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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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The authors would like to thank Dr Lewis for taking the time to read our manuscript and for the valuable comments. The manuscript was revised to reflect the reviewer's suggestions, and the detailed list of changes is presented here.

MAIN COMMENTS

Pollution plumes identification; Emission source assignment.

In the paper we have addressed the reviewer's questions about how geographic

sources were assigned to specific plumes (last part of first paragraph in section 3.1 of revised manuscript). Specifically, the trajectories were not calculated for the center time-point of the whole air sample; instead we obtained the specific time frame for each pollution event from the open time of the first and last canister of each episode (we previously identified the different pollution episodes based on enhancements of selected trace gases in at least five consecutively collected canisters). The minimum height above surface that trajectories had to follow was the 800 hPa pressure level, with no restrictions in terms of time spent within the boundary layer. In our opinion, air masses traveling below this altitude were able to capture the VOCs directly emitted from the source regions below and trapped within the boundary layer. Trajectories that had passed over source regions at any other altitude were discarded because of the significant dilution with free tropospheric air. The identification of the specific emission region was performed based on the geographical position (i.e. political boundaries) of the low altitude back-trajectories. We now include back trajectories in two new figures in the revised manuscript: Figure 3 (Asian plumes) and Figure 5 (Chinese and U.S. plumes).

We agree that the identification of the specific geographical source could be complex, therefore, we decided to remove the "geographical origin" column from table 1 and only label our pollution plums 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 more appropriate.

Comment on Page 7754. Both isolated samples and group of consecutively collected canisters with elevated VOC mixing ratios were encountered during the INTEX-B mission. In our analysis we decided to isolate samples that showed elevated mixing ratios in at least five consecutive canisters. Our intent was to isolate samples that could represent "defined" plumes and, hopefully, would offer the opportunity to characterize the VOC signature of plumes originating from different source regions (i.e. Asia-China versus North America plumes). In our opinion, isolated canisters with elevated mixing

ratios (i.e. one canister with high levels collected in between samples with "background" levels) could be the result of a pollution plume briefly encountered during the science flight (for instance, during ascents or descents), or could be due to the presence of isolated emission sources that most likely can not be well characterized in only one sample. For this reason, these isolated enhanced samples were not included in out data analysis.

PCA / Cluster analysis Reviewer 1 suggests the use of the principal component analysis to support our discussion based on VOC mixing ratio analysis. Here it is suggested that the cluster analysis could also be helpful. Because our research group has much more experience with the PCA, we decided to use this technique. We hope this will be acceptable to the second reviewer. We have now added an additional section at the end of the manuscript with the PCA results (section 3.5). Briefly, the PCA performed on the whole INTEX-B data set highlighted the impact of urban emissions with high loadings of trace gases associated with strong anthropogenic sources. 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 $\sim$70% of the 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).

Ethyne/CO ratio discussion The discussion on the ethyne/CO ratio calculated for the different pollution plumes was expanded (third paragraph of section 3.1 of revised manuscript). We found that the spread of ethyne/CO ratios in the five Chinese plumes was explained by a combination of different air mass ages and emission ratios. We now explain in greater detail how this ratio is affected by the aging of the investigated air masses but also by the spread in the emission ratio. In particular, we point out how this ratio has to be used carefully when air masses generated from different source region and influenced by different combustion processes are compared. In particu-

lar, we observed that the atmospheric processing of the air masses was overall well illustrated by the C2H2/CO ratio with the lowest ratio calculated for the stratospherically influenced air, followed by the samples with no pollution plumes, and the pollution plumes showed the highest ratios. However, when the ethyne/CO ratio was calculated for the individual plumes, we found that Chinese plumes #4 and #5 had the highest ratio, while the analysis of the backward trajectories suggested that the U.S. pollution plumes had the shortest transport time (3 days). We highlighted that the emission ratio of ethyne and CO greatly varies between different combustion processes (specific values of C2H2/CO are now reported in the manuscript – second part of third paragraph in section 3.1) but also depending on the specific source region. Therefore, the spread in source emission ratio can most likely explain this discrepancy (Chinese plumes with highest ethyne/CO ratio).

Background We thank the reviewer for this thoughtful comment. In the revised manuscript we decided not to use the background levels for INTEX-A as reported in Liang et al., which only included few gases. Using the same criteria, we calculated the INTEX-A background from the INTEX-A data set, as the average of lowest quartile (now listed in Table 3). In our comparison (third paragraph in section 3.2) we noted how the majority of the gases remained overall constant, with few exceptions (OCS, HFC-134a, HCFC-142b, methylene chloride, methyl chloride, 1,2-dichloroethane, ethane, and ethyne). In the new text we have pointed out how the differences in the sampling season, in the sampling regions, or in the emission strength over time were most likely responsible for the higher levels observed in 2006 during INTEX-B.

Halon-1211 We agree with the reviewer about the lack of significant enhancement in the Chinese plumes (with the exception of a limited number of samples) and we apologize for the lack of clarity in the original manuscript. Hopefully the new version of the manuscript better reflects both the reviewer's comments and our original intention for the Halon-1211 section and the paper, including emphasis on the need for a suite of compounds rather than just Halon-1211 to show origin from China. In particular,

the limited enhancement in the Chinese plumes made us wonder whether Halon-1211 could still be considered one of the most important VOC tracers for Chinese air masses. And yet, our group collected ground levels air samples in the Pearl River Delta region at the same time as INTEX-B which showed elevated Halon-1211 levels. In our opinion, background Halon-1211 levels can be found in China depending on the specific Chinese region investigated. In contrast to our ground-level samples, our INTEX-B samples may not have shown strong Halon-1211 enhancement most likely because of their specific source region and because of possible dilution of the plumes during the 5-7 day interception time by the airplane. Moreover, because of the limitations imposed by the Montreal Protocol, the role of Halon-1211 as a primarily Chinese tracer needs to be reassessed. In the revised manuscript we also include a paragraph discussing the few elevated samples collected within the U.S. plumes with high Halon-1211. Unfortunately the literature on Halon-1211 in US urban areas (actual measurements) is not extensive and we had to use some unpublished data (from a paper in preparation, Beyersdorf et al.) to show how Halon-1211 can be found at levels higher than background in US cities.

MINOR COMMENTS

Figure 8 has been removed.

More appropriate references (Khalil and Rasmussen, 1984, Chin and Davis, 1993, Watts, 2000) are now listed for the OCS biomass/coal burning sources (third line of section 3.4 of revised manuscript).

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