Comments on “A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane” by S. Gromov *et al*

Martin Manning (Referee)

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We are very grateful to Martin Manning for his detailed review and valuable comments. Below we hope to show that it is the putting right that counts.

General Comments

Given the number of recent papers that have proposed quite different explanations for the post-2006 rise in atmospheric CH_4, it is clear that there are still some major systemic uncertainties in our understanding of the CH_4 source – sink budget. While the increasing amount of isotopic ($\delta^{13}CH_4$) data should help to resolve these uncertainties, this has to deal with a limited understanding of removal by Cl with its very large kinetic isotope effect (KIE), and so a significant effect on $\delta^{13}CH_4$ even though most of CH_4 removal is by OH.

Analyses by Allan *et al* (2005, 2007) [NB additional references not included in the Gromov *et al* paper are given below] suggested that removal by Cl in the marine boundary layer can match $\delta^{13}CH_4$ data in the Southern Hemisphere, so long as there is a significant amount of interannual variability in the amount of this removal, but the driving factors for such variability in Cl still needed to be clarified. The Lassey *et al* 2011 analysis was then based on a simpler budget approach but showed that small interannual variations in the seasonal cycles for different sources can also lead to an ‘apparent KIE’ in the data that is quite different to that due to chemical removal processes alone.

More recent work by Hossaini *et al* (2016) has shown that, when a detailed form of tropospheric Cl chemistry is added to the TOMCAT chemical transport model, that sink for CH_4 appears to be about half what was used in Allan *et al*, but that there is also the potential for large scale regional effects and higher amounts of Cl in some places.

This new paper by Gromov *et al* is definitely a very important extension to the work cited above, because it now addresses the issue of how a highly fractionating removal of CH_4 would affect the atmospheric CO that is produced by both of the CH_4 + OH and CH_4 + Cl removal processes. A key point made in this paper is that the role of Cl in removal of CH_4 must be kept consistent with data and budget analyses for $\delta^{13}CO$, and that the long records of NIWA data in the Southern Hemisphere are very relevant for this. In addition, because CH_4 oxidation produces 40 - 50% of the CO that is observed in the Southern Hemisphere, the isotopic effects of removal by Cl should be more evident there.

The EMAC model that is used in this analysis, and the atmospheric chemistry that it covers, are quite well documented in a number of earlier papers and the tagging tools, described in Gromov *et al* 2010, provide a clear way of attributing CO to its different sources. So, the framework used in this paper has a clear basis.

However, there are some aspects of the paper that I find to be either not clear or incomplete as follows.

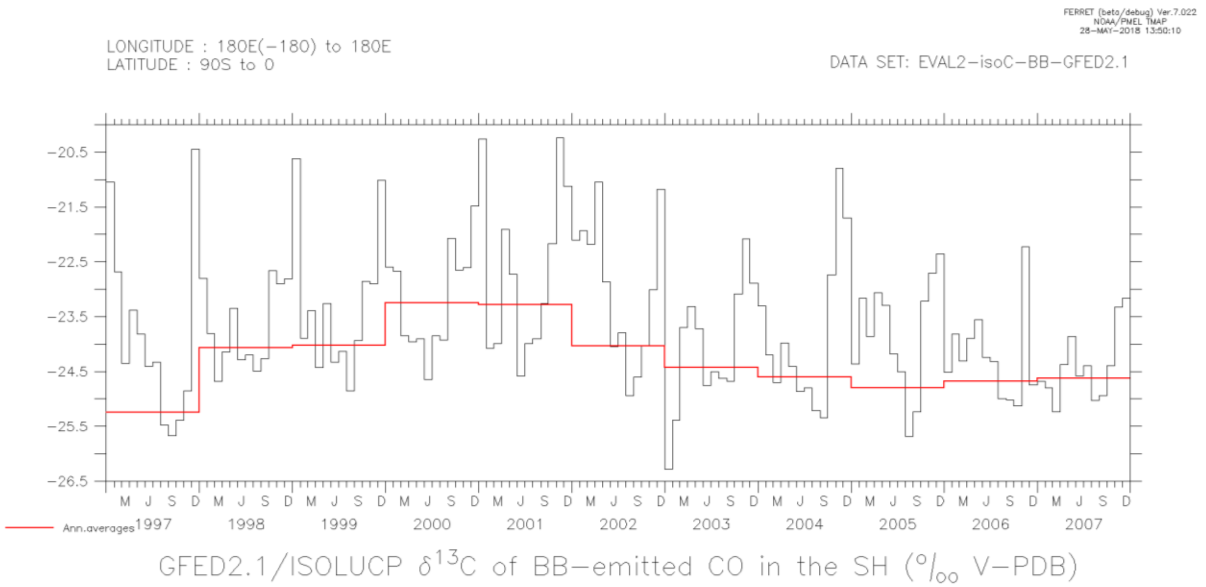
1) Use of the EMAC model in this work appears to have constant surface sources for CO over the 1994 – 2000 period and so does not include the effects of any trends or interannual source variations. Because the lifetime of CO is about forty times shorter than that for CH_4, its mixing ratio and $\delta^{13}CO$ are much more sensitive to interannual variations in its sources. In particular, biomass burning is a significant source of CO in the Southern Hemisphere and its interannual variations are not well known prior to 1996 (e.g. Giglio *et al* 2013). More generally, while burning in C4 ecosystems is known to be dominant, the interannual variations are larger for C3 ecosystems that have a quite different $\delta^{13}C$ (e.g. Randerson *et al* 2005) so there can be relatively larger interannual variability in the source's $\delta^{13}C$ than in its magnitude.

