

## ***Interactive comment on “20th Century trends and budget implications of trihalomethanes and dihalomethanes inferred from North GRIP firn air” by D. R. Worton et al.***

D. R. Worton et al.

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The authors would like to thank both reviewers for the very positive overall comments about our manuscript, which suggest the importance and relevance of our work to the literature. We also appreciate the referees comments regarding the analytical quality of our work and are grateful for the specific issues that are raised. We have addressed these issues in our response and they have been given substantial consideration during the revision of our manuscript.

Both reviewers suggest that the title of the paper should include the name chloroform since the majority of the discussion is dedicated to this species. Referee #1 also sug-

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gests removing the words North GRIP from the title since data from four sites are presented and discussed. Therefore, the title of the manuscript has been changed from “20th century trends and budget implications of trihalomethanes and dihalomethanes inferred from North GRIP firn air” to “20th century trends and budget implications of chloroform and related tri- and dihalomethanes inferred from firn air”. Referee #1 proposes developing a statistical error estimate of all contributing sources and sinks including uncertainty estimates of all steps and data that go into the analysis procedure, e.g., (a) firn air sampling procedure (b) chemical analysis error (c) firn air transport uncertainties (d) atmospheric model and the atmospheric oxidation sink (including its seasonality) and its potential change over the study period (e) all considered natural and anthropogenic sources. Referee #1 then suggests performing an error propagation error and from that conclude whether or not the observations indeed disagree (at the statistically significant confidence level) with what the model predicts. It is not possible to estimate an error associated with the firn air sampling procedure although we are confident about the reliability of the method from the monitoring of carbon dioxide during the sampling to ensure that only old air is being extracted during canister filling. The errors in the chemical analysis are represented as the error bars in figures 1, 2 and 3 and are less than 5% in all cases. As a result of the modelled firn tortuosity there are errors in the firn air model that result from the choice of the best diffusivity profile at each site, e.g., at NGRIP these were less than +8%/-27% between the methane and sulphur hexafluoride derived diffusivities and were most prevalent at depth where the largest discrepancies in the estimated diffusivities are observed. Uncertainties arising due to the parameterization of the transport scheme were considered in Sect. 3.2.6 of our manuscript, varying the position of the maximum anthropogenic emissions also simulated the effect of more or less northerly transport and gave an uncertainty of +7.6/-7.1%. The prescribed OH field, including its seasonality, in the 2D model has previously been evaluated and shown to be robust by Reeves (2003) by modelling the methyl chloroform trend as measured by the ALE/GAGE/AGAGE network. The possibility of an OH trend, as reported by Prinn et al. (2001) over the timescale of the 2D

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modelling is an important consideration. In Sect. 3.1.1 we describe the possible implications of the changing OH trend as reported by Prinn et al. (2001) and that this trend is disputed by continuing emissions of methyl chloroform from Europe. Recently, 2D modeling work by Martinere et al. (2006; unpublished work, CRYOSTAT final report to EU) has shown no evidence for an OH trend based on modeling measured atmospheric methyl chloroform derived from firn air. We constrain the magnitude of natural emissions based on the goodness of fits to the southern hemisphere firn air and the anthropogenic emissions are constrained by what is required to adequately model the northern hemisphere firn air, namely NGRIP. These model fits have an inherent uncertainty based on the goodness of fits for the model results relative to the measurements, which has a certain degree of subjectivity although the associated errors are likely to be small. We feel that although we have not conducting an error propagation calculation as suggested by referee #1 we believe that we have addressed the concerns raised by the referee.

Referee #2 comments that section 2.1 is too short as it only mentions the firn air samples collected at NGRIP. Hence, on page 705, line 11 has been changed “Details of the NGRIP site (Reeves et al., 2001)” to “Details of the NGRIP (Reeves et al., 2005) Devon Island, Dome C and DML (Sturges et al., 2001) sites”. The referee suggests that some clarification concerning which species were measured at which sites and the associated uncertainties should also be discussed in this section. The referee also states that the acronyms for the different sites should also be defined in this section. These issues have been addressed by the addition of the following text “CHCl<sub>3</sub> measurements are presented from all four firn sites whereas the brominated tri- and dihalomethanes are only presented for the NGRIP site. The brominated species have also been measured at the other three sites and were reported previously by Sturges et al. [2001].” at the end of line 17 on page 705, and the additional text “Firn air samples were collected at the North Greenland Icecore Project (NGRIP), Greenland (75°N, 42°W), Devon Island (DI), Canada (75°N, 82°W), Dronning Maud Land (DML), Antarctica (77°S, 10°W) and Dome Concordia (Dome C), Antarctica (75°S, 123°E) sites.” to the beginning of section

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## 2.1.

