Atmos. Chem. Phys. Discuss., 10, C4960–C4971, 2010
www.atmos-chem-phys-discuss.net/10/C4960/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The contribution of anthropogenic aerosols to aerosol light-scattering and CCN activity in the California coastal zone" *by* D. A. Hegg et al.

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Received and published: 8 July 2010

1. Reviewer no. 1.

1.1 Major Points

1.1.1 Discussion of UNMIX-PMF differences

The reviewer calls here for discussion of the differences in the PMF and UNMIX models and the circumstances under which one or the other of these models is best employed. More specifically, the reviewer feels more discussion of the reason(s) for the contrasting source attribution of CCN for cases 22-24 should be provided.

We note first that we have already given our main reason for our preference for the PMF over the UNMIX model for this data set, namely, the uncertainties in the data, particularly for the CARMA II and III data (page 11488, lines 16-22). Nevertheless, we do agree that this is an important issue and that more discussion would be valuable.

Numerous studies employing both the PMF and UNMIX models have been made in recent yearly (e.g., Pekney et al, Aerosol Sci & Technol., 40, 910-924,2006; Poirot et al, Environ. Sci. Technol., 35, 4622-4636, 2001; Kim et al, Environ. Sci. Technol., 38, 202-209, 2004; Chen et al, Environ. Sci. Technol., 41, 2818-2826, 2007). The models tend to be more or less in agreement when data sets have many cases and many analytical species. However, differences do occur, essentially on the order of those we see in this study and differences of a factor of two in the contribution of identified similar sources to particular samples are not uncommon. They arise from a number of factors that vary with data set. Typically, UNMIX resolves fewer factors than PMF and – very importantly for our purposes – the nature of the factors resolved is much more dependent on the precise choice of input species than is the case for PMF (cf., Maykut et al, Environ. Sci. Technol., 37, 5135-5142, 2003). The "edge" algorithm used in UNMIX will, in many instances, not yield a feasible solution if certain species are (or are not) included in the input and one commonly ends up running UNMIX with fewer and different species than PMF even for the same data set. (This issue is most acute for small data sets such as ours) For our data sets, a relatively small number of input species are available, and they vary from one study to the next. Hence, use of the UNMIX model is very problematic in the sense that quite different (and uncertain) factors would be resolved in each data set and inter-annual comparison – the main objective of the study - would be difficult. We will add a brief summary of this discussion to the text on page 11488.

With respect to the specific reason for the disagreement between UNMIX and PMF for cases 22-44, they arise from the issues discussed above. While the major component loadings for the marine source, for example, are the same for the two models, the

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pollution component loadings are somewhat different. UNMIX "markers" for pollution are, most importantly, Pb, NSS sulfate and aerosol hygroscopicity. For PMF, they are primarily, NSS sulfate and hygroscopicity. Lead was not included in the PMF model because it markedly degraded the regression, an effect presumably associated with its high uncertainty (mean normalized uncertainty of 100% as compared to $< 5\%$ for NSS sulfate and hygroscopicity). Because cases 22-24 are relatively low in Pb, UNMIX did not consider pollution a major source for these samples whereas PMF did. We will now note this in the text on page 11492, first paragraph, where the issue is discussed.

1.1.2 Possible inter-annual sampling bias

The reviewer raises the issue of possible inter-annual sampling bias, specifically with respect to cloudiness and sampling altitude. Because the main objective of the CARMA study was the interaction of aerosol with clouds, sampling was nearly always done under locally cloudy conditions for each of the study periods. Regionally, climatological data suggest a slightly higher low cloud fraction for July compared to August (i.e., for CARMA II as compared to CARMA III and IV) but the difference is well within the uncertainty in the data (38% for July as compared to 35% for August). Similarly, the mean sampling altitudes for the three study periods are not significantly different: CARMA IV 195 $\pm$ 59 m, CARMA III 141 $\pm$ 30 m, CARMA II 156 $\pm$ 38 m. There is also the possibility that mean offshore sampling distances differed from year to year but, again, such was not the case and the issue is subsumed in our back trajectory analysis. Finally, it is possible that the source strengths for pollutants varied from year to year. However, we have no information on this issue other than for biomass burning and, as noted already in the text, consider it unlikely.

The reviewer has suggested a table to convey the above information. While this could be done, we feel that the information can easily be summarized in the text itself without unduly lengthening the narrative and have taken this approach.

