Primary-marine-aerosol-cloud interactions off the coast of California

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Introduction

This supporting information section provides additional, detailed explanations of the experimental methods and data processing steps employed in this study, including description of the CVI inlet used during the SOLEDAD field campaign, the CCN-CVI measurements taken from the CIRPAS Twin Otter during the E-PEACE field campaign, the particle size distribution merging procedure, the processing of HR-AMS sea salt concentrations, the calculation of primary marine aerosol contributions to CCN concentrations, and the data processing procedures applied to produce Fig. 6 in the main text.

Text S1: SOLEDAD CVI inlet

The SOLEDAD CVI inlet only sampled cloud droplets larger than $11.6 \pm 0.7 \, \mu m$ diameter (CVI-$D_{50}$) during Clouds 1 and 3 and $11.5 \pm 0.7 \, \mu m$ during Cloud 2. The number fractions of droplets above this cut size were 43, 38 and 24% for Clouds 1, 2 and 3, respectively. The volume fractions of droplets above the cut size were 97, 91 and 68% for the 3 clouds. On average 27%, 26% and 45% of the droplets that were sampled made it to the exit of the CVI for Clouds 1, 2, and 3, respectively. We refer to these as Droplet Transmission (DT) factors. We hypothesize that DT values less than 1 are due to particle or droplet losses in the CVI, incomplete drying of the droplets, misalignment of droplets in the wind tunnel prior to entering the CVI, and insufficient acceleration of some of the larger droplets.

The droplets/residual particles that succeed in making it through the CVI get concentrated in the inlet. The ambient concentration Enhancement Factors (EF) were 7.3, 7.1, and 7.4 for Clouds 1, 2 and 3, respectively. Schroder et al. [2014] detail the calculation of these parameters from the properties of the CVI inlet and plots of the number concentration of cloud droplets greater than the CVI cut size versus EF-corrected residual particle concentrations.

These considerations have no bearing on relative parameters calculated with data collected behind the CVI (e.g. CCN activation ratios, relative mass fractions of chemical species measured by HR-AMS), other than limiting the applicability of the conclusions drawn from these analyses, since results are derived from only a subset of the total cloud droplet population. On the other hand, absolute mass concentrations measured by the HR-AMS behind the CVI inlet need to be corrected for the imperfect sampling through the inlet. To achieve this, CVI-HR-AMS mass concentrations were multiplied by factor of $\left(\frac{1}{\text{DT}} \times \frac{1}{\text{EF}}\right)$ to convert to equivalent ambient concentrations. This factor does not change the fact that the corrected concentrations still only apply to the subset of cloud droplets greater than the CVI cut-size.
Text S2: CCN-CVI measurements on the CIRPAS Twin Otter

The CCNC on board the CIRPAS Twin Otter during E-PEACE was operated in scanning flow CCN analysis (SFCA) mode [Moore and Nenes, 2009]. During SFCA operation, the instrument is kept at a constant pressure and applied temperature gradient while dynamically scanning the instrument flow rate produces a near-instantaneous change in supersaturation. A constant temperature gradient of 6 K was applied, and a critical flow orifice and active flow control system were employed to maintain a constant 700 mb pressure inside the instrument. Upscan and downscan ramp times of twenty seconds were used. Only upscan data were used in this analysis. The supersaturation in the CCNC was calibrated using classified ammonium sulfate from a DMA. Full details of the calibration procedure are given in Moore et al. [2012]. Uncertainty in the CCNC supersaturation is estimated to be ±0.04%.

The fraction of total aerosol that act as CCN as a function of supersaturation – the activation ratio, \( R_a(s) \) – was fit with a sigmoid function of the form

\[
R_a(s) = \frac{E}{1 + \left(\frac{s}{s^*}\right)^C}
\]

where \( E \) is the maximum activated fraction of CCN, \( s \) is the instrument supersaturation, \( s^* \) is the supersaturation at which half the particles have activated as CCN, and \( C \) is a parameter that describes the slope of \( R_a(s) \). The spectra fits were filtered to ensure reasonable fit values 0.2 < \( E \) < 1.2, -15 < \( C \) < -2, and \( ss_{\text{min}} < s^* < ss_{\text{max}} \) where \( ss_{\text{min}} \) and \( ss_{\text{max}} \) are the minimum and maximum instrument supersaturation during the spectra, respectively [Cerully et al., 2011].

