# Primary and secondary PM from shipping

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## Introduction

Emissions of exhaust gases and particles from seagoing ships contribute significantly to the anthropogenic emissions and thereby affect the chemical composition of the atmosphere and air quality both on the global, regional and on the local scale. On European level shipping in seas surrounding Europe emits 45, 52 and 22% of the EU-27 anthropogenic emission totals for $NO_X$, $SO_2$ and particulate matter (PM), respectively (www.emep.int). Uncertainties in emission inventory of PM emission from shipping are, however, large. In harbour cities the PM emissions from shipping can contribute to the total emission as much as the road traffic (excluding the road dust) (Haeger-Eugensson et al., 2010). In addition to the primary emitted PM the gaseous emissions contribute to air pollution with secondary PM after being processed in atmosphere. 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, acidification and eutrophication of waters and ecosystems in coastal areas and the climate impact (Eyring et al., 2010 and references there in).

The reason of the high contribution of navigation to the emission totals is the fact that shipping emissions have been, in difference from the land sources, for a long time unregulated and only in last few years regulation is gradually entering into force through Annex VI of the Marine Pollution Convention (MARPOL) that was adopted by the Marine Environmental Protection Committee (MEPC) of the International Maritime Organisation (IMO). Annex VI which came into force in May 2005 is mainly targeting emissions of sulphur through maximum allowed fuel sulphur content and to some extend emissions of $NO_X$ Emissions of PM are addressed only indirectly through decrease of formation of secondary PM from the reductions in $SO_2$ and $NO_X$. The Annex VI measures will also impact emissions of the primary PM due to enforced improvements in fuel quality associated with reduction of the fuel sulphur content and effect of engine improvements and installations of emission cleaning technologies. These effects are, however, very uncertain as only few measurements of PM and PM composition providing this information are available.

The contribution of PM emissions from shipping to the PM emission totals on local/urban scale frequently considers the primary particles only. Majority of the urban air quality studies neglect formation of the secondary PM as this effect is assumed to be small in polluted atmosphere of a city. However, meteorological conditions in harbour cities can often be favourable of more intensive chemistry as a relatively clean marine air enters a city over the harbour. In global and continental-scale studies formation and effects of the secondary inorganic PM is considered and makes a significant contribution to the PM concentration increase caused by shipping. E.g. c.a. 50% of the health effects from shipping-related PM in global study of Corbett et al. (2007) comes from the secondary PM. In this short paper the emission factors of primary PM from shipping and its components are reviewed and role of formation of the secondary PM on small-scale is discussed.

## Experimental

Emissions from a marine engine will depend on the type of fuel used as well as on characteristics of the engine. The most important fuel parameters are if the fuel is heavy fuel oil (residual fuel, HFO or residual oil, RO) or marine distillates (marine gasoil, MGO or marine diesel, MDO) and the sulphur content (FSC). Emissions have been found to vary significantly between engines. Probably the maintenance and age of the engine are important for certain emission factors. For calculating emissions one usually considers the engine power, the engine speed and the emissions standard. The latter applies to nitrogen oxides only. However, one can suspect that the emissions standard also will influence the emissions of particles and hydrocarbons, although there is, for most cases, not enough data available to draw conclusions about this. Here we present emission factors as emission per kg-fuel consumed meaning that the total emission is obtained from multiplying the emission factor with mass fuel consumed.

Emissions of some species like $SO_2$, $CO_2$ and metals are directly proportional to the SFC and fuel composition, regardless the type of engine or its operation regime (abatement techniques not accounted). Others, like $NO_X$, VOC, CO and PM are dependent on combustion regime and thus on type of engine, its power setting and on physical properties of the fuel. Here we present only the cruise-condition emission factors. More detailed review is given in Moldanová et al. (2012a).

The chemical transformation of ship emissions in plumes was investigated with a plume version of Model Of Chemistry Considering Aerosols (MOCCA) (Moldanová, 2010). The model includes comprehensive gas-

phase and condensed phase chemistry including NOx, SOx, organics, halogens and reactions on soot. The aerosol is treated with a segmental aerosol module consisting of 7 sea-salt and 7 sulphate bins. Background concentrations and emissions for Göteborg are used from the urban-scale simulations of TAPM (see below). The plume dispersion is simulated by two parallel boxes with the plume box entraining the background air simulated by the second box. The plume mixing is described by Gaussian dispersion, the dispersion parameters were also calculated with help of the TAPM simulations (see below).

