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Final Report for: The Interaction of Water and Aerosols in the Marine Boundary Layer: A Study of Selected Processes Impacting Radiative Transfer and Cloudiness

Dean A. Hegg

University of Washington
Department of Atmospheric Sciences
Box 351640
Seattle, WA 98195-1640

phone: (206) 685-1984 fax: (206) 685-7160 email: deanhegg@atmos.washington.edu

David S. Covert

University of Washington
Department of Atmospheric Sciences
Box 354235,
Seattle, WA 98195-4235

phone: (206) 685-7461 fax: (206) 685-3397 email: dcovert@u.washington.edu
Award #: N00014-07-1-0277

<http://www.atmos.washington.edu/academic/atmoschem.html>

LONG-TERM GOALS

The overarching, long-term goal of the study was to explore the profound effect of aerosol-water interaction both on radiation propagation in, and the thermodynamic structure of, the marine boundary layer. Specific goals as initially conceived were: 1) compile a climatology of aerosol hygroscopicity for use in the NAAPS and COAMPS models, and, further, to develop a model parameterization of hygroscopicity based on aerosol size and composition for such models, 2) explore the relative impacts of cross-inversion mixing and sub-cloud aerosol on cloud thickness and cloud base height, 3) quantify and parameterize the impact of precipitation scavenging on below cloud radiative transfer and cloud liquid water path. However, in the course of obtaining the measurements and analyzing them, our goals evolved as it became clear both that some particular tasks were infeasible with the resources available and other goals would be of more value to the overall objective of the study. The specific goals, or objectives, pursued in the study are given below. The sampling platform utilized throughout the study has been the CIRPAS Twin Otter research aircraft and the venue is the littoral environment off the California coast, representative of areas with high shipping densities.

OBJECTIVES

The specific objectives of the study have, as implied above, evolved as the study has developed. For example, we had initially hoped to examine mixed-phase clouds but the instrumentation for doing this, while included in various projected instrumentation lists for the CIRPAS facility, never actually materialized. Similarly, our initial measurements of the number of giant CCN in the marine atmosphere, which were substantially lower than values used in modeling studies that had prompted our interest, led us to abandon this issue as of little real significance. Despite such setbacks, a fairly extensive list of inter-related objectives remained viable. These objectives are listed below.

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- Characterize marine aerosol hygroscopicity as a function of particle size, relating it to chemical composition, both theoretically and experimentally

- Determine the sources of marine aerosol mass, CCN activity and aerosol light scattering

- Link the aerosol size and composition to CCN activity and cloud drop number concentration.

- Compile an aerosol "climatology," of aerosol hygroscopicity and optical properties for marine aerosol suitable for use in the NAAPS model

- Assess the secondary aerosol formation formulation in the NAAPS model

- Devise a strategy for including secondary organic aerosols in the NAAPS model with the objective of improving the prognostic power of the model for Aerosol Optical Depth (AOD).

APPROACH

The methodology used to address the objectives listed above was a judicious (we hope) mix of field, and theoretical studies. The field work involved data both from several projects dedicated nearly entirely to our goals (CARMA II, III, and IV) and from "external" projects within whose larger framework we could find appropriate data to address our goals (e.g., SAFARI, VOCALS). As mentioned above, the platform for the measurements taken in the dedicated projects was the Twin Otter research aircraft operated by CIRPAS, the joint ONR-Caltech research flight facility. In all of these dedicated studies we used various versions of our humidigraph (essentially 2-3 nephelometers measuring at different RH's) and, in the last two dedicated field studies (CARMA-III and IV), our new size resolving Aerosol Hydration Spectrometer (AHS) which allowed us to determine size-resolved aerosol hygroscopicity, as our primary tools for the determination of the impact of RH on aerosol properties. A host of ancillary instrumentation was used to address each specific goal, including various filter measurements for bulk chemistry, impactor data for size resolved chemistry, various aerosol sizing instruments (PCASP, FSSP, DMA, etc.), CCN spectrometers for CCN activity determination, and the numerous standard meteorological and cloud physics instruments that are part of the CIRPAS facility package. Additional data were derived from several well-known, satellite-born radiometers (e.g., MODIS, AVHRR). The flight plans formulated to address our goals were various but always involved measurements below, in and above marine stratocumulus or cumulus (moderatus) clouds.

Theoretical work centered around exercising the NAAPS model with various altered parameteric inputs to test the accuracy of the secondary aerosol (SA) formation mechanism currently in the model (solely oxidation of SO_2 to sulfate) and also to assess possible routes to improving the SA formation by inclusion of secondary organic aerosols (SOA).

WORK COMPLETED

All work under this grant has of course been completed – it is the final report after all.

RESULTS

Nine papers have been published based on the work done under this grant and several reports have been made to NRL-Monterey, the operators of the NAAPS model. Consequently, in the limited space available, we can only present the main highlights of this research.

Results relevant to our first goal, characterization of the aerosol hygroscopicity in the marine atmosphere as a function of size, and its relationship to composition, are shown in Figure 1,

