Anonymous Referee #2

My first concerns about the paper are over data quality, and until these issues–and the ones raised below–are dealt with satisfactorily, I'd argue that there is really no point in commenting on the later sections of the paper. We hope that we will be able to convince the referee that the data quality is not a major issue. **We hope that we will be able to convince the referee that the data quality is satisfactory.**

First, on P. 17574 the authors write: "At least once a week and when found visibly contaminated the wet-only collector was cleaned as part of quality control scheme using a plastic brush and de-ionized water (18MΩcm resistivity) from a spray bottle in different combinations."

What sorts of contaminants were seen on the funnels? How often were the samplers found to be contaminated? Was one of the samplers contaminated more often than the other? This is a serious concern because of the very high concentrations of nssCa++ found in some samples. Unless contamination can be discounted as a source for nssCa++, I'd argue that any detailed discussion of its sources would be overly speculative, and the data for the other ions may be compromised as well. {As an aside, I would be interested in seeing the high nssCa++ samples plotted with a different symbol in Fig. 2ăˇAˇThow were the ion balances for those samples?

For samples with concentration of nss-Ca^{2+} lager than 50, 75 and 90 percentiles (37, 50 and 87 μeq/l respectively), the mean difference between cations and anions are 6, 7 and 14 μeq/l respectively or only 0,5, 1 and 2 % of total amount of ions in the sample. There is clearly no indication that the high nss-Ca^{2+} levels should be due to an analytical error.

Also, it would be interesting to see the samples from the different trajectory groups plotted with different symbols in Fig. 2 and Fig. 3}. **We see no need to this.**