Southern Hemisphere data at the start of the 1998 – 2000 period will also be affected by the extensive biomass burning emissions from Indonesia that continued for a longer period than usual in 1997. This is seen in the NIWA data that have an (admittedly) noisy long-term maximum in CO mixing ratio in 1998 but a much clearer maximum in $\delta^{13}CO$ that year. It is still not clear to what extent these source variations will affect the relationships in the tightly coupled CH_4 – CO – OH system, but as noted in Lassey *et al*, 2011, the 'apparent KIE' for CH_4 is quite sensitive to variations in seasonal cycles for the sources.

Some structural differences between the two 3-year periods used in this paper are seen quite clearly in Fig S2, e.g. the much smaller amplitude for $\delta^{13}CH_4$ seasonal cycles over 1998 – 2000 as shown in Fig S2(d). Therefore, it would be better to show all of the data this way in the main text, rather than just the statistical summaries currently used in Fig 1. Similarly, Fig S3 is a very clear way of showing model results and would also be useful in the main text.

To summarize this point: given that CO and $\delta^{13}CO$ are much more sensitive to changes in sources than CH_4 and $\delta^{13}CH_4$, it is important to consider how the paper's use of a fixed non-CH_4 source for CO may have hidden some of the differences between the two periods.

We agree with this summary. Irrespective of the sensitivity of CH_4 and $\delta^{13}CH_4$, the use of CO poses upfront a dilemma. On the one hand, we use the sensitivity of ^{13}CO to changes in the Cl/OH ratio (thanks to the large KIE form Cl, this gives hope), for which the SH is the best region to test. On the other hand, just here biomass burning forms a major variable source, as pointed out by the Reviewer. The variability in ^{13}CO is partly decoupled from that of CO, due to variations in the relative contributions of CO from burning C4 (dominant) or C3 based vegetation. How serious is this effect? Taking the time series of biomass burning source $\delta^{13}C$ for SH (Gromov et al. (2017), Fig. 4 and Table 3), we can put an upper limit of 2‰ for this source $\delta^{13}C$ variation (between 1997 and 2000 averages, $1\sigma = 0.62$‰, see the Figure below). We may only speculate that the variations between in 1994–1996 and 1998−2000 did not exceed this range; on the other hand, about half of these 2‰ is due to the large $\delta^{13}C$ excursion in 1997 triggered by very strong Indonesian fires due to the ENSO pattern in those years.



If one assumes Cl being constant, one can compare the variability of ^{13}CO to that of CO to see if changes in biomass burning composition (C3/C4 distribution) have a substantial impact. Referring to Fig. 2, we have calculated the variations in δ^{13}C of CO and its non-CH_4 derived component, which is required to mask the Cl-induced changes. Indeed, it cannot be excluded, that some of the difference between the two periods may have been hidden, or likewise may have been augmented by variations in the contributions of burning of C3 vegetation compared to the total BB source of SH CO, but the effect is demonstrably negligible. We note uncertainties about δ_n (line 202) which exceed given above variation for BB source δ^{13}C; however even a 4‰ variation δ_n will add tangible uncertainty to $\Delta\delta_c$ value only at very low $\lambda < 0.25$. We added to the text that the use of a fixed non-methane source has a negligible effect.

