

How Important is Aerobic Methane Release by Plants?

Miko U. F. Kirschbaum^{1,2*} • Ülo Niinemets^{3,4} • Dan Bruhn^{5,6} • Anthony J. Winters^{7,8}

¹ Landcare Research, Private Bag 11052, Palmerston North, New Zealand

² Environmental Biology Group, Research School of Biological Sciences, Australian National University, GPO Box 475, Canberra ACT 2601, Australia

³ Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 64, Tartu 51014, Estonia

⁴ Department of Plant Physiology, University of Tartu, 23 Riia St., Tartu 51010, Estonia

⁵ Plant and Soil Science Laboratory, Dept of Agric. Sciences, Faculty of Life Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

⁶ Biosystems Department, Risø National Laboratory, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

⁷ School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney NSW 2052, Australia

⁸ Ecosystem Dynamics Group, Research School of Biological Sciences, Australian National University, GPO Box 475, Canberra ACT 2601, Australia

Corresponding author: * KirschbaumM@LandcareResearch.co.nz

ABSTRACT

The first research paper describing aerobic methane release from living plants and dead organic matter was published in early 2006. These original findings have yet to be independently repeated and confirmed. Instead, the only other detailed study that has been published did not find any significant aerobic emissions of methane. Concerns remain about possible artefacts, especially with respect to methane adsorption and desorption. Several questions are yet to be answered, such as identification of a plausible biochemical mechanism for the process, how CH₄ emissions might change with light, temperature or 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. Various studies have assessed the likely magnitude of aerobic methane release within a global context. Different estimates based on more or less sophisticated approaches have all indicated that the magnitude of aerobic methane release must be relatively moderate and contribute between 0-10% of modern and 0-30% of pre-industrial/pre-agricultural methane emissions. In the context of land-use change, consideration of aerobic CH₄ emissions from different plant types is only a small factor for overall greenhouse gas balances. Any carbon-offset benefit from planting trees is likely to be about 100 times as effective as any possible detrimental effect due to increased aerobic methane release. Land-use change, including the draining of wetlands, the establishment of paddy rice farming, or the introduction of ruminant animals, would produce emission changes that significantly outweigh any potential changes arising from differences in aerobic methane release by different plant types.

Keywords: adsorption, aerobic, climate-change mitigation, desorption, dissolution, global budget, Kyoto Protocol, land-use change, methane oxidation, trace gas

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INTRODUCTION

Methane is the second-most important greenhouse gas, contributing about 20% to the current radiative forcing of the enhanced greenhouse effect (Ramaswamy *et al.* 2001). It has been intensively studied and it had been thought that all of its sources and sinks had been identified. Hence, it came as a significant surprise when Keppler *et al.* (2006) reported a new finding of aerobic methane release by living plants and even dead tissue.

However, the question must be asked whether the apparent findings of significant methane emissions were actually just artefacts. The observed rates were exceedingly small, and measuring the minute emission fluxes at current high atmospheric methane concentration backgrounds constitutes a challenge to any experimental setup. Dueck *et al.*

(2007) used a different experimental approach to overcome some of these measurement challenges and did not report any significant methane emissions in their system.

If aerobic methane release does indeed occur, the question arises as to its global significance. There are inherent difficulties in extrapolating from a few measurements in the laboratory to global emissions from a variety of different plant species and under greatly varying conditions. Keppler *et al.* (2006) provided estimates of global emissions based on their measurements and derived large values, with as much as 1/3 of global emissions attributed to aerobic methane release.

However, the Keppler *et al.* (2006) method for scaling methane fluxes has been questioned by a number of workers (Kirschbaum *et al.* 2006; Parsons *et al.* 2006), and their global estimates were significantly smaller. Additional studies

based on detailed global modelling (Houweling *et al.* 2006) and isotope analyses (Ferretti *et al.* 2007) also concluded that aerobic methane release could at most be a minor contributor to total global emissions.

The original work of Keppler *et al.* (2006) also led to immediate questioning of tree plantings as a greenhouse mitigation option (Lowe 2006) although the original paper by Keppler *et al.* (2006) provided no support for that notion. This theme was, however, taken up strongly by the world media until studies with detailed calculations showed that any changes in aerobic methane release make almost no difference to the net benefit of tree plantings (Kelliher *et al.* 2006; Kirschbaum *et al.* 2006).

In the following, we discuss these various issues in greater detail. It draws on the small amount of material that has been published since the original findings of Keppler *et al.* (2006) were first reported. In addition, we assess in some detail the possibility of artefacts that might have added to observed apparent release rates.

EXPERIMENTAL EVIDENCE FOR AEROBIC METHANE RELEASE BY PLANTS

Keppler *et al.* (2006) enclosed various samples of live and dead plant materials in chambers, recorded subsequent changes in methane concentration over periods of minutes to hours and then calculated emission rates from the build-up of methane in their chambers. They observed methane release from living plants, dead plant material and even commercially available pectin (**Table 1**). The release of methane from pectin is perhaps the most remarkable observation. Pectin is a polysaccharide that is an important structural component of cell walls in most plants. Under anaerobic conditions and in the presence of a range of pectinase-containing micro-organisms, pectin can break down to methanol, with some methane produced as a by-product (Ollivier and Garcia 1990). While methanol formation from pectin has been known for some time (Fall and Benson 1996), formation of the more reduced methane from pectin under aerobic conditions goes against the expected direction of spontaneous chemical reactions. The 100-fold stimulation of methane release from pectin by sunlight (**Table 1**) is similarly highly surprising, and to our knowledge, no one has yet proposed a plausible mechanism for these observations.

In darkness, methane emissions from dead plant material were about an order of magnitude higher than from pectin. Emissions from dead plant material were also stimulated by exposure to sunlight, but the effect was not as pronounced as for pectin. Methane production was also observed to be stimulated by increasing the temperature up to 70°C (Keppler *et al.* 2006), which effectively excludes involvement of an enzymatic processes in this reaction as plant enzymes are expected to be completely denatured at temperatures above 50-60°C (Berry and Raison 1982).

Observed rates were about 100-fold higher for intact

plants than for dead plant material. This could mean that the same process of methane release is simply much more active in the reactive environment of a living cell than in dead tissue, or it could indicate that two separate processes are involved. One process might be non-enzymatic and the other might involve an enzymatic reaction and be capable of achieving much higher emission rates, but operate only in living tissue. All of these measured rates are exceedingly low, however, and Kirschbaum *et al.* (2006) calculated that at even the methane release rates in intact plants, about 30,000 mol CO₂ would be fixed per mol of CH₄ released.

