**Atmospheric
Chemistry
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Discussions**

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Comment

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 #3

This paper describes measurements of a suite of halocarbons over a potentially important urban source region in the US. Though a strength of their approach is the multiple gases measured and unique location sampled, the paper focuses primarily on inferring emissions of two HFCs with two different estimation methods. Though some limitations

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to these methods are discussed, the paper would be improved with a more complete discussion of these limitations. Furthermore, the description and text regarding many different details of the work could be improved.

The authors thank the referee for his or her suggestions. In the revised manuscript, the authors have improved parts of the methodology based on the referees' suggestions and included a more thorough discussion of the study's limitations.

1. On the HFC / CO ratio analysis: Orthogonal (2-sided) regression techniques seem necessary, but aren't mentioned. Were they used to calculate slopes, or were they derived with linear regression techniques that assume zero error in x? What do the errors on the regression slopes represent? Are these propagated directly to the derived emission magnitudes without consideration of any additional uncertainties, such as on the CO emissions? (what do we know about the accuracy of CO emissions for this region, have they been validated somehow?). Furthermore, how about additional errors when emissions are extrapolated to the SoCAB region or the whole of the US? Seasonal and regional variations in emissions are likely present for these HFCs, and though the magnitudes of these influences are difficult to estimate, surely some discussion of them is warranted, particularly with respect to uncertainties (and in addition to the discussion appearing on p. 28031).

In the revised manuscript, the slopes from the HFC vs CO data are calculated using orthogonal regression and the methodology used to determine the uncertainty in HFC-152a and HFC-134a emissions estimates is discussed in detail. The uncertainty in emission estimates is derived from (1) the uncertainties associated with the slope obtained from the orthogonal regression of the HFC vs CO data and (2) the uncertainty in the correction factors used to adjust for seasonal variability.

The total CO emitted by LA County and the SoCAB in 2008 is another potential source of error and should be considered when determining the uncertainty in emissions estimates. Unfortunately, the uncertainty in CO emissions has not been determined by

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the California Air Resources Board (CARB) and cannot be included in the analysis.

The referee is correct that the emissions estimates should account for the seasonal and regional variability of emissions. In the revised manuscript, HFC-152a and HFC-134a emissions are adjusted by examining the seasonal variability in the ΔCFC-11:ΔCO and ΔCFC-12:ΔCO ratios, respectively, as reported in Barnes et al. (2003). HFC-152a is used in applications that formerly used CFC-11, while HFC-134a is used in applications that formerly used CFC-12. The seasonality correction factor from Barnes et al. (2003), which was obtained for the Northeastern US, is adjusted further to account for differences between the Northeastern US and the SoCAB using data from Papasavva et al. (2009). In light of the data from Barnes et al. (2003) and Papasavva et al. (2009), the seasonal variability correction factors for HFC-134a and HFC-152a are 1.2 and 1.1, respectively.

Regional effects (warmer climates having greater leakage rates than colder climates due to higher temperatures and more frequent MAC usage) also may need to be considered, but are difficult to estimate. Papasavva et al. (2009) predicts that the leakage rate (gram per vehicle) of MAC refrigerants from cars in California will be about 4% higher than the national average in 2017. This result suggests that regional effects may not affect estimates of HFC-134a emissions significantly.

The revised manuscript and Supplementary Material discusses seasonality and regionality in greater detail.

2. On the discussion of the discrepancies in HFC-152a emission magnitudes derived in this study compared to previous ones: To make meaningful comparisons uncertainties need to be considered. What were the uncertainties given for US emissions in the Stohl work? Also, it would seem that conclusions drawn before 2004 with respect to the relative importance of the US compared to other nations (Ashford et al., 2004) have a time-dependence and might not be valid today (given the rapid economic growth in China, recessions, etc.). Some previous studies (Millet et al) have even made correc-

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tions on emissions determined in one season based on seasonal emission variations observed in other studies (Barnes et al).