Text S3: Size distribution merging procedure

Electrical mobility diameter measured by the SMPS was assumed to represent geometric physical particle diameter (\( D_p \)), i.e. shape effects were neglected. At each time point a power law function was fit to the SMPS size distribution between 0.2 and 0.5 μm (or 0.4 and 0.7 μm) to provide a reference distribution for the corresponding OPS (or APS) size distribution to be aligned with.

The positions of the 16 size bins of the OPS depend on particle refractive index. This parameter was adjusted until an optimal refractive index was found that resulted in the best match between the OPS and fitted SMPS size distributions in the overlap region 0.4 – 0.6 μm \( D_p \). The best match was represented by the minimum of the objective function defined by Khlystov et al. [2004] over the real refractive index range 1.2 – 1.7. The dependence of the OPS size bins on refractive index was calculated with calibration curves derived from the manufacturer’s software (Aerosol Instrument Manager), which is based on Mie theory calculations. The imaginary part of refractive index was neglected.

For E-PEACE data, a power law function was then fit to the shifted and merged OPS size distribution over the nominal diameter range 0.4 – 1 μm to provide a reference distribution for the corresponding APS size distribution to be aligned with. For the SOLEDAD Scripps Pier data, APS data were aligned to power law functions fit to the SMPS size distributions over the nominal diameter range 0.4 – 0.7 μm. Aerodynamic particle diameter measured by the APS depends on geometric physical diameter (\( D_p \)) through the following relationship
where \( \rho_o \) is the reference density (1 g cm\(^{-3} \)) and \( \rho_{\text{eff}} \) is the effective particle density, defined as the ratio of particle density (\( \rho_p \)) to its shape factor (\( \chi \)). Similarly to the OPS merging procedure, an optimal effective density was found that resulted in the best match between the APS and fitted OPS size distributions in the nominal diameter range 0.6 – 0.9 \( \mu \)m, represented by the minimum in the objective function defined by Khlystov et al. [2004] over the effective density range 0.9 – 3 g cm\(^{-3} \).

Total aerosol size distributions were created by joining the SMPS and shifted OPS and shifted APS size distributions for the E-PEACE and Mt. Soledad data, and the SMPS and shifted APS size distributions for the Scripps Pier data. There were appreciable discrepancies between the OPS and APS concentrations at large particle diameters. The APS data was considered more accurate since it was on a straighter sampling line during both campaigns, so only APS data was used at particle diameters greater than 0.8 \( \mu \)m.

**Text S4: HR-AMS sea salt concentrations**

The standard high resolution AMS data analysis software (PIKA v1.10h) was used to calculate the nitrate equivalent mass concentration of sea salt as the sum of the concentrations of a family of sea salt derived ions: NaCl\(^+\), KCl\(^+\), MgCl\(^+\) and the isotopes of each of these species. Ovadnevaite et al. [2012] explored including a wider range of ions in this family but ultimately decided to use only a single ion, NaCl\(^+\), to represent sea salt in order to avoid problems associated with ions that can become thermally ionized (e.g. Na\(^+\)) or ions that may have sources other than sea salt (e.g. Cl\(^-\)). Here we also added the KCl\(^+\), MgCl\(^+\) and related isotope ions into our sea salt family because they increased the total sea salt signal by a factor of 3.6 and did not have sources other than sea salt (their concentrations correlated well with NaCl\(^+\) concentrations, \( r > 0.93 \)).

Sea salt is a refractory compound that does not completely evaporate at the 600°C HR-AMS vaporizer temperature employed in these studies. Consequently the net overall transmission, ionization and detection efficiency of sea salt derived ions is much less than the corresponding efficiencies of ions derived from the non-refractory compounds typically quantified by the HR-AMS. Therefore, independent measurements are required to calibrate the raw sea salt concentrations calculated in the PIKA data analysis software. For E-PEACE, we regressed the XRF sea salt concentrations against the raw PIKA sea salt concentrations to derive a scaling factor of 96 (\( r = 0.91 \), N = 39). For SOLEDAD, we regressed the IC sea salt concentrations against the raw PIKA sea salt concentrations to derive a scaling factor of 145 (\( r = 0.59 \), N = 54). Since HR-AMS measured sea salt is calibrated against XRF and IC measured sea salt, which is calculated using the Bates formula (section 3.3), it also accounts for chloride depletion.

