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Aerosol dynamics in the equatorial Pacific Marine boundary layer: Microphysics, diurnal cycles and entrainment

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Abstract. During July-August of 1994 we measured the size-resolved physicochemical properties of aerosol particles at Christmas Island in the equatorial Pacific. In spite of rapid diurnal conversion of dimethylsulfide (DMS) to sulfur dioxide (SO_2) we found no evidence for new particle production in the marine boundary layer (MBL) and more than 95% of all particles were consistently larger than 0.02μm diameter, indicating an aged aerosol. The submicrometer aerosol number (size-distribution) was bimodal with peaks near 0.05μm and 0.2μm particle diameter (D_p) and had a cloud-processed intermode minimum at about 0.09μm that varied in phase with diurnal changes in ozone concentration. This suggests that the number distribution for condensation nuclei (CN) and cloud condensation nuclei (CCN) was maintained by a quasi-equilibrium between entrainment (estimated to be 0.6 +/-0.2 cm s^{-1}) from sources aloft and processes in the MBL. This implies a replenishment timescale for nuclei of about 2 and 4 days for this region. The stability of the distribution and the 0.09 μm cloud processed minima suggests trade wind cumulus supersaturations near 0.35% and updrafts near 1 m s^{-1}.

Introduction

Characterizing the response of the marine aerosol size distribution to the production of sulfate from DMS has been an elusive goal of numerous field programs because these particles are an important dynamic reservoir in the atmospheric cycling of species such as sulfur. Aerosol number, size and composition determine their effectiveness as cloud condensation nuclei [Pruppacher and Klett, 1990; Charlson, 1987] and their effect on atmospheric radiative transfer [Charlson et al., 1992]. However, direct evidence for diurnal conversion of DMS to sulfate mass has been difficult to observe because growth processes (eg. gas to particle conversion) often involve small changes in particle mass compared to other processes. The origin of MBL particle number is also uncertain, although evidence for particle production has been seen under unusual conditions [Covert et. al., 1992] or related to pronounced subsidence events [Clarke and Porter 1993; Covert et al, 1995]or in the vicinity of clouds [Hegg et al., 1992; Hoppel et al., 1994]. Even so, models differ regarding the likelihood of nucleation in the MBL although most models that include pre-existing aerosol surface area find that this suppresses MBL nucleation [Shaw, 1989; Raes and Van Dingenen, 1992]. Alternately, high nuclei concentrations measured in the clean upper troposphere suggest that aerosol formation and evolution aloft may supply the boundary layer with "new" CN and CCN [Clarke, 1993]. This is consistent with models that predict aerosol nucleation to be favored there [Raes and Van Dingenen, 1993] as well as a three year interhemispheric Pacific MBL study [Covert et al.,1995] that found more and smaller nuclei in high pressure (subsidence) regions than in low pressure regions, again consistent with a source of nuclei from aloft. The narrow range of CN concentrations observed in the remote MBL has also been predicted by this mechanism [Raes, 1995]. Even so, the most effective process for producing and sustaining MBL nuclei and their link to the sulfur cycle remains unclear.

Experiment

Christmas Island (CI) is located at 2°N-157°W and south of the Inter Tropical Convergence Zone in a region of equatorial upwelling with strong DMS emitted into an easterly flow of clean southern hemisphere air. The stable meteorology of this region and low precipitation with high insolation, provides optimal conditions for evaluating the DMS-aerosol sulfate link. Our cooperative experiment included extensive measurements of major gas phase sulfur species [Bandy et al., this issue] and aerosol chemistry [Huebert et al., this issue] along with our aerosol microphysics data.

A 20m sampling tower was located 10m from the coast on the NE shore of CI. The aerosol was transported from the top of the tower to instruments in 2-4sec. through a 10cm diam. aluminum tube with less than 10% particle loss. Meteorological variables were continuously recorded and profiles were obtained from 4 to 8 radiosonde launches per day. Particle data was obtained from an Ultrafine Condensation Nucleus counter (UCN-TSI 3025; Dp>0.003μm), a condensation nucleus counter (CN-TSI 3760; Dp>0.015μm), a scanning 17 bin differential mobility analyzer (DMA-TSI 3071; 0.02<Dp<0.5μm) and an ozone monitor (TECO-Model 49) with a separate teflon line. The DMA was operated near 20% relative humidity (RH) to get distributions of dry aerosol mass.

