Responses to Referee #1

General comments:

This manuscript presents new chemical data obtained from aerosols collected over the Arctic Ocean during summer. The manuscript is significant since it presents a new dataset that has been lacking in the literature, especially for the Arctic troposphere. This manuscript should certainly be published in Biogeosciences as a discussion paper. The authors should know that I have already carefully read through this paper and have several comments that I would like to make now, all of which I hope are constructive and useful in terms of improving the quality of the manuscript. The current quality of the manuscript is quite good; however, my comments will hopefully be useful in presenting these new exciting data in the clearest way possible. In order to jump start the review process, I will post my major comments below so that the authors can consider them during the discussion phase.

Response: We are grateful to the reviewer for the constructive comments and suggestions. Below are point-by-point responses with reviewer's comments in blue and authors' responses in black.

Major Comments/Suggestions:

1.) The major weakness of this study is that the authors could be missing important organic species that are not amendable to GC/MS analyses. By not measuring other tracer compounds, such as organosulfates that are easily observable by LC/ESI-MS techniques, the authors could be missing important sources or atmospheric processes. As clearly noted in a recent review article by Hallquist et al. (2009, ACP), in order to capture the organic aerosol formation well, several advanced analytical techniques should be used in tandem, as many individual techniques (such as GC/MS) have their respective weaknesses. For example, it is known with GC/MS that one can not characterize more than 10-20% of the organic aerosol mass at the molecular level.

Response: We agree with the reviewer's comment. There are many techniques have been applied to characterize the organic aerosols at a molecular level, including GC/MS, LC/ESI-MS, two-dimensional LC-MS, as well as high-resolution MS et al. All these off-line methods can only focus on a certain fraction of organic carbon mass. Although techniques such as LC/ESI-MS are not available in our laboratory, the authors still believe that the new dataset from GC/MS analysis for the Arctic Ocean aerosols is interesting enough for the readers in the community of atmospheric chemistry and biogeochemistry.

2.) Another issue I have with this study, which will not prevent this study from being published, is why wasn't a PM2.5 high-volume sampler used? This would help to isolate the collection of climatically relevant size ranges. With TSP you are getting everything that is present in the atmosphere at that time. As I'm sure the authors know, PM2.5 high-volume samplers certainly exist and would have been preferred here in the design of this study, especially if you argue the research you are doing is relevant to climate change, etc.

Response: It is a pity that PM2.5 high-volume air samplers were not available during the sampling period. In the pristine environment such as the Arctic Ocean, it would be difficult to collect aerosol samples by PM2.5 mid-volume air samplers during a short period of time. Thus, we just collected TSP samples using a high-volume air sampler (Kimoto AS-810B). By using such a sampler, we can collect the marine organic aerosols, both in fine and coarse modes.

3.) Why didn't the authors consider filtering solvent extracts through a Teflon membrane syringe filter instead of with their quartz wool packed in a Pasteur pipette approach? I worry the quartz wool might cause permanent absorption (and thus losses) of some organic constituents. Have the authors tried using authentic and surrogate standards to test for the recovery of compounds through this quartz wool?

Response: The recoveries of all the organic species measured by the method described in the manuscript have been checked using authentic and surrogate standards. Most of the organic compounds showed recoveries higher than 80%, except for several polyacids and pinonic acid whose recoveries are about 60% (Fu et al., 2009; Fu et al., 2010). Such information has been mentioned in Section 2.3 of the manuscript (see Page 5, Line 141-144).

4.) In section 3.1, it might be helpful to add a table (or to an existing table) that summarizes the origins of air masses for each filter collected. This might be easier for readers to find this information without having to search the manuscript for these details.

Response: Suggestion is taken. The information of primary source regions of air-mass back trajectories has been added in Table 1 in the revised manuscript. (see Page 27, Table 1).

5.) (a) Based on what is now known about isoprene SOA formation, I wonder if the authors have particulate sulfate (as well as particle-phase inorganic) data available from their campaign? Did anyone from your campaign make ion chromatography (IC) measurements from the aerosol samples? If so, it would be very interesting to know if the 2-methyltetrols and C5-alkene triols correlate with sulfate mass loadings.

(b) Further, do you or your colleagues from the campaign have gaseous chemical data? Specifically, it would be interesting to know if 2-methylglyceric acid correlates with NOx.

(c) Lastly, since you are using GC/MS, do you measure the other IEPOX-derived SOA tracers? Specifically, I mean do you measure cis- and trans-3-methyltetrahydrofuran-3,4-diols (see recent paper by Lin et al., 2012, ES&T). I would like to further note that since you see 2-methyltetrols and C5-alkene triols, you likely will observe the organosulfates derived from IEPOX if using ESI-MS techniques (operated in the negative ion mode). The organosulfate of IEPOX is an important compound since a recent study by Froyd et al. (2010, PNAS) showed that this compound is one of the single most abundant compounds in the free troposphere. This could indicate that it has a long atmospheric lifetime, allowing it to be transported long distances. The Froyd et al. (2010, PNAS) study used on-line aerosol mass spectrometry data collected from several aircraft campaigns. I should note that their aerosol mass spectrometer is equipped with laser ionization.

Response: (a) According to the reviewer's suggestions, we measured the inorganic ions in the Arctic aerosol samples using Ion Chromatography (IC) recently. The variations of sulfate and isoprene SOA tracers (2-methyltetrols and C_5-alkene triols), as well as aerosol acidity have been present in Figure 1 (as Figure 6 in Page 34 in the revised manuscript). The correlation between sulfate and 2-methyltetrols is insignificant, while a weak positive correlation (R^2=0.42) was obtained between sulfate and C_5-alkene triols.

