

Final author comments for manuscript acp-2019-1016

We want to thank the editor for considering our manuscript for review and publication. We also thank both referees for their comprehensive and valuable comments to our manuscript. We think that the changes implemented after careful consideration of the comments have improved the content and clarity of our manuscript.

This document contains the authors' response to the comments of both 'referee 1' and 'referee 2'. The comments are structured into three categories; 1) major/general, 2) minor/specific, and 3) technical, based on the specifications of the referees, or the judgement of the authors. All comments are followed first by a general author's response, and then by specifications about the changes done to the manuscript. New text which is added to the manuscript is marked in *italic*, and all changes are shown in the new manuscript document with "track changes".

Final author comment for Referee 1

1. Major/general comments:

Referee comment 1.1.

The Introduction is very brief and does not give a comprehensive review of literature on the topic of measurements and chemical characterization of ship emissions, see my specific points (2+3) below.

Author's response 1.1.

We agree that the introduction could be extended slightly to include examples from the literature on chemical characterization of ship plumes, and to guide the interested reader to further articles. We have added new text to the introduction, which gives examples from the literature of ship PM emission factors and chemical characterization. In order to make the introduction logical, some additional changes of the order of the paragraphs were made.

Author's changes in manuscript 1.1.

This is the new second paragraph in the section 1 Introduction:

"Ship emission properties, such as particle number and mass concentration, particle size, and chemical composition, depend on a variety of parameters and ships make up a heterogeneous mix of emission sources. Most particles emitted from ships are in the sub-micrometre range, typically with a diameter below 100 nm [Lack *et al.*, 2009]. Studies have shown a decrease in mean particle diameter when switching to a lower fuel sulphur content [Betha *et al.*, 2017; Zetterdahl *et al.*, 2016] as well as a decrease in emitted particulate matter (PM) [Lack *et al.*, 2009; Diesch *et al.*, 2013; Mueller *et al.*, 2015; Buffaloe *et al.*, 2014]. *Studies of chemical composition of ship PM have shown that the mass is typically dominated by organic matter, sulphate, and black carbon. Zetterdahl et al. [2016] measured PM*

35 emission factors on-board a ship in the Baltic Sea, running on heavy fuel oil (HFO) and low-sulphur
residual marine fuel oil, respectively. The total and non-volatile PM emission factors were
0.17 ± 0.03 g (kg fuel)⁻¹ and 0.12 ± 0.03 g (kg fuel)⁻¹, respectively for HFO, and 0.06 ± 0.03 g (kg fuel)⁻¹
and 0.04 ± 0.02 g (kg fuel)⁻¹, respectively for the low-sulphur fuel. The black carbon emission factor
40 ranged from 0.027 to 0.087 g (kg fuel)⁻¹, depending on engine load, and was slightly higher for HFO.
Lack et al. [2009] reported emission factors for 43 ship plumes based on ambient measurements using
aerosol mass spectrometry (AMS) for chemically resolved PM. They observed an average PM₁ emission
factor of 3.32 ± 4.04 g (kg fuel)⁻¹, and specifically 1.21 ± 1.50 g (kg fuel)⁻¹ (36 %) was sulphate, 1.26 ±
0.96 g (kg fuel)⁻¹ (38 %) was organic matter, and 0.85 ± 0.76 g (kg fuel)⁻¹ (26 %) was black carbon.
Sulphate and organic matter were linearly correlated with fuel sulphur content. In a study by Cappa et
45 al. [2014], the ship plume PM was varying with ship speed, with an EF_{PM1} ranging from 0.09 (slow
speed, 2.9 knots) to 1.5 g (kg fuel)⁻¹ (high speed, 12 knots). For this ship, running on a low-sulphur
marine gas oil, the PM sulphate content was below the detection limit of the AMS, while the primary
organic matter (pOM) made up 53 ± 14 % of the total mass (EF_{pOM} 0.39 ± 0.44 g (kg fuel)⁻¹), and BC
made up 47 ± 14 %. Similarly, Shen and Li [2019] also found negligible sulphate emissions from marine
50 HFO as fuel resulted in 75 % sulphate mass (including bound water), 21 % organic carbon, and the
rest was elemental carbon and ash. Plume studies of 139 ships in a 1 % sulphur emission control area,
presented in [Diesch et al., 2013], showed an average PM₁ emission factor of 2.4 ± 1.8 g (kg fuel)⁻¹,
and specifically 0.54 ± 0.46 g (kg fuel)⁻¹ (23 %) was sulphate and 1.8 ± 1.7 g (kg fuel)⁻¹ (75 %) was
organic matter. In a recent on-board study by Huang et al. [2018], it was also found that organic matter
55 was the most abundant PM fraction (45-65 %), while sulphate content was low compared to the values
listed above (2-15 %). The elemental carbon (or black carbon) PM mass fraction was low (1-6 %) for
the main engine used for propulsion, while higher (20 %) for the auxiliary engine used to generate
electricity. The PM composition, including other species than just sulphate, depend partly on fuel
sulphur content [Lack and Corbett, 2012]. There are several other parameters which affect the absolute
60 emission of PM as well as the particle composition, such as fuel type, operation conditions, engine load,
engine properties, and maintenance. Ship exhaust also contains elevated levels of nitrogen oxides (NO_x,
including NO₂ and NO), sulphur dioxide (SO₂), carbon monoxide (CO), carbon dioxide (CO₂), and
volatile organic compounds (VOCs) [Sinha et al., 2003; Chen et al., 2005; Alföldy et al., 2013;
Moldanová et al., 2009; Huang et al., 2018; Cooper, 2001].”

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Referee comment 1.2.

The study has been performed in the context of the new sulphur regulation that requires fuel sulphur content equal to or less than 0.1% by mass in 2015. It should be made clearer in the discussion of the results how the paper complements previous measurements or modelling of the ship contribution to ambient air concentrations before/after the new sulphur regulation.

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The new regulation has led to changes in the type of fuel used or to installation of scrubbers: I think the Introduction should inform more about the changes of the ship operation (fuels, engine operation, scrubbers, etc.) and their expected impact on exhaust composition, in response to the new sulfur regulation. The paper should also discuss whether the finding of relatively low contribution from shipping to coastal particle phase concentrations might suggest that the taken measures have not only affected the sulphur components but also other constituents of the ship exhaust.

75

Author's response 1.2.

The specific explanation on how we complement previous studies is given at the end of the introduction:

80 “The results complement previous studies in two ways. Firstly, due to the new measurement location at
an intermediate distance from the shipping lane. Secondly, due to the measurements being performed
after the recent fuel sulphur regulations within SECAs, which was introduced on January 1, 2015. The
estimation of how ship traffic along a major route contributes to the coastal particle concentrations can
contribute to the development of aerosol dynamic process models, regional aerosol particle models,
85 health assessment models and epidemiological studies.”

Regarding the specific changes in ship operation and fuel use in the Baltic region, we have added values
from the literature, which were the most relevant we could find, on e.g. fuel use in the North and Baltic
Sea during 2011, and information on scrubber use before and after the 2015 SECA. Additionally, our
observed AAE of 1 is in line with emissions from distillate fuels, and the conclusion from this
90 observation has been made clearer as well.

Regarding general impact of fuel change, we have described this in more detail in our new revised
version of the introduction section (see Author's response 1.1. above). The discussion has also been
extended to include more explanations of the observed low PM, including the effect of fuel sulphur
reductions (see details in comment 1.1 by Referee 2).

95 Author's changes in manuscript 1.2.

We have revised the following parts in the manuscript section 3.1 Plume identification and general
characteristics:

100 “Large variations between individual ships was also shown by Jonsson et al. [2011], at a measurement
distance of 0.5-1 km from the ships. In this study, there was no data *currently* available on the specific
fuel used by each ship *or in the Baltic Sea in general. However, according to Jonson et al. [2015], the
fuel distribution in the Baltic and North Sea in 2011 was around 74 % residual (e.g. HFO) and 26 %
was distillate fuels (MDO, MGO). Further, Johansson and Jalkanen [2016] reported a 88 % decrease
in SO_x and 36 % decrease in PM_{2.5} emissions from the year 2014 to 2015 in the Baltic Sea, based on
AIS data and emission modelling. Strong decreases in SO_x and PM_{2.5} due to SECA implementations
105 have also been predicted and reported in e.g. [Kalli et al., 2013] and Jonson et al. [2015]. Regarding
the use scrubbers to reduce airborne sulphur emissions, in the paper by Jonson et al. [2019] it is stated
that there was an increase in the number of scrubbers used globally, from 77 vessels in 2014 to 155 in
2016. Out of these, 85 vessels with scrubbers were operating in the Baltic Sea area in 2016. This is a
small fraction of the > 20 000 ships operating in the region [Johansson and Jalkanen, 2016].*

110 The fact that Falsterbo is often not affected by a large particle volume (or mass) contribution from ships
could potentially be explained by the recently implemented SECA regulations, making ship owners
improving or switching to other fuels. *The effect of sulphur regulations on the chemical composition is
discussed further in Section 3.4.*”

115 “During the years 2015 and 2016, the compliance level was 92 %–94 % in the region around Denmark.
*Also Jonson et al. [2019] have shown that there is a strong indication that ships are complying, based
on emission modelling before and after the 2015 SECA regulation.*”

We have added the following to the manuscript section 3.4. Contribution to BC and chemical
composition:

120 “Previous studies have shown an increase in light absorption at shorter wavelengths in plumes,
indicating a significant fraction of brown carbon (BrC) [Yu et al., 2018; Corbin et al., 2018; Corbin et
al., 2019]. This was not seen in our study in the Baltic Sea SECA, which is in line with Corbin et al.
[2018] who showed that burning of heavy fuel oil resulted in both BC and BrC, while marine gas oil or
diesel fuel resulted in negligible BrC fractions and an AAE close to 1, *suggesting that distillate fuel is
dominating in our sample.*”

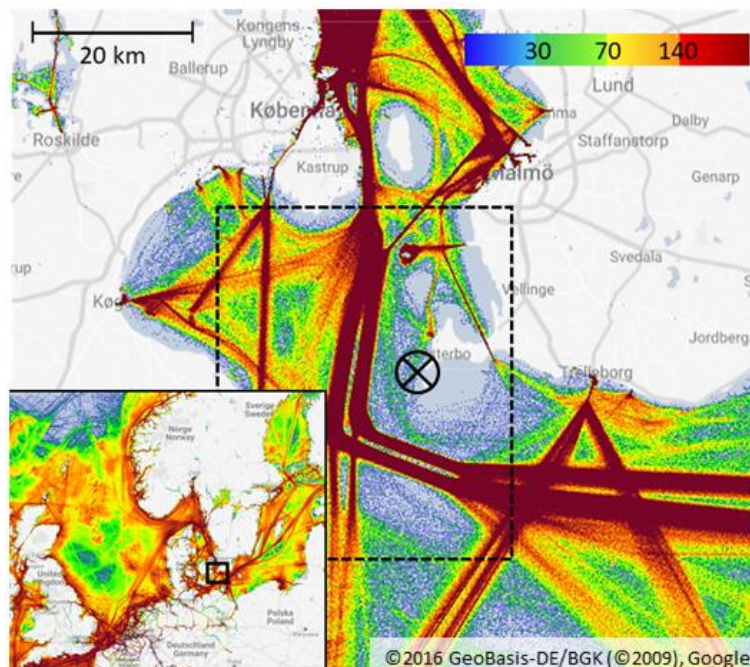
125

Referee comment 1.3.

The distance of 10 km, which corresponds approximately to a plume ageing time of 30 min, seems
long, even if it is considerable shorter than in a previous similar study by Kivekäs et al. (2014). At
this distance, the particle number concentrations in the plume are already approaching the
130 particle number concentrations in background air. Due to this distance, there is a chance that
ship plumes from somewhat further away, like 20 km, are already further diluted and might
contribute either to the background or to the plume signal of a “detected” ship. It should be
explained how the method deals with other ships in the source corridor and the possibility of
crossing or coinciding/indistinguishable ship plumes.

135 Author’s response 1.3.

We understand the referee’s concern about plumes from longer distances not being visible at the
measurement site. However, we found that almost all plumes (>95 %) were detectable with the method
presented in the manuscript. We base this on the AIS data, which is obtained from the geographical area
shown in the picture below (Fig. AC1).



140

Figure AC1. Location of the measurement station (circle with cross) at the Falsterbo peninsula
together with ship traffic density (www.marinetraffic.com, 2016). Dashed square shows the area in
which AIS positions are considered for ship identification. (From [Ausmeel et al., 2019])

145 That is, we could identify a peak in particle number concentration (PN) for most ships passing this
geographical area transmitting an AIS signal. This area includes the entire shipping lane described in
the manuscript, including the fraction of ships sailing the furthest away from the coastline. In our
previous paper [Ausmeel *et al.*, 2019], this method is validated. The Fig. AC2 below shows a typical
time series of particle number concentration and identified ship plumes at the Falsterbo field site. This
figure is representative for the entire measurement campaigns. We have added a sentence to the
150 manuscript, describing the success rate of the method in order to avoid misunderstandings or similar
concerns from future readers.

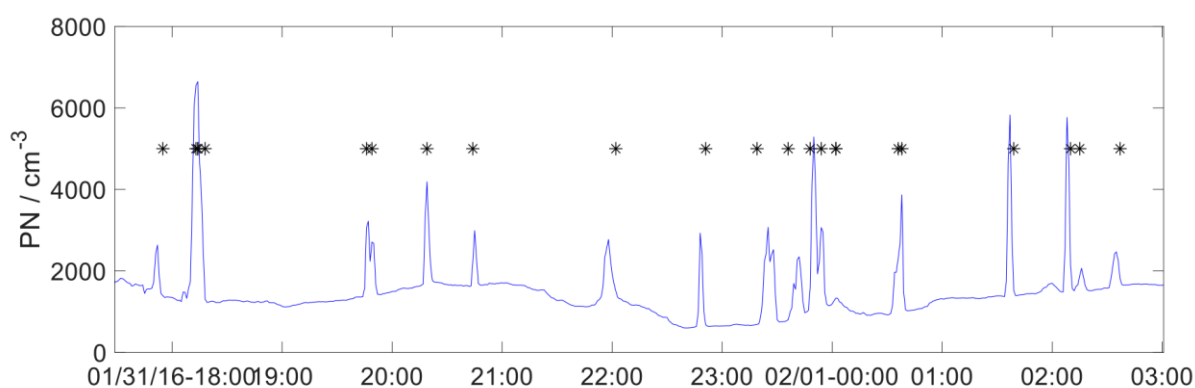


Figure AC2. Example of time series from total particle number concentration and the expected plume passages based on AIS and wind data (stars). (From [Ausmeel *et al.*, 2019])

155 It is still a valid and important comment that our study does indeed only deal with ships from the nearby
region and not from much further away, e.g. from the Baltic or North Sea. We raise this point on several
occasions; in the description of the method, in the discussion, and in the conclusions, specifically on p.
3-4, line 121-124, on p. 6, line 230, on p. 7, line 275, and on p. 10, line 388-390 in the first version of
the manuscript. In order to make this unambiguous throughout the manuscript, we have clarified this
160 also in the abstract and in the introduction.

Regarding crossing/coinciding plumes, it is described in the companion paper [Ausmeel *et al.*, 2019]
that we ignore plumes that are close to each other in time (based on PN and/or AIS data) in order to
keep the individual assessment of the plume contribution. Hence, this is not an issue for the
interpretation of the results. However, this is not explicitly mentioned in the summary of the method in
165 the current paper. We realize that this is a potentially important aspect for the interpretation of the
results, especially in the ways described by the referee. We have made this clearer in the Materials and
methods section.

Author's changes in manuscript 1.3.

The following two sentences have been changed in the manuscript abstract, and section 1 Introduction:

170 “The average emission contribution of the shipping *lane* was 29 ± 13 and 37 ± 20 ng m^{-3} to $\text{PM}_{0.5}$, 18 ± 8
and 34 ± 19 ng m^{-3} to $\text{PM}_{0.15}$, and 1.21 ± 0.57 and 1.11 ± 0.61 $\mu\text{g m}^{-3}$ to NO_2 , during winter and summer
respectively.”

175 “In the current paper however, we report the contribution from a *major shipping lane* to local particle
mass concentrations and chemical composition (organics, sulphate, black carbon), and NO_2 , as well as
the effects of additional aging simulated with an oxidation flow reactor.”