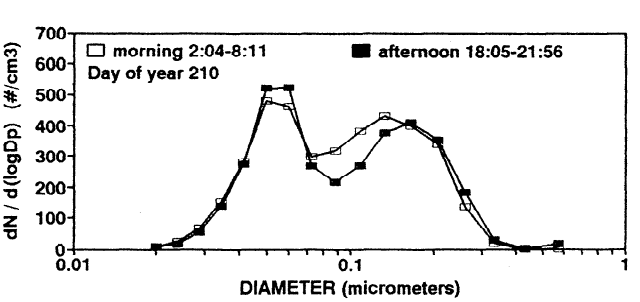

Fig. 1. Typical DMA dry size distributions. The change between these consecutive morning and afternoon averages reveals the number increase at night in the minima region and the growth out of that region during the day.

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Results

DMA distributions were taken every 20-30 minutes in order to assess the response of the size-distribution to factors controlling the CN and CCN population. Figure 1 shows two typical DMA number distributions revealing the bimodal nature characteristic of aerosol processed by clouds [Hoppel et al., 1994]. The mode at larger diameters reflects aerosol that were activated and grew into cloud droplets of several micrometer diameter while the smaller mode is comprised of unactivated nuclei. The rapid decrease in concentration for smaller sizes near 0.02μm (Fig. 1) is characteristic of an aged aerosol and consistent with other observations in this region [Clarke et al., 1987; Clarke and Porter, 1993; Covert et al., 1995]. The integral DMA number closely tracked those of total CN but were about 10-15% lower due to losses in the DMA [Covert et al., 1992]. The small difference between CN and UCN data confirmed that particles smaller than 0.02μm were less than 5% of the total CN (Fig. 2e). Furthermore, if significant nucleation had occurred near cloud level to result in nuclei

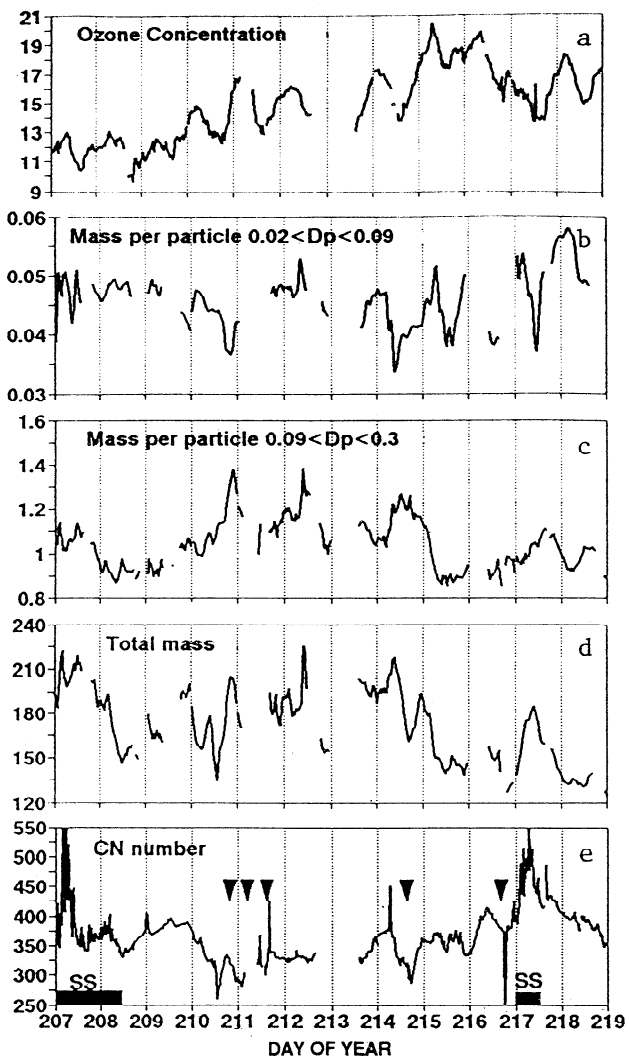

Fig. 2. A time series of key parameters measured at Christmas Island for DOY 207-219, 1994; (a) ozone (ppbv), (b) mass per particle (pptv/particle/cm^{-3}) for DMA nuclei mode, (c) mass per particle for DMA accumulation mode, (d) total mass (pptv) with D_p<0.3μm and (e) CN (#cm^{-3}). Local sea-salt from breaking waves are indicated as SS and squalls near the site suggested by RH jumps are marked as triangles.

