Supplementary Material

Emission datasets for the p-TOMCAT BASE scenario

The kinetic isotope effects for the methane reaction rates used in the model are listed in Table S1, and the emissions used in the p-TOMCAT BASE scenario described in Table S2. 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 $\delta^{13}C$ 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 $\delta^{13}C$ signatures and are therefore there is less information about how they vary with source type and region. Out of the $\delta^{13}C$ source signatures, there is a large uncertainty associated with the $\delta^{13}C$ 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 $\delta^{13}C$ signature of emissions from the coal industry (e.g. Zazzeri et al. 2015). In the results presented, we have used a $\delta^{13}C$ signature for emissions from the coal industry of -50 ‰. However, simulations in which emissions were assigned $\delta^{13}C$ 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.

References

Bergamaschi, P., Bräunlich, M., Marik, T., and Brenninkmeijer, C. A. M.: Measurements of the carbon and hydrogen isotopes of atmospheric methane at Izaña, Tenerife: Seasonal cycles and synoptic-scale variations, J. Geophys. Res., 105(D11), 14531–14546, doi:10.1029/1999JD901176, 2000.

Bilek, R. S., Tyler, S. C., Kurihara, M. and Yagi, K.: Investigation of cattle methane production and emission over a 24-hour period using measurements of δ13C and δD of emitted CH4 and rumen water, J. Geophys. Res., 106(D14), 15405–15413, doi:10.1029/2001JD900177, 2001.

Crowley, J. N., Saueressig, G., Bergamaschi, P., Fischer, H. and Harris, G. W.: Carbon kinetic isotope effect in the reaction CH4+Cl: a relative rate study using FTIR spectroscopy, Chemical Physics Letters, 303, 268-274, 1999.

Dlugokencky, E. J., Nisbet, E. G., Fisher, R., and Lowry, D.: Global atmospheric methane: budget, changes and dangers, Phil. Trans. R. Soc. A, 369, 2058-2072; doi: 10.1098/rsta.2010.0341, 2011.

Fisher, R. E., Sriskantharajah, S., Lowry, D. , Lanoisellé, M., Fowler, C. M. R., James, R. H., Hermansen, O., Lund Myhre, C., Stohl, A., Greinert, J., Nisbet-Jones, P. B. R., Mienert, J., Nisbet, E. G.: Arctic methane sources: Isotopic evidence for atmospheric inputs, Geophys. Res. Lett., 38, L21803, doi:10.1029/2011GL049319, 2011.

Fung, I., John, J., Lerner, J., Matthews, E., Prather, M., Steele, L. P., and Fraser, P. J.: Three-dimensional model synthesis of the global methane cycle, J. Geophys. Res., 96, 13033-13065, doi:10.1029/91JD01247, 1991.

Gierczak, T., Talukdar, R. K., Herndon, S. C., Vaghjiani, G. L., and Ravishankara, A. R.: Rate Coefficients for the Reactions of Hydroxyl Radicals with Methane and Deuterated Methanes, The Journal of Physical Chemistry, 101 (17), 3125-3134, doi: 10.1021/jp963892r, 1997.

Gupta, M., Tyler, S., and Cicerone, R.: Modeling atmospheric $\delta^{13}CH_4$ and the causes of recent changes in atmospheric CH_4 amounts, J. Geophys. Res., 101(D17), 22923–22932, doi:10.1029/96JD02386, 1996.

Gurney, K. R., Chen, Y.-H., Maki, T., Kawa, S. R., Andrews, A., and Zhu, Z.: Sensitivity of atmospheric CO_2 inversions to seasonal and interannual variations in fossil fuel emissions, J. Geophys. Res., 110, D10308, doi:10.1029/2004JD005373, 2005.

Levin, I., Bergamaschi, P., Dörr, H., Trapp, D.: Stable isotopic signature of methane from major sources in Germany, Chemosphere, 26, 161-177, 1993.

