

The contribution of anthropogenic aerosols to aerosol light-scattering and CCN activity in the California coastal zone

D. A. Hegg¹, D. S. Covert¹, H. H. Jonsson², and R. K. Woods²

¹Department of Atmospheric Sciences, University of Washington, Seattle, WA, USA

²Meteorology Department, Naval Post Graduate School, Monterey, CA, USA

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Abstract. Aircraft-based measurements of aerosol light-scattering coefficient, cloud condensation nuclei (CCN) measured directly or by proxy, and aerosol chemical composition are reported for three different years in the region of the large stratocumulus deck off the California coast. Receptor modeling is used to differentiate the contributions of the main aerosol sources to the light scattering and CCN activity. The contribution of anthropogenic sources to the two climatically important aerosol parameters (for direct and indirect forcing) varied from year to year but, on average, was found to be 67% in the case of CCN concentration and 57% in the case of light-scattering coefficient.

1 Introduction

It is now widely accepted that anthropogenic aerosols can have a significant impact on the albedo of the extensive subtropical stratocumulus decks that occur off the west coasts of Africa, and South and North America (e.g., Platnick and Twomey, 1994; Durkee et al., 2000; IPCC, 2001). These decks are a major factor in the radiative balance of the atmosphere (Klein and Hartmann, 1993) and, due to a combination of cloud extent, frequency, and the cloud type dependent sensitivity of cloud albedo to aerosol modulation, the climatic impact of aerosols on cloud microphysics (the indirect effect) is largely limited to these decks (Warren et al., 1988; Platnick and Twomey, 1994). More recently, it has been demonstrated that direct radiative forcing by aerosols above these cloud decks (or for aerosol absorption effects, even in them) can also be quite important, significantly impacting the apparent albedo as seen from space and some-

times partially offsetting the indirect forcing (cf. Hill and Dobbie, 2008; Chand et al., 2008; Keil and Haywood, 2003). 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 anthropogenic and natural sources has proven elusive. In part, this difficulty arises from the fact that a number of aerosol chemical components that strongly impact climatic properties have multiple sources, both natural and anthropogenic, the archetypical such component being sulfate. One methodology for addressing this quandary is to examine aerosols in venues in which particular sources, or at least either natural or anthropogenic sources, may be expected to dominate a priori; hence such studies as ACE-1 in the remote Southern Hemisphere (Bates et al., 1998) and TARFOX off of the east coast of the United States (Russell et al., 1999) or, for the particularly tricky issue of sources of CCN activity, the MAST experiment (Durkee et al., 2000). While all of these studies have added much to our understanding of aerosol impacts on climate, none have definitively addressed the issue of aerosol sources even for their extreme venues (cf. Hegg et al., 2009). For venues in which one might expect a mix of sources, both natural and anthropogenic, with none dominating, much remains to be done. Such is unfortunately likely the case for the regions of the three main stratocumulus decks of the world (Durkee et al., 2000; Huneus et al., 2006; Keil and Haywood, 2003).

To address the general problem of aerosol source attribution, various multivariate statistical techniques have long been employed (e.g., Cheng et al., 1993; Song et al., 1999; Kim et al., 2004; Chen et al., 2007). Such techniques, sometimes termed receptor modeling, have proven very versatile and useful in source attribution of aerosol mass and size distribution. We recently adopted this approach for CCN source attribution in the marine environment, using the results to distinguish anthropogenic and natural CCN for one of the



Correspondence to: D. A. Hegg
(deanhegg@atmos.washington.edu)

Table 1. Species analyzed from the filter samples obtained in the study and used in at least one of the PMF analyses. Technique acronyms are defined in the text. Mean concentrations found during the study are given ($\mu\text{g m}^{-3}$).

Species	Technique	Used in CARMA	Study mean (study)
Malate	IC	II	0.19 (II)
Formate	IC	IV, II	0.04 (IV), 0.04 (II)
Chloride	IC	IV, III, II	1.28 (IV), 1.27(III), 1.02 (II)
Nitrate	IC	IV, III, II	0.56 (IV), 0.31 (III), 0.24 (II)
Glutarate	IC	IV, II	0.01 (IV), 0.09 (II)
Succinate	IC	IV, II	0.01 (IV), 0.11 (II)
Sulfate	IC	IV, III, II	1.25 (IV), 1.30 (III), 1.19 (II)
Oxalate	IC	IV, III, II	0.09 (IV), 0.15 (III), 0.08 (II)
Levoglucosan	LC-MS	III, II	0.39 (III), 0.06 (II)
Calcium	ICP-OES	IV, III	0.03 (IV), 0.14 (III)
Iron	ICP-OES	II	0.03 (II)
Potassium	ICP-OES	IV	0.14 (IV)
Magnesium	ICP-OES	IV, II	0.04 (IV), 0.11 (II)
Sodium	ICP-OES	IV, III, II	0.81 (IV), 1.03 (III), 0.96 (II)
Lead	ICP-OES	IV	0.47 (IV)
Total dry mass	Gravimetric	IV, III, II	16.3 (IV), 3.93 (III), 3.12(II)
NSS Potassium	Derived	IV	0.11 (IV)
NSS Sulfate	Derived	IV, III, II	1.04 (IV), 1.30 (III) ³ , 1.34 (II) ³
Soluble mass	IC/ICP	IV	5.3 (IV)
Black carbon	Absorption photometer	IV, III	0.26 (IV), 0.30 (III)
Sub-H ₂ O ¹	AHS	IV	22.3 (IV)
Super-H ₂ O ²	AHS	IV	7.1 (IV)

1. water of hydration of the sub-micron aerosol (from AHS).

2. water of hydration for the super-micron aerosol (from AHS).

3. Averaged over a subset of the sulfate values due to missing data.

three stratocumulus decks of global climatological significance, that off the California coast (Hegg et al., 2009). However, as noted in that study, the occurrence of an exceptionally large forest fire near Santa Barbara during the study period, and the advection of smoke offshore, may well have rendered the source attribution results atypical. Indeed, this is an endemic problem with small time period studies. To address this issue, we present here results from three different years of data (2004, 2005 and 2007) in the same operational area, derived from the multi-year CARMA (Cloud Aerosol Research in the Marine Atmosphere) study using the same basic approach as that of Hegg et al. (2009). Additionally, we explore not only the issue of source attribution of CCN but also that of source attribution of aerosol light scattering, thus addressing the direct as well as indirect effects of anthropogenic aerosols in the study area.

