

Authors Response to Reviewer 1 for:

Journal: ACP

Title: Free Troposphere as the dominant Source of CCN in the Equatorial Pacific

Boundary Layer: Long-Range Transport and Teleconnections

Author(s): A. D. Clarke et al.

MS No.: acp-2012-895

MS Type: Research Article

Responses will follow issues raised by the reviewer in order presented unless otherwise noted. *Reviewer comments in italics.*

Reviewer 1

Summary concern – page C111

We appreciate the efforts and comments of the reviewer and their apparent following of this topic as we have presented it over the past several years. We note below that there may also have been some confusion we created by incorrectly mentioning that this paper included some related VOCALS results that have also “*long been suggested*”. That work is now part of another paper currently underway and is not part of this paper.

The reviewer’s first page also raises general concerns about the use of correlations employed and inferences made from our data to understand the entrainment process. The reviewer then questions generally whether the data set can be used to state that MBL CCN are always dominated by CCN entrained from the FT in this region. These general concerns concern the thrust of the paper and cannot be directly responded to without extensive reiteration of the paper. Consequently, we will address these issues raised in the introductory remarks in the context of the reviewers more specific comments raised below. Some similar comments are also addressed in our response to Reviewer 2.

One question we will address is:

The question in this work, though, is: does FT entrainment provide the dominant source of CCN to the MBL? I’m not entirely convinced it does and I also take issue with the “general” nature of the title of the paper that implies that FT is always the dominant source of CCN in the region. It may arguably be the dominant source during PASE but is that typical across the diurnal cycle, the meteorology and the seasons etc. I suspect it isn’t and the title should really reflect the necessarily limited scope of this study.

Although our experience beyond PASE and prior publications (see list below with related comments) also supports the original choice of our title, we agree there may be circumstances when it may not always be true.

Hence, we suggest the following modification.

New Title: “Free troposphere as a major source of CCN in the Equatorial Pacific boundary layer: long-range transport and teleconnections”

Away from regions of deep convection we have found entrainment to be common (see several of our papers below). Certainly, closer to continental sources, advection in the MBL may be dominant. However, entrainment in this region is well recognized. The previous 1994 Christmas Island surface experiment established entrainment rates of about 3-7 mm/s based on nighttime decrease in non-sea-salt sulfate concentrations (Huebert et al., 1996) and values of about 4-8 mm/s based upon fluctuation in ozone and aerosol dynamics (Clarke et al., 1996). Wood and Bretherton (2004) report values of 4-6 mm/s for the equatorial Pacific and Conley et al (2011) report a project average of 6.6 +/- 3.8 mm/s from their analysis of PASE data. Wind profiler data over CI (Ken Gage) reveals FT subsidence rates aloft of about 5-10 mm/s, consistent with subsidence in most of our HYSPLIT trajectories (see Freitag paper). Hence, subsidence and entrainment is the norm for this region and will bring whatever aerosol is present there into the MBL. This paper addresses the nature of this aerosol and the fraction of this aerosol most effective as CCN.

Diurnal Cycle – We agree that variations in entrainment over a diurnal cycle or even shorter/longer may be at work. However, such variations will not greatly change the mean concentrations and size distributions we discuss here as the lifetime in the MBL is on the order of several days or more.

Meteorology – Certainly variations in entrainment linked to meteorology are important and are part of our conclusions. The longer term coupling between FT and MBL mean concentrations discussed for Fig.11 implies synoptic scale variations and we will make this link to meteorology more clear.

Seasonality – Although we do mention these PASE data were for the biomass burning season in SA, it is true that we do not emphasize it. Indeed we have made related measurements in this region for both non-burning seasons (Clarke et al, 1996) and burning seasons (Clarke and Kapustin, 2010) and there is a seasonal cycle in pollution influence also mentioned in other papers on Ozone and CO in the FT for this region. **However, it should be recognized that a key motivation for our stratification for low and higher CO cases emphasized in this paper is to isolate and reveal the differences between clean and more polluted air mass properties evident in separate layers (eg. Fig. 2).** This is why we show these characteristics for two layers on the same flight (Fig. 1 and related discussion). With this approach we do not present just the mean properties of the season we were there but rather mean properties of the air masses stratified as clean and more polluted air masses (Figures 9 a-f, 10 a-f. The stratified mean clean behavior is then considered to represent the “clean season” whereas the more polluted mean is representative of the BB burning season influence. We will try to emphasize this point more carefully and include more references to earlier work in this area. (also see response to reviewer 2)

As evident in the publications below, we have a long history of demonstrating the lack of evidence for MBL nucleation in prior studies. We have also emphasized the importance of entrainment in prior studies that lacked the sustained repeated flight patterns available

in PASE, so this is not a new concept. Exceptional conditions can occur when nucleation near the top of the boundary layer can be found after heavy scavenging by rain has occurred, as discussed in our earlier Science paper (Clarke et al, 1998). We will include greater discussion and references to this in a revised version.

The reviewer also suggested that some inferences are overweighted and “A simple use of the word “suggests” rather than “confirms” throughout might go some way to address this. We will attempt to address this where appropriate in a final submission.

A few of Our Prior Relevant Publications for Nucleation, Cloud outflow and Entrainment

The first paper to provide evidence for enhanced nucleation in the FT

Clarke, A. D., “Atmospheric Nuclei in the Pacific Mid-Troposphere: Their Nature, Concentration and Evolution, Jour. Geophys. Res. Atmospheres, 98, D11, 20,633-20,647, 1993.

Our ASTEX paper showed Lagrangian evolution of aerosol in MBL under stratus was governed by entrainment of clean air form above diluting the MBL pollution aerosol.

