

# Transport and Transformation of Air Pollution from Road and Ship Transport - Joint Analysis of Regional Scale Impacts and Interactions

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**ABSTRACT:** The objective of the present work is to study the dilution and transformation processes and the interaction of the plumes generated by road and ship transport. The numerical simulations are carried out with the US EPA MODELS-3 system. A large number of numerical experiments were carried out, which makes it possible to distinguish the relative contribution of different air pollution factors. Careful and detailed analysis of the obtained results can outline the influence of the domain specific physiographic characteristics, road and ship emission impacts and meteorology conditions on the pollution characteristics

## 1 INTRODUCTION

The objective of the present work is to study the regional scale dilution and chemical transformation processes of pollutants generated by road and ship transport. More precisely the study aims at clarifying the interaction between the pollution from road and ship emissions their mutual impacts and contribution to the overall pollution.

It is expected the results of the current work to give some clues for specification of the “effective emission indices” linking emission inventories to the emissions to be used as input in large scale models.

## 2 METHODOLOGY

The US EPA Models-3 system (Dudhia, 1993, Grell et al., 1994, Byun et al., 1998, Byun and Ching, 1999, Byun and Schere, 2006) was chosen as a modelling tool. US NCEP Global Analyses data was used for meteorological background input: The data is with  $1 \times 1$  degree grid resolution covering the entire globe, the time resolution is 6 hours. The Models-3 system nesting abilities were applied for downscaling the problem to a resolution of 30 km for the domain discussed further.

Two sets of emission data are used in the present study:

- The data set created by Visschedijk and Denier van der Gon (2005) was used for the all the emissions but those from ship transport;
- The ship transport emissions were taken from the inventory created by Wang et al. (2007).

More details about emission processing (introducing temporal profiles, speciation, etc.) can be seen in Syrakov et al. (in press).

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The study was based on joint analysis of the results from the following emission scenarios:

- Simulations with all the emissions in the simulation domain, corresponding arbitrary (concentration, deposition, columnar value, process contribution, etc.) characteristic  $\phi$  denoted by  $\phi_{all}$ ;
- Simulations with the emissions from road transport excluded, corresponding arbitrary characteristic  $\phi$  denoted by  $\phi_{no,road}$ ;
- Simulations with the emissions from ship transport excluded, corresponding arbitrary characteristic  $\phi$  denoted by  $\phi_{no ship}$ ;
- Simulations with the emissions from both road and ship transport excluded, corresponding arbitrary characteristic  $\phi$  denoted by  $\phi_{no road \& ship}$ .

The most natural properties, which can be constructed from these scenarios are the relative (in %) contributions of road/ship emissions to the formation of the characteristic  $\phi$ :

$$\phi_{road} = \frac{\phi_{all} - \phi_{no,road}}{\phi_{all}} \cdot 100 \quad \text{and} \quad \phi_{ship} = \frac{\phi_{all} - \phi_{no ship}}{\phi_{all}} \cdot 100. \quad (1)$$

Some more “sophisticated” properties, like impact of road transport on the pollution from ship emissions (the ratio  $\phi_{ship}|_{road}$  of pollution from ship emissions when road emissions are also excluded to pollution from ship emissions, but with road emissions present) or vice versa ( $\phi_{road}|_{ship}$ ) can also be defined:

$$\phi_{ship}|_{road} = \frac{\phi_{no,road} - \phi_{no,road \& ship}}{\phi_{all} - \phi_{no ship}} \cdot 100 \quad \text{and} \quad \phi_{road}|_{ship} = \frac{\phi_{no ship} - \phi_{no,road \& ship}}{\phi_{all} - \phi_{no,road}} \cdot 100. \quad (2)$$

MM5 and CMAQ simulations were carried out for the periods January 2001-2005 and July 2001-2005.

Averaging the fields over the respective month produces a diurnal behavior of given pollution characteristic, which can be interpreted as “typical” for the month (respectively season). The characteristic, which will be mostly demonstrated and discussed as an example further in this paper is the surface concentration  $c$ . Moreover, what will be shown and discussed concerns not only separate pollutants, but also some aggregates like nitrogen compounds (GNOY=NO + NO<sub>2</sub> + NO<sub>3</sub> + 2\*N<sub>2</sub>O<sub>5</sub> + HONO + HNO<sub>3</sub> + PNA), organic nitrates (ORG\_N=PAN + NTR), hydrocarbons (HYDC=PAR + ETH + OLE + TOL + XYL + ISO), CAR\_PHE= FORM + ALD<sub>2</sub> + MGLY + CRES, aerosol NH<sub>4</sub>, SO<sub>4</sub> and H<sub>2</sub>O, PM<sub>2.5</sub> and PM<sub>coarse</sub>=PM<sub>10</sub>-PM<sub>2.5</sub>.