The revised manuscript now includes the uncertainty of HFC-152a and HFC-134a emission estimates from previous studies, if they are available. Additionally, Table 4 now lists emissions estimates from studies discussed in the manuscript for the reader's benefit.

The referee is correct that the relative contribution of HFC-152a emissions from different nations will change over time. The section of the paper discussing the role of the US as the main emitter of HFC-152a now reads,

"It should be noted that the United States generally is regarded as the "largest user" of HFC-152a (Ashford et al., 2004). Although much of the future growth in HFC-152a use is expected to come from East Asia, Stohl et al. (2010) estimates that the contribution of this region to the global emissions of HFC-152a in 2008 was only about 10% ($\sim$7% from China)."

The referee is correct that seasonal and regional variability of emissions should be accounted for when calculating emissions estimates. Please see the response to the previous comment for a more detailed description of how the emissions are adjusted.

3. For HFC-134a, estimates published previously by others are for different years. Are US emissions expected to be changing over time? What do EPA estimates suggest about trends and magnitudes expected for HFC-134a emissions (and, for that matter, HFC-152a)?

The revised manuscript now contains a comment that states the sampling period should be considered when comparing HFC emissions estimates.

The Advanced Global Atmospheric Gases Experiment (AGAGE) database shows that HFC-134a levels have increased steadily for the past decade, while the growth rate in HFC-152a levels has slowed down a little during the past five years (AGAGE, 2011).

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During the next decade, Velders et al. (2009) predicts that annual HFC demand in the US will increase by 7.4% per year.

In California, a large contribution to HFC-134a emissions is from the removal, recovery, and recycling of vehicle refrigerants from end-of-life vehicles (ELVs). During 2000-2008, the percentage of ELVs containing HFC-134a grew at approximately 3% a year and likely will continue to grow in the future (Wimberger, 2010).

A discussion about the current and predicted future trends of HFC-134a and HFC-152a use is included in the revised manuscript.

4. On the AQM approach. The lack of a "complete meteorological data set" for the period of sampling is a serious limitation. Using met fields from other years, and even different months in those different years is problematic, and it is very difficult to assess from the Supplement Tables if the met conditions are similar during those years to 2008 at the 3 sites for which information is given. In fact, the 2008 winds look substantially higher than in the other years at the Santa Ana site. Furthermore, it doesn't seem possible to know if a comparison of met data at 3 sites is sufficient to argue that met conditions were similar during the different periods.

The referee is correct that the lack of a "complete meteorological data set" during the period of sampling is a limitation of the AQM method, and the authors note this limitation in the manuscript. However, the authors believe that the emissions estimates from the AQM method are useful for comparison with the estimates from the tracer ratio method. The concentrations of HFC-134a and HFC-152a are governed primarily by emissions and transport (wind fields). The wind patterns of the sampling period are similar to the wind patterns of the six simulation scenarios (August 27 and 28, 1987 ; September 8 and 9, 1993 ; October 18 and 19, 1995), with a stronger onshore wind during the day and relatively low winds at night.

In the revised manuscript, the authors now include the standard deviation of the emissions estimates using the six wind fields. Additionally, the emissions calculated for

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each simulation are included in Supplementary Table 2. Providing this information will allow readers to view the variability in emissions estimates using different wind fields.

It should be noted that error in meteorological data still would exist even if the authors used June 2008 wind data from a limited number of locations in the SoCAB. There are 80 x 30 x 5 grid cells in the UCI-CIT airshed model and wind velocity would have to be extrapolated for most of these grid cells from data gathered at a relatively small number of locations.

The authors compared wind field data at multiple sites across the SoCAB, but only listed three locations (Long Beach, Hawthorne, Santa Ana) in Supplementary Table 1. The wind patterns of the six simulation wind fields and the June 2008 sampling days are similar for all locations examined.

