**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "HFC-152a and HFC-134a emission estimates and characterization of CFCs, CFC replacements, and other halogenated solvents measured during the 2008 ARCTAS campaign (CARB phase) over the South Coast Air Basin of California" *by* B. Barletta et al.

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Anonymous Referee #1

The paper by Barletta et al. describes the halocarbon flight-measurements as a part of the ARCTAS project and emission estimates of HFC-152a and HFC-134a in Los Angeles County as well as their extrapolation to the South Coast Air Basin of California (SoCAB) and US. The study presents a new data set concerning halocarbon emissions

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from mega cities, and I think this is publishable in ACP. However, I have some serious concerns about the presentation of the data and its interpretation, which are explained below. I recommend publication after these points have been addressed.

The authors thank the referee for his or her input. All points raised by the referee are addressed below.

1. Values of precision and accuracy for HFC-152a are missing.

The precision and accuracy for HFC-152a now are reported in the experimental section (10% for both parameters).

2. "Chemical ratio" defined in this study is practically the same as the "tracer ratio" which is more widely used for the top-down emission estimates. I think the authors should describe the technique as "tracer ratio". If this is deemed inappropriate, then please describe how "chemical ratio" differs from "tracer ratio".

The name of the method has been changed from "chemical ratio" to "tracer ratio" in the revised manuscript.

3. Please give the error range of the emission estimates from the AQM method. Since the authors conclude that the close agreement between the results from the two methods (tracer ratio method and AQM method) lends credence to the emission estimates presented in this paper, this should be important.

In the AQM method, emissions estimates of HFC-134a and HFC-152a are obtained using six different meteorological fields (six estimates are obtained). In the revised version of the manuscript, the mean and standard deviation of the six estimates are reported (see data in Table 4 and discussion in Section 3.2.2).

4. p.28038 line 7-13 – "Additionally, it is particularly important to assess accurately the atmospheric levels of CH_3CCl_3 because this species is used to estimate global concentrations the hydroxyl radical (OH). Errors in the determination of global OH levels can be significant if emission sources in developed areas are not properly character-

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ized. Millet and Goldstein (2004) calculate that global OH was underestimated by 7.2% for 2000 and 11% for 1997 by neglecting ongoing methyl chloroform emissions by non-Article 5 nations."

I don't understand why the authors state this in the Conclusion section. There is no discussion on CH3CCl3 data beforehand except that the authors found above baseline concentrations of this compound. I therefore think the statement should be deleted.

In consideration of both Referee #1 and #2's comments regarding methyl chloroform, this paragraph has been removed.

5. Please state the reason why only the field measurements obtained over the SoCAB were examined, and the data from the San Joaquin Valley were excluded.

There are two main reasons why the authors focus on the SoCAB:

(1) The authors were concerned about the length of the paper if data gathered over the San Joaquin Valley were included in the manuscript.

(2) The authors want to obtain HFC-134a and HFC-152a emissions estimates through multiple methods (tracer ratio method and AQM method), but only had access to a state-of-the-science air quality model that simulates air pollution formation and transport in the SoCAB, not the San Joaquin Valley.

It is possible that the data gathered over the San Joaquin Valley during the ARCTAS-CARB flights could be analyzed and presented in future publications.

6. p.28024 line 7-10 – "The original standard for the calibration of the NMHCs is gravimetrically prepared from National Bureau of Standards and Scott Specialty Gases standards (accuracy 5%). These standards are used for the calibration of the highly pressurized whole air standards (2000 psi) contained within aluminum cylinders."

I don't know why the authors describe the calibration of NMHCs (non-methane hydrocarbons), in spite that they report the measurements of halocarbons. This should be

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corrected.

The authors have removed the description of the standard calibration for NMHCs and included a description of the standard calibration for halogenated species. The description of the calibration now reads:

"Original standards for HFCs were from Scott-Marrin in the range of 10-300 ppb (nominal). These are checked against a butane/benzene NIST (National Institute of Standards and Technology) standard with an atomic emission detector. Dynamic dilutions of the high concentration standards and injection of variable volumes of these dilutions provided a calibration curve in the range of ambient concentrations. High pressure tanks were prepared by dilution of the high concentration tanks (also from Scott-Marrin). These tanks were used for more frequent comparisons and then also checked against the high concentration tank by dynamic dilution."

7. The authors emphasize the importance of CFC data for policymakers to assess the effectiveness of mitigation strategies. I just wonder why the authors did not try to estimate the emissions of CFCs, but only focused on the two HFCs.