The Models-3 “Integrated Process Rate Analysis” option is applied to discriminate the role of different dynamic and chemical processes for the pollution from road and ship transport. The processes that are considered are: advection, diffusion, mass adjustment, emissions, dry deposition, chemistry, aerosol processes and cloud processes/aqueous chemistry.

### 3 RESULTS AND DISCUSSION

The respective “typical” concentrations can be also averaged for the day and these will be (due to the volume limitations) most of the illustrations demonstrated, like on Figure 1.

The impact of road/ship emissions is rather complex and will take a lot of pages to be described. One could not help but notice, however, how well displayed the configurations of most intensive ship/road transport are. Due to the none-linearity of the processes their impact can be negative as well. Some big cities and the main ship routs are particularly well displayed as sinks in the July ozone plots.

The impact of road/ship emissions for a “typical” January day is again very complex. The difference, both qualitative and quantitative between “summer” and “winter” fields is quite evident (due to volume limitations not demonstrated in the present paper) for all the species, thou the configurations of most intensive ship/road transport are again very well displayed.

Ship/road emission relative contribution does have diurnal course, which is well displayed by Figure 2. Again the temporal behavior is complex and can not be described by some general statements. The most intensive ship/road sources are well visible as sinks and the sink locations do not

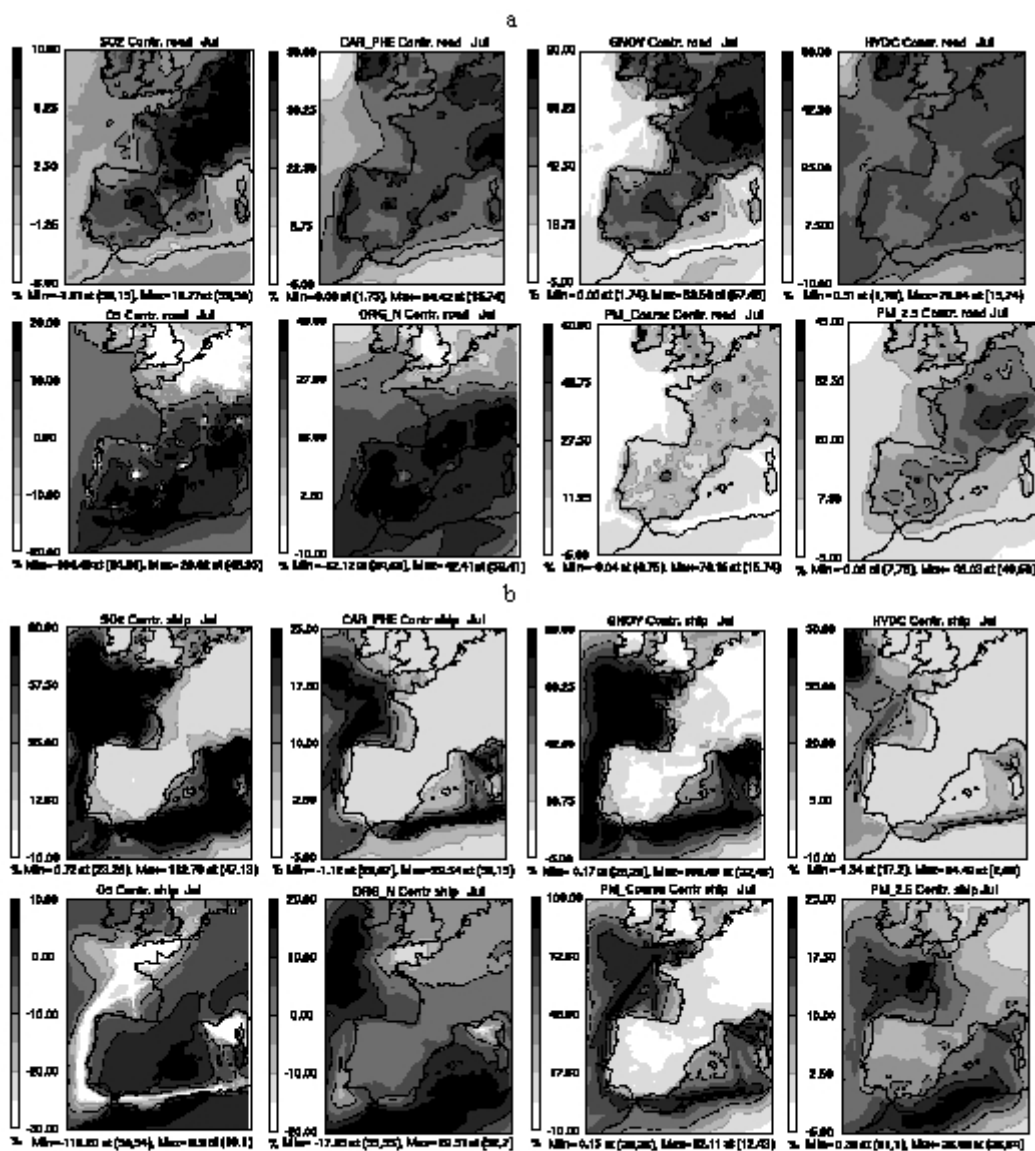


Figure 1. Averaged for a “typical” day in July fields of  $C_{road}$  [%] (a) and  $C_{ship}$  [%] (b) for ozone, PM2.5, nitrogen compounds, hydrocarbons, CAR\_PHE, PMcoarse, organic Nitrates and SO2

have dramatic diurnal change. The temporal variations of shape and location of areas with positive impact to the ozone levels generated by ship/road transport emissions are more prominent.

The more complex and sophisticated “road-to-ship” and “ship-to-road” contributions are illustrated in Figure 3. It is really hard to describe the plot, but they are a very good demonstration of how complex the interactions of the pollutants are and how strange and surprising the impact of one of the types of transport to the air pollution by the other is. The absolute value of these contributions in some points could be very large, but generally for most of the compounds the contributions vary within relatively narrow margins around 100%. The corresponding plots for January are of course different, but the most general features mentioned above are valid as well.

