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Interactive comment on “Increasing concentrations of dichloromethane, CH₂Cl₂, inferred from CARIBIC air samples collected 1998–2012” by E. C. Leedham Elvidge et al.

Anonymous Referee #1

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Review of: Increasing concentrations of dichloromethane, CH₂Cl₂, inferred from CARIBIC air samples collected 1998–2012 E. C. Leedham Elvidge, D. E. Oram, J. C. Laube, A. K. Baker, S. A. Montzka, S. Humphrey, D. A. O’Sullivan, and C. A. M. Brenninkmeijer

This paper presents discrete CH₂Cl₂ measurements from 1998–2012 collected at 10–12 km altitude. The paper suggests that CH₂Cl₂ levels have increased in the northern hemisphere over this time, possibly related to increased HFC-32 production. Regional

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emissions from the Indian subcontinent were also calculated and suggested to have increased.

While the paper uses a fine data set from the CARIBIC campaign, the analysis often stretches beyond what the sample size and variability of the data allow, especially when trying to calculate long-term trends at the regional level. For example long-term CH₂Cl₂ trends in Africa are attempted based on a sample size of as little as 3 at the beginning of the time series. Data time series need to be shown for each region so the reader can see the gaps in the data relative to the seasonality. The method used to calculate annual averages also needs to be clarified. Some conclusions are speculative and need to be clearly demonstrated, and several comparisons with the literature need to take into account factors such as seasonality and altitude. Overall the paper needs to be reworked within the limits caused by sample size, seasonality and spatial variability. In some cases it will not be possible to calculate a robust long-term trend. Specific comments are given below.

Page 20722: 1) L2-5: These sentences need references and are likely better placed in the Introduction. 2) L6: CH₂Cl₂ is a fairly minor contributor to overall stratospheric ozone depletion. Elsewhere in the text please provide specifics on the importance of CH₂Cl₂ relative to the other ozone depleting substances. 3) L8: The Simmonds et al. paper from 2006 reported CH₂Cl₂, C₂HCl₃ and C₂Cl₄. Did CARIBIC also measure other short-lived chlorinated compounds? Just curious why the focus here is limited to CH₂Cl₂. 4) L13: Global monitoring networks monitor CH₂Cl₂ at the Earth's surface. Is the CARIBIC time series being called 'unique' because it is collected at high altitude? 5) L16: The impact of seasonality on the long-term increase estimates needs to be presented. 6) L20: Likewise the possible impact of interannual variability on the long-term increase estimates needs to be discussed.

Page 20723: 1) L2: Provide a reference for the 90% industrial origin. Simmonds et al. (2006) suggested that ~70% of CH₂Cl₂ emissions were anthropogenic. 2) L5: Simmonds et al. used 10% to force their model to better fit Mace Head and Cape Grim

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observations, and they also tested 30% from natural sources. Please revise the text to reflect the uncertainty in natural sources. 3) L14: Specify that this is a ratio for the lower troposphere. 4) L16-17: Please provide a reference. This sentence can probably be combined with L22-24. 5) L16: The opening sentence of this paragraph is about trends; expand the discussion of trends for the SH, for example by folding in the trends reported at Cape Grim by Simmonds et al.

Page 20724: 1) L2-3: Provide some of this discussion here. For example cite the long-term downward trend at Mace Head from 1998-2004 reported by Simmonds et al. 2) L4-8: This discussion needs to be more quantitative. The contribution of short-lived chlorocarbons to stratospheric ozone depletion is minor, even considering the declining concentrations in long-lived halocarbons. Quantify the percent contribution of CH₂Cl₂ to ozone depletion relative to the other compounds. 3) L8-10: Please provide a reference. 4) L10: Provide a reference for the predominantly natural origin of CHCl₃. 5) L12: Be careful about citing a growth rate (8%) based on one year of change . . . a one-year growth rate isn't too meaningful without understanding year-to-year fluctuations in concentration, especially for a short-lived compound. This also contrasts with the NH declines presented in the previous paragraph. Try to synthesize the trends in CH₂Cl₂. For example the 1990 peak, decline till the mid-2000s, and apparent increase in recent years could be presented together in the same paragraph. 6) L15: The statement that CHCl₃ has 7% natural origin contradicts line 10, which said that CHCl₃ is primarily of natural origin. Also the Worton paper discusses a time-varying anthropogenic contribution to CHCl₃, peaking in 1990. In general the introduction needs tightening; often the same idea is presented several sentences apart. 7) L18-19: Please define EU and provide a reference to the regulations. Also according to the IARC CH₂Cl₂ is only a possible carcinogen; please clarify the text. 8) L20: General comment: The importance of CH₂Cl₂ needs to be put into perspective. CH₂Cl₂ is only a minor contributor to ozone depletion, a possible carcinogen, and its ambient concentration falls far below its permissible short-term exposure limit (12.5 ppm in 8 hours).

