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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 #3

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This work presents measurement results of halogenated ozone-depleting compounds and greenhouse gases based on aircraft sampling platforms. The results are used to deduce emission estimates for the study area and to scale this to larger regions, to the South Coast Air Basin of California (SoCAB), and to the entire US. This study provides some important information on emissions from urban regions, in particular from one of the larger emission centers on a global scale. Such 'top-down' emission estimates (based on atmospheric observations) are important tools to validate 'bottom-

up' estimates, which are based on instdustry information and coupled with release functions. The manuscript is prepared carefully and structured clearly. The number of figures and tables is adequate. I recommend publication after revision with the following major and minor comments

Major Comments:

The authors explain the spatial variability in their HFC-152a and HFC-134a measurements in the LA and SoCAB area with localized point sources. For HFC-152a the authors bring shredding facilitias into play as a possible source of HFC-152a and release of HFC-134a from accidents and dismantling lots. These possibilities seem very unlikely as pointed out further below. Is there a possibility that the enhanced concentrations simply stem from the variable loading due to enhanced mean residence times of the polluted air masses over the area, and that the emission fluxes over the area are actually relatively homogeneous? Could the authors offer a way to test such hypothesis?

If the many high-concentration samples had indeed derived from localized point sources, they would most likely not fit that nicely on the HFC-CO relationship plots. In fact, one of the fundamental assumptions, the co-location of the sources of the HFC and CO would clearly be violated and put this approach into question. How well do the large concentrations of HFC-152a agree with those of HFC-134a? They shouldn't, if the sources were local, unless shredders and car dismantling plants were co-located. In fact, as long as HFC-152a has not been used in MAC, a large concentration in one of the two compounds should certainly not be accompanied by a large concentration in the other. As far as the shredder hypothesis is concerned, there are a number of reasons why this seems to be unlikely to be a major source. HFC-152a is typically built into window foaming and used as an aerosol spray, and to my knowledge, its use as insulator in portable appliances is minor (e.g. new refrigerators). Also most appliances that are now shredded in the industrialized world are still dominated by CFC and HCFC foam blowing. Ultimately, shredders in industrialized countries are typically based on

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advanced technology, for example for refrigerator recycling (still with mostly CFCs) the refrigerant is carefully removed and the CFCs from shredded foam is trapped under sub-ambient pressure systems. It appears unlikely that a shredding plant would stick out as a large source in a such densely populated area with a general large release of anthropogenic substances.

Seasonality and regional effects in emissions. The authors hypothesize that the investigated regions in other studies may not be representative and hence leading to the differing emission in this study compared to others for the US. The authors should discuss the possibility of their own estimates not being representative. This could be due to seasonality of the emissions, in particular HFC-134a, with enhanced emissions during warmer periods. For this, the publication by S. Papasavva et al., 2009 Environ. Sci. Technol., 43, 9252-9259) may be of help, even though the substance discussed there is the potential successor of HFC-134a (HFC-1234yf). There could also be regionality within the US given that individual states have largely differing climate schemes, presumably with northern (colder) states having different emissions compared to southern (warmer) states.

The extrapolation of global HFC-152a abundances and emissions may have to be revisited possibly using NOAA/AGAGE data from data submission centres. HFC-152a has undergone significant slow-down in atmospheric growth over the past decade.

Minor Comments:

General comment throughout paper: usage of pptv instead of ppt. Suggest to use ppt only, in this context, the 'v' is not necessary. If you decide to keep the 'v' you should prove that the gases in discussion behave as ideal gases.

The first time a compound is mentioned (separately in abstract and text), its chemical formula or its chemical name should also be listed. E.g. p. 10, para 2, l. 8: 'halon-2402'. Check entired manuscript for this.

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Abstract: The mentioning of CFC-11 and CFC-12 enhancement in the abstract is strange given that these substances are no further discussed in the main text. Since the paper focusses on HFC-152a and HFC-134a, why not describe the enhancements (above background) for these two compounds?