Potential problems with methane flux measurements

The magnitude of these emission estimates readily explains why these emissions under aerobic conditions have been overlooked by previous generations of researchers. However, inherently low emission fluxes also pose the concern that the apparent aerobic methane release can be partly or entirely an artefact of the experimental design, and problems with methane emission flux measurements have been noted previously (e.g. Kim 1991).

There are at least three possible problems with methane emission measurements that all relate to the fact that methane is a constituent of the normal ambient atmosphere, which is currently around 1750-1800 ppb (Ehhalt *et al.* 2001; Frankenberg *et al.* 2005; 2006; see also <http://www.cmdl.noaa.gov/ccgg/iadv/> or <http://gaw.kishou.go.jp/wdceg.html> for the most recent data), as well as being present in gas- and liquid-phases in the soil and in plants.

By comparison, monoterpenes that are also emitted by plants at very low fluxes have atmospheric background concentrations of only 0.1-5 ppb. This means that measurements of very low methane flux rates must contend with interference, leakage, dissolution and desorption from an environment dominated by a large background concentration. Measurements of monoterpene fluxes, on the other hand, are simpler as these similarly low rates suffer much less from interference by high atmospheric background concentrations.

The first problem in methane measurements is the possibility of diffusion and mass flow leaks between the ambient atmosphere and measurement chambers. This problem is particularly significant if plant emissions are measured using an initially methane-free atmosphere as in most of the experiments of Keppler *et al.* (2006). As the measurement of very low fluxes is associated with long integration times, typically hours, even minor methane diffusion leaks from the ambient atmosphere into the chamber can significantly add to the calculated flux rates.

Keppler *et al.* (2006) were aware of that problem and tried to ensure that it was no problem in their work by measuring the change in methane concentration in their chambers when there was no plant material present and found no apparent emissions under those conditions. Provided that

Table 1 Summary of the rates of aerobic methane release from different plant materials under a range of conditions observed by Keppler *et al.* (2006). Shown are means with 95% confidence intervals which were calculated by taking all of the reported values for different materials as independent observations. Rate per unit area was calculated assuming a mass of 0.5 kgDW m⁻² as may be applicable for grasslands. An equivalent calculation was not done for forest vegetation as there is too much uncertainty with respect to equivalent treatment of metabolically active leaf and metabolically inert wood. 'Ratio' gives the ratio of measured rates relative to rates of the same material in darkness and at 30°C, where applicable.

Material	Condition	Rate (ngCH ₄ kgDW ⁻¹ s ⁻¹)	Grassland rate (ngCH ₄ m ⁻² s ⁻¹)	Ratio
Intact plants	dark	32 ± 13	16	
	sunlight	90 ± 19	45	2.8
Dead plant materials	30°C, dark	0.33 ± 0.25		
	30°C, sunlight	1.8 ± 0.8		5.6
	40°C, dark	0.6 ± 0.4		1.9
Pectin	30°C, dark	0.036		
	30°C, sunlight	3.8		105
	40°C, dark	0.053		1.5

Table 2 Calculation of the amount of methane physically held within living leaves. Water/air and lipid/air equilibrium partition coefficients of methane and calculations to calculate methane content per unit dry leaf tissue in equilibrium with an ambient air methane concentration of 2000 nmol mol⁻¹ at 25 °C.

Process	Phase	Mass of different constituents (kg kgDW ⁻¹)	Weight per unit volume (kg m ⁻³)	Volume of different constituents (m ³ kgDW ⁻¹) ^a	Equilibrium partition coefficient	Equilibrium methane concentration (ngCH ₄ m ⁻³)	Content per 1 kg dry leaf (ngCH ₄ kgDW ⁻¹)
Absorption	Gas			3.33·10 ⁻³		1,308,000	4356
	Water	2.33	1,000	2.33·10 ⁻³	28.2 ^b	46,420	108
	Lipid	0.05	800	6.25·10 ⁻⁵	2.29 ^c	571,090	36
	Total						4500
Adsorption	Cell walls	0.5	1,200	4.17·10 ⁻⁴		105,460,000 ^d	43975

^a assuming a leaf dry matter concentration of 150 kgDW m⁻³, fraction of leaf airspace volume of 0.5, leaf dry to fresh mass ratio of 0.3, lipid content of 5% DW, lipid density of 800 kg m⁻³, cell wall percentage of DW of 50% and density of cell walls of 1200 kg m⁻³. These are considered as typical values of leaf structural characteristics of grass leaves (Niinemets and Reichstein 2003b).

^b according to Falabella *et al.* (2006). Units are in molCH₄ m⁻³ air [molCH₄ m⁻³ H₂O]⁻¹

^c according to In *et al.* (2005). Units are in molCH₄ m⁻³ air [molCH₄ m⁻³ lipid]⁻¹

^d according to (Harrison *et al.* 2000) for coconut charcoal.

this was assessed in all of their measurements, leakage problems can probably be discounted as having interfered in those particular measurements.

However, it continues to be a significant potential problem in any measurement condition that combines the measurement of low flux rates and high concentration gradients between a chamber and the surrounding air. Leakiness has been recognised as a problem for gas exchange measurements in general (Long and Bernacchi 2003). As diffusion rates increase with increasing temperature (Bruhn *et al.* 2002), a diffusion leak can also lead to an apparent temperature sensitivity of emissions or, at least, an amplification of any actual emission sensitivity to temperature.

The second problem is that there is an equilibrium between methane in the gas phase and solubilised methane in the plant liquid and lipid phases (Table 2). As the methane concentration in the gas surrounding any sampled plant tissue changes, additional methane is either dissolved or comes out of solution, or simply enters or escapes from the intercellular air spaces.

Although, like most gases, methane is relatively insoluble in both water and lipids, release of this methane into methane-free air can provide an additional apparent emission that would decrease over time as the cell constituents come to equilibrium with the surrounding air (see Noe *et al.* 2006 and Niinemets and Reichstein 2002, for kinetic analysis of emission fluxes due to non-specific storage for non-methane plant volatiles).

This is a particularly significant problem if measurements are conducted in methane-free air, but it also constitutes a problem if methane concentrations in the air surrounding sample tissue are allowed to increase beyond atmospheric concentrations. In that case, the leaf or other sample tissue will absorb some of the released methane, and apparent fluxes would be less than true fluxes.

Furthermore, the equilibrium water/air partition coefficient (Henry's law constant) and the equilibrium lipid/air partitioning coefficients of methane decrease with increasing temperature (Falabella *et al.* 2005) as it does for other organic compounds (Copolovici and Niinemets 2005). This implies that any increase in temperature can result in apparent methane emissions even into air with high methane concentrations (see Noe *et al.* 2006 and Niinemets and Reichstein 2003a for analysis of physico-chemical characteristics on plant emissions).

