

Rapid communication:**A comment on the quantitative significance of aerobic methane release by plants**

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Abstract. A recent study by Keppler *et al.* (2006; Nature **439**, 187–191) demonstrated CH₄ emission from living and dead plant tissues under aerobic conditions. This work included some calculations to extrapolate the findings from the laboratory to the global scale and led various commentators to question the value of planting trees as a greenhouse mitigation option. The experimental work of Keppler *et al.* (2006) appears to be largely sound, although some concerns remain about the quantification of emission rates. However, whilst accepting their basic findings, we are critical of the method used for extrapolating results to a global scale. Using the same basic information, we present alternative calculations to estimate global aerobic plant CH₄ emissions as 10–60 Mt CH₄ year⁻¹. This estimate is much smaller than the 62–236 Mt CH₄ year⁻¹ reported in the original study and can be more readily reconciled within the uncertainties in the established sources and sinks in the global CH₄ budget. We also assessed their findings in terms of their possible relevance for planting trees as a greenhouse mitigation option. We conclude that consideration of aerobic CH₄ emissions from plants would reduce the benefit of planting trees by between 0 and 4.4%. Hence, any offset from CH₄ emission is small in comparison to the significant benefit from carbon sequestration. However, much critical information is still lacking about aerobic CH₄ emission from plants. For example, we do not yet know the underlying mechanism for aerobic CH₄ emission, how CH₄ emissions change with light, temperature and the physiological state of leaves, whether emissions change over time under constant conditions, whether they are related to photosynthesis and how they relate to the chemical composition of biomass. Therefore, the present calculations must be seen as a preliminary attempt to assess the global significance from a basis of limited information and are likely to be revised as further information becomes available.

Keywords: climate change, greenhouse gas, methane, plants, source.

Introduction

The atmospheric CH₄ concentration has increased from a pre-industrial concentration of less than 700 to ~1750 ppb at present, with little change over the last five years [Ehhalt *et al.* 2001; see <http://www.cmdl.noaa.gov/ccgg/iadv/> or <http://gaw.kishou.go.jp/wdcgg.html> (both verified 29 March 2006) for the most recent data]. It had been thought that all the major sources and sinks had been identified,

although with significant uncertainties still remaining about the exact magnitude of each identified source and sink (Ehhalt *et al.* 2001; Wang *et al.* 2004; Frankenberg *et al.* 2005; do Carmo *et al.* 2006).

Keppler *et al.* (2006) recently reported that CH₄ was emitted from dead and living plant material under aerobic conditions. This was a surprising finding as CH₄ emission and uptake from various systems has been studied for a long time

Abbreviations used: CO₂e, CO₂ equivalent; NPP, net primary production.

and it had always been thought that CH₄ production occurs only under anaerobic conditions, such as in flooded soils, guts of ruminant animals, or during incomplete combustion in fires. Keppler *et al.* (2006) also attempted to use their data to provide an estimate of the possible global significance of aerobic CH₄ emissions from plants. They derived a surprisingly large estimate of 62–236 Mt CH₄ year⁻¹, which suggested that the aerobic release by plants could constitute one quarter of total current global CH₄ emissions.

Hence, the new findings caused a flood of media statements, partly spurred on by an opinion piece by Lowe (2006) that accompanied the original article in *Nature*. This opinion article implied that the new finding by Keppler *et al.* (2006) will require a major rethink of the global CH₄ budget and a re-assessment of the value of planting trees as a greenhouse mitigation strategy.

The original study by Keppler *et al.* (2006) provided only scant data for extrapolation to the global scale. Nonetheless, such scaling up is required to evaluate whether the new findings might necessitate an immediate re-evaluation of current climate-change mitigation options, especially in relation to planting trees.

In this paper, we attempt to provide an estimate of the global significance of aerobic CH₄ emission from plants because we believe that the approach used by Keppler *et al.* (2006) contained some methodological inconsistencies. In our alternative approach, we used two different methods for estimating global emissions. We also attempt to quantitatively assess the significance of aerobic plant CH₄ emissions in modifying the value of planting trees for climate mitigation.

Methodology

Estimate of global methane emission

The Keppler approach

The only information currently available on aerobic CH₄ emissions is that published by Keppler *et al.* (2006) in their paper and its accompanying information. They found that CH₄ was emitted from dead and living tissue of several species, and that emission rates increased with increasing temperature or exposure to sunlight. However, we believe that their method for scaling to global emissions is inappropriate and dimensionally inconsistent. They multiplied their observed CH₄ emission rates (in units of CH₄ per unit of dry mass per unit of time), by estimates of net primary production (NPP in units of carbon per unit of area per unit of time) to estimate global CH₄ emissions per year. As both parameters are rates, their product attains the units of CH₄ per unit of time squared.