The following two sentences have been added to the manuscript section 2 Materials and methods:

“In order to assess individual ship plumes, no plumes that were overlapping or close to each other in time (less than five minutes) were included in the analysis.”

180 *“The expected plume passage based on AIS and wind data and the visible plumes in the particle counter agreed excellently, and a large fraction (>95 %) of the plumes (including all plume events, not only the plumes finally used for analysis for which 100 % were confirmed with AIS) were detectable as a distinct increase compared to background particle concentrations.”*

Referee comment 1.4.

185 **The method relies entirely on the accuracy and time resolution of the N measurements of the SMPS or particle counter. Kivekäs et al. (2014) apply a criterion for plume detection that the excess N has to be larger than 500 cm⁻³ for detection of a ship plume (one hour plume ageing). Why is no such criterion used here? Meandering of the plume would also cause a fluctuation of N measured, which may lead to obscured plume detection. How did you deal with rapid changes of**
190 **the background N?**

Author’s response 1.4.

In Kivekäs et al. (2014), the minimum plume PN criterion is used to include all clear ship plumes and to exclude peaks due to other variability in the data. Due to the high time resolution (5 or 30 seconds) of the PN measurements in our measurements in Falsterbo compared to Kivekäs et al. (5 minutes), we
195 did not experience any issue with potentially including other variability in the data than ship plumes. The background was never changing rapidly compared to the duration of the ship plumes (average 10 minutes). Additionally, the availability of AIS data in our study made the confirmation of the ship plumes unambiguous.

200 With meandering of the plume, we assume that it refers to the plume potentially fluctuating in strength or crossing the measurement site several times due to changing wind directions. However, this has not been seen at our site. Due to the geographical and meteorological conditions at the field site, we do also not expect such meandering transport of the ship plumes to any large extent during westerly winds which are associated with low pressure weather systems and higher wind speeds. These issues regarding accuracy and success of the PN and AIS data to detect and quantify plume contribution has already
205 been described in Author’s response 1.3, and also in detail in the companion paper Ausmeel et al. (2019).

Author’s changes in manuscript 1.4.

We have added the following parenthesis to the manuscript, section 2 Materials and methods:

210 The background level in this analysis was defined as the baseline concentration from which the identified plumes can be distinguished (*the background concentration was always relatively stable during onshore wind, see Fig. 2, and hence the background subtraction was straightforward*).

Referee comment 1.5.

215 **The study does not discuss the impact of meteorological conditions and atmospheric stability on the plume detection. A higher and well-mixed boundary layer allows more vertical mixing of the plume and would lead to lower particle numbers in the plume that can be measured at the site. There are also some effects due to the location of the measurement site at the interface between the marine boundary layer and the boundary layer over land. Sensible heat flux associated with solar heating of the land surface can lead to the growth of a thermal internal boundary layer (ITBL) at the shoreline. Stable onshore wind flow advected over a cold water surface during the daytime, when passing the shoreline can be eroded by the ITBL, that can intercept an elevated ship plume and fumigate it rapidly to the ground (Lyons and Cole, 1973; van Dop et al., 1979; Hanna et al., 1984; Nazir et al., 2005).**

Author's response 1.5.

225 The referee raises a relevant point regarding the impact of local meteorology when evaluating ambient measurements. Indeed, the boundary layer height (BLH) affects the vertical mixing and consequently the plume dilution. But since our aim is to quantify the contribution of ship plumes to the ambient air pollution, the different meteorological conditions will simply represent different realistic scenarios in the ambient air at Falsterbo. We are interested in presenting the absolute contribution at the coastal field site, and do not attempt to say anything about the emission concentration at the ship plume stack. We have highlighted this in the manuscript to avoid misunderstandings.

235 However, as the referee also seems to suggest, our results could still be affected if the dilution is so strong that the plumes are not visible to our instrumentation during certain meteorological conditions. After the referee's comment, we investigated the BLH at the field site during the measurement campaigns in more detail, using BLH values from HYSPLIT data. The BLH varied between 70 and 1400 m (average including standard deviation was 570 ± 290 m) in winter, between just a few and 1600 m (average including standard deviation was 490 ± 320 m) in summer. The BLH was indeed typically anti-correlated with aerosol concentrations on a longer time scale (hours to days). It could then be expected that the plume concentration is affected to some extent by the BLH as well. However, the BLH does not seem to affect our ability to detect plumes, but almost all (>95 %) expected plume passages based on AIS data are observed by the particle counter, also during periods with high BLH (see also Author's comment 1.3). Additionally, we investigated the particle number (PN) and volume/mass (PM) concentration of the quantified plumes as a function of the boundary layer height, see figure AC3. In this figure, the BHL does not appear to be correlated with plume concentrations, but both high and low concentrations are observed during both high and low BLH. The result is inconclusive and should need even more data to be able to draw any conclusions.

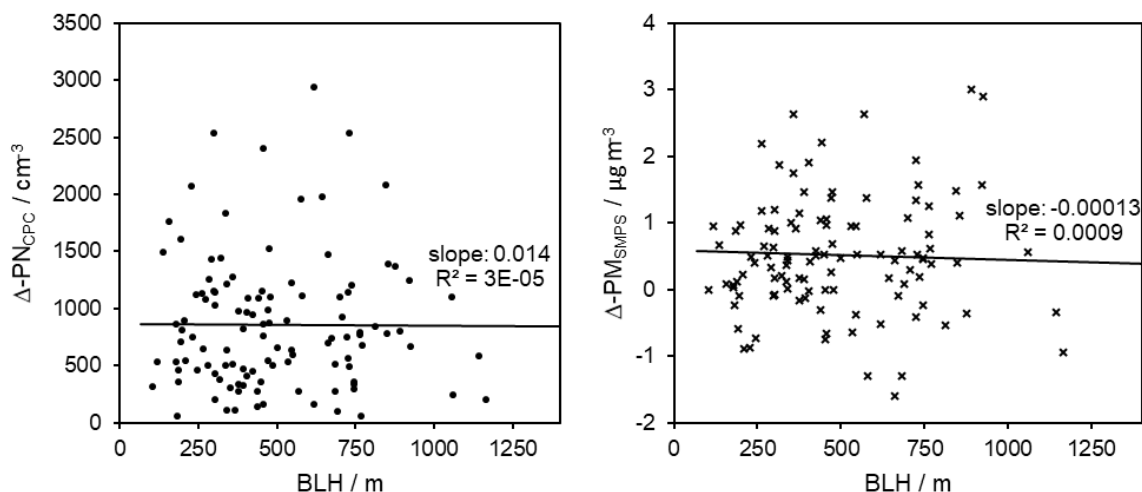


Figure AC3. Ship plume concentration (background subtracted) versus boundary layer height obtained from HYSPLIT. Left: Particle number concentration measured by CPC (circles). Right: calculated particle mass based on SMPS particle volume size distributions, assuming a particle density of 1.5 g cm^{-3} (crosses). The lines represent least square linear fits to the data.

Regarding the effect of ITBL, we do not think this is an issue at this particular field site. In the references suggested by the referee, the geography is different from the case in our manuscript. The references all describe a situation which can occur at a rather long coast line, separating a large body of water and a large body of land. The measurement site in our manuscript is located at the tip of a peninsula, which is a relatively small land mass surrounded by water (see Figure AC1, or the map in the response to referee 2). Hence, we assess the boundary layer over the Baltic Strait and the shipping lane not to be very different from the boundary layer over the field site. Still, such meteorological effects are indeed something to consider when doing other coastal measurements. Therefore, we have added an additional description of the field site and commented on the potential effects of an ITBL in order to make this clearer. Additionally, a map of the nearby region has been added to the manuscript, further helping the reader to interpret the effects of the boundary layer over sea versus land (see Author's changes in manuscript 2.1, in response to referee 2).

Author's changes in manuscript 1.5.

The following text has been added to the manuscript section 2 Materials and methods:

“When performing measurements along a coastline, the interface between atmospheric boundary layers over land and sea can cause a build-up of a thermal internal boundary layer at the shoreline. This has been described by e.g. Hanna et al. [1984] and is important to consider when doing plume measurements. However, due to the geographical surroundings at our field site, we do not expect this effect to be strong or exist at all, since the peninsula is a small land mass almost surrounded by water. The boundary layer height is likely a parameter which affects the dilution of the plumes and the background air and thereby the plume concentration. However, it seemed that boundary layer height did not affect the plume concentration in a systematic and reproducible way in Falsterbo as deduced using Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) [Stein et al., 2016] with meteorological data from Global Data Assimilation System (GDAS). Since this study aims at describing the ship emission contribution to inland aerosol burden and not the concentrations at the exhaust stack, the effects of boundary layer height has not been pursued any further in this paper.”

Referee comment 1.6.

280 **Aromatic VOC might also be good tracers for the ship plume. Toluene levels measured by PTR-TOF have been used to detect contamination by ship exhaust in a ship-borne measurement campaign (Chang et al., 2011). Were VOC measured at the site or is it considered to complement future campaigns with PTR?**

Author's response 1.6.

285 The referee raises a good suggestion for future ship emission studies, but unfortunately our campaigns did not include VOC measurements.

Author's changes in manuscript 1.6.

The following sentence has been added to the manuscript, section 3.5 Simulation of atmospheric processing:

290 No SO₂ data is available from the same period. *In future ship emission campaigns, both SO₂ and VOC measurements would be useful for evaluation secondary PM formation and as tracers for ship emissions in general.*

Referee comment 1.7.

295 **Murphy et al. (2009) reported a study with simultaneous shipboard and airborne measurements of the chemical composition and water-uptake of particulate ship emissions. One important finding of that study was that the in-plume organic-to-sulfate mass ratio did not change with increased plume ageing, indicating that the ship-originated particulate phase is not volatile enough to repartition back to the gas phase as the plume dilutes further. Please provide OC:SO₄dry ratios measured in the ship plumes at Falsterbo (and compare to values in the literature) as they could be helpful in deriving emission factors of OC for the ship fleet in the Baltic Sea. The ratio could also give valuable information about the ships with high sulfate formation in the OFR, obviously not complying with the new sulfur regulation.**

300

Author's response 1.7.

305 Out of the 33 plumes which were chemically resolved with AMS, there were 14 plumes with zero or close to zero ($< 0.01 \mu\text{g m}^{-3}$) sulphate content and two plumes with zero or close to zero organics. For the 17 plumes which contained both a sulphate and an organic fraction, the average OC:SO₄ (± 1 stdv) ratio was 2.3 ± 3.2 . We have added this value to the manuscript, together with a comparison with literature values.

Author's changes in manuscript 1.7.

310 The following text has been added to the manuscript section 3.4 Contribution to BC and chemical composition:

315 "For individual ships, there was a high variability in these fractions, but there seems to be a higher fraction of organics in the summer based on the 33 observed plumes. *Out of the 33 plumes which were chemically resolved with AMS, there were 14 plumes with zero or close to zero ($< 0.01 \mu\text{g m}^{-3}$) sulphate content and two plumes with zero or close to zero organics. The organic matter fraction (Org, OM) was translated to organic carbon (OC) using a conversion factor of 1.2, which is given by Canagaratna et al. [2015] for hydrocarbon-like organic aerosol (HOA). For the 17 plumes which contained both a*

320 sulphate and an organic fraction, the average $OC:SO_4 (\pm 1 \text{ stdv})$ ratio was 2.3 ± 3.2 . Studies of single
ships or test-bed engines show largely varying organics to sulphate ratios. In the study by Murphy et
al. [2009], the $OC:SO_4$ ratio was 0.30 ± 0.01 in an airborne exhaust plume. The ship in that paper was
325 running on a 3 % m/m sulphur heavy fuel oil. In a study by Moldanová et al. [2009], $OM:SO_4$ was
around 2.4 for HFO (or $OC:SO_4$ around 2.9, using the conversion factor $OC = 1.2 \cdot OM$ given above),
and in another study by Petzold et al. [2011], $OM:SO_4$ was around 0.38 for HFO and 16 for a marine
gas oil (or $OC:SO_4$ around 0.46 and 19, respectively). Mueller et al. [2015] reported an $OM:SO_4$ which
was around 3.8 for HFO and 515 for a marine diesel fuel (or $OC:SO_4$ around 4.6 and 618, respectively).
330 There are also studies reporting chemical composition for multiple ship, measured in ambient air,
which is more comparable to our observations. Based on the average OC and SO_4 in 43 ship plumes
measured by Lack et al. [2009], where the emission factors were $1.21 \pm 1.50 \text{ g (kg fuel)}^{-1}$ (36 %) for
sulphate, and $1.26 \pm 0.96 \text{ g (kg fuel)}^{-1}$ for OM , the corresponding average $OM:SO_4$ is then 1.04 (or
 $OC:SO_4$ around 1.25). Similarly, for the 139 ship plumes observed by Diesch et al. [2013], the average
335 $OM:SO_4$ was 3.3 (or $OC:SO_4$ around 4.0). Our ratio of 2.3 ± 3.2 is hence in the same range as previous
studies. Murphy et al. [2009] observed that the $OC:SO_4$ was constant during the first hour of plume
dilution into the marine boundary layer. To confirm this at our measurement site, more chemically
resolved ship plumes are needed.

335 In addition to a variable chemical content, there was also a large variation in total mass of the ship
plume aerosol,”

2. Specific comments:

Referee comment 2.1.

340 **P. 1 line 18: Please give percentage fraction of plumes that did not result in measurable secondary
PM.**

Author's response 2.1.

345 To quantify the fraction of plumes which do and do not produce secondary PM would indeed be
valuable information. However, due to the nature of the OFR experiments and our current setup, it is
not possible to give an exact fraction. The plumes are smeared in the PAM-OFR and individual
secondary PM plumes cannot be distinguished. Hence, during periods with secondary PM formation,
we cannot say if all plumes or a fraction of the plumes during such a period contributed to the additional
mass, or if it is even ships at all. We have not been able to completely rule out the possibility that it is
other sources in the background air which are the main cause of the secondary mass observed, and a
longer measurement period would be needed to investigate this further.

350 Still, in order to get a rough idea of the numbers, we made an estimation of the upper and lower fraction
of plumes responsible for the secondary PM formation. This is done by assuming that all plumes during
hours with secondary PM formation are contributing (upper limit), and then assuming that just one
plume per hour with secondary PM formation is contributing (lower limit). During periods without any
secondary PM formation, all plumes are counted as not contributing. The calculations are based on the
355 data presented in Figure 3 in the manuscript. A threshold of $1 \mu\text{g m}^{-3}$ secondary PM mass is used to not
include data noise.

This resulted in 39 hours with ship plumes present, but no secondary PM formation, and 19 hours with ship plumes present together with observed secondary PM. So about a third of the times when ship plumes were present, we saw secondary PM formation. During the 19 hours with secondary PM and ship plumes, the total number of ship plumes was 60. We now estimate the upper and lower number of contribution ships, as described above. Assuming only one ship per hour actually causing the secondary PM, results in 19 out of a total of 154 ships, i.e. 12 %. Assuming all ships per hour causing secondary PM results in 60 out of a total of 154 ships, i.e. 39 %. Hence, we conclude that the number of ships which result in measurable secondary PM formation is in the range 10-40 %, and consequently 60-90 % did not contribute to measurable secondary PM.

We have added the upper estimation to the manuscript. And, due to the uncertainties associated with the OFR experiment and the calculations above, we have also highlighted the uncertainties in determining the sources causing the secondary PM observed in order to not cause misunderstandings.

Author's changes in manuscript 2.1.

We have added the following text to the manuscript section 3.5 Simulation of atmospheric ageing:

“Assuming only one plume per hour is actually causing the secondary PM results in 19 out of a total of 154 ships, i.e. 12 %. Assuming all ships sampled in a given hour contributed to the secondary PM results in 60 out of a total of 154 ships, i.e. 39 %. As some of the 154 plumes may individually contribute below the detection limit (indeed this seems likely) and we cannot rule out interferences from non-ship sources, we consider 39% an upper limit on the fraction of ship plumes which contributed to secondary PM in our OFR experiment.”

Referee comment 2.2.

P. 2 line 48 - 50: It would be good to add a review of PM emission factors obtained by the CO₂ method, which is probably the most accurate method to infer real-world emissions, and compare to the PM emission factors obtained from testbed experiments.

Author's response 2.2.

See response to comment 1.1.

Author's changes in manuscript 2.2.