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Page 20725: 1) L4: Please provide basic information about this phase, including the total number of whole air samples that were collected. Also reference Figure 1 here. 2) L13: There are 28 samples/flight. Please state the typical interval between samples. Also change the semi-colon to a comma.

Page 20726: 1) L9: Change ‘to allow for’ to ‘to allow correction for’ or something similar. 2) L22: Change the comma to a period.

Page 20727: 1) L12: If the precision of the V.G. Autospec is better, why was it replaced by the Entech system? 2) L14-22: This paragraph is confusing. The V.G. Autospec was replaced by the Entech system, but now there is a Waters Autospec that is the direct replacement of the V.G. Autospec. Are there now two instruments, the Entech and the Waters Autospec? If the Waters Autospec system has higher precision, why is the Entech system being used? Also while comparison data have been presented (e.g. +/- 1 ppt agreement) please state the detection limit, precision and accuracy for each of the three instruments so their capabilities can be directly compared. (I see precision is included later on P20728; present it here or refer the reader to below.) 3) L29: Much of the analytical detail on P20726 (column details, temperature programs, etc.) could also be moved to the Supplementary Material.

Page 20728: 1) L1-10: This paragraph could be tightened. 2) L8: ‘compare well’ and ‘no apparent offset or change’ is too vague. 3) L16-18: The stated precisions have too many significant figures. 4) L19: As well as precision, detection limit and accuracy need to be stated. 5) L21-29: This paragraph could be tightened, with less qualitative description and some examples of the seasonal ozone thresholds that were used.

Page 20729: 1) L3: Without some indication of the O₃ thresholds that were used the reader can’t assess whether the 6-40% rejection is based on conservative estimates of stratospheric air. 2) L5: Please state the total number of non-stratospheric samples that were kept and how the number varied from year to year. Does Figure 1 show all the samples that were collected or just the non-stratospheric samples? 3) L6: Tell the

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reader the purpose of the CO measurements. Why only South Africa and India? 4) L6: The verb tense is changing from past to present; past is more appropriate. 5) L6-8: The availability of CO measurements was given on P20725 L18-19. Why does P20725 reference Brenninkmeijer et al. (2007) for CARIBIC2 while here it's Scharffe et al. (2012)? 6) L10: There is no need to abbreviate 'integrated' as 'int.' 7) L12: Change the comma to a period or semi-colon. 8) L20: 'a substantial portion' is likely overstated; in reality it is probably a very small percentage of the global free troposphere, especially because the measurements are limited to the upper free troposphere. 9) L21-22: So are only these five regions considered in this paper? Are the data in gray in Figure 1 not used? Overall please state what percentage of the data were used and how many samples this corresponds to. This is a 14-year data set and it seems that the data coverage could in fact be quite sparse both spatially and temporally, so not robust enough to pull out long-term trends. 10) L22: Is this the box shown in Figure 1? If so please state this in the Figure legend.

Page 20730: 1) L3: The legend in Figure 1 is confusing. What does the colour gray indicate? Aren't the regional samples (Africa, etc.) also CH₂Cl₂ samples? Some indication of the time frame for the different routes also needs to be given. 2) L4: What does 'this average' refer to? 3) L6: The Figure 2 legend is confusing. The text says 'NOAA Mace Head data' but Figure 2a shows a gray dot for 'NOAA' and a black diamond for 'Mace Head' (it took me a few minutes to work out that half the legend in Figure 2a is actually for Figure 2c). Please fix. Also I recommend presenting Figure 2c with Figure 1 and discussing it earlier in the text, say on P20725 L4. 4) L6-7: Instead of 'can be seen' use 'is shown'. 5) L8: The font size or figure size needs to be increased in Figure 2. 6) L9: Try to use more direct language. Instead of 'is mainly as a result of the fact that' use 'is mainly because' or something similar. 7) L10: Could the lower variability in the Mace Head data also be because these data have been edited for outliers? 8) L11-15: Even though Mace Head is a clean air site and CARIBIC can be impacted by pollution, the CARIBIC levels are still generally lower than the Mace Head values, most likely reflecting the vertical gradient of CH₂Cl₂ in the atmosphere.