Nakagawa, F., Yoshida, N., Nojiri, Y., Makarov, V. N.: Production of methane from alasses in eastern Siberia: Implications from its ^{14}C and stable isotopic compositions, Global Biogeochem. Cycles, 16(3), doi:10.1029/2000GB001384, 2002a.

Nakagawa, F., Yoshida, N., Sugimoto, A., Wada, E., Yoshioka, T., Ueda, S. and Vijarnsorn, P.: Stable Isotope and Radiocarbon Compositions of Methane Emitted from Tropical Rice Paddies and Swamps in Southern Thailand, Biogeochemistry, 61, 1-19, 2002b.

O'Shea, S. J., Allen, G., Gallagher, M. W., Bower, K., Illingworth, S. M., Muller, J. B. A., Jones, B. T., Percival, C. J., Bauguitte, S. J-B., Cain, M., Warwick, N., Quiquet, A., Skiba, U., Drewer, J., Dinsmore, K., Nisbet, E. G., Lowry, D., Fisher, R. E., France, J. L., Aurela, M., Lohila, A., Hayman, G., George, C. , Clark, D. B., Manning, A. J., Friend, A. D. and Pyle, J., Methane and carbon dioxide fluxes and their regional scalability for the European Arctic wetlands during the MAMM project in summer 2012, Atmos. Chem. Phys., 14, 13159-13174, doi: 10.5194/acp-14-13159-2014, 2014.

Quay, P., Stutsman, J., Wilbur, D., Snover, A., Dlugokencky, E. J., Brown, T., The isotopic composition of atmospheric methane, Global Biogeochem. Cycles, 13(2), 445–461, doi:10.1029/1998GB900006, 1999.

Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., Harris, G. W., Carbon kinetic isotope effect in the reaction of CH4 with Cl atoms, Geophys. Res. Lett., 22, 1225–1228, doi: 10.1029/95GL00881, 1995.

Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., Harris, G. W.: D/H kinetic isotope effect in the reaction CH4+Cl, Geophys. Res., 23, 3619–3622, doi: 10.1029/96GL03292, 1996.

Saueressig, G., Crowley, J. N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C. A. M. and Fischer, H.: Carbon 13 and D kinetic isotope effects in the reactions of CH4 with O(1 D) and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane, J. Geophys. Res., 106(D19), 23127–23138, doi:10.1029/2000JD000120, 2001.

Schoell. M.: The hydrogen and carbon isotopic composition of methane from natural gases of various origins, Geochimica et Cosmochimica Acta, 44, 649-661, 1980.

Snover, A. K., *and* Quay, P. D.: Hydrogen and carbon kinetic isotope effects during soil uptake of atmospheric methane, Global Biogeochem. Cycles, 14*(*1*)*, 25–39, *doi:*10.1029/1999GB900089, *2000a.*

Snover, A. K., Quay, P. D., and Hao, W. M.: The D/H content of methane emitted from biomass burning, Global Biogeochem. Cycles, 14(1), 11–24, doi:10.1029/1999GB900075, 2000b.

Sriskantharajah, S., Fisher, R. E., Lowry, D., Aalto, T., Hatakka, J., Aurela, M., Laurila, T., Lohila, A., Kuitunen, E. and Nisbet, E. G., Tellus B, 64, 18818, http://dx.doi.org/10.3402/tellusb.v64i0.18818, 2012.

Tyler, S. C., Zimmerman, P. R., Cumberbatch, C., Greenberg, J. P., Westberg, C., and Darlington, J. P. E. C.: Measurements and interpretation of $\delta^{13}C$ of methane from termites, rice paddies, and wetlands in Kenya, Global Biogeochem. Cycles, 2, 341–355, doi:10.1029/GB002i004p00341, 1988.

Tyler, S. C., Rice, A. L. and Ajie, H. O.: Stable isotope ratios in atmospheric CH4: Implications for seasonal sources and sinks, J. Geophys. Res., 112, D03303, doi:10.1029/2006JD007231, 2007.