2 Methodology

To characterize the chemical composition of the aerosol, filter sampling was employed. 47mm Teflo membrane filters with a 2 μm pore size were used. The substrates have collection efficiencies in excess of 99.99% for 0.2 μm particles and larger. After collection, samples were stored at a nomi-

nal 4 °C prior to analysis. The samples were analyzed over a week's time. All substrates were analyzed gravimetrically and then extracted in 10 ml of HPLC (High Performance Liquid Chromatography) water. The extracts were then analyzed by standard Ion Chromatography (IC) for anions (both organic and inorganic), Liquid Chromatography-Mass Spectroscopy (LC-MS) for carbohydrates, and Inductively Coupled Plasma-Optical Emission spectroscopy (ICP-OES) for a suite of trace elements (cf., Gao et al., 2003) as listed in Table 1. The hygroscopic properties of the aerosol were determined by measuring the light scattering coefficient at three relative humidity's, nominally 40, ambient and 85% (Gasso et al., 2000), and by use of an Aerosol Hydration Spectrometer (Hegg et al., 2008). Additionally, in order to quantify the concentration of light absorbing carbon present (important both optically and as an aerosol source tracer), we used a three wavelength Particle Soot Absorption Photometer (PSAP) to measure the aerosol absorption coefficient (Virkkula et al., 2005). We then employed a specific black carbon absorption coefficient of 7 m² g⁻¹ to convert the absorption at 530 nm to light absorbing carbon mass concentration (cf. Bond and Bergstrom, 2006).

The other main measurements in this study are the CCN concentration at some nominal supersaturation and the multi-wavelength aerosol light scattering coefficient. The measurement of the light-scattering coefficient is straightforward; we employed a TSI Inc. model 3563 three wavelength (450, 550 and 700 nm) nephelometer operating at a nominal 30% RH. For CCN, a more complex procedure was necessary. During the CARMA-IV study (2007), we used the DMT Inc. CNN-100 CCN spectrometer that employs the design described by Roberts and Nenes (2005). It measured cumulative CCN number concentrations at nominal supersaturations of 0.2, 0.3, 0.5, 0.7 and 1.0% (Hegg et al., 2009). However, for the two earlier studies (CARMA-II, 2004 and CARMA-III, 2005) this instrument was not available. Instead, a University of Wyoming model MA100 static diffusion chamber was utilized for CCN measurements. This instrument produced useful data but was plagued by calibration problems and operational breakdowns during the 2004 and 2005 studies. Furthermore, it required a relatively long measurement period (~ 15 minutes) to yield good data in marine air (Kaku et al., 2006). This resulted in sparse data sets for the 2004 and 2005 studies. For example, during the 2004 study, only six data points were available for comparison with filter measurements. Such a data set is simply too small to make receptor modeling viable. Hence, we have had recourse to a surrogate for the CCN concentration that has a much higher data density. This is the concentration of particles in a nominal range of 0.06 to 1.6 μm radius as measured by the PMS/DMT Inc. Passive Cavity Aerosol Spectrometer Probe (PCASP) model 100x. The PCASP concentration has in fact been used numerous times as a surrogate for CCN concentration (e.g., Hegg and Jonsson 2000; Kaku et al., 2006). Using the well-known parameterization of Fitzgerald (1973) relating particle size, soluble fraction and activation supersaturation, the concentration of particles measured by the PCASP would correspond to those active as CCN at a supersaturation of 0.3% assuming a mean particle soluble fraction of $\sim 30\%$, very reasonable based both on past work in the CARMA region and the results presented here. This supersaturation is in fact roughly the same as the effective supersaturations found in the stratocumulus clouds examined in the CARMA data base (cf., Hegg et al., 2009), and also in agreement with earlier studies in the same area (Roberts et al., 2006). Because of this, and because the 1 Hz measurement frequency of the PCASP results in very good counting statistics and hence small uncertainties, and a value can be associated with each filter measurement of composition, we use the PCASP number concentrations as a surrogate for the CCN number concentration active at 0.3% (CCN: 0.3%).

To test the validity of using the PCASP concentration as a CCN surrogate, simultaneous measurements of PCASP and CCN number concentration were compared via regression analysis for the CARMA-IV data set, in which good CCN measurements were available. A plot of the regression is shown in Fig. 1. The R^2 for the regression was a reason-

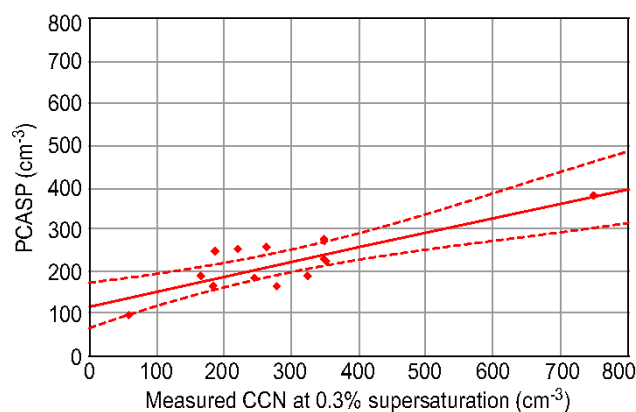


Fig. 1. Regression plot of the PCASP number concentration vs. the CCN number concentration active at 0.3% supersaturation for the CARMA IV study. The solid line is the best fit line and the dashed lines are the 95% confidence limits.

able 0.69. but the slope was only 0.3, suggesting far from complete closure. While the mean residual for the regression was 0.026 ± 11 with a skewness of -0.36 ± 0.62 indicating no bias, the low slope suggests that further investigation of the appropriateness of the linear relationship between the CCN and PCASP concentrations is in order.

To eliminate the possibility of a non-linear relationship, a power fit of the data was made and yielded an R^2 of 0.69, identical to that of the linear model. More plausibly, the unexplained variance could be due to variations in particle composition as a function of size, an issue we do not have data to address. This would not in itself greatly impact our source attribution, which is entirely determined by the bulk composition 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 that range acting as CCN, i.e., Aitken particles. To test this possibility, Aitken particle concentration was added to the CCN-PCASP regression (PCASP as the independent variable) as an additional term. The R^2 value moderately improved to 0.8 and an F test indicated that the additional term was significant, though the gain in variance reduction was quite small. Furthermore, the regression coefficients quite plausibly suggest that about 10% of the PCASP particles do not act as CCN, the deficit being made up by $\sim 8\%$ of the Aitken particles. On the other hand, the Aitken particle concentration is actually highly correlated with the PCASP concentration in this data set ($r = 0.79$, $p = 0.001$). This, taken together with the lack of bias apparent in the residuals, suggests that the Aitken term is merely effectively rescaling the PCASP concentration.

From the standpoint of source attribution, the most adverse possibility to which CCN activity in the Aitken mode gives rise is that the source of these particles is different from those in the PCASP range. This situation can certainly arise but

we feel it is unlikely for our data. Number size distribution measurements taken in the MBL (Marine Boundary Layer) 100 km north of the CARMA operational area a month prior to CARMA III by Roberts et al. (2006) show the PCASP lower limit of 60 nm roughly bisects their 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., 2004) and, while there is some evidence that external mixing occasionally occurs within the Aitken mode, based on hygroscopicity measurements (we are aware of no size resolved chemical measurements within the marine Aitken mode) there is no evidence that it is size-dependent (e.g., Swietlicki et al., 2000). Our own measurements during CARMA II, for example, show no systematic difference between the hygroscopicity of 25 and 50 nm radius particles (Kaku et al., 2006).