Beyond the visible contamination, I'm concerned about contamination that wasn't visible, and along these lines, I think some addition information on the sampling protocol needs to be included. What concerns me here is that there is no indication that the collector was cleaned after each sample was collected. What I'm wondering is whether all of the rain that falls on the funnel actually ends up in the collection bottle. If not, I'd be concerned that any droplets that remained on the funnel would evaporate and the ions that were in solution would carry over and be collected in the subsequent sample.
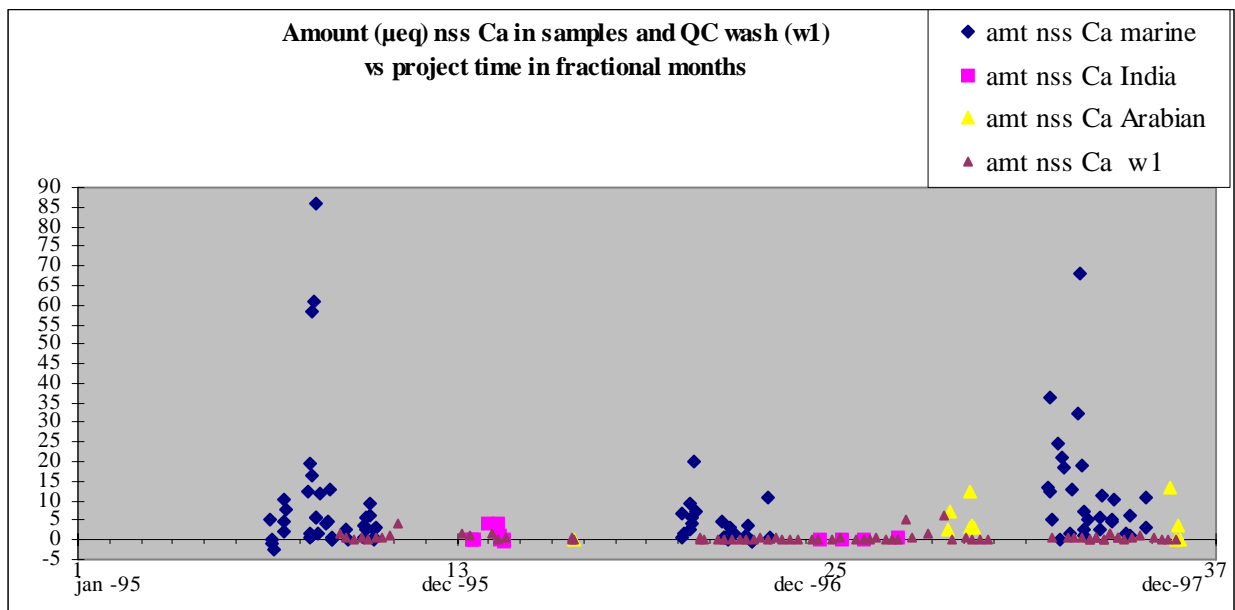**The operators were instructed to perform the quality control washings once a week. In addition, as a safety precaution, washing was also asked for if the funnel was found contaminated. We never found the collector contaminated during visits to the station, nor were there any comments on this in the protocols. Contaminations due to i.e. bird droppings do occur at many other locations, especially when using bulk collectors but no indications of such contamination was thus noticed at MCOH. We removed that sentence in the text as it obviously could be misunderstood.**
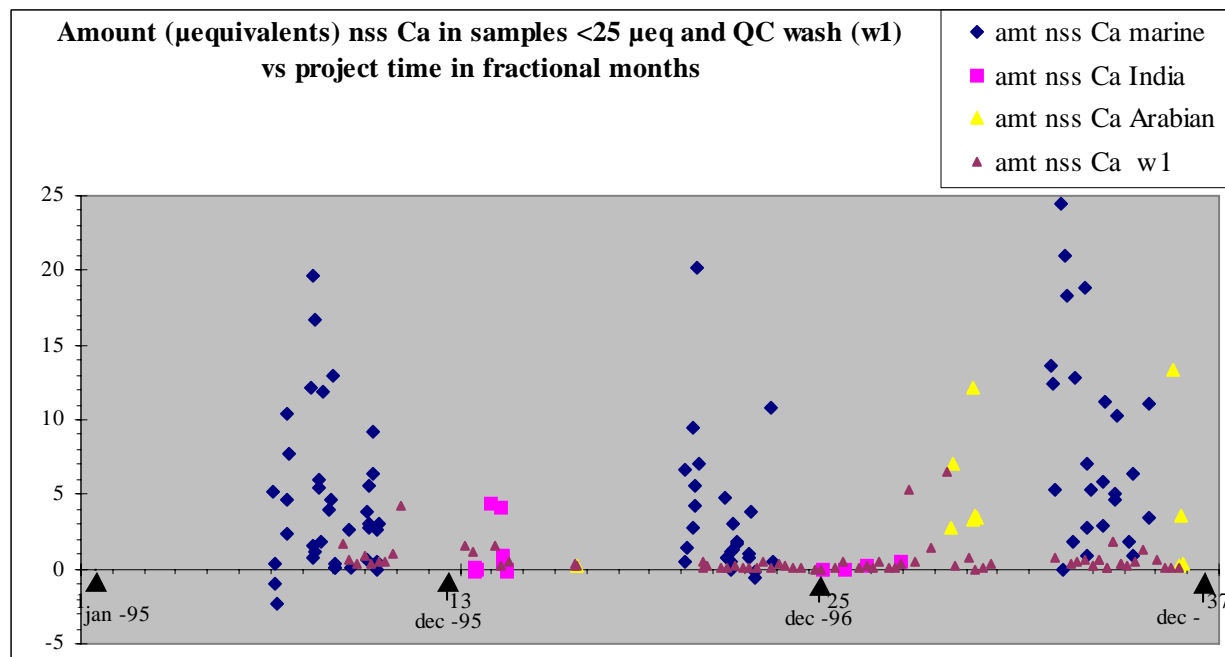
And of course, any droplets left on the funnel also would be prime sites for reactions with gaseous substances. So if the samplers were not cleaned between samples, I'd be concerned about sampling artifacts and their impact on data quality.

The amount of rain remaining on the funnel after a rain was estimated to be at most 0.5 ml. With a typical collected volume at each rain event of 190 ml (median of all rains) the contribution from remaining salt is negligible. The lid makes a tight seal against the funnel and the air volume from which gases could be extracted would thus be limited to about 2 l.

Along these lines, I didn't see any mention of blanks. These should be routinely collected for QA/QC and if any were collected, the data for them should be summarized, at least briefly as supplemental material if nothing else.

The blank issue is now made more explicit in the text. The so called w1 wash means washing all the interior of the funnel with DI water from a spray bottle that disperse water all over the surface. The amount of water is measured and later analyzed. The time since previous rain (or washing) can range from one week (previous w1 wash) to just after rain (w1 wash after that a rain sample was taken out). There was actually some material in w1 water, which can be attributed to factors such as contamination by the operator, very light "rain" that opened the collector or accidental opening of the lid during non rain conditions (e.g. due to small droplets from the surf activating the sensor). The following graphs are given to show how the amount of nss-Ca^{2+} in w1 wash compares with the amount in rain during the period of investigation. The second graph is an enlargement in the concentration region up to 25 microeq.