Closed systems without temperature control, like those used by Keppler *et al.* (2006), are particularly prone to such problems during measurements under natural light. Energy balance considerations and practical experience with plant gas-exchange systems suggest that the temperature is likely to increase by several degrees above ambient temperature in such enclosures (Field *et al.* 1989). As the equilibrium partitioning coefficients increase with temperature (typically about 2-fold for a 10°C temperature increase; Copolovici and Niinemets 2005), the apparent enhancement of methane release by light may be partly associated simply with the temperature-dependent physical pro-

cess of methane coming out of solution.

However, comparing the dissolved quantities in Table 2 with the flux rates observed by Keppler *et al.* (2006) as shown in Table 1, it is apparent that the release of methane physically held in leaves is likely to have made only a small contribution to observed apparent fluxes. According to Table 2, about 4500 ngCH₄ kgDW⁻¹ is held in the liquid and lipid phases and the air spaces inside leaves. For fluxes of 30-90 ngCH₄ kgDW⁻¹ s⁻¹ (Table 1), the release of methane physically held within intact leaves could amount to the equivalent of the observed fluxes over 50-150 seconds. As the measurements of Keppler *et al.* (2006) were conducted over periods of many minutes to hours, the methane physically held inside leaves could not account for the whole flux but would have added to it (for measurements in methane-free air). Observed flux rates were much smaller in dead tissue, but as there is presumably also much less water in which methane could dissolve as well as intercellular air spaces that are compressed and much reduced in volume, dissolution may have made a proportionately similar contribution to apparent fluxes in both dead and intact tissues.

Dissolved methane may also be transported from the roots to leaves in the transpiration stream and released through stomata (McBain *et al.* 2004; Loreto and Ciccioli, unpublished). This transport flux is likely to be small in most plants from terrestrial environments as those used by Keppler *et al.* (2006) but can be significant in wetland plants that have a large fraction of their stems composed of aerenchyma (Constable *et al.* 1992; Jackson and Attwood 1996; Blom 1999) and where the anaerobic conditions around the root zones of flooded plants typically provides a good environment for anaerobic methane formation. Chamber measurements in heterogeneous mire ecosystems suggest that most methane flux is associated with methane transported from the root zone of *Carex* species from a depth of 0.3-1.5 m through aerenchyma to the ambient air (Rinne *et al.* unpublished data).

The third, and potentially most serious, problem with methane measurements is that methane readily adsorbs to every surface, in particular to surfaces of hydrophobic compounds. Unfortunately, few data are available for low pressure methane adsorption capacities, and extrapolation from available adsorption isotherms to a low pressure range is inherently limited due to the very strong pressure-dependence of adsorption at low pressures (Shao and Wang 2004).

Chromatography studies provide some information of methane adsorption capacity at the relevant methane concentrations of 1-12 μmol mol⁻¹. These studies suggest that the methane adsorption capacity at 25°C may be between 0.24 g kg⁻¹ for charcoal and 0.85-14 g kg⁻¹ for typical porous trapping materials used in chromatography (Harrison *et al.* 2000; Thammakhetta *et al.* 2005; Pollmann *et al.* 2006).

These materials are characterized by high surface area, typically 100-1000 m² g⁻¹ for various adsorbents (Pollmann *et al.* 2006). Cell walls of plants consist of a complex net-

work of a highly porous polysaccharide matrix with typical pore sizes of around 5 nm (Carpita *et al.* 1979; Carpita and Gibeau 1993; Bauchot *et al.* 1999), which also provides potentially large effective surface areas.

It has been demonstrated that the methane adsorption capacity per unit of surface area is higher for organic matter than for inorganic minerals, because of the presence of these large number of small pores (Cheng and Huang 2004; Celzard and Fierro 2005). Wall pores are approaching the molecular diameter of methane which allows a strong interaction with methane molecules and that is largely responsible for the high adsorption capacities of organic matter (Biloe *et al.* 2002; Lozano-Castello *et al.* 2002).

The outer epidermis of all leaves is also covered by a highly porous and hydrophobic cuticle. There are also further lignified hydrophobic regions in cell walls. All of this suggests that large quantities of methane can potentially be adsorbed to the external and internal surfaces of leaves.

Using the numbers for the adsorption characteristics of plant cell walls based on that of coconut charcoal, we estimate an adsorption potential of about 40,000 ngCH₄ kgDW⁻¹. Even if the adsorption characteristics of cell walls were substantially less than those of charcoal, adsorption would still be a potentially large source of experimental artefacts. This is particularly significant for the release of methane from dead plant material such as pectin for which the desorption flux (see **Table 2**) could potentially be sufficiently large to fully account for the observed apparent emission rates (**Table 1**).

Given that an increase in temperature dramatically reduces the strength of hydrophobic interactions, a temperature increase reduces the methane adsorption capacity of leaves so that methane desorbs even if the external methane concentration does not change (Harrison *et al.* 2000; Shao and Wang 2004; Thammakhetta *et al.* 2005; Pollmann *et al.* 2006).

Adsorption and desorption are also relatively slow processes. Sorption exchange with organic materials, in particular, can be very slow (Pignatello and Xing 1996). Some studies have suggested that methane adsorbed to organic materials can be released into methane-free air at steady rates for periods of days to weeks (Zhang and Krooss 2001; Cheng and Huang 2004).

As adsorption/desorption is a basic physical process that occurs everywhere, one has to expect that it would modify any apparent emission fluxes, and, based on the numbers in **Table 2**, in quantitatively important ways. Reduced adsorption capacity at high temperature, in particular, could partly account for some, or all, of the apparent light and temperature dependencies observed in the experiments of Keppler *et al.* (2006).

In some of their work, Keppler *et al.* (2006) also exposed their plant material to methane concentrations above normal atmospheric concentrations, and methane release continued despite the build-up of methane in the air surrounding their samples. Under otherwise constant conditions, such an apparent flux would be inconsistent with desorption as a complete explanation for the observed fluxes. However, when sample temperatures were higher than the average temperature at which samples might have previously come to equilibrium with atmospheric conditions, desorption is potentially possible even into air of a higher concentration.

There is, therefore, a need for further research to determine the methane adsorption capacity of plant materials under a range of temperatures and methane concentrations in the relevant ambient range. While the determination of methane adsorption at current ambient methane concentrations poses challenges for experimental approaches, Higaki *et al.* (2006) demonstrated that use of triticated methane enables one to measure trace methane adsorption and desorption rates of even stainless steel tubes with very low surface areas.

Keppler *et al.* (2006) also recorded the isotopic compo-

sition of released methane and found it to be $-58.5 \pm 1.2\%$ (mean \pm 95% confidence limits; $n = 48$)¹ for methane released from C₃ plants and $-49.6 \pm 1.3\%$ ($n = 8$) for methane released from C₄ plants. In *Tillandsia usneoides*, the only CAM plant included in the samples analysed by Keppler *et al.* (2006), the discrimination was even more negative at about -68% . This evidence indicates that there must, indeed, have been some aerobic release from intact plants and dead plant material in the experiments of Keppler *et al.* (2006) although the emission rates, and the response to light and temperature, is likely to have been affected by methane adsorption and desorption.