Clarke, A.D., T. Uehara and J.N. Porter, Lagrangian evolution of and Aerosol Column during ASTEX, Jour. Geophys. Res., 101, p4351-4362, 1996.

Paper showing Entrainment Rate constrained at Christmas Island based upon aerosol size changes and ozone fluctuations at surface in Equatorial Pacific and also predicted the presence of a monmodal aerosol above inversion (later confirmed)

Clarke, A.D., Z. Li and M. Litchy, Aerosol Dynamics in the Pacific Marine Boundary Layer: Microphysics, Diurnal Cycles and Entrainment: Geophys. Res. Lett., 23, pg 733-736, 1996.

Paper confirming nucleation aloft from convective cloud outflow (ITCZ and other convective clouds) was a source of nuclei entrained into the MBL.

Clarke, A.D., J. L. Varner, F. Eisele, R. Tanner, L. Mauldin and M. Litchy, Particle production in the remote marine atmosphere: Cloud outflow and subsidence during ACE-1, Jour. Geophys. Res., 103, 16,397-16,409, 1998.

Paper demonstrating uncommon conditions in the equatorial MBL when nucleation was possible and observed to be consistent with the sulfur cycle from DMS

Clarke, A.D., D. Davis, V.N. Kapustin, F. Eisele, G. Chen, I. Paluch, D. Lenschow, A.R. Bandy, D. Thornton, K. Moore, L. Mauldin, R. Tanner and M. Litchy, M.A. Carroll, J. Collins, and G. Albercook, Particle nucleation in the marine boundary layer and its coupling to marine sulfur sources, SCIENCE, Oct 2., 1998.

Characterization of aerosol sizes and properties of cloud pumped aerosol between 6-8 km altitude over the equatorial Pacific

Clarke, A.D., F. Eisele, V.N. Kapustin, K. Moore, R. Tanner, L. Mauldin, M. Litchy, B. Lienert, M.A. Carroll, G. Albercook, Nucleation in the Equatorial Free Troposphere: Favorable Environments during PEM-Tropics, Jour. Geophys. Res, 104, 5735-5744, 1999a.

Nucleation Layers aloft in tropics and mid-latitudes are in accord with binary nucleation for conditions in evaporating cloud edges.

Clarke, A.D., V.N. Kapustin, F. L. Eisele, R. J. Weber, P. H. McMurry, Particle Production near Marine Clouds: Sulfuric Acid and Predictions from Classical Binary Nucleation, Geophys. Res. Lett., 26, 2425-2428, 1999b.

First paper to show clear entrainment of pollution (long range transport from China) being entrained into MBL and consistent with modeled transport. Strong entrainment near transition region in California stratus with large input of CCN sizes from the FT.

Clarke, A., V. Kapustin, W. Collins, P. Rasch, K. Moore, S. Howell and H. Fuehlberg, Dust and Pollution Transport on Global Scales: Aerosol Measurements and Model Predictions, Jour. Geophys. Res., 32, 555-32,569, 106, D23, 2001.

Multicampaign integrated study of the large scale features of the Pacific aerosol and the relative lack of nucleation in the MBL

Clarke, A.D., V. Kapustin, A Pacific Aerosol Survey – Part 1: A Decade of Data on Production, Transport, Evolution and Mixing in the Troposphere, Jour. Atmos. Sci., v59, 3, Part 1, 2002.

Global scale indication of the role of primary and secondary aerosol including volatile nuclei in Hadley cell for cloud outflow.

Clarke, A., and V. Kapustin, Hemispheric Aerosol Vertical Profiles: Anthropogenic Impacts on Optical Depth and Cloud Nuclei, Science, 329(5998), 1488-1492, 2010.

General Comments

1/ Airmass history assumptions

The assertion in the abstract that correlations in CCN.2 above and below the inversion “confirm” that FT entrainment dominate CCN is not correct. At best it may “suggest” it but what if the airmasses of the MBL and FT for the flights studied had similar aerosol backgrounds to begin with, e.g. that the deep convection that is later mooted as the source of FT aerosol, actually lofted BL aerosol above and over the MBL that is still carrying the same aerosol along with it at lower altitudes?

Trajectories could help to inform this argument (I’ll come back to the limitations of trajectories later) and trajectories from one flight are presented in Fig. 5, which all appear to show an easterly flow at all altitudes, with some trajectories passing over SA and some remaining over the MBL before being lofted. Interestingly (in this one

demonstrated example), the lofted airmass which is subsequently sampled in the FT, was lofted from the MBL, whereas the air sampled in MBL was always at low height (I use the word height and not altitude here) as the air seems to have hugged the ground as it moved over the Andes and SA (height ~3 km at ~80 degW, 6 degS). Now, if the lofted air was simply previously MBL air (ultimately of SA origin) with the same ultimate airmass history (S. America) and background aerosol character, then the reason the sampled FT air has similar CO and C112 CCN concentrations etc as the MBL would be very simply because the airmasses of the FT and MBL are still historically coherent.

We did not use the word “correlations” in the abstract or the text. We did say “Flight averaged concentrations of CCN.2 were similar for measurements near the surface, below the inversion and above the inversion, confirming that subsidence (*should read entrainment*) of FT aerosol dominated MBL CCN.2.” This one sentence summarizes a long discussion of the size distributions and concentrations etc. that support this argument in the text. This discussion points out that the smallest particles sizes are found in the FT associated with cloud outflow and that these smaller sizes are not evident in the MBL (also see references above and the discussion of Figure 10 distributions). Entrainment of these FT distributions and subsequent growth in the MBL is consistent with our prior observations, the physics of the meteorology involved, the gradient in concentrations (aloft toward the surface), and subsequent cloud processing in the MBL with a gas phase precursor surface source (DMS). As noted and referenced above, entrainment is active in this equatorial flow with a common value around 5 mm/s or about 432 m a day. Hence, a 10 day back trajectory should entrain about 4.3 km from above into the MBL. Our paper and many others point out such pollution layers are generally less than 1km thick. Even if the MBL and FT aerosol layer above the inversion had a similar origin near the coast of south America, (not generally the case in our experience) it would be entrained long before reaching Christmas Island. Moreover, trajectories in the FT go back over 12,000 km and air below the inversion has generally both different speed and direction relative to that above so these air masses are not coupled for long. Hence, as discussed in the text, we believe that the similarity in concentrations for CCN sizes in the FT, and MBL (as discussed in Fig. 11) and their covariance over a 5 week time period indicates entrainment dominates the MBL CCN.

