

# **TRANSPHORM**

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Collaborative Project, Large-scale Integrating Project

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### **Report on the description of near-field plume PM processes**

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Jana Moldanová

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# Report on the description of near-field plume PM processes

Jana Moldanová, Marie Haeger Eugensson, Lin Tang

IVL, Swedish Environmental Research Institute, Box 5302, 40014 Gothenburg, Sweden

## *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<sub>x</sub>, SO<sub>2</sub> and particulate matter (PM), respectively ([www.emep.int](http://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). 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 from PM-bound nitrate and sulphate 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<sub>x</sub>. Emissions of PM are though addressed indirectly through decrease of formation of secondary PM from the reductions in SO<sub>2</sub> and NO<sub>x</sub>. 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. Many urban air quality models neglect formation of the secondary PM as this effect is computationally expensive to calculate and it is assumed to be small in the polluted atmosphere of a city. However, emissions from ships around and in a harbour can experience more intensive chemistry as they are often emitted into a relatively clean marine air. In global and continental-scale studies formation and effects of the secondary inorganic PM is considered even though the gas-to-particle partition is parameterised and does not explicitly describe chemical composition of the aerosol particles. On this scale secondary PM makes a significant contribution to the PM concentration increase caused by shipping, e.g. approximately 50% of the health effects from shipping-related PM in global study of Corbett et al. (2007) is the secondary PM.

The secondary PM formed from shipping emissions comprises of nitrate, sulphate and secondary organics formed during atmospheric oxidation of NO<sub>x</sub>, SO<sub>2</sub> and VOCs, respectively. In this study we focus on contribution of shipping with nitrate and sulphate to the secondary PM on the local scale. This contribution is discussed in relation to the primary PM from shipping.

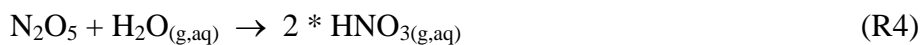
### *Theoretical background*

SO<sub>2</sub> is in atmosphere oxidised to SO<sub>3</sub> through its reaction with the OH radical, SO<sub>3</sub> will fast react with water forming H<sub>2</sub>SO<sub>4</sub>. Lifetime of SO<sub>2</sub> to this reaction is approximately a week. Dry deposition of SO<sub>2</sub> is typically much more efficient than the gas phase oxidation. At presence of clouds SO<sub>2</sub> is also efficiently oxidized in cloud particles, this SO<sub>2</sub> removal pathway can then exceed the dry deposition sink (Seinfeld and Pandis, 1996). In the gas phase H<sub>2</sub>SO<sub>4</sub> can either condense on existing particles or form new ones through the nucleation process. Due to the very low equilibrium vapour pressure of H<sub>2</sub>SO<sub>4</sub> the gas-to particle conversion of H<sub>2</sub>SO<sub>4</sub> is an irreversible process in atmospheric conditions. Gas-phase SO<sub>2</sub> can dissolve into the atmospheric aerosol and there be oxidised by ozone, H<sub>2</sub>O<sub>2</sub> or by oxygen in catalytic reaction chain involving Fe<sup>III</sup> or other metals. Both dissolution of SO<sub>2</sub> into the aerosol particles and some rates of its aqueous-phase oxidation are pH dependent and less efficient at low pH.

The main removal pathway of NO<sub>x</sub> in the atmosphere is its gas-phase oxidation initiated by OH radical giving nitric acid, HNO<sub>3</sub>, which is eventually deposited or scavenged:

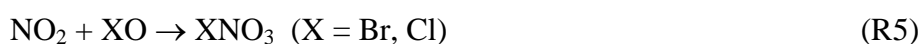


During the night a sequence of reactions R2-R4 can become important:

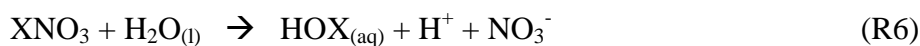


In the daytime, NO<sub>3</sub> formed in R2 is fast photolysed which makes the N<sub>2</sub>O<sub>5</sub> formation (R3) negligible. At night heterogeneous reactions (on aerosol particles and surfaces) or slow gas-phase hydrolysis of N<sub>2</sub>O<sub>5</sub> (R4) give HNO<sub>3</sub>. HNO<sub>3</sub> is subjected to partitioning between gas phase and particle phase and composition of aerosol particles, in particular of their pH, controls this mass exchange. When particles are fully acidified (in equilibrium with the gas phase HNO<sub>3</sub>), they can't absorb any further HNO<sub>3</sub> and absorption of further more soluble strong acids (H<sub>2</sub>SO<sub>4</sub>) will lead to the loss of HNO<sub>3</sub> to the gas phase.