While the information available to us did not allow an exact calculation of the rates at which methane might have been desorbed, information on the adsorption potential of other materials do indicate that it could have played a significant role in adding to the observed apparent flux rates. Methane may be simply adsorbed under cool conditions (i.e. night-time) and desorbed under warmer conditions (i.e. daytime). Dissolved methane coming out of solution would have added a small additional flux to apparent total fluxes.

Dueck *et al.* (2007) overcame some of these problems by growing plants in ¹³C- CO₂ and then measuring any methane release in an atmosphere containing only 22 ppb ¹³C-methane but a normal atmospheric concentration of about 2000 ppb ¹²C-methane. Their rationale was that any released methane of biogenic origin should also be labelled with ¹³C, and the low background concentration during measurements gave a higher detection limit for their analytical system. Using that approach, they observed an average methane emission rate from their intact plants of only 5.8 ± 3.1 (mean \pm S.E.) ngCH₄ kg⁻¹ s⁻¹ which is at least an order of magnitude less (see **Table 1**) than the rates observed by Keppler *et al.* (2006). When Dueck *et al.* (2007) recorded the build-up of methane in their growth chambers, they observed even lower apparent emission rates of only 0.1 ngCH₄ kg⁻¹ s⁻¹ which was not significantly different from 0.

The findings of Dueck *et al.* (2007) are thus clearly inconsistent with the observations of Keppler *et al.* (2006). While the rates observed by Keppler *et al.* (2006) could have been increased by desorption, methane desorption could not explain the plant-specific isotopic signature of released methane observed by Keppler *et al.* (2006). At present, we are unable to suggest any possible explanation for these conflicting findings.

Field measurements

In addition to the laboratory-based work of Keppler *et al.* (2006), a number of studies have measured methane exchanges in the field with more or less direct methods. Sanhueza and Donoso (2006) measured methane exchange of a tropical savannah in the field. They measured methane fluxes by enclosing an area of vegetation in a chamber and then recorded the subsequent change in methane concentration. Hence, they started from ambient methane concentrations so that any adsorption/desorption should have lowered their apparent rates, thus leading to an underestimation of true rates.

They also darkened their chambers prior to measurements and took their key reading about half an hour after placing the chamber. This helped to maintain a constant temperature but posed the problem that emissions were recorded under dark conditions whereas the work of Keppler *et al.* (2006) had illustrated the large stimulation of emissions by exposure to light (**Table 1**). However, it is not known over what time period emissions respond to changes in light levels, and whether 30 minutes after darkening,

¹ Calculated using the data in Table S1 in the supplemental information of Keppler *et al.* (2006), using information at different temperatures and with and without sunlight as separate observations. Data for *T. usneoides* was excluded as it has CAM rather than C₃ photosynthesis.

emission rates still reflected light conditions or were already responding to the darkened conditions.

Sanhueza and Donoso (2006) and Sanhueza (2007) studied both intact C₄-grass systems and systems where the grass was clipped close to the surface and removed together with any litter that was present. Their most significant finding in the present context was that net emissions from the system with intact grass were about 10 ngCH₄ m⁻² s⁻¹ higher than for the system without live plants and litter. The system without plants and litter instead was a slight sink of about 5 ngCH₄ m⁻² s⁻¹ (Fig. 1). This observation suggests that the plants were the source of methane although it does not completely discount the possibility of the flux being due methane desorption from plant tissue while exposed to higher daytime temperatures as discussed above.

Sanhueza and Donoso (2006) did not report on the amount of biomass removed in their study, but if one assumes that there was 0.5 kgDW m⁻², their measured rates are of the same order of magnitude, but still significantly less, than the rates reported by Keppler *et al.* (2006), especially if one were to compare it against the rates in the light (Table 1). It is possible that the differing effect of adsorption/desorption in the two studies could account for the difference. Other differences between species, growth or measurement conditions could, of course, also further account for any differences.

One interesting aspect of the study by Sanhueza and Donoso (2006) was their observed temperature response, with the difference between the systems with and without plants diminishing with increasing temperature. Below 30°C, there was about a 10 ngCH₄ m⁻² s⁻¹ difference attributable to methane release by intact plants, but above 30°C, the difference and the apparent methane release completely disappeared (Fig. 1). In contrast, Keppler *et al.* (2006) had shown that methane release from dead tissue increased strongly with temperature up to 70°C. The data of Sanhueza and Donoso (2006) suggested that methane release from intact plants may have a very different temperature response, thus possibly supporting the hypothesis that different processes may be involved in methane release in intact versus dead plant material.

Other indirect evidence for the occurrence of aerobic methane release comes from a study by Crutzen *et al.* (2006), who observed nocturnal build-up of methane in an inversion layer above mixed savannah and tropical forest vegetation. This could correspond to aerobic methane release by plants, but other possible sources of methane, such as termites, could not be excluded.

Sanhueza (2007) used the data of Crutzen *et al.* (2006) and the savannah measurements by Sanhueza and Donoso (2006) to deduce a forest emission rate of 70 ngCH₄ m⁻² s⁻¹, but the presence of other possible methane sources and the general difficulties of confidently quantifying fluxes with inversion techniques make that comparison uncertain.

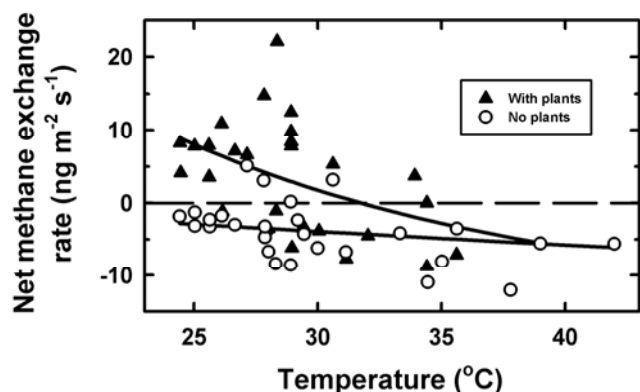


Fig. 1 Net methane exchange rates with and without plants as a function of temperature. Data redrawn from Sanhueza and Donoso (2006), with negative exponential curves drawn through the two data sets.