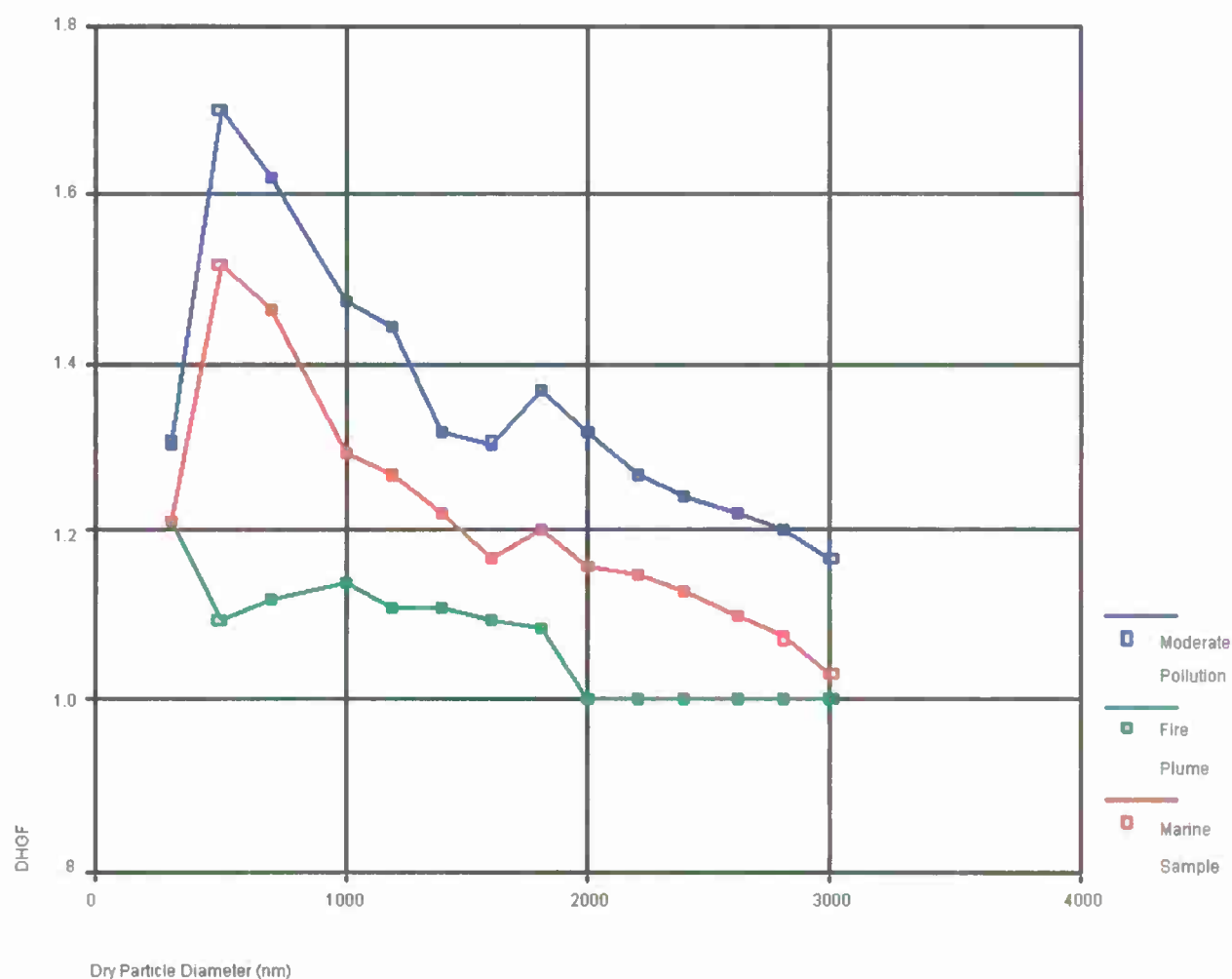


Figure 1. DHGF spectra measured during CARMA-IV for three different aerosol types. All the spectra show relatively low hygroscopicity at larger sizes but differ widely for submicron sizes, with the fire haze sample showing the lowest hygroscopicity.

There is a clear dependence of the hygroscopicity, as quantified by the DHGF (see Hegg et al, 2006), on both size and the nature of the aerosol. Both the size dependence and composition dependence are readily explicable and have been discussed in the published papers. Another aspect of the composition dependence is its variation with height in the MBL. An example of this is shown in Figure 2. The higher altitude samples are significantly more hygroscopic than the lower altitude sample. The simplest

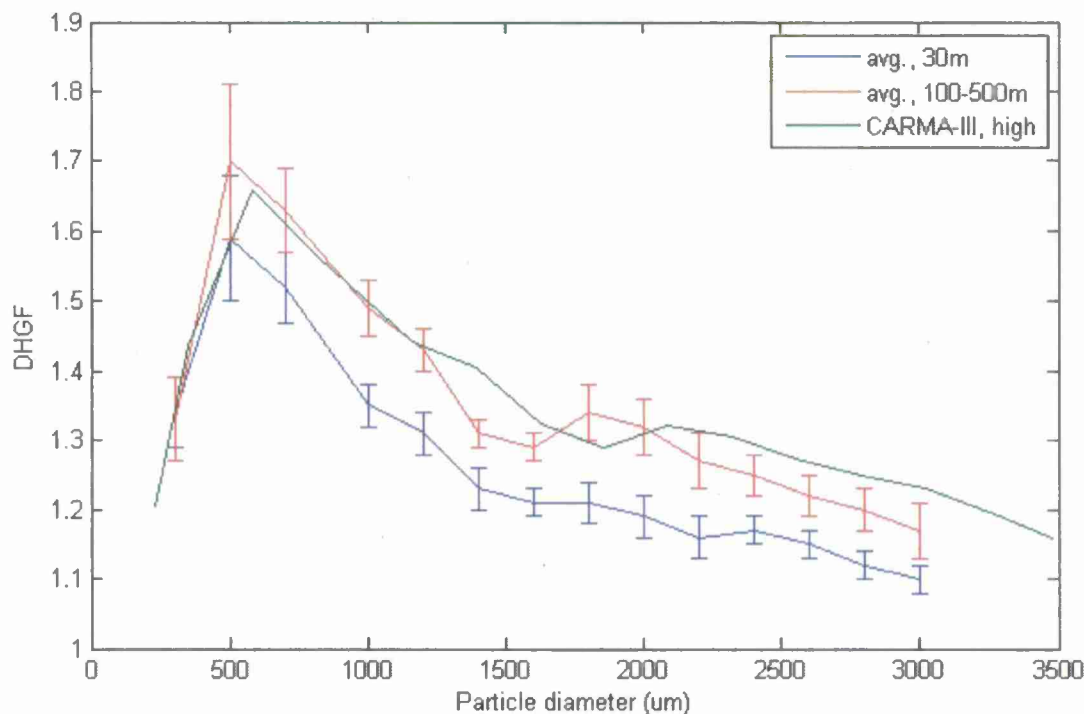


Figure 2. DHGF spectra measured during CARMA-IV for two different altitudes. For comparison, the mean spectrum from CARMA-III for the higher of the two altitude intervals is also shown. All the spectra show relatively low hygroscopicity at larger sizes but there is a significant difference in the mean spectra with altitude with the higher altitudes showing more hygroscopicity.

