Anonymous Referee #1

Overall, this represents an interesting dataset on precipitation composition from a remote location that is important for establishing the role of long-range transport, and differentiating source regions in this part of the world. I think the work should be published in ACP. However, there are a few serious issues with regard to data interpretation and conclusions drawn that must be addressed. Rather than just proceed through the paper as it is organized, I will begin with the bigger issues.

We thank this referee for a very thoughtful and constructive review.

1) The authors must provide a more thorough analysis of the origin of the extremely high non-seasalt calcium (actually, calcium carbonate) concentrations. These concentrations seem to be substantially greater than the enrichments suggested in work on exopolymer gels. The authors lob this idea out without any real discussion of this as a potential source. Hawkins and Russell (Advances in Meteorology Volume 2010 (2010), Article ID 612132, 14 pages doi: 10.1155/2010/61213) who have described the chemistry of these exopolymer gels, also note that these are marine primary aerosols, producing material in the fine particle mode via bursting bubbles (**Hawkins and Russell (2010) is added in the reference list as yet another example on the potential importance of exopolymer gels**). Granat et. al (JGR 2010, referenced in this manuscript and describing the same dataset) have found that nssCa++ is primarily present (90% for the marine trajectory group) in large aerosols. If primary marine aerosols were the most important source of these enrichments, wouldn't the nss-Ca++ observed in aerosols show a peak in the small particles? Seivering et al. seem to suggest the extreme Ca++ enrichment factors they observed and associate with plankton debris are a result of a

"large and variable upwind biogenic Ca source plus high wind speeds (~11m/sec) . . .make the site

atypical of many remote marine boundary layer regions". If the authors are still intent on invoking these mechanisms (exopolymer gels and calcium enriched plankton debris), they might look for evidence in ocean color data (as reported by Seivering, 2004) indicative of highly productive waters. Are these presumed to be local enrichments, or long range transport. This warrants more than a passing remark, forcing readers to search out information on how/where these possible sources may be contributing.

We agree with the referee that our suggestion of exopolymer gels as a possible source of the high rainwater concentration of Ca^{2+} was based on rather limited information and therefore somewhat premature. We have now considered in more detail other potential sources, including locally produced sea salt particles enriched in $CaCO_3$ from the soil dust and eroded corals. We tried to test this hypothesis by analyzing a few seawater samples collected near the shore of the Hanimaadhoo island. However, the result of this study was inconclusive; the amount of excess Ca^{2+} was variable but in general less than a few percent of the total Ca^{2+}.

Another possibility is dry deposition of locally produced soil dust during episodes when the lid was accidentally opened during non-rainy periods. Based on measured concentration in the weekly washings such contributions do not exceed 10 % of what was measured in the rain samples. This point is further elaborated in our response to reviewer 2.

In our discussion of the elevated Ca^{2+} concentrations we now mention several possibilities but leave the source attribution open. As discussed later in our response to Referee 2 we believe that artifacts associated with chemical analyses and sampling are unlikely explanations for the high Ca^{2+} values.

In contrast to these possible sources, I would encourage the authors to look for correlations with local wind speed and direction (is meteorological data available? **Unfortunately not**). If the trajectories are correlated with surface winds, then the marine transport category appears to be associated with a long fetch across the chain of islands and reefs of the Maldives. It seems very likely that the nss-Ca++, arriving with carbonate, is from production from local calcareous material, and in this sense it might be thought of as local contamination, local wind blown island material, or as noted wind-blown calcareous shell debris? It was noted by Granat that the enhancements of excess calcium were all in the coarse size fraction for particulates, wouldn't precipitation events associated with stronger local winds or wave action during the monsoon season produce these large paticles? Images of beaches and shoreline of Maldive coastal locations are abundantly available in Google Earth, and seem to suggest there is plenty of calcareous coral material available that could be kicked up by wind, waves and or alternatively, local construction. **Please see earlier comment**.

In addition to considering if these nss-Ca++ events are driven by a local source , it would be useful to provide some information on how often extreme events were sampled. It appears from Figure 5 that there were at least three events with concentrations over 150 ueq/l, and many events with concentrations over 50. Is there ever any other evidence to suggest a larger continental influence from Africa or Australia (which the authors acknowledge, is not supported by trajectory calculations), such as remotely sensed imagery of high MODIS AOD, that predates these major deposition events?