While the study of Crutzen *et al.* (2006) is thus consistent with the postulated magnitude of aerobic methane release, other possible explanations cannot be excluded on the basis of the available information.

do Carmo *et al.* (2006) observed nocturnal CH₄ emissions in a field study in Brazil by measuring the concentration profile in an undisturbed rainforest and obtained rates of 80 ± 64 (95% confidence limit) ngCH₄ m⁻² s⁻¹. This is of the same magnitude as the rates obtained by the other studies, but again other sources of methane, such as termites or anaerobic micro-sites, as well as the variable sink-source balance in the soil could not be further quantified. This study is thus also consistent with the notion of the presence of aerobic methane release, but other explanations could also account for it.

Frankenberg *et al.* (2005, 2006) reported satellite observations of the CH₄ profile across the globe and included comparisons with concentrations calculated from recognised sources and sinks. They found that there were higher than expected concentrations over tropical forest regions. Aerobic CH₄ emission from plants could possibly resolve this discrepancy. However, there is considerable uncertainty in all the other flux terms of the global budget as well, such as emissions from biomass burning, termites, wetlands, the CH₄ production/oxidation balance in partly wet soils, and oxidation rates by OH in the atmosphere (Allan *et al.* 2007) so that other possible explanations for the discrepancies cannot be ruled out, either. While global observations like those of Frankenberg *et al.* (2005, 2006) can pinpoint any discrepancies between observed and modelled budgets, there are, in principle, several possible adjustments that could be made to either source or sink terms to rectify those discrepancies.

In summary, the studies of Keppler *et al.* (2006) and Sanhueza and Donoso (2006) have demonstrated the apparent release of methane from plants under aerobic conditions. As the measured rates are exceedingly low, problems of potential artefacts, such as adsorption and desorption, are a persistent cause of concern and are likely to have added to any actual plant-derived emissions. The observation of plant-specific isotopic signatures of the released methane, however, strongly supports the notion that at least part of the observed emissions must be of biogenic origin. Dueck *et al.* (2007), on the other hand, found no significant aerobic methane release. While this could indicate that much of the flux observed by Keppler *et al.* (2006) and Sanhueza and Donoso (2006) could be due to desorption, methane desorption could not explain the plant-specific isotopic signature of released methane observed by Keppler *et al.* (2006). More work is clearly needed to further study the reasons for different observations and the possible role of artefacts in different experimental configurations.

In addition to these direct observations of aerobic methane release, the studies by Frankenberg *et al.* (2005, 2006), Crutzen *et al.* (2006) and do Carmo *et al.* (2006) all present evidence that would be consistent with the presence of aerobic methane release. However, without being able to better constrain other potential source terms, the support they lend to the existence of aerobic methane release is only slight.

Hence, at this point it is not yet possible to confidently conclude that aerobic methane release is, indeed, real and of the magnitude given by Keppler *et al.* (2006), or whether the apparent measurements were due to artefacts such as methane desorption. However, the following discussion will be based on the assumption that aerobic methane release is, indeed, occurring and at the rates reported in the original work of Keppler *et al.* (2006).

THE GLOBAL SIGNIFICANCE OF METHANE RELEASE BY PLANTS

Keppler *et al.* (2006) used their original measurements to extrapolate to total global emissions of 149 (range 62-236) MtCH₄ yr⁻¹, which would mean that this would constitute

about one quarter of total global sources. However, Keppler *et al.* (2006) had expressed their measured rates per unit of biomass, yet used estimates of net primary production to extrapolate their measurements to the global scale. Kirschbaum *et al.* (2006) and Parsons *et al.* (2006), instead, considered it to be more consistent if estimates of global leaf mass were used for scaling instead. Using this alternative assumption, they derived estimates of 36 and 42 MtCH₄ yr⁻¹, respectively. Parsons *et al.* (2006), additionally estimated that non-leafy biomass could emit a further 10 MtCH₄ yr⁻¹. Sanhueza and Donoso (2006) and Sanhueza (2007) also used the measurements from their savannah system and tried to extrapolate that to a larger scale, and with their estimates were within the range of values calculated by Kirschbaum *et al.* (2006) and Parsons *et al.* (2006) for savannah ecosystems.

A major problem with scaling estimates is that the original measurements were done at a particular temperature, light level and physiological state of the plants, and on a limited number of species, yet emission rates are likely to change with any of those conditions, but it is not known in what way. The extrapolation based on net primary production or leaf mass all rely on the implicit assumption that the original rates would be representative across all the various bioclimatic conditions that plants would experience across the world.

One approach to partly overcome that problem was used by Kirschbaum *et al.* (2006) by assuming that the ratio of photosynthesis to methane release would, instead, be a more conserved metric across the range of different environmental and plant physiological conditions. There is no direct evidence in support of this assumption, but it is just as plausible as the assumptions underlying the use of leaf mass as the basis of scaling. Using that approach, Kirschbaum *et al.* (2006) derived an even lower estimate for global emissions from living and photosynthesising plants of only 10 MtCH₄ yr⁻¹.

Ferretti *et al.* (2007) estimated likely global aerobic methane release by using constraints by isotopic ratios of methane recovered from ice core bubbles (Ferretti *et al.* 2005) and considerations of the mass balance of methane sources and sinks (Etheridge *et al.* 1998), especially pre-industrial². Based on those constraints, they concluded that aerobic methane release would have to be in the range of 0-46 MtCH₄ yr⁻¹ to be consistent with these measurements and remain within the uncertainty range of the other recognised sources and sinks.

Houweling *et al.* (2006) conducted an even more detailed analysis, including regionally based modelling of methane sources and sinks and compared that against the methane concentration profile observed by Frankenberg *et al.* (2005, 2006) as well as both present-day and pre-industrial isotopic composition and the overall budget. They concluded that aerobic methane release had to be in the range of 0-85 MtCH₄ yr⁻¹ to be consistent with those various constraints.

The pre-industrial budget constitutes a particularly strong constraint on maximum values for aerobic methane release. Any pre-industrial plant emissions presumably would have been as high or higher than they are currently, but other methane emissions would have been much smaller than they are currently (Etheridge *et al.* 1998) so that aerobic emissions from plants would have constituted a greater proportion of total emissions. This means that there is less scope for adding aerobic methane as an additional pre-industrial flux without conflicting with the current

understanding of other estimated pre-industrial fluxes and their uncertainties.

Houweling *et al.* (2006) specifically attempted to modify the size of the assumed aerobic methane source to reconcile modelled methane concentration surfaces with the satellite observations of Frankenberg *et al.* (2005, 2006). One problem with that work is that aerobic methane not only has some annual average rate, but is likely to also vary seasonally with factors such as temperature and physiological attributes of leaves. Hence, it would not be appropriate to just add an additional methane source of constant source strength wherever there are plants present. Instead, that source strength would have to be differentiated based on some environmental or plant attributes, but with current knowledge, it is not possible to add such differentiation.