To better understand the interaction of pollutants from road and ship transport, one should closely examine the contributions of different processes to the total pollution, in particular the “road-to-ship” and “ship-to-road” contributions to the respective processes. That is why the CMAQ “Integrated Process Rate Analysis” option was applied and the “portions” of the major processes which form the hourly concentration changes were calculated. The process “portions”  $\Delta c^{(proc)}$  can be treated like the concentrations and respective “road”, “ship”, “road-to-ship” and “ship-to-road” contributions can be estimated.

Plots of the horizontal fields of the “road-to-ship” ( $\Delta c_{ship}^{(chem)} \Big|_{road}$ ) and “ship-to-road” ( $\Delta c_{road}^{(chem)} \Big|_{ship}$ ) contributions to the chemical transformation processes “portion” of the surface ozone the hourly change concentrations are shown in Figure 4. The very complex and “mosaic” texture of the plots can hardly be discussed in details. This is simply an illustration of how discouragingly complex the mutual impacts of pollution from different source types is and how difficult the answer of a question “What is the impact of the pollution from road transport to the chemical transformation of the ozone from ship transport?” or vice versa could be.

#### 4 CONCLUSIONS

The numerical experiments performed produced a huge volume of information, which have to be carefully analyzed and generalized so that some final conclusions could be made. The conclusions that can be made at this stage of the studies are that the transport type/processes interactions are indeed very complex.

The results produced by the CMAQ “Integrated Process Rate Analysis” demonstrate the very complex behavior and interaction of the different processes – process contributions change very quickly with time and these changes for the different points on the plane hardly correlate at all. The analysis of the behavior of different processes does not give simple answer of the question what the impact of pollution from given source type to the process, which form the pollution from another source type, could be. The “Integrated Process Rate Analysis” is a fruitful approach, however, so an attempt should be made the evaluation and analysis of the processes to be presented in a more general way.