1.1.3 How to designate the "CCN" measurements.

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The reviewer raises the important issue of how we refer to our PCASP data. While the discussion in the text is deemed adequate, some of our figure captions are felt to be misleading and the reviewer suggests that that we universally refer to our PCASP data as CN. We prefer not to do this. CN generally refers to the number concentration measured by a CN counter, with a detection size limit on the order of 6 nm radius (for the CARMA data set). The CN number concentration is thus commonly dominated by particles that will not activate at cloud supersaturations characteristic of the Sc encountered in our study Hence we feel that so labeling the PCASP concentrations, which encompass only those particles above $\sim$ 60 nm in radius – and which WILL activate at cloud supersaturations – to be even more misleading than calling them CCN.

We currently refer to the PCASP concentrations as SURROGATE CCN in the text and feel that this term and the related discussion makes it quite clear that they are in fact proxies for actual CCN measurements. We do concede, however, that we have been lax in so designating them in the figure captions. While the axis labels in the figures properly refer to the particle concentrations as surrogate CCN, in some of the figure captions they are referred to as CCN and we will rectify this. In all instances, we will refer to them as surrogate CCN.

1.2 Minor points

1.2.1 P. 11488, lines 1-6

We now include a new figure showing the CARMA IV PCASP vs. CCN number concentration regression.

1.2.2 P. 11490, line 17

We used the term “secondary” in the sense of relatively low variance reduction and agree that the text is confusing here. We have altered the text to clarify this. We now state: “. . . produce additional, low-variance-reduction factors compared to the UNMIX model.”

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1.2.3 Various figure fonts sizes

We will increase the font size used in those figures that require it.

1.2.4 Color scheme in figures

We will render the color scheme consistent over all the figures

1.2.5 Figure 4

The upper most source is Marine 1. We will correct this.

1.2.6 Figure 10

The regression shown in Figure 10 is an EXAMPLE of the six regressions run in the measured/predicted comparison. All the R^2 and slope values for the regressions are given in Table 2. Note that the R^2 value for the regression shown is the second worst of those run – and the worst for CCN. Hence, we feel that it is a fair example. We do not wish to add additional figures but will now emphasize in the text that the other CCN regressions are BETTER than the one shown.

1.2.7 Figures 11-12

The uncertainties associated with the source contributions shown in Figures 11 and 12 are considerable though inter-annual differences are indeed significant, at least in some cases. However, it is difficult to add uncertainty bars to the type of graph we have utilized –and which we still feel best conveys our main point. Hence, we have added a table to the manuscript that contains both the source contributions and the associated errors and will refer to this table in the figure captions. In the table, it can be seen, for example, that the pollution contribution to CCN is significantly higher in CARMA III compared to CARMA IV but not compared to CARMA II with its unusually high uncertainty. For light scattering, on the other hand, the pollution contribution for CARMA III is significantly higher than that for either of the other studies. We will add discussion of these uncertainties to the text on page 11493, first paragraph, where

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inter-annual variability is discussed.

2. Reviewer no. 2.

2.1 Major point (General comment).

The issue raised by the reviewer here is somewhat similar to that raised by reviewer no 1 in 1.1.3. The recommended cure is similar as well: simply refer to the PCASP measurements as aerosol particles (accumulation mode) rather than surrogate CCN. It is in fact tempting to do this since we agree that it sidesteps the difficulties of assessing the impact of using a proxy for CCN. However, sidestepping the issue is not quite the same thing as resolving it. The two properties of accumulation mode aerosol that render them important to climate change are their optical properties and their CCN activity. We deal with the first by directly measuring the aerosol light scattering and doing a source attribution of this property. The other main reason for looking at accumulation mode aerosol at all – both by us and the community at large – is because of their presumed importance as the size range of most CCN activity under most circumstances. Even if we simply report our PCASP measurements as accumulation mode aerosol, the issue of how they correspond to CCN is still implicitly present. We feel that we have data available that help us assess this and wish to explicitly address the problem, though we readily admit that our analysis is far from definitive. On the other hand, we agree that we have not adequately explained what can and cannot be done with our model results given that we are using a surrogate for CCN rather than direct measurements and we now discuss this issue in the text.