Keppler *et al.* (2006) used NPP as the basis of their calculations to provide an estimate of the growth of new tissue formed within a given year. This estimate of functionally active biomass, they believed, could be equated with the biomass in their measuring system. Implicit in this calculation method are the assumptions that all newly formed tissue contributes equally to total CH₄ emissions and that emission rates are constant for a whole season and then cease.

However, this is likely to overestimate the amount of aerobic CH₄ emission because (1) a large part of NPP is allocated to roots which do not emit CH₄ at the same rate as light-exposed tissue, (2) woody material receives little light and is metabolically inert so that it is likely to also

emit less CH₄ than light-exposed and more metabolically-active tissue, and (3) a proportion of soft tissue, such as leaves, is shed in senescence or eaten by herbivores so that the duration of possible CH₄ emission extends for much less than the full growing season.

We, therefore, used two alternative methods that are methodologically consistent for scaling to the global rate. The first assumes that leaves are responsible for most aerobic CH₄ emissions, and we estimated global CH₄ emission by multiplying the observed emission rates per unit dry mass by estimates of the standing biomass of leaves in different biomes. The second method assumes that the ratio of photosynthesis to aerobic CH₄ emission is relatively constant and that global CH₄ emissions can be calculated from estimates of photosynthesis.

Leaf-mass-based estimates

For each of eight major biomes, we estimated CH₄ emissions, m_b , as:

$$m_b = asBf_f[Dm_l + (24 - D)m_d], \quad (1)$$

where a is the area of each biome (ha), B an estimate of biomass density in each biome (kg DW ha⁻¹), f_f the fraction of biomass contained in foliage, D effective daylight hours (h d⁻¹), m_l and m_d (kg CH₄ kg⁻¹ DW h⁻¹) the respective CH₄ emission rates in the light and dark as determined by Keppler *et al.* (2006) and s is season length (d year⁻¹), an estimate of the time in each year over which conditions are conducive for metabolic activity when temperatures are moderate and water is available for plants. We used the same categorisation into different biomes as Keppler *et al.* (2006) and scaled up to a global estimate of CH₄ emissions by simply summing the contributions from all biomes.

Photosynthesis-based estimates

The second method for estimating the global budget makes the assumption that the light-stimulated component of aerobic CH₄ emission is linked to photosynthesis. Hence, this provides a methodologically consistent means of scaling up based on the rate of net primary production instead of leaf mass in different biomes. This provides a convenient means of integrating across day and season length with conditions more or less conducive to metabolic activity. Hence, we expressed the rates observed by Keppler *et al.* (2006) as a function of the assumed photosynthetic rates of the leaves in their measuring chambers. We calculated the ratio of photosynthesis to CH₄ emission, r , in molar units as:

$$r = \frac{A}{m_l / 57\,600 S_l} \approx 30\,000, \quad (2)$$

where A is photosynthetic rate, conservatively estimated as 10 μmol m⁻² s⁻¹ (e.g. Peterson *et al.* 1999), m_l the average CH₄ emission rate from attached leaves in the light, measured at 374 μg kg⁻¹ DW h⁻¹ by Keppler *et al.* (2006), S_l is specific leaf area, taken to be 20 m² kg⁻¹ as an average for a range of species (Vile *et al.* 2005) and 57 600 is a constant to convert from hours to seconds and mass-based to molar units for CH₄ emission.

We then calculated CH₄ emission for each biome, m_b , as:

$$m_b = 2 \cdot (16/12) \cdot \frac{N}{r} \left(1 + \frac{24 - D}{D} \cdot \frac{m_d}{m_l} \right), \quad (3)$$

where N is NPP (kg C ha⁻¹ year⁻¹) of each biome. The constants 16 and 12 convert from mass-based carbon and CH₄ units to molar units. The constant '2' estimates annual photosynthesis from NPP. This implies that half of photosynthetically fixed carbon is lost again in autotrophic respiration (e.g. Gower *et al.* 1999). The term in the second set of brackets estimates the additional contribution from nighttime CH₄ emission, with the symbols the same as in Eqn (1).

Estimating the relevance for tree plantings

For estimating the relevance of CH₄ emissions for tree plantations, it is necessary to compare the difference in aerobic CH₄ emission from alternative vegetation types with the benefit from carbon sequestration.

We used representative global average tree-growth rates to estimate the carbon sequestration potential of tree plantings. For pasture, we assumed the system to be in steady state, with no change in carbon stocks (e.g. Murty *et al.* 2002). Calculations were based on either an estimate of standing leaf mass in the two systems, or estimates of photosynthesis as the basis for estimating CH₄ emissions. So, the difference in CH₄ emissions between a tree plantation and a pasture, m_{Δ} , was calculated as:

$$m_{\Delta} = d_t L_t / S_{1,t} [Dm_1 + (24 - D)m_d] - d_g L_g / S_{1,g} [Dm_1 + (24 - D)m_d], \quad (4)$$

where d_t and d_g are the number of days in the growing season (d year⁻¹) for trees and grass, respectively, L_t and L_g are leaf area indices (m² m⁻²) for plantation trees (8.7) and grass (2.5; Asner *et al.* 2003), $S_{1,t}$ and $S_{1,g}$ specific leaf areas (m² kg⁻¹ DW) for trees (8.3) and grass (23; Vile *et al.* 2005), m_1 and m_d and D the same parameters as used above. The same daylength was used for pasture and plantations, but season length could be different owing to the longer persistence of tree foliage with access to deeper water supplies in seasonally dry environments. Details used in respective simulations are given in the Tables below.

