Responses to Reviewer #2

We thank the reviewer for the detailed comments regarding our paper and for the suggestions.

(2.1) Nuleation. Fig. 2 appears to be only the direct validation of the ship-plume model, in terms of total aerosol number concentrations (also just over "70 minutes" after ship plume release). But it appears that the model does not include "nucleation" parameterization (based on Eq. 2). The nucleation is an important process for the "total aerosol number concentrations". Although I understand that it is extremely difficult to correctly simulate the aerosol number concentrations generated from the nucleation process, it is still of great significance, because inside the ship plume H_2SO_4 mixing ratios are so high (authors also mentioned the presence of high levels of NH_3 in the background air and high relative humidity of 90%). These conditions would create very favorable condition for nucleation. Therefore, without the consideration of the nucleation process, I do not think that the model can produce realistic total aerosol number concentrations.

> *We agree with the reviewer that the process of nucleation may be important for the ship plume environment and deserves more discussion in our manuscript. While PartMC-MOSAIC is in principle able to treat nucleation, the observations do not indicate that nucleation occurred, therefore we did not simulate this process. We included the following explanation in the paper to explain this (page 18, line 11):*

> *"The process of new particle formation was not included in this study. During the QUANTIFY study, there was no direct measurement of new particle formation due to the SMPS (size distribution) measurement range from 15 nm to 25 μm. However, the emission factor of total aerosol above 4 nm as well as for Aitken mode aerosol above 10 nm do not show a large difference. This suggests that nucleation was not occurring after the first plume crossing. Due to the high fraction of non-volatile particles providing a surface for secondary aerosol to condense on it is unlikely that nucleation ocurred before the first plume crossing, but we cannot exclude this possibility. The initial aerosol distribution shown in Table 3 indicated a volatile mode which consisted of 100% sulfate and a high number concentration of 2.29×10^{15} m^{-3}. We assumed that this volatile mode in the initial condition represents newly formed particles at the time of emission."*

(2.2) Dilution rate. Authors incorporated von Glasow et al.'s parameterizations in this study. But, the turbulent dispersion of the ship plumes is dictated primarily by the stability conditions of the marine boundary layer. The changes in the stability conditions would greatly affect the aerosol number concentrations by the orders of magnitude. This model validation issue is related to the omission of sensitivity analysis to the abovementioned factors such as nucleation, stability condition of the marine boundary layer and emission rates of particles from ship. Authors have to show some results of these sensitivity studies. Otherwise, there would be huge uncertainty (or possible errors) in keeping track of the aerosol number density inside the ship plume, e.g., in the analysis like Fig. 2.

> *We followed the reviewer's suggestion and performed additional sensitivity studies that explore the sensitivity to the handling of the dilution rate.*

> *We modified the manuscript as follows:*

> - *We added a sentence in Section 3.3 to clarify how we obtained the mixing height (Page 14, line 20): "The mixing height was derived from the vertical potential temperature profile."*

> - *We added a discussion about studies in the literature that explored the sensitivity to the dispersion parameters (Page 8, line 25): "von Glasow et al. [2003] evaluated the influence of mixing by varying α between 0.62 and 1. The value of $\alpha = 0.62$ was deemed unrealistic as it caused a strong and persistent separation between plume and background air, which is not expected to occur in the marine boundary layer. Values of $\alpha > 0.82$ caused very strong mixing, most likely only valid in extremely turbulent conditions. From this von Glasow et al.*

[2003] concluded that $\alpha = 0.75$ was appropriate to characterize the plume dispersion. Petzold et al. [2008] derived the values of α and β by fitting simulated excess CO_2 as a function of plume age to the observed data. The result of $\alpha = 0.74$ to 0.76 agreed well with the "best guess" from von Glasow et al. [2003], while their result for $\beta = 0.70$ to 0.80 was somewhat higher. While we will use the values of $\alpha = 0.75$ and $\beta = 0.6$ for our base case, we will also explore the sensitivity to changes in these parameters in Section 4.2 below."