**Text S5: Calculation of PMA contribution to CCN concentrations during E-PEACE**

PMA and CCN number concentrations were measured simultaneously during E-PEACE, which enabled the calculation of the contribution of PMA to CCN populations. For a given water vapor supersaturation, the contribution of PMA to CCN is represented by the percentage of PMA particles greater than a certain dry activation diameter, \( D_{\text{act}} \), to the total number of CCN particles. The activation diameter depends on the chemical composition of PMA and the
hygroscopicity of the different components. PMA is known to contain both inorganic (sea salt) and organic components. The $D_{\text{act}}$ of pure sea salt is lower than the corresponding $D_{\text{act}}$ of less soluble organic matter. For example, at 0.2% supersaturation pure sea salt particles greater than 0.07 $\mu$m dry diameter form cloud droplets [Fuente et al., 2011], while pure fructose or glucose particles need to be larger than 0.125 – 0.13 $\mu$m diameter to do the same [Koehler et al., 2006].

The apportionment of PMA across inorganic and organic chemical fractions as a function of particle size is still a subject of active research. At the particle sizes most relevant to CCN formation (0.06 < $D_{\text{act}}$ < 0.2 $\mu$m) PMA can be mainly saline [Modini et al., 2010; Fuentes et al., 2011; Cravigan et al., 2015] or organic [Keene et al., 2007; Facchini et al., 2008; Prather et al., 2013] depending on bubble properties and seawater composition. In this study, no size-resolved chemical composition data are available to determine the composition of PMA particles in the 0.06 < $D_{\text{act}}$ < 0.2 $\mu$m size range most critical for CCN activation. Therefore, we consider the extreme cases of completely saline and completely organic PMA to calculate ranges of possible PMA contributions to CCN concentrations during E-PEACE.

For the saline case, activation diameters as a function of supersaturation are calculated with the sodium chloride parameterization reported by Koehler et al. [2006]. Sodium chloride is the dominant component of sea salt, and Fuentes et al. [2011] have shown that the CCN activity of pure sea salt particles is similar to that of NaCl particles. For the organic case, activation diameters are calculated with the levoglucosan parameterization reported by Koehler et al. [2006]. This parameterization also agrees reasonably well with experimental data for glucose and fructose. Fructose and glucose are both saccharides, which is a major component of marine organic matter [Russell et al., 2010]. In addition, the hygroscopicity parameter $\kappa$ of levoglucosan (0.15 – 0.22 [Petters and Kreidenweis, 2007]) is very similar to the $\kappa$ values of organic-dominated PMA particles measured by Collins et al. [2013] (0.12 – 0.21).

Text S6: CDNC versus accumulation mode aerosol concentration plot

Fig. 6 plots CDNC versus accumulation mode aerosol concentration. For E-PEACE, CDNC is represented by the average of the top quartile of all the CDNC measurements taken during a single cloud water sampling period to minimize entrainment dilution effects. The CDNC measurements in perturbed clouds (determined by the f99 signal measured by AMS, see Coggon et al. [2012]) are not filtered out for this analysis, unlike for Fig. 4a, which displays the 1st-99th percentile range of only background (i.e unperturbed) CDNC. The accumulation mode number concentration is taken as the average integrated PCASP concentration below cloud (LWC < 0.01 g cm$^{-3}$, altitude < 100 m below cloud) in the 30 mins prior to collection of a cloud water sample. In-cloud sea salt concentration is the IC-measured sea salt concentration in cloud water samples. Thirty-two samples from 17 separate flight days had the required combination of data and are displayed in Fig. 6.