#### 5 ACKNOWLEDGEMENTS

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# Characterisation of particulate matter and gaseous emissions from a large ship diesel engine

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**Keywords:** Ship emissions, Particulate matter, chemical composition, elemental composition, microphysical characteristic, NOX, CO, SO<sub>2</sub>, hydrocarbons

**ABSTRACT:** Composition of exhaust from a large cargo vessel was investigated onboard a ship during the Quantify field campaign in June 2007. The emitted particulate matter (PM) properties were investigated along with composition of the gas-phase emissions. Mass, size distribution, chemical composition and microphysical structure of the PM were investigated. The emission factor for PM was 5.3 g/(kg fuel). The mass size distribution showed a bimodal shape with two maxima: one in the accumulation mode with mean particle diameter DP around 0.5 µm and one in the coarse mode at DP around 7 µm. The PM composition was dominated by organic carbon (OC), ash and sulphate while the elemental carbon (EC) composed only a few percent of the total PM. Increase of the PM in exhaust upon cooling was associated with increase of OC and sulphate. Laser analysis of the adsorbed phase in the cooled exhaust showed presence of a rich mixture of polycyclic aromatic hydrocarbon (PAH) species with molecular mass 178 – 300 amu while PM collected in the hot exhaust showed only four PAH masses. Microstructure and elemental analysis of ship combustion residuals indicated three distinct morphological structures with different chemical composition: soot aggregates, significantly metal polluted; char particles, clean or containing minerals; mineral and/or ash particles. Additionally, organic carbon particles of unburned fuel or/and lubricating oil origin were observed. Hazardous constituents from the combustion of heavy fuel oil such as transitional and alkali earth metals (V, Ni, Ca, Fe) were observed in the PM samples.

## 1 INTRODUCTION

Emissions of exhaust gases and particles from seagoing ships contribute significantly to the anthropogenic burden, thereby affecting the chemical composition of the atmosphere, local and regional air quality and climate. According to the global estimates shipping emits between 0.9 and 1.7 million tons of particulate matter annually. The fact that nearly 70 % of ship emissions occur within 400 km from land implies potential of these emissions to significantly affect air quality in coastal areas (Endresen et al., 2003, Eyring et al., 2005). Global-scale model study of Corbett et al. (2007) has shown a maximum increase of PM<sub>2.5</sub> due to shipping by 2 µg/m<sup>3</sup>. This study also indicated that shipping-related PM emissions on a global scale are responsible for around 60 000 cardiopulmonary and lung cancer deaths annually.

The radiative forcing of PM emitted by shipping is rather complex: radiative forcing of black carbon is positive, while radiative forcing of sulphate particles is negative (Endresen et al., 2003; Eyring et al., 2007; Lauer et al., 2007). The particles also affect the life cycle and radiative proper-

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ties of the marine stratus clouds at the top of the marine boundary layer and contribute with a negative radiative forcing. Current estimates indicate that the present-day net radiative forcing caused by ship emissions (including the gaseous species) could be negative (Endresen *et al.*, 2003; Eyring *et al.*, 2007; Lauer *et al.*, 2007).

The particles emitted from large marine diesel engines fuelled with residual oil represent a variety of compositions and sizes. Despite of many indications of their important role, both as air pollutant and for the climate change, information on emissions of ship-exhaust particles, such as detailed characterisation of chemical composition, microphysical characteristic and description of transformation processes in the marine environment, is only sparse. The ship-exhaust particles are composed by elemental, organic and inorganic carbon, sulphate and ash as well as nitrates. Quantification of aerosol mass emitted from the low-speed marine diesel engines has been investigated by few studies (Lyyräinen *et al.*, 1999; Cooper, 2003; Sinha *et al.*, 2003; Chen *et al.*, 2004; Petzold *et al.*, 2008, Fridell *et al.*, 2008). Size distributions are available both for ship plumes (e.g. Hobbs *et al.*, 2000; Petzold *et al.*, 2004) and for fresh emissions (e.g. Lyyräinen *et al.*, 1999; Petzold *et al.*, 2008, Fridell *et al.*, 2008). Microphysical and chemical studies of the PM generated by combustion of residual fuels have shown that the PM is composed of two different types of particles: graphitic soot aggregates in the size range tenths to hundred nm and larger carbon-rich char particles in size range of few  $\mu\text{m}$  containing also sulphur and other inorganic species (Ca, V, Ni, Fe) (Lyyräinen *et al.*, 1999; Chen *et al.*, 2005).

In this study we report properties of particles sampled in the exhaust of the main engine on a large cargo vessel together with their individual microphysical and chemical characteristics. Results from sampling both in hot and in diluted/cooled-exhaust gas are presented and the formation of particles during cooling of the exhaust is discussed. Composition of gaseous emissions was investigated to give a more complete picture of composition of the emissions.