explanation for this, formation of secondary soluble mass due to, for example, sulfate formation is not consistent with the compositional differences in the high and low altitude samples, which are shown in Figure 3. The soluble species most likely to form in the MBL, sulfate and nitrate are essentially invariant with altitude. On the other hand, the change in hygroscopicity seems to be associated with changes in formate and oxalate, both breakdown products of fatty acid oxidation. We hypothesize that surfactants from the marine surface layer coat much of the aerosol on emission and inhibit hydration of the marine aerosol, but are quickly oxidized, thus breaking the surfactant layer and increasing the aerosol hygroscopicity. This issue is discussed in Hegg et al (2008). Finally, given the different aerosol types shown in Figure 2, with their differing hygroscopicities, the question arises as to how to predict the overall aerosol hygroscopicity when multiple aerosol types are present, none dominant. We have found that the ZSR volume mixing rule works well in this regard. Again, this is discussed in Hegg et al (2008).

The application of the ZSR mixing rule requires quantitative information on the contribution of various aerosol types to the aerosol mass in the MBL. Because the types are essentially defined by composition, and this composition is determined by the aerosol source, the contribution of various potential sources

to MBL aerosol mass is a key aspect of marine aerosol studies. Indeed, the source attribution of not only mass but also such important related aerosol characteristics as CCN activity and light scattering

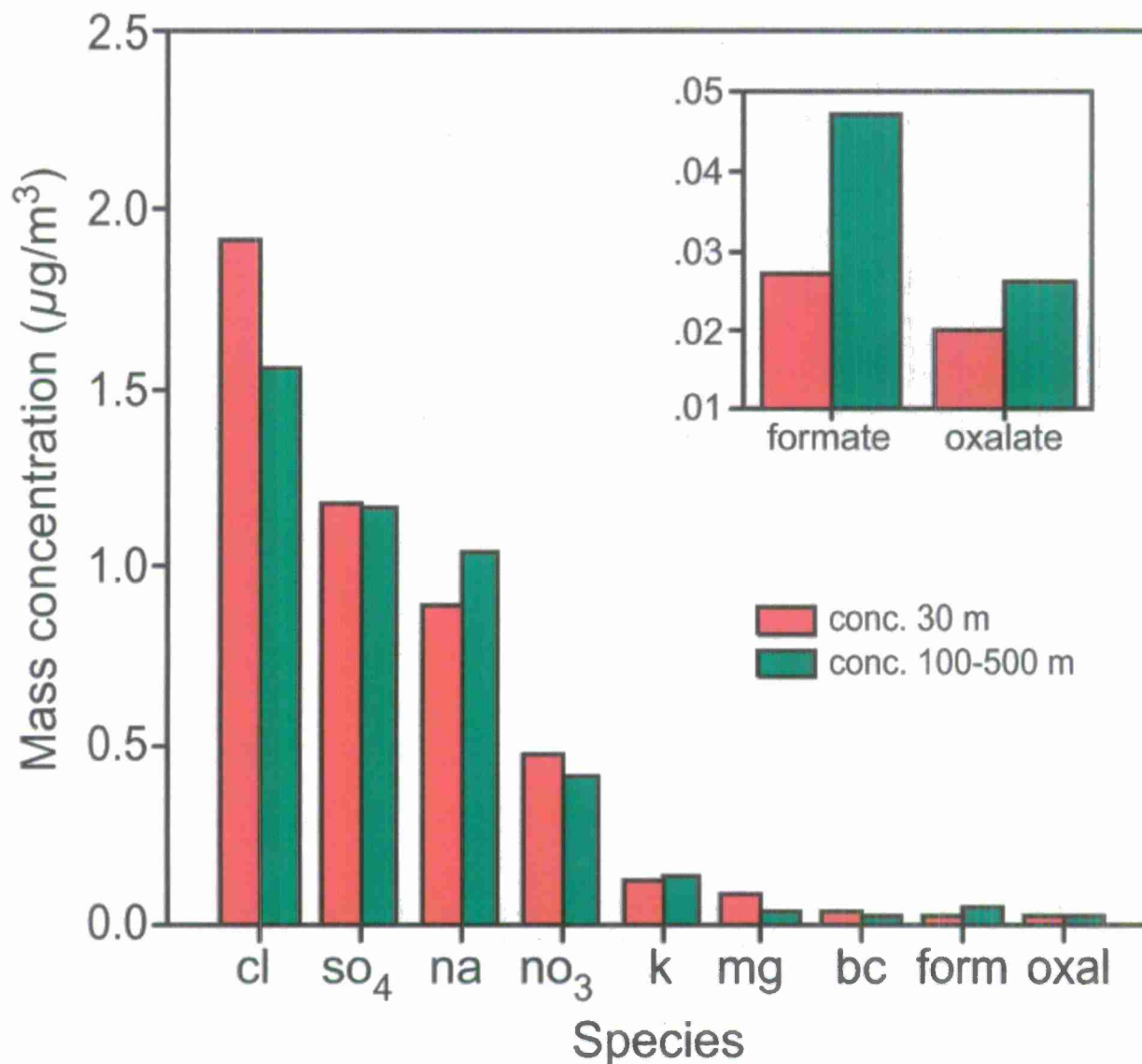


Figure3. Comparison of the mean chemical concentration of the dominant soluble chemical constituents of the aerosol at high (>160 m) and low altitude (30 m) during the study period. The associated DHGF spectra are shown in Figure 1. The insert shows more clearly the changes in formate and oxalate

efficiency has been a main objective of this study. To address this, we have exercised receptor modeling, specifically the EPA PMF and UNMIX models (cf., Hegg et al, 2009, 2010), on our aerosol composition data base. An example of the source attribution of CCN activity is shown in Figure 4, which compares the average contribution of the three main aerosol sources found in the CARMA operational area for three different intensive measurement periods, corresponding to summer of three different years. Similarly, Figure 5 shows data for the same three periods but now for the average

aerosol light scattering coefficient. It is interesting to note the differences between the sources of light scattering and CCN activity, with marine aerosols most important for the former and pollution aerosols