While the plume simulations provide qualitative information on formation of the secondary PM, a quantitative assessment needs to be done with a 3-d model. For this purpose the effect of the secondary PM on air pollution from shipping in Göteborg was studied with TAPM model. TAPM is a 3D consisting of two models, one meteorological and one dispersion model (Hurley et al, 2005). TAPM also includes chemistry such as NO/NO2, ozone formation, $SO_2$ and particle transformation. The meteorological model was run in 3 nestings, the largest covering Northern Europe, the second south-western past of Sweden and northern Jutland and the smallest for city of Göteborg on resolution 100x100m. Dispersion model with chemistry was run on the smallest scale only and the chemical fields were nested into the chemical fields produced by the EMEP model for gridcells on the border of the city. Emissions for Göteborg including shipping are from the database of Environmental Agency of Göteborg. Three simulations were run: 1. with all shipping emissions, 2. with shipping emissions of primary PM only and 3. without shipping emissions. Difference in PM results 1-2 gives primary PM, difference 1-3 giver primary plus secondary PM from shipping.

## Results and discussion

Particles emitted by marine engines consist of a volatile and non-volatile fraction. Volatiles are mainly sulphate with associated water and organic compounds. Non-volatiles consist of elemental carbon (soot, char) and of ash and mineral compounds containing Ca, V, Ni and other elements. Because of the high content of condensable matter in the exhaust the methodology of sampling impacts the PM mass found. Sampling directly in the hot exhaust captures to a large extend only the non-volatile part of PM while sampling in the diluted and cooled exhaust captures also some of the volatiles.

The PM emissions increase with fuel sulphur content. EFPM for engines using raw oil (RO) vary between 1 and 13 g/kg fuel with the mean around 7, and for engines using marine diesel (MD) between 0.2 and 1 g/kg fuel. Figure 1 shows a plot of the available data on EFPM at cruise conditions (engine load 75-90%) against the fuel-sulphur content (FSC). We can see a clear positive trend in emission factor for PM against the FSC for data measured on engines using RO.

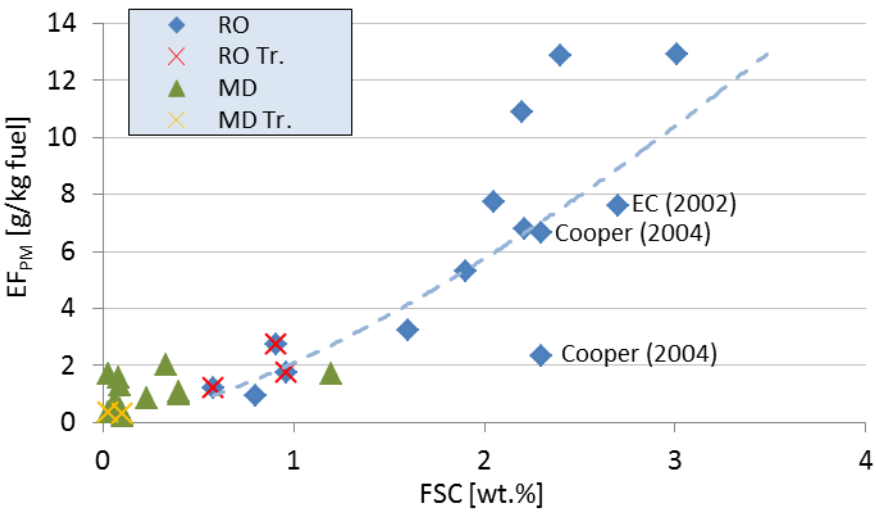


Figure 1. Emission factors for particle mass EFPM as a function of FSC (in wt. %). EFPM for RO is plotted in blue, EFPM for MD is plotted in green. Datapoints with crosses (Tr.) are from the Transphorm measurement campaigns (the dashed line fitted through the RO data has equation $EF(PM) = 2.084*FSC^{1.4633}$, $R^2 = 0.75$)