In the marine atmosphere NO<sub>x</sub> can be also oxidized in reaction with halogen oxides BrO and ClO (XO), species produced in the halogen catalytic cycle involving sea-salt aerosol particles (Vogt et al., 1996):



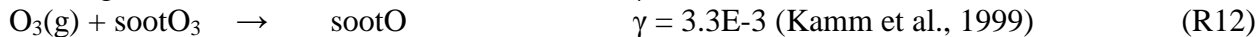
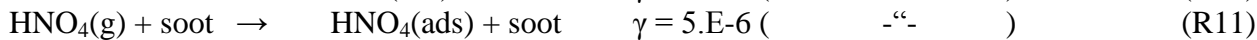
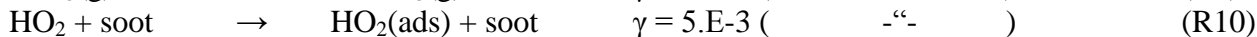
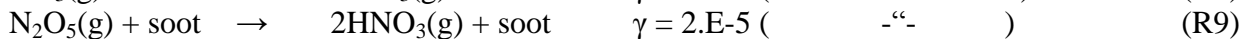
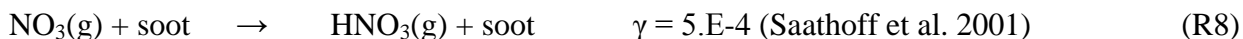
Model studies supported by observations indicate that in a clean marine atmosphere BrO is often the most abundant of the 2 XO species, however, in more polluted coastal areas ClO concentrations can dominate (Pszenny et al., 2004, Moldanova and Ljungström, 2001). Halogen nitrates (XNO<sub>3</sub>) will contribute to PM nitrate through heterogeneous reactions on aerosol particles:



Reactions R2-R3 followed by N<sub>2</sub>O<sub>5</sub> hydrolysis (R4) can significantly contribute to the NO<sub>x</sub> oxidation in urban areas during night and reactions R5-R7 in marine and coastal areas. At presence of non-acidic particles, such as sea-salt or ammonium containing particles, contribution of nitrate to the PM can be significant.

The plume model used in this study simulates background air with sulphate and sea-salt PM. The PM emitted by the ship consists of soot, organic matter, sulphate, and mineral compounds in both internal and external mixture (Moldanová et al., 2013). In this study 2 models of the ship-emitted PM were tested. The first assumed that all PM was coated with sulphate, i.e. the gas-particle interaction was with particles covered with sulphuric acid. The second model considered interaction

with pure soot particles, considering only the non-volatile part of the emitted PM. The following reaction scheme for the soot is implemented in the model:



The change of mixing ratio  $c_{ig}$  of species  $i$  in the gas phase due to the loss to the heterogeneous phase can be described by

$$\frac{dc_{ig}}{dt} = -Lk_t c_{i,g}, \quad (\text{E1})$$

where  $L$  is the volume fractional aerosol content and  $k_t$  is the transfer coefficient averaged over the size spectrum of particles.  $\gamma$  is dimensionless reaction probability which is used in calculation of  $k_t$ . Reaction R12 is fast destruction of ozone on ozone-specific reaction sites on fresh soot particles ( $\text{sootO}_3$ ). For this reaction the mass transfer is described using specific surface of soot instead of the fractional volume. Kamm et al. (1999) gives site density of  $6.5 \times 10^{14}/\text{cm}^2$  for the graphite spark generator soot. This site density and the specific surface of spark generator soot  $150 \text{ m}^2/\text{g}$  give as amount of ozone absorbed on the monolayer of  $1 \mu\text{g}$  soot being  $9.75 \times 10^{14}$  molecules. This means that  $1 \mu\text{g}/\text{m}^3$  soot would destroy 40ppt(V) ozone.

### *Experimental*

The chemical transformation of ship emissions in plumes was investigated with a plume version of Model Of Chemistry Considering Aerosols (MOCCA) Model results were published for the polluted marine boundary layer (MBL) (Sander et al., 1996) as well as for the remote MBL (Vogt et al., 1996, Pszeny et al, 2004). The model includes comprehensive gas-phase and condensed phase chemistry including NO<sub>x</sub>, SO<sub>x</sub>, organics, halogens and reactions on soot. Photochemical reaction rates vary as a function of solar declination. The chemistry scheme of the model was extended by the CBIV mechanism for hydrocarbon reactions (Gery et al., 1989). The particle population is partitioned into eight mono-dispersed size bins with median diameters equal to the corresponding size interval of the modelled continuous distribution. Particles emitted from the ship are treated either as sulphate-coated soot or as soot only, the soot is in the second case treated as a continuous lognormal distribution (Moldanová, 2010).

Initial concentrations and emissions for Göteborg are used from the TAPM urban scale model system setup for the city (see below). The plume is simulated with help of a single air box entraining the background air simulated by a second parallel box. Model simulation of both boxes is started several hours prior to the plume emission with clean maritime air. At the time point of plume initialization concentrations in the plume box are increased from the background concentration with initial concentrations in the plume. The plume initial concentrations are calculated from the emission factors of the species, specific fuel consumption, volume flux of the exhaust gas, wind speed relative to the ship movement direction and from the initial dispersion of the plume corresponding to the first few seconds. The emission fluxes and factors used in the model are shown in

Table 1. The plume mixing is further described by Gaussian dispersion. The dispersion parameters were obtained by fitting of the snapshots of ship plumes simulated with the TAPM model.