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This should be briefly pointed out and discussed here. 9) L16-17: Suggest rewording this because seasonality seems apparent in later years. 10) L21: While the Mace Head data are fairly evenly distributed so that annual averaging is reasonable, please describe how the CARIBIC annual averaging was done. Was any weighting done, for example averaging 12 monthly averages, or was it a straight average of all the data points in a given year, in which case the averaging could be biased if the data points are clustered. What tests were done to make sure the annual averaging calculation is robust? Also CARIBIC data time series need to be shown for each region, not just Europe. The reader needs to be able to see the gaps in the data relative to the seasonality, and whether the long-term averaging and trend analysis is reasonable. 11) L25-28: This discussion is very qualitative. What does ‘very similar’ mean? Does CH2Cl2 have a latitudinal gradient between Barrow and Mace Head?

Page 20731: 1) L2-5: This is also qualitative. What does ‘relatively stable’ mean? It seems very difficult to tell whether the concentrations are in fact relatively stable when a good portion of the data, including two sets of winter data, is missing. Do the data actually increase beginning in 2004, or does the increase begin more around 2006? What do linear fits to different subsets of the data show? 2) L4-8: I am concerned that trends are being deduced from data sets that are incomplete for each time period. The 1998-2001 CARIBIC data set for Europe (n = 16) is extremely sparse and almost entirely missing wintertime data, when concentrations will be the highest, whereas the last four years (2009-2012) have relatively more wintertime data. Therefore the latter data set can be expected to have higher concentrations on the basis of seasonality alone. The pre-2002 data do not seem nearly robust enough to be used for long-term trend determination. At very least you would need to compare data from similar months, but even this is questionable because unlike Mace Head, which is a fixed location, the location of the flight paths from CARIBIC may be different, introducing another difficulty in the comparison. A better starting point would be taking the Mace Head 2003-2004 data as a baseline and comparing it with Mace Head 2011-2012 data. What increase does this show? 3) L11-13: It is almost certainly because of

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the altitude difference so I recommend discussing vertical gradients of CH₂Cl₂ earlier in the text (see also comment for P20730 L11-14). 4) L15: Why is the Cape Grim data presented if it's not going to be discussed? 5) L17: Following from the above comments, I am concerned that the trends in Table 2 are questionable and will be misinterpreted; I recommend using more robust portions of the data set from long-term trend analysis, if the sample size and data coverage is adequate. 6) L17-18: The Simpson et al. altitudes were lower than CARIBIC (0.8-4.7 km instead of 10-12 km). Also the Simpson et al. measurements were only performed in the summer months so a better comparison would be with the CARIBIC summer data from 2008, though the effect of altitude still needs to be discussed. Please also provide an uncertainty on the average of 35.8. 7) L22: The legend for Figure 3a has many more colors than the three that are shown. 8) L24-25: The data are too sparse to infer any kind of long-term trend. 9) L25: Were the flights in 2000 and 2009-2011 made in the same season? Also provide uncertainties on the averages.

Page 20732: 1) L1-3: This conclusion is difficult to support without a more robust data set and full modeling analysis to understand all the sources and sinks of CH₂Cl₂. 2) L5: From Table 2 there are 3 samples in the north of 30 Africa data set. It is not possible to present a meaningful trend analysis with such small data sets. Please remove this discussion. 3) L8: Why does Table 2 present north of 30 data for Africa for 2000 but the text cites 1998-2001? How many samples are in the 1998-2001 data set? From Figure 3a it still only looks like a handful of data points and long-term trend analysis is not credible. Most of the discussion in this paragraph should be removed. 4) L16: Change 'trace gases' to 'trace gas emissions'.

Page 20733: 1) L6: Put 2011 before 2012. 2) L12-14: This is a bit confusing because flights before, during and after the ASM would cover all the 2008 data. Please clarify what time frame you mean. 3) L21: The elevated samples resulting from Southeast Asia influence is a good illustration of the difficulty in using small numbers of flights to assess long-term trends with time.

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Page 20734: 1) L1-10: The discussion is weakened when too much weight is placed on snapshot measurements. Is this a shift in latitude with time or just variability? More analysis and discussion is needed before such conclusions can be drawn. 2) L12: How large was the ‘small sample size’ in 2011-2012? Why weren’t the 2000 Africa data north of 30 degrees ($n = 3$) omitted for the same reason? 3) L13: There are too many significant figures. It is not possible to measure a change in CH_2Cl_2 to within 0.1 pptv over 10 years, especially with a relatively sparse data set. The impact of variability needs to be realistically addressed.