- *We have conducted sensitivity studies on different α and β values and updated Fig. 3 (used to be Fig. 2) to include the results from these sensitivity runs. We added a sentence in the caption of Fig. 3: "The four broken lines represent results from sensitivity runs with different sets of values for α and β."*

- *We added a new paragraph in Page 18, after line 21 to discuss the sensitivity results: "To explore the sensitivity to the choice of the dispersion parameters α and β, we conducted four sensitivity runs: Two sensitivity runs use the base case value of $\alpha = 0.75$, but combine it with $\beta = 0.7$ (lower end from the range in Petzold et al. [2008]) and $\beta = 0.5$, respectively. Two additional sensitivity runs use the base case value of $\beta = 0.6$, combined with $\alpha = 0.87$ and $\alpha = 0.62$, respectively (same range of values used in von Glasow et al. [2003]). The simulated number concentration from the sensitivity runs were added to Figure 3 as broken lines. The parameter combination ($\alpha = 0.62$, $\beta = 0.6$) results in a consistent overprediction of the number concentration by a factor of about 3, while the combination ($\alpha = 0.87$, $\beta = 0.6$) underpredicts the number concentration after a plume age of 30 min. Differences due to variations of β are most noticable during the first 20 min of the plume. Given the simplicity of the model assumptions, we do not attempt to perform a fitting procedure, but conclude from this exercise that using parameter set of our base case ($\alpha = 0.75$, $\beta = 0.6$) captures the observed data reasonably well. Importantly, the spread caused by varying α and β is less than the difference between the base case runs with and without coagulation."*

(2.3) Chemical composition. I wonder if the QUANTIFY aircraft measurement data did not include chemical composition such as the concentrations of sulfate, nitrate, ozone, HNO_3, NO_2, SO_2 etc.. If these are available, authors should compare this composition with the modeled ones for the model verification.

During the QUANTIFY campaign, no measurements were made that followed a particular plume for several hours, therefore there is no dataset available to compare our 14-h simulation to. However, some gas phase species were measured in the shipping corridor, which can be used for qualitative comparison. We included the following discussion on page 17, line 12: "No observations are available that followed the evolution of a particular plume for several hours, hence a quantitative comparison to our simulation results is not possible. However, mixing ratios of NO, NO_y, O_3, SO_2, and CO were measured in the shipping corridor on June 11 2007. These can be used for qualitative comparison with our model results. Peak values of NO, NO_y, and SO_2 mixing ratios were 4 ppb, 12 ppb, and 4 ppb, respectively. Mixing ratios for O_3 and CO are approximately 35 ppb and 105 ppb, respectively. These are values that are reached after appoximately 7 h of simulation time of the sensitivity run (right column in Figure 2). The mixing ratios of NO and O_3 of the base case are somewhat lower because this case extends into the nighttime."

(2.4) Condensation. This manuscript greatly focused on coagulation, and then investigated particle-based/resolved chemical (e.g. internal-external mixing) and physical (e.g. CCN activities) aging. However, the dominant factor determining the mixing state may not be coagulation but condensation, since coagulation is slow but condensation is much faster process. For instance, H_2SO_4 condensation onto BC and sea-salt particles would be faster and more effective than sulfate particle coagulation. Being related to this issue, Fig. 5 only shows the coagulation effects and pp.16737 -16740 concentrates on coagulation too much. How about the impacts of HNO_3 & N_2O_5 condensation onto particles (i.e., nitrate formation), e.g. on CCN activity?

The modeling focused on those properties which were accessible by observational data. Since aerosol data rely heavily on CPC data coagulation processes can be compared because they are reflected in the number concentration measured in the plume while condensation processes which do not change the number of particles but their size are not accessible by CPC data only.

The base simulation case started in the afternoon, at 2 pm local time, so the effect of condensation processes was limited. We contrast this with the sensitivity case starting from 6 am, where photochemical reactions play a bigger role. The effect of condensation can be seen in Fig. 5 and Fig. 9(b), where both of the particle size and CCN concentration were increased after about 6 hours of simulation.

Nitrate formation does play a role, especially for the sensitivity run, starting at 6am. We added the time series for the nitrate concentration to Fig. 2 (used to be Fig. 1). We also added a sentence on page 17, line 8:

"Likewise, the nitrate mass concentration increased to about $5.5\ \mu g\,m^{-3}$."

We also rephrased a sentence at the end of section 5 to highlight the importance of condensation:

"For conditions with higher formation rates of secondary aerosol mass, condensation and coagulation acted combined so that coagulation did have an impact on CCN concentration even at low supersaturation levels.

Other issues:

(2.5) P. 16734: 6 - 10. Again, this conclusion could be changed, if the nucleation parameterization and other dilution schemes were introduced to ship-plume modeling.

For the reasons mentioned in the response to point (2.1), we didn't consider nucleation in this study. The additionally performed sensitivity studies to explore the sensitivity to the dilution assumptions as discussed in the response to point (2.2) did not change this conclusion, so we left the text unchanged.