PM mass emission factors change with the engine load due to several processes. In the stack typically between 1 and 5% of sulphur is oxidized to SO3 (Moldanová et al., 2009, 2012b; Petzold et al., 2010) and contributes to the exhaust PM. Petzold et al. (2010) showed a positive correlation between the SO2 in-stack oxidation and the engine load for engines using HFO with similar fuel sulphur content (between 2 – 2.5%) (Figure 2a), Transphorm measurements showed an increase in S oxidation from 0.2 to 1.4%. While EF for sulphate is positively correlated to the engine power, i.e. contributes most to the PM emissions at high engine loads, emissions of black or elemental carbon and of organic carbon are higher at low engine loads and have their minima at loads around 50% and increases somewhat at cruise conditions (Figure 2b, Petzold et al., 2010). Emission factors of other elements, mostly metals, are related to the fuel composition

(V, Ni), lubricant composition (Ca, Zn and P) or can be associated with engine wear. The data in Moldanová et al., 2012a) show a good agreement between fuel composition and V and Ni found in PM. The ash-related elements make up 3-8% of PM in both HFO and MGO. The variability of the emission factors ter kg-fuel for metals is rather associated with fuel composition and composition and consumption of lubricant rather than with the engine load.

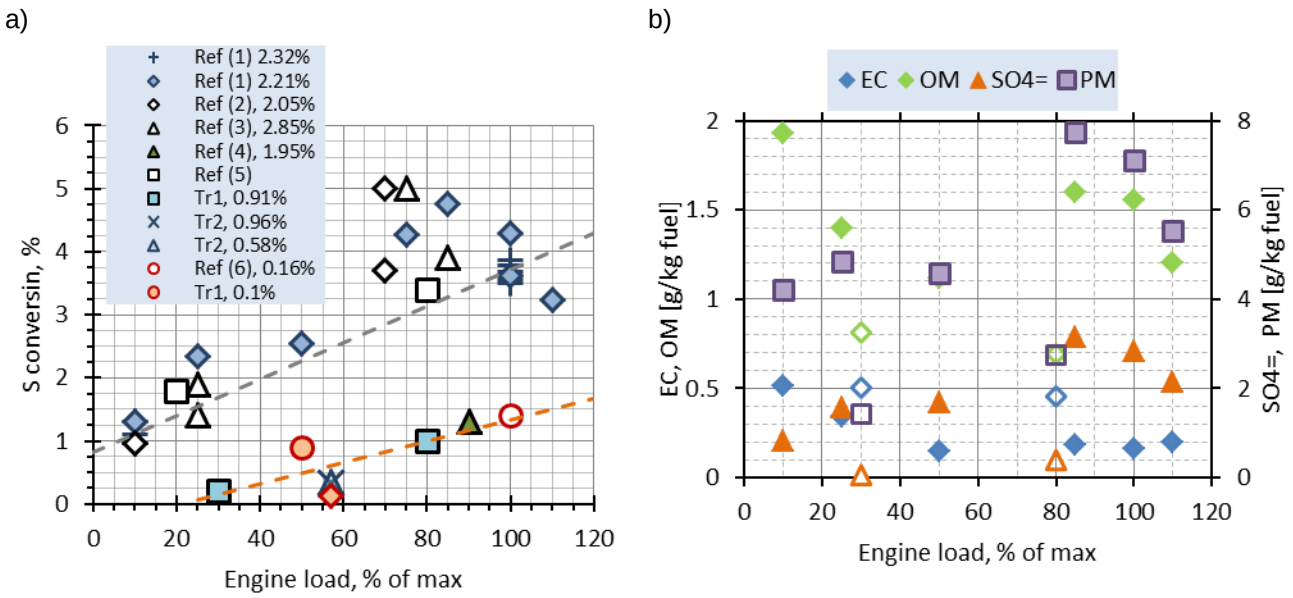


Figure 2. a - Efficiency for converting fuel sulphur to particulate-matter sulphate at various engine loads and for fuels with different sulphur contents given in wt-%; the dashed lines represent linear relationships between part of sulphur in exhaust converted to sulphate and engine load, the grey for HFO, the orange for MGO. (Ref (1): Petzold et al., 2010, Ref (2): Agrawal et al., 2008a; Ref (3): Agrawal et al., 2008b; Ref (4): Moldanová et al., 2009; Ref (5): Kurok, unpublished, Ref (6): Kasper et al., 2007, Tr1, Tr2: Data from Moldanová et al., 2012b, D2.1.4). b - Mass emission factors for carbon-containing compounds, sulphate and PM in the raw exhaust gas, FSC 2.40wt-% (filled symbols) and 0.91% (open symbols) (EC - elemental carbon, OM – organic matter, both analysed by multi-step combustion method) (from Petzold et al. 2010, data in their Table 1 and from Moldanová et al., 2012b).