## 2 METHODS

### 2.1 *Measurement campaign*

The measurements were performed in June 2007 as a part of a field campaign organized within the EU project QUANTIFY. The aim of the campaign was to investigate plume and corridor effects of ship emissions. The measurements were performed in area of the Celtic Sea, the English Channel and the North Sea. The campaign involved both measurements from the research aircraft that performed surveys in the ship corridors as well as plume chasing of a designated ship and measurements onboard this vessel. The onboard measurements presented here were performed on a combined Ro-Ro and container ship. The vessel was built in 1985 and is 292 m long and 32 m wide. The overall height is 52 m and the height from the sea level to the funnel top is 39 m. Further technical parameters of the ship engine and the cruise as speed, power, temperature and flux of the exhaust gases are presented in Table 1.

Table 1. Technical parameters of the ship and ship engine operation specific for the measurements performed 14/6 2007. The exhaust flow is given at normalized conditions (273.14 K, 1013.25 hPa)

Gross tonnage	58 438
Net tonnage	21 660
Main diesel engine	
Kincaid B&W 6L90 GBE	20 200 kW, 97 rpm *
Thrusters	2 × 1 398 kW
Full sea speed	17.5 knots (32.4 km/h)
Fuel consumption at sea	HFO** 3.2-3.4 m <sup>3</sup> /h
Brake Power Load, %	84
Brake Power, Main Engine, MW	17.0
Speed, km/h	31.5
Calculated Fuel Consumption, kg/h	3 263
Calculated Fuel Consumption, g/kWh	194
Exhaust temperature after the engine, °C	330
Exhaust flow, main engine, Nm <sup>3</sup> /h	110 000
Exhaust flow speed, m/s	25

\* rpm: rotations per minute, \*\* HFO: Heavy-Fraction Oil (residual oil)

Fuel analyses, one performed on routine basis after the fuel purchase on behalf of the ship owner and one performed on a fuel sample taken directly from the engine during the campaign have shown the following elemental composition: 86.5 % (mass) C, 0.7% O, 0.34% N, 1.9 % S, 107 mg/kg V, 35 mg/kg Ni, 5 mg/kg Si, 3 mg/kg Ca. The ash content was 0.03 % (mass).

## 2.2 Measured parameters and methodologies

The analysed exhaust from the 20.2 MW main engine was sampled through 3 holes in the exhaust pipe positioned c.a. 25 m behind the engine and 40 meters before the funnel exit plane. Properties of the particulate matter were investigated in the hot exhaust gas sampled directly in the exhaust pipe, in a diluted and cooled gas sampled in the dilution system, or in both, as indicated later in the text. The partial flow dilution system was used to mix the hot-exhaust gas with ambient air (26-30°C, 30% RH) and cool to around 40°C. The dilution factor was determined by continuous CO<sub>2</sub> measurements (International Organisation of Standardisation, 1996), and varied between 8 and 10. In addition, concentration of NO<sub>x</sub>, HC, CO, CO<sub>2</sub>, O<sub>2</sub> and SO<sub>2</sub>, as well as humidity, temperature and the gas flow were measured. More details about the sampling are described in Moldanová *et al.* (2009).

The size distribution of particles in the hot diesel exhaust was probed using a cascade impactor (Andersen Mark III Particle Sizing Stack Sampler) with eight stages and 47 mm diameter quartz filter. The impactor stages have cut-offs between about 10 and 0.2 µm. The filters were analysed gravimetrically. The total particle mass was measured using glass fibre, quartz and Teflon filters in the partial flow dilution system and quartz filters in the hot exhaust. The filters were analysed gravimetrically. Analyses of reference filters sampled behind the dilution system showed contribution of the background PM to the exhaust gas concentration by about 0.2%.

The morphology, microstructure and composition of individual carbonaceous particles on samples taken in hot and cooled exhaust were investigated by various electron microscopy techniques, including transmission electron microscopy (TEM) with the phase-contrast imaging method, energy-dispersive X-ray spectroscopy (EDS), and selected area electron diffraction (SAED) (Demirdjian *et al.*, 2007). The surface composition (especially in terms of adsorbed PAHs) of the carbonaceous material deposited on filters exposed in hot and cooled exhaust was investigated by two-step laser mass spectrometry (L2MS) (Bouvier *et al.*, 2007; Mihešan *et al.*, 2008).