The calculated differences in CH₄ emissions could then be used to calculate a CH₄ offset, m_o , of any carbon sequestration benefit. This was calculated as:

$$m_o = -wm_{\Delta} / C_e, \quad (5)$$

where C_e is the carbon stored in a plantation in CO₂ equivalents (CO₂e), and w is the relative greenhouse warming potential of CH₄ (23 for an assessment horizon of 100 years; Ramaswamy *et al.* 2001). The carbon storage benefit was calculated as:

$$C_e = (44/12) \cdot 0.5 \cdot W, \quad (6)$$

where W is the carbon storage benefit calculated as the biomass stored in wood, 0.5 calculates the fraction of woody dry mass that is carbon and 44/12 converts from carbon to CO₂ to allow a dimensionally consistent comparison between carbon storage and CH₄ emission effects. A generic carbon storage potential of 10 t DW ha⁻¹ year⁻¹ was assumed here (Schlamadinger *et al.* 2000). Adopting one global figure

hides a great diversity across the globe, with boreal regions generally having lower growth rates, but growth rates in tropical regions being able to exceed that figure, especially on soils with good nutrition (Schlamadinger *et al.* 2000).

The effect of tree plantations was also assessed using photosynthesis as the means of calculating aerobic CH₄ emission. Hence,

$$m_{\Delta} = \frac{16}{12} \cdot \frac{(P_t - P_g)}{r} \left(1 + \frac{24 - D}{D} \cdot \frac{m_d}{m_1} \right), \quad (7)$$

where r is the ratio of photosynthesis to CH₄ emission as defined before, P_t and P_g are the photosynthetic rates (kg C ha⁻¹ year⁻¹) of trees and grass, respectively and the constants 16/12 convert between mass and molar units for carbon and methane. The term in the second bracket accounts for the additional nighttime CH₄ emission as in Eqn (3). Photosynthesis of trees, P_t , was assumed to be related to carbon sequestration in wood by:

$$P_t = 2 \cdot 3 \cdot 0.5 \cdot W, \quad (8)$$

where W is the annual wood increment (kg DW ha⁻¹ year⁻¹), with the assumptions that one-third of NPP is stored in sequestered wood, that NPP is half of annual photosynthesis (e.g. Gower *et al.* 1999) and that half of dry mass is carbon. For grasslands, a range of assumptions was used as given in the Tables below. This was also combined with extremes in the assumption about the ratio of photosynthesis to CH₄ emission as shown below.

Results

Global up-scaling

Our first estimate of global aerobic CH₄ emissions used an approach similar to that of Keppler *et al.* (2006), except that we based our estimate on leaf mass in different biomes instead of NPP (Table 1).

With leaf mass as the basis for up-scaling, we derived an estimate of global CH₄ emissions of 36 (range 15–60) Mt CH₄ year⁻¹, with about half of estimated global emissions attributed to tropical forests. This estimate is substantially lower than the 149 (range 62–236) Mt CH₄ year⁻¹ estimated by Keppler *et al.* (2006).

Table 1. Global up-scaling of CH₄ emissions based on estimates of leaf mass

Area estimates are based on House *et al.* (2002) and estimates of biomass and the fraction in foliage, f_f , from Foley (1994). Biome types, estimates of season length and sunshine hours and specific emission rates were taken from Keppler *et al.* (2006), with the numbers in brackets showing calculated values with the minimum and maximum specific CH₄ emission rates reported by Keppler *et al.* (2006)

Biome	Area (10 ⁹ ha)	Season (d year ⁻¹)	Sunshine (h d ⁻¹)	Biomass (t DW ha ⁻¹)	f_f	Foliage (t DW ha ⁻¹)	Methane (Mt CH ₄ year ⁻¹)
Tropical forest	1.75	365	8	200	0.03	6	18.8
Temperate forest	1.04	250	6	100	0.03	3	3.4
Boreal forest	1.37	150	4	90	0.04	3.6	2.8
Mediterranean shrublands	0.25	200	8	40	0.1	4	1.0
Tropical savanna and grasslands	2.25	200	8	15	0.2	3	6.6
Temperate grasslands	1.0	150	6	12	0.2	2.4	1.6
Deserts	4.55	100	10	5	0.05	0.25	0.6
Crops	1.6	200	8	10	0.1	1.0	1.6
Total							36.4 (15.1–60.3)