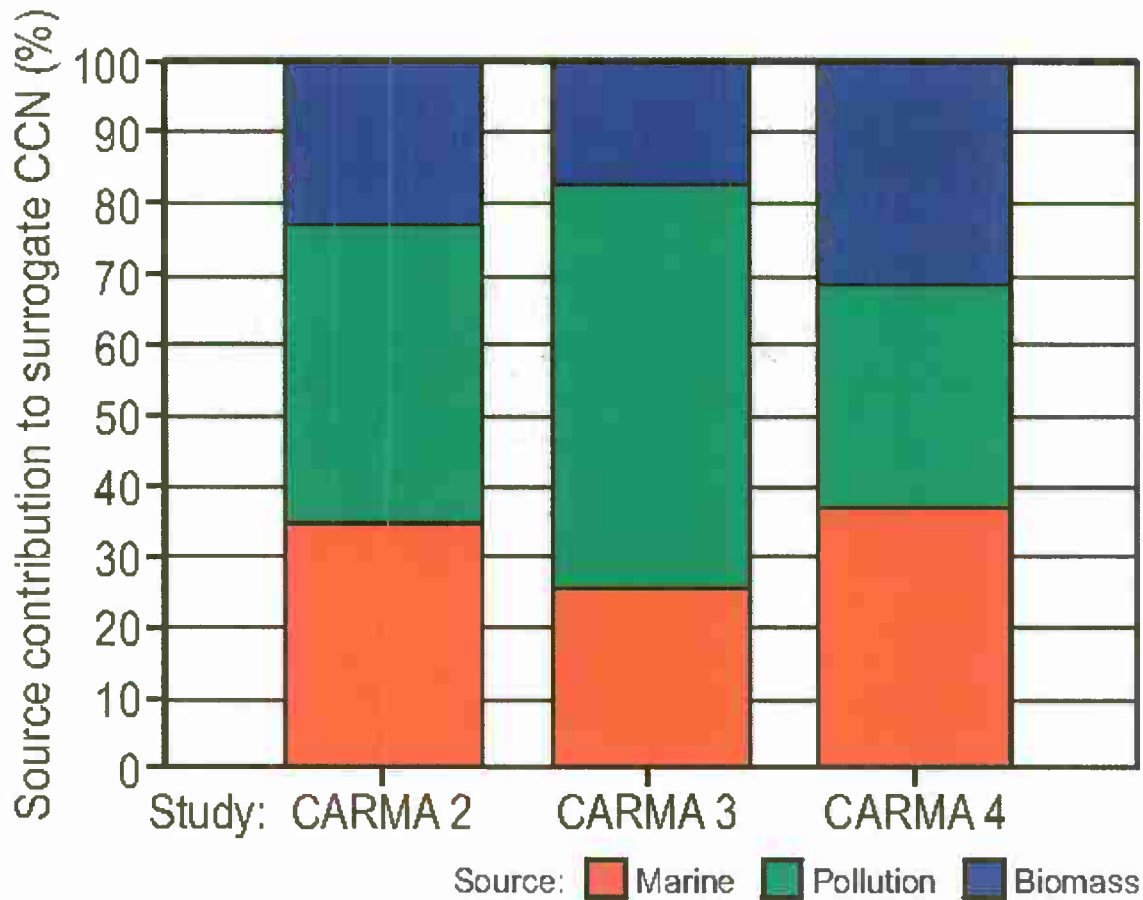


Figure 4. Bar graph showing the source contributions of the three main sources of CCN for three different years during the CARMA field campaign. For CARMA II, the largest source was pollution; for CARMA III, pollution dominated; for CARMA 4, marine aerosol was most important, closely followed by biomass burning.

for the latter. This is consistent with CCN being associated more with the aerosol number concentration and light scattering with the aerosol volume concentration.

One aspect of the data shown in Figure 4 leads naturally to another important topic in our study. The source attribution of the CCN activity is actually to “surrogate CCN” rather than CCN activity directly measured with a CCN spectrometer. An important finding of our work has been that, for the subtropical marine stratocumulus regimes that largely modulate the impact of anthropogenic aerosols on the aerosol indirect climate forcing, it is the Accumulation Mode Number Concentration (AMNC) of aerosol particles that is the best predictor of cloud drop number concentrations (CDNC) rather than the CCN concentration active at any particular supersaturation. This situation arises in part due to the feedback loop between CCN activation supersaturation and the peak supersaturation achieved in clouds. The issue is discussed in Hegg et al (2012). The prognostic power of the AMNC vis a vis CDNC is demonstrated in Figure 6. The R^2 value for the regression line shown is 0.91, which exceeds

the value of R^2 found for virtually all previous studies which have utilized values of CCN concentration active at any given supersaturation.