Evolved Gas Analyses (EGA) by thermal-optical analyzer (Johnson *et al.*, 1981; Birch and Cary, 1996) for determination of the sum of organic carbon and carbonates (OC) and of the elemental carbon (EC) content and ion-chromatographic analyses for determination of the sulphate content were performed at NILU laboratory on quartz filter samples. The samples were taken both from the hot exhaust and from the diluted exhaust.

Concentrations of a number of other gas constituents were measured continuously in the hot exhaust at point B. Nitrogen oxides (Horiba PG-250 chemiluminescence instrument), carbon monoxide and carbon dioxide (Horiba PG-250 NDIR), oxygen (Horiba PG-250 galvanic cell), total hydro-



carbons (Bernath Atomic BA 3006 FID), and sulphur dioxide (Horiba PG-250 NDIR) were monitored. The temperature and humidity of the inlet air were monitored. The exhaust gas flow was measured with a pitot tube at point A. The exhaust temperature in the hot exhaust was 300°C, and in the dilution system 40°C. Engine data were obtained from the ship's instrumentation. Further details of the individual measurement techniques are given in Moldanová *et al.* (2009) and references therein.

### 3 RESULTS AND DISCUSSION

#### 3.1 Exhaust composition and PM properties

A summary of measured emission indices of the engine, emission rates and concentrations of exhaust components are given in Table 2. The indices were calculated from measured concentrations and from the exhaust flow and fuel consumption presented in Table 1. Emission The emission factor for NO<sub>x</sub> is on the low side of the span of values of the global average EF<sub>NO<sub>x</sub></sub> for cargo ships, is lower for CO and significantly lower for hydrocarbons (EF comparison this work/global average values for cargo ships (in g/kg fuel): EF<sub>NO<sub>x</sub></sub>: 73.4/67.9–87; EF<sub>CO</sub>: 2.2/4.7–7.4; EF<sub>HC</sub>: 0.36/2.4–6.6). However, since emission factors are known to vary between ships, these results are not surprising. The SO<sub>2</sub> emission factor may be deduced directly from the sulphur content in the fuel assuming all sulphur is oxidized into SO<sub>2</sub> in the combustion chamber. Such a calculation gave 39.4 g/(kg fuel), a value close to emission factor 39.3 g/(kg fuel) obtained from the SO<sub>2</sub> measurements.

The PM emission factors, emission rates and concentrations given in Table 2 for the hot and for the diluted exhaust are calculated from gravimetric analysis of the total particle mass on filters. The value for the hot exhaust is an average of three samples, the value for the diluted exhaust is an average of five samples. The increase in PM observed after the dilution reflects condensation growth of particles during cooling from about 300°C to 40°C.

Table 2. Emission factors EF, emission rates Er and concentrations C in exhaust from the main diesel engine operating under conditions as listed in Table 1 (84% power load) and using the HFO. Concentrations are given at normalized conditions (273.14 K, 1013.25 hPa).

Exhaust component	EF g/kWh	EF g/kg fuel	Er kg/hr	C g/Nm <sup>3</sup>
NO <sub>x</sub>	14.22	73.4	241.7	2.20
CO <sub>2</sub>	667	3 441	11 339	103.1
CO	0.42	2.17	7.1	0.065
HC	0.07	0.36	1.2	0.011
O <sub>2</sub>	1270	6 553	21 590	196.3
SO <sub>2</sub>	7.62	39.32	129.5	1.18
SO <sub>3</sub>	0.11	0.57	1.9	0.017
Benzene	0.012	0.06	0.21	0.002
PM	0.29	1.49	4.86	0.044
PM*	1.03	5.31	17.43	0.158
OC*	0.30	1.58	5.15	0.047
EC <sup>†</sup>	0.02	0.13	0.42	0.004
Ash <sup>†</sup>	0.19	0.98	3.19	0.029
Sulphate*	0.15	0.76	2.47	0.022