For instance, Keppler *et al.* (2006) showed that rates increase with light exposure, but it is not known whether there is some saturation level. They also showed that the emissions from dead tissue increased strongly with temperature, but Sanhueza and Donoso (2006) found that emissions from intact plants appeared to decrease with increasing temperature (Fig. 1). Hence, while it seems likely that methane emissions will not be constant, it is unclear in what way and to what extent they may change with temperature or with any other environmental or plant-physiological variable. Depending on these relationships, the inclusion of aerobic methane release could possibly help to reconcile the discrepancy with current global observations, but more would need to be understood of the dependence of aerobic methane release on environmental and plant-internal conditions.

In summary, in the original publication, Keppler *et al.* (2006) proposed a potentially large global aerobic methane flux. However, that original estimate has not been supported by other studies that tried to estimate total global emissions. These studies ranged from simple scaling based on the original flux rates measured by Keppler *et al.* (2006), but using different and perhaps more consistent assumptions, to more sophisticated approaches that used full budgeting and isotopic constraints on the magnitude of this potential new source. All of these studies concluded that aerobic methane release would have to be a smaller source than that originally postulated by Keppler *et al.* (2006), contributing between 0-10% of current and 0-30% of pre-industrial emissions.

At the same time, all of these studies were hampered by a lack of even basic knowledge of the dependence of methane release on the bioclimatic condition of leaves. Further basic process studies and more sophisticated modelling approaches are required before the role of aerobic methane release can be more confidently quantified at the global scale.

CONTRASTING LAND-USE OPTIONS

Perhaps the most important consequence of the work of Keppler *et al.* (2006) was an immediate questioning of the value of tree plantings as a greenhouse response strategy, and various media commentators saw great importance in this new finding, some even casting doubt on the very basis of the Kyoto Protocol. At the same time, it is difficult to see where that assessment originated from as Keppler *et al.* (2006) had made no claim as to the potential significance of their findings for tree planting strategies.

The significance for tree plantings was alluded to in an opinion article (Lowe 2006) that accompanied the original publication of Keppler's work in Nature. However, that article also did not include any calculations of the quantitative effect of aerobic methane release on the value of tree plantings as a greenhouse mitigation option, and we are not aware of any published calculations that would have supported that early flurry of media activity.

A first quantification of the effect of aerobic methane release on negating the carbon storage benefit of tree plantings was provided by Kirschbaum *et al.* (2006). They used a range of assumptions covering the range of observed me-

² The reference to pre-industrial should more fully be expressed as pre-industrial/pre-agricultural as agriculturally-based emissions from rice cultivation and enteric fermentation in ruminants are quantitatively very important in addition to fossil-fuel based emissions and emissions from modern landfills. As a short-cut, this is referred to as just pre-industrial here and in the following.

Table 3 Methane fluxes due to aerobic methane release, soil oxidation and grazing sheep and combined net fluxes for a system studied in New Zealand. All fluxes are expressed in $\text{ngCH}_4 \text{ m}^{-2} \text{ s}^{-1}$ and given as means \pm standard deviations. Positive numbers are emissions to the atmosphere and negative numbers are uptake from the atmosphere. Modified from the data in Kelliher *et al.* (2006).

	Aerobic methane release	Soil oxidation	Ruminant emissions	Net emissions
Forest	51 \pm 35	-33 \pm 7	0	17 \pm 36
Grazed grassland	10 \pm 6	-4 \pm 1	304 \pm 82	310 \pm 83
Difference (Forest - grassland)	41	-29	-304	-293

thane release rates and assumptions that were representative of different tree-grass comparisons and concluded that the carbon storage benefit would be negated by aerobic methane release by only between 0 and 4.4%, with a most likely estimate of less than 1%.

In addition, soils of most ecosystems also oxidise CH_4 , and in the context of assessing the impact of land-use choices on the methane cycle, any effects of land use on aerobic methane production rates are as important as effects on methane oxidation rates in the soil. Oxidation rates are generally in the range of 3-15 $\text{ngCH}_4 \text{ m}^{-2} \text{ s}^{-1}$ (Smith *et al.* 2000; Mosier *et al.* 2004; Sanhueza and Donoso 2006), with a typical reduction by about 2/3 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).

As methane oxidation rates are largely diffusion limited (Striegl 1993; Ridgwell *et al.* 1999), the greater oxidation rates in forest soils may be related to soil structure and the properties of any litter layer. Inorganic nitrogen has also been shown to have a direct inhibitory effect on methane oxidation rates (Le Mer and Roger 2001). Methane oxidation rates are 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 CH_4 is produced rather than oxidised.

Hence, forests have the benefit, at least compared to cultivated soils, of encouraging CH_4 oxidation in the soil by $\approx 3\text{-}10 \text{ ngCH}_4 \text{ m}^{-2} \text{ s}^{-1}$ (Smith *et al.* 2000) which adds to the benefit of tree plantings. It is also important to treat methane oxidation not as a flux with a constant rate, but, as the work of MacDonald *et al.* (1996) and Price *et al.* (2004) has shown, as a flux that is highly dynamic and can even change from an uptake to a release with moderate changes in soil wetness. This creates significant problems for scaling net methane emissions to the global scale.

Other changes usually accompany the transition between forest and agricultural land uses, and Kelliher *et al.* (2006) showed that methane emissions from enteric fermentation from ruminant animals such as sheep or cattle are of the order of $\approx 300 \text{ ngCH}_4 \text{ m}^{-2} \text{ s}^{-1}$ and are likely to be quantitatively much more important than aerobic methane release from plants or methane oxidation in the soil. So, while aerobic methane release may be higher from a forest than a grassland (by 41 $\text{ngCH}_4 \text{ m}^{-2} \text{ s}^{-1}$ as calculated by Kelliher *et al.* 2006), the total net effect, including aerobic methane release, methane oxidation in the soil and animal emissions, means that net emissions are much higher from a grazed pasture than forests (by 293 $\text{ngCH}_4 \text{ m}^{-2} \text{ s}^{-1}$; Table 3).

CONCLUSIONS

When Keppler *et al.* (2006) early in 2006 described the first observations of aerobic methane release by living plants and dead organic matter, it caused major excitement and a re-think of the total global methane budget. However, at the time of writing this review, these original findings have not yet been independently repeated and confirmed, and the only other detailed laboratory based study (Dueck *et al.* 2007) reported findings that were inconsistent with the findings of Keppler *et al.* (2006). Some studies have lent circumstantial support to the existence of aerobic methane release, but the circumstantial nature of these observations

does not rule out alternative explanations, either. So far, no plausible chemical mechanism for the process has been postulated, and it is particularly puzzling how the process can occur abiotically.