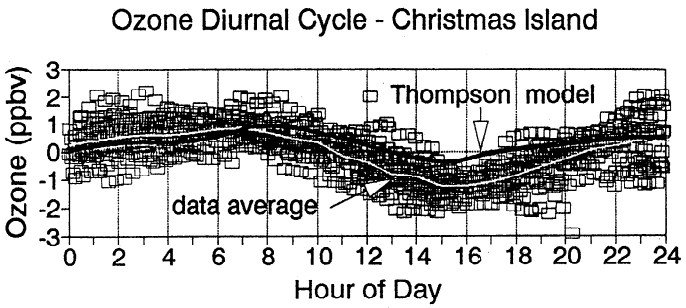

Fig. 3. Diurnal ozone variability (white line) relative to each daily ozone mean and Thompson et al., diurnal fit (black line) for the "low ozone" period (February-March).

similar to the observations (mean D_p <0.007 μm) at mid-latitudes [Hoppel et al., 1994] then the calculated lifetime for coagulation with the MBL aerosol is in excess of a day and longer than MBL mixing times. Both UCN counts and the lower tail of the DMA distribution (Fig. 1) should have regularly shown evidence of such nucleation but they did not. Hence, if gas to particle conversion occurred in the MBL the it was heterogeneous and did not form appreciable new nuclei.

The sulfate mass inferred from our dry DMA distributions (Fig. 2d) averaged about 200pptv and roughly 75% of the total measured non-sea salt sulfate (nss-SO_4) [Huebert et al., this issue]. If a significant fraction of the estimated daily DMS flux [Bandy et al., this issue] is converted to submicrometer nss-SO_4 then it should appear as a small change in the DMA size distribution. However, the size distribution may also vary with different source strengths, different trajectories, periodic precipitation events, varying dilution due to different entrainment etc. Indeed, marked fluctuations common to both DMA and CN data were evident and often persisted for several hours (Figure 2d). In order to help separate changes in mass through heterogeneous growth from other processes, we divide the distribution into two modes at 0.09μm (Figure 1) with the larger identified as the accumulation mode and the smaller the nuclei mode. We define the mass per particle (MP) of a mode as the integral mass divided by the integral number per cm^3 in that mode. This is an effective growth index for each mode and increases when the average particle size of the mode increases even if the total mass and/or number is reduced either from precipitation or prior history etc. Figure 2b and 2c show MP_a and MP_n for the accumulation and nuclei modes respectively. During periods when episodic squalls were at the site (Day of Year - DOY 216 @ 18:00; 211 @ 15:00) and when the excursion in RH (not shown) suggested earlier squalls upwind (DOY 214 @ 15:00) both CN number or total mass decrease significantly while the MP values show little change.

Regular diurnal excursions in ozone evident in Figure 2a also relate to aerosol behavior. A superposition of these measurements relative to each daily mean (Figure 3) for the experiment reveal a mean diurnal cycle consistent with a complete chemical model of the ozone budget for the equatorial Pacific [Thompson et al., 1993]. Our measurements have a greater amplitude because they were made near the seasonal ozone maximum, resulting in values approaching twice those of Thompson et al. measured in February-March near the seasonal minimum [Oltmans and Komhyr, 1986]. The diurnal decrease in ozone is due to photochemical destruction and formation of OH but the compensating increase in ozone at night (Figure 3) reflects a replenishment by subsidence and entrainment from

aloft where ozone concentrations are higher. This entrainment of ozone into the MBL must also be accompanied by an entrainment of aerosol from aloft.

Since entrainment rates could not be calculated without ozone profile information we interpret our data with reference to previous measurements (March, 1993) on CI (S.Oltmans, NOAA/CMDL, personal correspondence). These data show an increasing linear gradient in ozone concentrations between the surface and about 1,800m with higher and more variable values above. The ratio of values at 1,800m to surface values varied from 1.2 to 3.6 for the 9 cases we examined but averaged about a factor of 2. In order to assess the significance of the entrainment rate, we estimate it from a simple model that includes these previous observations and a constant surface deposition velocity (v_d) of 0.05 cm s^{-1} [Warneck, 1988], our mean measured daily surface ozone concentration (C_s) of 14.5ppb and the mean observed rate of increase (dC_s/dt) during the night of about 4.3 ppb day^{-1}.