In figure 1, referee #2 notes that only the northern hemisphere sites have associated error bars plotted with them and that an explanation of the associated experimental uncertainties should be discussed. Actually, all the data from all four sites have error bars plotted but as a result of the scale in figure 1 the errors on the southern hemisphere sites are actually smaller than the symbols used in the plot. To re-dress this, the symbols have been changed such that the error bars are more visible than before. The following text “The associated experimental uncertainties, as illustrated by the error bars in subsequent figures, were determined as the total analytical precision through duplicate analyses of samples at each depth” was also added at the end of section 2.1.

In section 3.2.2 (page 711, line 16) the sentence has been reworded to read “In the literature, the estimated anthropogenic source strengths of  $\text{CHCl}_3$  are reportedly small (Aucott et al., 1999) relative to the estimated natural emissions (Khalil et al., 1999). The associated uncertainties reported (Aucott et al., 1999; Khalil et al., 1999) with these estimates would suggest that the anthropogenic source strength is better constrained and hence more well known although this work, as will be shown, would suggest that this is unlikely to be correct.” following referee #2’s comment that this statement was contradictory to the conclusion of the paper.

Referee #2 comments that either in section 3.2.3 or in section 3.2.7 the uncertainties in the estimated emission factor described in section 3.2.3 should be discussed in more detail. It is important to point out that two different emission factor estimates are described in the text. The first is that determined during section 3.2.3 by the authors (page 712-713) to extrapolate the reported [Aucott et al., 1999] anthropogenic source emissions for 1990 back to the beginning of the 20th century by linked them to surrogates (i.e., paper production/consumption and population). The second are those reported by Aucott [1997] which were used to derive the global anthropogenic emissions for 1990 which were used as above to determine anthropogenic time trends (page 715, line 11). In order to clarify the above points and to address the referees comments the

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paragraph beginning on page 718, line 29 has been reworded to read “The modelling strongly suggests that the reported anthropogenic emission estimates are underestimated, especially for the P+P industry. The incorporated values for the WC and OI industries are within the described uncertainties of between a factor of 2 and 5 reported by Aucott (1997). However, the emission values used for the pulp and paper industry are outside the described uncertainties of a factor of 2 reported by Aucott (1997). This would suggest that the emission factors determined by Aucott (1997) to extrapolate the global emissions from the P+P industry are likely to be underestimated and need to be re-evaluated.”.

Referee # 2 comments that, inherent to studies like ours, lots of assumptions are made and discussed and that one very important assumption, i.e., that chloroform natural sources are known and constant, appears to have been overlooked and more discussion would be valuable to the paper. To address this issue we have added “A critical assumption is that the natural emissions from oceans and soils have not changed over this time frame. We concede that increased emissions from the biosphere could have taken place during the 20th century, e.g., as a result of increasing global temperatures. However, there is scant evidence to support such increases as a result of the apparent lack of increasing trends in the THM and DHM’s measurements in the southern hemisphere (Sturges et al., 2001) and the DHM’s in the northern hemisphere (Sturges et al., 2001; this work). The largest changes occur in the northern hemisphere and since it is hard to imagine a natural source that only operates in the northern hemisphere a large variation in the anthropogenic emissions needs to be invoked to describe the observations.” after “over this time frame.” on line 15 page 714.

Natural source emissions have been halved based on the assumption of different calibration scales, referee #2 asks how the conclusions of the paper would be affected if these natural emissions were larger than assumed. With the incorporated natural emissions the magnitude of the firm air measurements from the Antarctic are fairly well reproduced and so are the deepest samples at NGRIP, if the natural emissions are

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higher than this agreement is reduced which suggests that the values chosen are reliable. Larger values would not change the main conclusions of the paper but would not allow for good model fits of the deepest firn air samples in either hemisphere. This is discussed on page 717, lines 2-7.

