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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.

**Anonymous Referee #2**

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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 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.

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).

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 economoic growth in China, recessions, etc.). Some previous studies (Millet et al) have even made corrections on emissions determined in one season based on seasonal emission variations observed in other studies (Barnes et al).

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)?

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



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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.

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.

Many details of the paper need improving... see below.

Introduction

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

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.

Other terminology issues:

*Throughout the paper, enhancements are mentioned, I presume these are mean enhancements (I see that Table 2 includes mean enhancements)? Furthermore, I would



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expect an enhancement to represent a mixing ratio difference, not a measured mixing ratio.

*were emissions really extrapolated to larger regions based on population density, or was it population?

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

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.

Experimental section

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

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

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

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...

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



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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. . .

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

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?

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

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...

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?

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 den-



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sity, or evenly by area?

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).

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.

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.

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

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



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Interactive Comment