Subsidence into the MBL will result in both boundary layer growth (and/or divergence) while mixing both ozone and air into the MBL. Hence, the time rate of change of nighttime ozone mass [Mass=Concentration(C) x height (h) x Area] in a unit area column in the MBL can be approximated by:

$$C_{ave}\, dh/dt + h\, dC_{ave}/dt = C_t w_e + C_s v_d \qquad (1)$$

C_{ave} is average concentration in column, C_t and C_s the concentrations above the MBL (top of column) and at the surface respectively and w_e, the entrainment (subsidence) rate. For a linear gradient, C_{ave} can be written as $(C_s+C_t)/2$ and if C_t is assumed to vary slowly and randomly relative to diurnal changes in C_s then the mean $dC_t/dt=0$. If the increase in column volume represented above as dh/dt is replaced with w_e we get,

$$w_e = 1/(C_t/C_s-1)\,[\,(h/C_s)dC_s/dt + 2v_d\,] \qquad (2)$$

For our observed values of C_s and dC_s/dt this expression is most sensitive to the ratio of C_t/C_s and h. In Table 1 we select three ratios (R) that encompass most of the 9 profiles mentioned above and three heights that span the range of mixed layer heights suggested by our radiosonde data. Relatively constant ozone values between the equator and Samoa [Thompson et al., 1993] and the nine years of measurements at Samoa [Oltmans and Komyhr, 1986] that show a July-August peak in average monthly surface values of about 20ppb suggest that an estimate of about 30 ppb above the mixed layer is likely at CI., corresponding to about R=2 in Table 1. The underlined values in Table 1 reflect our favored assumptions that either R=2 is most representative and independent of height (vertical entries) or that R tends to increase with height (diagonal entries). Together these values show w_e=0.4-0.8 cm s^{-1} to be representative of our data and consistent with estimates [Huebert et al., this issue] from another method. The table also shows the related time to fill the mixed layer with subsiding air (replenish time or 50/50 dilution time) of 2-3 days.

Table 1. Estimated w_e (cm s^{-1}) and MBL replenishment time

	w_e			Days		
h(m)	R=1.5	R=2	R=2.5	R=1.5	R=2	R=2.5
800	<u>0.75</u>	<u>0.37</u>	0.25	<u>1.2</u>	<u>2.5</u>	3.7
1200	1.0	<u>0.51</u>	0.34	1.4	<u>2.7</u>	4.0
1800	1.4	<u>0.72</u>	<u>0.48</u>	1.5	<u>2.9</u>	<u>4.4</u>

In view of this entrainment, it is of interest to compare the size distribution in early morning, before the onset of photochemistry, to the distribution in the late afternoon. Figure 1 reveals aerosol number concentrations in the minima region are higher in the morning than the afternoon and have slightly larger sizes in the afternoon. Because this distinction is not always so apparent, we return to the notion of mass per particle introduced above for modes larger and smaller than 0.09μm. Note that the number increase (Figure 1) for the nuclei mode is greatest for the larger sizes in that mode, tending to raise values of MP_n, while for the accumulation mode the increase is at the smallest diameters and tends to lower MP_a. Consequently, an increase of particles distributed over the cloud-processed minima will have opposite effects on the values of MP_a and MP_n. This behaviour is clearly evident in Figure 2b and 2c both diurnally and over longer periods. The lack of variability for sizes below about 0.05μm (Figure 1) suggests that these sizes and concentrations are similar to values aloft. This implies that MBL removal mechanisms are slow for these sizes, consistent with both their slow diffusion/coagulation and their inability to activate in the non-precipitating cumulus typical for this region. Aerosol larger than 0.1μm tend to be fewer in the morning than the afternoon, indicating that the aerosol aloft has fewer large particles than in the boundary layer. These observations and the tendency for maximum change near the intermode minima, suggest that the aerosol aloft is monomodal with a number peak between about 0.06 and 0.1 μm. This agrees with modeled size distributions for aged subsiding aerosol nucleated in the upper troposphere [Raes, 1995].