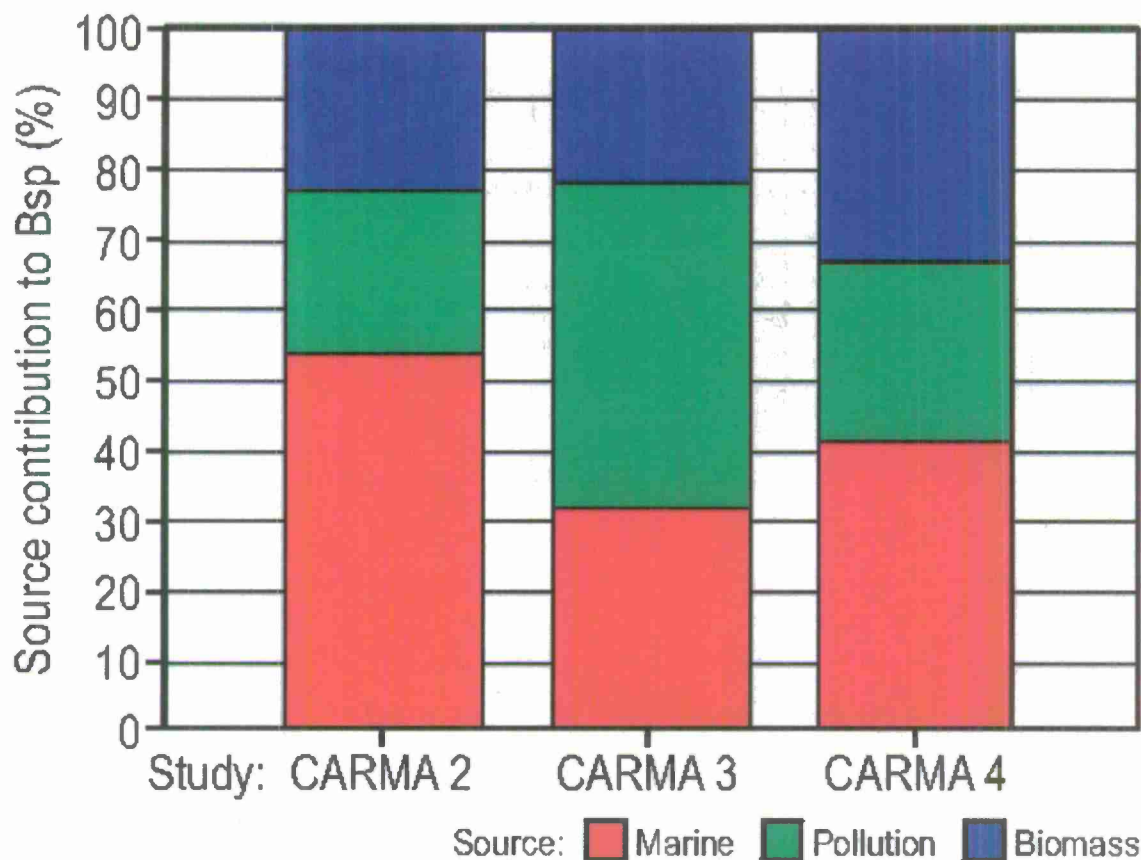


Figure 5. Bar graph showing source contributions to the aerosol light scattering for three different years during the CARMA field campaign. The marine source was the strongest during CARMA II, the pollution source the strongest during CARMA III and the marine and biomass sources the strongest during CARMA IV.

The next objective of this study, the aerosol optical climatology, has now been completed and the results conveyed to NRL. The data have been used in several different preliminary analyses to demonstrate their prospective value. One example is shown in Figure 7 for the CARMA II data alone. The aerosol single scattering albedo (SSA) at a wavelength of 550 nm has been plotted against altitude. Given that the mean inversion height for the CARMA II study was ~ 600 m, it is quite clear that significantly more absorbent (and perhaps more tellingly, variable in its absorbance) aerosol is commonly present above the MBL than in it, likely due to offshore transport of biomass burning aerosol and/or pollution. The aerosol hygroscopicity (now quantified by the gamma parameter; cf., Hegg et al, 2002) shows a similar dichotomy in vertical structure. This can be seen quantitatively in Figure 8, in which the distribution of aerosol hygroscopicity for both the MBL and the free troposphere is shown for CARMA IV. The normalized standard deviation of the mean hygroscopicity (gamma) for the free troposphere is almost 6 times that for the MBL. It is also worth noting that the central value for the MBL, 0.5, suggests that $\sim 50\%$ of the aerosol mass is organic (e.g., Hegg et al, 2002). This is consistent with the source attribution for this period, based on PMF modeling (Hegg et al, 2010).

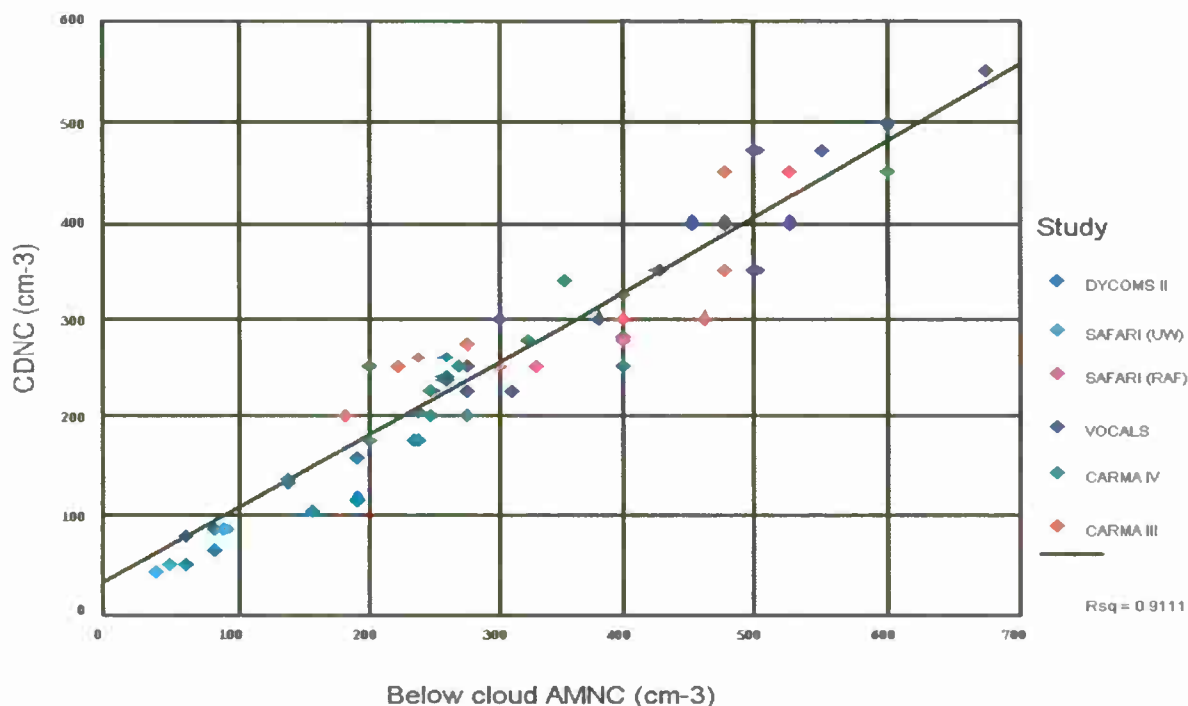


Figure 6. Regression analysis of the dependence of the CDNC on the AMNC for the three main stratocumulus decks of the earth system.

