Responses to Reviewer #1

We thank the reviewer for taking the time to review our paper and for the many insightful suggestions to improve it.

(1.1) In Table 2, the amounts of ship-emitted NMVOCs contribute ∼22 % to total pollutant emissions. However, several pervious studies have reported much lower contributions of NMVOCs (Entec Uk Limited, 2005; Eyring et al., 2005; Houyoux, 2005; Song et al., 2010). For instance, Erying et al. (2005) reported the global annual emissions of NO_x and NMVOCs from ocean-going ships to be 21.38 Tg and 1.96 Tg, respectively. Author should re-check the initial conditions of NMVOCs. In addition, authors seem to ignore the dilution of NMVOCs by turbulent dispersion. This can affect the model-estimated concentrations of gas-phase species and particulate matters. I believe that the dilution with background NMVOCs should be considered in the model simulations.

> *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].*
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> *The total mixing ratio of initial NMVOCs from the test-rig study was 1.39·10^5 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).*
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> *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.*
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> *The updated Table 2 is shown on the next page.*
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> *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]."*
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> *Dilution with background air is included for all species, as indicated in equation (3). To make this clearer we added "0" for the entry of background NMHC species in Table 2.*

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]
$\mathrm{NO_x}$	9.14×10^5	NO	8.77×10^5	1.86×10^{-2}
CO	3.4×10^4	$\mathrm{NO_2}$	3.7×10^4	3.95×10^{-2}
$\mathrm{SO_2}$	4.7×10^5	$\mathrm{HNO_3}$	0	3.29×10^{-1}
NMHC	1.39×10^5	$\mathrm{O_3}$	0	3.39×10^1
		CO	3.4×10^4	1.05×10^2
		$\mathrm{SO_2}$	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 $\mathrm{NO:NO_2}$ 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. $\mathrm{NO_x}$ to $\mathrm{NO_y}$ 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).

(1.2) As shown in Sec. 2, the turbulent dispersion parameters (alpha and beta) and meteorological conditions (mixing height, z) in this study were fixed (0.75, 0.60, and 400 m, respectively). In general, the magnitudes of these lateral and vertical dispersion parameters are a strong function of the MBL stability classes and other meteorological conditions, and mixing height is also time-variant. Since the model-estimated aerosol number concentration is mainly governed by the turbulent dispersion process, authors should discuss these issues in more detail or conduct sensitivity tests for alpha, beta, and z, in order to show the uncertainties caused by these fixed meteorological parameters.

> *To address the reviewer's questions, we performed additional sensitivity runs to explore the sensitivity to the parameters* α *and* β*. We modified the manuscript as follows:*
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> - *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* α *= 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* α *= 0.74 to 0.76 agreed well with the "best guess" from von Glasow et al. [2003], while their result for* β *= 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."*

(1.3) The evolution of gas and bulk aerosol species for two cases was summarized in Fig. 1. The results of the base and sensitivity cases relatively well represent the general trends of the ship-plume chemical evolution. However, the 0-d box modeling cannot represent the Gaussian-type horizontal and vertical pollutant distributions and their evolution throughout the entire ship-plume. Authors should discuss this part of model description more. Also, if the model-estimated mixing ratios are compared with observed values, the performance of the developed ship-plume model can be verified more clearly, considering the fore-mentioned issue.

> *We state the implicit assumption regarding the 0-D box modeling approach more clearly on page 5, line 15:*
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> *"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."*
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> *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."*

(1.4) In Fig. 2, the modeled aerosol number concentrations were compared with observed concentrations. However, the nucleation was not considered in this study. The mixing ratios of H_2SO_4 can be highly elevated within the ship-plumes. This elevation of H_2SO_4 can be particularly conducive to new particle formation (i.e. nucleation). In this study, the ship-plume release time for case study was 2 pm. I think the increase in aerosol number density due to the new particle formation cannot be negligible. In other words, I think that main governing equation of PartMC-MOSAIC has a limitation for simulating the aerosol number concentration without the consideration of nucleation. In addition, I also wonder if the observed aerosol number concentrations in Fig. 2 were measured at the ship-plume center line.