We note that we already had stated (Section 2.4, line 425-430) “unless masked by unrealistic concurrent increases in δ^{13}CO of the non-methane sources of about +(11.6-13.5)‰”.

2) It appears from this paper, and from the earlier Gromov (2013), that the EMAC model has produced CO mixing ratio values but not the δ^{13}CO values directly and that is why there is no analogue for Fig S3 showing model results for δ^{13}CO as well. Instead, section 2.4 gives formulae that bring together model and observational data, as summarised in Table 2, and then introduce the comparison between high Cl and low Cl periods shown in Fig 2.

Indeed, Gromov (2013) outlined the main problem of mass-balancing ^{13}CO for which an extensive modelling study were required. The current work, however, is mostly based on observational data, and we want to use model-derived information as little as possible in order to retain the observational nature of the evidence. Therefore, we use **only** model-derived γ and η_c values (which are difficult to obtain otherwise) and mass-balance the non-CH_4 CO sources’ δ^{13}C; for relevant components we show that their uncertainties are typically lower than that in the observed difference in δ^{13}C(CO) between the HC and LC. Another argument for using the approach via Eq. (1) is that we require annual averages (3-yr QAAs) in order to obtain low enough uncertainties (via larger statistic) about δ^{13}C(CO) changes.

However, while equation (1) is valid when CH_4 and CO are at equilibrium with their average sources and sinks, it does not apply more generally for the seasonal cycles in CH_4 and CO mixing ratios and δ^{13}Cs. Neither the mixing ratios nor δ^{13}Cs are at equilibrium due to the significant seasonal cycles in sources and removal rates. And, while large differences in lifetimes mean that the dis-equilibrium will be larger for CH_4 than for CO, in both cases the isotope ratios are expected be slower at reaching equilibrium than mixing ratios (e.g. Tans, 1997). Furthermore, the tightly coupled CH_4 – CO – OH system has different modes of variation (Prather, 1994, etc) and these are different again for the isotope ratios (Manning, 1999).

For the use of Eq. (1) is not relevant that CH_4 and its isotopic composition in response to inter- annual variations and short trend changes do not reach equilibrium. The impact of variations in CH_4 and $\delta^{13}CH_4$ is small compared to the impact of possible changes in Cl (to a degree as discussed by Allen et al. and in this paper) and of changes caused by a shifting in partitioning between the methane and the non-methane sources.

Concerning the applicability of Eq. (1) to CO and δ^{13}CO, phase ellipses of CO/δ^{13}CO would be highly adventurous in this sense. Tans, Prather and Manning have indeed pointed out that time constants are longer, especially for isotopic composition, than the commonly used life time or turnover time. If we for argument sake consider the SH OH seasonality to be the sole driving force of SH CO seasonality and we compare the phases of their seasonal cycles, we find a time lag of about 3 months. We compare in our paper however quasi annual averages (QAAs) for CO for the 2 periods of assumed high and low chlorine.

This difference between an equilibrium and dynamic situation appears when comparing the change in $\delta^{13}CH_4$ corresponding to equilibrium conditions for the HC and LC periods, as derived in section 2.4, with results shown in Fig 2b of Allan *et al* (2007), based on runs with the UK Met Office Unified Model, for the same estimates of Cl concentrations. The Allan et al difference in $\delta^{13}CH_4$ between the two different Cl concentrations is less than half that given in section 2.4. This point is mentioned again in specific comments on lines 181 – 193 below.

Therefore, it is not clear to what extent seasonal cycles in the dis-equilibrium and differences in that for both CH_4 and CO as well as for mixing ratios and δ^{13}Cs, will modify what is summarised in section 2.4. A more detailed summary of how the EMAC results are being used for δ^{13}CO might be helpful in this respect.