Table 2. Global up-scaling of CH₄ emissions using estimates of photosynthesis as the basis for up-scaling

Estimates of total NPP for each biome were taken from Saugier *et al.* (2001) and are the same as used by Keppler *et al.* (2006). These calculations assume a constant ratio of CH₄ emissions to photosynthetic rates

Biome	Area (10 ⁹ ha)	NPP (Gt C year ⁻¹)	NPP (t C ha ⁻¹ year ⁻¹)	Photosynthesis (t C ha ⁻¹ year ⁻¹)	Methane emission (kg CH ₄ ha ⁻¹ year ⁻¹)	Methane (Mt CH ₄ year ⁻¹)
Tropical forest	1.75	21.9	12.5	25.0	1.5	3.2
Temperate forest	1.04	8.1	7.8	15.6	1.0	1.4
Boreal forest	1.37	2.6	1.9	3.8	0.3	0.6
Mediterranean shrublands	0.25	1.4	5.6	11.2	0.7	0.2
Tropical savanna and grasslands	2.25	14.9	6.6	13.2	0.8	2.2
Temperate grasslands	1.0	5.6	5.6	11.2	0.7	1.0
Deserts	4.55	3.5	0.8	1.5	0.1	0.4
Crops	1.6	4.1	2.6	5.1	0.3	0.6
Total						9.6

The second approach relates CH₄ emissions to photosynthesis and uses independent estimates of photosynthesis as the basis for up-scaling. Using the same data for NPP as used by Keppler *et al.* (2006), and making a conservative assumption about photosynthetic rates in their plants resulted in a global emissions estimate of 9.6 Mt CH₄ year⁻¹ (Table 2), which was even lower than the leaf-mass-based estimate.

These two approaches are based on different assumptions, all of which are consistent with the currently available data. Both approaches result in estimates of global emissions that are much lower than that estimated by Keppler *et al.* (2006).

Tree plantings

The extent by which CH₄ emissions negate the benefit of carbon sequestration by tree plantings is shown in Table 3 with calculations based on leaf-mass estimates. For minimum, median and maximum calculations, the range of specific emission rates in the dark and light measured by Keppler *et al.* (2006) were used. In addition, different assumptions were used with respect to season length and sunshine hours. For the minimum calculation, the same short season length was assumed for trees and pasture. This might be applicable for a cool-temperate climate where cold winter temperatures equally inhibit grass and forest metabolic

activity. For the maximum calculation, it was assumed that trees would be active all year, whereas grass would be limited by drought conditions to only half a year. A longer daylength was also assumed for these conditions.

These detailed calculations showed that consideration of CH₄ emissions did little to negate the benefit from planting trees. Under our most likely assumptions, consideration of changes in CH₄ emission reduced the carbon sequestration benefit by only 1.1%. The greatest reduction in sequestration benefit by CH₄ emission was 4.4% when we employed the most extreme assumptions with respect to emission factors and season length.

Alternatively, the calculations were based on photosynthesis. We varied the assumed molar ratio of photosynthesis to CH₄ emissions between 60 000 and 10 000, and the assumption about photosynthesis of grasslands relative to that of forest stands to cover a range of possibilities.

With these assumptions, the benefit of planting trees would be negated by between 0 and 0.3% through consideration of CH₄ emissions (Table 4). Differences in methane emissions occur only when photosynthetic carbon gain from grasses is less than that from forests, which might be the case in seasonally dry environments where grass dies back at the onset of a dry season while trees might be able to continue

Table 3. Value of tree plantings (in t CO₂e ha⁻¹ year⁻¹), calculated CH₄ emissions for trees and grass and the net percentage reduction in net benefit due to inclusion of CH₄ emissions

Calculations were based on leaf-mass estimates. The same wood sequestration benefit (10 t DW ha⁻¹ year⁻¹ = 18.3 t CO₂e ha⁻¹ year⁻¹) was assumed for all calculations. We provide three estimates, a minimum and maximum estimate with extreme assumptions, and a median estimate, which we regard as the most likely

	C benefit (t CO ₂ e ha ⁻¹ year ⁻¹)	Season (d year ⁻¹)		Sunshine (h d ⁻¹)	Methane emission (kg CO ₂ e ha ⁻¹ year ⁻¹)			Methane offset
		Trees	Grass		Trees	Grass	Diff.	
Minimum	18.3	183	183	6	77	8	69	-0.4%
Median	18.3	183	183	8	216	22	194	-1.1%
Maximum	18.3	365	183	12	850	44	806	-4.4%

Table 4. Value of tree plantings (in t CO₂e ha⁻¹ year⁻¹), calculated CH₄ emissions and the percentage reduction in net benefit due to inclusion of CH₄ emissionsCalculations were based on photosynthesis estimates with different assumed ratios, *r*, of photosynthesis to CH₄ emissions

	C benefit (t CO ₂ e ha ⁻¹ year ⁻¹)	Photosynthesis (t DW ha ⁻¹ year ⁻¹)		<i>r</i>	Methane emission (kg CO ₂ e ha ⁻¹ year ⁻¹)			Methane offset
		Trees	Grass		Trees	Grass	Diff.	
Minimum	18.3	60	60	60 000	30	30	0	0.0%
Median	18.3	60	40	30 000	50	33	17	-0.1%
Maximum	18.3	60	30	10 000	121	61	61	-0.3%

to photosynthesis with access to water deeper in the profile. In systems without water limitations, photosynthetic rates of trees and grasses are likely to be similar, with consequently no expected differences in CH₄ emissions.

