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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Regional differences in organic composition of submicron and single particles during INTEX-B 2006" *by* D. A. Day et al.

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Reply to comments of Referee #2

We thank the reviewer for his/her careful reading of our manuscript. While we are sympathetic to the reviewer's desire to obtain more measurements of organic composition than were possible in this single campaign and reported in this single manuscript, we agree with Referee #1 that "The work will be helpful in adding information to the existing knowledge base regarding sources and processes responsible for OM in different regions of USA" and as such merits publication in ACP. Specific points and broader context for this statement are described in further detail below.

General and Specific Comments

1. The reviewer wrote: "It is also implicit that, even after the present study, our knowledge of the composition and sources of that OM are rudimentary." and "Given the importance of the topic, I was frustrated by the meager new results that are presented here."

We agree with the reviewer that our knowledge of the composition and sources of OM in the free troposphere, particularly over the eastern Pacific, remain rudimentary, which highlights the need for reporting even a limited number of unique measurements. We acknowledge that it is frustrating that a more comprehensive dataset was not obtained in this particular campaign. However, considering the analytical and logistical challenges of studying organic composition in this region, the dearth of organic aerosol information available for this region (including the INTEX-B campaign), and the uniqueness of our observations, the results presented in this manuscript reflect substantial new findings that merit publication in ACP.

2. The reviewer wrote: "Relatively few samples were collected (just 72 filters over 12 flights for FTIR and XRF analyses, and only 113 individual particle from 10 samples for STXM-NEXAFS), and then a surprisingly small fraction of these samples yielded reliable results (only 17 FTIR spectra allowed quantification of 2-3 functional groups out of the 8 target groups."

The major new results of this work are from organic single-particle composition by NEXAFS-STXM. The reviewer appears to suggest that 113 particles for STXM analysis were somehow fewer than planned. We note that this represents more than 3 people-years of STXM measurements and analysis; in addition, 113 particles constitute more than 10% of particles analyzed by our group in almost 10 years of synchrotron beam allocations (Russell et al., 2002; Maria et al., 2004; Takahama et al., 2007; 2009). In addition, the 113 particles are probably more than 8% of atmospheric particles EVER analyzed by this technique by any group (Tivanski et al., 2007; Hopkins et al., 2007;

Vernooij et al., 2009). As such, the limitation had nothing to do with sampling problems or detection limits (as the reviewer implies), but with synchrotron beamtime and personnel funding to analyze the results. The results presented using the 113 particles analyzed with STXM-NEXAFS are interesting, appropriate, and new. Moreover, we note that the results and coverage are more than expected, and the information provided by this technique is unique as it identifies organic functional group composition at the single-particle level (Braun, 2005). From this information we examine mixing states (internal or external), identify possible sources (Takahama et al., 2007), and examine composition as a function of size (Maria et al., 2004).

FTIR measurements were added to this study at relatively low cost to quantify the submicron particle masses associated with the limited number of single particles. The 76 samples represent nearly every level leg that was flown for a duration exceeding 5 minutes during this budget-limited-flight-hour campaign. Collecting filter samples (or online size distributions) during ascents and descents when the aircraft traversed a large range of altitude would produce quantitatively meaningless data. It is not uncommon for techniques characterizing aerosol chemical composition, to require modest intervals of integration (e.g. filter sampling), collection (e.g. TDMA), or averaging (e.g. AMS) to produce meaningful results, especially when sampling particle concentrations that were lower than those expected for “pollution layers." These sampling requirements were considered by the leadership of this multi-objective project, but the objectives associated with identifying the somewhat sparse Asian transport layers necessitated devoting a considerable fraction of the flight time to vertical profiles. The reasons for lower FTIR coverage on INTEX-B relative to four previous aircraft-based projects (Gilardoni et al., 2007; Liu et al., 2009; Maria et al., 2002; Maria et al., 2003) were:

a) Competing Aircraft Priorities: Planned horizontal sampling legs for this project were reduced to save flight hours for vertical profiles; as a result, several flights included legs less than 10 min rather than 30-40 min legs planned. Such decisions are always

a trade-off made by the in-flight mission scientist, and in this case the horizontal extent of all of the organic composition measurements (by FTIR, AMS, and PILS) did not benefit. The authors certainly agree that such decisions about priority measurements are ideally made in coordination with all techniques during the planning phase, but we see no way in which a discussion of the planned vs. actual atmospheric conditions (as Referee #2 recommends in comment 4 below) is relevant to the scope of this work.