On the issue of trajectories, we note that a separate PASE companion paper (**Assimilating airborne gas and aerosol measurements into HYSPLIT: A visualization tool for simultaneous assessment of air mass history and back trajectory reliability; Freitag et al.**), was submitted to ACP at the same time as this paper with the hope that readers would be able examine that paper to get a better sense of the trajectories and their characteristics over the PASE campaign. Hence, we only present one illustrative example here. Although the Freitag paper a good review, the reviewer and editor suggest it be resubmitted to the related journal AMT due to its technical content. This required some modification and delay. It was resubmitted to AMT on March 15 and it will help address a lot of related trajectory questions, including most of those raised here. We will reference it accordingly.

The trajectory analysis and integrated data assimilation is a topic in its own right and was simply too much information to try to include in this paper. We consider this high resolution visualization tool a powerful way to assess airborne data but it requires more discussion than we could accommodate here. Originally we had multiple references to this trajectory paper but these had to be removed when it was delayed. It discusses the relation of air mass properties, physical/chemical properties and sources in detail. Numerous papers identify entrainment rates for the region and 10 day HYSPLIT trajectories almost invariably shows similar subsidence as that for our example case.

The reviewers hypothesis of coherent air masses in the FT and MBL persisting back to SA was not evident in PASE, nor would they persist in the face of recognized subsidence and entrainment over 10-12 days. Even if originally coherent near the source, they would not remain so for long under the vertical gradient in wind speed and the shear evident across the inversion. Moreover, coherence was not evident in the experiments near the source regions [see Moore et al, 2003 in references for the PEM-Tropics Expt., also Allen et al. for the VOCALS Expt.] (see below and to be added to references) and others. Hence, the notion of a general coherence between FT and MBL air masses over 10 days or so transport is inconsistent with the dynamics and lacks support in our measurements for PASE and for measurements near SA or the literature.

The heavily polluted air lofted over the Andes to 5 km and advected over the ocean is decoupled from the MBL air over the Pacific until it subsides to the inversion (near Christmas Island and giving rise to the teleconnections we describe) and certainly does not have the same air mass history. Again the Freitag et al. trajectory paper will make this discussion more clear.

For RF14, a MODIS plot (with no timestamp) is presented in Fig. 3 (with no recognition of where the plot was taken from as this is clearly extracted from and not a plot generated by the authors from raw data). It is referred to on P.1287, line 15, to discuss CTH and outflow from a line of convection. In the text, it appears to be a MODIS image taken "the night before" the flight, which was used to select a cloud for flying the next day. But why isn't a MODIS image that corresponds to the time of the flight shown – perhaps with the position of the aircraft labeled at the corresponding time? I would expect ITCZ-type convection to wax and wane with the diurnal cycle and I simply can't take imagery from the night before as evidence of the same cloud structure that was sampled the next day. In the text, we are told that "cloud top temperatures are indicative of outflow near 5 km" – then why isn't the plot a plot of cloud top temperature? Or what was the cloud top temperature? We are asked to believe generalities about satellite data that may not have been examined properly.

We believe that this analysis was done properly and it was similar to our previously published approach (referenced in Clarke et al. 1998). We have also employed it on various other airborne experiments and we felt it was not very unusual so we did not belabor the details. We are not clear on what satellite generalities we are asking people to believe. We are simply using the described IR product to get cloud top temperatures

(commonly done) and combine that with commonly used model forward trajectories as a tool to enable us to predict the location suitable target cloud cluster.

We agree the MODIS time stamp should be included in Figure and the MODIS origin acknowledged. It was taken from a MODIS image at 22:30 GMT during the RF04 flight and was selected to correspond to the cloud profiles made and discussed here. The cloud selection process is outlined briefly in the text and we agree it could be expanded somewhat.

The process is as follows:

In order to accommodate pilot flight planning the evening before the flight one has to identify a suitably a convective cloud cluster by its lower cloud top temperature. This needs to be done as late as possible but before the cutoff for pilot flight planning. This requires going through cloud IR imagery using IR temperature to select a cloud higher than the warmer trade wind Cu but lower than the maximum flight altitude for a fuel loaded aircraft (about 5 km). One then needs to plot trajectories using model wind fields for a suitable cloud group advecting in a way that would: 1) allow us to predict it to come within aircraft range (preferably no more than 500km distant) at the time we could reach the station in a flight plan filed for the next day and 2) that allows for enough sample profiling (about 5 hours) on station near the cloud to complete the characterization and then return. Once filed the night before the flight plan can only be modified a little in the morning so there is a lot of pressure on to get this right. This takes careful planning and considerable time examining mult-hour IR imagery along with projected meteorological forecast data and preferably some experience. If you are lucky, as we were, you will have chosen a cloud cluster where suitable convection is still active at the **predicted location and altitude**.