> *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):*
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> *"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."*
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> *Since the ship plume encounter time is very short, we assume the observations were conducted at the plume center. We added a sentence in Page 17, line 23:*
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> *"Due to the short encounter time with the ship plume, we assumed that the measurements were conducted at the ship plume center line."*

(1.5) In comparisons presented in Sec. 4.2, the model simulation conditions and the gas-phase and aerosol initial conditions were obtained from HERCULES (initial conditions) and from Pfaffenberger et al. (2013)

(background conditions). Although information for model simulation conditions has been illustrated in the cited references, it is necessary to clearly present the relevant information in this manuscript, such as observed species, research domain, and metrological condition, for the benefit of the readers. Further, since the article by Pfaffenberger et al. (2013) has not been published yet, I cannot see detailed information on the QUANTIFY campaign. The model simulation parameters for QUANTIFY can be different from those for HERCULES. More detailed explanations for model simulation conditions should be discussed in the manuscript.

> *In response to the reviewer's comment, we removed the reference to Pfaffenberger et al. (2013).*
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> *In addition we made the following changes to section 3.3 to improve the explanation of the model simulation conditions:*
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> - *We added a sentence in Page 14, line 4: "These exhaust conditions are expected to be similar to the ones encountered in the QUANTIFY SHIPS study, therefore the aerosol population and the gas phase concentrations present in the engine exhaust served as input for the model."*
> - *We added more specific information on the model simulation conditions in section 3.3. The entire revised paragraph reads as follows: "During the QUANTIFY SHIPS field study in June 2007, airborne measurements of a single ship plume (June 14, 2007) as well as aged aerosol in highly frequented sea lanes (June 11, 2007) were performed. During the single-plume study the plume was crossed several times during the time interval of approximately one hour. As in-plume total particle number concentrations we considered the maximum measured concentration during one plume crossing ($D > 4$ nm). Size distributions of both the polluted and the clean marine boundary layer were determined using a combination of instruments capable of measuring in different size ranges. The research domain with the flight path for June 11 is shown in Figure 1. The location of the shipping corridor is marked. In addition to the size distributions observed in the shipping corridor, we also used measurements of gas phase species (NO, NO_y, O_3, SO_2, and CO) to qualitatively compare to our simulations. Last but not least, the following meteorological parameters in the well-mixed marine boundary layer were measured and used for the model runs: a relative humidity of $RH = 90$ %, a temperature $T = 289$ K and a boundary layer mixing height $z_{MBL} = 300$ m. These parameters were obtained from observations on June 14, 2007. The mixing height was derived from the vertical potential temperature profile."*
> - *We added a new figure (Figure 1 in the revised paper)showing the flight path on June 11 and the location of the shipping corridor and the region that we used to derive the background conditions. The new figure is included below.*

(1.6) In Fig. 7, two-dimensional number distributions are compared. In Table 1, the values of the hygroscopicity (κ) were shown. According to my understanding, the value of the hygroscopicity (κ) varies along the chemical aging of aerosols. Since, as shown in Eqs. (14)-(16), the value of hygroscopicity is one of the key parameters in the CCN activity, authors would better discuss how the κ values change in accordance with the chemical aging of aerosols in the manuscript.

> *In PartMC-MOSAIC, an aerosol particle can contain up to 20 constituent species. The effective hygroscopicity for each particle, denoted by κ_i in our paper, is the volume-weighted mean of the individual κ-values of each constituent species, according to Petters and Kreidenweis [2007] and as described in (Section 3.2). For each particle κ_i changes indeed as the aerosol particles evolve since their composition changes. The evolution of κ_i values in the plume is discussed in Section 4.5.*
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> *Table 1 provides the κ values for different chemical species. In contrast, in Fig. 8 (used to be Fig. 7), the y-axis represents the κ-value of individual particles*