**Table 1. Emission fluxes (g/s) and emission factors (EF, g/kg-fuel) initiating the plume**

Parameter	Flux [g/s]	EF [g/kg-fuel]
NO <sub>x</sub>	1.91	54.6
SO <sub>2</sub>	0.75	21.4
PM <sub>10</sub>	0.07	2.0

The model simulated plume moving from the harbour area over the city. Emissions from the urban background were inserted both to the background and to the plume box, these emissions started prior to the plume emission simulating conditions of the estuary harbour of Göteborg. The plume simulations were performed for 2 different seasons, 1 for summer (June) and 1 for fall (October). The plumes were initiated every 2<sup>nd</sup> hour of the day. Sensitivity of the plume processes to concentration levels of the urban background were studied by changing the urban emissions by factors 0, 5 and 10. Concentrations of NO<sub>x</sub> and ozone in the background air mixed into the plume in different simulations are shown in Table 2. Sensitivity tests were performed for processes on primary PM emitted by ship on the secondary PM formation.

**Table 2. Mixing ratios of NO<sub>x</sub> and ozone (in ppb) in the background model box after time indicated in h in the left-most column. Average ± standard deviation for simulations with plume initiated in all day-hours is presented. Mixing ratios in model simulations with background NO<sub>x</sub> emissions corresponding to clean MBL (0x), with urban emissions corresponding to Göteborg (1x) and 5x and 10x increased Göteborg emissions (10x) are shown.**

NO <sub>x</sub> [ppb]		0 x	1 x	5 x	10x
1h	June	0.27 ± 0.13	1.63 ± 0.35	7.8 ± 0.62	15.8 ± 0.60
	October	1.67 ± 0.08	6.27 ± 0.09	24.5 ± 0.10	47.4 ± 0.16
2h	June	0.22 ± 0.12	1.40 ± 0.47	7.5 ± 0.81	15.8 ± 0.78
	October	1.46 ± 0.08	5.95 ± 0.20	24.6 ± 0.41	48.6 ± 0.35
4h	June	0.14 ± 0.09	1.12 ± 0.53	7.2 ± 1.17	16.2 ± 1.24
	October	1.11 ± 0.07	5.49 ± 0.46	25.0 ± 0.93	51.2 ± 0.71
8h	June	0.06 ± 0.03	0.79 ± 0.37	6.8 ± 1.17	17.1 ± 1.41
	October	0.65 ± 0.07	4.92 ± 0.66	26.1 ± 1.56	56.7 ± 1.24
Ozone [ppb]					
1h	June	42.1 ± 3.1	42.1 ± 3.9	36.3 ± 4.1	29.6 ± 4.4
	October	30.6 ± 2.1	26.5 ± 2.1	11.9 ± 4.2	3.5 ± 4.6
2h	June	41.6 ± 2.9	42.4 ± 4.5	35.6 ± 4.2	28.3 ± 4.1
	October	29.5 ± 2.1	25.1 ± 2.0	10.1 ± 4.4	3.2 ± 4.1
4h	June	40.3 ± 2.5	42.7 ± 5.0	34.4 ± 4.1	26.2 ± 3.3
	October	27.6 ± 2.3	22.7 ± 1.7	7.9 ± 4.3	2.6 ± 3.4
8h	June	37.8 ± 1.9	42.9 ± 4.2	32.4 ± 3.4	22.3 ± 2.1
	October	24.4 ± 2.5	18.9 ± 1.4	4.7 ± 4.6	2.0 ± 2.6

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 an Eulerian 3D model consisting of two modules, one meteorological and one dispersion model (Hurley et al, 2005). TAPM includes simplified chemistry of NO<sub>x</sub>, ozone titration, ozone formation driven by VOC reactivity, SO<sub>2</sub> oxidation and gas to particle partition of sulphate and nitrate. The N<sub>2</sub>O<sub>5</sub> formation and halogen chemistry are not included in the model. Also the gas-to particle partition of HNO<sub>3</sub> is parameterised and does not account for the aerosol composition explicitly. The chemistry of TAPM was tested against that of MOCCA in Haeger-Eugensson et al. (2010) and the comparison showed good agreement. The meteorological model was run in 3 nested scales, the largest covering Northern Europe, the second south-western part 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 those for 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. Differences in PM concentrations 1-2 gives secondary PM from shipping, difference 1-3 gives primary plus secondary PM from shipping.