In summary, the linear relationship between the CCN and PCASP concentrations appears appropriate and, while particles in the Aitken mode may also be acting as CCN, at least at times, they are highly correlated with the PCASP particles and unlikely to have different sources from them. Hence, the use of PCASP particles as a proxy for CCN active at 0.3% supersaturation appears valid. Nevertheless, the non-unitary nature of the CCN-PCASP regression slope must be kept in mind when interpreting the receptor model results. While the source attribution of the CCN will be valid, the parameter which will be predicted by the model will be surrogate CCN concentration, not the actual CCN concentration at 0.3% supersaturation.

The instruments described above were deployed from an airborne platform, the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS) Twin Otter research aircraft. This platform, and its associated facility instruments, has been described in a number of publications (e.g., Wang et al., 2002; Schmid et al., 2003; Hegg et al., 2005). More specific information will be related, as necessary, in the discussion.

Because the aerosol sources for the CARMA study area are not well characterized and mass conservation cannot be assessed, fully deterministic source apportionment, using tools such as a chemical mass balance model, is not really feasible. As in Hegg et al. (2009), we therefore use receptor modeling to address the issue of sources of CCN activity and aerosol light scattering. However, while the EPA (Environmental Protection Agency) UNMIX 2.3 model (Henry, 2003) was used in Hegg et al. (2009), in this study we use the EPA PMF (Positive Matrix Factorization, see Paatero and Tapper, 1994) model 3.0.

Numerous studies employing both the PMF and UNMIX models have been made in recent yearly (e.g., Pekney et al., 2006; Poirot et al., 2001; Kim et al., 2004; Chen et al., 2007). The models tend to be more or less in agreement for large data sets but differences of a factor of two in the contribution of identified similar sources to particular samples are not

uncommon. 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 (Maykut et al., 2003). 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 could be resolved in each data set and inter-annual comparison – the main objective of the study – would be difficult. Additionally, the larger uncertainties associated with the reduced data sets for the 2005 and 2004 studies render the error-weighted variance reduction of the PMF approach preferable. Nevertheless, we take advantage of the previous UMMIX results for the 2007 data set, using them to inform our choice of factors in PMF.

3 Venue

The measurements reported here were acquired during three CARMA field campaigns, as alluded to above. The operational area for the CARMA measurements extended from 37.2°N Latitude to 34°N latitude and from the coastline to ~300 km offshore. This location is one in which the aerosol is impacted by a number of different sources, including biomass burning, pollution and the ocean surface (Hegg et al., 2008). This leads to a wide range in both aerosol size and composition, and other derivative properties such as the CCN activity (cf., Roberts et al., 2006). Airborne sampling was done throughout this region in the course of 15 flights conducted during August 2007 (CARMA-IV), 17 flights in August of 2005 (CARMA-III) and 14 flights in July of 2004 (CARMA-II). Horizontal traverses of the marine boundary layer (MBL) were made. There were normally at least three per flight, typically at 30 m m.s.l. and also 100–500 m but below cloud base (when cloud was present). During the traverses, filter samples were obtained, typically one per traverse, while the PCASP and aerosol scattering measurements were continuous and could be averaged over the filtering times. Traverses with sufficiently complete chemical data to permit inclusion in receptor modeling analysis were selected from this data base. From the standpoint of inter-annual comparison, it is important to note that general meteorological conditions were similar during all three studies, with percent low cloud fraction essentially the same (35–38%). The sampling altitudes were also quite similar, with mean sampling altitudes of 195 ± 59 m, 141 ± 30 m and 156 ± 38 m for CARMA IV, III and II, respectively.

4 Results and discussion

4.1 Chemistry and aerosol sources from receptor modeling

The available data set consists of the concentrations of chemical species analyzed on each of the filter samples together with concurrently measured values of CCN activity and aerosol light scattering. From CARMA II, 21 such samples are available, from CARMA III 29 and from CARMA IV 24. From these chemical concentrations, several derivative variables such as non sea salt (NSS) sulfate and potassium, and water of hydration were calculated (Hegg et al., 2008). However, several species were eliminated from use a priori due to a low incidence of above detection limit concentrations – which led to a poor signal-to-noise ratio. Such eliminations varied from study to study, resulting in a non-uniform set of chemical measurements across the three years investigated. This precluded a meta analysis using all of the data in a single receptor model. Instead, separate models were run for each study (year). The species included in each receptor model are listed in Table 1.

Hegg et al. (2008, 2009) exercised the EPA receptor model UNMIX 2.3 on the data set for CARMA IV to derive sources for aerosol hygroscopicity and CCN activity. The model found feasible solutions to the matrix inversion only for three factors or sources using the detection algorithm of Henry (2003) that finds data “edges” in sets of data points in N-dimensional space. These sources were interpreted as representing, marine, biomass burning and pollution emissions. The source identification was based primarily on Na and Cl for the marine factor, black carbon and NSS potassium for the biomass and Pb and NSS sulfate for the pollution factor (see Hegg et al 2008 for details). As discussed above, we now use the more recent and, for these data sets taken as a whole, more appropriate EPA PMF model 3.0. Exercised on the CARMA IV data set, the PMF model yields a four source/factor solution (shown in Fig. 1) as compared to the three source solution of the UNMIX model. However, the additional source, which is dominated by Mg, water of hydration and formate, is also quite plausibly a marine source. When summed with the more obvious marine source (dominated by Na and Cl), the factor loadings are quite similar though not identical with those from the earlier UNMIX model. The reason for the disaggregation of the marine source into two factor in the PMF analysis is not clear but PMF is well known to produce additional, low-variance reduction factors compared to the UNMIX model (cf., Pekney et al., 2006; Poirot et al., 2001; Kim et al., 2004; Chen et al., 2007).

Turning to the CARMA III and CARMA II data sets, the PMF model produces the source profiles shown in Figs. 2 and 3, respectively. For CARMA III, the model optimum solution is for three sources or factors. The first of these, heavily loaded by Cl and Na is obviously a marine source. A pollution source is indicated for the second factor given

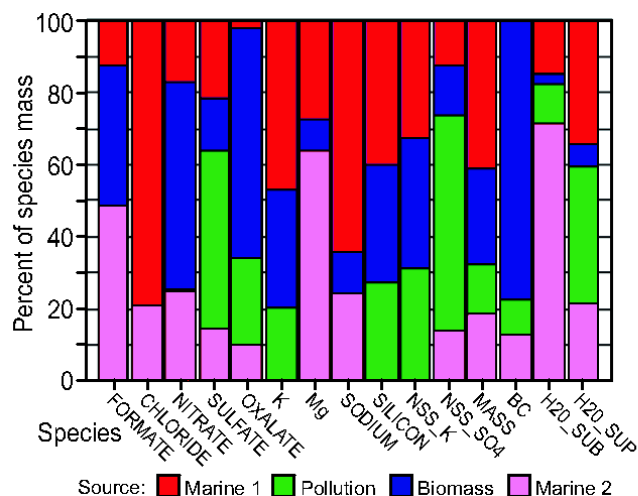


Fig. 2. Source profiles for the four sources identified by the PMF model for the CARMA-IV (2007) data set.

