

Comments on:
**“Interpreting methane variations in the past two decades using
measurements of CH₄ mixing ratio and isotopic composition”,
by G. Monteil, S. Houweling, E.J. Dlugokencky, G. Maenhout, B.H.
Vaughn, J.W.C. White, and T. Rockmann
Atmos. Chem. Phys. Discuss., 11, 6671–6803**

Substantive comments:

1. The authors undertake a nice study of the global methane budget and its likely evolution over the past two decades, including a few scenarios that test assumptions about key source and sink strengths. However, in my view, the range of scenarios is quite restrictive, failing to consider the possible implications of some recent developments reported in the literature. These are covered in the remaining “substantive comments”.
2. The authors do not address the possibility of a tropospheric chlorine sink which according to Allan et al. (2007) removes about 25 Tg yr⁻¹ (inter-annually varying with a range 13–37 Tg yr⁻¹) from the marine boundary layer. Such a sink, although natural, should be seen in the context of a mismatch between the authors’ modelled source and sink, $\Delta F(t)$, (source exceeds sink by too much) during the anthropogenic era, averaging 25.9 Tg yr⁻¹ over 2000–08 (p. 6783). The chlorine sink has strong ramifications for isotopic balance as it strongly discriminates between ¹³CH₄ and ¹²CH₄, suggesting that a sink-weighted isotopic fractionation factor for tropospheric removal could be near 0.992 (Lasseby et al., 2007).
3. In discussing natural geologic emissions, the authors attribute to Etiope and Klusman (2002) a range of 30–70 Tg yr⁻¹ from “terrestrial [sources] and oceanic mud volcanoes” (p.6778). Yet the authors restrict consideration to a single “intermediate value” of 15 Tg yr⁻¹, supplemented by oceanic emissions of 28 Tg yr⁻¹, the latter given a biogenic signature without attribution (Table 1). However, in their abstract Etiope and Klusman (*op cit*) describe mud volcanoes as “the largest visible expression of geologic methane emission”, attesting to their terrestrial (not oceanic) manifestation. In a more recent paper, Etiope et al. (2008) assess the global geologic source as dominantly terrestrial with strength 53±11 Tg yr⁻¹. Moreover, the mud volcanoes at least are predominantly thermogenic, with ¹³C “more isotopically enriched than -50‰” (Etiope et al., 2009). The strength of the geologic source has an appreciable effect on isotope balance.
4. A recent paper by Neef et al. (2010) reported a comparable study that looked at the present-day global methane budget constrained by ¹³C/¹²C ratios, including the consideration of various scenarios of source and sink strengths that include the tropospheric chlorine sink and a strong geologic source, favouring a 19–30% fossil source. The present authors do not cite the Neef et al. study, despite its topicality and the relevance of its conclusions about the strengths of sources and sinks.

Minor comments:

5. On p. 6773, Lines 10–11, how can a 2003 paper (by Dlugokencky et al.) support a statement about “the stable methane concentration between 1999 and 2007”?
6. On p. 6779, Lines 4–10, I cannot follow what is being described. It looks like the “original inventories” of 182 Tg yr⁻¹ for wetlands (p. 6778, Line 11) and for biomass burning (unquantified on p. 6777, yet probably in the range 14–88 Tg yr⁻¹) are being scaled by 1.45 and 2 respectively leading to “global emissions ... listed in Table 1”. Yet

the respective values in Table 1 are 182 and 30 Tg yr⁻¹. To what does the “scaling” refer, and why is it undertaken?

7. On p. 6780, Line 20 and p. 6781, Line 2, Allan et al. (2005) are cited (but with an truncated authorship) as the source of NIWA ground-based measurement — and, moreover, the source of such measurements to 2007! Allan et al. do not present NIWA measurements in detail such as through charts or tables (that paper is about the chlorine sink: see Comment #2). A better reference with the most up-to-date NIWA records would be Lassey et al. (2010).
8. The multiplier H introduced on p. 6782 does not seem to be mentioned again after Equation (6). The ‘optimal’ value for H would be very useful to many readers. It appears to be analogous to the value 2.767 Tg ppb⁻¹ apparently first proposed by Dlugokencky et al. (1998).
9. On p. 6783, Lines 10–11 read rather oddly: “ $\Delta F(t)$ starts to increase rapidly, reaching a minimum value of -40 Tg in 2005”. I think it should be the magnitude of $\Delta F(t)$ that increases rapidly, and that its minimum value has units Tg yr⁻¹. On Line 12, the standard deviation of 9.4 should also have these same units.

References cited:

- Allan, W., Lowe, D.C., Gomez, A.J., Struthers, H., Brailsford, G.W., 2005. Interannual variation of ¹³C in tropospheric methane: Implications for a possible atomic chlorine sink in the marine boundary layer. *J. Geophys. Res.* 110, D11306, doi:11310.11029/12004JD005650.
- Allan, W., Struthers, H., Lowe, D.C., 2007. Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with southern hemisphere measurements. *J. Geophys. Res.* 112, D04306, doi:04310.01029/02006JD007369.
- Dlugokencky, E.J., Masarie, K.A., Lang, P.M., Tans, P.P., 1998. Continuing decline in the growth rate of the atmospheric methane burden. *Nature* 393, 447–450.
- Etioppe, G., Klusman, R.W., 2002. Geologic emissions of methane to the atmosphere. *Chemosphere* 49, 777–789.
- Etioppe, G., Lassey, K.R., Klusman, R.W., Boschi, E., 2008. Reappraisal of the fossil methane budget and related emission from geologic sources. *Geophys. Res. Lett.* 35, L09307, doi:09310.01029/GL2008033623.
- Etioppe, G., Feyzullayev, A., Baciu, C.L., 2009. Terrestrial methane seeps and mud volcanoes: a global perspective of gas origin. *Mar. Petrol. Geol.* 26, 333–344.
- Lassey, K.R., Etheridge, D.M., Lowe, D.C., Smith, A.M., Ferretti, D.F., 2007. Centennial evolution of the atmospheric methane budget: What do the carbon isotopes tell us? *Atmos. Chem. Phys.* 7, 2119–2139.
- Lassey, K.R., Brailsford, G.W., Bromley, A.M., Martin, R.J., Moss, R.C., Gomez, A.J., Sherlock, V., Allan, W., Nichol, S.E., Schaefer, H., Connor, B.J., Robinson, J., Smale, D., 2010. Recent changes in methane mixing ratio and its ¹³C content observed in the southwest Pacific region. *J. Integr. Environ. Sci.* 7, 109–117.
- Neef, L., van Weele, M., van Velthoven, P., 2010. Optimal estimation of the present-day global methane budget. *Global Biogeochem. Cycles* 24, GB4024, doi:4010.1029/2009GB003661.