### ***Results and discussion***

In a clean atmosphere oxidation of the emitted  $\text{SO}_2$  proceeds and in a photochemically active atmosphere sulphate becomes the dominant component of PM in a ship plume (Chen et al., 2005). Also  $\text{NO}_x$  can significantly contribute to the PM mass with nitrate, however, due to the volatility of  $\text{HNO}_3$  nitrate can be kept in particles only when these are not fully acidified. Our plume model simulations show that in a clean marine atmosphere (the  $0\times$  case) under summer daytime conditions 20 – 30% of the plume  $\text{SO}_2$  is lost after 4 h, ca. 12% loss is the  $\text{SO}_x$  deposition while  $\sim 10\text{--}20\%$  are oxidised to  $\text{H}_2\text{SO}_4$  which condensates both on sea salt and sulphate particles (Figure 1a). This corresponds to contribution to the PM mass with particulate  $\text{H}_2\text{SO}_4$   $\sim 6\text{--}12$  g/kg-fuel (EF for the primary PM is 2 g/kg-fuel). In October case only 0.4% of the plume  $\text{SO}_2$  contributes with the secondary sulphate to the PM mass in plume which corresponds to  $\text{EF}_{\text{PM}}$  0.2 g/kg-fuel (Figure 1b). Also nitrate formed from  $\text{NO}_x$  in the ship plume contributes to the PM as long as the sea-salt particles are alkaline enough to keep  $\text{HNO}_3$ . In our clean atmosphere case  $\sim 30\text{--}40\%$  of the plume  $\text{NO}_x$  was lost within 4 hours in daytime simulations with 8 – 12% deposited on sea and land surfaces and 20 – 27% contributing with nitrate to the sea-salt particles (Figure 1c). This corresponds to contribution to the PM mass with particulate  $\text{HNO}_3$   $\sim 15\text{--}20$  g/kg-fuel. Majority of the gas to particle exchange is through the dissolution of gaseous  $\text{HNO}_3$  in sea-salt, however, in dark hours significant part goes via heterogeneous reactions of  $\text{N}_2\text{O}_5$  with water and halogens present in aerosol particles (e.g. Moldanová et al., 2001) (Figure 1d). The heterogeneous reactions take 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  $\text{HNO}_3$ . In October case the nitrate partition into the PM from day-time oxidation of  $\text{NO}_2$  is relatively small (1.5% of  $\text{NO}_x$  emission), however, the night-time formation of nitrate through heterogeneous processes is still important (5.5%) (Figure 2). In the clean case the secondary sulphate and nitrate together contribute in summer day-time plume within 4 hours after the plume start with 19-29 g/kg fuel of secondary PM, the corresponding contribution in October case is 1.2 g/kg-fuel (EF for the primary PM is 2 g/kg-fuel).

Table 3 summarizes results of the plume model simulations for 4 different air pollution cases for 1, 2, 4 and 8 hours of plume processing. In clean and less polluted cases under summer conditions the secondary PM formed from ship-emitted  $\text{NO}_x$  and  $\text{SO}_2$  make a high contribution to the primary PM in the plume, already within 1 h travel distance from the source. In heavily polluted atmosphere and under winter conditions the contribution of secondary inorganic PM in ship plume is much lower, however, in many cases still comparable to the primary PM from shipping. The resulted contributions to secondary PM are presented first as particulate  $\text{H}_2\text{SO}_4$  in molar % of  $\text{SO}_2$  and particulate  $\text{HNO}_3$  in molar % of  $\text{NO}_x$  emission (100%  $\text{EF}(\text{SO}_2)$  21.4 g/kg-fuel corresponds to  $\text{EF}(\text{H}_2\text{SO}_4)$  59.1g/kg fuel, 100%  $\text{EF}(\text{NO}_x)$  54.6 g/kg-fuel corresponds to  $\text{EF}(\text{HNO}_3)$  74.7). The net secondary PM mass formed is also presented as wt% of the primary PM emission (4 right-most columns). The negative values of the contributions of nitrate to PM are mainly caused by the fact that the sulphate absorbed by acidified particles expels out  $\text{HNO}_3$ .

In some cases, however, also decrease in oxidation capacity in plume comparing to the plume background slows down formation of the secondary PM relatively to the plume background. This is clearly illustrated by the case  $5\times$  urban emissions of  $\text{NO}_x$ , October simulation where large negative values also for the net secondary PM formation occurred. In the  $10\times$  emission case, October, the net secondary PM formation is either positive or only slightly negative, this due to the fact that the oxidative capacity of the plume background is already low in this higher  $\text{NO}_x$  simulation and the additional  $\text{NO}_x$  has only a small effect. Figure 3 shows gas-to-particle exchange processes for N species in all simulations. These are masses accumulated over the plume volume from its start during the 1 hour. Situations when  $\text{HNO}_3$  scavenging on sea-salt particles is negative, heterogeneous  $\text{NO}_x$  reactions on sulphate is negative while the  $\text{HNO}_3$  scavenging on sulphate particles is positive (all comparing to the same processes in the plume background) are those with large decrease in oxidative capacity in the plume.