\*after cooling in the dilution system, †average hot exhaust and diluted exhaust

The mass particle size distribution measured in the hot exhaust is presented in Figure 1. It is a fit for the PM mass data from the stage-impactor measurement. The hot-exhaust mass distribution shows clearly two main modes: one in the accumulation mode at diameter DP around 0.5 µm and one in the coarse mode at DP around 7 µm. The coarse particles around 7 µm constitute a major mode of the ship-exhaust particulates' mass size distribution. Exhaust particulate residuals from medium-speed diesel engines operated with HFO investigated by Lyyränen *et al.* (1999) also demonstrated the bimodal mass size distribution with the main mode at 0.1 µm and a second mode at about 10 µm. The presence of coarse particles along with fine aerosols is probably associated with HFO combustion and may be explained by the various nature and composition of the ship-exhaust par-

ticulates. The findings of TEM observations can confirm this assumption. This size distribution is strongly different from typical automobile diesel soot where the mean diameter around 1  $\mu\text{m}$  is emphasized (Kerminen et al., 1997). The difference is due to very different chemical composition and physical properties of the marine HFO and car diesel fuel and different conditions of combustion.

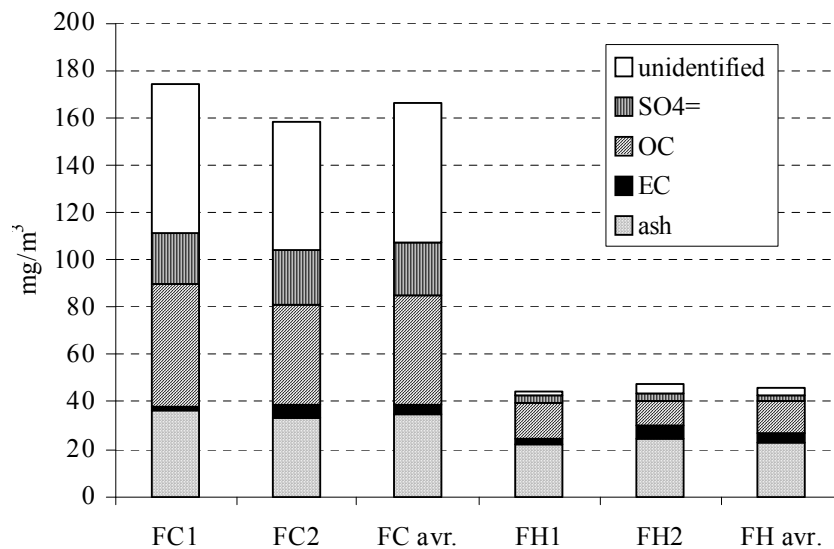


Figure 1. Particle mass size distribution measured on stage impactor in the hot exhaust gas.

The composition of PM with respect to the content of EC, OC (is OC + carbonate), sulphate and fly ash is presented in Figure 2. Organic matter (OM) was calculated from organic carbon via the relationship  $\text{OM} = 1.2 \times \text{OC}$  (Petzold et al., 2008). Figure 2 shows clearly that OM and sulphate increase after the cooling of the exhaust gas while content of EC and ash remains unchanged, which is consistent with the expected condensation of  $\text{H}_2\text{SO}_4$  and hydrocarbons due to the cooling of the exhaust gas. The unidentified PM in Figure 2 represents a fraction obtained by subtracting the sum of OC, EC, fly ash (from the EGA analysis) and sulphate (from the ion chromatography) from the total PM concentration on the filter obtained by gravimetry. Part of this mass may be water associated with sulphate.

