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Stable isotopes provide revised global limits of aerobic methane emissions from plants

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Abstract. Recently Keppler et al. (2006) discovered a surprising new source of methane – terrestrial plants under aerobic conditions, with an estimated global production of 62–236 Tg yr^{-1} by an unknown mechanism. This is ∼10–40% of the annual total of methane entering the modern atmosphere and ∼30–100% of annual methane entering the pre-industrial (0 to 1700 AD) atmosphere. Here we test this reported global production of methane from plants against ice core records of atmospheric methane concentration (CH_4) and stable carbon isotope ratios ($\delta^{13}CH_4$) over the last 2000 years. Our top-down approach determines that global plant emissions must be much lower than proposed by Keppler et al. (2006) during the last 2000 years and are likely to lie in the range 0–46 Tg yr^{-1} and 0–176 Tg yr^{-1} during the pre-industrial and modern eras, respectively.

1 Introduction

Atmospheric methane (CH_4) is an important greenhouse gas that impacts atmospheric chemistry and has almost tripled in abundance since pre-industrial times. The inclusion of large methane emissions from plants via an unknown biological production mechanism as proposed by Keppler et al. (2006) has important multidisciplinary scientific implications. Consequently the discovery is currently subject to methodological scrutiny and requires substantial experimental validation under realistic field conditions. The Keppler et al. (2006) methodology assumed that measured emissions from chambered plants were globally representative and scaleable to annual net primary production (adjusted for seasonal and daylight lengths for different plant types). Extrapolation of their bottom-up measurements resulted in large uncertainties and could overestimate global plant emissions.

Emitted methane from tropical plants has been suggested (Keppler et al., 2006) to help explain the surprisingly high methane concentrations observed by satellite over tropical forests (Frankenberg et al., 2005, 2006). Recently reported methane emissions from Brazilian forests (4–38 Tg yr^{-1} Carmo et al., 2006) and from Venezuelan savannah and forests (∼30–60 Tg yr^{-1} Crutzen et al., 2006) may be produced by plants but could also include some contribution from anaerobic methane sources. Alternative calculations to extrapolate the Keppler et al. (2006) results to the global scale, however, estimate that global plant emissions are only ∼10–60 Tg yr^{-1} based on foliage biomass and photosynthetic rates (Kirschbaum et al., 2006) or ∼53 Tg yr^{-1} based on leafy and non-leafy biomass (Parsons et al., 2006), and are much lower than the 62–236 Tg yr^{-1} deduced by Keppler et al. (2006), while other model simulations suggest that modern and pre-industrial global plant emissions are as large as ∼125 Tg yr^{-1} and ∼85 Tg yr^{-1}, respectively (Houweling et al., 2006) – see Schiermeier (2006) for summary of recent estimates.

Although a prominent role of plant emissions in the pre-industrial atmosphere was proposed by Keppler et al. (2006), here we show that plant emissions are likely to be much smaller than they initially proposed and are not essential to close the isotopic mass balance of atmospheric methane.

2 Methods

To determine tighter limits on global plant emissions we first postulate fossil and biomass burning emissions in the pre industrial and modern eras then calculate anaerobic and aerobic sources to balance observed atmospheric composition. The

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Table 1. Upper limits of global CH_4 emissions from plants.

To calculate the "Maximum Estimate" of the plant source, we use lowest reported values of fossil and biomass burning emissions (see notes a and b). The plant source upper limits decrease further in the "Best Estimate" calculations where more likely values are used for fossil and biomass burning emissions (see notes c and d). A C_3:C_4 plant type ratio of 60:40 is consistent with previous studies (Ferretti et al., 2005; Keppler et al., 2006) and with global $\delta^{13}CH_4$ source signatures from biomass burning, plants, and anaerobic sources of −19.8‰, −49.8‰, and −60‰, respectively. Anaerobic and aerobic plant emissions cover a range because we allow for: (i) uncertainties in the weighted-mean value of the CH_4 sink fractionation factor between −7‰ and −5‰ (Lassey et al., 2005); and (ii) variations in the C_3:C_4 plant type ratio from 40:60 to 60:40. The resulting variation in the weighted-mean $\delta^{13}CH_4$ source signatures are: biomass burning (−19.8 to −17.2‰), plant (−49.8 to −48.7‰), and anaerobic sources (−60 to −58‰) (see Table 2). The fossil source signature is held constant at −40‰.