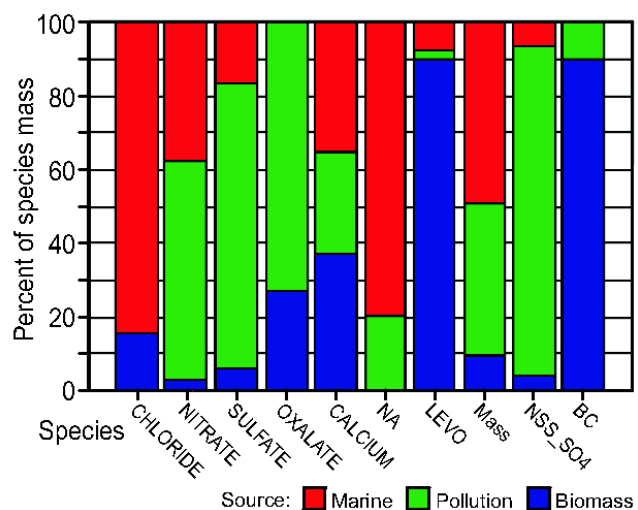


Fig. 3. Source profiles for the three sources identified by the PMF model for the CARMA-III (2005) data set.

the high loadings of nitrate and NSS sulfate while the third factor is identified as biomass burning by having virtually all of the levoglucosan and black carbon loaded on it. For CARMA II, a slightly more complex scenario is evident. While a clear marine source is once again evident, with high Na and Cl, a pollution source with high nitrate and NSS sulfate, and a biomass burning source with high levoglucosan, there is now a fourth source as well. This source displays high loadings of the three dicarboxylic acids analyzed and is the only source loaded by the single hydroxy dicarboxylic acid present. Although these species do have a number of possible sources, they are well known secondary photochemical species in marine air (e.g., Satsumabayashi et al., 1990; Kawamura and Sakaguchi, 1999). Furthermore,

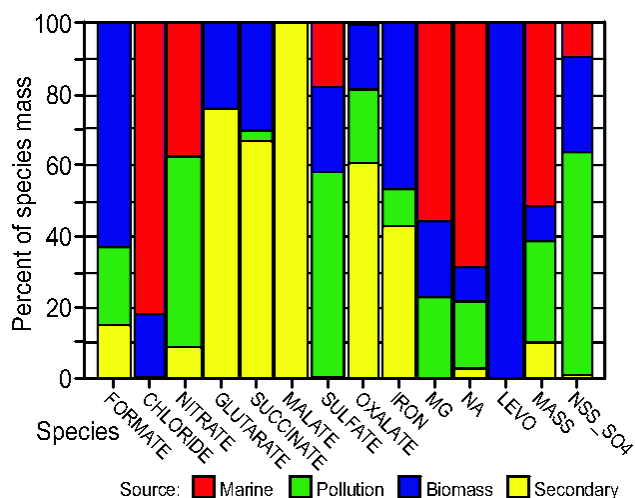


Fig. 4. Source profiles for the four sources identified by the PMF model for the CARMA-II (2004) data set.

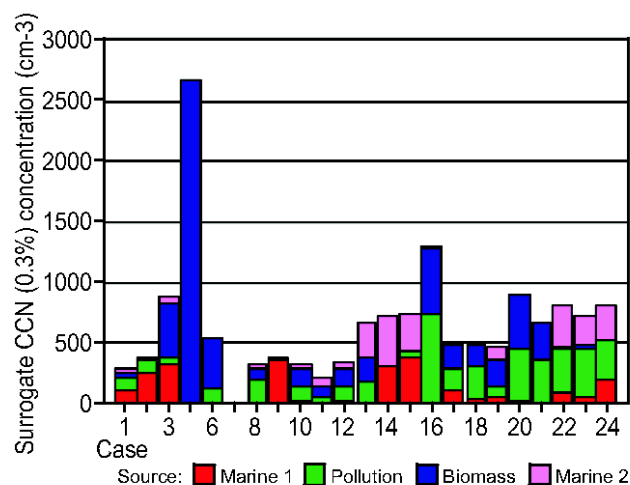


Fig. 5. Source contributions to the surrogate CCN (0.3%) concentration of each of the four sources to each sample taken during the CARMA IV study. The samples shown were taken consecutively between 11 and 27 August 2007. As noted in the text, in this figure and in all succeeding figures CCN(0.3%) refers to the concentration of CCN active at 0.3% supersaturation.

previous studies in roughly the same sampling venue as the CARMA studies, have pointed out the importance of secondary or in situ processes on aerosol properties (e.g., Furutani et al., 2008). Hence, we designate this source as a secondary aerosol source. The reason why the CARMA II data set could preferentially distinguish this factor is not entirely clear. This study did take place in July while the other two CARMA studies were in August and would thus have a slightly higher clear sky actinic flux. However, it is unlikely that this alone could be responsible for a more distinct secondary component and the explanation likely involves differ-

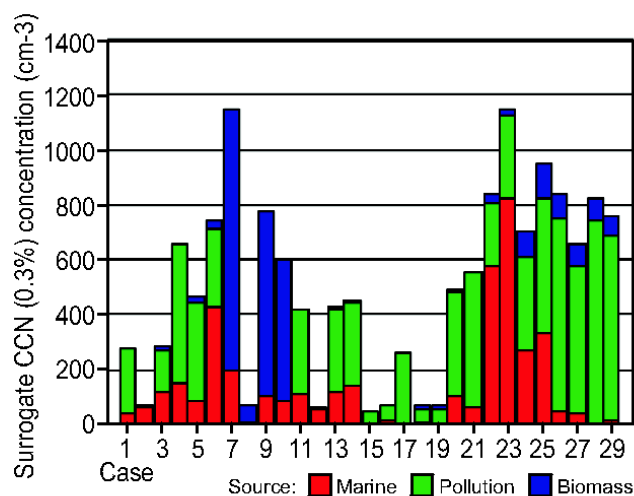


Fig. 6. Source contributions to the surrogate CCN (0.3%) concentration of each of the three sources to each sample taken during the CARMA III study. The samples shown were taken consecutively between 6 and 26 August 2005.

ential emissions, transport and low-cloud statistics between the study periods. Further analysis is beyond the scope of this study.

Having plausible source profiles in hand, the next step in the receptor modeling exercise is to quantify the contribution of each source to each of the samples in the database with respect to the specific aerosol property of interest.