We have added new text according to the answer to referee comment 1.1.

Referee comment 2.3.

P. 2 line 50 - 51: Please explain: “It is difficult to simulate atmospheric dilution in testbed experiments, which has large effects on nucleated nanoparticles”. Please explain the effects on nucleated nanoparticles in more details and add literature references. Does “atmospheric dilution” refer to the fast cooling and expansion of the exhaust plume at stack exit or the dilution due to atmospheric turbulence?

Author's response 2.3.

The intention of this sentence was not mainly to explore details of dilution processes, but to highlight the fact that dilution processes is something that can matter for particle formation, and hence support the need for atmospheric observations in addition to e.g. laboratory studies where conditions might differ. With dilution, we hence mean all relevant processes, including both processes mentioned by the referee, but mainly the first one (fast cooling and expansion at stack exit). Since we do not explore dilution processes further in our manuscript, we find such a review of the literature outside of the main scope. We realize that this sentence and statement might rather cause confusion for the reader. Since the statement does not have a significant impact on our results and our manuscript, we choose to completely remove the sentence.

Author's changes in manuscript 2.3.

We have removed this sentence from the manuscript section 1 Introduction:

~~*It is difficult to simulate atmospheric dilution in testbed experiments, which has large effects on nucleated nanoparticles.*~~

Referee comment 2.4.

P. 6 line 216 - 220: The explanation of the differences of PM_{0.15} in ship plumes to the study by Kivekäs et al. (2014) is somewhat speculative. What about the influence of different atmospheric chemistry regime or seasonal differences? The statement “these effects are likely cancelling each other out” is too strong. Simulations and observations of the particle number concentrations in ship plumes reported by Tian et al. (2014, figure 3 therein) show that after rapid dilution in the first minutes, total particle number concentration change only slowly between 30 and 60 minutes. This means that the effect of longer dilution period would be small. On the other hand, the ship contribution determined by Kivekäs et al. covers a larger source corridor, a fact that is not discussed here.

Author's response 2.4.

We agree with the referee and are thankful for pointing out the detailed limitations of the discussion. We have made some statements weaker, in accordance with the uncertainties associated with the results. We have also extended the discussion to include more possible differences between the two measurement sites compared in this paragraph.

Author's changes in manuscript 2.4.

The new paragraph in the manuscript section 3.2 Contribution to particle mass concentrations now reads:

“In a similar study to ours by Kivekäs et al. [2014], their reported PM_{0.15} values were 100 ng m⁻³ within plumes, and 23 ng m⁻³ daily contribution. This compares well to our values of about 50 ng m⁻³ within plumes and 26 ng m⁻³ daily contribution. *However, there are several factors impacting the particle concentrations which differ between the locations, which makes a detailed comparison for e.g. evaluating the effect of SECA regulations difficult. In the study by Kivekäs et al., the data covers a larger ship corridor in the North Sea. Hence, the ships were also larger (had higher gross tonnage and deadweight) and the particle source is consequently not the same as in Falsterbo. Additionally, the*

435 distance between the ships and the station is larger in the Kivekäs et al. study, suggesting that plumes could be more diluted. However, the most rapid dilution occurs directly after emission, and then much slower after around 30 minutes of atmospheric transport [Tian et al., 2014], which suggests that this should not constitute a large difference between the observed particle concentration between the sites. The particle mass can also be affected by the current chemical state of the atmosphere, e.g. by differences in seasons and meteorology.

Referee comment 2.5.

440 **P. 7 line 267 - 269: The average BC fraction of 2% of the total PM_{0.5} mass is very low compared to previous studies of ship exhaust, which may be explained in part by different fuels, operating conditions or the use of scrubbers. For a better understanding of this result, please provide the BC fraction, if only the plumes with detectable eBC increase were included in the analysis.**

Author's response 2.5.

445 First of all, thanks to drawing our attention to these values, we have found that there is an error in the eBC fractions presented in the results. It now states that the total eBC contribution compared to background levels was 12 % (p. 7, line 251) and that the eBC fraction within ship plumes was 2 % (p. 7, line 254, line 267 and p. 10, line 383). This is incorrect and the values should be 2 % and 5 %, respectively (in agreement with the values presented in table 1).

450 Hence, the eBC fraction is not as low in the ship plumes as previously stated. Still, the eBC fraction is indeed low in ship plumes in Falsterbo in general. The suggestion from the referee to specifically look at the “high BC emitters” is very good and in line with the approach we used to look at the top PM emitters for chemical speciation in Figure 2 in the manuscript. Hence, we selected the 10 % of the plumes ($n = 15$) with the highest eBC mass contributions (all $> 20 \text{ ng m}^{-3}$) and compared these to the corresponding PM_{0.5} contributions, which are calculated from size distributions as described in the manuscript. For these ship plumes, the average $\Delta\text{PM}_{0.5}$ was ($\pm 1\sigma$) $120 \pm 90 \text{ ng m}^{-3}$, and the ship plume eBC fraction was 0.40 ± 0.20 . It should again be remembered that both the eBC and PM_{0.5} plume concentrations have large uncertainties for individual ship plumes due to the low absolute concentrations. Still, there appears to be a substantial fraction of eBC in some plumes, and the total average eBC contribution of 2 % is then consequently a result of many ships having even lower or zero eBC emission. The 10 % of the ship plumes with the highest eBC concentrations were from eleven separate days of the campaign and during different parts of the day, with different meteorological conditions, so there is no apparent bias in the selection of these high eBC-emitters.

Author's changes in manuscript 2.5.

465 We have corrected the percentage values of eBC everywhere in the manuscript, so that 2 % refers to the contribution compared to background levels, and that 5 % refers to the plume composition.

We have added the following sentence to the manuscript section 3.4 Contribution the BC and chemical composition:

470 *“An eBC fraction of 5 % is very low compared to previous ship emission studies. The individual eBC fraction varied a lot from ship to ship, which can depend on many factors including engine operation, fuel type, and use of scrubbers. The 10 % of the plumes ($n = 15$) with the highest eBC mass contribution*

($> 20 \text{ ng m}^{-3}$) had an average eBC fraction ($\pm 1\sigma$) of $40 \pm 20 \%$ of the $PM_{0.5}$ calculated from SMPS size distributions.”

475 Referee comment 2.6.

P. 9 line 339-340: Please discuss in more detail the (only) moderate increase of nitrate and ammonium in the OFR. Formation of ammonium nitrate requires the presence of sufficient ammonia, which may be the limiting factor during the time when the measurements were made. Thus, nitrate and ammonia could be higher during the spring season with more agricultural activity. The gas-phase/particle partitioning is also very sensitive to changes in temperature and relative humidity inside the reactor compared to ambient air.

Author's response 2.6.

The referee is correct that ammonia may have been a limiting factor in particulate nitrate formation. Concentrations of ammonia in Sweden seem to be highest between April-August, up to around $1 \mu\text{g m}^{-3}$ in southern Sweden (1993-2010 average) [Ferm and Hellsten, 2012]. Although we did not measure NH_4 , we expect the concentrations to be lower than the measured NO_2 found in table 1 [Ferm and Hellsten, 2012]. Using the OH exposures of the reactor and a reaction rate of $9.2 \cdot 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ [Mollner et al., 2010] between 50 and 90 % (depending on the OH concentrations which in turn depends mostly on the absolute humidity) of the NO_2 entering the reactor should have reacted. This translates to between 2-10 $\mu\text{g m}^{-3}$ of nitrate. However, to form particulate nitrate the formed HNO_3 must be neutralized by the limited ammonia but is also limited by the reactor condensation sink, in a similar fashion as for LVOCs (Fig S4). Setting up a model for nitrate is possible, but not necessary for any conclusions in this manuscript. The temperature effect in reactors could be significant and is known to affect both organics and ammonium nitrate [Nenes et al., 2020]. However, if it was important in this campaign, the nitrate already in the particle phase should also have evaporated, and the difference between reactor and ambient measurements would be negative, which was not the case. Further, pH of the particles, in combination with liquid water content affects the sensitivity to ammonia and nitrate. A lot of the above discussion is important for ambient OFR studies, but does not affect any of the conclusions in the present manuscript.

500 Author's changes in manuscript 2.6.

We have added the following to the manuscript section 3.5 Simulation of atmospheric processing:

“Modelling of the fate of produced low-volatile species (Supporting Information and Fig. S4) suggests that a significant portion (~60-90%) of the oxidation products do not enter the particle phase due to the low condensation sink. *Although the model was set up for organics, this is true for all secondary aerosol species formed in the reactor. Particulate nitrate formation will also be sensitive to the availability of gas-phase ammonia to neutralize the aerosol.*”

Referee comment 2.7.

510 **P. 9 line 351-353: How likely is it that heterogeneous oxidation of organic aerosols happens in the real plume ageing where the environment is much less oxidative?**

Author's response 2.7.

515 Heterogeneous oxidation surely happens in the atmosphere as well, but is likely different in an OFR, since the particle surfaces in the atmosphere are not as static as in the OFR, due the dynamics of a specific air mass (emissions and mixing). *Renbaum and Smith* [2011] showed that the radical concentration and time are interchangeable variables in lab experiments, i.e. OFR experiments can simulate the atmospheric oxidation, but that heterogeneous oxidation can be affected by adsorption of O₃ to particle surfaces. We don't find it necessary to add any of this discussion to the manuscript.

Author's changes in manuscript 2.7.

No changes were done to the manuscript.

520 **3. Technical corrections:**

Referee comment 3.1.

P. 4 line 143: "Chemical composition" would be better here.

Author's response 3.1.

We agree with the referee.

525 **Author's changes in manuscript 3.1.**

We have changed the word "*content*" to "*composition*".

Referee comment 3.2.

Figure 1: Please add a panel with wind direction and wind speed below the current plots.

530 **Author's response 3.2.**

535 We think that the suggestion from the referee to include wind data, is mainly in order to show that the changes in particle concentration are not due to these factors but indeed due to ships as we state in the manuscript. As can be seen in the Fig. AC3 below, the wind speed and direction are fairly constant during the period (255-282 degrees and 7.6-9.6 m s⁻¹). We do not think that these figures are contributing with enough relevant information to be included in the manuscript. However, we recognize the potential risk of other readers wondering about the same thing, hence we have added a comment about this in the figure caption.

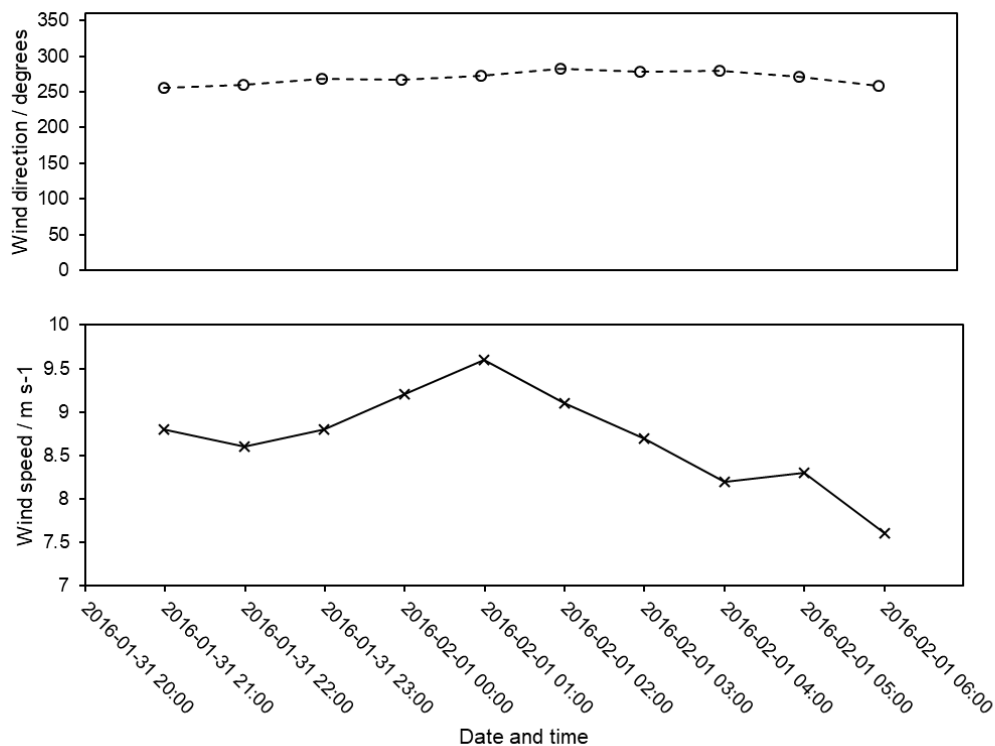


Figure AC4. Wind direction and wind speed during the same period which is shown in the Fig. 1 in the manuscript.

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Author's changes in manuscript 3.3.

We have added the following phrase to the end of the caption of Figure 1:

“The wind direction (269 ± 14 degrees) and wind speed (8.7 ± 1.1 m s⁻¹) can be considered stable during this period.”

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Referee comment 3.3.

Figure 3: The orange line for ammonium is hardly visible.

Author's response 3.3.

We appreciate the feedback on the visibility of the data in the plot. We agree that both ammonium and nitrate are not clearly visible, but this is mainly due to the often zero change in concentration of these species. In order to improve the middle panel of Figure 3, we made a new version with the relatively brighter line for ammonium in front for comparison (see Figure AC5 and AC6 below). The figures are similar, but due to the colors of the lines (which are the standard colors for these aerosol species within the field), we think that the new version (AC6) is slightly more clear.

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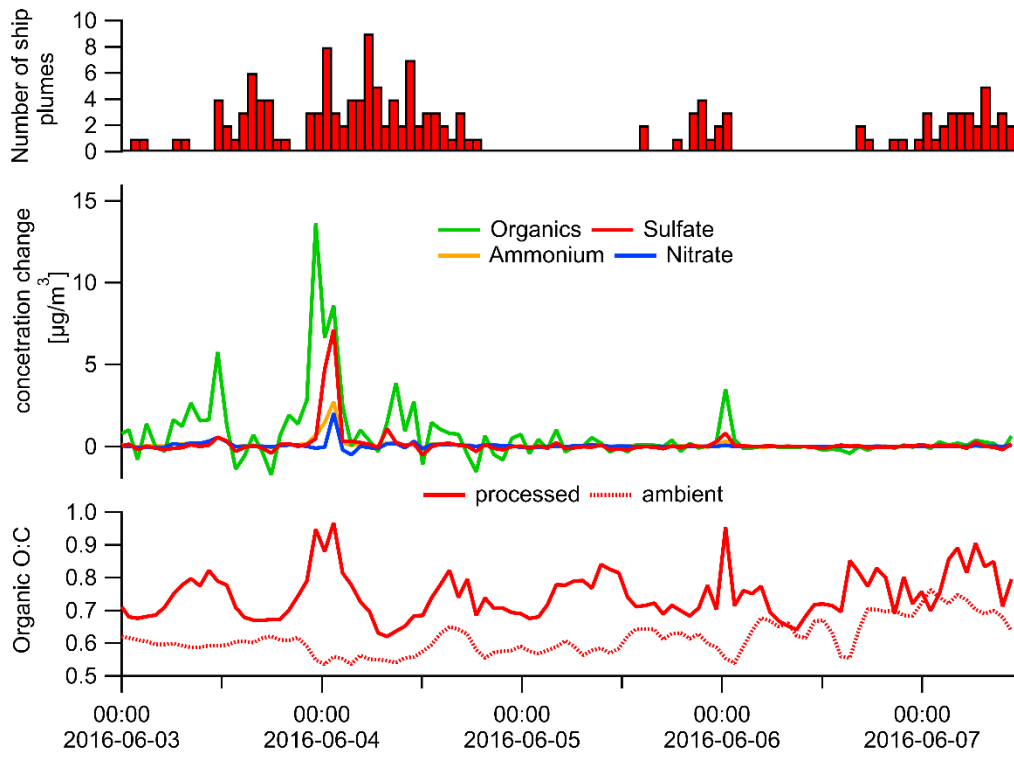


Figure AC5.