We do not present/regard the difference in $\delta^{13}C(CH_4)$ between the HC and LC periods in Sect. 2.4. Perhaps, Reviewer implied those shown in Sect. 2.2, which do not exceed 0.1‰ (in terms or 3-yr averages in QAAs), which is a negligible change for the CH_4-derived ^{13}CO. The largest effect on the latter are indeed driven by changes in the average CH_4 sink fractionation (ε_m) and should be pronounced in δ^{13}C(CO), however not in δ^{13}C of CH_4 due to its large inventory and potentially varying sources strengths/signatures. The question of equilibrium indeed is key here for CO, whose average lifetime is ~2 months in the troposphere, which means its inventory is reset within one year. We do not regard CH_4 at equilibrium here at all (and we do not need to) – therefore we use the QAAs only. Figs. S2 and S3 evidence that there is no disequilibrium in observed/simulated CO. Our approach also does not require de-trending, as compared to phase ellipses method. We are also concerned about Allan et al. (2007) approach using equilibrated CH_4 tropospheric inventory in a transport model with composite SST and wind fields, i.e. which likely produce unrealistic CH_4 distributions based on atmospheric dynamics and tracer transport/mixing different from those corresponding observational data. To recap: due to much shorter lifetime of CO, our approach is negligibly influenced by the disequilibrium in tropospheric CH_4 and its δ^{13}C. However, it is sensitive to rapid changes in CH_4 sink ^{13}C KIE, which should occur under large Cl variations.

We have amended Sect. 2.3 (also following the comment of Reviewer #2) regarding the use of EMAC results. We also add the seasonal cycles of η_c to Fig. S3 in order to facilitate the explanation of this parameter.3) While I agree with significant parts of this paper, the third paragraph of section 3 has several things that I cannot agree with. For example, the Allan *et al* papers did not just consider seasonal cycles in the CH_4 data. Their consistency with a total CH_4 budget based on other work was inherent throughout those analyses – e.g. see Table 1 of Allan *et al* (2001a). Similarly, early work to extract phase diagrams for variations in $\delta^{13}CH_4$ vs those in CH_4 mixing ratio, as shown in Figs 8 and 9 of Allan *et al* (2001a), had explicitly removed trends from the data using the very detailed Seasonal-Trend-Loess (STL) method and so it is not correct to imply that these results would have been sensitive to long term trends.

Perhaps, we misinterpreted the statement from Allan et al. (2001a), Sect. 5: “Thus we are averaging over interannual variations and assuming that disequilibrium effects and trends can be taken to be *linear over the period 1993-1996*.” However, we note here that assumption on linearity of trends is not applicable (will lead to wrong mixing vs. isotope ration slope or phasing) when actual trend (e.g. Loess component) of $\delta^{13}C(CH_4)$ reverses earlier than that of CH_4.

We change the text of our manuscript to do justice to also the earlier paper by Allan et al. (2001a) which is now included in the literature cited.

Also, the point about having to take account of a reversal in the long-term trend for $\delta^{13}CH_4$ as shown in Nisbet *et al* (2016) will apply to the analysis done in this paper as well. In particular, although not shown in Nisbet *et al* explicitly, that analysis has a reversal in trends for the CH_4 source $\delta^{13}C$ occurring around 1994 – 1996 which is also when there is a maximum in $\delta^{13}CO$ in the ETSH. That shows, again, the much faster response of the short-lived CO than the longer-lived CH_4. Consequently, concerns about dealing with trends in the CH_4 budget can be even more pertinent for this analysis.

We believe that proper dealing with annual cycles, their phases, inter-annual changes and trends of CH_4 and $\delta^{13}CH_4$ is extremely critical. We have in the case of CH_4 a lifetime of a decade and relatively small changes and trends. Tens of papers have dealt with this problem set and uncertainties persist.

For our approach, the changes in CH_4 and $\delta^{13}CH_4$ are not critical as we consider CO and $\delta^{13}CO$. The fast responses of CO and $\delta^{13}CO$ make our analysis much more robust. If Cl had indeed been elevated during the high chlorine period by 19×10^3 atoms cm^{-3}, the impact on $\delta^{13}CO$ would have been fast and detectable.