4.2 Source apportionment of CCN activity and aerosol light scattering

The methodology for partitioning of a variable into the various source components is well established. To arrive at the contribution of each source to the CCN concentration or aerosol light scattering in each sample, linear regressions of the property of interest in each sample onto the factor source contribution (factor scores) for each factor in each sample (as shown in Figs. 1–3) are made. The linear regression coefficients are then multiplied by the source contributions to arrive at the contribution of each source to the measured property in each sample. In this instance, such an analysis is made for both the surrogate CCN concentration (PCASP number concentration) and the aerosol light scattering coefficient onto the factor scores. The results of this for the CCN activity are given in Figs. 4–6 for CARMA IV, III and II, respectively. Corresponding results for aerosol light scattering are shown in Figs. 7–9.

Perhaps the first point of interest is to compare the results for the CARMA IV PMF analysis of CCN with the previously reported results using the UNMIX model (Hegg et al., 2009). Compared to the earlier results, those shown in Fig. 4, although broadly similar, suggest a somewhat reduced role for the marine source. However, this arises due to the impact

Table 2. Values of R^2 for linear regressions of measured aerosol properties onto those predicted by the PMF model.

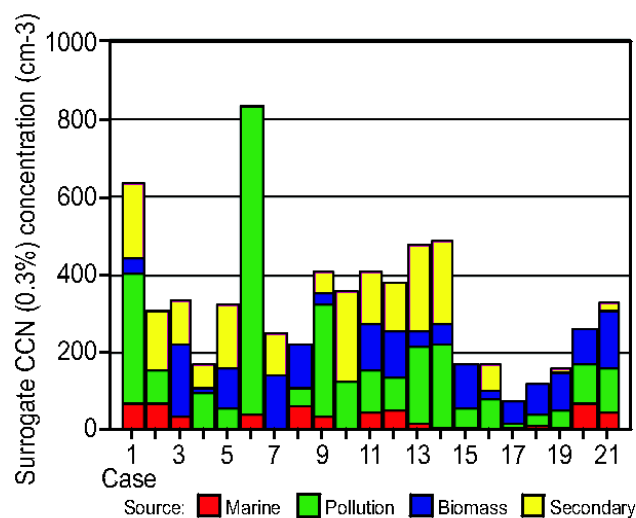
Study	Aerosol parameter	Regression R^2	Slope	Intercept	No intercept slope
CARMA IV	CCN	0.86	0.92 ± 0.085	-228 ± 72	0.7 ± 0.06
CARMA IV	Light scattering coefficient	0.85	1.01 ± 0.09	-37 ± 9	0.7 ± 0.07
CARMA III	CCN	0.70	0.54 ± 0.08	98 ± 45	0.7 ± 0.04
CARMA III	Light-scattering coefficient	0.61	0.51 ± 0.09	3.8 ± 4.2	0.6 ± 0.05
CARMA II	CCN	0.75	0.86 ± 0.15	9 ± 50	0.9 ± 0.05
CARMA II	Light-scattering coefficient	0.71	0.53 ± 0.09	-3.5 ± 3.0	0.4 ± 0.03

Table 3. Study mean values of the source contributions to both CCN activity and aerosol light scattering for each of the CARMA studies, together with their associated uncertainties. Values are in percentages of the total contribution.

Property	CARMA study	Marine source	Biomass source	Pollution source
CCN activity	II	35 ± 6	23 ± 4	42 ± 11
CCN activity	III	26 ± 5	17 ± 5	57 ± 6
CCN activity	IV	37 ± 6	31 ± 6	32 ± 4
Light scattering	II	54 ± 9	23 ± 4	23 ± 7
Light scattering	III	32 ± 5	22 ± 5	46 ± 6
Light scattering	IV	42 ± 7	33 ± 6	25 ± 3

of a small subset of the samples. Firstly, a key sample from the earlier analysis is that taken on 14 August at an altitude of 30 m, which UNMIX designated as virtually pure marine. This sample was not included in the PMF analysis due to a malfunction of the PCASP during the sample period. More tellingly still, the last set of samples (cases 22–24), taken on 27 August which had rather high CCN concentrations, were designated as predominately marine by the UNMIX analysis but only partially marine by PMF. The UNMIX attribution was based primarily on a lack of Pb in these samples, Pb being a main component of the pollution profile in UNMIX. However, Pb, due to its very large uncertainty (100%), was not included in the PMF source profile. The PMF attribution is based on high NSS sulfate and hygroscopicity. The total particle concentrations for these samples (based on measurements with a TSI 3010 CN counter, particle diameter detection limit of ~ 10 nm) were of order 10^3 cm^{-3} and we thus find the PMF designation of the samples as a mix of marine and polluted air more plausible.

Another important facet of assessing the value of the results is a comparison of values of CCN and light-scattering coefficient predicted by the model (the sum of the contribution from each source) with the actual measured values of the CCN (PCASP) and aerosol light scattering coefficient. An example of such a regression comparison (measured regressed onto predicted) is shown in Fig. 10 for the CARMA III data and R^2 values and slopes for the comparisons for each study and both aerosol properties, are given in Table 2. (Note that the regression shown is the worst of the three CCN regressions.) The results of the regressions suggest that the

**Fig. 7.** Source contributions to the surrogate CCN (0.3%) concentration of each of the four sources to each sample taken during the CARMA II study. The samples shown were taken consecutively between 1 and 21 July 2004.

PMF model does a quite reasonable job of predicting the CCN concentrations and, to a somewhat lesser degree, the light-scattering coefficient. Interestingly, the slopes of the regressions with the regression lines forced through zero – a good metric for bias – are systematically below one, indicating that the models always over predict the aerosol properties.

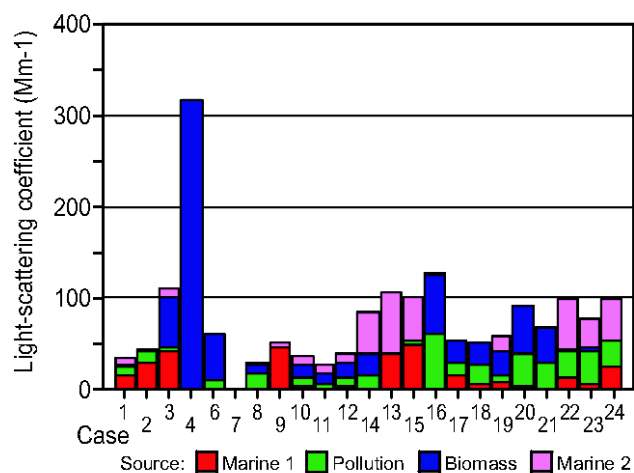


Fig. 8. Source contributions to the aerosol light-scattering coefficient (σ_{sp}) for each of the four sources to each of the samples taken during the CARMA IV study. The samples shown were taken consecutively between 11 and 27 August 2007.