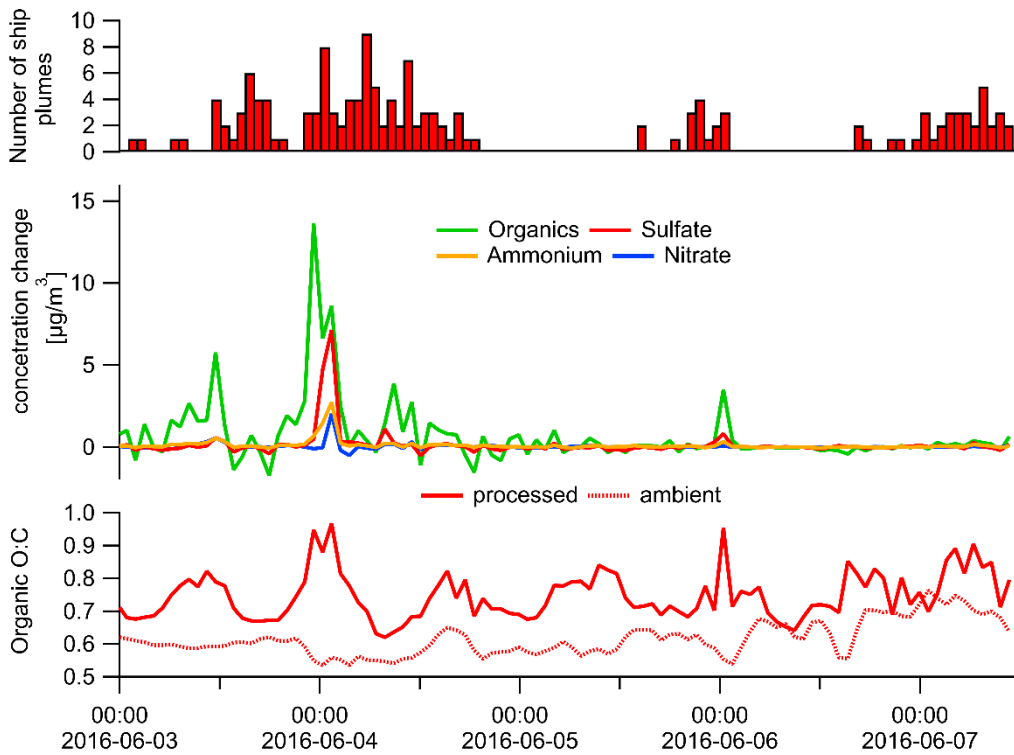


Figure AC6.

Author's changes in manuscript 3.3.

560 We have replaced Figure 3 (now Figure 4) with the new version, where all the data is identical but the ammonium concentration time series is moved to the front (i.e. the Figure AC6 above).

Referee comment 3.4.

565 **Table 1: Please give the number of plumes in summer and winter somewhere in this table. It would be better to replace “average plume concentration” by “Delta plume” since the column gives the excess concentration due to the ship plume and not the in-plume concentration.**

Author's response 3.4.

570 We agree with the referee regarding the use of “delta plume” instead of “average plume concentration”. Regarding the number plumes, this is already given in the table. The rightmost column shows the number of plumes (n) per season and per aerosol variable. To make this even clearer, we have added an explanation in the table headline.

Author's changes in manuscript 3.4.

We have changed the table heading in Table 1 from “*Average plume conc.*” To “ Δ plume”.

We have added the phrase “*a number (n) of*” to the table headline in Table 1, which now reads:

575 “*Table 1: Average absolute contribution of particle mass (PM), NO₂, equivalent black carbon (eBC), particle number concentration (PN), SO₂, and CO₂ to local air quality due to a number (n) of ship plumes, from two measurement campaigns at the Falsterbo coastal site.*”

Final author comment for Referee 2

580 1. Major/general comments:

Referee comment 1.1.

The evaluated impact on of ship plume is really low, by reading the manuscript I do not understand what are the authors conclusions, is this due to the application of SECA rules? Or to other meteorological effect? This aspect is fundamental to give guideline to environmental policies. Please authors improve the discussion on this aspect.

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Author's response 1.1.

We acknowledge that the conclusions regarding the cause of the low PM is not clear. However, we also think that with the current data set, we cannot exclusively point to a simple explanation for the observed levels. Since there are no similar measurements in the region before the SECA, we cannot compare the PM levels before and after regulation. We could find several explanations for the observed low PM contribution from ships in this study. Firstly, the SECA regulation could indeed be a cause of PM reduction, as is now more clearly stated in the introduction (see Author's response 1.1 to referee 1). Secondly, we only consider one shipping lane with the method used, and the total contribution from shipping is then larger due to ship emissions being a source to the regional background aerosol. We raise this point in the description of the method, in the discussion, and in the conclusions, specifically on p. 3-4, line 121-124, on p. 6, line 230, on p. 7, line 275, and on p. 10, line 388-390 in the first version of the manuscript and have clarified this also in the abstract and in the introduction (see Author's response 1.3 to referee 1) Thirdly, the ships in Falsterbo are smaller than in the rest of the Baltic and on larger seas elsewhere. This could be an additional reason for a lower impact at our field site. And, since most other ambient studies have been performed on ship fleets with larger sized vessels, this will affect comparisons with emission factors from literature. We do not think the observations of low PM are due to meteorology only, even if meteorology has an impact on observations (see Author's response 1.5 to referee 1). This is partly based on the fact that measurements were performed in both summer and winter and yielded similar results. We have extended the discussion to make all of the previously not mentioned factors above more clear to the reader.

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Author's changes in manuscript 1.1.

We have made the following changes to the manuscript section 3.2 Contribution to particle mass concentrations:

“Most ships have a small contribution to PM, of less than 100 ng m⁻³. A relatively low PM is expected in the strictest SECA regions compared to elsewhere, due to the strong reduction in particulate sulphate. However, there are multiple reasons for the low PM contribution observed in Falsterbo. The fuel sulphur content and the small, but existing, use of scrubbers is the first explanation, and the compliance with these regulations is indeed high. Secondly, the impact presented is from one shipping lane, and the total contribution from shipping is hence larger due to ship emissions being a source to the regional background aerosol. Thirdly, the ships in Falsterbo are relatively small compared to the rest of the Baltic and on larger seas elsewhere, since they have to pass the Øresund Strait and under bridges. Smaller ships typically have a lower engine power and emit less air pollutants on an absolute

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620 *scale. Meteorological factors did not seem to influence the plume detection to any large extent, and the shipping lane contribution to ambient concentrations was similar in both the summer and winter campaign. However, longer measurements would be needed to study the effect of meteorological parameters on plume detection, and this will be of even larger importance in other measurement sites where there is risk of a build-up of a thermal internal boundary layer at the shoreline.”*

Referee comment 1.2.

625 **The result of the scarce increases of secondary aerosol obtained in the OFR measurements is not fully supported. I think that a comparison with data from other sites could help the discussion (e.g. Contini et al., 2011 and especially Perez et al., 2016 for the evaluation of secondary aerosol).**

Author's response 1.2.

630 We do not fully understand what the referee means with “not fully supported”. The OFR results show increases in secondary aerosol production in some occasions, while not in others. It is important to understand the limitations of the OFR measurement technique, but since this is a minor part of the manuscript, we do not want to extend the description of these results too much. See also the Author's response 2.1 to referee 1, about an upper estimation of ships contributing to secondary aerosol.

635 Regarding the references suggested, we think these are not easily comparable to our results. Contini et al. (2011) describes diurnal patterns of primary PM_{2.5} and PM₁₀, not measurement or modelling of secondary aerosol formation. There is a statement in the introduction about the possible contribution to secondary inorganic aerosol due to sulphur, and a statement about the difficulties to extract the contribution to secondary aerosol from the data. In Perez et al. (2016), the SOA is obtained from PMF and they explicitly state the difficulties in quantification and highlight the need for further research. We have chosen not to add any detailed comparison with the suggested papers, but rather our manuscript highlights the first ambient OFR studies on ship emissions and the associated observations.

Author's changes in manuscript 1.2.

We have not made any changes to the manuscript.

645 Referee comment 1.3.

Besides, the statement that background particles are already aged is not correct in my opinion, as the author state the time required to air masses from ship plume to the sampling site is 90 min in the measuring condition, this time is not sufficient for the ageing of aerosol, nether in summer.

Author's response 1.3.

650 Here, we think there is a misunderstanding about what is meant with “background particles”. With “air masses being somewhat aged” we mean air that is not coming from the shipping lane, but the regional background. This aerosol is hence much more aged than the stated 90 minutes, more like days up to a week. That this air is at least partly aged is shown in the ambient AMS O:C ratio in figure 4 [Canagaratna et al., 2015]. We have made some linguistic changes in the manuscript in order to make this unambiguous.

Author's changes in manuscript 1.3.

We have revised the following sentence in the manuscript section 3.5 Simulation of atmospheric processing:

660 “This may be caused by the *background* air masses reaching the site already being somewhat aged and precursor concentrations being low.”

And revised the following sentences in the manuscript section 4 Summary and conclusions:

“We suggest that the reason for this is that the *regional* background particles *from long-range transport* arriving at Falsterbo are already relatively aged.”

665 Referee comment 1.4.

I think that information on the height of planetary boundary layer are fundamental to understand secondary aerosol formation processes and especially the real contribution of ship aerosol to background aerosol budget. By considering this aspect, conclusions can change substantially. I strongly suggest adding a discussion on the effect of PBL height on the contribution of both primary and secondary ship aerosol respect to background.

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Author's response 1.4.

The topic of planetary boundary layer effects was also brought up by referee 1. We have therefore treated these comments together, see the response to referee 1 (“Referee comment 1.5”).

675 Regarding secondary aerosol formation, we are not sure how the referee means that this should be affected in a different way compared to the primary aerosol. As stated in the manuscript, the PAM-OFR measurements were limited in time and we cannot make any conclusive statements regarding this matter.

Author's changes in manuscript 1.4.

See the response to referee 1 (Referee comment 1.5).

680 2. Minor comments:

Referee comment 2.1.

A map with the sampling site and surrounding areas with the urbanization level can be useful to interpret the data set.

Author's response 2.1.

685 We agree with the referee. Additionally, since both referees brought up boundary layer effects as a concern, the map will also help the reader to interpret the geographical and meteorological conditions (see Author's response 1.5 to referee 1).

Author's changes in manuscript 2.1.

We have added the following figure and caption to the manuscript section 2 Materials and methods.
690 The map is now “Figure 1” in the manuscript, and all other figures have changed number accordingly.



695 “Figure 1. Map of the Baltic Sea region (left) and the nearby region around the field site (right). The measurement site Falsterbo is marked with blue pin, and the nearby large cities Copenhagen and Malmö are marked with red circles. The red line shows a typical route of a ship following the main shipping lane around the Falsterbo peninsula, based on AIS position data.”

Additionally, the following text has been updated in section 2 Materials and methods:

700 “The field site and the measurement methods have been described in Ausmeel et al. [2019] and is only briefly outlined here. The measurements took place at the Falsterbo peninsula, Southern Sweden, during January-March and May-July, 2016. The location of the field site and the surrounding area are shown in Fig. 1. The largest nearby cities are Copenhagen (Capital of Denmark) and Malmö, with populations of about 800 000 and 300 000, respectively. All water in this figure is within the North Sea and Baltic Sea SECA. ~~This location is within the Baltic Sea SECA.~~ The field site is located at the tip of a peninsula, around which a frequently trafficked shipping lane is passing (illustrated by a red line in Fig. 1).”

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Referee comment 2.2.

Section 3.1 Plume identification and general characteristic seems more a methodology to recognize ship plume than results, I suggest moving this part in the Materials and methods section.

710 Author’s response 2.2.

We think that just a part of the section could be considered to be method, while a large part of the section is relevant to keep in the results, since it describes the general observations of plumes and evaluation of successful measurement techniques. We have moved a part of this section, in order to keep methods and results more clearly separated.

715 **Author's changes in manuscript 2.2.**

The following text has been moved from section '3.1 Plume identification and general characteristics' to section '2 Materials and methods'. In order to make the text fit into the new location, a few structural and linguistic changes have been made, this is the new text:

720 "The average concentration for each plume was calculated by integrating the total area under the plume peak. The values were then normalized by the plume duration to give an average plume peak concentration. All ship passages that resulted in an elevated particle number concentration, *fulfilling the criteria for plume selection listed above*, and which could be connected to an individual ship with AIS were included in the calculation of the average contribution from the fleet. Daily and seasonal contribution values *from the shipping lane* are *calculated* based on AIS data, which showed an average of 73 and 63 ships passing per day in winter and summer respectively. During periods when the wind blows from the Øresund Strait (i.e. across the shipping lane), the Falsterbo site is *hence* affected by the nearest shipping lane approximately 51% of the time in the winter, and 44% in the summer, based on the average observed plume duration of 10 min *multiplied with the average number of ships per day*. Based on historical wind data from the last 20 years (Swedish Meteorological and Hydrological Institute, SMHI), the wind intercepts the shipping lanes in Øresund Strait about 70% of the time in both summer and winter, which was used to estimate the seasonal contribution from ships. For the daily and seasonal estimates, it was assumed that the average *ship plume* contribution ($\Delta plume$) in Table 1 is representative for all plumes. For calculation of the uncertainty in the daily and seasonal contribution, the uncertainty in aerosol number concentration was estimated to 30 %, the uncertainty in particle loss estimation was 30 %, the variation in ship traffic density was 17-34 %, and the uncertainty in seasonal wind pattern was estimated to 5 %. These values were used to calculate the total uncertainty with error propagation, i.e. added in quadrature."

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Referee comment 2.3.

740 **Lines 339-340. The sentence is not completely correct, it is true that nitrate arises from oxidation of NO_x, but ammonium arises from neutralization of ammonia on both HNO₃ and H₂SO₄, the latter is preferred over ammonium nitrate formation due to the lower vapor pressure of sulfuric acid than nitric acid (Hauglustaine et al., 2014).**

Author's response 2.3.

745 We have removed the incomplete explanation of the chemical origin of the (low) formation of particulate nitrate and ammonium and revised the sentence.

Author's changes in manuscript 2.3.

The revised sentence reads:

The increases in nitrate and ammonium were moderate on an absolute scale.

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Ship plumes in the Baltic Sea Sulphur Emission Control Area: Chemical characterization and contribution to coastal aerosol concentrations

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Abstract. In coastal areas, there is increased concern about emissions from shipping activities and the associated impact on air quality. We have assessed the ship aerosol properties and the contribution to coastal particulate matter (PM) and nitrogen dioxide (NO₂) levels by measuring ship plumes in ambient conditions at a site in Southern Sweden, within a Sulphur Emission Control Area. Measurements took place during a summer and a winter campaign, 10 km downwind of a major shipping lane. Individual ships showed large variability in contribution to total particle mass, organics, sulphate, and NO₂. The average emission contribution of the shipping lane fleet was 29±13 and 37±20 ng m⁻³ to PM_{0.5}, 18±8 and 34±19 ng m⁻³ to PM_{0.15}, and 1.21±0.57 and 1.11±0.61 μg m⁻³ to NO₂, during winter and summer respectively. Sulphate and organics dominated the particle mass and most plumes contained undetectable amounts of equivalent black carbon (eBC). The average eBC contribution was 3.5±1.7 ng m⁻³ and the absorption Ångström exponent was close to 1. Simulated aging of the ship aerosols using an oxidation flow reactor showed that during a few occasions, there was an increase in sulphate and organic mass after photochemical processing of the plumes. However, most plumes did not produce measurable amounts of secondary PM upon simulated ageing.

1 Introduction

Air pollution from shipping is a global concern due to its climate and health effects [Oeder et al., 2015; Brandt et al., 2013; Corbett et al., 2007; Eyring et al., 2010; Lack et al., 2011]. In many places, there is an increase in shipping activities as a result of increased international trade. Ship emissions are an increasingly important source of air pollution, especially in coastal areas and harbours [Corbett and Fischbeck, 1997; Eyring et al., 2005]. Ship emission properties, such as particle number and mass concentration, particle size, and chemical composition, depend on a variety of parameters and ships make up a heterogeneous mix of emission sources. Most particles emitted from ships are in the sub-micrometre range, typically with a diameter below 100 nm [Lack et al., 2009]. Studies have shown a decrease in mean particle diameter when switching to a lower fuel sulphur content [Betha et al., 2017; Zetterdahl et al., 2016] as well as a decrease in emitted particulate matter (PM). The International Maritime Organization (IMO) have regulated fuel sulphur content in several steps in recent years, from 1.5% to 0.1% mass fraction between the years 2010 and 2015 in sulphur emission control areas (SECA). The fuel sulphur limit is still has been 3.5% outside SECA but is planned to be was restricted to 0.5% in 2020.