Using this calculation method, we found the effect of including CH₄ emissions to be negligible under all combinations of assumptions, with a 0.1% reduction as the most likely estimate, and an estimate of a 0.3% reduction only under the most extreme assumptions.

Discussion

We believe that the procedure used by Keppler *et al.* (2006) to calculate global aerobic plant CH₄ emissions from their chamber measurements overestimates the likely magnitude of emissions. We, therefore, used two different methods with independent assumptions to scale up from their measurements to the globe.

Leaf-mass-based estimation

Keppler *et al.* (2006) presented rates of aerobic methane release per unit of plant dry mass, which in most cases was mainly leaf material. We therefore calculated global fluxes on the basis of estimates of leaf mass, which is dimensionally consistent.

This approach was based on estimated leaf mass in different biomes and resulted in an estimate of 36 Mt CH₄ year⁻¹. The NPP-based estimate of Keppler *et al.* (2006) greatly exceeds the leaf-mass-based estimate because the numeric value of NPP considerably exceeds the average amount of living foliage. For tropical forests, for example, we estimated an average leaf mass of 6 t DW ha⁻¹ (Table 1), whereas NPP is estimated at 25 t DW ha⁻¹ year⁻¹ (equivalent to 12.5 t C ha⁻¹ year⁻¹; Table 2). Consequently, the leaf-mass-based estimate of CH₄ emissions is only about one quarter of the NPP-based estimate.

For these calculations, we had to assume that leaves emit methane at a constant rate throughout their life. One could also estimate CH₄ emissions on the basis of annually produced new leaf mass. This would be appropriate if the mechanism of aerobic CH₄ emission were such that the source of carbon of the emitted CH₄, such as available

methoxyl side chains, is exhausted within one year of formation. CH₄ emissions might cease even earlier, such as upon cessation of growth processes in newly formed leaves. As no information about the time course of CH₄ emission is yet available, it was not possible to use this calculation method. CH₄ might also be emitted from other light-exposed soft tissues, such as flowers, but the quantitative contribution of such tissues is likely to be small.

Our estimate is also based on assumptions of season length and effective daylength because methane emissions were stimulated by sunlight. We used the same season and daylength estimates as Keppler *et al.* (2006), which implicitly assumed that the CH₄ release rates in the light have a high light threshold. Effects of temperature or other physiological variables had to be ignored because there is no information yet about their possible effect on emissions.

Photosynthesis-based estimation

Our second approach for scaling up is based on the ratio of photosynthesis to CH₄ emissions. This approach assumes that CH₄ emissions are in some way linked to the production of new carbohydrate, or directly involve the electron transport chain so that ratio of photosynthetic carbon gain to CH₄ emission might be conserved across different physiological states and conditions.

If photosynthesis were directly involved in CH₄ production it could be by providing reducing equivalents for methane production which would provide a mechanistic explanation for the light stimulation of emissions. Highest CH₄ emission rates were also observed for the C₄ plants maize and sorghum and the lowest rates for Norway spruce, a C₃ plant, which would be in line with expected photosynthetic rates for these species.

This method thus requires no assumptions about season length as this is implicitly included in the estimates of photosynthesis for different biomes. An assumption about daylength was only required to estimate the (smaller) contribution from nighttime CH₄ emissions. Estimates of daylength and NPP for different biomes, which we used to estimate photosynthesis, were taken from Keppler *et al.* (2006).

We used a conservative estimate of photosynthesis to calculate the ratio of photosynthesis to CH₄ emission so that our estimate is more likely to overestimate CH₄ emissions. Nonetheless, despite assumptions that were biased towards higher emissions, our derived estimate of global aerobic CH₄ emissions was only 10 Mt CH₄ year⁻¹, and thus even lower than the leaf-mass-based estimate.

Methane oxidation in soils

Soils of most ecosystems also oxidise CH₄. This is estimated to consume between 10–44 Mt CH₄ year⁻¹ globally (Ehhalt *et al.* 2001), with oxidation rates strongly dependent on soil moisture conditions, being highest at intermediate soil moisture (e.g. MacDonald *et al.* 1996; Price *et al.* 2004). When soils are too wet, soil micro-sites become anaerobic and CH₄ is produced rather than oxidised.