Before turning to the main discussion proposed to address the reviewer's point, we address a more specific issue raised in conjunction with it, namely the measurement conditions within the PCASP as compared with the CCN counter. The reviewer notes that the PCASP is heated and that sampling conditions within it our likely poorly controlled. The PCASP heating in fact leads to a typical RH in the scattering volume of $\sim$ 30% but never more than 40% unless the intake air is actually close to saturation

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(based on direct measurement of the temperature in the PCASP scattering volume and assumed water vapor conservation between the intake and the scattering volume). The samples utilized in this study had ambient RH's below $\sim$ 85%. For hygroscopic growth factors measured during CARMA (e.g., Kaku et al, Atmos. Chem Phys., 6, 4101-4115; Hegg et al Atmos. Chem. Phys., 8, 7193-7203), this would lead to at most a 10% change in particle diameter (relative to "dry" particles) and more typically 5% - within the instrument measurement error. Hence, in our view, the sizes given by the PCASP are essentially dry diameters and thus usable in our CCN proxy calculations.

Turning to the larger issue raised by the reviewer, we note first that our main goal in this study has been source attribution of the CCN activity of the aerosol. For this, so long as the PCASP and CCN number concentration measurements covary, the attribution is valid. However, because we have used a proxy for the CCN activity rather than direct CCN measurements, what one recovers from the model (in a diagnostic, NOT prognostic, sense since receptor models are diagnostic only) are SURROGATE CCN concentrations, i.e., PCASP concentrations, not CCN concentrations. That is why, for example, the ordinates in Figures 4 and 6 are labeled surrogate CCN (0.3%) concentrations. To recover the actual CCN measurements, one would have to additionally employ something like the regression we used to establish the link between the CCN and PCASP variance. We have not done this because it was beyond the scope of our analysis, i.e., source attribution. Perhaps more importantly, the fact that the R^2 value for the PCASP-CCN regression is 0.69 indicates that about a third of the CCN variance is not being explained by the PCASP particles. Quite likely the extra variance is due to variations in the particle composition as a function of size, an issue we do not have the data to address but which would not in itself greatly impact our source attribution based on bulk chemistry, which is entirely determined by the composition of particles within the PCASP measurement range. However, it might also be due to a combination of pathological chemistry within the PCASP range and other particles outside of the PCASP range acting as CCN, i.e., Aitken particles. If so, then in so far as these particles have a different source from the PCASP particles, our source attribution would

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not be applicable to them. We do not think this is likely but it certainly could happen (for example if the Aitken particles were purely secondary in origin) and we now discuss this issue in the text.

2.2 Minor points

2.2.1 Acronyms

We now define all acronyms.

2.2.2 Clarification of prose

Perhaps we are trying to say too much in a single sentence here. We have altered the text to read: “However, it has proven difficult to quantitatively deconvolute the impact of various aerosol sources on such aerosol mean properties as light scattering and CCN activity. Even differentiating between the impact of natural and anthropogenic sources has proven elusive.” Hopefully this clarifies our meaning.

2.2.3 Dates vice cases in figures

It would be difficult, we feel, to substitute dates for case numbers on the figure abscissas since the sampling was not uniform from campaign to campaign in terms of dates and flight time intervals. However, we have added the date and time interval over which the sampling was done in each campaign to each relevant figure caption.

2.2.4 Model references

We now provide citations for the models when they are first introduced.

2.2.5. Reference for the nature of biomass burning in the study region.

We have added the requested citation to the text (Chow et al, 2010).

3. Reviewer no. 3

3.1 General comments

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The reviewer has two main concerns. The first of these, the use of the PCASP measurements as proxies for CCN, is shared, more or less, by the other two reviewers. We address it in responses to the other two reviewers (responses 1.1.3 and 2.1) in addition to our response to this reviewer. The second main concern, the robustness of the results given the relatively small number of cases is presented more substantively in the second of the reviewer's specific comments and we differ discussion until we address that comment.

3.2 Specific comments

3.2.1 Page 11488, lines 1-6.

In the last paragraph of our response to reviewer no. 2's main concern (response 2.1) we address the consequences of the PCASP vs CCN regression only explaining 69% of the variance. This discussion is now summarized in the text. Essentially, one possible consequence – the most adverse from the standpoint of our study goal – is that we are not accounting for the source of perhaps one third of the CCN. If these particles had a different source from those in the PCASP size range, our conclusions would be at least somewhat different. We now explicitly acknowledge this but feel it is unlikely. Number size distribution measurements taken in the MBL 100 km north of the CARMA operational area a month prior to CARMA III by Roberts et al (J. Geophys. Res., 111, doi: 10.1029/2005JD006661, 2006), show that the PCASP lower limit of 60 nm roughly bisects their observed MBL Aitken mode. One would have to hypothesize that the upper and lower halves of this mode were chemically (and source) distinct to impact our analysis. In general, the various aerosol modes are assumed to be well-mixed (cf., Easter et al, J. Geophys. Res., 109, doi:10.1029/2004JD004571, 2004) and, while there is some evidence that external mixing occasionally occurs within the marine Aitken mode, based on hygrosocpicity measurements (we are aware of no size-resolved composition measurements across the marine Aitken mode), there is no evidence whatsoever that it is size-dependent (e.g., Swietlicki et al, Tellus, 52B, 201-228, 2000). Hence, we feel reasonably secure in our conclusions. Once again, we now

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discuss this issue in the text.