Amount (μequivalents) nss Ca in samples <25 μeq and QC wash (w1) vs project time in fractional months

In the Marine and Arabian Sea groups the amount in w1 is practically without any influence on the measured nss-Ca^{2+} amounts (and thus concentrations) except for the cases with very low measured values. In the Indian group the w1 during the beginning of 1996 are in level with the amount in rain and in three cases actually higher. We believe that the two high values for w1 in months 27 and 28 are either heavily contaminated or not even real w1 samples. The concentration of all other components except nss-Ca^{2+} was much higher than those in these two w1 samples.

The amounts in the wash water (concentration times amount of water) compared with amounts in rain was less than 9 % in case of nss-Ca^{2+} down to less than 2 % in case of nss-SO$_4^{2-}$ based on medians of amount in w1 and collected rain. The collection is therefore clearly "wet only" and the high nss-Ca^{2+} concentrations in the "marine" trajectory group and is not due to deposition of nss-Ca^{2+} rich material between rain events.

If blanks were not collected, I would consider this a serious flaw in the experimental design, possibly a fatal flaw, depending upon the authors' response to the possible lack of cleaning issue raised above. **We hope that the reviewer is satisfied with the explanations and data given above. The DI (18MΩcm) water in the spray bottle used up in the tower was also checked regularly and found to be clean.**

I may have missed it, but I didn't see some information that I think should be included in the paper. First are at least summary statistics for the numbers of samples and the volumes of the samples. This information should be included in Table 1 and it should be given for each trajectory group. **This information is now included in Table 1.**

I'm concerned about the volumes of the samples because of possible volume effects on concentrationsâ˘Aˇ Tit appears (Fig. 5) that there are higher concentrations of some the analytes, such as NO3-, in the lower volume (more concentrated?) samples. Are the volumes of the samples comparable for all of the trajectory stratified groups?

The variation of concentration in rain is - as is often the case with this type of data - large variability at low rainfall amounts and a tendency towards generally lower concentrations with increasing rain fall amount. The typical rainfall amount for each of the trajectory classes are given in Table 1.

[Perhaps a bit tangential, but I would also be interested in knowing what time of day the rain events most often occurred for the various groups, i.e., are the "photochemical environments" similar among groups?] **Not considered. No systematic information is available on the timing of the rainfall. It is really hard to believe that local photochemistry should be an important factor.**

On P. 17576, the quality of the NH4+ and nssK+ data is discussed, and it raises some flags about the validity of the results. I am particularly concerned about the nssK+ data because in two of the trajectory-defined groups (marine and mixed), nssK+ is a very small percentage of the total K+. More to the point, the concern is that for those groups nssK+ is a small difference between two large numbers, and so very noisy and likely with little meaning. I'm particularly concerned about the inclusion of this variable in the PCA because of the large uncertainties in its concentrations (I have somewhat lesser concerns over using the NH4+ data in the PCA for the same reason). Although I admittedly have limited experience with the technique, I have found that the inclusion or exclusion of a single variable can greatly influence the outcome of PCA. Even if not the results are not presented in the final version, I'd suggest that authors try several runs of the PCA with and without nss Ca++, nssK+ and NH4+ to see how robust the results are.

Some of the nss fractions, especially those for K$^+$ and Mg^{2+}, are indeed small compared to the total and therefore inevitably more uncertain. For this reason we have now excluded nss-K$^+$ and nss-Mg^{2+} from the PCA analysis.

As noted in the review RC already posted, PCA requires a large number of samples, and this is another reason I'm concerned about the number of samples. The following quote is from SAS support: "Principal component analysis is a large-sample procedure. To obtain reliable results, the minimal number of subjects providing usable data for the analysis should be the larger of 100 subjects or five times the number of variables being analyzed." (http://support.sas.com/publishing/pubcat/chaps/55129.pdf)

We share this concern about the limited number of observations in two of the groups. We have tried to take this uncertainty into account when formulating our conclusions.

Further, I am curious about the way in which the relationships among the ions were evaluated. The relationships are presented in several tables of correlations, but there is no evidence that the variables are in fact linearly related. It's generally known that a relatively small number of extreme points can exert a disproportionate influence on correlations, i.e., leading to "significant" correlations when the data are not really linearly related. Some x-y plots might be added, even if as supplemental material.