b) Lower Aerosol Loadings: We note the paucity of organic aerosol measurements in general during this project (see response 4 below), in part resulting from short level legs preventing meaningful averaging (e.g. of AMS measurements), and in part resulting from the cleaner-than-expected conditions that were encountered. Based on studies conducted over the western Pacific (Heald et al., 2005; Maria et al., 2003) there was reason to believe that OM concentrations would be significantly higher than were observed, especially in Asian pollution plumes (the target of this campaign), which were only sampled during a small fraction of the flight time. FTIR sampling on INTEX-B was riskier than previous aircraft missions but still provided useful information to supplement the single-particle STXM measurements.

3. Regarding the reviewer’s note that we “report 2-3 functional groups out of the 8 target groups," we cannot report groups that are not present in the particles. The reviewer seems to imply that these groups constituted a significant fraction of the particles; on the contrary, our measurements show in most cases their potential contribution was small at best - and there is certainly no published evidence to the contrary. Three of these functional groups are typically below detection limit in 24 hr samples in many regions (aromatic, alkene, organosulfate groups), simply because they represent 1% or less of OM. While a more sensitive technique might have quantified the potential presence of low concentrations, in the absence of such a technique we have identified upper bounds to guide future studies. It is worth noting that prior to these measurements, no such bounds existed.

4. The reviewer wrote: “As a result, it is my opinion that one of the conclusions that

could/should be drawn from this study is that the combination of sampling and analysis protocols adopted herein are not really suitable for airborne sampling in the remote troposphere."

See response to comment 2 above with respect to the respective roles of STXM and FTIR measurements in this paper, noting that for STXM there were no “sampling and analysis protocol" (by which we understand the reviewer intends sensitivity or detection limit problems) that in any way make this technique "not really suitable" for airborne sampling; the number of particles analyzed and reported for this campaign exceed those of all but one campaign ever studied by STXM (ground or airborne). (ACE-Asia is the aircraft-based campaign that exceeds it at 185 particles, for which additional beam and personnel resources were available. Additional INTEX-B particles were collected and stored, in the event that future resources become available.) It is also appropriate to point out that "coverage" is not an appropriate metric for the unique single-particle organic composition measurements enabled here. Because of this unique information, several important studies have been published based on many fewer particles (Russell et al., 2002; Maria et al., 2004; Tivanski et al., 2007; Hopkins et al., 2007; Vernooij et al., 2009). So the number 113 is intended to remind the reader that it is not sufficient for statistical significance or global (or "remote troposphere") extrapolation - which would be folly regardless due to the limited geographic and altitude range of the 10 flights - but rather to provide examples of the types of particles found.

In addition, we note that FTIR has been successful on four previous aircraft missions marked by successful aircraft-based sampling, good horizontal and vertical coverage, and valuable insights into the role and contribution of organic aerosols aloft: ACE-Asia (Maria et al., 2003), PELTI (Maria et al., 2002), ICARTT-Twin Otter (Gilardoni et al., 2007), and MILAGRO (Gilardoni et al., 2009; Liu et al., 2009). In Figure 1 below, we compare recommended and actual organic particle sampling conditions for INTEX-B to sampling conditions during three previous campaigns. Ranges of the sample collection duration and the OM concentrations are shown for: 1) proposed conditions for

INTEX-B, 2) actual conditions during INTEX-B (OM estimated from AMS measurements), and 3) actual conditions during previous projects where FTIR - OM sampling was conducted. The resolved FTIR measurements for INTEX-B are also shown. The “Actual INTEX-B Sampling Conditions" box was estimated using AMS organic measurements averaged for each FTIR sampling period. In addition, we indicate limits for the collection duration - OM concentration space for which application of our method during aircraft projects is recommended. We applied this limits in planning our sampling strategy during INTEX-B, and they should be applied to future projects. While we are happy to have these recommendations archived as part of this discussion, we find it has no bearing on the scope and conclusions presented in our manuscript.