The objective of this exercise was to find such convection at altitudes above surrounding clouds that allows one to isolate cloud outflow nucleation layers when you get there. As we did find such clouds at the predicted location, as seen in this image, our approach achieved our goal. We do not recall the exact IR temperature but clouds further north (lower IR temp) and nearer the ITCZ had outflow too high for us to reach while further south they were not convective enough (high IR temp) to get to altitudes favorable for precipitation scavenging and nucleation. If one goes to the MODIS website and looks at ITCZ cloud loops over these scales it is clear such convective cloud groupings can last a day or more even if an individual cloud might vary. We have successfully used this predictive approach to target more convective clouds on other experiments like ACE1 and INDOEX. We can perhaps discuss this more and give the IR cloud location but we do not see a need to include or discuss the IR imagery. (One is included in the Fretag discussion of ITCZ convection on another flight). We will give enough information such that the truly interested reader can go to the MODIS website and go through the worthwhile exercise of doing this for themselves. Yes, there is a diurnal cycle and you try to take off early enough to reach your objective when the cloud is still active but not too active (too high), as it can be if convection intensifies.

However, despite the above, the use of volatility information used later in the discussion

is alot more encouraging and I enjoyed the discussion of new nucleation in deep convective outflow and the reasons for contrasts in volatility. This, when taken with the above, does begin to build a convincing case for the airmass history conclusions made, but again it must be stressed that this is all still (interesting) inference but not conclusive proof.

The volatility behavior and associated size distributions in ITCZ cloud outflow has been presented in our papers for well over a decade, including many of our included references. We felt it was necessary to present a specific case for PASE that showed nucleation at altitudes relevant to PASE flights and trajectories but did not want to repeat prior work more than necessary. Hence, we carried out RF04 during PASE to confirm our earlier studies of clean and nucleation below the 5 km altitude most likely to influence our PASE measurements (much higher altitudes are expected to subside fast enough to reach the inversion near CI). The clean layers are characteristics of the non-biomass burning season. The biomass burning season simply has a greater number of combustion layers present (*Schultz, M., JGR, 104, 1999*). The entrained aerosol in both seasons are still the dominant source of larger aerosol at CCN sizes and (as argued in this paper).

As reported in most of our previous papers (and reviews by others – eg. Quinn and Bates, *Nature*, 2012), little evidence for a widespread MBL nucleation source has been found for most of the remote Pacific. We will make more direct references to our published data so that this is clear. Again, the trajectory assessment is best revealed in the Freitag et al. paper that focuses on that process for PASE. As the paper is longer than this one, clearly we could not include the kind of flight by flight analysis in this paper. We are not sure what could be done to establish “conclusive proof”. We have tried to present an argument that we feel is most consistent with all of the observations available.

In summary, I really don't buy the current mismatch of satellite imagery, trajectories, in situ trace gas data and aerosol spectra that are potentially cherry-picked for analysis C114 to fit the hypothesis. I'd be much more convinced if I could see a complete flow of analysis (trajectory to cloud imagery to in situ data or the other way around) on a flightby-flight basis (or even for one single flight), rather than snapshots of each data type from different flights all linked together in an unclear manner to “confirm” a favoured hypothesis.

We do not understand the notion that we have presented “...snapshots of each data type from different flights all linked together in an unclear manner to “confirm” a favoured hypothesis.”

We methodically proceed from individual cases that illustrate the data types and their differences in cleaner and more polluted air (higher CO). We then pointed out the layered behavior of CO and aerosol over different altitude ranges before stratifying size distributions and other data into profiles and groupings of higher and lower CO. This was followed by analysis of the results of this grouping. We then analyzed the flight to flight

means of key quantities above and below the inversion that illustrate the coupling of the FT and MBL etc.

As mentioned, flight 4 was the only ITCZ flight in PASE dedicated to characterize the cloud outflow and nucleation relevant to the PASE region.

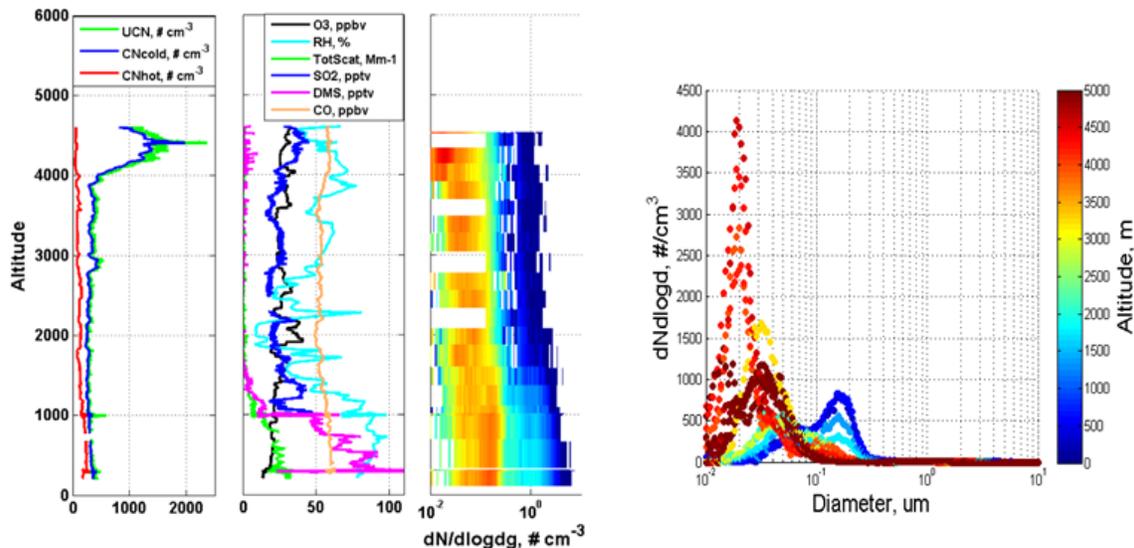
The flight 14 discussion was presented precisely to illustrate an example flight profile in detail for flight data linked to trajectories before moving into the discussion of mean PASE data and statistics. We take exception to the assertion that case flight 14 reflects a presentation that is a mismatch of “*cherry picked*” imagery. It is our data from this flight mapped exactly onto the trajectory path for every 10 sec of flight path (see Freitag et al. paper for details). The CALIPSO satellite image corresponds to the trajectory shown for flight 14 as close as possible to the time the HYSPLIT trajectory passed over this location viewed by the satellite. Again, the Freitag paper discusses the trajectory types in much greater detail.