5. Given the absence of concurrent met data it seems some additional effort on validation is warranted in order to justify retaining this second approach to deriving emissions in this paper. The authors have used a CO emissions inventory for the area in deriving emissions from the ratio method. Why not try to calculate CO mixing ratio enhancements with the 2008 CO emission inventory for the periods that you have met data and compare to those observed during 2008? This should provide some information on whether or not the results from this approach should be retained in the paper: More specifically, such a validation effort seems essential before one can conclude that these emission estimates are credible, despite assertions given on p. 28037.

The authors are not quite sure what the referee is asking for. It sounds like he or she believes that the authors possess a 2008 CO emissions inventory for each grid cell in the UCI-CIT model. This is not the case; the authors only possess CO emissions inventories for each grid cell for 1987, 1993, and 1995, the same years as the meteorological fields. For 2008, CARB provides an estimate of the total CO emissions for the SoCAB, but not an estimate for each grid cell.

The authors understand the referee's concerns about the reliability of the emissions es-

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timates using the AQM method. However, although the authors are not able to validate the model in the manner suggested by the referee, the fact that most field measurements are within a factor of two of the mean concentration predicted in the LA area and SoCAB provides some measure of validation to the model (see Figure 9 and Supplementary Figures 3-5). The authors believe that inclusion of a second, independent method of estimating HFC emissions provides a valuable check to the estimates from the tracer ratio method. The authors have attempted to provide all necessary caveats in the manuscript to allow the reader to decide the usefulness of each method.

Introduction:

6. McCullock, 2001 and McCullock et al., 2003 are not listed in the reference section (these are likely typos).

In the revised manuscript, this typo has been corrected ("McCullock" is changed to "McCulloch").

7. Terminology related to the Montreal Protocol needs some cleaning up. No compounds have had their production totally phased out. There continue to be allotments for critical uses and non-dispersive uses. Uses listed for these chemicals are given in the present tense... this implies that they still are used for these purposes.

In the revised manuscript, the paragraph discussing the Montreal Protocol now reads,

"A phase-out for the production and consumption of CFCs, methyl chloroform (CH_3CCl_3), halons, and carbon tetrachloride (CCl_4) was imposed in developed countries in 1996 (although allotments for critical and non-dispersive uses are allowed), and a global ban was scheduled for 2010 (2015 for CH_3CCl_3; UNEP, 2003). Methyl chloroform was used as an industrial cleaner and degreaser (McCulloch, 2001), halons were used in fire-fighting (Butler et al., 1998), and CCl_4 was a solvent and chemical intermediate for CFC production (Altshuller, 1976; Sturrock et al., 2002)."

8. Throughout the paper, enhancements are mentioned, I presume these are mean

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enhancements (I see that Table 2 includes mean enhancements)? Furthermore, I would expect an enhancement to represent a mixing ratio difference, not a measured mixing ratio.

In the revised manuscript, the term "enhancement" is used more precisely.

9. Were emissions really extrapolated to larger regions based on population density, or was it population?

Population data, rather than population density, is used to extrapolate the emission estimates from the SoCAB to the US. The word "density" has been removed from the manuscript.

10. p. 28021, It seems appropriate to cite previous studies that have also used the "top-down" method here:

Additional references to publications that utilize top-down methods have been added to the manuscript (e.g., Yokouchi et al., 2006; Greally et al., 2007; Millet et al., 2009).

11. p. 28022, The authors write "this work makes an important contribution of the validation and improvement of California emissions inventories..." Yet, with the exception of CO, no bottom-up emissions data are considered... and the accuracy of the CO inventory isn't mentioned. It would seem that validation of an inventory should include comparing the results you get to that (bottom-up) inventory.