Ship emission properties, such as particle number and mass concentration, particle size, and chemical composition, depend on a variety of parameters and ships make up a heterogeneous mix of emission sources. Most particles emitted from ships are in the sub-micrometre range, typically with a diameter below 100 nm [Lack et al., 2009]. Studies have shown a decrease in mean particle diameter when switching to a lower fuel sulphur content [Betha et al., 2017; Zetterdahl et al., 2016] as well as a decrease in emitted particulate matter (PM) [Lack et al., 2009; Diesch et al., 2013; Mueller et al., 2015; Buffaloe et al., 2014]. Studies of chemical composition of ship PM have shown that the mass is typically dominated by organic matter, sulphate, and black carbon [Zetterdahl et al., 2016; Cappa et al., 2014; Lu et al., 2006; Anderson et al., 2015; Beecken et al., 2014]. Zetterdahl et al. [2016] measured PM emission factors on-board a ship in the Baltic Sea, running on HFO and low-sulphur residual marine fuel oil, respectively. The total and non-volatile PM emission factors were 0.17 ± 0.03 g (kg fuel)⁻¹ and 0.12 ± 0.03 g (kg fuel)⁻¹, respectively for HFO, and

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40 $0.06 \pm 0.03 \text{ g (kg fuel)}^{-1}$ and $0.04 \pm 0.02 \text{ g (kg fuel)}^{-1}$, respectively for the low-sulphur fuel. The black carbon emission factor ranged
from 0.027 to $0.087 \text{ g (kg fuel)}^{-1}$, depending on engine load, and was slightly higher for HFO. *Lack et al.* [2009] reported emission
factors for 43 ship plumes based on ambient measurements using aerosol mass spectrometry (AMS) for chemically resolved PM.
They observed an average PM_{10} emission factor of $3.32 \pm 4.04 \text{ g (kg fuel)}^{-1}$, and specifically $1.21 \pm 1.50 \text{ g (kg fuel)}^{-1}$ (36 %) was
sulphate, $1.26 \pm 0.96 \text{ g (kg fuel)}^{-1}$ (38 %) was organic matter, and $0.85 \pm 0.76 \text{ g (kg fuel)}^{-1}$ (26 %) was black carbon. Sulphate and
45 organic matter were linearly correlated with fuel sulphur content. In a study by *Cappa et al.* [2014], the ship plume PM was varying
with ship speed, with an $\text{EF}_{\text{PM}_{10}}$ ranging from 0.09 (slow speed, 2.9 knots) to $1.5 \text{ g (kg fuel)}^{-1}$ (high speed, 12 knots). For this ship,
running on a low-sulphur marine gas oil, the PM sulphate content was below the detection limit of the AMS, while the primary
organic matter (pOM) made up $53 \pm 14 \%$ of the total mass ($\text{EF}_{\text{pOM}} 0.39 \pm 0.44 \text{ g (kg fuel)}^{-1}$), and BC made up $47 \pm 14 \%$. Similarly,
50 *Shen and Li* [2019] also found negligible sulphate emissions from marine diesel oil, which was dominated purely by organic and
elemental carbon. In the same study, the use of HFO as fuel resulted in 75 % sulphate mass (including bound water), 21 % organic
carbon, and the rest was elemental carbon and ash. Plume studies of 139 ships in a 1 % sulphur emission control area, presented in
[Diesch et al., 2013], showed an average PM_{10} emission factor of $2.4 \pm 1.8 \text{ g (kg fuel)}^{-1}$, and specifically $0.54 \pm 0.46 \text{ g (kg fuel)}^{-1}$
(23 %) was sulphate and $1.8 \pm 1.7 \text{ g (kg fuel)}^{-1}$ (75 %) was organic matter. In a recent on-board study by *Huang et al.* [2018], it was
also found that organic matter was the most abundant PM fraction (45-65 %), while sulphate content was low compared to the
55 values listed above (2-15 %). The elemental carbon (or black carbon) PM mass fraction was low (1-6 %) for the main engine used
for propulsion, while higher (20 %) for the auxiliary engine used to generate electricity. The PM composition, including other
species than just sulphate, relative distribution of these species depend partly on fuel sulphur content [*Lack and Corbett*, 2012].
There are several other parameters which affect the absolute emission of PM as well as the particle compositions, such as fuel type,
operation conditions, engine load, engine properties, and maintenance, which makes ship exhaust a heterogeneous aerosol for
60 different ships and geographical locations [*Anderson et al., 2015; Brandt et al., 2013*]. Ship exhaust also contains elevated levels of
nitrogen oxides (NO_x , including NO_2 and NO), sulphur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), and volatile
organic compounds (VOCs) [*Sinha et al., 2003; Chen et al., 2005; Alföldy et al., 2013; Moldanová et al., 2009; Huang et al., 2018;*
Cooper, 2001]. Concentrations of CO_2 can be used to estimate emission factors of gases and particles. NO_x emissions from ships
have also been shown to depend on, at least, both fuel type and on ship speed [*Beecken et al., 2014; IPCC, 2013*].

65 One way to characterize and quantify ship emissions is through ambient measurements in coastal areas, downwind of shipping lanes.
This method makes it possible to register an increase in aerosol levels and potential exposure in an area when individual ship
emission plumes pass the measurement station. Other methods include e.g. measurements on laboratory engine emissions [*Anderson*
et al., 2015; Kasper et al., 2007; Lyyränen et al., 1999; Petzold et al., 2010] or measurements on board or following a sailing ship,
intersecting the emission plume [*Chen et al., 2005; Murphy et al., 2009; Petzold et al., 2008; Aliabadi et al., 2016; Lack et al.,*
70 *2011*]. However, while these methods can provide detailed knowledge on fresh emissions from a specific ship, they do not give
information about the variety of particle properties between different ships, how the plume evolves during transport in the
atmosphere, human exposure over land areas, and these methods can be more cost-intensive. By measuring in ambient conditions
on the coast, emissions from a large part of the shipping fleet can be captured, and atmospheric measurements are needed to give
information on emissions, dilution, and impact on environment and local air quality. Atmospheric measurements of elevated CO_2
75 concentrations close to (less than a few minutes downwind) shipping lanes, can give emission factors during atmospheric conditions,
which differ from testbed conditions. It is difficult to simulate atmospheric dilution in testbed experiments, which has large effects
on nucleated nanoparticles.

To date, a number of atmospheric studies of individual ship plumes have been conducted in harbour areas [*Alföldy et al., 2013;*
Healy et al., 2009; Jonsson et al., 2011; Lu et al., 2006; Westerlund et al., 2015], and also in the Arctic [*Aliabadi et al., 2015*]. One
80 study of aged plumes from a shipping lane has been performed by *Kivekäs et al.* [2014], outside the west coast of Denmark,
measuring plumes with an atmospheric age of about one hour. In the study by *Kivekäs et al.*, ship plumes were measured at a coastal
station about 25-50 km from the shipping lane, where there was good potential to study the impact of ship emissions on land

concentrations and how particles are aged during semi-long range transport. However, the authors suggested shorter distances to be able to detect elevated particle number concentrations from each individual ship passing along the lane when winds blew from the ships to the coastal stations. In this study, we have performed measurements 10 km (corresponding to approximately 30 minutes of plume aging) downwind of a major shipping lane in southern Sweden. With this setup, we were able to measure elevated particle number concentration for a majority of the ship plumes. The distance is nevertheless large enough to represent typical shipping lanes around the globe which influence inland air-pollution, as well as to observe some effects of particle aging.

The measurements presented here were performed in the Baltic Sea SECA during 2016 in order to study ship emission properties after the newest regulation of fuel sulphur content (0.1% by mass). In a report by *Mellqvist et al.* [2017], the compliance levels to the most recent SECA regulations was studied in the nearby region of where our measurements were conducted. During the years 2015 and 2016, the compliance level was 92 %–94 % in the region around Denmark. [Also *Jonson et al.* \[2019\] have shown that there is a strong indication that ships are complying, based on emission modelling before and after the 2015 SECA regulation.](#) The method for individual ship plume identification and the contribution to particle number concentrations have been described in detail in *Ausmeel et al.* [2019]. In the current paper however, we report the contribution from [a major shipping laneships](#) to local particle mass concentrations and chemical composition (organics, sulphate, black carbon), and NO₂, as well as the effects of additional aging simulated with an oxidation flow reactor. The results complement previous studies in two ways. Firstly, due to the new measurement location at an intermediate distance from the shipping lane. Secondly, due to the measurements being performed after the recent fuel sulphur regulations within SECAs, which was introduced on January 1, 2015. The estimation of how ship traffic along a major route contributes to the coastal particle concentrations can contribute to the development of aerosol dynamic process models, regional aerosol particle models, health assessment models and epidemiological studies.

2 Materials and methods

The field site and the measurement methods have been described in *Ausmeel et al.* [2019] and is only briefly outlined here. The measurements took place at the Falsterbo peninsula, Southern Sweden, during January-March and May-July, 2016. [The location of the field site and the surrounding area are shown in Fig. 1. The largest nearby cities are Copenhagen \(Capital of Denmark\) and Malmö, with populations of about 800 000 and 300 000, respectively. All water in this figure is within the North Sea and Baltic Sea SECA. This location is within the Baltic Sea SECA. The field site is located at the tip of a peninsula, around which a frequently trafficked shipping lane is passing \(illustrated by a red line in Fig. 1\). When performing measurements along a coastline, the interface between atmospheric boundary layers over land and sea can cause a build-up of a thermal internal boundary layer at the shoreline. This has been described by e.g. *Hanna et al.* \[1984\] and is important to consider when doing plume measurements. However, due to the geographical surroundings at our field site, we do not expect this effect to be strong or exist at all, since the peninsula is a small land mass almost surrounded by water. The boundary layer height is likely a parameter which affects the dilution of the plumes and the background air and thereby the plume concentration. However, it seemed that boundary layer height did not affect the plume concentration in a systematic and reproducible way in Falsterbo as deduced using Hybrid Single Particle Lagrangian Integrated Trajectory Model \(HYSPLIT\) \[*Stein et al.*, 2016\] with meteorological data from Global Data Assimilation System \(GDAS\). Since this study aims at describing the ship emission contribution to inland aerosol burden and not the concentrations at the exhaust stack, the effects of boundary layer height has not been pursued any further in this paper.](#)

In order to measure particle number size distribution, and estimate mass concentrations for particles with a mobility diameter up to 0.15 μm (PM_{0.15}) as well as 0.5 μm (PM_{0.5}), a custom built scanning mobility particle sizer (SMPS) was used (DMA, Hauke type medium, custom built; CPC 3010, TSI Inc., USA) [*Svenningsson et al.*, 2008]. The scan time of the DMA was two minutes and the particle size range measured was 15–532 nm. SMPS size distributions were corrected for sampling losses using the Particle Loss Calculator tool [*von der Weiden et al.*, 2009].

The particle chemical composition was evaluated online with a Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc.) [Onasch *et al.*, 2012]. The SP-AMS was alternately run in single and dual vaporizer mode during winter and only in single vaporizer mode during summer. In single vaporizer mode, particles are flash vaporized upon impaction on a heated (600 °C) tungsten surface. In the dual vaporizer mode, particles containing refractory black carbon (rBC) are vaporized by an Nd:YAG laser (1064 nm). The vapours are then ionized (70 eV electron ionization) and detected in a high resolution time of flight (HR-ToF) mass spectrometer. The SP-AMS ionization efficiency with respect to nitrate was calibrated using 300 nm ammonium nitrate particles and for rBC calibration, regal black was used. The relative ionization efficiency for ammonium (RIE- NH₄) was 3.8 in winter and 4.0 in summer, and the collection efficiency (CE) was assumed to be 0.5 for both campaigns. SP was not used in the summer in order not to affect the detection of other compounds, since the BC levels were found to be low in the winter campaign. SP-AMS data analysis was performed using Igor Pro 6.37 (Wavemetrics, USA), Squirrel 1.571, and PIKA 1.161. In addition to the SP-AMS measurements, equivalent black carbon (eBC) content was measured with online, filter based optical absorption methods, using a seven wavelength Aethalometer (model AE33, Magee Scientific) [Drimovec *et al.*, 2015] and a 637 nm Multi Angle Absorption Photometer (MAAP, Thermo Fisher Scientific) [Müller *et al.*, 2011], both with a sample time of one minute. For the gaseous compounds, CO₂ was measured at 1 Hz with a non-dispersive infrared gas analyser (LI840, LI-COR), NO_x was measured every minute using a chemiluminescence monitor (CLD 700 AL, Eco Physics), and SO₂ was measured every minute using a UV fluorescent SO₂ analyser (S.A AF22M, Environnement).

A potential aerosol mass (PAM) oxidation flow reactor (OFR) [Kang *et al.*, 2007; Lambe *et al.*, 2011] was alternately connected before the SP-AMS, SMPS, and Aethalometer to simulate atmospheric aging during parts of the summer campaign. The reactor is a 13.2 l aluminium cylinder with two UV lamps mounted inside. The reactor produces high levels of ozone and hydroxyl radicals (OH), and has been shown to produce similar yields and mass spectra to those from traditionally used smog chambers [Bruns *et al.*, 2015; Lambe *et al.*, 2015]. The flow through the reactor was 5 litres per minute, which gives an average residence time of 160 s. The particle instruments sampled air from the radial centre of the reactor while ozone was sampled from a perforated Teflon tube ring. The reactor and bypass sampling was controlled using an automated 3-way valve which was switching every 30 minutes. The first five minutes of ambient data and the first ten minutes of reactor data were not analysed, in order to give the sampling line time enough to stabilize flows. In some previous field studies with the PAM-OFR [Ortega *et al.*, 2016; Palm *et al.*, 2016], it has been placed outside with the end plate removed, directly sampling ambient air. This has been shown to minimize losses [Ortega *et al.*, 2013]. Due to the location, this was not possible in the present study. A fine metal mesh grid, which is usually installed at the inlet side of the reactor to help develop a laminar flow, was removed in order to minimize losses. Further details about the simulated atmospheric aging, including calibration, particle losses, and fate of produced low-volatile species, are discussed in the S.I. (Fig. S3-5).

Individual ship plumes were extracted from the data set based on a set of criteria, which are described in the companion paper [Ausmeel *et al.*, 2019]. In brief, plumes were initially selected by inspection of the time series, choosing peaks in particle number concentration where there was a clear increase above the background and noise level. This increase should not be longer than about 20 minutes and not shorter than about 5 minutes, to exclude other potential sources than ship plumes from the nearby lane. In order to assess individual ship plumes, no plumes that were overlapping or close to each other in time (less than five minutes) were included in the analysis. Plumes were only selected when the wind was blowing over the shipping lane to the measurement station. Further, automatic ship identification system (AIS) position data was used to confirm that the increase in particles was due to a passing ship. This was performed by calculating a trajectory of the emission plume from the ship using wind data. The expected plume passage based on AIS and wind data and the visible plumes in the particle counter agreed excellently, and a large fraction (>95 %) of the plumes (including all plume events, not only the plumes finally used for analysis for which 100 % were confirmed with AIS) were detectable as a distinct increase compared to background particle concentrations. Background concentrations were subtracted from the total plume concentration to get only ship emission contributions. The background level in this analysis was defined as the baseline concentration from which the identified plumes can be distinguished (the background concentration was

always relatively stable during onshore wind, see Fig. 2, and hence the background subtraction was straightforward). The background aerosol contains particles from several emission sources, including ship emissions from other regions which are well-mixed in the air. Hence, the contribution from ships presented in this paper is not necessarily the total contribution from shipping, but only from one shipping lane of interest at a specific distance from the measurement site. For other variables, such as eBC measured with the Aethalometer, aerosol mass measured with SP-AMS, and aerosol number concentration of larger particles (diameter above 530 nm) measured with APS, most individual plumes were not observable through a visual inspection of the time series. For these, the contribution during the plume duration was still calculated in the same way as for particle number concentration using the same time stamps, followed by a statistical analysis (t-test) of whether this contribution was significantly larger than the background concentrations [Ausmeel et al., 2019].