Oxidation rates are generally in the range of 1–5 kg CH₄ ha⁻¹ year⁻¹ (Smith *et al.* 2000; Mosier *et al.* 2004), with a reduction by about two-thirds when soils are cultivated (Smith *et al.* 2000). Oxidation rates can increase again under forests when soils remain uncultivated, but the recovery generally takes decades to centuries (Smith *et al.* 2000).

Hence, forests have the benefit, at least compared with cultivated soils, of encouraging CH₄ oxidation in the soil by ≈1 kg CH₄ ha⁻¹ year⁻¹ (Smith *et al.* 2000), corresponding to ≈23 kg CO₂e ha⁻¹ year⁻¹ for a greenhouse warming potential of 23 for methane relative to CO₂ based on an assessment horizon of 100 years (Ramaswamy *et al.* 2001). This approximately balances the estimated extra aerobic CH₄ emission by trees relative to grass calculated by the photosynthesis-based method (Table 4).

The global methane budget

Our estimate for global aerobic CH₄ emissions can be readily accommodated within the estimates of the established sources and sinks in the present global budget (Table 5). The uncertainty in emissions from wetlands alone has been calculated by different workers to be over 100 Mt CH₄ year⁻¹. An additional source term of up to 60 Mt CH₄ year⁻¹, as calculated here, would require no adjustment to any of the more established terms. By contrast, an additional flux of the order of 149 Mt CH₄ year⁻¹, as calculated by Keppler *et al.* (2006), could not be reconciled with the other terms in the budget without requiring substantial re-assessment of their magnitudes.

The possible magnitude of aerobic CH₄ emissions from plants must also be consistent with the pre-industrial/agricultural CH₄ budget when aerobic plant CH₄ emissions were presumably no less than they are at present but emissions from burning fossil fuels, domestic livestock, flooded rice cultivation and landfills were much less than at present. Based on the global mean CH₄ concentration of 695 ppb for the period 1000–1800 AD and

Table 5. Summary of key CH₄ sources and sinks

Minimum and maximum estimates reported in the literature are summarised in the IPCC's third assessment report (TAR; Ehhalt *et al.* 2001), together with the final estimate reported in the TAR. The numbers given in bold type are our current estimate as described in this paper. All fluxes are in Mt CH₄ year⁻¹

Methane sources and sinks	Min.	Max.	TAR
Natural sources			
Wetlands	115	237	
Termites	20	20	
Ocean	10	15	
Methane hydrates	5	10	
Anthropogenic			
Energy transformations	75	110	
Landfills	35	73	
Ruminants	80	115	
Waste treatment	14	25	
Rice cultivation	25	100	
Biomass burning	23	55	
Other	15	20	
Aerobic methane emissions	10	60	
Total sources			598
Sinks			
Soils	10	44	
Tropospheric OH	450	510	
Stratospheric loss	40	46	
Total sinks			576
Imbalance (atmospheric increase)			22

estimates of its atmospheric lifetime of 8–11 years, the total of all CH₄ sources must have been in the range of 200–250 Mt CH₄ year⁻¹ (Etheridge *et al.* 1998). Houweling *et al.* (2000) estimated the pre-industrial emissions from wetlands as 163 (uncertainty range 130–194) Mt CH₄ year⁻¹ and the sum of all other sources (termites, rice farming, ruminants, biomass burning, waste treatment, oceans, volcanoes) at 88.5 (53.5–143.5) Mt CH₄ year⁻¹, for a total of 251.5 (183.5–337.5) Mt CH₄ year⁻¹.

This suggests that an additional source of 10–60 Mt CH₄ year⁻¹, as calculated here, could be accommodated within the uncertainties of the pre-industrial/agricultural CH₄ budget provided that the estimates of all other individual source terms and the atmospheric lifetime of CH₄ were at the lower end of estimates. Aerobic CH₄ emissions rates of 149 (62–236) Mt CH₄ year⁻¹, as estimated by Keppler *et al.* (2006), in contrast, would be too large to be reconciled with the current understanding of the pre-industrial/agricultural budget.

Frankenberg *et al.* (2005, 2006) recently reported space-based observations of the CH₄ profile across the globe and a comparison with concentrations calculated from global sources and sinks. The comparison pointed to higher than expected concentrations over tropical forest regions, especially in South America. Aerobic CH₄ emission from plants may resolve that discrepancy, and our calculations

suggest that aerobic CH₄ emissions are of the same magnitude as total CH₄ emissions reported in a field study from Brazil by do Carmo *et al.* (2006). Other components of the global budget, such as emissions from biomass burning, termites, wetlands, and the CH₄ production/oxidation balance in partly wet soils, as well as oxidation by OH in the atmosphere, however, are all sufficiently uncertain to further account for any remaining discrepancies.

