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

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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 summarise 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.

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 $\delta^{13}CO$ values directly and that is why there is no analogue for Fig S3 showing model results for $\delta^{13}CO$ 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.

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 $\delta^{13}Cs$. Neither the mixing ratios nor $\delta^{13}Cs$ 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).

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 $\delta^{13}Cs$, will modify

what is summarised in section 2.4. A more detailed summary of how the EMAC results are being used for $\delta^{13}CO$ might be helpful in this respect.

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.

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.

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.

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.

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.

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.

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%.

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.

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).

47 – 55: This is an important point – i.e. that anomalies observed for $\delta^{13}CO$ 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.

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.

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 CH4, ~~why~~ is this effect ~~not~~ visible as concurrent isotope depletion in CO?

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.

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

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

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.

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

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.

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].

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.

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.

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

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.

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.

References for the comments above that are not included in the paper by S. Gromov *et al*.

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