The referee is correct and the paragraph has been revised,

"Although previous studies use top-down methods to estimate HFC emissions (Yokouchi et al., 2006; Greally et al., 2007; Millet et al., 2009), report emissions of HFCs (Reimann et al., 2002; Buchmann et al., 2003; Reimann et al., 2004; Maione et al., 2008; Kim et al., 2010) and emissions of regulated CFCs and other halogenated compounds in North America (Hurst et al., 2006; Millet et al., 2009; Barletta et al., 2009), this study is the first time that halocarbons from the SoCAB have been examined and compared to samples obtained from relatively clean inflow air masses. This work

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makes an important contribution to understanding the tropospheric composition of a highly urbanized and industrialized region, such as the SoCAB, through the characterization and quantification of several halogenated species. These halogenated species include selected greenhouse gases that are used extensively in California (i.e., CFC replacement compounds) and species regulated by the Montreal Protocol and subsequent amendments, including CFCs. Accurate knowledge of halocarbon levels in the atmosphere allows policymakers to access the effectiveness of mitigation strategies."

12. p. 28023, if this information is indeed in the Colman et al paper, it doesn't seem necessary to repeat here.

In the revised manuscript, the sentence has been rephrased to state, "The analytical system used in this study is similar to the system described in Colman et al. (2001)."

13. HFC/CO slopes have unusual units. The use of pmol/nmol or 10E-3 seems more appropriate and clearer.

The slope units have been changed to mmol mol-1 in the text, and 1E-3 in Figures 7 and 8.

14. p. 28024, para starting "The original standard..." is unclear and needs improving.

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."

15. Discussion section problems: Para 1. Flight 14 in Figure 1 is not identifiable, though it is called out in the text. I'm not clear why results from this flight don't represent regional background concentrations; perhaps as a result of me not being able to discern the sample locations.

The authors intentionally did not use the term "background" to characterize the inflow samples obtained during Flight 14 (collected 250-450 km off the California coast). Previous studies (Barletta et al., 2009 and references therein) document how polluted air masses emitted from the Asian Continent can be intercepted and transported across the Pacific Ocean. The presence of "non-background" levels in the inflow samples from Flight 14 is indicated by the elevated maximum mixing ratio reported for many species. For example, the range in HFC-152a concentrations in the inflow samples was 5.1-31 ppt.

In the revised manuscript, the locations of the off-shore samples collected during Flight 14 now are clearly indicated in Figure 1. As stated in the figure caption, a red oval encircles the Flight 14 off-shore samples. The authors decided to omit the specific flight path for each flight to limit the length of the paper. The revised manuscript now includes a link to the official website of the ARCTAS campaign for readers interested in the flight paths (http://www.espo.nasa.gov/arctas/). Flight path information also can be found in the ARCTAS overview paper, Jacob et al. (2010).

16. Para 2. It doesn't seem true that the average mixing ratios for ALL compounds in the inflow air was less than the mean measured in the LA and SoCAB area. Measurement precision needs to be considered before these conclusions can be drawn... Perhaps add another column to Table 2? This would seem more useful than the subset of general precisions quoted on p. 28024 (and what is measurement precision for HFC-152a?). The 'differences' for halons and some CFCs appear small enough that they may not be larger than measurement imprecision:

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The referee is correct. In the revised manuscript, the sentence now reads, "As expected, the average mixing ratios for the majority of the halogenated compounds in the inflow air were lower than the average levels measured over the LA area and SoCAB."

The precision and accuracy for HFC-152a (10% for both parameters) is stated in the revised manuscript.

17. Para 4, information about extremely high levels seems more useful if trajectory or even wind direction information was supplied.

The wind speed and wind direction for the set of 8 samples with extremely elevated concentrations are included in the revised manuscript.

18. Figure 6 points are very small and it is difficult to distinguish their color, as is the star indicating downtown LA. Why not include the line distinguishing the LA Basin area in this figure? Perhaps at the least refer to Figure 2 where this region is indicated. What was used to delineate the "LA Basin" area? And the SoCAB area? What justification is given to use LA County CO emissions to apply to LA Basin results? If they are co-located it isn't readily apparent from the maps, please make clearer. Do these distinctions influence the emissions inferred from the ratio method given that LA County CO emissions are used in the ratio-derived emissions?