Abstract and first-time mentioning in main text. The chemical names and formula should also be mentioned the first time HFC-152a and HFC-134a are mentioned in the abstract and in the main text (e.g. for HFC-152a: 1,1-difluoroethane, CH3CHF2)

Abstract, last sentence. Could a quantitative comparison been given instead of the 'agree well' statement?

p. 2, para 1, l. 2: 'McCullock' reference. This should probably read 'McCulloch' (c instead of k). This error appears at various places in the manuscript, but not in the reference list, suggesting that the authors are not using an automated referencing tool. The authors should therefore carefully re-check their citations and references.

p. 2, para 2, l. 4: suggest to change '... considered a transitional species ...' to '... considered transitional species'.

p. 3, para 1, l. 7: Suggest to reverse 'mainly is'.

p. 4, para 1, l. 1: Suggest to change '... by California ...' to '... by the California ...'

p. 4, para 2, l. 8: Suggest to change '... on other sides ...' to '... on the other sides ...'

p. 5, para 1, l. 5: CO should be spelled out the first time used in the abstract and main text.

p. 5, para 1, l. 7: suggest to change '... then are ...' to '... are then ...'

p. 6, para 2. It should say somewhere early in this paragraph, that gas chromatographs (GCs) are used, best to mentioned where the columns are mentioned.

p. 6: Could the authors mention how many replicate measurements are done on a

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single sample? Does this depend on the detector (GC vs MS)?

p. 7, para 2: The use of the words 'precision' and 'accuracy' is confusing. Accuracy of a measurement includes the uncertainty of the calibration scale (and the measurement precision plus some other uncertainties), so how can the measurement accuracy (e.g. 2% for CFCs) be smaller than the accuracy of the standards (5%)? Is it correct that the authors mean these halogenated compounds when mentioning 'NMHCs'? It may be clearer to change the naming. Also, if the authors stay with the expression 'NMHC', this needs to be spelled out the first time mentioned.

p. 7, para 3, l. 2: Are the standards provided by the National Bureau of Standards also in the ppt range like the air samples. If not, it should be explained how this is dealt with, and how potential nonlinear effects are avoided. Is the naming 'National Bureau of Standards' correct, is this an US institution (it is not NIST, correct?).

p. 7, para 3, l. 7. 'A higher degree of stability ...' compared to what? Compared to not storing in pontoon, or compared to other substances? Please specify.

p. 7, para 4, l. 1: Suggest to replace 'Carbon monoxide levels were measured ...' by 'CO was measured ...'.

p. 9, para 2, l. 2: Suggest to use plural (concentrations, were)

p. 9, para 2, l. 3: 'far'. Could you give a quantitative estimate instead of 'far', e.g. ∼xx km offshore

p. 9, para 2, l. 11: Plural for 'Figure' (Figures 4b and 4C)

p. 11, para 1, l. 1: latitude and longitude numbers need units (degree N or S, degree E or W). Check entire manuscript and Tables and Figures for this (e.g. Figures 1, 2, 5, 6 need units on their x and y axes).

p. 14, para 1, l. 2, and Figures 7 and 8: Explain how regression was done. This should be an orthogonal regression (i.e. minimize with respect to both x and y) and take into

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account the (presumably different) uncertainties in x and y.

p. 14, para 1, l. 6/7: it is not necessary to list 2 numbers, either use the tons/day or the grams/day, but not both.

p. 14, para 1, l. 8: Uncertainty of 0.05 Gg etc. What do these include? They look very small, it is difficult to believe that these are the overall uncertainties on these emission estimates. If these are the uncertainties in the regression, then it should be clearly stated. Also, these numbers also appear in the abstract and may have to be revised accordingly, because in the context of the abstract, there should be a mentioning of the overall uncertainties. Also, can you assign an uncertainty on the CO emissions?

p. 14, para 2, l. 1: Suggest to change '... assuming ...' to '... assuming that ...'

p. 14, para 2: Again, one would expect some regional differences in the emissions of these HFCs within the USA also due to different usage/climate pattern.

p. 15, para 1: Could you compare your results with bottom-up estimates for these compounds, e.g. from UNFCCC, from the EPA, or from Ashford et al (by using some methods to extract the US emissions)?

p. 16, para 4, l. 1: Suggest to use plural (concentrations, ..., were ...)

Figure 6, caption: Suggest to replace 'indicated' by 'indicates'. Also, spell out 'LA'.

Figure 7: In my printed version, there is a fine horizontal dashed line at 20 ppt. Explain what this line means (or remove if not necessary). Similar lines appear in Figure 8. Suggest to remove these. I suggest to change the units of the slopes to pmol/nmol, or leave them out alltogether and add a 10 E-3.

Table 4: This table would greatly benefit if the results of other studies were listed for comparison.

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