Figure 1 shows that our expected INTEX-B OM samples fall within the limits of previously successful aircraft OM measurements. No organic aerosol measurements (AMS, FTIR, STXM, WSOC) are reported in the literature from individual vertical profiles, only average profiles representing measurements from multiple flights and geographic locations (Dunlea et al., 2009; Peltier et al., 2009). Almost two-thirds of the research flight time was used for vertical profiles. Of the remaining 35% used on horizontal legs, FTIR measurements are reported for all legs of 15 min or more, less than a half of the time requested for our somewhat conservative, planned sampling strategy.

We also wish to provide some context for organic aerosol measurements aloft (including those in the remote free troposphere) so that the reviewer can better understand the importance of this manuscript despite the limitations that we have clearly identified: a) the shortage of published organic measurements from INTEX-B, b) the uniqueness of the single particle STXM measurements, and c) bulk organic information obtained with the analytical measurement techniques described in the manuscript:

a) Limited number of organic aerosol measurements: Only a few papers that report organic aerosol have appeared to date from the INTEX-B studies of the troposphere: Leaitch et al. (2009), Dunlea et al. (2008) and Peltier et al. (2008). Leaitch et al. (2009) presents a small subset of the STXM results presented in this paper, for which

this paper provides context and additional findings. Dunlea et al. (2008) describe inorganic and organic particle measurements made with a HR-ToF-AMS on board the C-130. The paper focuses primarily on one research flight (and also reports average inorganic/organic concentrations and correlations for different air masses for the entirety of the campaign). No organic particle size distributions are reported in that work, despite the nominal size resolution of the technique. The limited number of papers on this topic illustrates the scarcity and need for additional measurements.

b) Unique STXM results: STXM single particle measurements did not suffer from aircraft or concentration-related sampling issues, and as discussed above these results provide unique particle type and morphology information that is not available from other techniques. This emphasis is improved in the revised manuscript by reorganizing the order in which information is presented. We note several aspects of the STXM analysis presented in this manuscript that were missed by Reviewer 2 in assessing the results being too few, which highlight the reasons for publication based on the quality and novelty of the information despite its limited quantity. The STXM results and discussion show: i) a wide range of particles types (combustion, secondary, biomass) over a large range of locations and for a large range of particle sizes. ii) external and internal mixing of organic components and similarity of particle types to those observed over the western Pacific during ACE-Asia. iii) condensation/surface-limited oxidation contributing to the growth of Secondary particles in Pacific and Continental air masses. iv) dust scavening of combustion particles and SOA precursors.

c) Unique information provided by FTIR analysis: We argue that FTIR filter measurements also offer a unique measure of OM in the atmosphere. The capability of FTIR to quantify organic functional groups provides chemical specificity not attainable with techniques such as AMS and PILS. The FTIR method quantifies OM that is both soluble and insoluble and quantifies the organic component of aerosol that is contained within both refractory and non-refractory particles.

Collection efficiency: In comparison to AMS, the FTIR-filter method (while not as fast or

as size-resolved) can provide a measure of the total OM when organics are mixed with non-refractory material or other materials with low collection efficiency due to bounce. The collection efficiency of the AMS has been parameterized in relation to NH4/SO4 ratios (Quinn et al., 2006); however the effects of organic/inorganic/refractory mixing have not been studied extensively. For the INTEX-B dataset, we observed a correlation between the differences of FTIR and AMS organic mass with dust tracers. For example the correlation of the FTIR-AMS OM (difference) showed a mild correlation with Al (r =0.5) suggesting that at higher dust loadings AMS may be missing organic mass. Comparison of AMS OM to WSOC and FTIR OM to WSOC also reveals differences in OM quantification. Organic carbon (OC) can be directly calculated from the FTIR functional group quantification. The average ratio of WSOC to FTIR OC for overlapping periods (12 level legs) was 0.75, suggesting that 75% of OC was soluble. By contrast, even if a low OM/OC of 1.4 is assumed for the project average, the corrected AMS measured project average is below the WSOC by 25% – suggesting that some OM has a different AMS collection efficiency than is currently applied. Another example of the added detail that functional group characterization can provide is illustrated by the strong correlation between the FTIR OM - WSOC difference vs. alkane functional group concentration (r = 0.75). The ability of FTIR to quantify alkane functional group mass or to differentiate between oxygenated groups such as alcohol and carboxylic acid functional groups is not available from the INTEX-B AMS or WSOC measurements. It is therefore prudent to retain slower measurements to provide simultaneous in-flight evaluation of collection efficiency and complementary chemical information. As such, the FTIR filter method complements faster organic aerosol measurements, providing significant value for improving our understanding of organic aerosol on any platform.