	Source Type	0 to 1000 AD emissions ($Tg\,yr^{-1}$)	Changes 1000 to 1700 AD[e] (Tg)	1700 AD emissions ($Tg\,yr^{-1}$)	2000 AD emissions ($Tg\,yr^{-1}$)
Maximum Estimate	Fossil[a]	10	(0)	10	82
	Biomass burning[b]	10	(−5)	5	21
	Anaerobic	178–91	(+41)	222–128	487–274
	Aerobic plant	34–121	(−22)	9–103	0–213
Best Estimate	Fossil[c]	19	(0)	19	91
	Biomass burning[d]	25	(−10)	15	26
	Anaerobic	188–144	(+22)	212–166	473–297
	Aerobic plant	0–44	(+2)	0–46	0–176

[a] The fossil source includes CH_4 emissions from natural geologic and ocean sources together with anthropogenic coal mining and energy use with a $\delta^{13}CH_4$ signature of −40‰. We assume no anthropogenic fossil emissions in the interval 0–1700 AD and take the lowest reported estimates of both natural (Judd et al., 1993) and anthropogenic (Scheehle and Kruger, 2006) fossil emissions.

[b] A lower natural limit of ~1.2 Pg C yr^{-1} from lightning induced wildfires (Venevsky, 2006) translates to ~10 Tg yr^{-1} of CH_4 from biomass burning, using a typical emission factor of 9 mmol CH_4/mol C derived from Andreae and Merlet (2001). We ignore pre-industrial anthropogenic biomass burning emissions. Our lower limit of modern biomass burning emissions is determined by neglecting natural biomass burning emissions and assuming only anthropogenic emissions (Scheehle and Kruger, 2006).

[c] Here we use larger and more commonly reported values for natural fossil emissions (Houweling et al., 2000) although it is possible that natural fossil emissions could be much higher (e.g. Etiope, 2004). We use a conservative estimate for modern anthropogenic fossil emissions (Scheehle and Kruger, 2006).

[d] Here we use larger and more likely pre-industrial biomass burning emissions (Ferretti et al., 2005; Venevsky, 2006; Subak, 1994). We use conservative values for modern biomass burning emissions from natural (5 Tg yr^{-1}) and anthropogenic (Scheehle and Kruger, 2006) sources.

[e] These source changes are approximate and required to match the 2‰ $\delta^{13}CH_4$ depletion and the 14 Tg total source increase between 1000 to 1700 AD determined from ice core data (Ferretti et al., 2005). Note 0 to 1000 AD has a total source of 232 Tg yr^{-1} and $\delta^{13}CH_4$≈-47‰, 2000 AD has a total source of 590 Tg yr^{-1} and $\delta^{13}CH_4$≈−47‰.

[f] We have deduced the individual methane source components so that the overall isotopic signature of the "Maximum Estimate" and "Best Estimate" are identical. However our presented results have been rounded so recalculating the overall isotopic signature of the "Maximum Estimate" and "Best Estimate" should not be expected to give exact results.

atmospheric constraint is given by CH_4 mass balance and stable carbon-isotope ratios ($\delta^{13}CH_4$) over the last 2000 years recovered from ice core air bubbles (Ferretti et al., 2005). From independent assessments of fossil and biomass burning we take the lowest reported emissions to constrain the anaerobic/aerobic mix in our "Maximum Estimate" of the plant source, while higher and more probable fossil and biomass burning emissions constrain our "Best Estimate" of the plant source (see Table 1). We allow for $\delta^{13}CH_4$ source signature variations and CH_4 sink fractionation uncertainties (see Tables 1 and 2).