In section 3.2.5, referee #2 comments that the discussion relating to the hypothesis of constant emissions from water chlorination (WC) and other industrial processes (OI) between 1990-2001 is to much of a coincidence that this occurs in the same year that the pulp and paper emissions began to decline. Referee #2 suggests removing this scenario from figures 8 and 9 and from the discussion as it is noted that this hypothesis does not bring a conclusive result to the discussion. Therefore, the scenario has been removed as suggested and as a result the model has been re-run to provide data that excludes this scenario, which has led to some changes to the figures and to the associated discussion of these figures. The following changes have been made: Page 714, lines 13-17 now read “The temporal variations, over a 100 year period, for all source terms, including a trend that incorporates a changing soil source (Sect. 3.2.4), are shown in Fig. 8.” Page 715, line 4 added “and is shown in Fig. 8.” to the end of the sentence. Page 715 line 16 - page 716 line 3 inclusive has been removed from the manuscript. Page 716 lines 14-18 changed to now read “The magnitude of the WC and OI emissions were fixed at either the reported values (Aucott et al., 1999) or at double these values dependent on the particular run.”

In section 3.2.6, it is stated that China is responsible for <10% of global pulp and paper production. Referee #2 requests a comment about the contribution that Russia makes. Therefore, page 718 lines 11-13 now read “However, the effects are likely to be small as China and Russia are responsible for <10% and <5%, respectively, of global pulp and paper production (Johnston, 1996)”.

In section 3.2.7, referee #2 comments that it is not clear why the changing soil source (dSS), which represents an anthropogenic perturbation of the soil emission, therefore affecting mainly the Northern Hemisphere would improve the Southern Hemisphere

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simulation. The authors concede that this is a very good point and in fact the improved fits most likely arise as a result of the soil coverage and not necessarily as a result of any anthropogenic influence. If the soil emissions have changed as a result of some natural change then the improved fits from the dSS scenario would be more readily understandable. As a result the best fit model scenarios no longer incorporate the dSS term and instead incorporate a reduction in natural emissions of 20%, which was necessary to improve the model fits to the southern hemisphere firn air data. Therefore the following changes were necessary: Page 716, line 24 changed “varied between ~3-4 times” to read “varied between ~4-5 times” Page 717, lines 19 removed “with constant values between 1990-2002” and replaced “treble” with “four times” Page 718, lines 17-19 have been reworded to now read “The four scenarios shown incorporate either 4 or 5 times the reported P+P emissions (Aucott et al., 1999), double the reported WC and OI emissions (Aucott et al., 1999) and either natural emissions of 280 Gg or 224 Gg (a reduction of 20%). The reduced natural emissions were introduced to improve the fits to the Antarctic firn air data and are well within the estimated uncertainties reported by Khalil et al. (1999). The total anthropogenic emissions associated with these four scenarios are 190 - 230 Gg at the peak in atmospheric CHCl<sub>3</sub> around 1990.” Page 718, lines 21 - 22 have been reworded to read “These anthropogenic emissions are significantly larger than the estimated 66 Gg CHCl<sub>3</sub> reported by the RCEI (Aucott et al., 1999) and arise as a result of doubling the emissions from WC and OI and multiplying those from the P+P industry by a factor of 4 or 5.” Page 719, lines 5 - 15 have been removed and replaced with the following “At NGRIP, three of the four best fit trends model the measured maxima well. At Dome C and DML, the trends which incorporate natural emissions of 280 Gg over predict the measurements although the general trend is well simulated (Fig. 14).

However, reducing the natural emissions by 20% to 224 Gg results in significant improvements in the model fits to the majority of the data except the shallowest firn where concentrations are slightly under estimated (Fig. 14).” Page 719, line 16 replaced “~40%” with “~41 - 50%” Page 719, line 22 replaced “~19%” with “25 - 29%” Page 719,