The resulting dependence of $EF_{PM}$ on engine load thus varies with fuel sulphur content and potentially also with fuel type. One should remember that the fuel consumption varies also with the engine load making the emissions (in g/hour) higher at cruising that at low loads.

In a clean atmosphere the oxidation of the emitted $SO_2$ proceeds and in ship plumes sulphate becomes the dominant component of the PM (Chen et al., 2005). Our plume model simulations show that in a clean marine atmosphere under summer daytime conditions ca. 30% of the plume $SO_2$ is lost after 4 h, almost 50% of this loss is SOx deposition while the other c.a. 50% is $SO_2$ oxidised to $H_2SO_4$ and lost to both seasalt and sulphate particles. Also nitrate from $NO_X$ in the ship plume contributes to the PM as long as the sea-salt particles are alkaline enough to keep $HNO_3$. In our clean atmosphere case c.a. 45% of the plume $NO_X$ was lost in 4 hours with ca. 10% deposited on sea and 35% contributing as nitrate into seasalt particles. Majority of the gas to particle exchange is through $HNO_3$ dissolution in sea-salt, however, in dark hours significant part goes via heterogeneous reactions of $N_2O_5$ with particulate water and halogens (e.g. Moldanová et al., 2001). The heterogeneous reactions takes place both on alkaline sea-salt and on acidic sulphate particles, in the second case the nitrate is expelled back to the gas phase as $HNO_3$. Table 1 summarizes the plume model simulations. It shows that in polluted atmosphere and under dark conditions the contribution of secondary inorganic PM from $NO_X$ and $SO_2$ in ship plume is much lower, however, still significant when compared with the primary PM from shipping. When 1% of sulphur emitted from combustion of HFO with 1% FSC is oxidised and condenses on particles, it corresponds to emission factor for particulate $H_2SO_4$*$nH_2O$ of 0.67 g/kg fuel, for $NO_X$ the corresponding $EF_{HNO3}$ is 0.82 assuming $EF_{NOx}$ 70 g/kg-fuel. The total $EF_{PM}$ for this fuel is ca. 2 g/kg-fuel. Results in Table 1 show that in polluted situations the sea-salt particles get acidified by nitrate and as sulphate condenses on these acidified sea-salt particles it expels nitrate out.

Table 1. Contribution of sulphur emitted as $SO_2$ and nitrogen emitted as $NO_X$ into the PM expressed as part of the total $SO_2$ and $NO_X$ emission from the ship stack. The 'CBgnd $NO_X$' is level reached in the model during the first 2 hours outside the plume (city background). The negative values in $NO_X$ to PM contribution are for cases when shipping sulphate expelled $HNO_3$ originating from background pollution.

| | CBgnd NOx | $SO_2$ to PM | | | | $NO_X$ to PM | | | |
|---|---|---|---|---|---|---|---|---|---|
| | (ppb) | 1h | 2h | 4h | 8h | 1h | 2h | 4h | 8h |
| October-day | 1.2 | 0.15% | 0.28% | 0.42% | 0.49% | 0.03% | 0.19% | 0.60% | 4.51% |
| | 5.1 | 0.12% | 0.25% | 0.40% | 0.48% | -0.05% | 0.06% | 0.75% | 2.46% |
| | 20.7 | 0.09% | 0.15% | 0.22% | 0.50% | -0.06% | -0.10% | -0.13% | -0.16% |
| October-night | 1.4 | 0.03% | 0.05% | 0.05% | 0.09% | 0.56% | 2.96% | 7.34% | 11.25% |
| | 5.1 | 0.03% | 0.06% | 0.11% | 0.22% | 0.27% | 1.51% | 3.81% | 5.30% |
| | 42.0 | 0.03% | 0.04% | 0.10% | 0.45% | -0.04% | -0.04% | -0.06% | -0.10% |
| June-day | 0.1 | 1.71% | 6.00% | 12.70% | 15.30% | 3.92% | 13.58% | 27.83% | 35.09% |
| | 0.9 | 0.85% | 2.61% | 7.55% | 11.77% | 1.42% | 4.98% | 15.72% | 27.21% |
| | 12.6 | 0.43% | 0.86% | 1.49% | 2.03% | -0.21% | -0.52% | -1.10% | -1.69% |
| June-night | 0.2 | 0.21% | 0.43% | 0.76% | 4.81% | 3.98% | 11.78% | 20.36% | 30.82% |
| | 1.5 | 0.23% | 0.48% | 0.99% | 4.52% | 1.76% | 5.44% | 12.36% | 23.76% |
| | 13.5 | 0.18% | 0.36% | 0.62% | 1.17% | 0.24% | 0.74% | 1.61% | 1.54% |