Page 20735: 1) L1: Change ‘us’ to ‘use’. 2) L2: Change ‘ CH_2Cl ’ to ‘ CH_2Cl_2 ’. 3) L6: Is it realistic to estimate emissions based on just 35 samples? 4) L10: Fix the subscript. Also show Equation (1) immediately after it is cited. 5) L14: The justification for not using an excess concentration needs to be briefly presented here (not just referring the reader to two other papers). 6) L19: CO is a combustion tracer and CH_2Cl_2 is primarily industrial. Why is CO’s biofuel source being highlighted here? How large is India’s biofuel source of CO compared to its other CO sources such as fossil fuel and biomass burning? 7) L20: This argument isn’t convincing. Even if CO is the best option it still doesn’t guarantee that it’s a good option. Also remove the comma after ‘Other’. 8) L27: Do not hyphenate ‘air masses’. In Table 3 add a space between ‘airmass’. 9) L26: What was the correlation between CO and CH_2Cl_2 in the 35 samples? Is there evidence that they were co-located? (I see that it is presented later . . . please provide it here.)

Page 20736: 1) L1-2: Were all the referenced comparisons between CO and CH_2Cl_2 based on surface studies or were any high altitude studies like yours? 2) L15: Add error bars to all slopes given in Table 3 and if possible to the Baker et al. slope (the significant figures will probably need to be adjusted). In the ‘other study’ part of Table 3 adjust the significant figures (e.g. ‘Urban, California’ should be 3.1 not 3.10 if the error is 0.3). 3) L24: Some of the arguments on P20735-36 seem weak. Better correlation in the India samples than the Africa samples still doesn’t exclude some impact of transport

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or different lifetimes on the CH₂Cl₂/CO ratio.

Page 20737: 1) L2-6: Many of the arguments in this paper refer the reader to other papers; the assumptions need to be quantified here. How much is 'minimal'? 2) L10-15: A general comment is to try to rearrange the flow of the paper. Many times a result is presented but not supported until later. Try to bring common ideas together. This will also help condense the text and avoid repetition. 3) L19: State the lifetime of CO. Why does CO with a 2-month lifetime experience changes in 4 days but not CH₂Cl₂ with a 5 month lifetime? 4) L23: The emissions occur at the surface and are measured at 10-12 km. Is 298 K appropriate? By 'average concentration of OH' do you mean throughout the troposphere?

Page 20738: 1) L5: State the magnitude of the two errors so the reader can see how much smaller the first is compared to the second. 2) L26: What is the basis for assuming CO emissions are constant year-round?

Page 20739: 1) L3: 'hopefully' – not sure what is meant by this. 2) L6: It's difficult to follow all the assumptions in this paper. Some seem unsubstantiated and it's difficult to know which assumptions are negligible and which are assumed to be negligible but it's not really known. 3) L8: As noted above this correlation could be presented and discussed earlier. 4) L15: Remove the semi-colon. 5) L18-20: 'the rest of the ratios show a consistent increase over time due to increased emissions of CH₂Cl₂'. This conclusion seems to come out of the blue. What evidence is there that there is a quantitative increase and that it's related to increased CH₂Cl₂ emissions rather than variability? Are you just talking about the urban ratios or also the biomass burning ratio of Rudolph et al.? Even if it were possible to draw such a conclusion, the 2006 ratio from Mexico City for example is lower than the 2005 ratio from Los Angeles. 6) L20: Which ratio is 'this ratio'? 7) L22: What about seasonality in CO emissions? 8) L28: I'm not convinced that all the uncertainties have been addressed well enough to draw this conclusion.

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Page 20740: 1) L8: What is the uncertainty on these estimates? 2) L10: Or emissions of CO could decrease with time because of catalytic converter technology. What is the situation in India? 3) L22: Change '200' to '2000'. 4) L23: It isn't clear to me that uncertainty has been handled well enough to provide confidence in these results. 5) L26: Does 'North and central Atlantic' correspond to 'C. America' in Figure 1 (green)? If so this should be clarified.