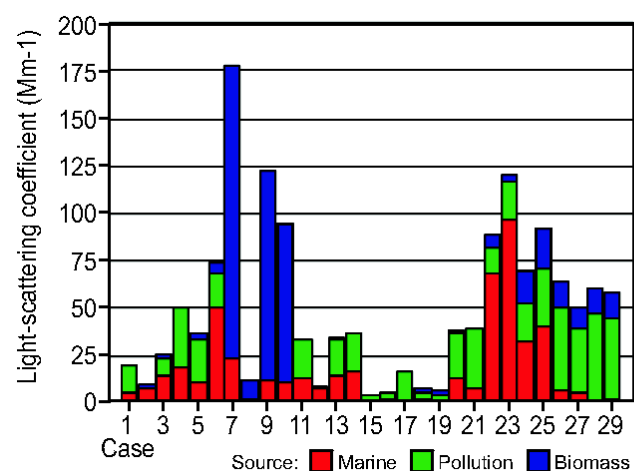


Fig. 9. Source contributions to the aerosol light-scattering coefficient (σ_{sp}) for each of the three sources to each of the samples taken during the CARMA III study. The samples shown were taken consecutively between 6 and 26 August 2005.

Turning to a year-to-year comparison of the sample source attribution, perhaps the most striking difference between the study years is the relatively high values for pollution during the 2005 study (CARMA III), in the CCN comparison. There is a similar difference in the light-scattering coefficient source attribution but it is somewhat attenuated, reflecting a disproportionate impact of pollution on particle number compared to cross section or mass. Systematic differences between the study years are most clearly seen, however, by looking at the differences in source attribution averaged over all sample for each study year. Such comparisons of study means are given in Fig. 11 for CCN and Fig. 12

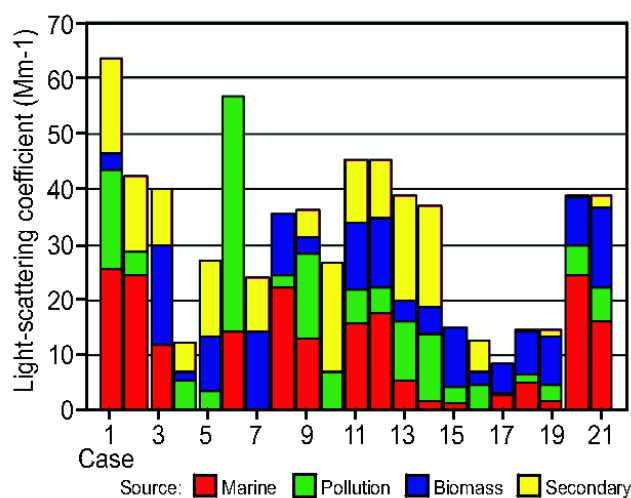


Fig. 10. Source contributions to the aerosol light-scattering coefficient (σ_{sp}) for each of the four sources to each of the samples taken during the CARMA II study. The samples shown were taken consecutively between 1 and 21 July 2004.

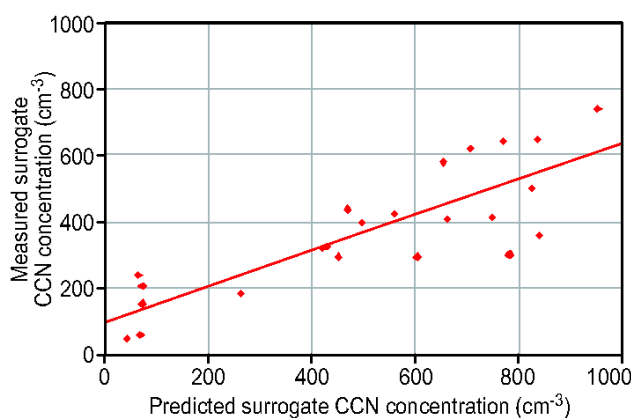


Fig. 11. Comparison via linear regression of the measured surrogate CCN(0.3%) concentration with that predicted by the PMF model for the CARMA III data set.

for aerosol light-scattering (Note that the uncertainties in the study mean source contributions are given in Table 3) To facilitate these comparisons, the two marine sources identified in the CARMA IV study have been grouped into a single marine component. Similarly, the secondary component resolved in the CARMA II study has been folded into the marine source since the origin of the organic acids is in the marine atmosphere and likely at least partially due to emissions from the ocean surface (long chain fatty acid precursors). With this admittedly somewhat ad hoc reclassification, the relative importance of pollution in the CARMA-III data is still quite clear. Taking into account the uncertainties given in Table 3, the pollution contribution to the surrogate CCN concentration is significantly higher in CARMA III than in

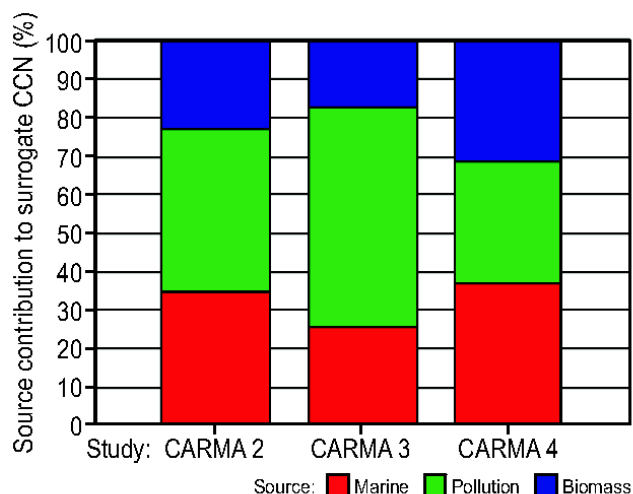


Fig. 12. Study average source contributions by each of three source categories (see text) to the surrogate CCN(0.3%) concentration. Uncertainties associated with the mean source estimates are given in Table 3.

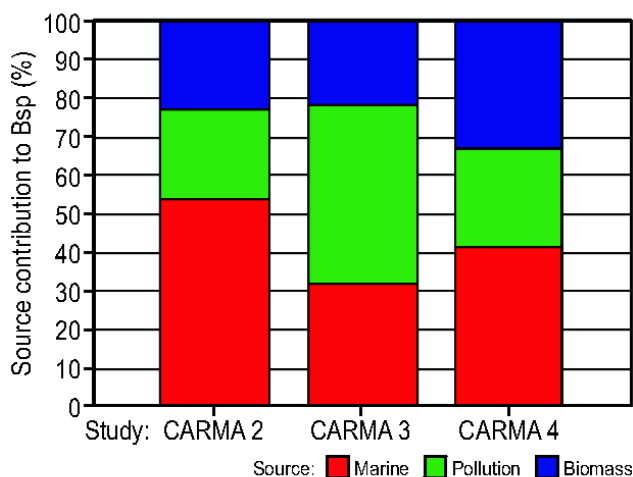


Fig. 13. Study average source contributions by each of three source categories (see text) to the aerosol light-scattering coefficient (Bsp). Uncertainties associated with the mean source estimates are given in Table 3.