4) A broader concern that I have with section 3 is that this is not covering how the EMAC model may differ from other models such as TOMCAT used in Hossaini *et al* (2016) and which produces a much higher estimate for Cl in the marine boundary layer. These estimates will be very dependent on how details such as aerosol transport and DMS chemistry are treated. But comparison of the MESSy AIRSEA submodel used in EMAC with the GLOMAP aerosol microphysics model used in TOMCAT does not seem to have been considered anywhere so far. George Box is often cited as saying “All models are wrong, but some are useful” but the bigger problem with atmospheric chemistry models is that they all tend to hide the details at levels that make it virtually impossible to decide which is actually the useful one. Solving that problem is outside the scope of this paper, but it would be helpful if the issue was raised.

In our discussion, section 3, we do not discourse upon how the EMAC model may differ from other models such as TOMCAT used in Hossaini et al (2016) (the latter produces similar [Cl] in similar setup to that of EMAC, but not in the more complex setups which derive much higher local [Cl] in MBL). This is beyond the scope of this paper. We agree with the reviewer that there are shortcomings in the models and that sources of these shortcomings are hard to identify. The only crucial parameter which adds model-derived uncertainty is the yield value, for which we provide sensitivity.

5) The conclusion in section 4 may be the only part of this paper that some will read. On that basis I would argue that it should have a short summary of the range of different estimates for CH_4 removal by tropospheric Cl and their basis. E.g. Vogt *et al* (1996) showed that autocatalytic release of halogens from sea salt should be expected and several subsequent publications on aerosol chemistry have made similar points. Allan *et al* (2001b) then used such estimates of Cl concentration to derive an initial estimate for the magnitude of this sink, but that estimate tended to increase in subsequent papers to become as large as 25 ± 12 $TgCH_4$/yr. The more recent Hossaini *et al* (2016) treatment of marine air chemistry derived a tropospheric Cl methane sink of ~12–13 $TgCH_4$/yr and noted that there could be some larger regional effects. Then this paper is reducing the Cl sink again and now even more significantly. The basis for such a reduction and its implications for the CH_4 and CO budgets can then be summarised much as is done currently.

Perhaps it is a process akin to humans with their innate hopeful and positive nature doing science. After sheep were identified as a source of methane, estimates peaked. After termites were identified as a source of methane, estimates peaked. After plants were identified as a source of methane, estimates peaked. After methane hydrates were identified, estimates peaked. After tundras were identified, estimates peaked. After atomic chlorine gained attention and was suspected to play a significant removal role in the troposphere, estimates peaked. There may be a gold rush, but not all luster is gold. There is no doubt about the importance of chlorine in chemical /physical process in the troposphere in different environments. Our paper casts, in a largely model independent fashion, very strong doubt on the existing high tropospheric free chlorine estimates.

We note that in two publications, each by many experts on tropospheric methane, the estimated removal of 25 Tg CH_4 per year by tropospheric chlorine is listed, based on using the CH_4 and $\delta^{13}CH_4$ based estimate. Several studies deal with mechanisms of Cl production, yet global scale estimates are not available, apart from model studies. Much emphasis is on different chemical environments (marine and polluted especially) with little predictive power for the global troposphere. In our paper we cannot make a balance of major studies involved because they mostly deal with different aspects.

In conclusion, I would restate that this paper sets out an important extension of the work done previously on the potential role of CH_4 + Cl in explaining the $\delta^{13}CH_4$ data. E.g. while Lassey *et al,* 2011, sets out the sensitivity of an ‘apparent KIE’ to small variations in the sources, that made no mention of how this might be seen in $\delta^{13}CO$. This paper also sets out a reason why all future analyses of $\delta^{13}CH_4$ data would ideally include a consistency check with $\delta^{13}CO$, but unfortunately the limited spatial and temporal coverage for $\delta^{13}CO$ data will still prevent that.

At the same time, I do not think that this treatment of the two periods 1994 – 1996 and 1998 – 2000 is conclusive. In particular the much shorter lifetime of CO makes interpretation of its data much more susceptible to interannual changes in the source $\delta^{13}C$, and in the Southern Hemisphere these are expected to be relatively larger than in the Northern Hemisphere. Also, coverage of the seasonal cycles for $\delta^{13}C$ in both CH_4 and CO, with their variations from an equilibrium state, are not clear. The significant differences between two recent and detailed atmospheric chemistry model-based estimations of Cl in the MBL also raises other questions.