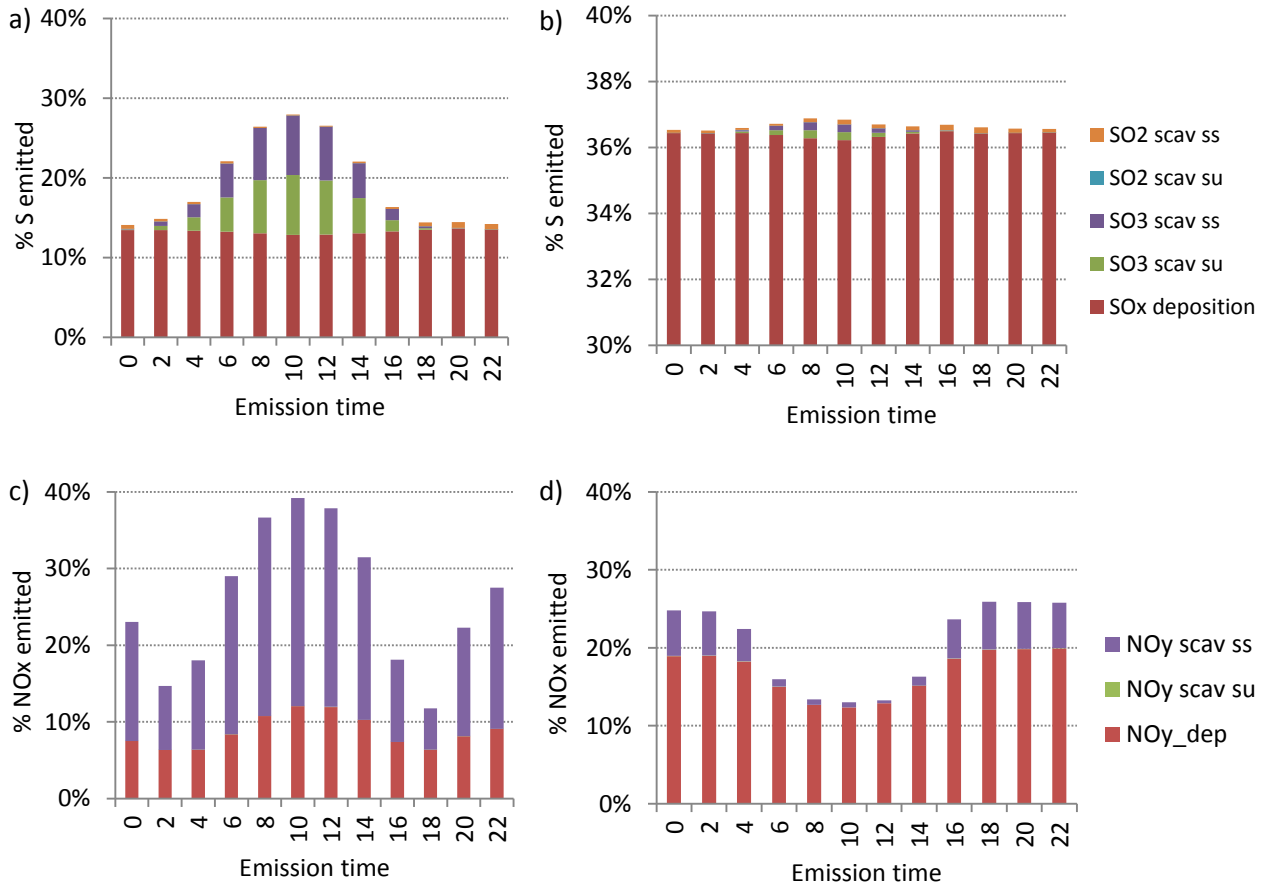


Figure 1. a, b – Part of SO<sub>2</sub> emission deposited and converted to PM-bound H<sub>2</sub>SO<sub>4</sub>\*nH<sub>2</sub>O within 4 hours from the plume start (a – June, b – October, observe that the y-axes scale for October starts at 30%) and c, d – part of NO<sub>x</sub> emission deposited as NO<sub>y</sub> and converted to PM-bound NO<sub>y</sub> within 4 hours from the plume start (c – June, d – October). The ship plumes are emitted in time of the day as indicated on the x-axes. Legend: ss is contribution do sea-salt particles, su to sulphate particles, NO<sub>y</sub> to ss and su assumes both scavenging and heterogeneous reactions.