(2.6) P. 16739: Eqs. 3&4. In Eq. 2, authors have to explain how to calculate "water transfer". I guess that the thermodynamic aerosol module (MTEM & MESA) may have a calculation component, but the important thing is again that the water condensation (particulate water formation) would be one of the main processes that can determine "aerosol size distribution" (such as Fig. 3), particularly under such a high relative humidity condition at RH=90%. In addition, in Eq. 3, authors have to explain more about gas-particle transfer (i.e., condensation of atmospheric species), because this is very important process in determining the aerosol mixing state and aerosol size distribution.

We agree with the reviewer that the water uptake of the particles will greatly alter the particles' wet diameters, and thus the size distribution based on wet diameter will change. However in our paper we always use particle dry diameter for size distribution plots which is common in the literature.

We intentionally separated the governing equations (Section 2) from the numerical implementation (Section 3), but we inserted an additional sentence after equation (3) (page 8, line 5): "The relevant references regarding the numerical implementation are provided in Section 3".

The details of the thermodynamic module MESA-MTEM and the gas-particle partitioning module ASTEM are described in detail in the cited papers [Zaveri et al., 2008, 2005b,a], and since these are well-established model capabilities at this point, we refer to these papers without explaining the details.

(2.7) P. 16740: 6-12 & p.16741: 1-3. Authors should show some sensitivity analysis about α and β. In the same context, the initial ship-plume cross section (w_0 and h_0) can also be important parameters.

We performed additional simulations to explore the sensitivity towards α and β (see response to point (2.2)). We did not perform additional sensitivity studies regarding w_0 and h_0, since these parameters do not appear in the expression for the dilution rate coefficient λ_{dil} (equation 6), which is the relevant parameter that enters equations (2) and (3).

(2.8) P. 16742:9-27. This is a bit lengthy explanation about particle-resolved MC model. I understand this is a stochastic model, but is there such a big computation burden, because this is a "box model" simulation?

"Box model" simulation simply means that we simulate a well-mixed box, without resolving spatial gradients. We included a sentence on this modeling approach, which is very common in the literature, on page 5, line 15:

"Inherent to the parcel modeling approach is the assumption that the plume is immediately well-mixed. Within the air parcel we do not track the physical location of aerosol particles, and we assume homogeneous meteorological conditions and gas concentrations. Concentration gradients across the plume cannot be resolved with this approach and would require the use of a spatially-resolved 3D model framework".

The computational burden arises because we resolve many individual aerosol particles and their composition. We shortened this paragraph somewhat to make it more concise. Specifically we removed the following sentences: "For example, for the simulations presented in this paper, the initial number concentration of the coarse mode was around 10^{10} m^3 and approximately 10^{15} m^3 in the volatile nucleation mode (see Table 3)." "We computationally overrepresent the rare but important particles and underrepresent the common particles."

(2.9) P. 16743: 2-5. Coagulation may be important (or fast) only between very small particles and large particles. However, again nucleation governs the number concentrations of the very small particles (nucleation-mode particles).

As explained in the response to point (2.1), we did not explicitly simulate the process of nucleation. However, we assume that the particles represented by the "volatile mode" of the initial condition (Table 3) originate from nucleation, and are therefore included in the simulation. These are indeed small particles (geometric mean diameter of 15 nm), and they are initially present in high concentrations, however their concentration quickly decreases due to coagulation (in addition to dilution) as is shown in Figure 5.

(2.10) P. 16747: 14-19. Again, more important process for aerosol chemical evolution is condensation (of H_2SO_4, HNO_3, N_2O_5, SOA precursors etc.) than coagulation. This chemical modification is important further for CCN activity, as discussed by authors.

The reviewer is right in that condensation can be important for CCN activity, and we show this in section 4.5. We conducted a sensitivity simulation starting from 6 am local time to investigate the effect of condensation, and we quantify the impact of condensation on CCN activity (as a function of environmental supersaturation) in Figure 8.

The modelling focused on those properties which were accessible by observation data. Since aerosol data rely heavily on CPC data coagulation processes can be compared because they are reflected in the number concentration measured in the plume while condensation processes which do not change the number of particles but their size are not accessible by CPC data only.

(2.11) P. 16748: 16-20. Denitrogen pentoxide (N_2O_5) is NOT reservoir species in NO_y. N(V) species such as HNO_3 and nitrate are reservoirs in NO_y.

We changed the sentence in Page 16, line 15, now the sentence reads: "The NO_2 mixing ratio was further decreased after 6 h due to nighttime chemistry to form dinitrogen pentoxide (N_2O_5) and other reservoir species."

(2.12) P. 16748: 24. Sulfate and BC were "diluted", not "depleted". Words should be used more carefully.