There are a few reasons why this study focuses only on HFC emissions rather than CFC emissions:

(1) The authors want to focus on one class of species for this paper. Future articles may examine HCFCs and CFCs in the same thorough manner as HFCs in this paper.

(2) The authors are concerned about the length of the paper if HCFCs and CFCs were analyzed in the same manner as HFCs in this paper.

(3) The AQM methodology is time-consuming and the authors want to submit the article for consideration in the ARCTAS special edition of ACP before it was too late.

8. As suggested in the manuscript, the extrapolation using population data is likely to be overpredicting. I encourage the authors to consider a different approach using anthropogenic species such as CO, which should have closer relationship with HFCs

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than population. The authors have actually found good correlation between CO and HFC-152a in this study.

In the previous version of the manuscript, the authors obtained estimates of the 2008 HFC-152a and HFC-134a emissions in the LA area using the tracer ratio method. The SoCAB emissions were obtained by extrapolating the LA area emissions using population data (1.25 ± 0.16 and 1.77 ± 0.34 Gg for HFC-152a and HFC-134a, respectively).

It is possible to calculate the 2008 emissions in the SoCAB using the tracer ratio method instead of the population-based method. The HFC:CO ratio is obtained from the samples collected within the SoCAB and the total CO emitted by the SoCAB in 2008 is obtained from the California Air Resources Board (CARB). The resulting emissions estimates (1.60 ± 0.22 and 2.12 ± 0.28 Gg for HFC-152a and HFC-134a, respectively) are within the uncertainties of the two methods. A paragraph comparing the HFC-152a and HFC-134a emissions estimates in the SoCAB using both the tracer ratio method and the population-based method is included in the revised manuscript.

As discussed by Stohl et al. (2009), using population data to extrapolate HFC emissions from a region in the United States (such as the SoCAB) to the entire world likely would result in an overprediction of global HFC emissions because this method does not consider different degrees of industrialization in developing (or less developed) countries. However, it is expected the use of population data to extrapolate HFC emissions from the SoCAB to the entire United States would cause significantly less error since the SoCAB has similar levels of industrialization as other regions of the United States. It should be noted that other authors also have used population data to extrapolate regional halocarbon emissions to the entire US (e.g., Millet and Goldstein, 2004; Li et al., 2005; Stohl et al., 2009).

It is possible to extrapolate the SoCAB emissions to the entire US using the ratio of the total CO emitted in US to the total CO emitted in SoCAB, but this would imply that the HFC:CO ratios in the SoCAB and US are the same. If this assumption is

made, nationwide CO emission estimates for the year 2008 can be obtained from EPA National Emission Inventory by interpolating between the 2005 inventory and the 2009 model predicted inventory (EPA, 2009). Using the estimated value of 212,836 tons day-1 for 2008, the emission rate of HFC-152a and HFC-134a in the US for 2008 were 100 and 132 Gg, which are about a factor of three greater than the population-based estimates and much greater than estimates from all other studies (see Table 4 in the revised manuscript). The reason for this discrepancy likely is due to the assumption that the HFC:CO ratio observed in the SoCAB is representative of the entire nation.

9. I would recommend adding another reference "Yokouchi et al., Geophys. Res. Lett., 2006" where the tracer ratio technique was used to estimate emission of selected halocarbons including HFC-134a and HFC-152a.

The suggested reference is included in the revised manuscript.

References for Referee #1:

Li, J., Cunnold, D. M., Wang, H.-J., Weiss, R. F., Miller, B. R., Harth, C., Salameh, P., and Harris, J. M.: Halocarbon emissions estimated from advanced global atmospheric gases experiment measured pollution events at Trinidad Head, California, J. Geophys. Res., 110, D14308, 2005.

Millet, D. B. and Goldstein, A. H.: Evidence of continuing methylchloroform emissions from the United States, Geophys. Res. Lett., 31, L17101, 2004.

Stohl, A., Seibert, P., Arduini, J., Eckhardt, S., Fraser, P., Greally, B. R., Lunder, C., Maione, M., Muhle, J., O'Doherty, S., Prinn, R. G., Reimann, S., Saito, T., Schmidbauer, N., Simmonds, P. G., Vollmer, M. K., Weiss, R. F., and Yokouchi, Y.: An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, Atmos. Chem. Phys., 9, 1597–1620, 2009.

United States Environmental Protection Agency (EPA), National Emis-

sions Inventory (NEI) Air Pollutant Emissions Trends Data, 2009. <http://www.epa.gov/ttn/chief/trends/index.html>. Accessed on February 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28017, 2010.

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