In addition, there are still important methodological concerns, particularly with respect to adsorption/desorption processes that are likely to have modified any observed apparent emission rates, but the likely magnitude of these problems has yet to be determined. Until there is a better quantification of the effects of adsorption/desorption, in particular, one needs to be cautious about the acceptance of any observed apparent emission rates. It would be preferable if experimental procedures could be devised to overcome these concerns of possible artefacts. Kirschbaum *et al.* (2006) also suggested a range of additional experiments that could be conducted to allay concerns about possible artefacts and better determine the physiological relationships between aerobic methane release and temperature, light level, length of exposure, differences between species and the actual biochemical compounds from which methane is derived.

Within the global context, aerobic methane release is, however, likely to only play a minor role in any case. All studies have consistently shown that aerobic methane release is unlikely to be responsible for more than about 10%, at most, of current emissions although may have contributed a more significant proportion to pre-industrial emissions.

In the context of land-use change, consideration of aerobic CH_4 emissions from different plant types is a small factor and likely to be outweighed by effects on soil oxidation and ruminant emissions, where they occur. The effect of carbon sequestration in greenhouse gas equivalent terms is likely to be more than 100 times as important as any change in aerobic methane release.

Aerobic methane fluxes are exceedingly small even at the rates reported by Keppler *et al.* (2006). While a more complete understanding of aerobic methane release is important in terms of completing our understanding of all methane sources and sinks, it is unlikely to require a major re-think of the global distribution of sources and sinks. It is also unlikely to have any significant bearing on greenhouse mitigation strategies.

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REFERENCES

- Allan W, Struthers H, Lowe DC (2007) Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: global model results compared with Southern Hemisphere measurements. *Journal of Geophysical Research* **112**, Art. no 4306
- Bauchot AD, Hallett IC, Redgwell RJ, Lallu N (1999) Cell wall properties of kiwifruit affected by low temperature breakdown. *Postharvest Biology and Technology* **16**, 245-255
- Berry JA, Raison JK (1982) Responses of macrophytes to temperature. In: Lange OL, Nobel PS, Osmond CB, Ziegler H (Eds) *Physiological Plant Ecology I. Responses to the Physical Environment*, Encyclopedia of Plant Physiology, New Series Vol. 12A, Springer-Verlag, Berlin, pp 277-338
- Biloe S, Goetz V, Guillot A (2002) Optimal design of an activated carbon for an adsorbed natural gas storage system. *Carbon* **40**, 1295-1308
- Blom CWPM (1999) Adaptations to flooding stress: From plant community to molecule. *Plant Biology* **1**, 261-273