The average concentration for each plume was calculated by integrating the total area under the plume peak. The values were then normalized by the plume duration to give an average plume peak concentration. All ship passages that resulted in an elevated particle number concentration, fulfilling the criteria for plume selection listed above, and which could be connected to an individual ship with AIS were included in the calculation of the average contribution from the fleet. That is, even if no plume peak was observed with e.g. BC measurements, it was still included in the calculation of the average BC. A t-test was performed to check that the value of the BC contribution within the plume was significantly higher than the background. The daily and seasonal contribution values from the shipping lane are calculated based on AIS data, which showed an average of 73 and 63 ships passing per day in winter and summer respectively. During periods when the wind blows from the Øresund Strait (i.e. across the shipping lane), the Falsterbo site is hence affected by the nearest shipping lane approximately 51% of the time in the winter, and 44% in the summer, based on the average observed plume duration of 10 min multiplied with the average number of ships per day. Based on historical wind data from the last 20 years (Swedish Meteorological and Hydrological Institute, SMHI), the wind intercepts the shipping lanes in Øresund Strait about 70% of the time in both summer and winter, which was used to estimate the seasonal contribution from ships presented in Table 1. For the daily and seasonal estimates, it was assumed that the average ship plume contributions (A_{plume}) in Table 1 is are representative for all plumes. For calculation of the uncertainty in the daily and seasonal contribution, the uncertainty in aerosol number concentration was estimated to 30 %, the uncertainty in particle loss estimation was 30 %, the variation in ship traffic density was 17-34 %, and the uncertainty in seasonal wind pattern was estimated to 5 %. These values were used to calculate the total uncertainty with error propagation, i.e. added in quadrature. For a ship plume event, the average concentration in the plume during the entire duration of the plume was used as the contribution value of that ship at Falsterbo.

3 Results and discussion

3.1 Plume identification and general characteristics

An example of a time series from the SMPS (size distribution and number concentration) and SP-AMS (chemical speciation) during wintertime is shown in Fig. 42. The middle panel also displays the times when ship plumes were expected to arrive at the measurement station based on ship position (AIS) and wind data. The plumes can visibly be distinguished from the background concentration in the time series of the particle number concentration (Fig. 42, upper and middle) as relatively short (ca 10 minutes) and intense peaks, generally matching well with expected passages. Most particles are in the lower range of the size spectrum, below 100 nm in diameter (Fig. 42, upper). This is also reflected in the volume concentration (Fig. 42, middle), which does not increase during all plume events, since the small particles do not contribute largely to the total volume compared to the background concentrations. This means that most particles from ship emissions do not contribute directly to local particle mass concentrations while the contribution to number concentration is larger. Note that this is valid at the measurement site, ca 30 min downwind of the emission source. Secondary aerosol formation can still contribute to larger mass further downwind, which is discussed in the Sect.

3.5 Simulation of atmospheric processing. In summary, several hundred ships passed the measurement station during the campaigns (approximately 70 per day), and those that were possible to attribute to a specific ship were studied in detail. Mass concentrations,

PM_{0.15} and PM_{0.5}, were calculated from particle number size distributions and evaluated for 113 plumes in the winter. Chemical composition content from SP-AMS measurements was evaluated for 15 and 18 plumes in winter and summer respectively. 76 plumes were evaluated for NO_x and 100 plumes for eBC in the winter. The lack of eBC and NO_x data as well size distributions in the summer was due to either instrument malfunction or unfavourable winds. Particles with an aerodynamic equivalent diameter larger than 530 nm did not contribute significantly to the particle number or mass concentration. This was shown by the aerodynamic particle sizer (APS 3321, TSI Inc. USA) measurements (0.5 – 20 µm). For all identified plumes, the contribution to PM_{2.5} and PM₁₀ was assessed based on APS size distribution (assuming spherical particles with unit density). For the plumes observed in this study, there was no contribution to PM_{2.5} or PM₁₀ distinguishable from background levels.

A general feature observed in both measurement campaigns is that the particle properties varied from ship to ship. As described in Ausmeel *et al.* [2019], the ships evaluated in this study varied in size, load etc. The deadweight tonnage was 1-140 kilo tonnes, (10th and 90th percentile) with a median of 6 kt. The ship speed was 5-19 knots, (10th and 90th percentile) with a median of 11 kn. The ships observed in this study were mainly of the types cargo ship, tanker, and ro-ro ship. A correlation test with linear least square regression was performed on all plume aerosol variables versus all ship properties. No significant correlation was found, even when normalizing plume concentrations for plume transport time. Hence, we could not conclude any relation between observed aerosol emissions 30 min downwind of the emission source and specific ship properties. However, for some variables there were few plumes observed, e.g. during summer when AIS data was lacking and for particle mass measurements (see table 1 and Fig. 23). A larger set of plumes would be needed for such relations to be observed, if present. Large variations between individual ships was also shown by Jonsson *et al.* [2011] at a measurement distance of 0.5-1 km from the ships. In this study, there was no data currently available on the specific fuel used by each ship or in the Baltic Sea in general. However, according to Jonson *et al.* [2015], the fuel distribution in the Baltic and North Sea in 2011 was around 74 % residual (e.g. HFO) and 26 % was distillate fuels (MDO, MGO). Further, Johansson and Jalkanen [2016] reported a 88 % decrease in SO_x and 36 % decrease in PM_{2.5} emissions from the year 2014 to 2015 in the Baltic Sea, based on AIS data and emission modelling. Strong decreases in SO_x and PM_{2.5} due to SECA implementations have also been predicted and reported in e.g. Kalli *et al.* [2013] and Jonson *et al.* [2015]. Regarding the use scrubbers to reduce airborne sulphur emissions, in the paper by Jonson *et al.* [2019] it is stated that there was an increase in the number of scrubbers used globally, from 77 vessels in 2014 to 155 in 2016. Out of these, 85 vessels with scrubbers were operating in the Baltic Sea area in 2016. This is a small fraction of the > 20 000 ships operating in the region [Johansson and Jalkanen, 2016]. Another potential explanation for the variation in plume properties could be meteorological factors. In this study we have considered wind speed and precipitation, but no detailed analysis of the plume dispersion was performed and is outside the scope of this paper. Large variations between individual ships was also shown by Jonsson *et al.* [2011] at a measurement distance of 0.5-1 km from the ships.

The fact that Falsterbo is often not affected by a large particle volume (or mass) contribution from ships could potentially be explained by the recently implemented SECA regulations, making ship owners improving or switching to other fuels. The effect of sulphur regulations on the chemical composition is discussed further in Section 3.4. In this study, we are only considering emissions from the shipping lane passing about 10 km from the measurement location. Depending on wind direction, it is also likely that the background particle concentrations contain emissions from ships in other regions, making the actual effect of ships on the local air quality larger. In a region with more ship traffic or in harbour areas, the local effects on particle levels and consequently health implications will be of larger concern.

In Table 1, the average measured plume concentration is presented together with the background concentration (i.e. without local plume contribution) as well as estimated corresponding daily and seasonal contributions of the shipping lane during winter and summer to PM_{0.15}, PM_{0.5}, NO₂, eBC, and particle number (PN) levels. The average concentration for each plume was calculated by integrating the total area under the plume peak. The values were then normalized by the plume duration to give an average plume peak concentration. All ship passages that resulted in an elevated particle number concentration and which could be connected to an individual ship with AIS were included in the calculation of the average contribution from the fleet. That is, even if no plume peak was observed with e.g. BC measurements, it was still included in the calculation of the average BC. A t-test was performed to

250 check that the value of the BC contribution within the plume was significantly higher than the background. The daily and seasonal values are based on AIS data, which showed an average of 73 and 63 ships passing per day in winter and summer respectively. During periods when the wind blows from the Øresund Strait (i.e. across the shipping lane), the Falsterbo site is affected by the nearest shipping lane approximately 51% of the time in the winter, and 44% in the summer, based on the average observed plume duration of 10 min. Based on historical wind data from the last 20 years (SMHI), the wind intercepts the shipping lanes in Øresund Strait about 70% of the time in both summer and winter, which was used to estimate the seasonal contribution from ships presented in Table 1. For the daily and seasonal estimates, it was assumed that the average contributions in Table 1 are representative for all plumes. For calculation of the uncertainty in the daily and seasonal contribution, the uncertainty in aerosol number concentration was estimated to 30 %, the uncertainty in particle loss estimation was 30 %, the variation in ship traffic density was 17-34 %, and the uncertainty in seasonal wind pattern was estimated to 5 %. These values were used to calculate the total uncertainty with error propagation, i.e. added in quadrature. For a ship plume event, the average concentration in the plume during the entire duration of the plume was used as the contribution value of that ship at Falsterbo.

The measured ambient concentrations of SO₂ and CO₂ are also shown, although individual plumes were not distinguishable from the background. SO₂ is typically of interest in ship emission studies, due to the fuel sulphur content, especially [before regulations and outside SECAs](#). At the current distance of ca 10 km from the shipping lane, SO₂ plume concentrations were too diluted to be detected and separated from ambient background levels in the winter campaign with an instrument noise level of 0.5 ppb. No measurements of SO₂ were performed during the summer campaign. It is still possible that there is a ship contribution to SO₂, but the individual peaks are smeared out so that it appears as a general increase in background level. SO₂ concentrations in Falsterbo were in general low, below 1 ppb. Ship contributions to CO₂ were also not detected, with an instrument noise level of less than 1 ppm. Therefore, it was not possible to calculate emission factors at this distance from the shipping lane.

270 3.2 Contribution to particle mass concentrations

Particulate mass concentrations were calculated from the SMPS size distributions, assuming spherical particles with a density of 1.5 g cm⁻³ [Matthias *et al.*, 2010]. Mass concentration values presented here are given in PM_{0.15} or PM_{0.5} (particulate matter in the in the range 15-150 nm or 15-500 nm). The PM_{0.15} contribution was included in this study to be able to compare with Kivekäs *et al.* (2014), who also presented this contribution. Figure S1 shows the frequency distribution of the 113 individual contributions of plumes to PM_{0.5} during the winter campaign. Most ships have a small contribution to PM, of less than 100 ng m⁻³. [A relatively low PM is expected in the strictest SECA regions compared to elsewhere, due to the strong reduction in particulate sulphate. However, there are multiple reasons for the low PM contribution observed in Falsterbo. The fuel sulphur content and the small, but existing, use of scrubbers is the first explanation, and the compliance with these regulations is indeed high. Secondly, the impact presented is from one shipping lane, and the total contribution from shipping is hence larger due to ship emissions being a source to the regional background aerosol. Thirdly, the ships in Falsterbo are relatively small compared to the rest of the Baltic and on larger seas elsewhere, since they have to pass the Øresund Strait and under bridges. Smaller ships typically have a lower engine power and emit less air pollutants on an absolute scale. Meteorological factors did not seem to influence the plume detection to any large extent, and the shipping lane contribution to ambient concentrations was similar in both the summer and winter campaign. However, longer measurements would be needed to study the effect of meteorological parameters on plume detection, and this will be of even larger importance in other measurement sites where there is risk of a build-up of a thermal internal boundary layer at the shoreline.](#)

A few ships can be regarded as relatively high mass contributors. It cannot be concluded from our results, whether the high contributors to observed plume peaks at the coastline were non-compliant to the SECA regulations. Based on the number of plumes which resulted in high PM concentrations (either BC, organics or sulphate, or all of these), compared to the number of plumes that should have intersected the measurement site based on AIS and wind data, about 2-5 % were detected by our aerosol instrumentation. This number is in the same order of magnitude as the level of non-compliance reported by [Mellqvist *et al.*, 2017], and could be related to the potentially higher emissions from such ships. In order to link these plumes to non-compliance, a more detailed study

of the stack emission and the fuel properties (or use of exhaust scrubbers) is needed. Using the average PM for all ships, the contribution to the daily PM_{0.15} and PM_{0.5} levels in Falsterbo are around 8% and 1%, respectively. The contribution during the summer and winter measurements (assuming winds carrying ship emissions during 70% of the year) was ca 8-10% and 1% for PM_{0.15} and PM_{0.5} respectively (Table 1). Hence, we show that ships in this part of the Baltic SECA generally contribute with low PM concentrations. However, although mass contributions are low in this study, they can still be higher in areas with even more intense ship traffic, or close to harbours.

In a similar study to ours by Kivekäs *et al.* [2014], their reported PM_{0.15} values were 100 ng m⁻³ within plumes, and 23 ng m⁻³ daily contribution. This compares well to our values of about 50 ng m⁻³ within plumes and 26 ng m⁻³ daily contribution. ~~There is a plausible reason why the contribution to PM_{0.15} should be similar in both the Kivekäs *et al.* [2014] and the current study. However, there are several factors impacting the particle concentrations which differ between the locations, which makes a detailed comparison for e.g. evaluating the effect of SECA regulations difficult. Namely, on the one hand, In the study by Kivekäs *et al.*, the data covers a larger ship corridor in the North Sea. Hence, the ships were also larger (had higher gross tonnage and deadweight) and the particle source is consequently not the same as in Falsterbo, and the measurements were performed before the new 2015 sulphur content regulation in the SECA in the Kivekäs study and thereby likely had higher particle mass emission factors than at Falsterbo. Additionally, On the other hand, the distance between the ships and the station is larger in the Kivekäs *et al.* study, suggesting that plumes are could be more diluted. However, the most rapid dilution occurs directly after emission, and then much slower after around 30 minutes of atmospheric transport [Tian *et al.*, 2014], which suggests that this should not constitute a large difference between the observed particle concentration between the sites. The particle mass can also be affected by the current chemical state of the atmosphere, e.g. by differences in seasons and meteorology. Hence, these effects are likely cancelling each other out, why the absolute plume PM_{0.15} contribution becomes similar in both studies.~~ According to Kivekäs *et al.* (2014), the maximum distance between ship and measurement site, for which plumes were still visible as an increase in number concentration, was about 50 km, and they suggested measurements to be performed at distances shorter than 45 minutes of transport time. In this study, we registered all plumes in particle number concentration at a distance of less than 45 minutes. However, mass concentrations and some gaseous compound were still not detectable for all ships.

In a model study by Karl *et al.* [2019], three different regional chemistry transport model systems were used to study the influence of shipping in the Baltic Sea region, including the Øresund region in which our measurements took place. The maximum annual mean PM_{2.5} contribution from shipping in the Øresund region was reported as 0.9 µg m⁻³, corresponding to a relative contribution of 10%. From our observations, ship plumes contributed with 0.029 ± 0.013 µg m⁻³ (winter) and 0.037 ± 0.020 µg m⁻³ (summer). Since we only observe the contribution from a single shipping lane, the comparatively low PM_{2.5} contribution is not unexpected. However, the factor 20-30 difference between our observations and the contribution modelled by Karl *et al.* [2019] is still large. This could potentially be explained by the emission inventory used in model simulations being older than the most recent SECA regulation. Further studies of SECA regions and the typical fuels used within these would be valuable for confirming a potential decrease in the total PM contribution from ships due to the sulphur regulations.

3.3 Contribution to NO₂

Plumes contained about 0-10 µg m⁻³ of NO₂, with a similar distribution among ships as for PM concentrations, i.e. that a few ships contributed with high concentrations while the majority of the plumes were diluted to below the detection limit of the instrument (0.1 ppm). The plume NO₂ concentrations, with background subtracted, are shown in Fig. S2, and average NO₂ values are presented in Table 1. There was in general no increase in NO concentration associated with the ships in this study. One instance of elevated NO was recorded and attributed to a pleasure craft passing very close to the station (less than 1 km away and about 5 minutes of plume transport). This type of ship is not representative for the fleet in general, and not considered in further results or discussion. Except for this case, all contribution to NO_x was in the form of NO₂ both during winter and summer, and during day and night-time. This implies that the plume transport in this case results in a well-mixed plume reaching the coast line. In a study by Karl *et al.*

[2019], the ship-related NO₂ concentrations in the Baltic Sea region were evaluated using three regional chemistry transport model systems. It was found that the contribution was 3-5 µg m⁻³ along the main shipping routes. Our observed seasonal contribution in Falsterbo of 1.21 ± 0.57 µg m⁻³ (winter) and 1.11 ± 0.61 µg m⁻³ (summer) are lower than the one presented by Karl et al. Since our measurement campaign is limited to one shipping lane, we are likely treating diluted ship emissions from further away as background emissions, and hence our calculated contribution is likely a lower estimate. The measurements presented here are also limited in time and do not cover a full year of observations.