We changed the phrasing of this sentence on Page 16, line 22. The sentence now reads: "sulfate and BC started out with high initial mass concentrations and their concentrations decreased very quickly due to dilution. "

(2.13) P. 16749: 1-4. SOAs were formed via the oxidation of alkenes with ozone and NO_3, too.

We modified the sentence in Page 16, line 27, now it reads: "The lack of production of secondary aerosol mass was a result of the low mixing ratios of oxidants (such as OH, O_3 and NO_3) in the plume,"

(2.14) P. 16752: 16-20. Particle growth due to condensation of atmospheric species and water can also alter the aerosol number-size distribution greatly.

We added the following sentence to clarify this point (page 21, line 20):

"Note that other secondary aerosol species form as well and contribute to a change in mixing state, such as secondary organic aerosol and aerosol nitrate, however for brevity we do not include these results as figures."

Note that we plot size distribution versus particle dry diameter.

(2.15) P. 16764 Table 2. The level of paraffin carbon (PAR) is almost the same level of sulfur dioxide (SO_2) and is even higher than that of CO. This is really high level (or large emission). NMVOC emission is usually from evaporative and fugitive emissions (from engines, pump, joints, and storages...), not from combustion. It appears that this level is too high. Obviously, this will affect ozone and OH mixing ratios, SOA formation, and particle growth and chemical evolution inside the ship plumes. Therefore, authors have to consider this factor more seriously. Regarding the NMVOC emissions from ships, there are numerous articles available.

The NMVOC mixing ratios in Table 2 appear high because we report mixing ratios of the surrogate model species as appropriate for the carbon bond mechanism (CBM-Z) used in this study. In the framework of a carbon bond mechanism the model species represent the mixing ratios of constituent groups regardless of the molecule to which they are attached. For example, suppose there was a mixture of 1.0 ppmV of butane and 1.0 ppmV of propene. These chemical species would be grouped as 4.0 ppmC PAR ("paraffin carbon") from the butane and additional 1.0 ppmC PAR and 1.0 ppmC OLET ("terminal olefin") from the propene for a total of 5.0 ppmC PAR and 1.0 ppmC of OLET [Stockwell et al., 2012].

The total mixing ratio of initial NMVOCs from the test-rig study was $1.39 \cdot 10^5$ ppb [Petzold et al., 2008]. We then partitioned the total NMVOCs to different categories including (1) hexanes and higher alkanes, (2) ethene, (3) propene, (4) toluene, (5) xylene, (6) trimethylbenzenes and (7) other alkenes based on the composition fraction provided in Eyring et al. [2005]. Finally, we converted the mixing ratio of these measured species to model surrogate species mixing ratios (see Table 10 in Zaveri and Peters [1999] for a mapping of chemical species and their CBM-Z representation).

Table 2. Gas phase initial and background conditions.

Ship-engine exhausts[a]		Model inputs		
Measured species	Conc. (ppbV)	CBM-Z species[b]	Initial (ppbV/ppbC)[c]	Background (ppbV)[d]
NO_x	9.14×10^5	NO	8.77×10^5	1.86×10^{-2}
CO	3.4×10^4	NO_2	3.7×10^4	3.95×10^{-2}
SO_2	4.7×10^5	HNO_3	0	3.29×10^{-1}
NMHC	1.39×10^5	O_3	0	3.39×10^1
		CO	3.4×10^4	1.05×10^2
		SO_2	4.7×10^5	1.55×10^{-1}
		HCl	0	[e] 5.99×10^{-1}
		PAR	3.09×10^5	0
		ETH	2.94×10^4	0
		OLET	3.38×10^4	0
		OLEI	1.55×10^3	0
		TOL	2.56×10^4	0
		XYL	6.06×10^3	0

[a] Ship exhaust data are obtained from HERCULES measurement in 2006 under 75 % engine load condition (Petzold et al., 2008, 2010). NMHC refers to non-methane hydrocarbon.
[b] PAR, ETH, OLET, OLEI, TOL, XYL stand for paraffin carbon, ethene, terminal olefin carbons, internal olefin carbons, toluene and xylene, respectively.
[c] Initial data are based on HERCULES measurement data. A $NO:NO_2$ ratio of 96:4 is assumed for the ship exhaust (von Glasow et al., 2003). The attribution of non-methane hydrocarbons are based on Table 2 in Eyring et al. (2005). The units of inorganic and organic species are ppbV and ppbC, respectively.
[d] Background data are obtained from European program QUANTIFY in 2007. NO_x to NO_y ratio is 0.15 based on Table 2 in Shon et al. (2008) in the marine boundary layer.
[e] Value from Table 2 in Keene et al. (2007).