The final two objectives of the study, assessing SA formation in the NAAPS model and devising a strategy for incorporating SOA into the model arise because of a low bias in the prediction of AOD by NAAPS. Such underprediction is fairly commonplace in GCM's and can arise for several different reasons, depending on the specific model examined. As discussed in our various annual reports, it was initially thought that the relatively primitive parameterization of sulfur chemistry in the model was leading to the observed underprediction of AOD. However, a comparison of measured and model predicted precipitation and sulfate deposition in the arctic did not reveal any systematic low bias in the deposition of sulfate. Furthermore, model sensitivity studies showed that varying the sulfate precursor input or model oxidation within any reasonable bounds could not correct for the aerosol mass underprediction. For example, shown in Figure 9 is a comparison of a base model run with one in which the input of SO₂ has been doubled and essentially instantly oxidized to sulfate. Clearly the column mean sulfate concentration has not doubled. In fact, the annual average global mean column burden has increased by only ~ 35%. Since the doubling of SO₂ is a highly implausible scenario, this result, coupled with the previous reasonable agreement of model/observed sulfate deposition, render it quite clear that the low model bias for AOD is not due to sulfate chemistry. It in fact almost certainly resides in the lack of organic aerosol in the model.

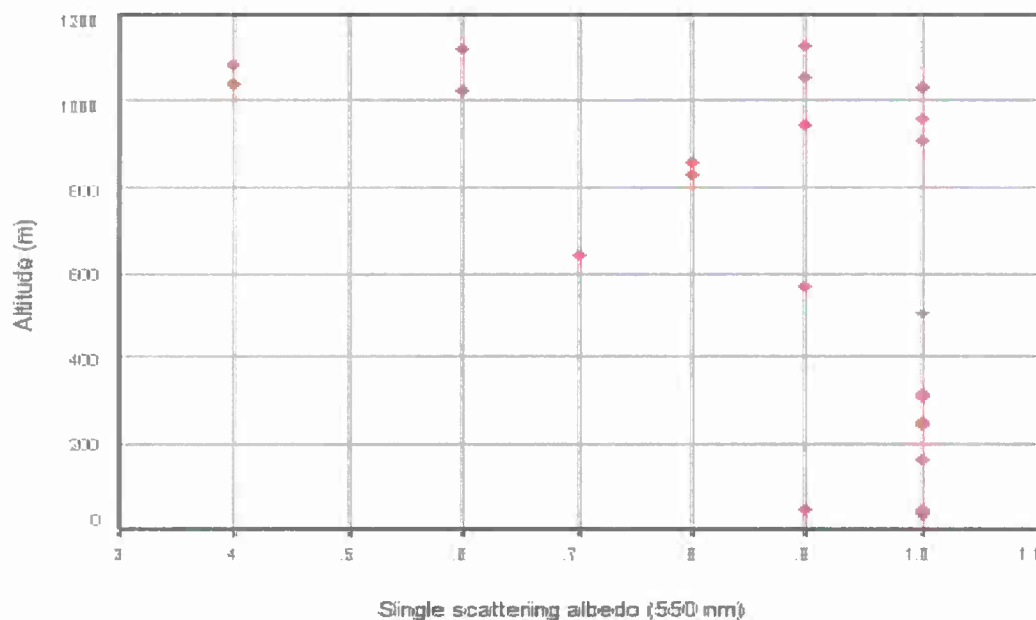


Figure 7. The aerosol single scattering albedo (SSA) at 550 nm plotted against altitude for transects from the CARMA II study. For reference, the mean inversion height defining the top of the MBL was ~ 600 m during CARMA II.

To address this issue, an extensive literature survey has been undertaken of the impact of organic aerosols in global models. Briefly, the results indicate that most of the organic aerosol is secondary and is of biogenic origin. With respect to the chemistry necessary to include in a global model for optimum prognostic power, Figure 10 shows the results of sensitivity studies done by Ahmadov et al (2012) with the WRF-CHEM model and a state-of-the-art chemistry parameterization. The sensitivity studies suggest that the process that is most important is the multi-generational chemistry of organic aerosol precursors. These findings (in greater detail) have been conveyed to NRL-Monterey (Frascati ICAP meeting, May, 2012).

On this basis, a strategy has been formulated to incorporate SOA into the NAAPS model. It will involve the following steps.

- Incorporate both the MEGAN and POET data bases into the NAAPS model. The databases contain reasonable suits of volatile organic carbon (VOC) species that can act as organic aerosol precursors
- Utilize the oxidation rates of Ahmadov et al (2012) for the VOC classes involved in SOA formation
- Employ the VBS4 approach to partitioning of the SOA precursors into the condensed phase as per Ahmadov et al (2012) and Farina et al (2010)
- Incorporate the strategy of Ahmadov et al (2012) for the aging of the SOA in the NAAPS model

A number of these steps will involve modification of the existing parameterizations in the NAAPS model. For example, a new aerosol type (SOA), with a variable initial hygroscopicity will be included in the