3 Results and discussion

Our results (Table 1) show that the "Maximum Estimate" of pre-industrial and modern global plant emissions are in the ranges 34–121 Tg yr^{-1} and 0–213 Tg yr^{-1}, respectively, lower than reported by Keppler et al. (2006). However, global biomass burning emissions at 1700 AD are very unlikely to be as low as 5 Tg yr^{-1} because even lightning-induced wildfires alone (i.e. zero anthropogenic contribution) are likely to be more than 5 Tg yr^{-1} (see Table 1, note b) and higher pre-industrial biomass burning and fossil emissions in our "Best Estimate" compare well with other studies (Ferretti et al., 2005; Subak, 1994; Scheehle and Kruger, 2006; Houweling et al., 2000). Thus our "Best Estimate" is a more reasonable methane budget reconstruction, suggesting that pre-industrial and modern plant emissions are most likely to be in the ranges 0–46 Tg yr^{-1} and 0–176 Tg yr^{-1}, respectively. In our approach for constructing the "Best Estimate" of the methane budget, we use a comprehensive and very recent reconstruction of pre-industrial biomass burning emissions (Ferretti et al., 2005) that was constrained by the large atmospheric $\delta^{13}CH_4$ depletion from −47 to −49 ‰ during 1000–1700 AD. While it is possible to construct a 1000 AD budget with 85 Tg yr^{-1} of plants, as suggested by Houweling et al. (2006), and with only 15 Tg yr^{-1} of biomass burning, balancing the atmospheric variations during 1000–1700 AD requires a reduction in biomass burning to less than 10 Tg yr^{-1} by 1700 AD. However, lightning-induced wildfires alone are very likely to be more than 10 Tg yr^{-1} (Table 1, note b) so the Ferretti et al. (2005) estimate of pre-industrial biomass burning is still the most reasonable

Table 2. Uncertainties in the global methane budget for sources (a) and sinks (b).

[a] C_3 and C_4 components from Ferretti et al. (2005), Keppler et al. (2006).

[b] Values from Lassey et al. (2005), Table II. ε_{sink} is the sink "kinetic isotope effect" (KIE).

[c] Methane is largely removed from the stratosphere by various processes that discriminate against $^{13}CH_4$ leaving a minor return flux of ^{13}C-enriched methane that we ignore. Consequently, and consistently with IPCC assessments, the stratosphere is viewed as a transport-mediated tropospheric sink, a process which is isotopically neutral.

[d] If the recent Allan et al. (2006) estimate of the global chlorine sink strength is used (25±12 Tg yr^{-1}) the upper limits of global CH_4 emissions from plants presented in Table 1 would decrease even further.

(a) Source $\delta^{13}CH_4$(‰) [a]	C_3	C_4	40:60	60:40
Biomass Burning	−25	−12	−17.2	−19.8
Aerobic Plant	−52	−46.5	−48.7	−49.8
Anaerobic	−64	−54	−58	−60

(b) Sinks[b]	(Tg yr^{-1})	ε_{sink} (‰)
OH	490±85	−4.65±0.75
Soil	30±15	−20±0.2
Stratosphere	40±8	0±0 [c]
Chlorine	10±9 [d]	−60±1
TOTAL	570±87	−6±1

reconstruction, even with the inclusion of plant emissions into the methane budget.

The Ferretti et al. (2005) reconstruction of biomass burning is based on a top down approach in which atmospheric measurement uncertainties translate to a reconstructed biomass burning emission uncertainty of ±1 Tg. If the biomass burning source varies by this uncertainty, then plant emissions only vary by ±8 Tg yr^{-1}. Therefore small changes in biomass burning do not significantly affect plant emissions and our conclusions. Considering fossil emission uncertainties (±1 Tg yr^{-1}) in a similar way, plant emissions only change by ±2 Tg yr^{-1}, so our conclusions are also not significantly affected by uncertainties in our postulated sources.

To account for the uncertainties associated with the stable carbon isotope values of each source, including that of the plant source isotope value, our approach is to consider two scenarios in which we vary the C_3:C_4 plant type ratio between 40:60 and 60:40. As well as being a plausible range of environmental change, this introduces an uncertainty in the isotopic composition of each source which is similar to that associated with bottom up estimates of the isotopic composition of each source type (Table 2a). Since the assigned isotope values of plant emissions are still not known with certainty, the range of C_3:C_4 mix allows us to gauge the effect of this uncertainty. We also consider sink uncertainties in the global methane budget so that the total aggregate sink encompasses a large range of errors (Table 2b) and is not significantly affected by estimated changes in OH between modern and pre-industrial times (Houweling et al., 2000). These source and sink uncertainties in the global methane budget cause our calculated results of revised global limits of aerobic methane emissions from plants to contain accumulated uncertainties that are reflected as a relatively large range of possible values (Table 1).