Analysis of MODIS AOD data for dates preceding high nss-Ca^{2+} observations did not show any obvious plumes. But the extent of cloud-free regions was rather limited.

If not, again, it would seem that a bit more consideration should be given to local effects, driven largely by wind direction (and speed) transporting material from local calcareous debris. This local source in particular, is not even mentioned in the abstract for the paper. The authors should consider the work of a few other remote Island stations, which might be exhibited for comparison. For example, Galloway et al., 1988 (Tellus, 1988, 40B, 178-188), looked at the local influences of Bermuda on precipitation composition. They compared two island sites, and found that the enrichment of nss-Ca++ appeared to vary as a function of wind direction and local activities such as nearby construction or wind speed generated turbulence generating calcareous dust from the island. It seems that it would be very useful to add a table that puts MCOH precipitation composition into the context of composition observed in other remote locations. **Such comparison has now been added in Table 1.** Rather than simply providing a comparison of measured annual wet deposition for a number of locations as shown in Table 9 (including rural continental sites from the Eastern US, from NADP), it seems that it would be valuable to include marine sites like Bermuda, and possibly even Amsterdam Island (from the Southern Indian Ocean, Moody et al., JGR, 1991), as well as a rural Indian site (as noted in Table 9), etc., to bracket the range of observations found in the Maldives. For example, comparing data from the Galloway '88 paper, they report annual volume weighted average (VWA) nss-Ca++ on the order of 3.5, and nss-SO4= on the order of 11 ueq/l . By comparison, Amsterdam Island, in the Southern Indian Ocean, measured VWA nss-Ca++ on the order of 0.4 and

nss-SO4= on the order of 5 ueq/l. Marine trajectory events (monsoon rain events?) on MCOH observed nss-Ca++ of 20 and nss-SO4= of 6.8 in marine flow. These comparisons to other published data sets could be included in Table 1. Done. Perhaps there are other precipitation observations that should be included. This should be far more useful to the reader than just the summary material in Table 9. Table 9 has been removed. A comparison between data from MCOH and India has been included in the text.

2) The authors conflate the concepts of seasonality and source region. They define two seasons, and they also define three transport patterns, and then leave a substantial amount of data unexplained (defined as mixed transport). The implicit suggestion of the paper is that the marine flow is entirely monsoonal while the Indian flow is nonmonsoonal and occurs exclusively in the dry season only, between November and April. If this is true, then it should be stated explicitly; if it is not true, then the text is misleading. Do these trajectory categories in fact cleanly and perfectly partition the data into seasons? If not, if any of the marine events (defined by their transport) occur during the non-monsoonal or dry season, then this should be clearly indicated. **This has now been clarified both in the main text and in the abstract. We now use trajectory groups rather than seasons throughout the paper.**

Similarly, does any of the Indian or Arabian flow occur during the monsoon (or anytime from May to October)? The text as written is confusing with regard to these distinctions. Are the Mixed group trajectories that couldn't be visually clustered into one of the other categories, or are they in fact Marine type events that occurred in the winter season, etc? (Some of these trajectories do not look very different from the Marine group).

3) I am concerned that the authors are misinterpreting the results of the PCA. First, some caution should be exercised in basing principle components on datasets that are this small. For example, the Indian transport events appear to represent about 10 cases, and the PCA uses 10 variables, I believe this makes it difficult to consider these results robust (the authors should clearly indicate the number of observations for each transport group, I had to estimate from the plots of pH). The danger is that one data point can have a major influence on the correlation data, and the resulting factor analysis. Furthermore, some of the correlation between non-seasalt species can arise from the fact that they are all derived from relatively large sodium concentrations.

We have redone the PCA analysis excluding some of the more uncertain components (nss-K^+ and nss-Mg^{2+}) and completely rewritten the discussion in this section. The conclusions have been formulated in a more tentative way.