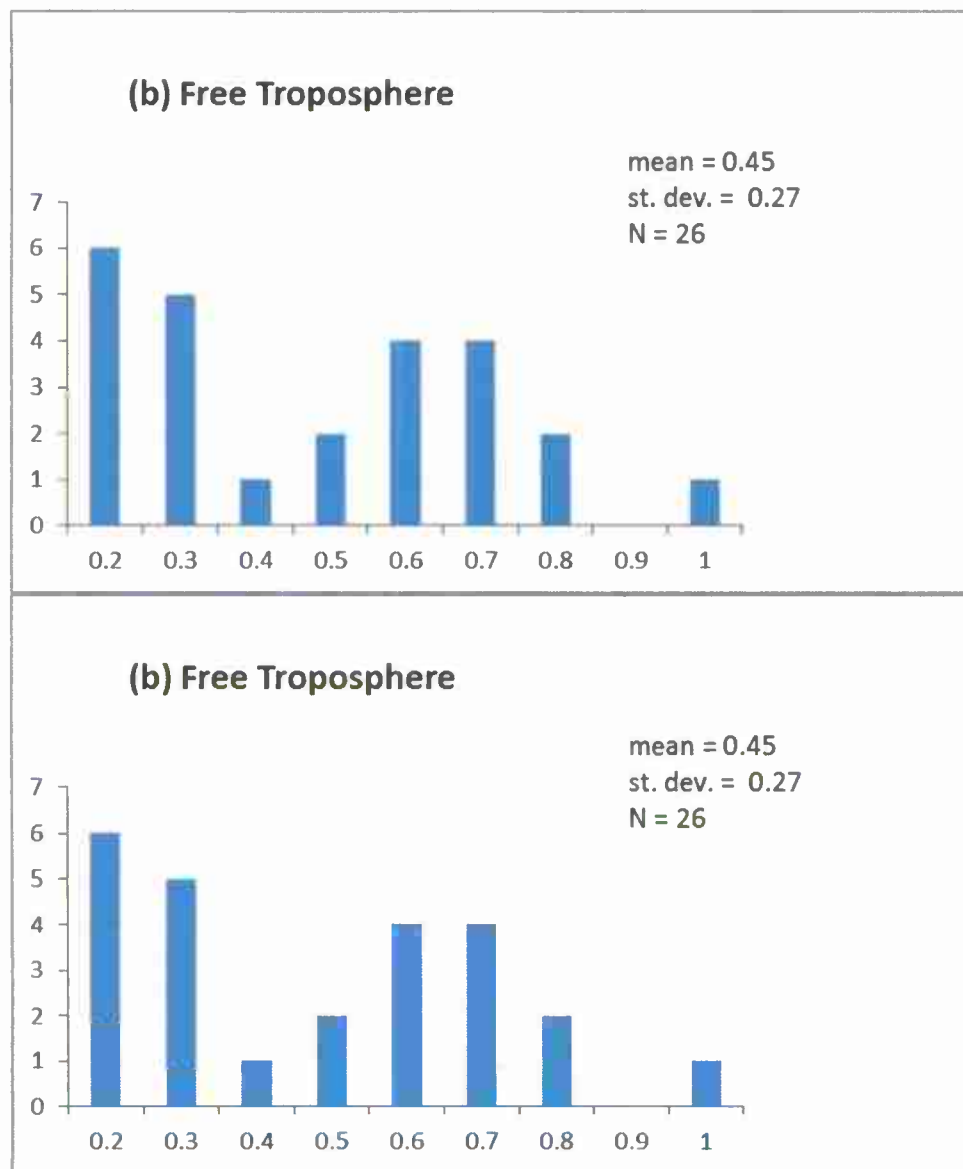


Figure 8. Histograms of aerosol hygroscopicity for transects from the CARMA IV study. (a) in the MBL and (b) in the free troposphere.

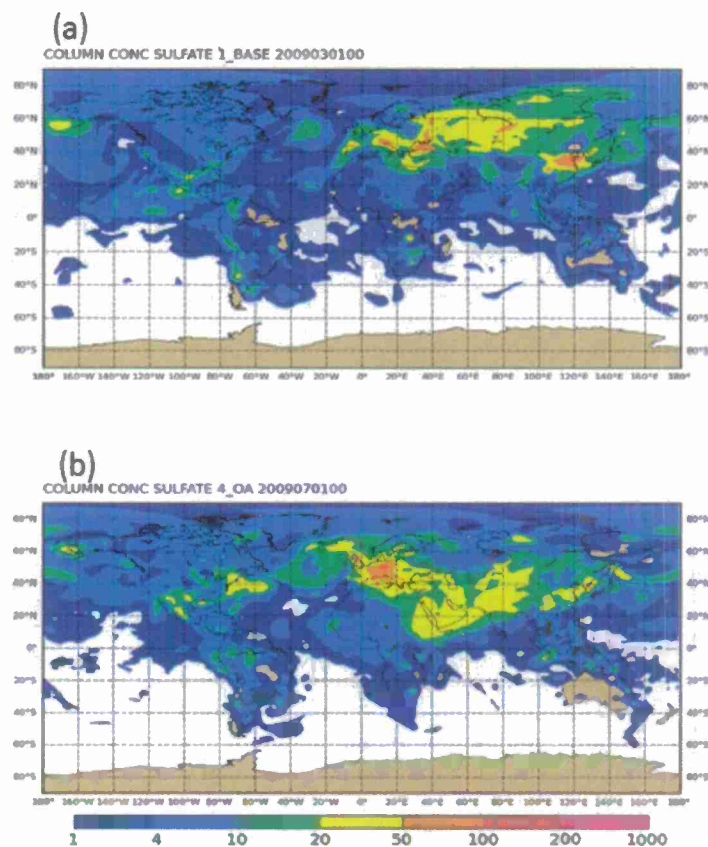


Figure 2. Sulfate column burden predicted by the NAAPS model with, (a) standard input based on widely used emissions inventories and, (b) double the standard SO_2 emission with immediate conversion to sulfate. The units are mg m^{-2} .

model. Furthermore, the hygroscopicity of this aerosol will evolve with the aging of the SOA. Hence, the overall aerosol hygroscopicity will also evolve with time and require the application of a mixing rule to quantify. Removal processes for the aerosol will now vary appreciably with the aerosol type and the age of the aerosol in the model domain.

The implementation of the SOA incorporation strategy is tentatively scheduled for the first half of 2013 by NRL. The Principle investigator of this study will participate in this implementation.