CARMA IV, though not higher than that in CARMA II, largely due to the high uncertainty in the CARMA II estimate. For aerosol light-scattering, pollution contributes significantly more as a source in CARMA III than in either of the other CARMA studies. It is also clear that biomass burning emissions play a role in all three study periods though, as expected, they were more marked in the 2007 study period.

The reason for the enhanced impact of pollution during the 2005 study is worth a bit more analysis since one would not expect industrial pollution sources to display much inter-annual variation in this region and biomass burning, as already remarked, was higher in 2007 than in the other two

study periods. The other obvious explanation is differential transport and we explore this using back trajectories generated by the HYSPLIT IV model. Isentropic, 96 h back trajectories were generated every six hours for each day of the study period, originating near the middle of the CARMA operational area at the top of the MBL. To facilitate comparison, a cluster analysis was then done, specifying three clusters. For the CARMA II and CARMA IV studies (2004 and 2007), all three clusters were offshore throughout the 96 hour trajectory period. However, for the CARMA III study, one of the three clusters, containing 17% of the trajectories, went onshore about three days back from the starting point. Hence, the enhanced pollution observed during CARMA III is likely due at least in part to more offshore flow during the 2005 study period.

5 Conclusions

The analysis presented suggests that, with respect to both CCN activity and aerosol light-scattering, anthropogenic aerosols have a large impact on climate critical cloud systems such as the stratocumulus off the California coast. Biomass burning in the continental region adjacent to the CARMA operational area (offshore, marine cloud-topped boundary layer) is largely human-induced (either accidentally, through prescribed burns or as fuel; see Chow et al., 2010). Hence, the anthropogenic component of the aerosol sources in this area might plausibly be considered to be the sum of the explicit pollution and biomass sources in the PMF analysis. With this grouping, for CCN activity, the fraction arising from anthropogenic sources varies from 63% in CARMA IV to 74% in CARMA III. For aerosol light-scattering, the anthropogenic portion varies from 45% in CARMA II to 68% in CARMA III. Hence, while there is considerable year-to-year variation in the relative impact of the three main source categories (marine, pollution and biomass), the anthropogenic component is always the most important source.

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References

- Bates, T. S., Huebert, B. J., Gras, J. L., Griffiths, F. B., and Durkee, P. A.: International Global Atmospheric Chemistry (IGAC) Project's First Aerosol Characterization Experiment (ACE 1): Overview, *J. Geophys. Res.*, 103, 16297–16318, 1998.
- Bond, T. C. and Bergstrom, R. W.: Light absorption by carbonaceous particles: an investigative review, *Aerosol Sci. Technol.*, 40, 1–41, 2006.
- Chand, D., Anderson, T. L., Wood, R., Charlson, R. J., Hu, Y., Liu, Z., and Vaughan, M.: Quantifying above-cloud aerosol using spaceborne lidar for improved understanding of cloudy-sky direct climate forcing, *J. Geophys. Res.*, 113, D13206, doi:10.1029/2007JD009433, 2008.
- Chen, L.-W. A., Watson, J. G., Chow, J. C., and Magliano, K. L.: Quantifying PM_{2.5} source contributions for the San Joaquin Valley with multivariate receptor models, *Environ. Sci. Technol.*, 41, 2818–2826, 2007.
- Cheng, M. D., Hopke, P. K., Barrie, L., Rippe, A., Olson, M., and Landsberger, S.: Qualitative determination of source regions of aerosol in Canadian high Arctic, *Environ. Sci. Technol.*, 27, 2063–2071, 1993.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L.-W. A., and Motallebi, N.: Black and organic carbon emission inventories: review and application to California, *J. Air Waste Manag. Assoc.*, 60, 497–507, 2010./
- Durkee, P. A., Noone, K. J., Ferek, R. J., Johnson, D. W., Taylor, J. P., Garrett, T. J., Hobbs, P. V., Hudson, J. G., Bretherton, C. S., Innis, G., Frick, G. M., Hoppel, W. A., O'Dowd, C. D., Russell, L. M., Gasparovic, R., Nielsen, K. E., Tessmer, S. A., Ostrom, E., Osborne, S. R., Flagan, R. C., Seinfeld, J. H., and Rand, H.: The Impact of Ship-Produced Aerosols on the Microstructure and Albedo of Warm Marine Stratocumulus Clouds. A Test of the MAST Hypothesis Li and Lii, *J. Atmos. Sci.* 57, 2554–2569, 2000.
- Easter, R. C., Ghan, S. J., Zhang, Y., Saylor, R. D., Chapman, E. G., Laulainen, N. S., Abdul-Razzak, H., Leung, L. R., Bian, X., and Zaveri, R. A. MIRAGE: model description and evaluation of aerosols and trace gases, *J. Geophys. Res.*, 109, D22207, doi:10.1029/2004JD004939, 2004.
- Fitzgerald, J. W.: Dependence of the supersaturation spectrum of CCN on aerosol size distribution and composition, *J. Atmos. Sci.*, 30, 628–634, 1973.
- Furutani, H., Dall'osto, M., Roberts, G., and Prather, K. A.: Assessment of the relative importance of atmospheric aging on CCN activity derived from field measurements, *Atmos. Environ.*, 42, 3130–3142, 2008.
- Gao, S., Hegg, D. A., Hobbs, P. V., Kirchstetter, T. W., Magi, B. I., and Sadelik, M.: Water-soluble organic compounds in aerosols associated with savanna fires in southern Africa: Identification, evolution and distribution. 2003. *J. Geophys. Res.*, 108(D13), 8491, doi:10.1029/2002JD002324, 2003b.
- Gasso, S., Hegg, D. A., Covert, D. S., Collins, D., Noone, K. J., Ostrom, E., Schmid, B., Russell, P. B., Livingston, J. M., Durkee, P. A., and Jonsson, H.: Influence of humidity on the aerosol scattering coefficient and its effect on the upwelling radiance during ACE-2, *Tellus*, 52B, 546–567, 2000.
- Hegg, D. A. and Jonsson, H. H.: Aerosol number-to-volume relationship and relative humidity in the eastern Atlantic, *J. Geophys. Res.*, 105, 1987–1995, 2000.
- Hegg, D. A., Covert, D. S., Jonsson, H., and Covert, P. A.: Determination of the transmission efficiency of an aircraft aerosol inlet, *Aerosol Sci. Technol.*, 39, 966–971, 2005.
- Hegg, D. A., Covert, D. S., and Jonsson, H. H.: Measurements of size-resolved hygroscopicity in the California coastal zone, *Atmos. Chem. Phys.*, 8, 7193–7203, doi:10.5194/acp-8-7193-2008, 2008.
- Hegg, D. A., Covert, D. S., Jonsson, H. H., and Woods, R.: Differentiating natural and anthropogenic cloud condensation nuclei in the California coastal zone, *Tellus*, 61B, 669–676., 2009.
- Henry, R.: Multivariate receptor modeling by N-dimensional edge detection, *Chemometr. Intell. Lab.*, 60, 43–48, 2003.
- Henry, R. C.: Duality in multivariate receptor models, *Chemometr. Intell. Lab.* 77, 59–63, 2005.
- Hill, A. A. and Dobbie, S.: The impact of aerosols on non-precipitating marine stratocumulus. II: The semi-direct effect, *Q. J. Roy. Meteor. Soc.*, 134, 1155–1165, 2008.
- Huneeus, N., Gallardo, L., and Rutllant, J. A.: Offshore transport episodes of anthropogenic sulfur in Northern Chile: potential impact on the stratocumulus cloud deck, *Geophys. Res. Lett.*, 33, L19819, doi:10.1029/2006GL026921, 2006.
- IPCC, Climate Change 2001.: The Scientific Basis: contributions of Working Group I to the Third Assessment Report of the IPCC, edited by: Houghton, J. T., Ding, Y., and Griggs, D. J. et al., Cambridge University Press, New York, USA, 881 pp., 2001.
- Ishizaka, Y. and Adhikari, M.: Composition of cloud condensation nuclei, *J. Geophys. Res.*, 108, 4138, doi:10.1029/2002JD002085, 2003.
- Kaku, K. C., Hegg, D. A., Covert, D. S., Santarpia, J. L., Jonsson, H., Buzorius, G., and Collins, D. R.: Organics in the Northeastern Pacific and their impacts on aerosol hygroscopicity in the subsaturated and supersaturated regimes, *Atmos. Chem. Phys.*, 6, 4101–4115, doi:10.5194/acp-6-4101-2006, 2006.
- Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, 104, 3501–3509, 1999.
- Keil, A. and Haywood, J. M.: Solar radiative forcing by biomass burning aerosol particles during SAFARI 2000: a case study based on measured aerosol and cloud properties, *J. Geophys. Res.*, 108, 8467, doi: 10.1029/2002JD002315, 2003.
- Kim, E., Hopke, P. K., Larson, T. V., and Covert, D. S.: Analysis of ambient particle size distributions using unmix and positive matrix factorization, *Environ. Sci. Technol.*, 38, 202–209, 2004.
- Klein, S. A. and Hartmann, D. L.: The seasonal cycle of low stratiform clouds, *J. Climate*, 6, 1587–1606, 1993.
- Maykut, N. N., Lewtas, J., Kim, E., and Larson, T. V.: Source apportionment of PM_{2.5} at an urban IMPROVE site in Seattle, Washington, *Environ. Sci. Technol.*, 37, 5135–5142, 2003.
- Paatero, P. and Tapper, U.: Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, 5, 111–126, 1994.
- Pekney, N. J., Davidson, C. I., Robinson, A., Zhou, L., Hopke, P., Eatough, D., and Rogge, W. F.: Major source categories for PM_{2.5} in Pittsburgh using PMF and UNMIX, *Aerosol Sci. Technol.*, 40, 910–924, 2006.
- Platnick, S. and Twomey, S.: Determining the susceptibility of cloud albedo to changes in droplet concentration with the Advanced Very High Resolution Radiometer, *J. Appl. Meteor.*, 33,