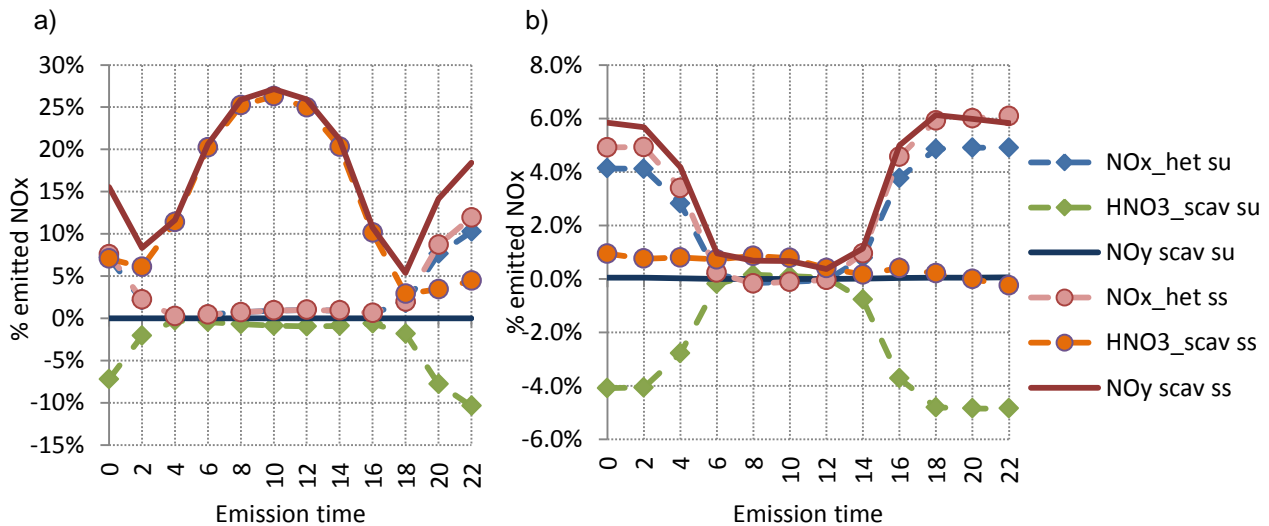


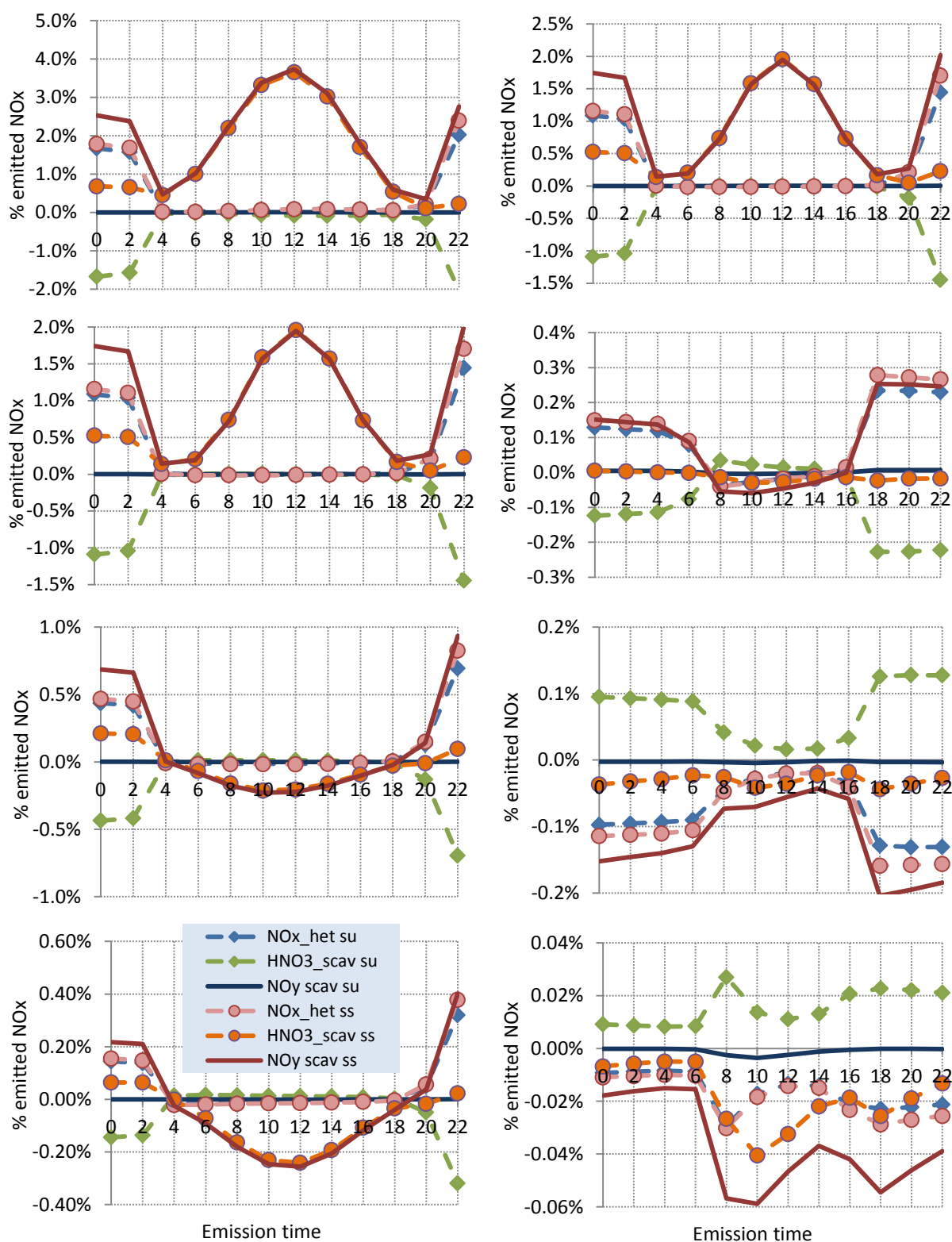
Figure 2. Difference between net gas-to particle conversion of HNO<sub>3</sub> through different processes in plume and in a same volume of the background air after 4 h of simulation in clean-air simulations (0x) starting the plume at time indicated on x-axes. a – June simulation, b – October simulation. ss - exchange on sea-salt particles, su – exchange on sulphate particles. NO<sub>y</sub> scav ss and su: scavenging of gasepus NO<sub>y</sub> by sea-sat and sulphate particles, respectively. HNO<sub>3</sub>\_scav ss and su: scavenging of gaseous HNO<sub>3</sub> by the respective particle types. NO<sub>x</sub>\_het su and ss: Heterogeneous reactions. Negative values mean loss of PM mass to gas phase.

**Table 3. Simulated molar parts of emissions of SO<sub>2</sub> and NO<sub>x</sub> in a ship-stack contributing to the secondary PM (columns with headings SO<sub>2</sub> and NO<sub>2</sub>). The ‘Background NO<sub>x</sub> emissions’ refers to the multiplier of the NO<sub>x</sub> emissions in background, the corresponding NO<sub>x</sub> levels reached are shown in Table 2. The negative values of N contributing to PM are cases when HNO<sub>3</sub> is expelled from the particles. Columns with heading ‘Net PMsec/PMprim is a sum of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub><sup>2</sup>·nH<sub>2</sub>O contributions to the secondary PM mass expressed as % of emission of primary PM mass.**