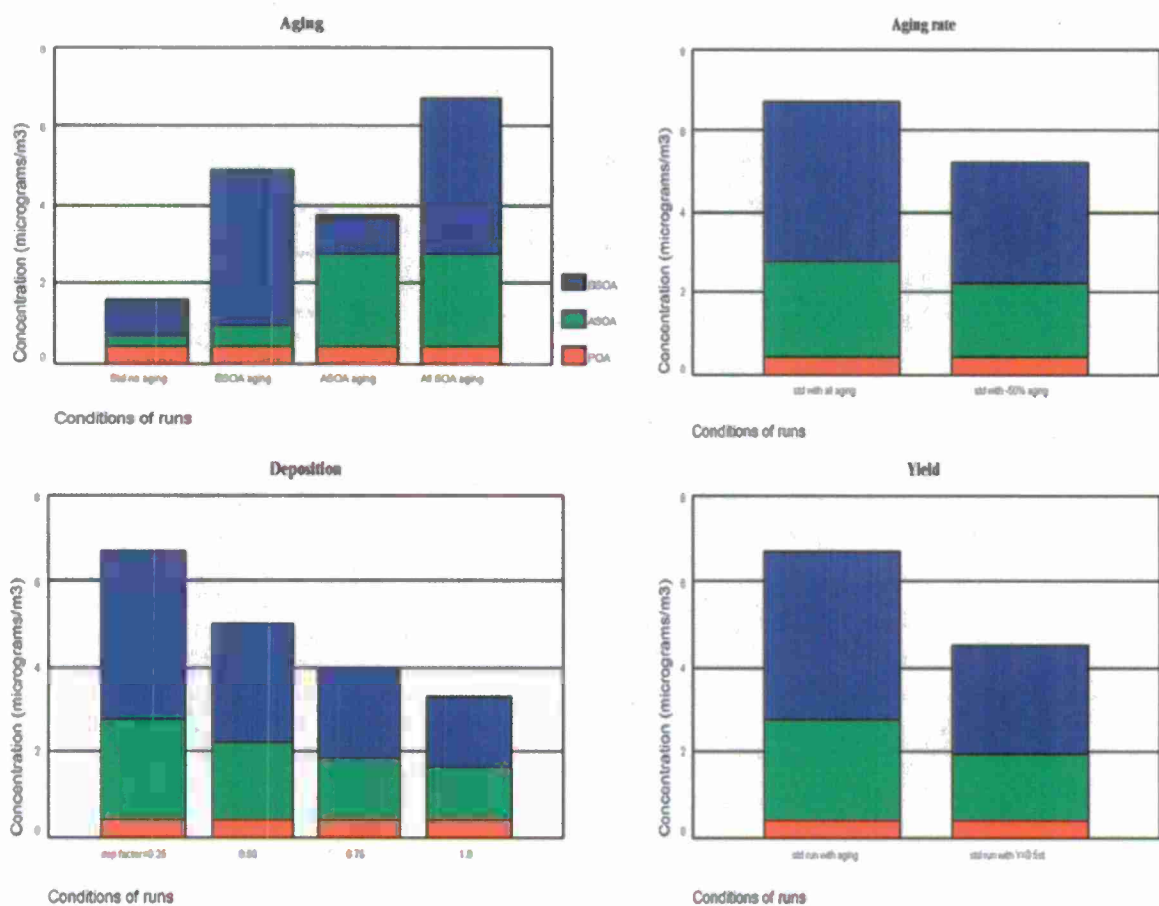


Figure 10. Results of sensitivity studies done with the WRF-CHEM model to test the relative importance of precursor aging, aging rate, reaction yield and deposition on the concentration of secondary organic aerosol. Concentrations are averages over the model domain (based on Ahmadov et al, 2012).

TRANSITIONS

None.

RELATED PROJECTS

The research described above is clearly related to a host of issues of importance to the physics and chemistry of the MBL.

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PATENTS

None

Subject: RE: Final report on ONR N00014-07-0277 (fwd)
From: Dean A Hegg <gwillam@u.washington.edu>
Date: 1/24/2013 4:25 PM
To: Andrew Sattler <acs29@u.washington.edu>

Dear Andrew,
Here is both the letter to Ron, and his response.

Regards, Dean

----- Forwarded message -----

Date: Wed, 16 Jan 2013 15:53:52 -0500
From: "Ferek, Ronald CIV ONR 322" <ron.ferek@navy.mil>
To: "'deanhegg@atmos.washington.edu'" <deanhegg@atmos.washington.edu>
Subject: RE: Final report on ONR N00014-07-0277

Thanks Dean. It was money well spent. Enjoy the time at NRL. See you around, Ron

-----Original Message-----

From: gwillam [<mailto:gwillam@u.washington.edu>]
Sent: Wednesday, January 16, 2013 3:24 PM
To: Ferek, Ronald CIV ONR 322
Subject: Final report on ONR N00014-07-0277

Dear Ron,

Attached is the Final Report on the CARMA work. I am also submitting it through the UW system but wanted to get it through to you directly (you never know). It has been a long haul but I think we have gotten some interesting results - and will be applying some of them to work at NRL (I am off Saturday to work with Jeff down there). Let me take this opportunity to thank you for the support you have given us over the years. It has been very pleasant to work with you. Now that I am no longer working for you, I think I can buy you a beer when we next meet.

Regards, Dean



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UNIVERSITY of WASHINGTON

January 25, 2013

Defense Technical Information Center
8725 John J Kingman Road Ste 0944
Fort Belvoir, VA 22060-6218

Naval Research Laboratory
ATTN: CODE 5596
4555 Overlook Avenue SW
Washington, DC 20375-5320

Re: Final Technical Report for ONR award N00014-07-0277, PI: Dean Hegg

Please find enclosed a copy of the email to Ron Ferek, the program manager for the above award, along with a copy of the Final Technical Report that was attached to that email.

Sincerely,

Andrew Sattler
Grants Manager

cc: ONR REG OFFICE SEATTLE-N63374
1107 NE 45TH STREET SUITE 350
SEATTLE, WA 98105-4631

