**Atmospheric
Chemistry
and Physics
Discussions**

# Interactive comment on "Chemical composition of rainwater at Maldives Climate Observatory at Hanimaadhoo (MCOH)" *by* R. Das et al.

**Anonymous Referee #1**

Received and published: 13 September 2010

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.

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. Granat et. al (JGR 2010, referenced in this manuscript and describing the same dataset) have found that nss-Ca++ 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 ($\sim$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.

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?). 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.

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? 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. 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. 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.

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 non-monsoonal 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. 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.

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.

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 anti-correlated) 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.

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).

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? 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).

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? Is there a greater contribution from continental regions like Africa or Australia as you go higher in the atmosphere? 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.

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."

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. "

Again, please provide a better explanation of the mixed transport group.

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. 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.

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.

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.

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.

Hawkins, L.N, and L.M. Russell, Advances in Meteorology Volume 2010 (2010), Article ID 612132, 14 pages doi:10.1155/2010/61213.

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.

C7504