Our inability to directly confirm this inferred monomodal size distribution for the subsiding air at CI prompted related measurements one year later at Mauna Loa Observatory (MLO, alt. 3,400m) and a coastal site, Kumukahi, in Hawaii on July 23-24, 1995. Although Hawaii is not in the same equatorial air mass, at this time of year it is characterized by pollution-free long-range transport, a regional scale subsidence into the MBL and comparable meteorology. We chose a period with E-NE flow both at the surface and at MLO with wind speeds about 6 ms^{-1} for both so that air above and below the inversion would have moved together for several days. The meteorological condition most different from CI was the presence of more developed cumulus in the MBL accompanied by occasional showers. DMA distributions were accumulated at MLO during nighttime downslope flow (01:00 LST) characteristic of the free troposphere and compared with a sea-level distribution from later that day during onshore flow.(ca. 14:00 LST). Figure 4 show that the nighttime MLO distribution is monomodal with a peak diameter near 0.06μm while the coastal MBL aerosol is bimodal with an intermode "cloud processed" minima at about the same diameter as CI. These data reveal a higher concentration of monomodal nuclei aloft (3,400m) that can subside into the MBL where they both grow and are removed in response to cloud processes, as described for CI. In both regions the cloud processed minima for the ammonium sulfate aerosol distribution (Figures 1 and 4) would be expected after activation in cloud at about 0.35% supersaturation (consistent with updrafts of about 1 m s^{-1}) [Pruppacher and Klett, 1980].

The time series of MP_a values for the CI accumulation mode tend to increase during daytime and decrease at night (Figure 2c). This suggests a daytime growth in response to photochemical production of sulfate [Huebert et al., this issue] or aqueous phase oxidation of SO_2, that is sufficient to overcome the decrease arising from the continuous entrainment

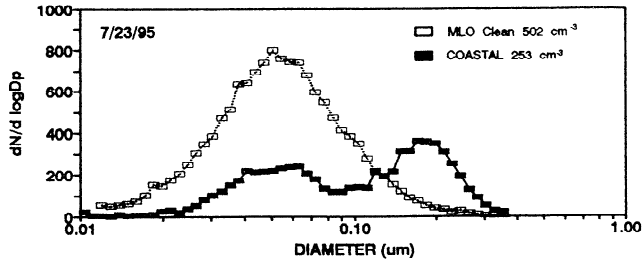

Fig. 4. Averaged DMA number distributions corrected to effective concentrations at surface pressure: measured at MLO (3,400m) during clean free troposphere conditions (solid square) and a clean surface marine case measured at the Kumukahi coast (open square) measured within 16 hours of each other under steady trade wind flow similar to conditions at Christmas Island.

of smaller particles. The average apparent daytime increase in MP_a (in units of pptv per particle per cm^3) over the 12 days is about 0.18 (Figure 2c). The average nighttime decrease of 0.20 is assumed to reflect constant entrainment so we must increase the "apparent" daytime increase in Mp_a to 0.38 to account for this continuous loss term. For a mean MBL accumulation mode aerosol concentration of 150 cm^{-3} this implies about 55pptv sulfate formed per day or 25% of the total in this mode. This suggests a replenishment time for aerosol mass in the region of about 4 days. This is about 70% of the 74pptv reported for total filter measurements [Huebert et al., this issue]. Although uncertainties in absolute quantities present in the combined techniques (about 20% for DMA data and 10% for filter data) could account for this difference, we expect that some of this is due to accumulation of sulfate on sizes larger than the 0.4μm measured by the DMA.

Conclusion

We have characterized the changes in submicrometer MBL aerosol in response to diurnal processes associated with entrainment and aerosol growth in the remote MBL. We found no evidence for significant particle production in the MBL. The variability of ozone is consistent with photochemical models for this region and suggests an entrainment rate of about 0.6 cm s^{-1} that can replenish MBL aerosol number in about 2-4 days with aged nuclei from the free troposphere. The data also suggest that about 20% of the measured DMS flux is eventually converted to sulfate on the accumulation mode particles with diameters below 0.3μm. A combination of cloud processes (nonprecipitating) and photochemical formation appears to result in preferential growth of cloud activated aerosol (D_p>0.07μm) that amounts to about 25% of the mean submicrometer sulfate. This suggests a 4 day replenishment time for aerosol mass that is similar to the entrainment time scales and helps explain the quasi-stable size distribution and submicometer mass in this low precipitation region.

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