Supplement of

Using $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ to constrain Arctic methane emissions

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Supplementary Material

Further details on the p-TOMCAT BASE scenario

The kinetic isotope effects for the methane reaction rates used in the model are listed in Table S1. Prescribed surface methane fluxes from anthropogenic sources are taken from EDGAR v4.1 [http://edgar.jrc.ec.europa.eu/overview.php?v=41] for 2005. A seasonal variation has been applied to the EDGAR v4.1 fossil fuel source, following Gurney et al. (2005). Biomass burning emissions are taken from a GFEDv2 climatological average (Van der Werf et al. 2006), and are scaled to 31 Tg yr⁻¹. The geographical and temporal distribution of natural methane emissions from termites, hydrates and wetlands is taken from Fung et al. (1991). Tropical and mid-latitude wetland emissions (<50° N) are scaled to 200 Tg yr⁻¹ (wetland emissions >50° N are left unscaled). Table S2 also shows the source-specific δ¹³C and δD signatures used in the model. As for the fluxes, the isotopic signatures used are all subject to a level of uncertainty. Measurements of source δD signatures are currently much more limited than the δ¹³C signatures and are therefore there is less information about how they vary with source type and region. Out of the δ¹³C source signatures, there is a large uncertainty associated with the δ¹³C isotopic signature of methane emissions to the atmosphere from subsea permafrost and hydrates. This is discussed in Section 6.3. Observations also suggest a wide geographical spread in the δ¹³C signature of emissions from the coal industry (e.g. Zazzeri et al. 2015). In the results presented, we have used a δ¹³C signature for emissions from the coal industry of -50 ‰. However, simulations in which emissions were assigned δ¹³C values of both -35 ‰ and -40 ‰ only had a small impact on the modelled distribution relative to using -50 ‰ and did not influence our conclusions.

Figure S1 shows a comparison of modelled and observed seasonal cycles of methyl chloroform from the NOAA-ESRL halocarbons in situ program at Barrow, Alaska, indicating that the seasonal cycle of the model prescribed OH concentrations is well represented in the Arctic region.

References


### Table S1. Kinetic isotope effects for methane sinks in p-TOMCAT

<table>
<thead>
<tr>
<th>Methane Sink</th>
<th>KIE$^{12C/13C}$</th>
<th>KIE$^{H/D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ + OH</td>
<td>1.0039$^1$</td>
<td>1.29$^5$</td>
</tr>
<tr>
<td>CH$_4$ + Cl</td>
<td>1.066$^{2,3,a}$</td>
<td>1.508$^{4,a}$</td>
</tr>
<tr>
<td>CH$_4$ + O($^1$D)</td>
<td>1.013$^1$</td>
<td>1.06$^1$</td>
</tr>
<tr>
<td>Soil Oxidation</td>
<td>1.018$^6$</td>
<td>1.083$^6$</td>
</tr>
</tbody>
</table>

$^1$Saueressig et al. (2001), $^2$Saueressig et al. (1995), $^3$Crowley et al. (1999), $^4$Saueressig et al. (1996), $^5$This value is within a range of quoted literature values (DeMore et al., 1993, Gierczak et al., 1997, Saueressig et al. 2001, Bergamaschi et al., 2000, Tyler et al., 2007), $^6$Snover et al., (2000), $^a$Kinetic isotope effects are temperature dependent, the value quoted is for 298 K.
Figure S1: A comparison of observed and modelled seasonal cycles for methyl chloroform at Barrow, Alaska (157ºW, 71ºN). NOAA-ESRL observations are shown in black and are for the year 2009; error bars show +/- 1 s.d.. Model data uses 2009 meteorology and is shown in red. Linear trends and annual mean mixing ratios have been removed from both the observational and modelled data.