Large pre-industrial $\delta^{13}CH_4$ variations have been partially explained by natural temperature and precipitation changes causing anaerobic and biomass burning emission variations (Ferretti et al., 2005). Even though there is no evidence yet for significant temperature dependency of methane emissions from plants over ambient ranges (∼10–30°C) it is likely that during 1000–1700 AD a cooling climate with increasing moisture availability, together with changes in both anthropogenic deforestation and natural vegetation re-growth, may have combined to maintain near-constant plant emissions, thus explaining the relatively small change in "Best-Estimate" plant emissions during 1000–1700 AD (see Table 1).

The "Maximum estimate" of plant emissions is a scenario in which we minimize pre-industrial biomass burning levels and variations in a very conservative way by ignoring both pre-industrial anthropogenic and modern natural biomass burning emissions (see Table 1, note b). However our "Best Estimate" scenario, which is based on more complete and recent evidence of comparatively higher fossil and biomass burning emissions (see Table 1, notes c and d), is more likely to occur than the "Maximum Estimate" scenario. Thus, while Keppler et al. (2006) argue that pre-industrial $\delta^{13}CH_4$ variations (Ferretti et al., 2005) could not be reconciled with a wetland-dominated source, our analysis shows that a wetland-dominated pre-industrial source reconstruction with variable biomass burning emissions is more likely to have caused pre-industrial $\delta^{13}CH_4$ variations than one controlled by large plant emission variations.

4 Conclusions

Our "Best Estimate" of the methane budget suggests that pre-industrial and modern plant emissions are likely to be in the ranges 0–46 Tg yr^{-1} and 0–176 Tg yr^{-1}, respectively. Therefore, while there is scope in the methane budget for plant emissions, they are not essential to reconcile either the pre-industrial or the modern methane budgets.

Although our top-down approach allows increased plant emissions during the industrial era, modern plant emissions are likely to be lower than pre-industrial plant emissions due to the reduction in total biomass that has occurred from anthropogenic deforestation and land use change during 1700–2000 AD (Schlesinger, 1991). Therefore, during both the pre-industrial and modern eras, the best estimate of global plant emissions is likely to lie in the range 0–46 Tg yr^{-1} and be at least 80% lower than proposed by Keppler et al. (2006). The good agreement between our top-down best estimate (0–46 Tg yr^{-1}) and bottom-up reassessments of plant emissions ($\sim$10–60 Tg yr^{-1} Kirschbaum et al., 2006; $\sim$53 Tg yr^{-1} Parsons et al., 2006) corroborates our conclusion that plant emissions are likely to be much lower than initially reported by Keppler et al. (2006).

The plant source limits are most sensitive to the sink fractionation and if a larger magnitude fractionation is used (e.g. $-7.4‰$, Ferretti et al., 2005, which is consistent with a global chlorine sink of 25 Tg yr^{-1} – see Allan et al., 2006) the upper limits of our best estimate of the plant source would decrease even further.

Besides some small differences between the assumed atmospheric composition and sink-weighted fractionation factor, the main reason for our lower estimate of pre-industrial plant emissions (46 Tg yr^{-1}) compared to the Houweling et al. (2006) estimate (85 Tg yr^{-1}) is that the Houweling et al. (2006) estimate of biomass burning emissions at 1000 AD (15 Tg yr^{-1}) is significantly lower than ours (25 Tg yr^{-1}). However, the atmospheric constraint during 1000–1700 AD causes biomass burning in the Houweling et al. (2006) budget to decrease below the lower feasible limit of natural wildfires.

Clearly, a lot remains to be learnt about the pre-industrial and modern methane budgets. Further field and laboratory studies are needed to better define methane emissions from plants and new ice core records of carbon and hydrogen isotopes in atmospheric methane throughout the Holocene are required to better constrain the pre-industrial methane budget.

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