The value of tree plantings

Our quantitative assessment of the value of plantation establishment as a greenhouse mitigation option is also only marginally affected by consideration of aerobic CH₄ emissions. Our best estimate was that the carbon sequestration benefit might be negated by between 0.1 and 1.1% by such CH₄ emissions. At the same time, long-established forests provide the additional benefit of encouraging greater CH₄ oxidation in soils than in cultivated soils. Hence, there is no justification for questioning the value of planting trees on the grounds of aerobic CH₄ emissions.

Carbon sequestration, the process of removing CO₂ from the atmosphere and storing it in an increasing pool of woody biomass does, however, continue only over the growth phase of forests. After forests reach maturity there is no further carbon uptake whereas any difference in CH₄ emission can be maintained indefinitely. Nonetheless, because the effect of CH₄ emissions is of such minor importance, the value of tree plantings is overwhelmingly determined by considerations of its carbon balance.

*The observations by Keppler *et al.* and their interpretation*

The primary focus of this paper is to question the methods that Keppler *et al.* (2006) have used to scale up from their chamber observations to estimate global aerobic CH₄ emissions from plants. Given that their experimental results form the basis of these global estimates, it is appropriate to scrutinise the experimental methods that underpin these estimates.

We accept that the experimental methods did indeed demonstrate that CH₄ could be emitted under aerobic conditions. The most obvious alternative sources of methane could be either microbial or atmospheric. The authors were able to satisfactorily exclude anaerobic processes as the source of CH₄ emissions by irradiating plant material yet still observing CH₄ emissions. In principle, it is also possible that the observed CH₄ emissions were the result of desorption of atmospheric CH₄ following the flushing of chambers containing plant material with CH₄-free air. This possibility was partly discounted by demonstrating that emitted CH₄ had an isotopic signature similar to the esterified methoxyl groups (Keppler *et al.* 2004) of the C₃ and C₄ plants that were being studied.

However, that isotopic work does not fully allay our concerns about the reliability of measured methane emission

rates because of the use of static chambers and CH₄-free air. This approach inherently introduces some limitations into emission rate studies. The study used static chambers that were generally flushed with CH₄-free air, and emission rates were calculated from the build-up of CH₄. This inevitably necessitated plant exposure to a wide range of CH₄ concentrations over the course of the observation period. Lowest CH₄ concentrations observed were in the parts per billion range after flushing the chambers with CH₄-free air, while the highest concentrations were attained at the end of the observation period. These levels were often in excess of normal ambient concentrations.

Over this range in concentrations, CH₄ may have physically absorbed or desorbed from plant surfaces or the chamber materials, especially the plexiglass chambers used for experiments with intact plants, thus adding to or subtracting from plant-derived CH₄ emissions. The change in CH₄ concentration might also have stimulated or inhibited plant emissions. The importance and magnitude of these processes remains unknown until an underlying mechanism responsible for CH₄ emissions can be demonstrated.

Concerns also relate to the draw-down in CO₂ concentrations while CH₄ was building up. Keppler *et al.* (2006) reported that CO₂ concentrations did not fall below 250 ppm but did not report an upper limit of CO₂ concentrations. If there is a metabolic link between photosynthetic and methane pathways, any changes in CO₂ concentration could have affected CH₄ emission rates.

A further concern relates to the light-exposure experiments with intact plants. The authors suggest that exposure to sunlight greatly increased CH₄ emission rates. However, temperature was not tightly controlled in this set of experiments, and the possibility cannot be excluded that the apparent response to sunlight was, at least in part, a response to temperature, which had been shown to have a highly stimulatory effect on emissions.

If one accepts the basic veracity of the observations, the question turns to its possible interpretation. CH₄ is a reduced compound, and some bacteria can generate energy from its oxidation to CO₂ and water. CH₄ production under aerobic conditions, however, runs counter to the expected direction of chemical reactions in an oxidising atmosphere. The production of CH₄ from purified pectin is particularly difficult to understand, given that it involves the reduction of pectin to the more highly reduced CH₄. The continued increase in the rate of CH₄ emission up to 70°C suggests that no enzymes are involved.

Rates of CH₄ emission from both live and dead material, as well as from pectin, were also stimulated by light. The rates of release were, however, nearly 100 times greater from attached than detached or dried tissues. It may simply mean that rates occur faster in the more metabolically reactive conditions of a living cell or that two independent processes are involved. The slower process may be able to occur in dead tissues, but higher

rates might require living tissues where the cell's metabolism, especially in the presence of light, can facilitate the reduction of CH₄. No specific mechanism has yet been suggested for the production of CH₄ under aerobic conditions.

Future work

The calculations reported here are carried out under considerable uncertainty as much critical information that is required for up-scaling is not yet known. Additional research is needed to overcome this uncertainty. We consider the following as deserving priority.