The effect of secondary PM from shipping in a more quantitative manner was tested with the TAPM model. The TAPM model does not have an explicit sea-salt chemistry which means that the nitrate contribution from shipping to PM is underestimated. Figure 3 shows PM concentration isolines around a harbour in estuary of Göteborg city simulated for October. A clear shift to higher PM concentrations can be seen when secondary PM is considered. In a 1 km distance the contributin of secondaru PM in almost as high as that of the primary PM.

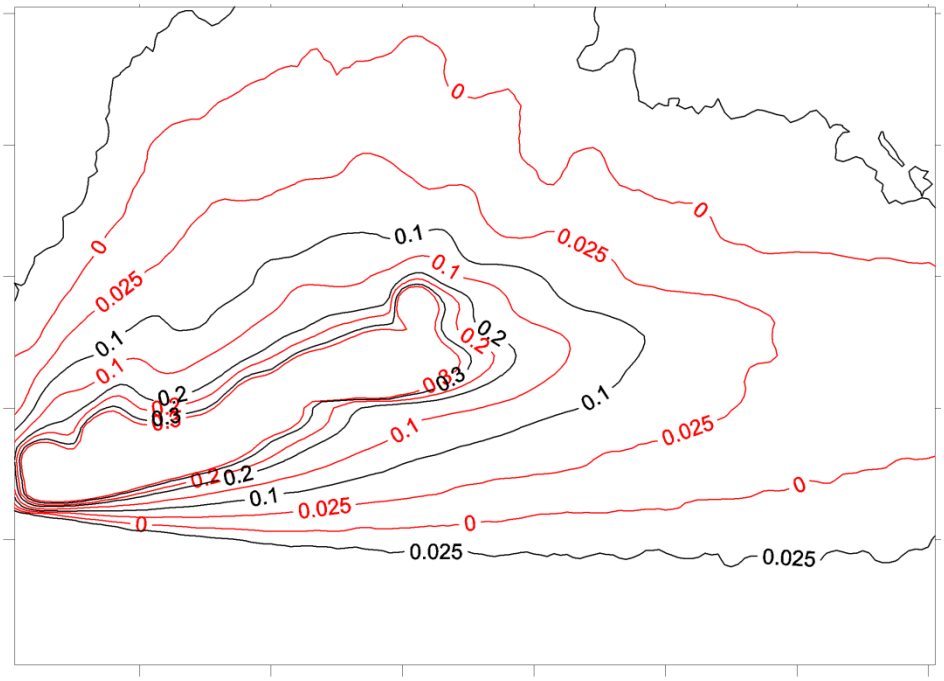


Figure 3. Conntribution of primary PM (red) and primary and secondary PM (black) from shipping emissions to the PM concentrations in Göteborg. The numbers are µg/m$^3$ and the scale on axes is 1 km. The highest shipping PM contributions in the harbour are 10 µg/m$^3$ (not shown).

## Conclusions

The primary PM from shipping main components are non-volatile elemental (or black) carbon and mineral compounds and volatile fractions sulphate, organic carbon and associated water. With exception of mineral compounds, emissions of all other PM compounds were shown to be dependent both of the fuel quality and of the engine operation. The measured volatile part is sensitive to sampling methodology.

The model simulations have shown that secondary sulphate and nitrate from shipping $SO_2$ and $NO_X$ emissions makes a significant contribution to the shipping related PM. On a regional scale under clean and moderately polluted background conditions this contribution can highly exceed the primary PM emissions. Also in the polluted environment and under low photochemistry this contribution can be in similar order of magnitude as contribution of the primary PM. Contribution of PM from shipping to the high PM concentrations at street level in cities is, however, small regardless if the secondary PM is considered or not. The contribution of shipping to PM levels is rather significant in the urban background and here the secondary PM should be considered. As the primary PM emissions are an important and often dominating part of the total when urban air pollution is concerned an accurate determination of emissions of primary particulate sulphate and OC is very important for correct evaluation of health effects of PM from shipping.

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