The "SoCAB points" include the samples filled while the DC-8 airplane was within the SoCAB boundaries, which are indicated in Figures 2, 5, and 6. The "LA points" include all the samples collected within the portion of LA County that lies within the SoCAB boundary. Nine points in the northern section of the LA County are excluded from the LA points because of the poor sampling coverage of that area (only four samples had a CO concentration greater than 100 ppb). However, these nine samples are included in the SoCAB points.

In the revised manuscript, Figures 6a and 6c have been moved from the main text to the Supplementary material. Figures 6b and 6d have been enlarged allowing the

reader to view the data more clearly. As a result of these changes, the caption for Figure 6 now reads:

"Figure 6. Mixing ratios (in ppt) of (a) HFC-152a and (b) HFC-134a measured over the SoCAB (boundary indicated by the solid gray line). The samples included within the red dotted line are the data points used to calculate emissions from LA County. Downtown Los Angeles is indicated by the red star."

In the original manuscript, HFC emissions in the SoCAB are estimated by extrapolating the estimates from the LA area using population data. In the revised manuscript, HFC emissions from the SoCAB also are calculated using the tracer ratio method. In the tracer ratio method, the HFC:CO ratio is determined from field measurements over the SoCAB and this value is multiplied by the amount of CO emitted in the SoCAB in 2008 (available from the CARB inventory).

HFC emissions estimates obtained using the tracer ratio method and population-based method are compared in the revised manuscript. There is good agreement in the emissions estimates predicted by the two methods. For the tracer ratio method, the HFC-152a and HFC-134a emissions are 1.60 ± 0.22 Gg and 2.12 ± 0.28 Gg, respectively. For the population-based method, the HFC-152a and HFC-134a emissions are 1.25 ± 0.16 Gg and 1.77 ± 0.34 Gg, respectively.

19. Aren't mobile air conditioners the known dominant use of HFC-134a? Not that they "may contribute significantly to HFC-134a emissions"?

The referee is correct. Mobile air-conditioner (MAC) systems are the largest and most emissive sales market for HFC-134a (Papasavva et al., 2009). Approximately half of the annual consumption of HFC-134a is for the manufacture and service of MAC systems (Velders et al., 2009). This information is included in the revised manuscript.

20. Requirements to apply the "ratio" method don't seem quite right. Isn't it that the emissions should be co-located and the lifetimes should be long relative to transport?

This would lead to strong correlations...

The referee is correct. In the revised manuscript, the sentence discussing the tracer ratio method now reads,

"The validity of the tracer ratio method relies on three main assumptions: (1) the HFC and CO sources are co-located, (2) the emission rate of one of the two species is well-known (CO in this case), and (3) the chemical compounds have a lifetime longer than the typical transport time, which is true for CO (lifetime $\sim$ two months), HFC-152a ($\sim$ 1.5 yr), and HFC-134a ($\sim$ 14 yr) (Forster et al., 2007)."

21. It is stated that lower-mixing ratio data were excluded from Figures 7 and 8. On what basis were they excluded? The magnitude of analytical precision around some background? Does including these points change the slope? Including them seems to involve fewer assumptions. Perhaps these data should at least appear in these figures as different symbols?

Statistical outliers (> 98 percentile) and samples with a CO mixing ratio lower than 100 ppb are excluded from Figures 7 and 8. The 100 ppb threshold is the average CO mixing ratio of the inflow samples (discussed in Section 3.1).

In the figure here attached, all HFC-152a and CO data are plotted against each other. The unfilled dots are data points where CO < 100 ppb. The HFC:CO slope of these data points is much flatter than the HFC:CO slope of the data points where CO > 100 ppb. The authors believe that the CO < 100 ppb data points represent cleaner ocean air entering the SoCAB prior to mixing with HFC emissions and should not be included in the tracer ratio analysis.

