Atmos. Chem. Phys. Discuss., 10, C13879–C13892, 2011
www.atmos-chem-phys-discuss.net/10/C13879/2011/

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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Received and published: 21 February 2011

Anonymous Referee #2

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 industry 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.

The authors thank the referee for his or her suggestions. All suggestions and comments raised by the referee are addressed below.

Major Comments:

1. 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 facilities 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?

Upon further deliberation, the authors agree with the referee that the build-up of pollutants likely is due to meteorology and not localized point sources. These two possibilities are discussed in greater detail in the next comment.

2. 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

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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 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.

The referee is correct that most of the spatial variability of HFC levels likely is due to meteorology and not due to localized point sources for the following reasons:

(1) Both HFC-152a and HFC-134a levels often are elevated at the same time. This could occur if the HFC-152a and HFC-134a point sources were co-located or if the two species are emitted more evenly across the SoCAB and influenced by the same wind patterns. It is unlikely that the HFC points sources would be co-located, leaving wind patterns to explain most of the variability in HFC levels.

(2) The ethyne:CO ratios measured in the SoCAB during this study are indicative of aged air masses. Therefore, it is possible that pollutants, such as HFC-152a and HFC-134a, accumulated in the SoCAB due to due to variable wind patterns.

In the revised manuscript, the following paragraph is added:

“There is considerable spatial variability of HFC concentrations across the SoCAB. However, elevated levels of both HFC-152a and HFC-134a often are observed simul-

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taneously (coefficient of determination of 0.84 in the SoCAB). Therefore, the spatial variability likely is not due to localized point sources since emissions by point sources would selectively enhance only one species. Instead, the presence of stagnant air around the sampling area may be the cause of the observed build-up in trace gases. Air stagnation events in the US are most prevalent in the southern states and during the summertime when the winds are weaker (Wang and Angell, 1999). The wind speed was 4 ± 3 m s-1 during the time the LA area samples were collected.

It is possible to gain insight into the degree of stagnation and atmospheric processing of an air mass by examining the ratio of hydrocarbon species with common emission sources but different atmospheric lifetimes (Parrish et al., 2007 and references therein). The ethyne:CO ratio is of particular interest because combustion is the main emission source for both species and their removal from the troposphere is controlled primarily by reaction with hydroxyl radicals (OH), with a faster removal rate for ethyne (lifetime of about two-three weeks; Xiao et al., 2007) than CO (lifetime of about two months; Logan et al., 1981). Typically, these two trace gases are strongly correlated and the ethyne:CO ratio decreases with time due to the faster removal rate of ethyne. A ratio of about 9 ppt ppb-1 has been observed for air masses less than one day old (Talbot et al., 2003), while lower ratios have been observed for highly aged air masses (< 1 ppt ppb-1; Barletta et al., 2009). The SoCAB is a coastal area receiving highly aged air masses from Asia due to the long transport time required to cross the Pacific Ocean. The average ethyne:CO ratio in the 60 inflow air samples was quite low, 0.8 ± 0.5 ppt ppb-1. In order to examine the ethyne:CO ratio in samples that have been influenced by emissions from the SoCAB, only samples with a CO levels higher than the average mixing ratio measured for the inflow samples (100 ppb) are selected for analysis. After removing samples with [CO] < 100 ppb, the average ethyne:CO ratio in the SoCAB samples was 2.2 ± 1.2 ppt ppb-1, suggesting that the air masses investigated in our study were subject to atmospheric processing before being sampled. Therefore, it is possible that pollutants, such as HFC-152a and HFC-134a, can accumulate in localized areas due to due to variable wind patterns.

The main uses of HFC-152a and HFC-134a support the idea that emissions are spread more evenly across the SoCAB. HFC-152a is used widely as an aerosol propellant in many commercial products. Mobile air-conditioner (MAC) systems are the largest and most emissive sales market for HFC-134a (Papasavva et al., 2009). The HFC-134a leakage rate from MAC systems increases during the summer when MAC units are used more frequently. Significant amounts of the refrigerant can be lost during a vehicle's lifetime; Wimberger (2010) took HFC-134a samples from vehicles on dismantler lots in California and found that on average only 27% of the initial HFC-134a remained in the MAC system before dismantlement."

3. 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 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.

4. 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.

The authors only extrapolate to the US in this study.

Minor Comments:

5. 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 authors changed the “pptv” notation to “ppt” throughout the manuscript and added the following sentence to the Table 2 caption: “Data in parts per trillion by volume, unless otherwise specified (indicated as “ppt” throughout the paper).”

6. 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 entire manuscript for this.

In the revised manuscript, a chemical compound's name and formula is listed the first time the compound is mentioned.

7. 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?

The CFC-11 and CFC-12 enhancement findings have been removed from the abstract.