Independent confirmation of the observations of aerobic methane release

The original study by Keppler *et al.* (2006) appears to have been carried out with care and considerable attention to possible problems and artefacts although only scant details of methods were given. Nonetheless, we urge caution in accepting its implications until there is independent confirmation of the findings. The emission rates also need to be quantified more reliably. Given this, any extrapolation of these findings to the global scale needs to be done with extra care and mindful of the possibility of artefacts.

Identification of the underlying mechanism

Elucidation of the underlying biochemical pathway for aerobic CH₄ production is crucial for gaining a full understanding of its role and possible global significance. Other experiments suggested here will provide the observational base to allow identification of these underlying processes.

Is there a temporal component?

Once leaves are exposed to light, does the rate remain constant? If it does it would indicate that CH₄ is released as a by-product of some on-going reaction. Alternatively, rates may decrease over time. If rates decrease slowly (in the order of days to weeks), it might indicate that CH₄ is released slowly from a large pool. If rates change relatively quickly (over minutes to hours) after a change in conditions, then it lends support to the possibility that one might simply be observing an artefact of CH₄ absorption / desorption.

Any possible change in emission rates over time is crucially important for up-scaling. If rates change over days to weeks, it would imply that annual rates cannot be estimated simply by multiplying short-term rates by the length of time over which plants are assumed to remain under the same condition.

From which plant tissues or compounds does CH₄ originate?

Keppler *et al.* (2006) found that CH₄ can be emitted from pure pectin, although at much smaller rates than from intact plants. It would be useful to test for any possible release

from other compounds as well, including some with and some without methoxyl groups to help identify the chemical reactions that are involved in aerobic CH₄ production.

At the whole-plant level, it is important to know whether CH₄ is emitted from photosynthesising leaves, from growing tissues or from all metabolically active tissue. Do metabolically inert tissues, such as fully formed xylem, or tissue shielded from light, such as roots, also emit CH₄? This again will be important for estimating annual emissions.

More species comparisons

The number of species tested is still very small. Only one tree species has been assayed using intact tissue and no species from tropical forests. While CH₄ emission rates were measured from detached leaves of a greater number of species, these rates were nearly two orders of magnitude lower than those measured for intact plants. Hence, scaling to the globe is uncertain when a large part of the overall flux is likely to originate from species for which no measurements have yet been taken.

Temperature dependence of CH₄ emission in the light

Keppler *et al.* (2006) presented the temperature response of CH₄ emission in the dark, which showed a continued increase in rates up to 70°C, suggesting a non-enzymatic reaction mechanism. The temperature response of CH₄ emission in the light needs to be measured to indicate whether plant metabolism is involved. If the light stimulation in intact leaves were to continue up to high temperatures, it would exclude an enzymatic process and indicate a non-enzymatic reaction as in non-living organic matter.

Irradiance dependence of CH₄ emission

Keppler *et al.* (2006) have shown a dark–light modulation of emission rates. This response needs to be confirmed under more tightly controlled conditions. If it can be confirmed, it would be valuable to know more about the light-response curve. Do CH₄ emissions increase linearly with light? Do they saturate? Is there some low-light threshold?

Action spectrum of CH₄ emission

Is UV radiation involved in CH₄ emission, or does the spectral dependence of CH₄ emission mirror the action spectrum of photosynthesis? If it is driven by UV, then we might be dealing with a non-biological action, but if it mirrors the action spectrum of photosynthesis, it would indicate the involvement of photosynthetic electron transport.

It is noteworthy that the experimental work on dead plant materials was done in glass vials whereas the work on intact plants used plexiglass chambers (Keppler *et al.* 2006). As these chambers could possibly have different UV transmission properties, it raises the possibility that the apparent difference in CH₄ emissions between dead and

intact plants might have simply been due to the different amounts of UV the materials were subjected to. A carefully constructed action spectrum of CH₄ emissions should show whether different amounts of UV could have played a role in these findings.

Do rates change with the physiological state of leaves?

Are rates higher or lower in water stressed leaves? How do rates change with plant nutrition? Are rates more constant if they are expressed as a function of photosynthetic rates across differences in nutrition or stress levels?

Conclusions

The work of Keppler *et al.* (2006) has identified a new source of CH₄ emission from plants under aerobic conditions. If this can be confirmed by independent research, preferably by different methodologies, it will need to be incorporated into our understanding of CH₄ budgets. Identifying the mechanism of aerobic methane formation would assist in scaling from the laboratory to the globe.

We reassessed here the global significance of aerobic CH₄ emission and derived a much smaller estimate than that of Keppler *et al.* (2006). While the magnitude of the contribution from this additional source to the global CH₄ budget is uncertain, our estimate can be readily accommodated within existing uncertainty in the established sources and sinks of both the present and pre-industrial/agricultural global CH₄ budget.

For mitigating climate change, we also believe that the carbon sequestration benefit from planting trees far outweighs the warming associated with aerobic CH₄ emissions by a factor of about 100. Statements in the media that have questioned the benefit of trees as a mitigation strategy are therefore unsubstantiated.

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