Page 20741: 1) L4-9: The text is vague. Quantify 'very little variation', 'increases over time', 'less pronounced' and 'slight decrease'. Are the differences statistically significant? As before, was annual averaging based on a bulk average of all samples, which will bias the average towards heavier sampling times, or was some kind of seasonal weighting performed? 2) L10-11: The long-term trend in Figure 6c does not look statistically significant. 3) L13-14: As with other regions a better uncertainty analysis needs to be provided. Is it realistic that a long-term trend can be assessed to within 0.7 ppt from this data set? 4) L17: What time of year did Scheeren et al. make their measurements? Is it an annual average like the CARIBIC data or over a shorter time period (in which case the comparison is not meaningful without a discussion of seasonality)? Also 'Similarly low' does not seem like a correct interpretation of 16 versus 23. 5) L18: Why is the Scheeren discussion paper cited rather than a final published version? 6) L20-21: Similar to elsewhere in the paper, before the data can be used to look at changes in CH₂Cl₂ with time there needs to be a full analysis of other impacting factors such as variability, seasonality, sample size, etc.

Page 20742: 1) L2-3: Where can the reader see that the samples were evenly distributed across many months? What about elsewhere in this paper where samples were not evenly distributed over time, but long-term trend analysis was still performed? 2) L3-4: The statement that 'it is unlikely that seasonal bias plays a role' needs to be substantiated . . . in other words time series need to be shown for all regions, not just Europe. 3) L6-8: This type of argument applies everywhere in the paper. A few low or high samples will affect each average and the sample size is too small for long-term

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trend analysis, especially when seasonality hasn't been factored in and the averaging seems to have been done in bulk. 4) L22: Figure 8 is very hard to read. 5) L22: Not sure it's a 'clear increase' ... the error bars are so large that none of the differences look significant. The maximum increases for 2007-2008, decreases for 2009-2010, and increases for 2011-2012, so even if the differences were statistically significant this could just be interannual variability rather than a long-term increase. Also it would help to have all five graphs on the same scale for CH₂Cl₂. 6) L27-28: Again avoid 'clear increase'. If you omit 2011-2012 instead of 2009-2010 then it would be a decrease.

Page 20743: 1) L2: In what season did Schauffler et al. make their measurements? How does seasonality affect CH₂Cl₂ measurements at 15.3-17.2 km, and how might this affect the comparison? 2) L2-8: It's unlikely that the Schauffler average is 'lower' than the early CARIBIC value because the range shown in Figure 8a is so large. What is 1-sigma error on the CARIBIC value of 18.1 (13.0-25.0; n = 20) for 1998-2002? Is 18.1 significantly different from 14.9 +/- 1.1? Variability and small sample size are two other considerations that also need to be discussed. 3) L19-20: This statement is speculative. When did the rise of industrial activity begin in Asia? The CARIBIC data set spans 1998-2012 and the very high values of Barletta et al. were already observed in 2001, so it's unclear why a flight in 2012 is highlighted and linked to a rise in industrial activity. 4) L22: Add an error bar to the value of 226 ppt.

Page 20744: 1) L4: Avoid using 'about' with a number as precise as 95.9%. Are the NH emissions of HFC-32 really known to this level of precision? 2) L8-9: Is it a rate of increase or just an increase? You could also just use 'growth'. 3) L16: Use a semicolon instead of a comma. 4) L16-17: Why is India in particular highlighted here? What are the world's first and second largest consumers of CH₂Cl₂? Are they experiencing rapid growth? 5) L21-22: Change 'the O'Doherty et al. (2014) study' to 'O'Doherty et al. (2014)'. 6) L22: The inter-hemispheric gradient of which compound? All HFCs or just HFC-32? Suggest condensing and clarifying the text in L21-25.

Page 20745: 1) L3-6: It is difficult to know whether large point source emissions trans-

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late into a major emission source at a national level. Does the Majumdar and Srivastava study discuss this? 2) L9-11: While this could be the case, the arguments leading to this conclusion seem speculative. Also the following sentences in this paragraph seem to contradict the importance of India on a global scale . . . if it's 4% then it's not an important source. Try to draw out a clear conclusion in this paragraph. 3) L14: What year does the 515 Gg/yr apply to? Is it closer to 2008 or 2005? 4) L20: The paper and its conclusions need to be reworked within the limitations of what the CARIBIC data set can provide.

Page 20746: 1) L2: 'must be linked' is too strong without direct evidence. 2) L11: The minor contribution to ozone depletion should be mentioned in the introduction.

Figure captions: The captions would be easier to read if they had full sentences. For example try 'Error bars are given for combined values based on multiple measurements' instead of 'Error bars given for combined value based on multiple measurements'.

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