2/ MBL nucleation

In the abstract, (line 25) we are told that the “measurements confirm that nucleation in the MBL was not evident during PASE”. Do they? Have I missed something? This isn’t discussed in the text so far as I can tell. Is the LDMA instrument used in this study on the C130 sensitive to ultrafine particles (~10 nm) that would see MBL nucleation. Perhaps it is but would be good to say this.

The absence of nucleation in the typical MBL has been a theme in many of our earlier papers for over a decade, with the noted exception of the post scavenging case discussed in the referenced Clarke et al, 1998. We note it again here on pg 1302 in conjunction with the lack of evidence for significant small nuclei in our size distributions shown in Fig 10. Perhaps we have slipped into taking this for granted although others reach similar conclusions based upon our work and others (Quinn and Bates, 2012). We can and will discuss this issue more in conjunction with this size data and will include more references to our prior work and those of others, including modelers, that show nucleation is rare in the MBL unless it has been heavily scavenged. While we could add more on this point in this paper, we feel it has been adequately addressed in prior papers.

We also plan to replace the RF04 fig 4 with another near cloud profile (see Fig. 3) when DMS measurements were available in the FT (see Fig. below left). Surface derived DMS (and MBL CO and SO₂) is clearly enhanced in the outflow region near 4km where nucleation is observed and where the larger CN_{hot} are scavenged. Recent nucleation is evident in the size distributions in the outflow (see Fig. below right) compared to layer below (yellow) and above (brown) while no small particles are seen in the mBL (blue). (also see response to reviewer 2)



3/ Use of VOCALS data?

Sorry. This was an error and we neglected to delete this VOCALS reference. We are writing a separate VOCALS entrainment paper and we initially considered adding some VOCALS observations to this paper for related issues. However, it became complicated, unwieldy and required too much discussion of the VOCALS experiment such that we felt it muddied up this paper. Hence, we removed the VOCALS discussion a long time ago but failed to remove this sentence.

4/ Section 9: I found this section very confusing.

Yes, there are awkward places here where we try to lead the reader through some complicated relationships. The second reviewer also had difficulty with this text. We will greatly revise this section for clarity.

To our knowledge there is no way to measure supersaturation directly in cloud. This is reason for our use of the Hopple minimum as a measurable aerosol feature that directly reflects the integrated impact of cloud supersaturation and its variability upon the MBL size distribution. This minimum (its diameter and variability) provides the constraint on cloud supersaturation mean and variability (respectively) that are present. We can include greater discussion of this for those unfamiliar with it.

5/ P.1299, line 5+: This paragraph discussed inter-flight variability between the FT and MBL and “confirms” that the apparent consistent variability of FT and MBL profiles over similar time-frames was due to entrainment. This may not be true for reasons discussed above – both FT and MBL airmasses could still be historically (and therefore chemically) coherent.

As noted earlier the notion of coherency over these scales is not consistent with observations and layered structures observed. We can spend more time in this paper (and in Freitag paper) to show the suggested “coherency” over 10 days is not a plausible hypothesis if this is not now clear.

6/ Discussion and conclusions: This section is very long and mostly repetitive of earlier sections. This needs to be more concise. —————

Specific/technical comments:

1/ P. 1286, line 3 change “with them nucleated” to “with nucleation”

2/ p. 1287, line 8: Change “(see below)” to (see Figure 5).

3/ P. 1291, line 4. Needs a period mark after “ranges”

4/ P. 1298, line 8. A mismatch in CNVol is explained away by “unresolved cloud processes”

– could you expand on this?

5/ P. 1301, line 4: What’s a “V pattern”? And what are “Vs”?

C116

6/ P.1301, line 29, Change “after they reaches”.

7/ P.1302, line 1. What is “cloud density”? Droplet number, optical thickness, cloud fraction, thickness. . . ?

8/ P.1302, line 8; rephrase “cloud free regions along the wind that may travel together for several days” – I don’t understand what this means here.

Yes. We will abbreviate conclusions and make suggested corrections.

Response to Reviewer 2

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Title: Free Troposphere as the dominant Source of CCN in the Equatorial Pacific

Boundary Layer: Long-Range Transport and Teleconnections

Author(s): A. D. Clarke et al.

MS No.: acp-2012-895

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Responses will follow issues raised by the reviewer in order presented unless otherwise noted. *Reviewer comments in italics.*

Reviewer 2

We thank the reviewer for their comments and will address them below and and/or incorporate them into an improved revised paper. We also note that some comments are also addressed in our response to reviewer 1 and these also be considered.

The data set is large enough to explore some key features of the CCN particles (volatility, size distribution, transport), but the measurements coincide with highly active biomass burning episode downwind in SA (Aug-Sep 2007) that is only briefly mentioned in the paper, and not discussed in the abstract or in the conclusions. As mentioned in Section 2, the CN and CCN concentrations during PACE campaign were unusually high compared to other clean MBL regions. It appears that the patchy pollution episodes are the ones that raise the concentrations to high levels during the time of year when biomass burning in SA is particularly active. Therefore it is unlikely that the data represents average conditions in Equatorial pacific boundary layer.