In section 3.2 it is noted that the moderately high loading of nss-SO4= in Marine Factor 1 points to a marine biogenic source. I don't see this at all? Based on the loadings, and data correlations, Factor 1 in the marine dataset, appears to indicate strong evidence of an anthropogenic/biomass burning source, it is high in NO3-, NH4+, nss-K+ and nss-SO4=, there is in fact no evidence of this as a biogenic component (no significant loading of Na+). The second factor, with high loadings of Na+ and Cl- seems to represent the sea-salt source or component, while the third factor exhibits high loadings of nss-calcium and carbonate, indicative of an independent source of calcareous material (this may very well be the marker for local contamination, a local source of wind blown material). It is also worth noting that none of these dominate as a major factor controlling the variance, since they explain 28%, 21% and 20% respectively (and over 30% of the variance remains unexplained). Just because

the actual contributions of the NO3-, NH4+ and nss-SO4= are low (especially relative to the Indian transport group), does not mean that there would not be any background chemical signature that is anthropogenic or biomass burning in nature. Factor loadings are describing correlations between ions, how they rise and fall together, not their magnitude. The authors refer to concentrations of MSA, however, there is no inclusion of this ion in the correlation matrix, or in the factor analysis (presumably it was often below detection limit, or unmeasured based on insufficient sample volumes, this is not discussed) therefore there is no real chemical evidence for a marine biogenic component in the factors presented. **MSA has now been included in the correlation matrices (Marine and Indian trajectory groups).**

Further evidence that factor 1 of the Marine transport PCA is anthropogenic/biomass burning in nature is the fact that most of the chemical loadings are very similar to factor 1 loadings in the Indian PCA 1 (Table 5), with the exception of hydrogen ion. Most of the variability in this transport from India (48%) is associated with this first factor which the authors do identify as anthropogenic in nature (combustion, and agriculture). The loadings are also similar for Factor 1 in the Arabian group with the addition of crustal components (dust). Furthermore, each of these sets of transport defined events (Indian and Arabian), also have a seasalt factor that explains on the order of 21% of the overall variability (a little more for the Indian data set).

I suggest that the authors label each of these factors with a source term indicative of the loadings and discuss each of the Tables in order (currently Table 7 is never even referenced). The correlations seem to suggest Marine transport is composed of three factors, which make similar contributions to observed variability. They could be thought of as background pollution (anthropogenic/biomass burning, maybe a marine biogenic contribution as well?), sea salt, and local surface material. The Indian transport is composed of three factors, with the greatest variance explained by the acidic pollution (anthropogenic and biomass burning factor), sea salt, and a factor that is low (or anticorrelated) with local surface material (and probably associated with transport from the NE). The Arabian transport is composed of two factors, with the majority of variance explained by the buffered pollution (anthropogenic and biomass burning along with crustal dust), and sea salt. The discussion of pH in this section seems out of place, it warrants a separate section. **The discussion has been reorganized according to the suggestion.**

If you are going to do the PCA for each transport pattern, why not include Mixed? From its composition, it looks like marine air with lower wind speeds and higher MSA, which is probably consistent with a number of trajectories that circle the region at low speeds (it looks like there are trajectories of this type, although its hard to tell from this spaghetti plot). **We have chosen not to include the mixed trajectory class in any of the statistical analyses. The reason is that this group is less well defined with trajectories of different arrival heights showing substantially different transport patterns.**

I have also provided more minor and specific suggestions by section.

Section 2.2, in the analysis of rain samples, it is mentioned that different ion chromatograph columns were used to measure cations before and after February 2007. Did the occurrence of extreme Ca++ concentrations occur to a greater/lesser extent in relation to this change in analytical technique? No! The authors note that Na+ was used as the seasalt reference species, but they then go on to discuss the possible influence of crustal material. It seems warranted to evaluate the dataset to

ensure selection of the appropriate reference species (Keene et al, 1986). **We have decided to keep to the use of Na^+ as reference.**

Section 2.4, it is noted that the trajectories were calculated to arrive at three different heights of 50, 1000 and 2000m, at 12GMT, which of these heights are plotted in Figure 4? **We missed to point out that the plots refer to 50 arrival height. This is now corrected**. Is there a greater contribution from continental regions like Africa or Australia as you go higher in the atmosphere? **The trajectories with greater arrival heights are on average somewhat longer, but even these trajectories for the high Ca^{2+} days did not explicitly indicate a continental origin within the ten days followed.** It might be important to acknowledge that back trajectories through deep convection are inherently uncertain, since the model representation of the ITCZ and the real ITCZ cannot be assumed to match. These trajectories may still describe the evolution of the large scale flow, but I it is difficult to directly think of them as accurately representing the source region of all material incorporated into the deep convection of monsoonal precipitation. We are well aware of this limitation in the interpretation of trajectory data. The fact that we only classified (in the three main categories) days when all trajectories had a similar shape is believed to make the classification reasonable.