For SOLEDAD, CDNC is represented by the average of the top quartile of CDNC measurements over 10 min intervals. Accumulation mode number concentration is represented by the average integrated number concentration above 100 nm diameter for the total particle size distributions measured from the total inlet (interstitial + droplets) over the same 10 min intervals. In-cloud sea salt concentration is the HR-AMS measured sea salt concentration in the dried cloud droplet residuals, measured at 10 min resolution.
Figure S1. Scatterplots used to determine the E-PEACE HR-AMS collection efficiency. Left panel: AMS SO$_4^-$ mass concentrations versus XRF SO$_4^-$ mass concentrations. Right panel: total mass concentration of AMS species (including sea salt, section S4) versus mass concentrations derived from the particle number size distributions (PSDs). Two values of density were used to convert PSD number to mass as indicated in the legend. The following transmission curve was applied to the PSD data to represent the transmission efficiency of particles through the AMS aerodynamic lens: 0% transmission below 40 nm $d_{va}$ (vacuum aerodynamic diameter); linear increase in transmission from 0% at 40 nm $d_{va}$ to 100% at 100 nm $d_{va}$; 100% transmission from 100 – 650 nm $d_{va}$; linear decrease in transmission from 100% at 550 nm $d_{va}$ to 0% at 2 μm $d_{va}$. A CE of 1 was applied based on the slopes that were fit to the data in both panels.
Figure S2. Scatterplots used to determine the SOLEDAD HR-AMS collection efficiency. Left panel: AMS SO$_4$ mass concentrations versus IC SO$_4$ mass concentrations. Right panel: total mass concentration of AMS species (including sea salt, section S4) versus mass concentrations derived from the particle number size distributions (PSDs). Two values of density were used to convert PSD number to mass as indicated in the legend. The following transmission curve was applied to the PSD data to represent the transmission efficiency of particles through the AMS aerodynamic lens: 0% transmission below 40 nm $d_{va}$ (vacuum aerodynamic diameter); linear increase in transmission from 0% at 40 nm $d_{va}$ to 100% at 100 nm $d_{va}$; 100% transmission from 100 – 550 nm $d_{va}$; linear decrease in transmission from 100% at 550 nm $d_{va}$ to 0% at 2 μm $d_{va}$. A CE of 0.6 was applied based on the slopes that were fit to the data in both panels.

Figure S3. Sensitivity of the integrated number concentrations in the fitted PMA mode to the constraints placed on the PMA modal parameters. Left panel: percentage change in integrated number concentration for different ranges of allowable PMA mean diameters relative to the range that was actually used (0.2 μm ± 30%). Right panel: percentage change in integrated number concentration for different ranges of allowable PMA mode geometric standard deviations relative to the range that was actually used (2.5 – 3).
Figure S4. A version of Fig. 4 in the main text with the integrated number concentrations of particles in PSD modes 1, 2, and 3 plotted instead of the integrated mass concentrations of particles in those modes.
Figure S5. Organic aerosol (OM) mass concentrations measured by FTIR and HR-AMS versus sea salt mass concentrations measured by XRF and HR-AMS, respectively. FTIR OM refers to the sum of all the functional group concentrations measured by FTIR. HR-AMS refers to ‘Org’ concentrations measured by HR-AMS.
Figure S6. Organic aerosol (OM) concentrations (left panel) measured by FTIR and HR-AMS and sea salt concentrations (right panel) measured by XRF and HR-AMS versus locally measured wind speed. FTIR OM refers to the sum of all the functional group concentrations measured by FTIR. HR-AMS refers to ‘Org’ concentrations measured by HR-AMS. Poor correlation was observed between organic aerosol mass concentrations and local wind speed. However, local wind speed likely does not equal the wind speed at the time of PMA production, although the two may be related (e.g. across mesoscale weather systems, or if the PMA is freshly produced). Therefore, the sea salt plot is also included in the right panel to show the relationship between an unambiguously primary species and local wind speed. Only poor to moderate correlation was observed between sea salt mass and wind speed, but a clear and sharp increase in sea salt concentrations was observed at the highest local wind speeds. This feature was not observed for organic aerosol mass concentrations.

Figure S7. 5-min averaged CCN-CVI concentrations versus the concentrations of cloud droplet residuals over all three SOLEDAD cloud events. The left panel contains CCN concentrations measured by the CCN counter that was kept at constant supersaturation (CCN_{S=0.3%}) and the right panel CCN concentrations measured by the scanning CCN counter (CCN_{S=0.1-0.74%}). The two counters were run in parallel but instrument malfunction resulted in less data being collected with the scanning CCN counter.

References.