We now also include a plot of the PCASP-CCN regression in the text, as requested by the reviewer. As for the residuals, the mean residual is 0.026 $\pm$ 11 (SE) while the skewness of the distribution is -.36 $\pm$ 0.62 (SE), i.e., there is no significant evidence of a systematic bias. With regards to the completeness (appropriateness?) of the linear model, we also tried a power fit to the data which yielded an R^2 =0.686, indistinguishable from the value of 0.69 for the linear model. Perhaps more tellingly, we tested the addition of other predictors to the linear regression. We first ran a regression of the CCN onto PCASP that, of course, yielded the same R^2 value as we obtained for the inverse regression. We then added the Aitken particle concentration to the regression (particles in the size range from 6 to 60 nm radius base on the difference between the PCASP and CN concentrations), the only other really plausible predictor for CCN concentration. The R^2 value improved to 0.8 with regression coefficients for PCASP, Aitken and the constant of 0.89 $\pm$0.54, 0.08 $\pm$ 0.03, and 27 $\pm$ 101, respectively. Given that the regression constant does not significantly differ from zero, one could interpret the two predictor coefficients as indicating that roughly 10% of the PCASP particles do not act as CCN at 0.3% supersaturation while $\sim$ 8% of the Aitken particles do. It is certainly plausible that $\sim$ 10% of the PCASP particles could be relatively insoluble and thus not active, the deficit being made up by Aitken particles above $\sim$ 32 nm radius. However, while the R^2 value for the multiple regression is indeed higher than that for PCASP alone, it is not significantly higher given the change in degrees of freedom incident on adding another prognostic variable. And, of course, the actual prognostic power of the regression has been reduced by this addition.

In summary, while there are certainly some issues associated with the R^2 value of the PCASP-CCN regression, we feel that the value less than unity reflects parametric rather than structural uncertainties, i.e., uncertainties in the measurements rather than an inappropriate linear model. In our view, the above discussion in its entirety is too lengthy – and distracting – to put into the text but a brief summary has been included.

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3.2.2 Pages 11488 to 11490, justification for using PMF vice UNMIX

We have already addressed this issue, at least in part, in our response to reviewer 1 in paragraph 1.1.1. Essentially, we agree that the edge algorithm is very attractive but it does have its problems. It presupposes that there are some samples in the data base that have no contribution from this or that source – this is what leads to the "edges". If such is not the case, if there is a least SOME contribution from all of the sources to each sample (or at least most of them), UNMIX will have trouble doing the inversion. Conversely, if there is some species that has a nice edge, i.e., is not present at all in some samples and markedly so in others, it will strongly influence the source profiles and source attribution irrespective of the uncertainty in its measurement. As per our response 1.1.1, this is what we feel happened with Pb in CARMA IV – and the major source of the UNMIX-PMF discrepancy for that study. Given the differences in the species available for inclusion in each of the respective CARMA studies, it would be difficult to differentiate, in our view, between actual differences in source profiles and source contributions due to real source differences, and those induced in the model due to its sensitivity to individual species. Again as per our earlier response, we now make this point in the text.

3.2.3 Page 11485, lines 15-19

We had used ANOVA as an abbreviation for analysis of variance in a broad sense: statistical models used to partition variance into components due to different sources of variation. However, after polling numerous colleagues we now agree that this is not the currently common usage of this term and have changed the text to label the general approach of receptor models as multivariate statistics, as suggested by the reviewer.

3.2.4 Page 11490, lines 17-18

References for the additional factors produced by PMF have been added to the text (as per those in response 1.1.1). The (0.3%) in the ordinate labels is the activation supersaturation. We clarify this in the figure captions.

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3.2.5 Table 2

The regression intercepts, and their uncertainties, have been added to Table 2. All uncertainties are for a 95% confidence interval, i.e., they are standard. Because the reviewer indicates his concern is with possible bias, we also now include the slopes of the regressions with the regression line forced through zero, a straightforward way of assessing bias. All of the forced slopes are below one, indicating that the models systematically over predict the scattering and surrogate CCN concentrations. We now discuss this briefly in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11483, 2010.