June	S	N				Net PMsec/PMprim							
		1h	2h	4h	8h	1h	2h	4h	8h				
Bgnd 00	day	1.23%	4.47%	10.84%	14.67%	2.85%	10.09%	22.19%	31.18%	143.07%	509.39%	1150.21%	1599.75%
	night	0.21%	0.45%	1.45%	7.17%	1.70%	5.30%	13.62%	27.12%	69.60%	211.61%	552.47%	1226.40%
	average	0.66%	2.24%	5.93%	10.90%	2.03%	6.97%	17.09%	29.09%	95.43%	326.85%	814.52%	1410.10%
Bgnd 01	day	0.83%	2.62%	7.99%	13.05%	1.31%	4.40%	12.61%	20.51%	73.49%	242.07%	707.49%	1152.54%
	night	0.19%	0.38%	0.79%	4.76%	1.17%	3.74%	8.56%	15.56%	49.28%	151.06%	343.68%	722.69%
	average	0.47%	1.36%	4.06%	9.03%	1.06%	3.49%	9.67%	18.10%	53.63%	170.56%	481.63%	943.72%
Bgnd 05	day	0.58%	1.32%	2.64%	4.03%	-0.18%	-0.50%	-1.11%	-0.78%	10.14%	20.20%	36.25%	89.69%
	night	0.16%	0.32%	0.59%	1.63%	0.49%	1.76%	3.66%	3.82%	22.94%	75.50%	154.27%	191.21%
	average	0.35%	0.77%	1.54%	2.83%	0.12%	0.50%	1.12%	1.54%	14.60%	41.24%	87.07%	140.87%
Bgnd 10	day	0.41%	0.84%	1.50%	2.09%	-0.20%	-0.47%	-0.91%	-1.09%	4.65%	7.17%	10.21%	20.94%
	night	0.14%	0.28%	0.47%	1.02%	0.17%	0.51%	0.91%	0.57%	10.53%	27.39%	47.91%	51.22%
	average	0.27%	0.53%	0.94%	1.55%	-0.02%	-0.01%	-0.04%	-0.26%	6.88%	15.08%	26.36%	36.01%

Table 3. Continued

October		S				N				Net PMsec/PMprim			
		1h	2h	4h	8h	1h	2h	4h	8h	1h	2h	4h	8h
Bgnd 00	day	0.11%	0.22%	0.40%	0.56%	0.01%	0.29%	1.58%	5.55%	3.64%	17.44%	70.95%	223.9%
	night	0.03%	0.06%	0.12%	0.53%	0.42%	2.16%	5.55%	9.15%	16.45%	82.55%	211.11%	357.9%
	average	0.06%	0.14%	0.26%	0.57%	0.24%	1.26%	3.56%	7.36%	11.00%	51.17%	141.07%	292.3%
Bgnd 01	day	0.10%	0.21%	0.36%	0.47%	-0.04%	0.02%	0.48%	1.86%	1.46%	6.90%	28.68%	83.6%
	night	0.02%	0.05%	0.10%	0.30%	0.19%	1.07%	2.84%	3.89%	7.85%	41.74%	109.15%	154.4%
	average	0.06%	0.12%	0.23%	0.40%	0.09%	0.57%	1.65%	2.78%	5.15%	25.01%	68.57%	115.9%
Bgnd 05	day	0.08%	0.15%	0.24%	0.29%	-0.06%	-0.24%	-0.84%	-1.98%	0.10%	-4.45%	-24.41%	-65.3%
	night	0.02%	0.03%	0.05%	0.11%	-0.17%	-0.92%	-2.67%	-3.85%	-5.73%	-33.39%	-98.43%	-140.9%
	average	0.05%	0.09%	0.15%	0.21%	-0.12%	-0.60%	-1.78%	-2.94%	-3.24%	-19.93%	-62.31%	-103.9%
Bgnd 10	day	0.07%	0.13%	0.19%	0.24%	-0.05%	-0.08%	-0.11%	-0.13%	0.20%	0.61%	1.51%	2.20%
	night	0.02%	0.03%	0.05%	0.09%	-0.03%	-0.03%	-0.04%	-0.06%	-0.50%	-0.32%	-0.15%	0.15%
	average	0.04%	0.08%	0.12%	0.17%	-0.04%	-0.06%	-0.08%	-0.10%	-0.18%	0.09%	0.68%	1.34%



**Figure 3.** Difference between net gas-to particle partitioning of nitrate through different processes in plume and in a same volume of the background air after 1 h of simulation in 0x (row 1), 1x (row 2), 5x (row 3) and 10x (row 4) Göteborg city emissions simulations starting the plume at time indicated on x-axes in June (column 1) and in October (column 2). ss - exchange on sea-salt particles, su – exchange on sulphate particles. NO<sub>y</sub> scav ss and su: scavenging of gaseous NO<sub>y</sub> by sea-salt and sulphate particles, respectively. HNO<sub>3</sub>\_scav ss and su: scavenging of gaseous HNO<sub>3</sub> by the respective particle types. NO<sub>x</sub>\_het su and ss: Heterogeneous reactions. Negative values mean loss of PM mass to gas phase.