According to the new datasets, the following sentences have been added in the revised manuscript:

"Such a pattern is consistent with those of sulfate loading (Figure 6e), indicating an influence of aerosol acidity.

Aerosol acidity has been reported to have significant impacts on SOA formation from the oxidation of isoprene and other biogenic VOCs (e.g., Surratt et al., 2007; Offenberg et al., 2009). In the present study, the aerosol acidity (Ziemba et al., 2007) was roughly estimated by $[H^+] = 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$, where the brackets represent ion concentrations in molar units that were measured using ion chromatography (761 Compact IC, Metrohm, Switzerland). As shown in Figure 6f, the $[H^+]$ values ranged from 0.002 to 0.060 μmol m^{-3}.

QFF3357 showed much stronger acidity than the other samples, which indicates that the aerosol acidity may enhance the formation of C_5-alkene triols rather than 2-methyltetrols in the pristine atmosphere over the Arctic Ocean. Furthermore, aerosol acidity can favor the formation of 3-MeTHF-3,4-diols and 2-MGA (Figure 6c-d). Interestingly, a strong positive correlation (R^2=0.95) was observed between 3-MeTHF-3,4-diols and C_5-alkene triols (Figure 8) in marine aerosols over the Arctic Ocean, which supports the idea that both of them can be formed through the oxidation of IEPOX under low-NO*x* conditions (Surratt et al., 2010; Lin et al., 2012)." (see Page 14, Line 415-430).

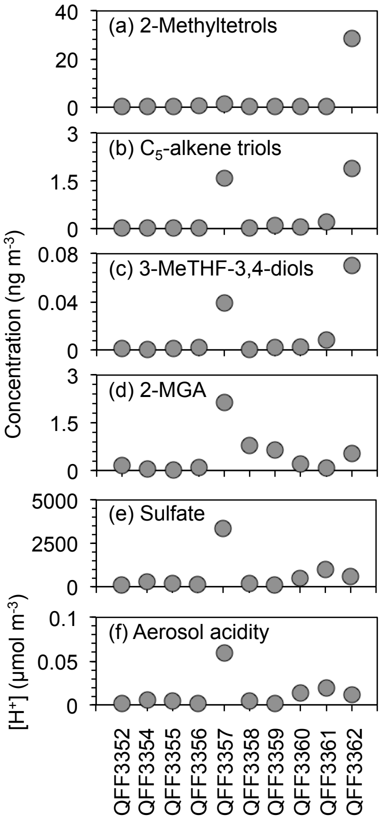

Figure 1. Concentrations of isoprene SOA tracers and aerosol acidity measured in the marine aerosols collected over the Arctic Ocean during the MALINA campaign in August 2009.

(b) During the MALINA field campaign, there was no gaseous chemical data recorded.

(c) LC/ESI-MS was not available in our laboratory, thus we cannot provide the data of organosulfate of IEPOX. Alternatively, by revisiting our GC/MS TIC data, we detected *cis*- and *trans*-3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4-diols) (Lin et al., 2012) and estimated their concentrations of using *meso*-erythritol as a surrogate. Interestingly, a strong linear correlation (R^2=0.95) was obtained between the concentrations of 3-MeTHF-3,4-diols and C_5-alkene triols (Figure 2, as Figure 8 in Page 36 in the revised manuscript).

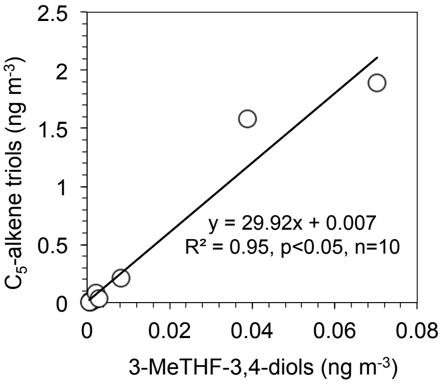

Figure 2. Correlations between 3-methyltetrahydrofuran-3,4-diols and C_5-alkene triols.

7.) The authors seem to indicate that the ratios of 2-methylerythritol to 2-methylthreitol are lower than what has been seen before, especially at lower latitudes. They suggest that this could indicate that some of the 2-methyltetrol contribution is derived from primary biogenic emissions, as recently proposed by Noziere et al. (2011). However, could this be due to one isomeric epoxide produced in the gas-phase oxidation of isoprene (Paulot et al., 2009, Science) leading to this difference?

Response: Suggestion is taken. The following sentence has been added in the revised manuscript. "Another possibility is that such a difference may be due to one isomeric epoxide preferentially produced in the gas phase oxidation of isoprene (Paulot et al., 2009)." (see Page 15, Line 442-444).

8.) The authors discuss that the C5-alkene triol to 2-methyltetrol ratio was high on one foggy (humid) day and lower on another foggy (humid) day. If the authors had IC data, they could see if this is due to sulfate loading. Furthermore, since aerosol acidity has been previously shown by Surratt et al. (2010, PNAS) and Lin et al. (2012, ES&T) to be important in promoting the heterogenous chemisty of gaseous IEPOX, have the authors also considered trying to estimate aerosol acidity from IC data (if available)?

Response: Based on the IC data, we estimated the aerosol acidity, which was calculated as below:

$[H^+]=2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$

where [X] represents the molar concentration of the ions. The data of aerosol acidity are present in Figure 1f (as Figure 6f in the revised manuscript) with discussion in Page 14, Line

415-430 in the revised manuscript.

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