5. The reviewer wrote: “Clearly, using very small filters resulted in small sampling flow rates that limited the mass of particles collected in each sampling interval."

Both volumetric flow rate and absorption scale with area for fixed face velocity and particle concentration. Flow through a larger area results in particles collected outside

of the FTIR beam used, which does not increase the absorption signal. The size of the filters used for collection was optimized for the beam size of the Bruker FTIR (1 cm diameter).

6. The reviewer wrote: “It is obvious that the authors realized they would be fighting detection limits in advance, and used the longest sampling intervals possible (duration of each level leg). While this did create some samples with “above detection limit" data, it also meant that most of these samples inevitably included multiple air masses from different source regions."

We understand this comment to apply to the supporting FTIR measurements rather than the STXM measurements, as the latter had short collection times and no "detection limit" losses of data. The FTIR sampling intervals were designed to maximize the functional group information obtained. Since the study and the interpretation was not designed to interpret differences in local sources, but to distinguish broad categories such as long range transported dust and local continental emissions, this design was appropriate. The manuscript is entirely consistent with the reviewer’s comment, identifying only broad regions rather than individual sources.

7. The reviewer wrote: “And, analysis of the sparse data set revealed no clear new insights into spatial distribution, or predominant sources, of the OM in aerosol over the study region (e.g., “OM concentrations showed greater variability within air mass categories as compared to averages among them")."

We feel that this observation is relevant and interesting. One might have expected these different geographical regions to have very different OM concentrations, on average. Our observations show that this is not the case and variance of regional sources and processing may often be more important for both OM concentration and composition. A recent compilation of global OC measurements showed similar behavior for OC within the boundary layer (Bahadur et al., 2009).

8. The reviewer wrote: “Given the small size of the data set, it is far from clear that

dividing it into smaller subsets is appropriate. For example, is it realistic to suggest that as few as 2 samples (author note: 3 samples) can really represent any of the defined geographic regions? Similarly, applying “clustering analysis" to 17 FTIR spectra in order to define 5 clusters seems a bit ambitious. In this case it is stated that just two of the clusters included “more than half of all samples", implying that the other three clusters had to split < 8 samples between them. The rationale for using this statistical approach seems to be that it has previously been used for much larger data sets, since it is noted that the two dominant clusters identified in this work were “similar to three cluster averages identified by Liu et al. (2009). . ." Perhaps this is encouraging, but what is meant by aligning two clusters in one study with three from another one, and more to the point, were Liu et al. able to draw any insight about sources/processing, etc, for their clusters? A similarly broad brush approach is used to examine the small data set on elemental tracers."

In this study, the point of using multivariate statistical tools (like cluster analysis) is to show the agreement (and discrepancies) between these results and those discussed in Liu et al. (2009). As such, we are doing due diligence by comparing to relevant published results in other regions. The groups that showed similarity in Liu et al. were mostly composed of samples collected from the aircraft platform in that study and were associated with a wide range of sources. This point is interesting, and suggests a similarity of well aged free tropospheric aerosols that are thousands of miles apart - and a much greater similarity than the local ground-based samples. The clustering analysis provides a convenient methodology to obtain this useful result. The associated results have been clearly presented to show its limitations so as to prevent over-interpretation.

9. The reviewer wrote: “In summary, I feel that the title of this manuscript promises much more than is delivered. The data are unfortunately just too few."