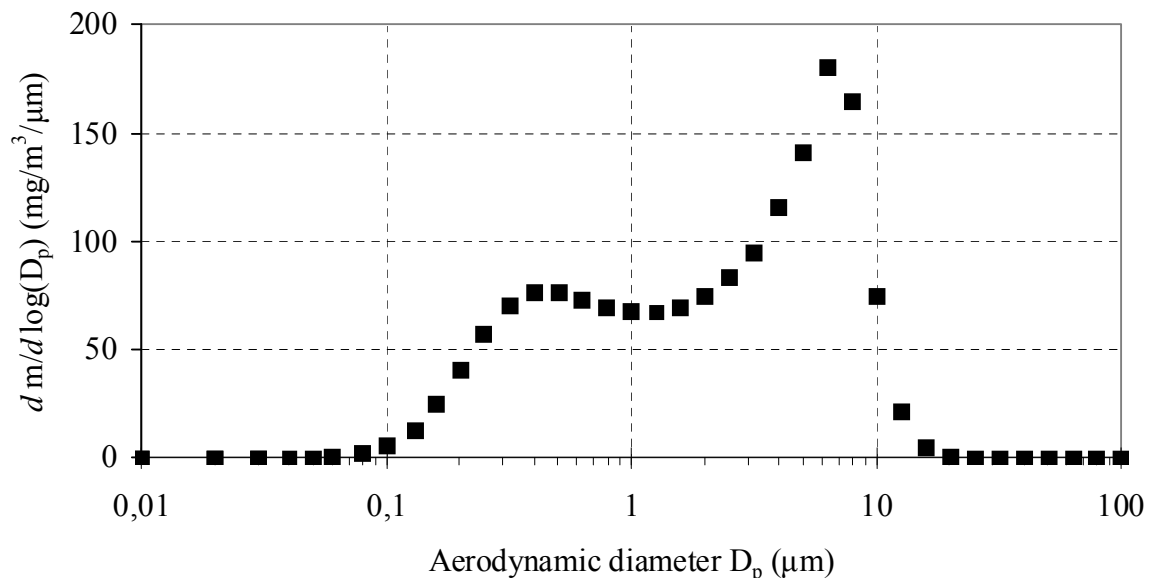


Figure 2. Composition of PM (as  $\text{mg}/\text{m}^3$  exhaust gas) collected on filters in the diluted (FC) and hot (FH) exhaust gas. FC1, FC2, FCavr. and FH1, FH2, FHavr. are individual filter samples and their average values collected in the diluted and hot exhaust, respectively.

The emission factors derived for EC and ash in Table 2 are calculated as an average from filter samples taken both in the hot and in the cooled exhaust while emission factors for OC and sulphate were derived only from filter samples taken in the cooled exhaust with much higher content of these species. For EC, ash and OC our results are consistent with values derived from data published by

Petzold *et al.* (2008) (0.174, 1.18 and 0.28 g/kg of OC, EC and sulphate, respectively) and Agrawal *et al.* (2008) (0.08, 1.22 and 0.58). The L2MS analysis have shown that the high OC-content of the PM collected in the cooled exhaust is accompanied also by much more rich composition of PAH species comparing to few PAH species observed in PM collected in the hot exhaust. The emission factor for sulphate derived from the FC samples was substantially lower than factors derived from Agrawal *et al.* (2008) and Petzold *et al.* (2008). The difference was due to a lower conversion ratio of S<sup>IV</sup> to S<sup>VI</sup> in the exhaust (Moldanová *et al.*, 2009). Emission factor 5.3 g/(kg fuel) for the total PM (EF<sub>PM</sub>) obtained from our measurements was lower than EF<sub>PM</sub> 6-7 g/(kg fuel) obtained in Petzold *et al.* (2008).

### 3.2 Microphysical properties of individual particles

In general, microstructure and elemental analysis of ship combustion residuals sampled in the hot and diluted exhaust indicate three distinct morphological structures with quite different chemical composition: Soot aggregates, significantly metal polluted; Char particles, clean and containing minerals; Mineral and/or ash particles. The soot aggregates dominate in the sub-micrometer fraction. Vanadium, nickel and sulphur are gathered within the soot matrix forming composite submicron particles. Spherically shaped char particles are abundant in the micrometer size fraction. They can be found as almost clean spherical carbonaceous particles or mixed with alkali-earth compounds, e.g. V, Ni, Ca, included in partly burnt carbonaceous matrix. Spherically or irregularly shaped mineral and/or ash particles have typically size 200 nm to 10 µm. They are characterized by a dominant content of Ca, V and Ni and by having mineral dust structure of elongated prismatic crystals related to mineral compounds. Their formation may be explained by coalescence of molten grains of minerals during combustion. Additionally, organic carbon particles with a size of about 100 nm, of unburned fuel or/and lubricating oil origin, were observed.

Sulphur was detected by EDS analysis in almost all individual particles. Soot particles contain on average the smallest amount of sulphur, typically less than 1% and also have lower content of O, V and other inorganic elements. The highest S content is associated with large amount of V and other inorganic elements from the parent fuel oil in char particles. These composition differences are consistent with formation mechanisms of particles; since the char particles do not undergo evaporation – condensation process, inorganic elements from parent oil fuel are more readily preserved there.

The ship-emitted PM with surfaces covered with transition metals and organics has a potential to cause reverse health effects. Armstrong *et al.* (2004) have shown potential impact of PAHs on human health. Study by Mudway *et al.* (2004) have shown that the residual oil using diesel exhaust particles cause higher oxidative stress on epithelial lining fluid in lungs than particles not having their surface covered with oxidants. The oxidative stress increases the relative health risk of the PM.

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