by high content of catalytically active contaminants; in particular in the HFO exhaust PM for which the ED XRF analyses showed high content of V, Ni and S.
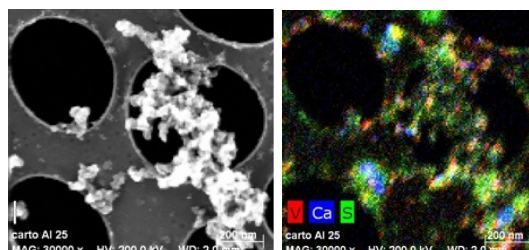

Figure 1. STEM image of an agglomerate of soot-type particles in ship exhaust (left) and their elemental composition map of V, Ca and S (right).

The data obtained during the experiments add information on emission factors for both gaseous and PM-bound compounds from ship engines using different fuels and under different engine load conditions. Observed variability of the EFs illustrates uncertainties of these emission factors as a result of measurement uncertainties, influences from trace components of fuels and lubricants and from differences between individual engines.