Indeed, the patchy layers are the ones that raise the concentrations of CO and aerosol and CCN active aerosol to higher values. This is actually at the foundation of our approach and we do not represent the data as an annual average. Instead of averaging our observations for this campaign we carefully stratify all the data with CO (as described in the text) so that we can assemble separate profiles of data for “clean only conditions” (low CO) and for “combustion influenced” layers (higher CO). This allows us to present the stratified profiles (eg. see fig 1, fig 9 and fig 10) that describe air masses most influenced by combustion (biomass burning) compared to air that has no evidence of influence (more representative of the clean part of the year). This was done to reveal characteristic differences to be expected in different periods of the year. We discuss the enhancements associated with the higher CO cases but also note that aerosol and larger CCN size concentrations in the clean air masses can also be high enough to act as a source of MBL CCN for these clean cases. We will reference the biomass burning in 2007 (see reviewer 1) and make an effort to make this approach more clear.

1. The results are based on a relatively short measurement campaign, and there is no discussion how well the results are expected to represent annual averages in the region. It is mentioned in Section 2 that PACE campaign took place during the time

of active biomass burning in the Amazon region, and the abstract should clearly point this out as well. The biomass burning episodes in South America tend to be sporadic with high interannual variability. According to Giglio et al. (2010), burning in SA peaked during the measurement period and was higher than normal in 2007. This should be discussed in the paper.

Although this airborne campaign duration was about typical for deployments of this type, it is true it only samples a limited time period. Because we and others find the more combustion influenced air usually travels in FT layers a few hundred meters deep (eg. Thouret et al., JGR, 2001) with cleaner air separating them, this stratification effectively separates our data into those more characteristic of the cleaner and the more polluted seasons. Seasonal differences in layer occurrence and concentrations of O₃ and CO are pronounced in the 2-6 km altitude range (Schultz, M., JGR, 104, 1999). Our resulting stratified profiles should therefore bound the range of conditions at different times of the year. If we had simply averaged all of our data without this stratification then we agree our observations would only apply to this time period. We will emphasize that objective of this effort was to capture this variability expected between clean and more polluted time of year. We were unaware of the Giglio reference and will note it.

It would be a good to separate “clean, CO below 63 ppbv” and “polluted” cases in the abstract and in Table 1.

We are reluctant to push our stratification any further than we have. As described in the paper, there were relatively few profiles flown aloft compared the boundary layer and not all instruments were operating at all times. Moreover, as discussed in section 10, there is not only variability in the FT (Fig. 2) but also in the MBL. The much less data for FT (Fig 8) means that, although there is enough data for representative comparisons between flights (Fig. 11), it is more limiting when individual comparisons are made for each profile above and below the inversion. This is more serious for the slower measurements like number greater than 80nm. Consequently, and along with occasional missing measurements on the profiles, the data from FT profiles are less robust than lower altitudes. Hence, while figure 11 reveals interesting overall trends and behavior, the relative variation in bar heights for a given flight are influenced by these considerations. We feel that Fig. 11 better provides the reader with the variability in the observations and we feel further stratification of the data is hard to justify.

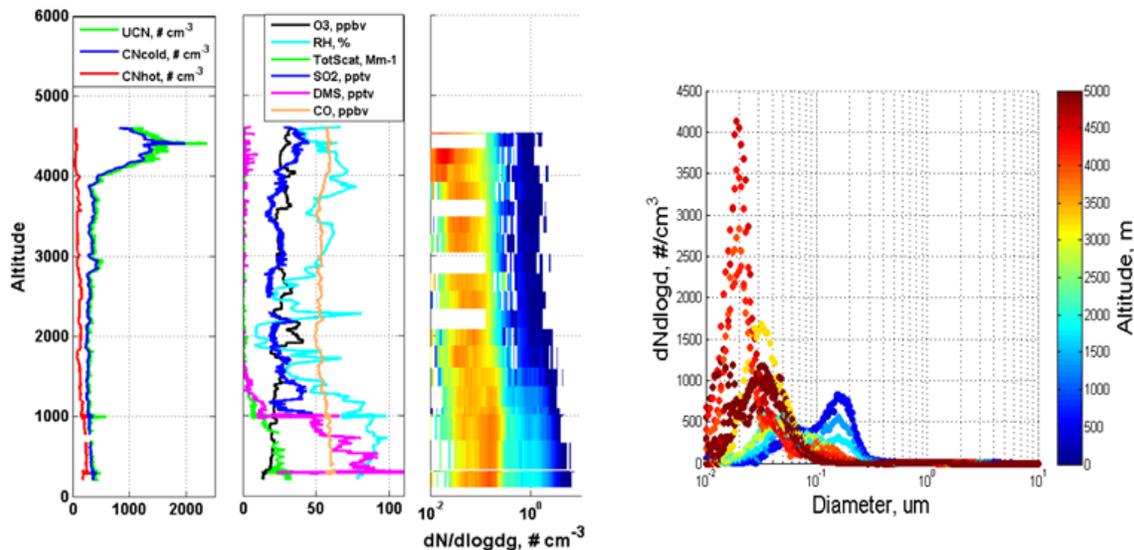
Also changes in wind speed affect sea salt aerosol emissions, and their variability should be discussed in connection with winds speeds during the campaign.