lines 24-26 removed “However, it is likely that the anthropogenic contribution is actually slightly higher than these values since to improve the model fits at all three firn sites would involve slightly lowering the natural and slightly increasing the anthropogenic emissions.” Page 719, line 29 replaced “440 - 480 Gg CHCl<sub>3</sub>/yr” with “417 - 506 Gg CHCl<sub>3</sub>/yr” Page 720, line 1 replaced “340 Gg CHCl<sub>3</sub>/yr” with “315 - 373 Gg CHCl<sub>3</sub>/yr” Page 720, line 2 replaced “20%” with “25%” Page 720 line 5 reworded to now read “The absolute values for the global and hemispheric averages, corresponding to the scenario incorporating a 20% reduction in natural emissions and P+P emissions 5 times those reported by Aucott et al. (1999)” Page 720 line 6 replace “5.4 pptv” with “5.6 pptv” Page 720, line 11 replaced “10.2 pptv” with “10.4 pptv” Page 720, line 12 replaced “-0.29 pptv/yr” with “-0.42 pptv/yr” Page 725, line 24 replaced “~40%” with “~50%” Page 702, line 16 replaced “~40%” with “~50%” Page 702, line 17 replaced “~19%” with “~29%” Page 720, lines 15-18 removed “The over estimates in the southern hemisphere that result by assuming constant natural emissions over the time frame of the modelling suggest that the absolute magnitude of the natural emissions could be slightly lower than those incorporated within the model.” Page 725, lines 24 - 27 the following text has been removed “Our results also suggest that the soil source may not have been constant over time and could have been increasing over the 20th Century possibly as a result of agricultural interference.” Page 720 lines 14 - 15 replaced the sentence “These would suggest that there are still some uncertainties with the results and budget implications of this modelling.” with “This would suggest that there are some limitations resulting from the global extrapolation of the rapid decline in CHCl<sub>3</sub> emissions from the USA pulp and paper industry. A possible explanation for the discrepancies of the modelled rate of decline and the higher estimated contemporary concentrations is that the global P+P market has responded at a slower rate relative to the USA”. Table 1 now reads as below: Year Emissions Gg yr-1 Anthropogenic Contribution (%) Anthropogenic Total 1950 46 - 55 270 - 335 14 - 20 1990 193 - 226 417 - 506 41 - 50 2001 91 - 93 315 - 373 25 - 29

Referee #2 comments that the changing soil source (dSS) scenario should be com-



pared to the other scenarios that involve anthropogenic changes (i.e., Figures 9 and 10). In response to this, we have added the dSS into Figure 9 to illustrate the effect it has on the model fit to NGRIP and this has also resulted in the additional text “The changing soil source (dSS) scenario is also shown in Fig. 9 and the effects observed at NGRIP are reasonably small with slightly lower values being modelled in the deeper part of the profile whilst the opposite is apparent for the near surface. The effect of this scenario is more significant for the southern hemisphere sites (not shown) where the higher values in the shallow firn and lower values in the deeper firn appear to improve the fit to the measurements. However, these improved fits are more likely reflecting the consequence of the distribution of soil coverage within the model as opposed to a definitive anthropogenic perturbation.” being added on page 715 at the end of line 15.

Page 703, lines 8-12 referee #1 suggests that this sentence should either be explained in more detailed or removed. We have removed it, as we believed a lengthy explanation would have been necessary that would not have added additional benefits to the paper.

Page 704, line 21-23 referee #1 points out that the sentence describing the current decline in the tropospheric bromine burden is miss leading with respect to the halon gases which are still growing in the atmosphere. Hence, this sentence has been reworded to read “However, this decrease is reportedly driven by the reduction in atmospheric methyl bromide and the contributions of the very short lived bromocarbons are considered to have remained constant (Montzka et al., 2003) as they are generally assumed to be almost entirely of natural origin.”

Page 708, line 28 referee #2 comments that the reference (Sect. 3.1.2) from this section should be checked. This reference was corrected to read Sect. 3.1.1.

Page 709, line 4 referee #1 requests a definition of ‘gravitational settling’. Hence the sentence has been reworded to now read “As a result of the seasonally influenced concentrations the samples collected in the shallow firn (<30m) are not included in this plot and the remaining data have been corrected for the effects of gravitational settling,

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which causes heavy molecules to be enriched at depth in the firn column relative to lighter ones.”

Page 709, line 19-21 referee #2 comments that the references to Khalil should be checked as some should be referenced as Khalil and Rasmussen and not as Khalil et al. This led to the lines 19-21 being corrected to read “Khalil et al. (1983) and Khalil and Rasmussen (1998) whose calibration scale for CHCl<sub>3</sub> has been shown, through an intercomparison of measurements at Cape Meares (45°N, 124°W) (Khalil and Rasmussen, 1999) and Trindad Head (AGAGE; 41°N, 124°W) (O’Doherty et al., 2001)”

Page 715, line 12 referee #2 notes that in the modeling approach the scenarios use emission magnitudes that are a factor of 2 higher than the figures reported by Aucott et al. [1999] for water chlorination (WC) and other industrial processes (OI) and a factor of up to 5 times for pulp and paper manufacture (P+P). The uncertainty ranges being described here are those reported by Aucott (1997) that were estimated to arise from their extrapolation approach were a

factor of 5 for WC and OI and a factor of 2 for P+P. Therefore to clarify the paragraph (page 715, lines 11-15) has been reworded to read “The reported (Aucott 1997) uncertainty levels associated with each of the anthropogenic source terms suggest that the reported values (Aucott et al., 1999) could be up to a factor of 2 larger. Therefore, all the anthropogenic emissions were doubled, which resulted in a better approximation to the NGRIP data (Fig. 9).”