Umezawa, T., Machida, T., Ishijima, K., Matsueda, H., Sawa, Y., Patra, P. K., Aoki, S. and Nakazawa, T.: Carbon and hydrogen isotopic ratios of atmospheric methane in the upper troposphere over the Western Pacific, Atmos. Chem. Phys., 12, 8095-8113, doi:10.5194/acp-12-8095-2012, 2012.

Van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., and Arellano, Jr., A. F.: Interannual variability in global biomass burning emissions from 1997 to 2004, Atmos. Chem. Phys., 6, 3423–3441, 2006.

Waldron, S., Lansdown, J. M., Scot, E. M., Fallick, A. E., and Hall, A.. J.: The global influence of the hydrogen isotope composition of water on that of bacteriogenic methane from shallow freshwater environments, Geochimica et Cosmochimica Acta**,** 63, 2237-2245**,** doi:10.1016/S0016-7037(99)00192-1**,** 1999.

Whiticar, M. and Schaefer, H.: Constraining past global tropospheric methane budgets with carbon and hydrogen isotope ratios in ice, Philos. Trans. R. Soc. A, 365, 1793-1828, 2007.

Zazzeri, G., Lowry, D., Fisher, R. E., France, J. L., Lanoisellé, M. and Nisbet E. G., Plume mapping and isotopic characterisation of anthropogenic methane sources, Atmos. Environ. 110, 151-162, doi:10.1016/j.atmosenv.2015.03.029, 2015.

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

Methane Sink	$KIE^{12C/13C}$	$KIE^{H/D}$
CH_4 + OH	1.0039[1]	1.29[5]
CH_4 + Cl	1.066[2,3,a]	1.508[4,a]
CH_4 + $O(^1D)$	1.013[1]	1.06[1]
Soil Oxidation	1.018[6]	1.083[6]

[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 (Gierczak et al., 1997, Saueressig et al. 2001, Bergamaschi et al., 2000, Tyler et al., 2007), [6]Snover et al., (2000a), [a]Kinetic isotope effects are temperature dependent, the value quoted is for 298 K.

Table S2. Global methane source magnitudes and isotopic signatures used in p-TOMCAT

Surface Source/Sink	Global flux (Tg/yr)	High latitude (>50°N) flux (Tg/yr)	$\delta^{13}C-CH_4$ (‰)	$\delta D-CH_4$ (‰)
Northern Wetlands	30	30.0	-70[d,h,l,n*]	-360[f,n*]
Tropical Wetlands	200	0.0	-55[b,m*]	-320[g,o*]
Hydrates	5	5.0	-55[d*]	-190[p]
Coal	40	3.2	-50[i,q*]	-140[p]
Gas	63	15.3	-40[b,n*]	-185[i,j,n*]
Biomass burning	31	3.1	-26[b]	-210[k]
Ruminants	110	8.0	-63[a,c*]	-360[a*]
Landfills	27	4.6	-53[b]	-310[i,p]
Sewage	29	1.8	-57[b]	-310[r]
Rice	33	0.0	-62[b,g,m*]	-330[p*]
Termites	20	1.1	-57[e,m*]	-390[p]
Total	588	72.1		

Source isotopic signature data are based on reported values from: [a]Bilek et al., 2001, [b]Dlugokencky et al., 2011, [c]Levin et al., 1993, [d]Fisher et al., 2011, [e]Gupta et al., 1996, [f]Nakagawa et al., 2002a, [g]Nakagawa et al., 2002b, [h]O'Shea et al., 2014, [i]Quay et al., 1999, [j]Schoell, 1980, [k]Snover et al., 2000b, [l]Sriskantharajah et al., 2012, [m]Tyler et al., 1988, [n]Umezawa et al., 2012, [o]Waldron et al., 1999, [p]Whiticar and Schaefer, 2007 , [q]Zazzeri et al., 2015, [r]value used taken from landfill data, *value is within a range of quoted literature estimates..