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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of volatile organic compounds (VOCs) in Asian and North American pollution plumes during INTEX-B: identification of specific Chinese air mass tracers" *by* B. Barletta et al.

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We thank the reviewer for taking the time to read and comment on the manuscript. Here is a detailed description of the changes made to the revised paper according to the reviewer's suggestions.

MAIN COMMENT: pollution plumes identification/segregation

The main issue raised by the reviewer is the source region identification of the plumes. We fully agree that pollution plumes originating from source regions close to each other,

such as China and other Asian countries will be diluted and hard to distinguish when intercepted after several days (i.e. 5-7 days). We recognize that plumes #1, #2, and #3 were much diluted with respect to pollution plumes #4 and #5 (and we are now pointing this out in the manuscript as clearly as possible, as discussed later in this document), and the inclusion of these air masses in the more general Asian plume classification, as proposed by the reviewer, is very reasonable. However, we believe that the VOC composition of plumes #1 - #3 is consistent with Chinese emissions, as follows. A figure is here attached showing plots of OCS and CH3Cl (two recognized coal burning tracers) vs ethyne (combustion tracer) for all of the Chinese plumes (all samples aggregated and for the individual plumes), Asian plumes (all samples aggregated and for the individual plumes), and U.S. plumes. Consistent with widespread use of coal in China and the usefulness of CH3Cl and OCS as Chinese tracers, the plots show very good OCS vs C2H2 and CH3Cl vs C2H2 correlations (R2 0.91-0.92) in the Chinese plumes. By contrast, the Asian plumes have low R2 values of 0.17 (OCS vs C2H2) and 0.10 (CH3Cl vs C2H2), and the U.S. plumes have an R2 of 0.01 for both the OCS and CH3Cl vs C2H2 plots. Further, when the individual plumes were separated, the Chinese plumes #1, #2, and #3 (suggested by the reviewer to be included in the Asian plumes) show excellent correlations, with R2 of 0.91, 0.87, and 0.97 for the OCS plot, and 0.96, 0.66, and 0.73 for the CH3Cl plot, which is an additional indication that these plots do belong to the “Chinese” group of samples (by contrast all of the Asian plumes have R2 < 0.5). In the manuscript we are now including a table (Table 2 in the new manuscript) where the coefficient of determination (and slopes) of all the plots here included are reported. This additional discussion is now reported in the last paragraph of section 3.1 of the revised manuscript. In addition to the above, in the new manuscript we further verify our VOC analysis based on the identified pollution plumes, with the principal component analysis (section 3.5). The analysis of the major principal components extracted for the Chinese and U.S. pollution plumes pointed to the presence of sources consistent with Chinese and North American influence. In particular, the main principal component extracted for the Chinese data matrix (accounting for ∼70% of the

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variance) showed high loadings of many anthropogenic emitted trace gases including the Chinese tracers suggested by the VOC data analysis (namely OCS, CH3Cl, 1,2-dichloroethane, ethyl chloride, and Halon-1211). The PCA was also performed on the whole INTEX-B data set, highlighting the impact of urban emissions with high loadings of trace gases associated with strong anthropogenic sources.

Moreover, we now include in new figures (Figure 3 and 5 in the revised manuscript) the path of the back trajectories for the Asian plumes, for plume #4 and 5 (Chinese plumes with highest levels), for U.S. air masses.