Section 3.1, I suggest changing the first sentence to something like: "Figure 5 shows the data at a monthly resolution depicting individual events and volume weighted mean (VWM) values for each month." **Changed accordingly**.

Section 3.2, I suggest changing the first sentence to something like: "To evaluate possible source region for the precipitation collected at the MCOH observatory, the events were separated into three well defined trajectory groups, Marine (1), Arabian Sea (2), Indian (3), and Mixed (4), a less well defined transport group. Volume weighted means were calculated for each group and are shown in Table 1, along with published VWM concentrations from some other remote locations for comparison. " **Changed accordingly**. Again, please provide a better explanation of the mixed transport group. **Done.**

Section 3.3, discussed above.

Section 3.4 It is not at all clear why the authors note in the discussion of Marine PCA factor 1 that "this moderately high loading of nss-SO4=. . ..points toward a marine biogenic sulfur source", since they don't include MSA in the analysis, and the factor includes high loadings of NO3- and NH4+. In this section, they use the molar ratio of MSA to nss-SO4=, but its not clear if this is for all events, or a subset of events for which MSA was available. If MSA is available for every event, put it into the PCA. Done. If its not, then be careful, and state how many observations the conclusions are based upon. A plot of this relationship or an indication of the strength of the correlation would be more useful that just a reference to the mean molar ratio of an unspecified number of observations.

Section 3.5, the authors need to explain why a correlation between NO3-, NH4+, and nssSO4= would not indicate an anthropogenic background signal. Again, it might be useful to compare these values with precipitation data from other remote locations. **This discussion is reformulated to accommodate i.a. this issue.**

Section 3.6, I am not sure it makes sense to compare the wet deposition of sites driven by monsoon conditions with subtropical or mid-latitude locations. Furthermore, when the authors discuss the

overall nutrient loading of NO3-, they indicate that a large part is due to natural sources. It doesn't seem that there is anything conclusive about the source, especially given that the authors speculate on biogenic nss-SO4= correlated with a lightening source for NO3-, primarily on the basis of a PCA, which they potentially misinterpret. **Table 9 has been removed. Comparison with other remote marine sites has been included in Table 1.**

Section 4 Conclusions

My greatest concern is that the authors overstate their ability to infer sources, both in the physical sense (based on trajectories that can be invalid for tracing air parcel motion during deep convective precipitation) and the chemical sense (biogenic sources based on little evidence, PCA based on small datasets). They also go on to state that wet deposition of NO3-, NH4+ and nssSO4= is an order of magnitude greater at MCOH than Amsterdam Island, and indicate that this shows "the chemical climate of the Maldives is clearly affected by pollution sources of the Asian continent during the winter season." Both these statements may be true, but the implication is that the wet deposition differences are driven or caused by this pollution source, neglecting the fact that there are very large differences in precipitation amount at a monsoonal location versus a mid-latitude location. And in fact, the authors already showed that deposition is driven by summer rainfall amounts. The authors seem to have preconceived ideas of what is driving the chemistry in the Maldives, perhaps they are right, but it does not appear that they have shown enough data to demonstrate their conclusions. **The conclusions regarding sources have been modified to reflect the referee's concerns.**

References:

Galloway, J.N, J.J. Tokos, A.H. Knap, W.C. Keene, Local influences on the composition of precipitation on Bermuda, Tellus, 40B, 178-188.

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Moody, J.L., A.A.P. Pzenny, A. Gaudry, W.C. Keene, J.N. Galloway, and G. Polian, Precipitation composition and its variability in the Southern Indian Ocean: Amsterdam Island, 1980-1987, JGR, 96, 20769-20786, 1991.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17569, 2010.