We looked into wind speed dependencies of coarse particle light scattering and larger aerosol sizes. The results were not clear in view of the limited range of wind speeds encountered and the influence of more pollution often under higher winds with more direct transport from SA etc. It is also likely that, when winds are low, higher wind shear will increase entrainment that acts to dilute (reduce) MBL coarse particle concentrations faster than production can increase them. This weak relation was also found in the PASE CCN data (Hudson et al, “On the relative role of sea salt cloud condensation

nuclei CCN”, J Atmos Chem. ,2011, DOI 10.1007/s10874-011-9210-5) compared to a similar RICO experiment that showed a strong relation. Their argument was that the much lower cloudiness/precip on PASE led to long aerosol residence times (except for very large particle > 9um) and this undermined the relation between concentration and wind speed for sea-salt.

2. I feel that there is some inner conflict in some of the conclusions: the growth of small particles to CCN sizes is claimed to be important (p. 1299), and this growth is linked to sulfuric acid produced from DMS (p. 1295). However, in Discussion and conclusions (p.1307) it is claimed that CLAW is not effective since all sulfate produced is accumulated on larger entrained aerosols. This claim is then stated in the abstract as well. Also I think it is wrong to claim that CLAW requires BL nucleation to be effective. While the CLAW hypothesis has been recently shot down by several other studies, I don't think that the data presented here justifies strong conclusions about the CLAW hypothesis.

CLAW argues that an increased DMS flux will lead to increased CCN number. We argue from size distributions here (and generally in other papers for many years) that we do not see new particle formation in the PASE BL and similar regions. Here the source of particles is from aloft where many are already larger than the Hoppel minimum (Fig.4, 10) and the subsequent growth through the Hoppel minimum is a relatively small sink for sulfate mass from DMS.



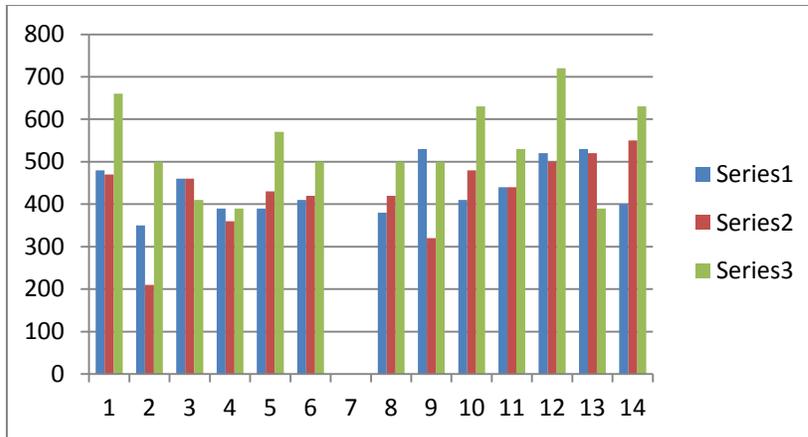
We will add a revised figure 4 (see above) to include these more standard size distributions plots that more clearly reveal the size distributions of nuclei mode in cloud outflow and their absence in the MBL. It is clear that DMS and CO have been pumped up to the region of nucleation from the MBL and that in spite of higher DMS in the MBL there is no evidence of nucleation there. The absence of the latter in the MBL was evident throughout PASE as can be seen in Fig 10. Moreover, the nucleation aloft occurs where mass (and surface areas, and CCN effective sizes) are lowest. Size distributions from below the outflow (yellow) reveal the “background” FT distributions (those above were

similar to the yellow from higher profile – see Fig 2b). Distributions below 2km show the progressive development of a Hopple minimum and increased number (and mass) in the CCN size range. SO₂ in the outflow is about 20pptv higher than in background air and could increase nucleated mass (and size) to about 80 ng/m³ compared to background aerosol sulfate on RF04 of about 250 ng/m³ below the outflow on RF04.

One might argue that the aerosol below the outflow nucleated similarly elsewhere with higher SO₂ and grew to these sizes and that these are also linked to surface DMS via the cloud pumping evident. However, it is problematic to assume that a doubling of DMS would lead to doubling of nuclei aloft. As discussed in our prior references (see response to reviewer 1), such production is a nonlinear function of conditions in the outflow [temperature, relative humidity, actinic flux, aerosol surface area (controlled by prior scavenging in cloud and the FT aerosol into which the outflow mixes as well as DMS and SO₂ pumped aloft)]. Concentrations produced increase with altitude (Clarke et al., 1999) into the tens of thousands per cc. due more favorable T, RH and low surface areas. However, this does not imply more DMS pumped aloft as detrainment at higher altitudes into cleaner and colder air will prompt greater nucleation, the number nucleated depends upon not just the DMS and SO₂ pumped up but the environmental conditions [temperature (altitude, Fig. 11c), RH, actinic flux, OH, scavenging (removal of surface area), mixing (surface area of aerosol mixed into), etc.]. In our PASE flight 4 they were ~1,000/cc in outflow with SO₂ about 35 pptv. Moreover, the entrained sizes most effective at becoming CCN will be the larger sizes (Fig 10) and not the smallest that are more closely linked to recent nucleation. These will include other sources that contributed to the “background” aerosol present near cloud outflow. Hence, the link proposed between a surface DMS source and increased cloud nuclei will far less simple or linear than the CLAW hypothesis proposed. However, we agree with the reviewer that some link to this cycle, via nucleation in the FT followed by entrainment, is likely. We will mention this and alter our text to reflect this process.

3. In section 9 it is suggested that 30-40nm volatile particles entraining to BL are rapidly removed by some unidentified cloud processing, and therefore do not contribute to BL CCN. This sounds quite suspicious, but seems to be a rather important assumption when calculating the contribution of CCN originating from UT nucleated particles. A few lines earlier it is suggested that the uptake of sulfate by volatile particles entraining from UT may convert CN_vol to be detected as CN_hot. Is this not a more plausible explanation for the smaller CN_vol than unidentified cloud processing?

These losses are most evident for all sizes below 40nm (Fig 10) and show up in the measurement of total CN in the FT, BuL and BL that was not included in Fig. 11 but is shown below.