We show absence of a systematic difference in ^{13}CO assuming the two periods of high and low chlorine published in the literature. Such large differences in chlorine abundance lasting several years would have affected δ^{13}CO significantly, especially because of CO its short lifetime. A corresponding “compensation” or “hiding” by changes in the ratio of C3 to C4 biomass burning CO is unrealistic because it would not suffice and one would have to assume a coincidence, because no common mechanism can be identified. We further support this in our preceding study (Gromov et al., 2017). Even more so, for such large variations in chlorine on such a large scale, one still has no explanation.

Some of my concerns may be too deep to be resolved by one paper, but I would like some parts of this one to be improved, and that it then be published in order to move towards a more conclusive understanding of how we should interpret the growing amount of CH_4 isotopic data.

We deeply appreciate this thorough review and hope that the changes to the manuscript do justice to this.

Specific comments

line(s): 12 – 18: Another point that should be brought into the introductory paragraph is that the growing spatial and temporal coverage in $\delta^{13}CH_4$ data means that they are now being used for top-down estimates of changes in the source – sink budget to the order of ~1%.

Thank you, we do so.

30 – 39: I would suggest that this coverage of KIE also mention Barker *et al*, 2012 (references given below) which used an *ab initio* approach in quantum chemistry to determine the KIE for CH_4 + Cl. That showed theoretical calculations for ^{12}C/^{13}C rate constants are close to experimental estimates but a bit smaller. However, the authors accept that there are still some issues to be resolved with that method.

Barker et al. conclude in their paper that their KIEs for ^{12}C/^{13}C are probably still not satisfactory at the level of theory used. With two existing experimental laboratory studies, results from this model study add little weight.

40 – 46: Somewhere, and probably in this paragraph, the point should be made that, while there is also a CO + Cl removal process, the rate constant for that is typically six times smaller than that for CO + OH, whereas the rate constant for CH_4 + Cl is typically 20 times larger than that for CH_4 + OH. Therefore, Cl is not expected to play a significant role in tropospheric CO removal, except possibly at polar sunrise (Hewitt *et al*, 1996) and it is included in some stratospheric chemistry analyses, see Sander *et al* (2011).

It is normally not considered. None of a few of papers on tropospheric CO mention chlorine as a sink because of the extremely low abundance of Cl and its negligible reaction rate constant with CO. We are glad about this, because the reaction product is not so nice.

We add a paragraph mentioning that after Par. [6], respectively.

47 – 55: This is an important point – i.e. that anomalies observed for δ^{13}CO in both the Antarctic and Arctic are very likely to be caused by stratospheric Cl as shown by Jobson *et al*, 1994, so they do not provide evidence for a wider role due to tropospheric Cl.

We are confused by this statement. Jobson used NMHC ratios changes as evidence for chlorine and bromine during polar sunrise, at the surface. They write: “Thus the data from Alert and the ice floe site provide evidence for Cl and Br atom chemistry during the ozone depletion episodes observed at polar sunrise.”

62: The Young *et al* reference mentioned here is for a study of the night time urban atmospheric chemistry budget in Los Angeles. So, it is not clear why that might be relevant here.

In this short paragraph of the introduction we list some of the recent work on chlorine chemistry research. When we conclude in our paper that there is little tropospheric chlorine, or less than estimated in some papers, we in no way want to injustice to tropospheric chlorine chemistry research.

77: I would suggest that the wording be changed here to avoid this sounding like the work has a foregone conclusion. E.g. it could be “… inferred from ^{13}C isotope enrichment in CH_4, why is this effect not visible as concurrent isotope depletion in CO?

Thank you, we have changed “has been” to “could be”.