In the revised manuscript we also presented pollution plumes #4 and #5 in greater detail and we mostly use the VOC levels measured within these two specific plumes for the overall discussion about VOC characterization in Chinese plumes (last paragraph of section 3.2). We recognize that the mixing ratio difference between the Chinese and Asian plumes is small for many VOCs when all 5 Chinese plumes are considered together, but following the reviewer suggestion, plume #4 and #5 are now discussed separately from the other Chinese plumes highlighting the enhenced levels of many trace gases with respect to the background. The following paragraph has been added at the end of section 3.2 in the revised manuscript:

"Chinese plumes #2 and #3 (and to some extent plume #1) were diluted compared to the other Chinese air masses, and the average mixing ratios for many species were not significantly different than background levels (Table 4). When Chinese plumes #2 and #3 are excluded, the HCFC-134a enhancement is 38 $\pm$ 1 pptv (11% enhancement). Further, when plumes #4 and #5 are considered separately from the other three Chinese air masses, the trace gas mixing ratios show a considerable increase with respect to background levels. For instance, the average OCS and CH3Cl mixing ratios were about 30% higher than background when the 13 samples included in these two plumes were considered (622 $\pm$ 44 pptv for OCS, 687 $\pm$ 53 pptv for CH3Cl). An average Halon-1211 mixing ratio of 4.90 $\pm$ 0.39 pptv was measured in the same plumes (#4 and #5), representing an enhancement over background of 18%. Finally,

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elevated levels of industrial halogenated solvents were also observed in the Chinese air masses. In particular, high enhancements of chloroform (up to 37 pptv average), methylene chloride (up to 135 pptv), and trichloroethene (up to 6.6 pptv) were measured in pollution plume #4."

As suggested by the reviewer, we also decided to keep table 4 with the mixing ratios of the individual Chinese plumes to clearly show the differences among these plumes.

We apologize for the limited information given in the original manuscript on how the pollution plumes were identified. In the new paper, we describe how polluted air masses were segregated from clean tropospheric air and the criteria used to classify polluted air masses as "pollution plumes" (end of first paragraph in section 3.1). In particular, we added the minimum altitude that a trajectory had to follow over a source region (800 hPa pressure level) and we described how the time frame of each pollution event was calculated.

Finally, as mentioned in the reply to reviewer 2, because we fully agree that the identification of the specific geographical source could be complex, we removed the "geographical origin" column from table 1 and only label our pollution plumes as from "China", "Asia", and "U.S.". This will not undermine our discussion and conclusions, but at the same time will make our geographical source identification less specific.

DETAILED COMMENTS

The sentence "The INTEX-B mission. . ..out of Honolulu and Anchorage" has been removed from the introduction.

Text and references to ozone formation, greenhouse and health effects are now reduced. The passage now reads : "Ozone is a recognized greenhouse gas (e.g. Berntsen et al., 1997) and is unhealthful at enhanced concentrations (Bell et al., 2004)".

Page 7755. Table 1: The reviewer is correct in that we had reported a variable transport time in the original manuscript. For instance, the "7-9 days transport time" indicated for

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pollution plume #6 indicated that both 7-day and 9-day back trajectories showed low altitude air masses traveling over Asia. We agree with the reviewer that this can be confusing; therefore, we decided to indicate only the longest traveling time suggested by the back trajectories (i.e. 9 days for plume #6).

Page 7757. Following the suggestion of reviewer #1, Figure 4 was eliminated and the INTEX-A background data (in the new manuscript now calculated with the same criteria used for the INTEX-B background – i.e. average of lowest quartile of the INTEX-A data set) are now listed in Table 3. This will allow the reader to clearly see the background mixing ratio measured for INTEX-A and the background mixing ratios calculated from the present study.

The comparison between the background measured in 2006 (INTEX-B) and 2004 (INTEX-A) now reflects the new background levels calculated for INTEX-A. We agree that the difference in CFC-12 mixing ratios between 2004 and 2006 must be evaluated within a statistical context (CFC-11 remained constant within the statistical error with the new INTEX-A background levels). In Table 3 (Table 2 in the original manuscript) we now show background trace gas mixing ratios (including CFC-12) for INTEX-A and INTEX-B based on the lowest quartile of data. The 25th percentile yielded a reasonable background without limiting too much the number of samples available (third paragraph of section 3.2 of revised manuscript). These give background (1-sigma) CFC-12 mixing ratios of 536 (2) pptv in 2004 and 525 (4) pptv in 2006, corresponding to a $\sim$2% decline that lies outside of the statistical uncertainty. This decline suggests that, although much more limited in size, our data set was able to correctly capture (within the stated uncertainty) long-term trends in this gas. The NOAA global monitoring network also measured a decline in CFC-12 for the same time period (but at a slower rate - 0.5%). A similar decline ($\sim$2%) was observed for CFC-113 as well. These issues have been addressed in the revised manuscript in section 3.2 (third paragraph).