- 334–347, 1994.
- Poirot, R. L., Wishinski, P. R., Hopke, P. K., and Polissar, A. V.: Comparative application of multiple receptor methods to identify aerosol sources in Northern Vermont, *Environ. Sci. Technol.*, 35, 4622–4636, 2001.
- Roberts, G., Mauger, G., Hadley, O., and Ramanathan, V.: North American and Asian aerosols over the eastern Pacific Ocean and their role in regulating cloud condensation nuclei, *J. Geophys. Res.*, 111, D13205, doi:10.1029/2005JD006661, 2006.
- Roberts, G. and Nenes, A.: A continuous-flow streamwise thermal-gradient CCN chamber for airborne measurements, *Aerosol Sci. Technol.*, 39, 206–221, 2005.
- Russell, P. B., Hobbs, P. V., and Stowe, L. L.: Aerosol properties and radiative effects in the United States east coast haze plume: an overview of the Tropospheric Aerosol Radiative Forcing Observational Experiment (TARFOX), *J. Geophys. Res.*, 104, 2213–2222, 1999.
- Schmid, B., Hegg, D. A., Wang, J., Bates, D., Redemann, J., Russell, P. B., Livingston, J. M., Jonsson, H. H., Welton, E. J., Seinfeld, J. H., Flagan, R. C., Covert, D. S., Dubovik, O., and Jefferson, A.: Column Closure Studies of the Lower Tropospheric Aerosol and Water Vapor during ACE Asia Using Airborne Sunphotometer, Airborne In-Situ and Ship-Based Lidar Measurements, *J. Geophys. Res.*, 108, 8656, doi:10.1029/2002JD003361, 2003.
- Song, X.-H., Hopke, P. K., Fergenson, D. P., and Prather, K. A.: Classification of single particles analyzed by ATOFMS using an artificial neural network, ART-2A, *Anal. Chem.*, 71, 860–865, 1999.
- Swietlicki, E., Zhou, J., Covert, D. S., Hameri, K., Busch, B., Vakeva, M., Dusek, U., Berg, O. H., Widensohler, A., Aalto, P., Makela, P., Martinsson, B. G., Papaspiropoulos, G., Mentes, B., Frank, G., and Stratmann, F.: Hygroscopic properties of aerosol particles in the northeastern Atlantic during ACE-2, *Tellus*, 52B, 201–227, 2000.
- Virkkula, A., Ahlquist, N. N., Covert, D. S., Arnott, W. P., Sheridan, P. J., Quinn, P. K., and Coffman, D. J.: Modification, calibration and a field test of an instrument for measuring light absorption by particles, *Aerosol Sci. Technol.*, 39, 68–83, 2005.
- Wang, J., Flagan, R. C., Seinfeld, J. H., Jonsson, H. H., Collins, D. R., Russell, P. B., Schmid, B., Redemann, J., Livingston, J. M., Gao, S., Hegg, D. A., Welton, E. J., and Bates, D.: Clear-Column Radiative Closure during ACE-Asia: Comparison of Multiwavelength Extinction Derived from Particle size and Composition with Results from Sunphotometry, *J. Geophys. Res.*, 107(D23), 4688, doi:10.1029/2002JD002465, 2002.
- Warren, S. G., Hahn, C. J., London, J., Chervin, R. M., and Jenne, R. L.: Global Distribution of Total Cloud Cover and Cloud type Amounts Over the Ocean. NCAR Technical Note NCAR/TN-317+STR, 1988.