Yes, some CNvol could be converted to CNhot but that will not account for the depletion of total number evident above and in table 1 or the lower number of CNhot in the MBL as seen in Fig. 11b. There is clearly a net loss of particles and these are primarily in the smallest volatile sizes. We agree that the marked depletion of these small sizes was not expected but this not an assumption. Their loss is clearly evident in the size distributions and in the summary concentrations seen in Table 1. We do have a mechanism involving thermophoretic forces that we are investigating but it is speculation at this point and we are reluctant to suggest it in this paper.

4. I am confused of the nature of particles that grow to CCN sizes in the boundary layer, that contribute 25% (50 particles/cc) to MBL CCN on average. Are these combustion aerosols? Or is this UT nucleated aerosol (as suggested by intercept of the linear line with y-axis in Fig 7b)? Please discuss

We feel figure 7b clearly shows a relation between CCN and CNhot but the intercept varies from flight to flight and would include both combustion aerosol and larger volatile sulfates. We do not want to over-interpret this intercept. Both combustion and clean outflow aerosol that are introduced into the MBL should grow larger heterogeneously in response to DMS emissions *Bandy, A. R., et al., JGR (1996)* with the larger ones likely to take up most of the mass. There will also be compensation in the sense that for a given MBL DMS flux the entrainment of fewer and smaller sizes under clean conditions can be expected to experience the greatest relative size increase via this process and with a greater fraction moved through the Hopple minimum. The 55/cc we discuss can be either clean or combustion aerosol. We are just trying to eliminate the sea-salt aerosol (SSA) from the total that grow to identify the non-SSA CCN that grow in the MBL. We agree the argument was hard to follow and we will work on improving, simplifying and clarifying this discussion.

5. The paper considers three sources of CCN: combustion aerosol, sea salt aerosol, and aerosol nucleated in cloud outflow. The abstract mentions that no boundary layer nucleation was observed, but this discussion is very limited in the rest of the paper. The authors claim that all observed volatile MBL aerosols originated from UT nucleation in cloud outflow, but I find this highly speculative. Nucleation also takes place in very

large air volumes close to tropopause (for example Young et al., 2007 and references within), and the subsequent entrainment of these particles could be responsible for the majority of the volatile UT aerosol. I find it difficult to believe that cloud outflow nucleated particles with concentrations around 3000 particles/cc around noon right after nucleation could generate a stable background aerosol of some hundreds particles/cc some 3000 km away, after being distilled into such a large airmass. Please discuss other UT nucleation as well or justify why cloud outflow nucleation should be the only source.

As both reviewers commented upon this we were clearly remiss in not giving this topic more attention. In fact we were the first to publish on this topic almost two decades ago and have published a number of papers on this issue since. Others have found that same and we have fallen into the mode of thinking nucleation in the FT and entrainment into the MBL were common knowledge (*See the recent 2011 Quinn and Bates paper in Nature paper that summarizes some of these observations*). Also, see our response to reviewer 1 where we identify these prior publications.

However, particles are not “distilled into a large airmass” but rather clean scavenged air with precursors of DMS, SO₂, and water vapor are injected as plumes at their potential temperature established by the cloud height and thermodynamics (eg. Clarke et al., 1999a,b). Once detrained into quiescent FT air these layers can and do travel thousands of kilometers, often with little mixing and particle growth stops when available precursor gases are depleted. Coagulation also becomes effective as concentrations drop.

As noted in our publication listed in response to reviewer 1, we published the first paper on nuclei in the FT (Clarke et al., 1993) and later demonstrated the increase in nuclei altitude toward the tropopause (Clarke et al, JGR, 1999a) and also documented a case of nucleation at the top of the boundary layer (Clarke et al, Science, 1998). However, our studies in the equatorial Pacific found most layers linked to cloud outflow at most altitudes (Clarke et al, GRL, 1999b). As discussed in these papers, nucleation in the equatorial MBL is rare because there is usually enough aerosol surface area to suppress nucleation. The profiles shown here are consistent with our prior studies and more recent ones (Twohy et al., 2002) clearly show nucleation is most active aloft in cloud outflow, many of which will be higher than the 4km outflow illustrated in this paper. The Young paper mentioned also identifies convection as possible source for those measured near the tropopause. Even so, we believe that high concentrations found near the tropical tropopause associated with convection or any other process are unlikely to subside to altitudes in the equatorial zone that will impact our PASE “clean” layer observations but we agree that it would help add to the global background of FT nuclei via the Hadley circulation (Clarke and Kapustin, Science, 2010).

Our purpose in flying and including the RF04 study (our only cloud outflow study on PASE) was to confirm our prior observations of nucleation in outflow was active at locations and altitudes (near 4km) most germane to the PASE study (see Fig. 5 example trajectory and the Freitag trajectory paper). We do not claim that this outflow creates a “stable background” of aerosol but that they generate characteristic clean layers with low

CNhot and increased volatile CN compared to background and/or more polluted layers. To the extent it exists, a background should reflect the aged scavenged air masses into which convection (both clean ITCZ and polluted continental) will introduce their convected air masses. Such layers can and should persist at their lifted potential temperature for thousands of kilometers as the aerosol coagulation rates rapidly slow and the distribution will stabilize until these aerosol are exposed to a resupply of precursor gases (eg. after subsiding to the MBL).

6. Introduction should include more discussion about previous measurements and modeling studies of marine CCN. Also, discussion about combustion aerosol and its role as CCN should be included.

Yes, this is now clear and we will summarize the nucleation story outlined in the papers above as well as more discussion of combustion aerosol properties characterized with similar airborne instrumentation (see response to reviewer 1).