The sentence referring to enhanced CFC replacement compounds in U.S. has been eliminated from the revised manuscript and we now point out that HFC-134a in par-

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ticular shows high levels in the U.S. pollution plumes. The analysis of the HFC-134a enhancement in the Chinese plumes highlights how plumes #1-#3 were, in fact, very diluted giving us the opportunity to begin the analysis of pollution #4 and 5 in greater detail (last paragraph of section 3.2).

p. 7758: The passage "It appears the Chinese plumes #2 and 3 were diluted compared to the other plumes." has been eliminated from the revised manuscript following the reviewer's suggestion to analyze with more detail pollution plumes #4 and #5. The new paragraph added at the end of section 3.2 in the revised manuscript was reported earlier in this document.

We apologize for the confusion. The sentence "Both the Asian and Chinese plumes were elevated in HFC-134a, but with lower enhancements compared to the background" has been reworded as follows: "Both the Asian and Chinese plumes also showed elevated HFC-134a levels, but with lower enhancements than the U.S. air masses: 37 $\pm$ 2 pptv measured in the Asian plumes (8% enhancement) and, 36 $\pm$ 4 pptv in the Chinese air masses ($\sim$6% enhancement)."

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 7747, 2009.

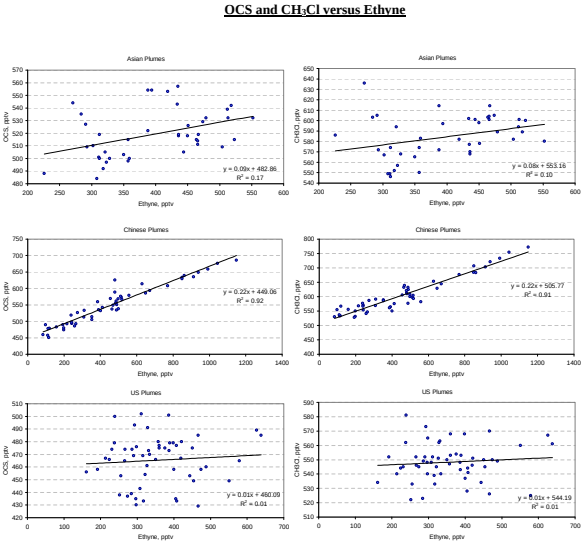

Fig. 1.

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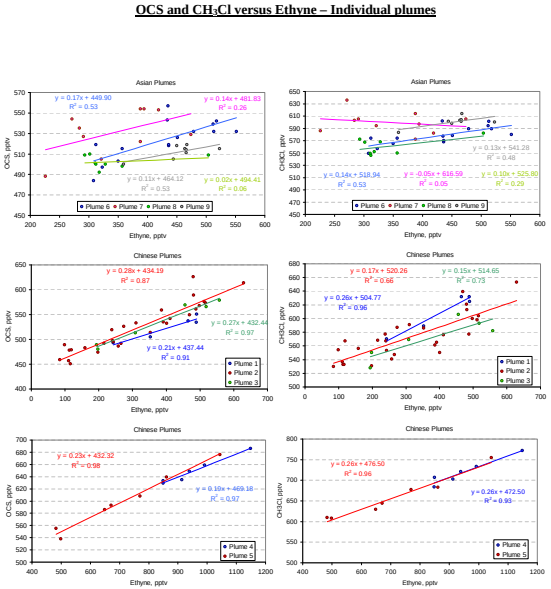

Fig. 2.

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