22. Model description: what happens at the boundaries to the model? Is there no means for emissions to escape the model domain? It is not clear how emissions are distributed between the different urban cells of the model domain, on the basis of population density, or evenly by area?

The concentrations of HFC-152a and HFC-134a at the boundaries of the model domain are the same as the inflow concentrations (9 ppt for HFC-152a and 46 ppt for HFC-134a). As winds blow across the domain, "clean" air (at inflow concentrations) enters the domain while "polluted" air (at elevated concentrations due to emissions and transport) is removed downwind. During most of the simulations, clean air enters from the western edge of the domain and polluted air leaves through the eastern edge of the domain.

In the UCI-CIT model, cells are labeled as "urban" or "rural," with various subcategories within the two groups. For the simulations in this study, it is assumed that emissions from all urban cells are the same at all hours of the day. As mentioned on page 28037, "In the simulations, it was assumed that the HFC emission rates were constant for all urban cells at all times. The true emission rates are not constant in time and may vary significantly among urban cells. This constant emission rate assumption was made to compare emissions determined from the AQM method to emissions determined by the tracer ratio method, which uses the 24-h average CO emission rate in LA County. Both methods assume a constant emission rate during all hours of the day."

Additional information regarding the simulations has been added to the paragraph in question. This paragraph now reads:

"The UCI-CIT model spins up for five simulation days allowing the system to reach a steady diurnal cycle. The data presented here are from the last simulation day. In the simulations, it is assumed that HFC-152a and HFC-134a are emitted evenly across all urban cells at a constant rate every hour, while emissions from rural cells are zero. Separate sets of simulations were conducted to determine the emission rates in the LA area and SoCAB. As in the tracer method, simulation results from the LA area were extrapolated to LA County. The inflow concentrations for HFC-152a (9 pptv) and HFC-134a (46 pptv) were obtained from field measurements over the Pacific Ocean. As winds blow across the domain, "clean" air (at inflow concentrations) enters the domain while "polluted" air (at elevated concentrations due to emissions and

transport) is removed downwind. During most of the simulations, clean air enters from the western edge of the domain and polluted air leaves through the eastern edge of the domain."

23. Some of the straightforward technical details and formulas related to deriving weighted average emissions owing to changes in pressure and the ideal gas law, etc., seem more appropriate for the Supplement (e.g., much of the information on p. 28033 and the first part of p. 28034).

In the revised manuscript, some of the formulas related to the AQM method have been moved to the Supplementary Material.

24. The first paragraph of the conclusions is introductory material; no conclusions from this work are given in it. Furthermore, the information isn't relevant to the main points made in the paper.

In the revised manuscript, this paragraph has been moved to the Introduction.

25. The last sentence of the conclusion section also is out of place. I can't think of any results given in the paper that allow for this comment.

In the revised manuscript, the last sentence of the Conclusions section was removed.

26. The title of the McCulloch, Midgley, and Ashford paper is incorrect in the reference section.

This error has been corrected in the revised manuscript.

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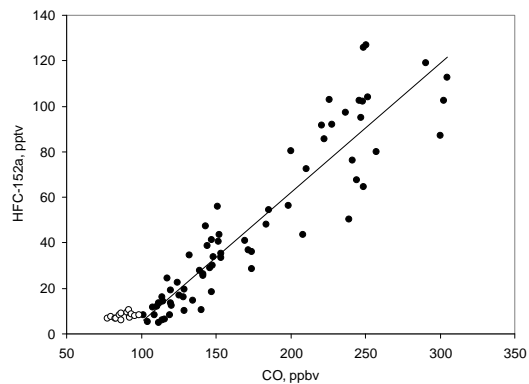**Fig. 1.** Figure: HFC-152a (ppt) and CO (ppb) measurements over the SoCAB. The unfilled circles are samples where CO < 100 ppb, while the filled circles are samples where CO > 100 ppb