We found the separation into geographical air masses regions to be a useful and sensible framework by which to present the observations. We suspect that presenting these observations only as overall averages for the campaign, lumping together mea-

surements from the diverse geographic sampling regions, would not be acceptable to any reviewer or reader. We present both relevant and interesting differences and similarities among the air mass regions, despite the possibility of subtle trends that are not detectable due to the limitations. We do not overreach in our conclusions and make a concerted effort to accurately represent our uncertainties. Nevertheless, we have changed the title of the revised manuscript to de-emphasize the focus on differences between air masses. We feel the revised title “Organic composition of single and submicron particles in different regions of western North America and the eastern Pacific during INTEX-B 2006" accommodates the reviewer's concern and simultaneously provides a more informative title. In addition, we refer the Referee #2 to the comments of Referee #1 on the value of these results, our intended emphasis on the single-particle STXM measurements rather than the sampling-limited FTIR (discussed in our response to comment 2 above), and the specific value added by these measurements to the limited published information about organic particles in the Eastern Pacific region of the troposphere (discussed in detail in our response to comment 4 above).

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Figure Captions

Figure 1. OM concentrations detected by FTIR plotted vs. collection duration. Collection altitude is indicated by colored shading. Boxes (solid borders) enclose the 70th inter-percentiles ranges of OM concentrations and sample collection duration (level legs) measured with FTIR during three other aircraft studies using this method (Liu et al., 2009; Maria et al., 2002; Maria et al., 2003). The dashed grey box shows corresponding limits for INTEX-B, but representing the central 90th percentile ranges for OM measured with a HR-ToF-AMS on board the C-130. The grey curve indicates the collection duration - OM concentration sampling space for which application of this method is recommended and should be a guide for future experiments. The range of proposed INTEX-B level leg duration is shown above the figure.

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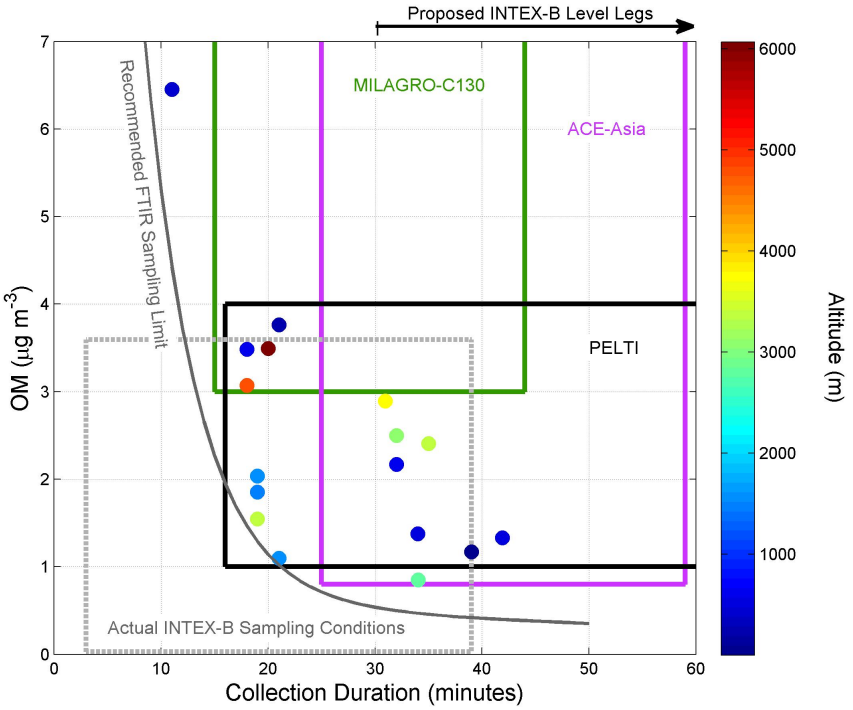
Proposed INTEX-B Level Legs
MILAGRO-C130
ACE-Asia
PELTI
Recommended FTIR Sampling Limit
Actual INTEX-B Sampling Conditions
OM (μg m-3)
Collection Duration (minutes)
Altitude (m)
0
1
2
3
4
5
6
7
0
10
20
30
40
50
60
1000
2000
3000
4000
5000
6000

Fig. 1.