3.4 Contribution to BC and chemical composition

The contribution from ships to measured eBC during winter was $3.5 \pm 1.7 \text{ ng m}^{-3}$, which is 42 % compared to background eBC levels (Table 1). For eBC, a very small number of ships are contributing. Most plumes show no eBC contribution at all while still increasing the particle number and mass concentration to some degree, indicating other major particle components. Within the ship plumes, the average eBC fraction correspond to approximately 52 % of the total PM_{0.5} mass. An eBC fraction of 5 % is very low compared to previous ship emission studies. The individual eBC fraction varied a lot from ship to ship, which can depend on many factors including engine operation, fuel type, and use of scrubbers. The 10 % of the plumes (n = 15) with the highest eBC mass contribution (> 20 ng m⁻³) had an average eBC fraction (±1σ) of 40±20 % of the PM_{0.5} calculated from SMPS size distributions. The absorption Ångström exponent (AAE) was calculated for the plumes, using seven wavelengths of the Aethalometer, after background subtraction, and was on average ~1, which is typical for fresh BC [Kirchstetter et al., 2004; Sandradewi et al., 2008; Zotter et al., 2017].

Previous studies have shown an increase in light absorption at shorter wavelengths in plumes, indicating a significant fraction of brown carbon (BrC) [Yu et al., 2018; Corbin et al., 2018; Corbin et al., 2019]. This was not seen in our study in the Baltic Sea SECA, which is in line with Corbin et al. [2018] who showed that burning of heavy fuel oil resulted in both BC and BrC, while marine gas oil or diesel fuel resulted in negligible BrC fractions and an AAE close to 1, suggesting that distillate fuel is dominating in our sample. Heavy fuel oil is not expected to be used to any large degree within the SECA. For the MAAP, the plumes were not distinguishable from the background due to the detection limit of the instrument. The rBC content was also measured with the SP-AMS in the winter campaign, showing similar results with low contribution in general. There are however studies that have shown a significant BC fraction in ship exhaust. Lack et al. [2009] reported an average particle composition of 15 % BC, 46 % sulphate, and 39 % organic matter. Cappa et al. [2014] measured emission factors of BC from a ship running on low-sulphur marine gas oil and found extremely small sulphate fractions, while organic matter and BC dominated the particulate matter, with approximately 63 % BC at a speed of 6.9 kn, and 25 % at a speed of 12 kn. Hence, the average BC fraction of 25 % observed in Falsterbo appears to be relatively low, even with an average speed closer to 12 kn. It has been shown that BC emission factors depend on operating conditions, fuel quality and the potential use of scrubbers for reducing sulphur emissions [Lack and Corbett, 2012]. Jonsson et al. [2011] showed that the non-volatile fraction of fresh ship emissions in a region close to Falsterbo (Gothenburg, west coast of Sweden) contributed to slightly less than 50% of the total particle population. However, it cannot be concluded whether the non-volatile fraction is consisting of soot particles or non-volatile organic compounds. In the model study of the Baltic region specifically [Karl et al., 2019], the shipping contribution to aerosol elemental carbon (EC) was found to be 0.03–0.04 µg m⁻³ along the main shipping routes and in the main ports. This is a factor of ten larger than our measured contribution of 3.5 ng m⁻³, similar to the discrepancy in NO_x, possibly due to the emission inventory being from before the most recent SECA regulation as well as the difference between the total influence from shipping contra that from one shipping lane.

Due to the small particle sizes and consequently the low mass concentration when diluted, the filter based measurement techniques are not optimal for investigating the presence of soot particles with our type of set-up (there could potentially be a high number concentration of small soot particles, while at the same time the BC concentration is low due to low light absorption). Also, the SP-AMS has a detection limit for particle size and hence some ship emitted particles at small sizes are not measured by the SP-AMS, and those that are, still contribute with a relatively small mass fraction. For further studies of ship BC emissions, other measurement

techniques, such as the Single Particle Soot Photometer (SP2) which measures individual soot particles down to ~0.3 fg, could be useful. Also extracting microscopy pictures of the PM_{0.1} fraction in fresh ship emission plumes could be useful for determining the presence of smaller sized soot particles.

The chemical composition of the ship plumes with relatively high PM contribution was provided by the SP-AMS measurements. In summary, the contribution to total PM is low with a very small or non-distinguishable refractory BC (rBC) fraction. Figure 2-3 shows the chemical composition of all plumes with a total mass concentration of more than 0.1 µg m⁻³ (in order of decreasing mass).

The average composition is inserted for each season. As seen in Fig. 23, when plumes have relatively high mass concentrations, the particles contain mainly sulphate and organics. For individual ships, there was a high variability in these fractions, but there seems to be a higher fraction of organics in the summer based on the 33 observed plumes. Out of the 33 plumes which were chemically resolved with AMS, there were 14 plumes with zero or close to zero (< 0.01 µg m⁻³) sulphate content and two plumes with zero or close to zero organics. The organic matter fraction (Org, OM) was translated to organic carbon (OC) using a conversion factor of 1.2, which is given by Canagaratna et al. [2015] for hydrocarbon-like organic aerosol (HOA). For the 17 plumes which contained both a sulphate and an organic fraction, the average Org:SO₄ (± 1 stdv) ratio was 2.3 ± 3.2. Studies of single ships or test-bed engines show largely varying organics to sulphate ratios. In the study by Murphy et al. [2009], the OC:SO₄ ratio was 0.30 ± 0.01 in an airborne exhaust plume. The ship in that paper was running on a 3 % m/m sulphur heavy fuel oil. In a study by Moldanová et al. [2009], OM:SO₄ was around 2.4 for HFO (or OC:SO₄ around 2.9, using the conversion factor OC = 1.2·OM given above), and in another study by Petzold et al. [2011], OM:SO₄ was around 0.38 for HFO and 16 for a marine gas oil (or OC:SO₄ around 0.46 and 19, respectively). Mueller et al. [2015] reported an OM:SO₄ which was around 3.8 for HFO and 515 for a marine diesel fuel (or OC:SO₄ around 4.6 and 618, respectively). There are also studies reporting chemical composition for multiple ship, measured in ambient air, which is more comparable to our observations. Based on the average OC and SO₄ in 43 ship plumes measured by Lack et al. [2009], where the emission factors were 1.21 ± 1.50 g (kg fuel)⁻¹ (36 %) for sulphate, and 1.26 ± 0.96 g (kg fuel)⁻¹ for OM, the corresponding average OM:SO₄ is then 1.04 (or OC:SO₄ around 1.25). Similarly, for the 139 ship plumes observed by Diesch et al. [2013], the average OM:SO₄ was 3.3 (or OC:SO₄ around 4.0). Our ratio of 2.3 ± 3.2 is hence in the same range as previous studies. Murphy et al. [2009] observed that the OC:SO₄ was constant during the first hour of plume dilution into the marine boundary layer. To confirm this at our measurement site, more chemically resolved ship plumes are needed.

In addition to a variable chemical content, there was also a large variation in total mass of the ship plume aerosol, where many of the plumes detected by the CPC were not seen at all in the volume and mass concentration time series (SMPS and SP-AMS), hence the relatively small number of plumes in Fig. 23. Most plumes were simply not above the SP-AMS detection limit (<50 nm) with the settings used, which was also confirmed with the SMPS particle volume. However, the particles with diameter below 50 nm will not contribute largely to the total mass and the results presented here are hence focusing on the plumes with the largest PM contribution. Whether the difference in mass and specifically, the organic fraction, is significant between seasons require further measurements.

In one instance, the plume from an individual ship was detected multiple times. This is indicated with symbols in Fig. 23, where the ship passed the Falsterbo peninsula on three different occasions during the winter campaign. All plumes were detected during night time, and the ship-to-site distance and the transport time was similar (12-15 km and 20-30 minutes) during all occasions. The chemical composition and the total mass is similar for the plumes from this ship, with similar fractions of sulphate and organics, compared to the large variability between different ships. This suggests that there is reproducibility in the method. For future studies, AIS data can be used to deduce which ship and engine types and fuels used are responsible for the increases in number and mass concentrations. For the organic fraction of the particles from all of the 33 ships plumes measurable by the SP-AMS, a larger amount of organics was seen in the plumes during summer. Comparing the mass spectra (Fig. 23) shows that the organic ship aerosol is very similar in winter and summer, which strengthens the validity of the method used. The organic aerosol mass spectrum of the ship plumes in Falsterbo is similar to that measured in a laboratory study by Mueller et al. [2015], as well as in ambient conditions measured by Murphy et al. [2009] and Lu et al. [2006]. The dominant hydrocarbon fragments are in general similar to those observed

in aerosols from other traffic sources such as diesel emissions [Canagaratna et al., 2004]. Elemental analysis of carbon, oxygen, and hydrogen content was performed according to Canagaratna et al. [2015] and resulted in similar O:C and H:C ratios in both campaigns. The O:C ratio in the plume was 0.20 in winter and 0.21 in summer, while the H:C ratio was 1.89 in winter and 1.73 in summer. Hence, there is no indication of particularly stronger oxidation or aging of the plumes in the summer, possibly due to the relatively short transport time.

3.5 Simulation of atmospheric processing

Figure 3-4 shows an overview of the results from simulated aging with an OFR of ship plume aerosol during the summer campaign. During the reactor period, the ambient aerosol particles were dominated by organics (78% by mass) and sulphate (14% by mass). The wind direction during the OFR experiment was mostly 90-180°, making the distance to ship lanes a few kilometres longer compared to periods with westerly winds. Also, the wind speed was typically lower during the OFR period, making the transport time of the plume about 90 minutes long compared to about 30 minutes during westerly winds. The reactor mainly changed the aerosol in two ways. A large number of small particles were produced and the O:C ratio was increased. The number of particles increases because a super saturation of condensable vapours is produced as the aerosol enters the highly oxidizing environment. In the atmosphere, the production rate of these vapours is lower and instead of nucleating they would likely condense onto pre-existing particles. The ratio between reactor and ambient mass was mostly between 0.8 and 1.2. Much of this variation can be explained by the naturally changing ambient concentrations, since the enhancement is calculated as an average of reactor and bypass measurements varying with time. Notably there is no PM formation in the OFR in periods where no plumes are predicted. The contribution of precursors from individual ships cannot be extracted from the data due to mixing in the OFR. Although there are periods of significant secondary PM formation (Fig. 3-4), considering the predicted number of plumes impacting the site, it is clear that most plumes did not contribute measurable amounts of secondary PM (as produced by the OFR). For example, none of the plumes (n=28) that were sampled during the last day (2016-06-07) of the experiment resulted in a net increase in PM₁ after simulated aging. However, for the period during which plumes produced secondary PM in the reactor (2016-06-03 and 2016-06-04), rather high concentrations (several µg/m³) were produced (see Fig. 3-4). Assuming only one plume per hour is actually causing the secondary PM results in 19 out of a total of 154 ships, i.e. 12 %. Assuming all ships sampled in a given hour contributed to the secondary PM results in 60 out of a total of 154 ships, i.e. 39 %. As some of the 154 plumes may individually contribute below the detection limit (indeed this seems likely) and we cannot rule out interferences from non-ship sources, we consider 39% an upper limit on the fraction of ship plumes which contributed to secondary PM in our OFR experiment. Considering that none of the observed plume concentrations was above one µg/m³ without OFR processing (see Fig. 2-3), this suggests that more PM forms in the plumes further downwind of the measurement site.

As shown in Fig. 3-4, some periods of secondary particle formation were observed in the reactor. The increase was due to sulphate and secondary organic aerosol (SOA) formation. Figure 4-5 shows one of these periods with a higher time resolution, where several consecutive OFR engagements result in high (up to a factor ~2) increases in PM₁ from secondary aerosol formation. Particle volume increases during the periods with secondary PM formation in the OFR was a factor 1.5-2.5 and the absolute mass increase was several µg m⁻³. While both estimated volume from the SMPS and mass concentration as measured by the SP-AMS increased simultaneously during OFR processing, the magnitudes of the increase are not the same due to changes in the SP-AMS collection efficiency, as further discussed in the OFR section of the S.I. The increases in nitrate and ammonium (~~from oxidation of NO_x followed by neutralization by ammonia~~) were moderate on an absolute scale. During the periods where no ship plumes were predicted, the difference between reactor and ambient measurements was close to zero, suggesting no net secondary formation from aging of the background air mass, and negligible particle losses on a mass basis.

Modelling of the fate of produced low-volatile species (Supporting Information and Fig. S4) suggests that a significant portion (~60-90%) of the oxidation products do not enter the particle phase due to the low condensation sink. Although the model was set up for organics, this is true for all secondary aerosol species formed in the reactor. Particulate nitrate formation will also be sensitive to

465 [the availability of gas-phase ammonia to neutralize the aerosol](#). There was no diurnal trend in the enhancements, in contrast with previous OFR field campaigns in urban [Ortega *et al.*, 2016] and forested areas [Palm *et al.*, 2016]. This may be caused by the [background](#) air masses reaching the site already being somewhat aged and precursor concentrations being low. Further, the fact that the reactor was kept in an air-conditioned space increases the losses when it is colder outside (e.g. during nights), which was also seen by Ahlberg *et al.* [2019]. No trend in the enhancement of particle mass with OH exposure was seen, likely due to the comparably low exposures. Ambient O:C and H:C ratios, commonly used as a proxy for atmospheric age, were on average 0.62 ± 0.15 and 1.53 ± 0.15 (1σ) respectively. The reactor produced an organic aerosol with a significantly higher O:C ratio (0.76 ± 0.17) while H:C was not affected to any large degree (1.51 ± 0.16). The O:C increase at times when aerosol mass was not increased (i.e., for the background aerosol and the majority of the plumes), suggests either heterogeneous oxidation or that SOA mass was formed and lost in similar magnitudes.

470 While the bulk of the secondary PM formed was due to organic compounds (see Fig. 34) two OFR engagements, shown in Fig. 45, additionally resulted in high sulphate formation. The increase in sulphate upon processing, which was not observed for the vast majority of the approximately 100 plumes sampled, was possibly due to failure to comply with the Sulphur Emission Control Area regulations. No SO₂ data is available from the same period. [In future ship emission campaigns, both SO₂ and VOC measurements would be useful for evaluation secondary PM formation and as tracers for ship emissions in general.](#) OFRs can be used for qualitatively observing ships that contribute a lot to secondary aerosol inland, but should preferably be placed closer to the shipping lanes. Care must also be taken to ensure that reported secondary particle formation is not influenced by the background condensation sink [Palm *et al.*, 2016; Ahlberg *et al.*, 2019].

4 Summary and conclusions

480 Ship emission plumes from the Øresund Strait were sampled with several on-line aerosol measurement techniques at a coastline in Southern Sweden during the winter and summer of 2016. A few up to a hundred plumes were analysed for particle mass contribution (PM_{0.15} and PM_{0.5}), particle chemical composition, and gaseous NO₂. The aerosol particles were exposed to additional atmospheric ageing using an oxidation flow reactor. The ageing of the background aerosol at Falsterbo in the oxidation flow reactor did not show significant increases in secondary mass, despite an increase in the O:C ratio. We suggest that the reason for this is that the [regional](#) background particles [from long-range transport](#) arriving at Falsterbo are already relatively aged. During the limited flow reactor measurements, there were a few cases with clear increase in sulphate and organic mass behind the flow reactor. However, the distance from ships during these days is relatively large and the contribution from individual ships is not clear, which means that further studies are needed to infer how aged shipping particles can influence particle exposure. Falsterbo would be a good place to do further oxidative ageing experiments, but with slightly different setup than used in this study and for a longer time period. A common observation for all aerosol parameters was large ship-to-ship variations in aerosol properties and plume concentrations, and these variations were not found to be correlated with any specific ship properties or plume transport time. Hence, the differences can be attributed to meteorological effects or variable exhaust properties. To determine which effect is most dominating, further studies are required. For example, successful CO₂ measurements would make it possible to calculate emission factors of the aerosol species. To measure CO₂ in ship plumes, the measurements should either take place closer than 10 km from the emission source, or instruments with high sensitivity (better than < 1 ppm) must be used. During these measurement campaigns, ships in this part of the Baltic Sea SECA did generally contribute with low PM concentrations. The PM was dominated by organics and sulphate, in varying fractions, and the organic mass spectrum did strongly resemble that of typical diesel emissions. We were able to detect BC in plumes with one out of three instruments measuring BC, namely the Aethalometer. The AAE of the ship BC was close to 1, indicating diesel like fuel being common rather than heavy fuel oil, which is to be expected within a SECA. The contribution to eBC concentrations was relatively small, on average 3.5 ng m^{-3} , like the contribution to PM_{0.5} exposure in general. The eBC fraction of the total mass was approximately 25 % in the diluted plumes, which is small compared to other ship emission studies. The BC

contribution of ships sailing along shipping routes in this region is relatively small as has been demonstrated in this study. This indicates smaller health impact due to BC compared to other anthropogenic BC sources. However, health effects due to other particle parameters might be significantly larger. For example, exposure to particle number concentration (Ausmeel et al., 2019), organic compounds, and NO_x is higher. Although PM contributions are low in this study, they can still be higher in areas with more intense ship traffic, close to harbours, or in non-SECA regions. The regional impact of ships is higher than that measured in this study, since the background levels in Falsterbo also contain ship emissions from more distant shipping activities. This contribution is diffuse compared to the individual ship plumes and therefore not possible to assess with our method. Hence, we expect an additional gaseous and primary and secondary aerosol particle contribution from ships sailing further away than about 30 km from the coastline. In addition, our OFR measurements indicate a possible secondary aerosol PM influence.