We have made such plots for all trajectory groups. A summary of these plots is given below with both slope (concentration ratio) and correlation given for those pairs where the correlation is significant.

		NH_4^+		$nss\text{-}Ca^{2+}$		NO_3^-		$nss\text{-}K^+$	
marine	NH_4^+							0.15	0.10
arabian								0.09	0.92
indian								0.04	0.60
marine	$nss\text{-}Ca^{2+}$	0.10	-					0.01	0
arabian		1.0	0.69					0.09	0.64
indian		10	-					0.21	0.83
marine	NO_3^-	0.58	0.40	5.6	0.20			0.12	0.20
arabian		1.1	0.83	0.90	0.74			0.09	0.83
indian		0.64	0.40	0.17	0.82			0.04	0.69
marine	$nss\text{-}SO_4^{2-}$	0.26	0.30	3.2	0.60	0.42	0.50	0.06	0.20
arabian		0.56	0.90	0.50	0.79	0.52	0.85	0.05	0.91
indian		0.60	0.70	0.09	0.30	0.73	0.53	0.03	0.91

[I don't actually know how the data should be handled for these analyses, but are the correlation calculations weighted by volume?] Yes.

Back to PCA. One of the assumptions of PCA is this:

Linearity. The relationship between all observed variables should be linear. (same SAS reference as above)

We have checked this and found no large deviations from linearity. We have also checked that the correlations are not critically dependent on individual 'ouliers'.

Thus I think it would be important to address the linearity issue in some detail.

****
My next concern is over the use of trajectories in interpreting the precipitation data. First, the trajectories are calculated for one point in time (5 pm) each day. I'm wondering how representative these will be relative to the actual time the rain event occurred. For example, the 5 pm trajectory could be more than 12 hrs after the event occurred if the rain fell shortly after midnight. Second, and more problematic in my mind: how are the heights of the trajectories matched to the rain event? My understanding is that in-cloud processes are much more important determinants of what gets into the

rain than below-cloud scavenging. So, are the trajectories matched to the altitude where the precipitation formed, and if so how? In the same vein, how do the trajectories deal with convective precipitation? Wouldn't the strong vertical motions in convective storms make the trajectories almost meaningless? Wouldn't convective events upwind of the sampling site similarly limit the usefulness of trajectories? Even for stratiform precipitation, I'd think the trajectories would need to be carefully matched to the heights of the air masses where the droplets formed–as the term "stratiform" would imply.

We are well aware of these issues regarding representativeness of air mass trajectories. A more detailed analysis, including consideration of short time (sub-day) variations, is hindered by lack of information about temporal distribution of rainfall during the day. The relative steadiness of the flow patterns in this part of the world and the broad classification that we have applied are likely to reduce the problems associated with the issues raised by the referee. The main problem, as we see it, is the low number of rainfall events in the Indian and Arabian Sea groups, which contribute to making the statistics of the data in these groups uncertain.

I think the authors also need to provide some more detailed information on how the trajectory groups were defined. Was a clustering algorithm used to objectively establish groups, or was this done by eye? The clustering was done subjectively. I suspect the latter, and if so, was information on the vertical dimension of the trajectories taken into account? **A specific day was considered to belong to one of the three main groups only if the trajectories for the three arrival heights (50, 1000 and 2000 m) had a similar shape.** Frankly, to my eye, at least some of the mixed trajectories look quite similar to those in the marine group. **Since only the 50 m trajectories were included in the diagrams several members of the mixed group do look like the marine trajectories. On those days trajectories for the other heights had a different shape. This has now been clarified in the text.** At the very least, Fig. 4 should include plots showing the vertical characteristics of the trajectory groups, and this dimension should be given considerably more attention. In particular, the heights of the trajectories as they passed over potential source regions could well determine whether pollutants and other continental substances were entrained into the air that eventually was sampled at MCOH. **In the Indian group all trajectories arriving at 50 m had remained below 800 mbar except two, which reached 700. Out of the 12 trajectories in the Arabian Sea group 9 had stayed below 800 mbar. The remaining three reached levels between 600 and 800 mbar during their first days.**

As the stratification of the data by trajectories is the foundation for much of the interpretation of the results, I think the authors need to establish that their approach is robust. **The fact that we excluded all days with uncertain transport patterns (different directions for the different arrival heights) we believe that the classification of the remaining days is reasonable robust.**

Again, until these questions about data quality and the approach used to interpret the data are addressed, I think further comments on the results would be unwarranated. Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17569, 2010.