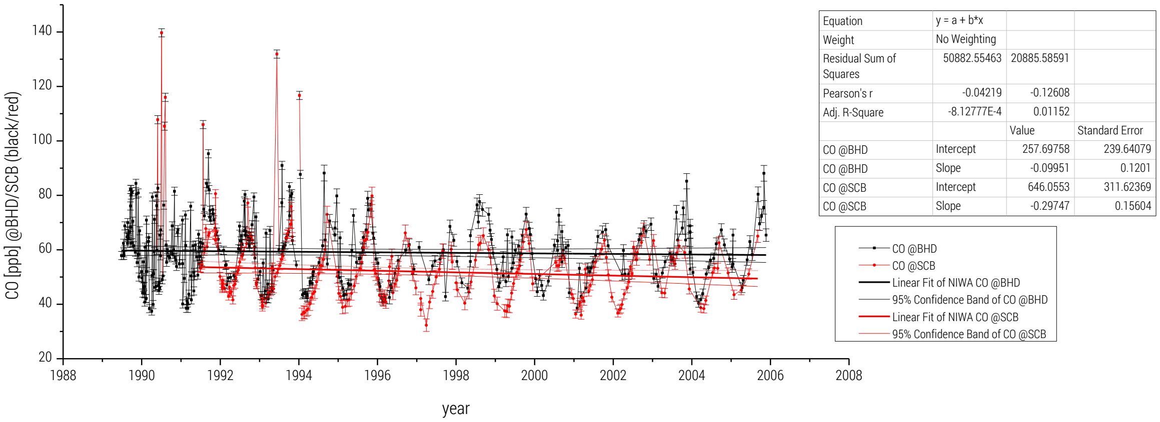
120: this is a minor point, but the samples classified as ‘Scott Base’ in this paper were actually collected at Arrival Heights which is about 4 km from Scott Base in a fenced area labelled ‘entry by permit only’ and reserved for clean air and electromagnetic studies. Some of the NIWA datasets use the abbreviation AHT for this site.

We have added a respective elucidation.

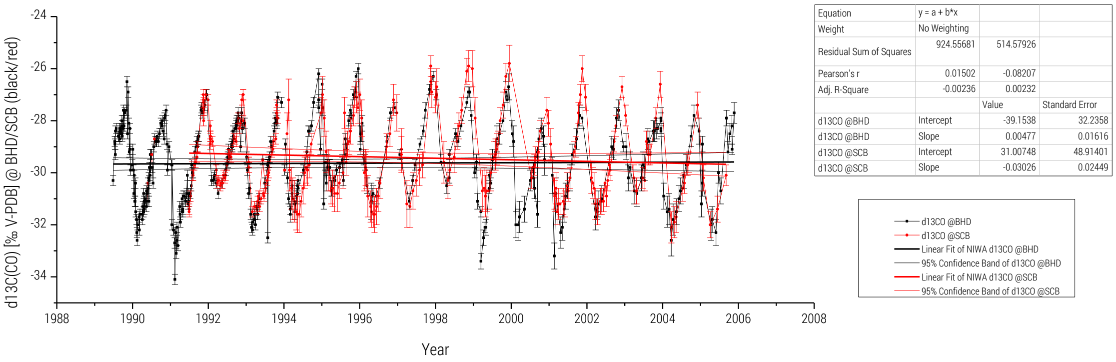
126 – 132: As noted in the general comments, the longer-term records for CO and δ^{13}CO show a decreasing trend in the CO mixing ratio after 1998 and a more obvious trend to lower δ^{13}CO values.

But a more significant issue for the analysis done in this paper is the extent to which interannual variability in the CO budget can alter results based on a constant budget.

Our analysis (see the figure below) of the NIWA station data between 1990−2006 does not confirm any significant trends in CO (we note that the extreme outliers are removed, as described in the manuscript). That is, for [CO] we obtain −0.10±0.12 [nmol/mol/yr] and −0.3±0.16 [nmol/mol/yr] at BHD and SCB, respectively. For δ^{13}C(CO), the slopes are +0.005±0.016 [‰/yr] and −0.030±0.025 [‰/yr] at BHD and SCB, respectively.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	50882.55463	20885.58591	
Pearson's r	-0.04219	-0.12608	
Adj. R-Square	-8.12777E-4	0.01152	
		Value	Standard Error
CO @BHD	Intercept	257.69758	239.64079
CO @BHD	Slope	-0.09951	0.1201
CO @SCB	Intercept	646.0553	311.62369
CO @SCB	Slope	-0.29747	0.15604



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	924.55681	514.57926	
Pearson's r	0.01502	-0.08207	
Adj. R-Square	-0.00236	0.00232	
		Value	Standard Error
d13CO @BHD	Intercept	-39.1538	32.2358
d13CO @BHD	Slope	0.00477	0.01616
d13CO @SCB	Intercept	31.00748	48.91401
d13CO @SCB	Slope	-0.03026	0.02449

Regarding the non-CH_4 CO sources interannual variability issue, please see our reply to the general comment above.