To avoid this confusion, and we modified Table 2 as follows: We added a column to report the actual, measured concentrations as determined in the test-rig study by Petzold et al. [2008] separately from the model inputs. Note that the initial measured NMVOC mixing ratios indeed only contribute about 9% to the total pollutant mixing ratios. We then separately list the mixing ratios that we use as model inputs, after converting the NMVOC mixing ratios to the CBM-Z model species mixing ratios. These mixing ratios are now reported in ppbC.

The updated Table 2 is shown above.

We added a sentence in Section 3.3 (Page 14, line 25) to clarify this issue: "We partitioned the total mixing ratio of NMVOCs to different categories based on the composition fractions provided in Eyring et al. [2005], including (1) hexanes and higher alkanes, (2) ethene, (3) propene, (4) toluene, (5) xylene, (6) trimethylbenzenes and (7) other alkene. We then converted these to model surrogate species mixing ratios as listed in Table 2 suitable for the use in CBM-Z. Note that CBM-Z is a carbon bond mechanism, and the model species represent the mixing ratios of constituent groups regardless of the molecule to which they are attached [Stockwell et al., 2012]."

(2.16) P. 16766 Fig. 1. In the modeling results, very near the ship stack, OH is depleted, but HNO_3 is not depleted. Could you explain this? Because HNO_3 is produced by NO_2+OH reaction in the presence of the third body (M).

For HNO_3 a non-zero background concentration was prescribed. The HNO_3 concentration that is seen very close to the ship stack occurs because HNO_3 is diluted in from the background.

We explain this on page 16, line 17: "The HNO_3 mixing ratio reached quickly its background value within the first 10 min, then showed a slight increase during daytime as a result of photochemical processes, and a subsequent decrease due to reaction with sea salt to form sodium nitrate."

(2.17) P. 16770 Fig. 5. Again, the composition change can be due to condensation of many gas species such as H_2SO_4, HNO_3, N_2O_5 and SOA precursors.

We added the following sentence to clarify this point (page 21, line 20) (compare to point (2.14):

"Note that other secondary aerosol species form as well and contribute to a change in mixing state, such as secondary organic aerosol and aerosol nitrate, however for brevity we do not include these results as figures."

References

V Eyring, HW Köhler, J van Aardenne, and A Lauer. Emissions from international shipping: 1. The last 50 years. *J. Geophys. Res.-Atmos*, 110(D17), SEP 15 2005. ISSN 0148-0227. doi: 10.1029/2004JD005619.

A. Petzold, J. Hasselbach, P. Lauer, R. Baumann, K. Franke, C. Gurk, H. Schlager, and E. Weignartner. Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. *Atmos. Chem. Phys.*, 8:2387–2403, 2008.

William R. Stockwell, Charlene V. Lawson, Emily Saunders, and Wendy S. Goliff. A review of tropospheric atmospheric chemistry and gas-phase chemical mechanisms for air quality modeling. *Atmosphere*, 3(1): 1–32, 2012. ISSN 2073-4433. doi: 10.3390/atmos3010001.

R. von Glasow, M. G. Lawrence, R. Sander, and P. J. Crutzen. Modeling the chemical effects of ship exhaust in the cloud-free marine boundary layer. *Atmos. Chem. Phys.*, 3:233–250, 2003.

RA Zaveri and LK Peters. A new lumped structure photochemical mechanism for large-scale applications. *J. Geophys. Res.-Atmos.*, 104(D23):30387–30415, DEC 20 1999. ISSN 0747-7309.

RA Zaveri, RC Easter, and LK Peters. A computationally efficient multicomponent equilibrium solver for aerosols (MESA). *J. Geophys. Res.-Atmos.*, 110(D24), DEC 23 2005a. ISSN 0148-0227. doi: 10.1029/2004JD005618.

RA Zaveri, RC Easter, and AS Wexler. A new method for multicomponent activity coefficients of electrolytes in aqueous atmospheric aerosols. *J. Geophys. Res.-Atmos.*, 110(D2), JAN 21 2005b. ISSN 0148-0227. doi: 10.1029/2004JD004681.

Rahul A. Zaveri, Richard C. Easter, Jerome D. Fast, and Leonard K. Peters. Model for Simulating Aerosol Interactions and Chemistry (MOSAIC). *J. Geophys. Res.*, 113(D13), JUL 3 2008. ISSN 0148-0227. doi: 10.1029/2007JD008782.