8. 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)

The chemical names and formulas for HFC-152a and HFC-134a have been added to the abstract and introduction.

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

In the revised manuscript, the last sentence in the abstract states the difference in HFC emissions estimates obtained using the tracer ratio method and AQM method. The sentence now reads, "Emissions estimates obtained using both methods differ by less than 25% for the LA County and less than 45% for the SoCAB."

10. 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.

This typo has been fixed in the revised manuscript.

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

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The phrase has been changed to, “are considered to be a transitional species” in the revised manuscript.

12. p. 3, para 1, l. 7: Suggest to reverse ‘mainly is’.

The sentence now reads, “HFC-152a is used mainly as a foam-blowing agent and in aerosol spray applications, and is a possible alternative to HFC-134a in car air-conditioning systems due to its lower GWP.”

13. p. 4, para 1, l. 1: Suggest to change ‘... by California ...’ to ‘... by the California ...’

This change has been incorporated into the revised manuscript.

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

This change has been incorporated into the revised manuscript.

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

Carbon monoxide now is spelled out in the abstract and introduction the first time it is mentioned.

16. p. 5, para 1, l. 7: suggest to change ‘... then are ...’ to ‘... are then ...’

This change has been incorporated into the revised manuscript.

17. 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.

This sentence has been changed to, “The sample is heated to approximately 80ïĆřC and split into six different column/detector combinations housed in three gas chromatographs (GCs) using UHP helium as the carrier gas. . .”

18. p. 6: Could the authors mention how many replicate measurements are done on a single sample? Does this depend on the detector (GC vs MS)?

There were no replicate measurements for individual samples. A working standard was analyzed every 8 samples and absolute standards were analyzed once a day.

19. 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.

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.”

20. 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?).

In the revised manuscript, the paragraph describing the calibration of the samples has been rewritten (see the reply to the previous comment).

21. 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.

In the revised manuscript, the sentence describing the stability of certain species inside the electropolished stainless steel pontoon reads, “A higher degree of stability inside the electropolished stainless steel pontoon compared to storage in an aluminum cylinder has been determined for higher molecular weight hydrocarbons, alkyl nitrate, sulfur species and some of the halocarbons.”

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

This change has been incorporated into the revised manuscript.

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

This change has been incorporated into the revised manuscript.

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

The distance between the coastline and the location of the inflow measurements is provided in the revised manuscript. The sentence discussing the inflow samples reads, “. . .the inflow concentrations of halocarbon species were determined from a set of 60 air samples collected about 250-450 km offshore during Flight 14 along a south to north leg over the Pacific Ocean (Figure 1).”

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

This change has been incorporated into the revised manuscript.

26. 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).

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In the revised manuscript, latitude and longitude coordinates in Figures and throughout the text are reported as “Latitude N” and “Longitude W.”

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

In the revised version of the manuscript, an orthogonal regression on the experimental data to determine the HFC:CO slope is presented. The HFC:CO slopes calculated from orthogonal regression (minimizes the squared residuals in both the x- and y-directions) are similar to the slopes calculated from simple linear regression (minimizes the squared residuals in the y-direction).

28. 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.

In the revised manuscript, the amount of CO emitted from the SoCAB is expressed as g day-1.

29. 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?

The revised methodology used to determine the uncertainty in HFC-152a and HFC-134a emission estimates is discussed in the revised manuscript. Now, the uncertainty 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 the California Air Resources Board and cannot be included in the analysis.

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

This change has been incorporated into the revised manuscript.

31. 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.

The referee is correct that the HFC-152a and HFC-134a emissions estimates should account for the seasonal and regional variability of emissions. As discussed in an earlier comment, seasonality correction factors for HFC-152a and HFC-134a emissions are obtained from Barnes et al. (2003) and adjusted using the findings of Papasavva et al. (2009). Regionality correction factors are more difficult to determine, but analysis of the data from Papasavva et al. (2009) suggests that regional effects may not affect the US emissions estimates calculated in this study greatly.

A detailed description on how these adjustment factors are calculated is included in the Supplementary Material.

32. 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)?

Such a comparison would be interesting, but to the authors' knowledge bottom-up estimates are not available for HFC-152a and HFC-134a in the SoCAB or the US.

The implementation of methods to extract US emissions from global estimates, such as those obtained by Ashford et al. (2004), is beyond the intentions and expertise of the authors. In this study, the authors focus on how experimental measurements from an extensive airborne study, such as ARCTAS, can be used to derive regional emissions

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estimates using both the tracer ratio method and AQM method.

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

This change has been incorporated into the revised manuscript.

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

These changes have been incorporated into the revised manuscript.

35. 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.

These changes have been incorporated into the revised manuscript.

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

In the revised manuscript, Table 4 has been updated to include the data on HFC-152a and HFC-134a emissions estimates from the studies discussed in the manuscript.

References for Referee #2:

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