

### Response to Reviewer #3

Responses to general concerns follow. Reviewer comments are in bold text, followed by author's responses, while additions/corrections to a revised version of the manuscript are indicated by italicized font:

Reviewer wrote: **“It needs to be made clear that the AMS data provide only mass concentrations of organics, not number concentrations (the relevant parameter for CCN and aerosol-cloud interactions). A low submicrometer mass concentration does not necessarily imply a low number concentration. Could it be that the number concentration of organic containing particles in the 30 to 300 nm size range was larger than the number concentration of sulfate-containing particles? Several studies have shown the existence of 50 nm organic inclusions coated by sulfates (e.g., Leck and Bigg, GRL, vol. 32, 2005).”**

We acknowledge that a low submicrometer mass does not necessarily imply a low number concentration, and that there could be a large number of small organic particles which constitute little mass. However, we make no effort in this paper to link organic mass to CCN concentrations, or make suggestions on how OM might affect aerosol-cloud interactions. The purpose of the manuscript was an attempt at describing the background aerosol mass concentrations over the remote Pacific. However, in cases where the authors are making claims such as those on page 16913, lines 14-15, that *“the ocean in this remote region is not a significant source of Org to the marine atmosphere”*, we changed instances of *“Org”* to *“Org mass”*.

Reviewer wrote: **“The use of the org/so4 ratio needs to be discussed in more detail given the different production mechanisms. Oxidation of DMS to so4 has been shown to occur in the upper troposphere. The resulting so4 may be transported long distances from the point of emission. Organic aerosols may be produced locally through wind-driven mechanisms or may result from gas to particle conversion. How do the spatial and temporal scales of these different production mechanisms impact the utility of the org/so4 ratio in looking for evidence of marine organics?”**

The intent of using the Org/SO<sub>4</sub> ratio was not to make assumptions about the relative production of particulate Org and SO<sub>4</sub>, but rather to demonstrate that in the absence of pollution and possible long range transport, the amount of Org mass in the MBL in the areas we sampled is small compared to that of SO<sub>4</sub>. This is a major conclusion of the paper. Being that Org and SO<sub>4</sub> measurements are common across all studies compared in the paper, particularly in the absence of CO and BC measurements (e.g. our TAO cruise), this seemed a convenient and consistent way to compare and contrast fundamental aerosol properties for different geographical regions. True, the spatial and temporal scales of the different production mechanisms (of SO<sub>4</sub> and organics) impacts the variability in this ratio. Therefore, differences in the Org/SO<sub>4</sub> ratio are not a direct reflection of the sources, however the ratio may reflect common characteristics of different air masses and serves to illustrate the variability over various data sets. A sentence was added to the end of the Introduction section (Sect. 1) that states: *“The use of the mass fraction of Org relative to SO<sub>4</sub> (Org/SO<sub>4</sub>) will be used to illustrate that under the clean conditions established in this study, little submicron non-refractory aerosol*

*mass can be attributed to Org. Org and SO<sub>4</sub> are the two largest components of submicron aerosol mass and are therefore two components that are commonly and consistently measured. Though Org and SO<sub>4</sub> have different production rates and chemical reactivity in the atmosphere, the ratio of Org/SO<sub>4</sub> is a useful and convenient tool for comparing submicron aerosol chemical composition across different geographical regions.*” The purpose of Fig. 6 and the associated analysis was intended to isolate natural aerosol (i.e., no relation to combustion indicators), and demonstrate that in those instances there was a relationship, albeit weak, between Org and SO<sub>4</sub>, possibly indicating a common source.

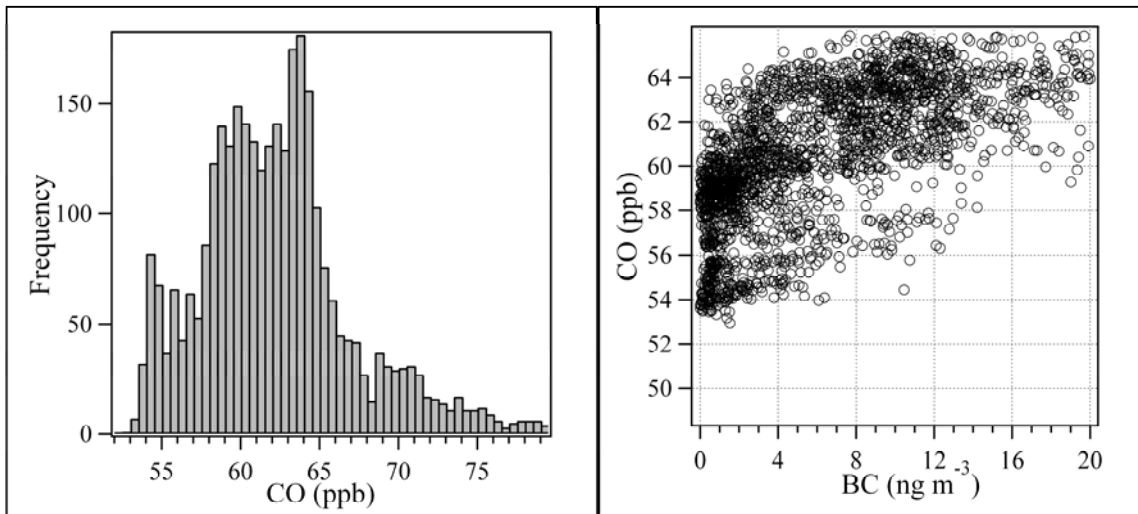
Responses to specific comments:

p. 16898, lines 11-17: The statement in question will be changed to *“Both satellite-derived mean chlorophyll-a and trajectory-weighted chlorophyll-a concentrations have been weakly correlated ( $R^2 \sim 0.25$ ) with OC concentrations in clean marine aerosols collected there.”*

p. 16902, lines 26-27: In the less-polluted southern hemisphere it is recognized (Staudt, 2001) that background levels of CO and BC are lower than in the North Atlantic where there is more land mass, more human population, and therefore more combustion sources. The purpose of our “clean” division was to establish background concentrations representative of the SEP in order to more directly compare to the background conditions in the North Atlantic. Histograms of CO in the VOCALS MBL show a division between two modes at about 61 ppb. The lower CO mode appears to be related to trajectories coming from the Southern Ocean, while the higher CO mode correspond to MBL trajectories that often appear to contact the South American continent, perhaps bringing air masses influenced by the Santiago region over the SEP. The lower CO mode (CO < 61 ppb) was therefore chosen as representative of background concentrations in this region. Also, a plot of CO versus BC indicated that when BC goes to zero (no pollution), CO values range from ~53-61 ppb, another indication that this CO value might represent the upper limit of background conditions in the SEP. A BC concentration of 5 ng m<sup>-3</sup> was established because it represented the approximate average BC concentration (actual average was 4.09 ± 4.75 ng m<sup>-3</sup>) in the low CO mode (CO < 61 ppb). Therefore, these concentrations were considered background conditions for the SEP, and represent a tool for comparing this data set with that collected at Mace Head. The following addition was made to the manuscript:

*“In the less-polluted southern hemisphere, one would expect the background levels of CO and BC to be lower than in the North Atlantic where there is more land mass, more human population, and more combustion sources. By establishing background concentrations for the SEP, we can more directly compare to the background conditions in the North Atlantic. Histograms of CO in the VOCALS MBL (not shown) reveal two modes that occur below and above 61 ppb. Trajectory analyses (Steffen Freitag, personal communication) indicate the lower CO mode appears to be related to trajectories coming from the Southern Ocean, while the higher CO mode correspond to MBL trajectories that appear to contact the South American continent, apparently*

bringing air masses influenced by continental emissions and the urban region near Santiago over the SEP. The lower CO mode (CO < 61 ppb) was therefore chosen as representative of background concentrations in this region. Also, a plot of CO versus BC indicated that when BC approaches zero (e.g. no combustion aerosol), CO values range from ~53-61 ppb, another indication that this CO value might represent the upper limit of background conditions in the SEP. A BC concentration of 5 ng m<sup>-3</sup> was chosen because it represents the average BC concentration (actual average was 4.0 ± 4.8 ng m<sup>-3</sup>) in the low CO mode (CO < 61 ppb). Therefore, these concentrations were considered background conditions for the SEP, and data that can be directly compared with background data reported from Mace Head.”



Reviewer wrote: “ACE Asia: How were the “org” values determined since only impactor measurements of C measured?”

Quinn et al., 2004 and Quinn and Bates 2003 are the references for the Ace-Asia data presented in both Fig. 1 and Table 1. The filter measurements of OC (in  $\mu\text{g m}^{-3}$ ) were converted to particulate organic matter (POM) through multiplication of factors 2.1 for marine environments, and 1.6 in others. POM is used interchangeably with Org in our paper, and while this is not technically correct, as the term Org is often used to represent the amount of POM resolved by the AMS, and may exclude some refractory mass that the AMS cannot measure, it does not affect the logic of the paper. The following paragraph was added to “Sampling bias” section:

*“Not all measurements of Org compared in this study are equal. Some studies (O’Dowd et al. 2004, Cavalli et al., 2004, Quinn and Bates 2003, Phinney et al., 2006) rely on filter-based measurements of OC. Filter measurements have significant biases, including negative artifacts from volatilization of particulate-phase organics from the filter surface, and positive artifacts from adsorption of gas-phase organics onto the filter (Turpin et al., 2000). Filter measurements do not, however, suffer from the potential refractory -Org losses as the AMS does. There is also the issue of particle bounce off the collection*

*substrate of an impactor stage during sampling, leading to inaccurate size classifications. Also, in order to convert total organic carbon (TOC) from bulk filter measurements to water soluble and insoluble organic carbon (e.g. Cavelli et al., 2004) and particulate organic matter (e.g. Quinn and Bates, 2003), TOC measurements from filters are multiplied by a conversion factor which represents a ratio between molecular mass and carbon mass. These factors, when added to the AMS biases, can contribute to possible differences when comparing studies of OM measurements. It should be noted that for the purposes of this study the term Org, which is used in the AMS community to represent the amount of POM resolved by the AMS, is used interchangeably with POM from e.g. Quinn and Bates, 2003 and water insoluble and soluble organic carbon (WIOC+WSOC, e.g. from Cavelli et al., 2004).”*

**p. 16905, line 14:** References were added, replacing Charlson et al., 1987:

Andreae, M.O. and Barnard, W.R.: The marine chemistry of dimethylsulfide, *Mar. Chem.*, 14, 267-279, 1984.

Cline, J.D., and Bates, T.S.: Dimethyl sulfide in the Equatorial Pacific: A natural source of sulfur to the atmosphere, *Geophys. Res. Lett.*, 10, 949-952, 1983.

**p. 16906, line 25:** Sentence in question was changed to “*In contrast, during periods of high biological production activity, O’Dowd et al. reported a tenfold increase...*”

**Figure 7: Include a legend or list in the caption label for the different colored lines in 7c.**

Fig. 7 caption was changed to indicate that the colored lines in Fig. 7c and 7d are represented by the same legend shown in Fig 7a.

**p. 16909, line 22-27:** Unfortunately there was not enough signal in the VOCALS MBL to get size distributions for the organics. We only operated in the PToF mode when there was a large Org signal, which incidentally, only occurred when flying in pollution plumes, and even then the distributions are too noisy to resolve.

**p. 16909, line 23:** Changed to “*vacuum aerodynamic diameter*”.

**p. 16910, lines 11-12:** The short answer is no, m/z ions that result from wind-driven production of sea spray organic aerosol cannot be missed (or not chosen) by the analysis. The fragmentation table in SQUIRREL takes those signals known to occur from air species (i.e., N<sub>2</sub>, Ar, etc), and those from sulfate, nitrate, and ammonium species, subtracts them from the total signal at that mass, and essentially calls the leftover signal Org. The only way an Org peak can be missed is if the signal from one of the known species is too high. This can occur, and does often occur at m/z 29, which corresponds to a peak containing both N<sup>15</sup>N<sup>+</sup> and CHO<sup>+</sup>. The CHO<sup>+</sup> signal is sometimes overwhelmed by the N<sup>15</sup>N<sup>+</sup> signal. In the fragmentation table frag\_air[29] is calculated by multiplying the N<sub>2</sub><sup>+</sup> peak by an isotopic fraction. However, depending on the threshold setting and possible saturation effects, this isotopic factor may be slightly different than predicted. The CHO<sup>+</sup> peak is calculated by subtracting frag\_air[29] from the total signal at m/z 29, and the remaining mass corresponds to frag\_organic[29]. In the case of negative CHO<sup>+</sup>

values, the isotopic fraction can be multiplied by a factor, close to 1, in order to account for the overwhelming of the CHO<sup>+</sup> signal. For example, we adjusted the isotopic fraction to give zero Org signal at m/z 29 during filter periods, avoiding negative Org artifacts. This information has been added to the AMS instrumentation description.

**p. 16914, lines 11-16:** The authors agree that the inclusion of this paragraph, and Fig. 10, appear as if attempting to improve the results of O'Dowd and others. This was not the intended use of the figure and accompanying text. However, in light of the reviewer's concerns, Fig. 10 will be removed from the manuscript. The paragraph in question will be reworded: "*Comparison of Org and satellite-derived chlorophyll-a concentrations for VOCALS, TAO, and IMPEX yielded a relationship that goes through the origin and with a slope of  $34.3 \pm 0.1$ . This slope is similar to others reported in the literature for this relationship (Langmann et al., 2008; O'Dowd et al., 2008; Vignati et al., 2010) but their non-zero intercept at zero chlorophyll-a concentrations does not reflect the lower values we find here for low chlorophyll-a regions. If employed in models, this may improve consistency between measurements and model observations, particularly over more unproductive regions of the oceans.*"