Sensitivity of the secondary PM formation to the processes on the emitted PM were investigated by using 2 different models of the ship PM (sulphate coated soot and pure soot) and 1 simulation not including any primary PM in the plume emissions. Table 4 summarises results of these simulations. We can see that the secondary PM formation takes to large extent place on the background PM and only small part is due to the processes on ship-emitted PM (compare Table 4 with right-most columns of Table 3). This is not surprising as the sulphate particles do not affect oxidation and neither accommodate nitrate and the modelled soot processes are slow. These 2 models are, however, very simple, processes are not well known and more research in this area is needed.

**Table 4. Result of the sensitivity simulations for processes on primary ship-emitted PM in plume expressed as % of primary PM emission, all simulations use the  $\times 1$  Göteborgs emission case. Soot – no-PMprim is difference between simulation with ship-emitted PM as pure soot and simulation without ship-emitted PM, Sulphate – no-PMprim is difference between simulation with ship-emitted PM as  $H_2SO_4$ -coated soot and simulation without ship-emitted PM.**

	Net PMsec /PMprim							
	June				October			
	1h	2h	4h	8h	1h	2h	4h	8h
<b>Soot – no-PMprim</b>								
day	-0.30%	-1.44%	-5.54%	-3.29%	-0.06%	-0.003%	1.05%	8.45%
night	0.29%	1.78%	5.87%	3.18%	-0.45%	-0.014%	3.19%	8.81%
average	-0.02%	0.06%	-0.03%	2.05%	-0.28%	-0.023%	2.10%	8.47%
<b>Sulphate – no-PMprim</b>								
day	4.8%	9.7%	15.7%	18.1%	1.6%	3.7%	6.3%	10.0%
night	4.1%	10.0%	18.7%	27.8%	2.0%	5.6%	9.6%	17.7%
average	4.3%	9.6%	17.0%	21.9%	1.8%	4.9%	8.2%	13.6%

Effect of the secondary PM from shipping on PM concentrations in a more quantitative manner was tested with the TAPM model. TAPM does not employ an explicit aerosol chemistry which means that the nitrate contribution from shipping to the PM is underestimated when significant quantities of sea-salt are present, especially at nighttime. However, effects of the formation of the secondary PM from emissions from ships operating in the Göteborg harbour on shipping-related PM concentrations were found. Figure 4 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 contribution of secondary PM is almost as high as that of the primary PM.

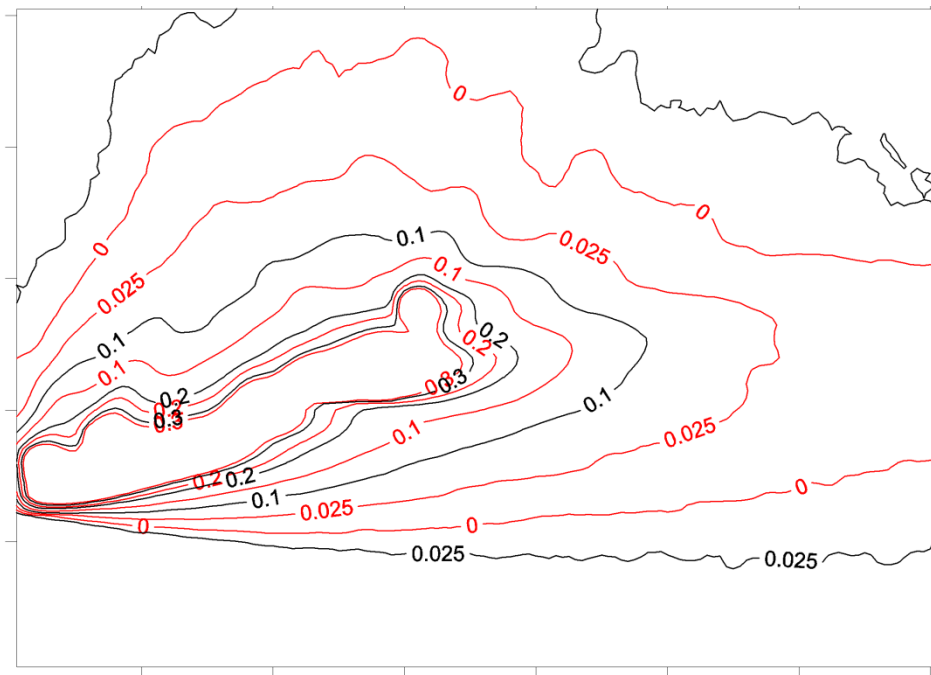


Figure 4. Contribution of primary PM (red) and primary and secondary PM (black) from shipping emissions to the PM concentrations in Göteborg located in the middle part of western half of the depicted area. The numbers are  $\mu\text{g}/\text{m}^3$  and the scale on axes is 1 km. The highest shipping PM contributions in the harbour are  $10 \mu\text{g}/\text{m}^3$  (not shown).

### Conclusions

The model simulations have shown that secondary sulphate and nitrate from  $\text{SO}_2$  and  $\text{NO}_x$  emissions from shipping can significantly contribute 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 from shipping. Also in the polluted environment in summer conditions or under low photochemistry at moderately polluted conditions this contribution can be in similar order of magnitude as contribution of the primary PM. Contribution of PM from shipping to the highest PM concentrations at street level in cities is, however, relatively small regardless if the secondary PM is considered or not. Instead, the contribution of shipping to PM levels may be rather significant in the urban background and here the secondary PM should be considered.

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