128: It seems that this should be citing Gromov, 2013, Sect 4.1.1.

Yes, indeed, thank you for this correction.

150 – 155: This part of the paragraph brings in results from the following sections and so is hard to follow. Also it is noted here that the data errors are too large to dismiss this ‘Cl-driven difference’ but the conclusion suggests that such a difference can be dismissed. So I would suggest that these points be moved to section 2.4.

We agree to refrain from using the EMAC-derived estimate here. Indeed, it is enough to conservatively assume up to 50% of CO derived from CH_4 and project the Cl-driven change using this figure.

151 – 152: Also the numeric value for ‘times smaller than the errors in Δ‘ is missing in the text.

Corrected.

163 – 166: This paragraph is setting out the basis for Table S1 that gives a global average Cl concentration of 261 atoms cm-3 and which is five times less than the equivalent value given in Hossaini *et al* (2016). As noted in general comment #4, because the same emissions and precursors are being used here as in Hossaini *et al* (2016), it raises questions about the models and the need for some explanation as to why the estimated MBL Cl concentrations can differ this much.

We are confused about this statement. Hossaini *et al.* (2016) write (Sect. 3.4): "Figure 9 shows the simulated annual mean surface [Cl]. We find that CH_3Cl oxidation provides a small [Cl] background of around **$0.5–2\times10^2$ atoms cm^{-3} throughout most of the global boundary layer**. When VSLSs are also considered (i.e., ORG2), annual mean [Cl] reaches a **maximum of 0.5×10^3 atoms cm^{-3}** in ***some coastal regions of the NH***." Inspecting Fig. 9 (ibid.), the latter figure is simulated maxima; we do not see such concentrations the SH MBL, however. We remark that the setup of EMAC resembles the ORG2 setup of Hossaini et al. (2016), which we communicate in Sect. 2.3.

170 – 172: This point could be made more clearly by noting that the very small seasonal cycle seen in CH_4–derived [CO] is largely due to both its production and its removal being proportional to [OH].

Thank you, we agree, simultaneous sink/production of CH_4 and CO via OH is indeed the key factor here. We amend the statement accordingly.

181 – 193: Equation (1) is written as an approximation and part of the reason for that is that it applies to a theoretical equilibrium between the sources and sinks rather than to the continual seasonal changes in both. As noted in the general comments, this appears to be the reason why the net fractionation effect seen here is a lot larger than that derived in Allan *et al* (2007), using the UK Unified Model. Also, the seasonal cycle for Cl removal used in the Allan *et al* papers puts this at a significant level for only 3 months. Consequently, if there is a way to give approximations for the non-equilibrium effects then that could clarify this analysis.

We reiterate that fractionations derived in Allan *et al* papers cannot be compared here – we also do not derive them. Instead we use nominal KIE (ε_m) which should have caused fractionations derived by Allan *et al.* In other words, Allan *et al.* values are what we denote "effective fractionation" η_c for CO. For CH_4, we use nominal sink fractionation ε_m (and denote it with different symbol), which shows how much different in $^{13}C/^{12}C$ ratio the portion of reacted CH_4 molecules (that will become CO) differs from the leftover CH_4. We are not affected by the disequilibrium issues whilst regarding short-lived CO, not long-lived CH_4 (see other comments above).

Table 2: The layout used for this table could be improved to make it clearer by separating the three sections, which each have different column headings. Also, as the ‡ symbol is only used for the last part of the table it could be made clearer by using a subheading mentioning the Allan *et al,* 2007, paper at the top of that section.

We add indent between the sections of this table (it is favourable to use two columns for the variables always distributed in two categories). Thank you for the hint, we add the footnote ref. to the entire subsection.

212: It would read a bit better if this sentence started with "Finally, …"

Changed.

223: This reference to using the same seasonal cycle for OH and Cl is not quite correct as Allan *et al* (2007), and its preceding papers, have used a seasonal variation for Cl in the marine boundary layer based on DMS related species in the Southern Hemisphere and that has a much shorter seasonal cycle than OH.

We have corrected the statement.

254: "none of which" can be read as meaning none of the analyses mentioned in this paragraph, whereas Nisbet *et al* (2016) did explicitly consider different spatial and seasonal distributions of Cl removal – see Table 1 in that publication.

We drop the last part of this sentence.

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