Page 715, lines 16-21 referee #2 suggests shortening this sentence if possible. The sentence has been rewritten to now read “Trudinger et al. (2004) had difficulties modelling the recent observed declining CHCl<sub>3</sub> trend at Cape Grim (O’Doherty et al., 2001) using the global population as a surrogate for anthropogenic emissions. As a result Trudinger et al. (2004) suggested that the anthropogenic emissions were most likely to have increased with population until 1990 before decreasing slightly contrary to the

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continued population growth.”

Page 718, line 24 referee #2 suggests removing “the” from “the these”, this has been done.

Page 721, line 23 referee #2 suggests removing “the” before “whether”, this has been done.

Page 710, line 8 referee #1 suggests a definition of RCEI should be included, this abbreviation was defined earlier in the paper (page 704, line 5) and so is not defined again here.

Page 712, line 25 referee #1 suggests rewording the sentence to read “The relationship between  $\dot{E}$  ought to be linear and in  $\dot{E}$ ..” and this has been corrected in accordance with this recommendation.

Page 720, line 11 referee #1 requests a reference for the given average global concentration (10.2 pptv). However, this value is from the output of the 2D model used in this work and therefore there is not a literature reference. This issue has been addressed by clarifying the origin of the 10.2 pptv value.

Page 723, line 10 referee #1 comments that “bottom of the firn” is not specific enough such that this sentence has been rephrased to read “Between the firn close off depth and”.

Page 725, line 18 referee #1 suggests correcting “shows” to “show”, this correction has been made.

Figure 6 caption has been modified following a comment from both referees to include the full names of ECF and TCF in the text.

Figure 8 caption has been modified following a comment from referee #2 to include a definition of  $\sigma_{SS}$  and the legend has also been changed to read “(oceans + dSS)/5”.

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Both referees comment that although plotting  $\text{CHCl}_3$  and the other trihalomethanes versus CFC-12 instead of depth is convincing for illustrative purposes a second axis with an approximate date scale would also be helpful or at the very least for the year 1990. As a result of the differing diffusion rates within the firn for the various species we are reluctant to add an additional axis as a date scale although we agree that indicating the year 1990 would be beneficial to the reader and as such have added this to Figures 1 and 3. Additionally, in figure 3 linear fits have been added to better illustrate the increases of the brominated trihalomethanes relative to CFC-12. Figure 2 referee #1 suggested that for better comparison it would be good to plot the  $\text{CHCl}_3$  data in the same format alongside the other trihalomethanes in figure 2, which has been done. The caption for figure 2 has also been modified to read “Depth profiles of the THM and DHM in firn air from NGRIP (symbols). Model lines corresponding to constant atmospheric burdens incorporating seasonal cycles, where appropriate, are also shown.” in order to take account of these changes.

Figure 4 referee #1 suggests using different line patterns such that the ND1 and ND2 lines can be distinguished in black and white format. Also, the x axis has been changed to latitude instead of model box in both figures 4, 11 and 12. This changed axis has resulted in the additional sentence “The x axis represents the latitude with positive values reflecting the northern hemisphere and negative values the southern hemisphere” being added to the figure captions for figures 4, 11 and 12. We believe it is not possible to incorporate uncertainty ranges as the associated uncertainties as reported by Khalil et al. (1999) were quoted for the global emissions and were not given for any specific latitudinal range.

Figure 5 the abbreviation FAOSTAT has been defined in the legend following the suggestion by referee #1. Also, all shown abbreviated data series from figures 8-14 have been defined in the figure captions and the lines have been modified such that they can be distinguished in black and white format following the suggestion by referee #1. These corrections have changed the captions to these figures to incorporate the defi-

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nitions of the abbreviations.

Referee #2 suggests that the depth axis on figures 9, 10 and 13 could be reversed so as to be more consistent with the time trends shown in figures 5, 8, 15. However, we prefer to keep the depth axis the same so as to be consistent with the other depth profiles presented in figure 2.

In table 1 the word “global” has been added before “CHCl<sub>3</sub>”.

Referee #2 notes an inconsistency between the text in table 1 and the legend where both dates have now been corrected to read 2001.

In table 5 the words “Northern Hemisphere” have been added before “increases in the brominated”

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