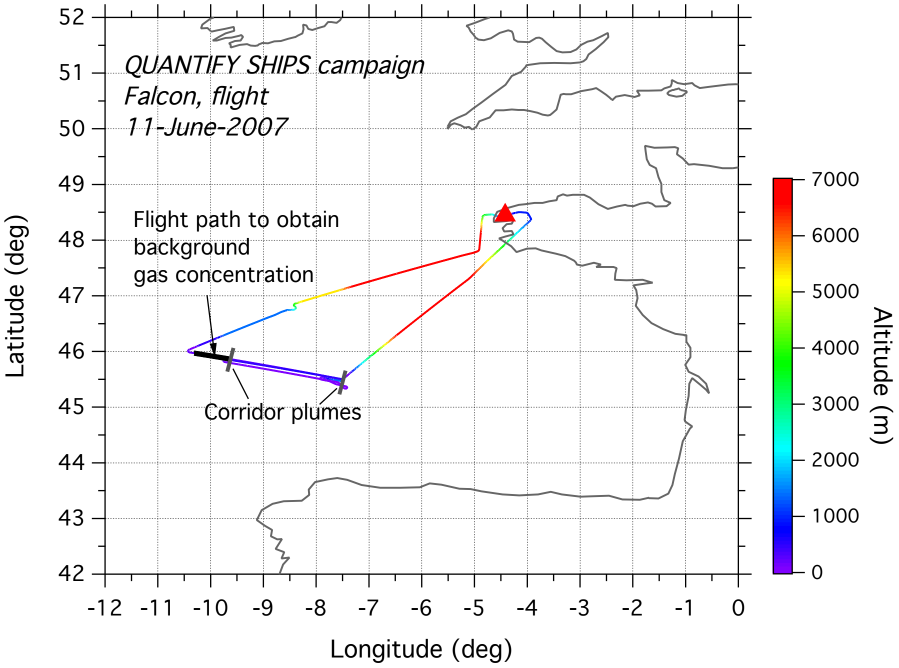

Figure 1: New figure addressing the reviewer's comment (1.5).

> *To clarify this point, we changed the caption of Table 1. The new caption reads: "Hygroscopicity values, κ, for individual model species". We also changed the y-axis label in Figure 8 from "Hygroscopicity parameter" to "Hygroscopicity parameter κ_i", indicating that this refers to the value for individual particles.*

Minor comments:

(1.7) In Fig. 2, in order to scientifically quantify the model simulation performance, the statistical variabilities (e.g., error and bias) should be included, although the results of modeled aerosol number density showed reasonable agreement with observations.

> *Following the reviewer's comment we added a table showing the statistics of the error and bias in Table 4, and added the following text in Page 18, line 6:"A list of error metrics, including mean bias, mean error, mean normalized bias and mean normalized error, is provided in Table 4 for the comparison of simulated and observed number concentrations."*

(1.8) In conclusion, the author states that "the model results agreed well with observed particle number concentration and size distributions." However, the comparison study (Figs. 3 and 4) did not sufficiently verify model simulation performance for aerosol size distribution. The above sentence would better be replaced by "the model results agreed well with observed particle number concentration."

> *As suggested by the reviewer we have removed "and size distributions" on Page 24, line 9. The sentence now reads: "the model results agreed well with observed particle number concentrations."*

(1.9) In order to clearly express the results of this study, the labels of figures should be consistent. - p. 32, in Fig. 2: "Number Concentration" should be replaced by "Number concentration". - p. 33-37, in Figs. 3-5:

“No Coag” and “With Coag” should be replaced by “Without coag.” and “With coag.”. - p. 33-34, in Figs. 3-4: “Dry Diameter” should be replaced by “Dry diameter D”. - p. 36-39, in Figs. 5-7: “Dry Diameter D” should be replaced by “Dry diameter D”. - p. 36-39, in Figs. 5-7: “number conc.” should be replaced by “Number concentration”. - p. 40, in Fig. 8: “CCN Concentration” and “Local Time” should be replaced by “CCN concentration” and “Local time”.

> *Thanks for pointing out these inconsistencies. We have made all the corresponding changes and updated the figures, except for Figure 6 due to the limited space on the graphs. So in Figure 6 we used “w/o coag.” and “w/ coag.” instead of “Without coag.” and “With coag.”.*

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