Data availability

The data sets used in this study are available upon request from the authors.

Supplement

Frequency distribution of the individual contributions of ship plumes. Technical details regarding the oxidation flow reactor, including measured and modeled losses. Comparison of SP-AMS and SMPS mass measurements during OFR periods.

Author contributions

SA analysed the aerosol data, was responsible for project administration during the summer campaign and prepared the manuscript. AE was involved in the aerosol sampling and assisted in the data analysis and in the writing process. EA was involved in the aerosol sampling, conducted PAM-OFR experiments and analysis, prepared this section of the manuscript, and assisted in the data analysis and in the writing process. MKS generated trajectories used in the PAM-OFR analysis and assisted in the writing process. MS was involved in the aerosol sampling and in the writing process. AK designed the study, developed the model code, was responsible for project administration during the winter campaign and assisted in the writing process.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgement

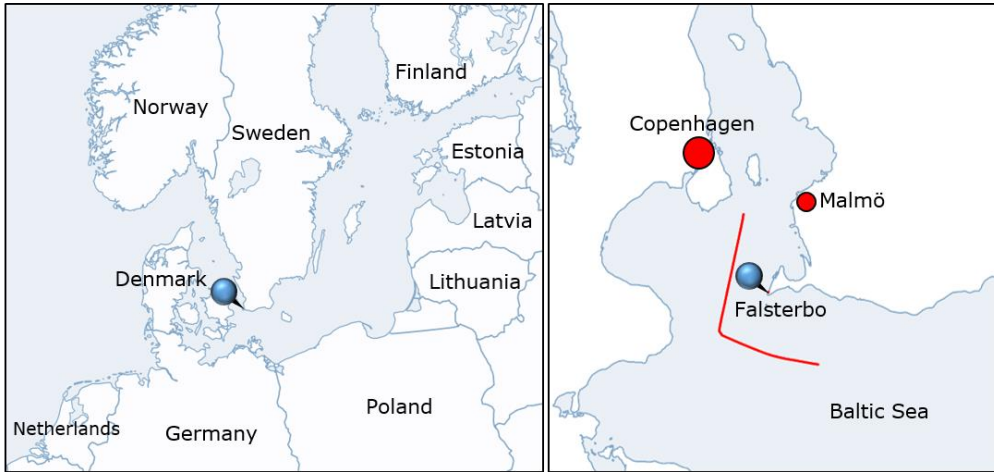
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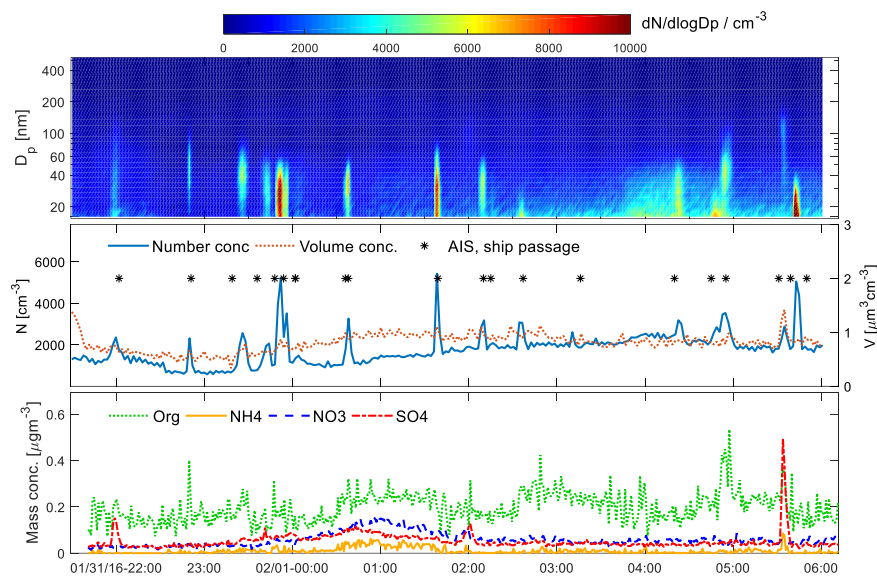
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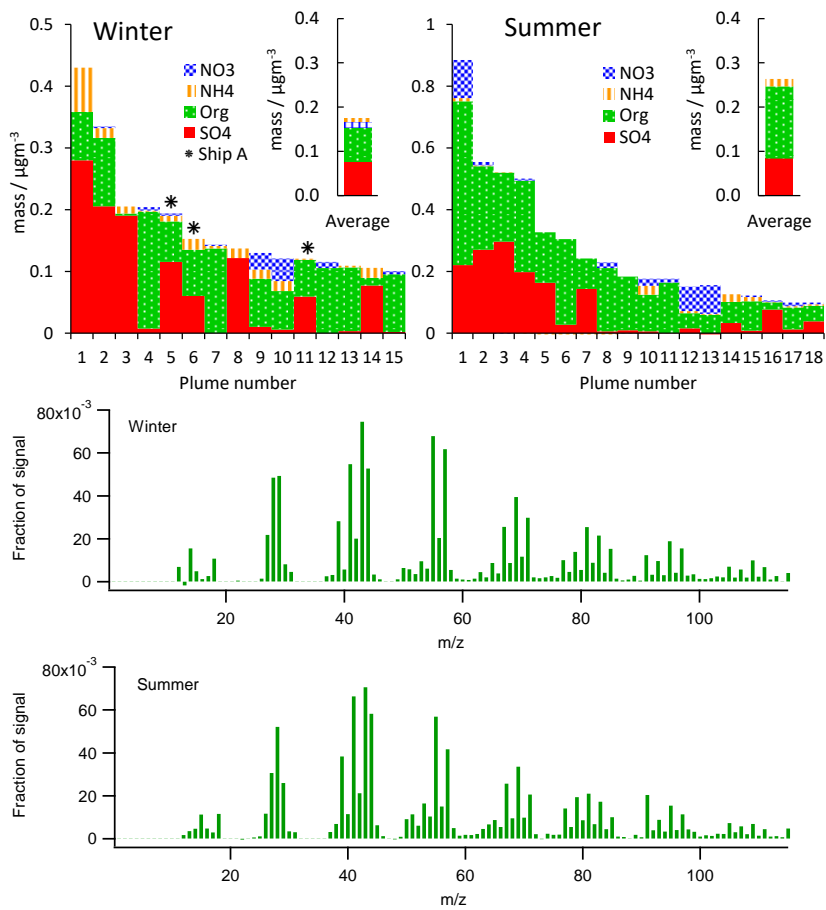


715 **Figure 1.** Map of the Baltic Sea region (left) and the nearby region around the field site (right). The measurement site Falsterbo is marked with blue pin, and the nearby large cities Copenhagen and Malmö are marked with red circles. The red line shows a typical route of a ship following the main shipping lane around the Falsterbo peninsula, based on AIS position data.

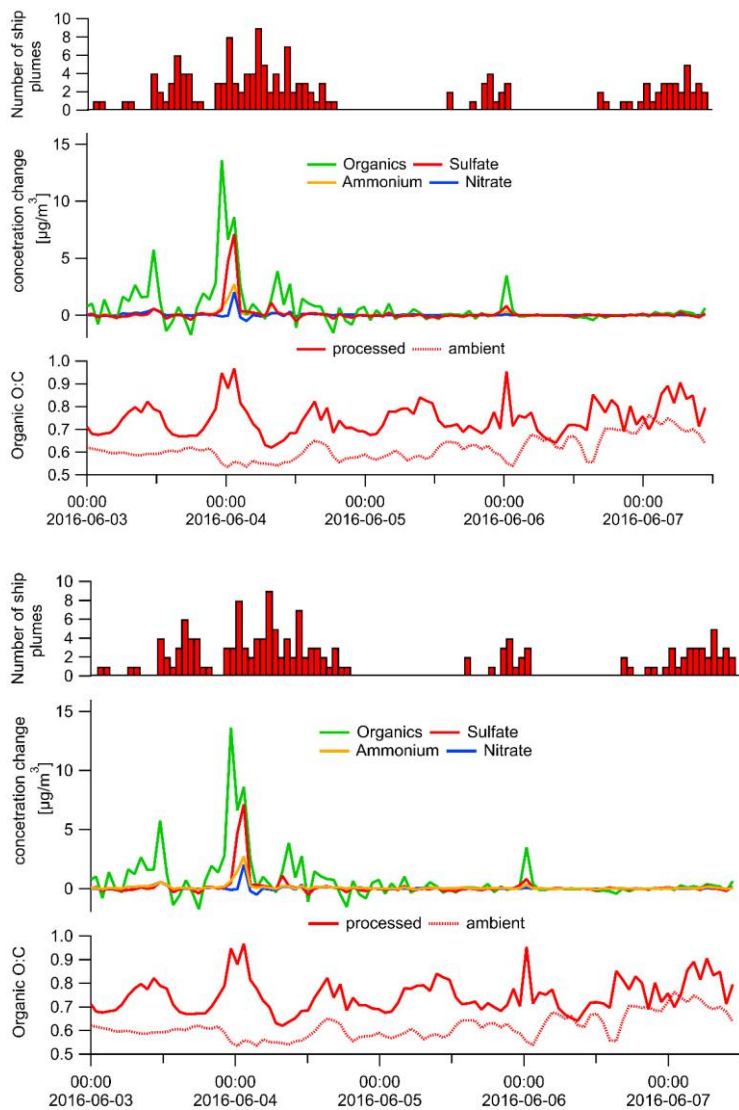


735 **Figure 12.** Aerosol particle properties measured with an SMPS and an SP-AMS versus time (31 Jan. – 1 Feb. 2016), from measurements at the coastline in southern Sweden during an episode with westerly winds blowing from the Øresund Strait to the coastal station Falsterbo. The concentrations are those of the total aerosol, i.e. background concentrations are not subtracted. Top panel: 2D-Colour plot of total particle number size distribution from the SMPS. Middle panel: The total number- and volume concentrations from the SMPS and incidents of ship plume passages determined with AIS and meteorological data. Bottom panel: Concentration of the chemical constituents from the SP-AMS; total organics (Org), ammonium (NH₄), nitrate (NO₃), and sulphate (SO₄). The wind direction (269±14 degrees) and wind speed (8.7±1.1 m s⁻¹) can be considered stable during this period.

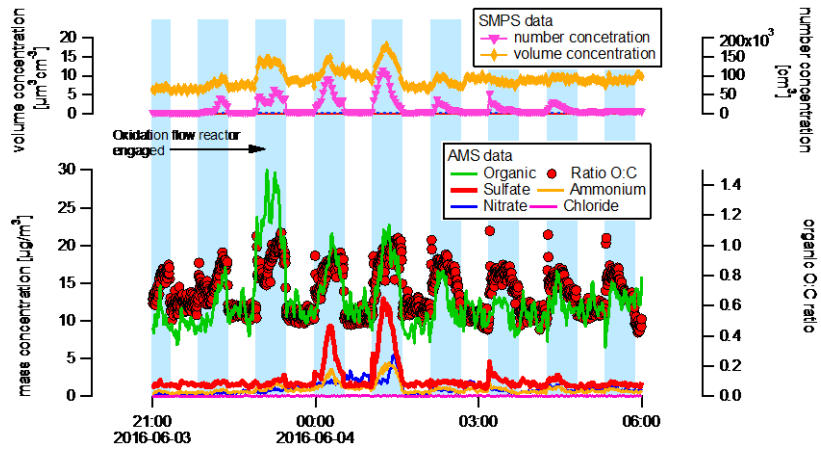
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745 | **Figure 23:** Top panel: Mass concentration and composition of the particle constituents nitrate (NO₃), ammonium (NH₄), total organics (Org), and sulphate (SO₄) of ship plumes with an average mass content larger than 0.1 μg m⁻³, measured with the SP-AMS. Left plot shows plumes in winter and right shows plumes in summer sorted in decreasing order of total mass conc. Inserted bar plot shows the average of all plumes. The stars mark the plumes from the same ship passing at three different occasions (plume no. 5, 6, and 11). Middle and bottom panel: average organic mass spectra of plumes in the winter and summer measured with the SP-AMS.



750 **Figure 34:** Overview of an Oxidation Flow Reactor (OFR) experiment in the summer. Top panel: Number of ship plumes sampled. Middle panel: chemical species concentration change upon OFR processing. Bottom panel: organic O:C ratio after (processed) and before (ambient) OFR. Due to the alternating OFR/bypass sampling all data are hourly averages.



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Figure 45: Atmospheric processing simulated through an Oxidation Flow Reactor (OFR). OFR measurements are shown in light blue background. Top panel: SMPS number and estimated volume concentration. Bottom panel: SP-AMS chemical species concentrations and organic O:C ratio.

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Table 1: Average absolute contribution of particle mass (PM), NO₂, equivalent black carbon (eBC), particle number concentration (PN), SO₂, and CO₂ to local air quality due to a number (*n*) of ship plumes, from two measurement campaigns at the Falsterbo coastal site.

Season	Variable	Back-ground conc. ^g	Average plume conc. ^g	Contribution		<i>n</i>
				Daily ⁱ	Seasonal ⁱ	
Winter	PM _{0.15} (ng m ⁻³) ^a	280	50	26 ± 12	18 ± 8	113
	PM _{0.5} (ng m ⁻³) ^a	2440	80	41 ± 19	29 ± 13	113
	NO ₂ (µg m ⁻³)	4.4	3.4	1.73 ± 0.81	1.21 ± 0.57	76
	eBC (ng m ⁻³) ^b	210	9.9	5.0 ± 2.4	3.5 ± 1.7	100
	N / cm ⁻³ (CPC ^c , 4 nm-10 µm)*	1320	750	380 ± 180	270 ± 130	109
	N / cm ⁻³ (SMPS ^d , 15-532 nm)*	1200	700	360 ± 170	250 ± 120	113
Summer	PM _{0.15} (ng m ⁻³) ^a	500	110	48 ± 27	34 ± 19	8
	PM _{0.5} (ng m ⁻³) ^a	2720	120	53 ± 29	37 ± 20	8
	NO ₂ (µg m ⁻³)	3.6	3.6	1.58 ± 0.88	1.11 ± 0.61	17
	N / cm ⁻³ (CPC, 4 nm-10 µm)*	2610	860	380 ± 210	260 ± 150	61
	N / cm ⁻³ (SMPS, 15-532 nm)*	2530	1470	650 ± 360	450 ± 250	8
Both	SO ₂ (ppb) ^e	0.20	<DL ^h	-	-	-
	CO ₂ (ppm) ^f	430	<DL	-	-	-

* Value from [Ausmeel et al., 2019]

^a Based on size distribution data.

^b Based on Aethalometer data (880 nm).

^c Condensation Particle Counter

^d Scanning Mobility Particle Sizer

^e Plume concentrations not distinguishable from background, instrument noise level is < 1ppm, according to manufacturer.

^f Plume concentrations not distinguishable from background, instrument noise level is < 0.5 ppb, according to manufacturer.

^g The background particle and gas concentrations (Background conc.) and the contribution due to ships (Average plume conc.) to different pollutants. Each value represents an average of a number of plumes (*n*) and are calculated from the ship plume peaks average concentration (i.e. concentration per unit time).

^h Below detection limit (<DL).

ⁱ "Daily" values refer to days with wind directions where ships affect Falsterbo (mainly westerly) and "Seasonal" values refer to the average contribution observed at each campaign extrapolated over one season, including all wind directions.

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