- Bruhn D, Mikkelsen TN, Atkin OK (2002) Does the direct effect of atmospheric CO₂ concentration on leaf respiration vary with temperature? Responses in two species of *Plantago* that differ in relative growth rate. *Physiologia Plantarum* **114**, 57-64
- Carpita N, Sabularse D, Montezinos D, Delmer DP (1979) Determination of the pore size of cell walls of living plant cells. *Science* **205**, 1144-1147
- Carpita NC, Gibeaut DM (1993) Structural models of primary cell walls in flowering plants – consistency of molecular structure with the physical properties of the walls during growth. *The Plant Journal* **3**, 1-30
- Celzard A, Fierro V (2005) Preparing a suitable material designed for methane storage: A comprehensive report. *Energy and Fuels* **19**, 573-583
- Cheng A-L, Huang W-L (2004) Selective adsorption of hydrocarbon gases on clays and organic matter. *Organic Geochemistry* **35**, 413-423
- Constable J VH, Grace JB, Longstreth DJ (1992) High carbon dioxide concentrations in aerenchyma of *Typha latifolia*. *American Journal of Botany* **79**, 415-418
- Copolovici LO, Niinemets Ü (2005) Temperature dependencies of Henry's law constants and octanol/water partition coefficients for key plant volatile monoterpenoids. *Chemosphere* **61**, 1390-1400
- Crutzen PJ, Sanhueza E, Brenninkmeijer CAM (2006) Methane production from mixed tropical savanna and forest vegetation in Venezuela. *Atmospheric Chemistry and Physics Discussions* **6**, 3093-3097
- do Carmo JB, Keller M, Dias JD, de Camargo PB, Crill P (2006) A source of methane from upland forests in the Brazilian Amazon. *Geophysical Research Letters* **33**, Art. no L04809
- Dueck TA, de Visser R, Poorter H, Persijn S, Gorissen A, de Visser W, Schapendonk A, Verhagen J, Snel J, Harren FJM, Ngai AKY, Verstappen F, Bouwmeester H, Voeseek LACJ, van der Werf A (2007) No evidence for substantial aerobic methane emission by terrestrial plants: A ¹³C-labelling approach. *New Phytologist* **175**, 29-35
- Ehhalt D, Prather M, Dentener F, Derwent R, Dlugokencky E, Holland E, Isaksen I, Katima J, Kirchhoff V, Matson P, Midgley P, Wang M (2001) Atmospheric Chemistry and Greenhouse Gases. In: Houghton JT, Ding Y, Griggs DJ, Noguera M, van der Linden PJ, Dai X, Maskell K, Johnson CA (Eds) *Climate Change 2001: The Scientific Basis*, IPCC Working Group I, Third Assessment Report, Cambridge University Press: Cambridge, UK, pp 239-288
- Etheridge DM, Steele LP, Francey RJ, Langenfelds RL (1998) Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions and climate variability. *Journal of Geophysical Research* **103**, 15979-15993
- Falabella JB, Kizzie AC, Teja AS (2006) Henry's constants of gases and volatile organic compounds in aqueous solutions. *Fluid Phase Equilibria* **241**, 96-102
- Fall R, Benson AA (1996) Leaf methanol - the simplest natural product from plants. *Trends in Plant Science* **1**, 296-301
- Ferretti DF, Miller JB, White JWC, Etheridge DM, Lassey KR, Lowe DC, MacFarling Meure CM, Dreier MF, Trudinger CM, van Ommen TD, Langenfelds RL (2005) Unexpected changes to the global methane budget over the past 2000 years. *Science* **309**, 1714-1717
- Ferretti DF, Miller JB, White JWC, Lassey KR, Lowe DC, Etheridge DM (2007) Stable isotopes provide revised global limits of aerobic methane emissions from plants. *Atmospheric Chemistry and Physics* **7**, 237-241
- Field CB, Ball JT, Berry JA (1989). Photosynthesis: principles and field techniques. In: Pearcy RW, Ehleringer JR, Mooney HA, Rundel PW (Eds) *Plant Physiological Ecology. Field Methods and Instrumentation*, Chapman and Hall, London, pp 209-253
- Frankenberg C, Meirink JF, Bergamaschi, P, Goede APH, Heimann M, Körner S, Platt U, van Weele M, Wagner T (2006) Satellite cartography of atmospheric methane from SCIAMACHY onboard ENVISAT: Analysis of the years 2003 and 2004. *Journal of Geophysical Research* **111**, Art. No. D07303
- Frankenberg C, Meirink JF, van Weele M, Platt U, Wagner T (2005) Assessing methane emissions from global space-borne observations. *Science* **308**, 1010-1014
- Harrison D, Seakins PW, Lewis AC (2000) Simultaneous monitoring of atmospheric methane and speciated nonmethane hydrocarbon concentrations using Peltier effect sub-ambient pre-concentration and gas chromatography. *Journal of Environmental Monitoring* **2**, 59-63
- Higaki S, Oya Y, Makide Y (2006) Emission of methane from stainless steel surface investigated by using tritium as a radioactive tracer. *Chemistry Letters* **35**, 292-293
- Houweling S, Dentener F, Lelieveld J (2000) Simulation of preindustrial methane to constrain the global source strength of natural wetlands. *Journal of Geophysical Research* **105**, 17243-17255
- Houweling S, Röckmann T, Aben I, Keppler F, Krol M, Meirink JF, Dlugokencky EJ, Frankenberg C (2006) Atmospheric constraints on global emissions of methane from plants. *Geophysical Research Letters* **33**, Art. No. L15821
- In YY, Chai HH, No KT (2005) A partition coefficient calculation method with the SFED model. *Journal of Chemical Information and Modeling* **45**, 254-263
- Jackson MB, Attwood PA (1996) Roots of willow (*Salix viminalis* L.) show marked tolerance to oxygen shortage in flooded soils and in solution culture. *Plant and Soil* **187**, 37-45
- Kelliher FM, Clark H, Zheng L, Newton PCD, Parsons AJ, Rys G (2006) A comment on scaling methane emissions from vegetation and grazing ruminants in New Zealand. *Functional Plant Biology* **33**, 613-615
- Keppler F, Hamilton JTG, Braß M, Röckmann T (2006) Methane emissions from terrestrial plants under aerobic conditions. *Nature* **439**, 187-191
- Kim BK (1991) Unexpected errors in gas-chromatographic analysis of methane production by thermophilic bacteria. *Applied Environmental Microbiology* **57**, 1866-1869
- Kirschbaum MUF, Bruhn D, Etheridge DM, Evans JR, Farquhar GD, Gifford RM, Paul KI, Winters AJ (2006) A comment on the quantitative significance of aerobic methane release by plants. *Functional Plant Biology* **33**, 521-530
- le Mer J, Roger P (2001) Production, oxidation, emission and consumption of methane by soils: a review. *European Journal of Soil Biology* **37**, 25-50
- Long SP, Bernacchi CJ (2003) Gas exchange measurements, what can they tell us about the underlying limitations to photosynthesis? Procedures and sources of error. *Journal of Experimental Botany* **54**, 2393-2401
- Lowe DC (2006) A green source of surprise. *Nature* **439**, 148-149
- Lozano-Castello D, Alcaniz-Monge J, de la Casa-Lillo MA, Cazorla-Amoros D, Linares-Solano A (2002) Advances in the study of methane storage in porous carbonaceous materials. *Fuel* **81**, 1777-1803
- MacDonald JA, Skiba U, Sheppard LJ, Hargreaves KJ, Smith KA, Fowler D (1996) Soil environmental variables affecting the flux of methane from a range of forest, moorland and agricultural soils. *Biogeochemistry* **34**, 113-132
- McBain MC, Warland JS, McBride RA, Wagner-Riddle C (2004) Laboratory-scale measurements of N₂O and CH₄ emissions from hybrid poplars (*Populus deltoides* x *Populus nigra*). *Waste Management Research* **22**, 454-465
- Mosier A, Wassmann R, Verchot L, King J, Palm C (2004) Methane and nitrogen oxide fluxes in tropical agricultural soils: sources, sinks and mechanisms. *Environment, Development and Sustainability* **6**, 11-49
- Niinemets Ü, Reichstein M (2002) A model analysis of the effects of nonspecific monoterpenoid storage in leaf tissues on emission kinetics and composition in Mediterranean sclerophyllous *Quercus* species. *Global Biogeochemical Cycles* **16**, Art. No. 1110
- Niinemets Ü, Reichstein M (2003a) Controls on the emission of plant volatiles through stomata: sensitivity or insensitivity of the emission rates to stomatal closure explained. *Journal of Geophysical Research - Atmospheres* **108**, 4208
- Niinemets Ü, Reichstein M (2003b) Controls on the emission of plant volatiles through stomata: a sensitivity analysis. *Journal of Geophysical Research - Atmospheres* **108**, 4211
- Noe SM, Ciccioli P, Brancaleoni E, Loreto F, Niinemets Ü (2006) Emissions of monoterpenes linalool and ocimene respond differently to environmental changes due to differences in physico-chemical characteristics. *Atmospheric Environment* **40**, 4649-4662
- Ollivier B, Garcia J-L (1990) Thermophilic methanogenesis from pectin by a mixed defined bacterial culture. *Current Microbiology* **20**, 77-81
- Parsons AJ, Newton PCD, Clark H, Kelliher FM (2006) Scaling methane emissions from vegetation *Trends in Ecology and Evolution* **21**, 423-424
- Pignatello JJ, Xing B (1996) Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology* **30**, 1-11
- Pollmann J, Helmig D, Hueber J, Tanner D, Tans PP (2006) Evaluation of solid adsorbent materials for cryogen-free trapping – gas chromatographic analysis of atmospheric C₂-C₆ non-methane hydrocarbons. *Journal of Chromatography A* **1134**, 243-248
- Price SJ, Kelliher FM, Sherlock RR, Tate KR, Condon LM (2004) Environmental and chemical factors regulating methane oxidation in a New Zealand forest soil. *Australian Journal of Soil Research* **42**, 767-776
- Ramaswamy V, Boucher O, Haigh J, Hauglustaine D, Haywood J, Myhre G, Nakajima T, Shi GY, Solomon S (2001) Radiative forcing of climate change. In: Houghton JT, Ding Y, Griggs DJ, Noguera M, van der Linden PJ, Dai X, Maskell K, Johnson CA (Eds) *Climate Change 2001: The Scientific Basis*, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, pp 349-416
- Ridgwell AJ, Marshall SJ, Gregson K (1999) Consumption of atmospheric methane by soils: A process-based model. *Global Biogeochemical Cycles* **13**, 59-70
- Sanhueza E (2007) Methane soil-vegetation-atmosphere fluxes in tropical ecosystems. *Interciencia* **32**, 30-34
- Sanhueza E, Donoso L (2006) Methane emission from tropical savanna *Trachypogon* sp. grasses. *Atmospheric Chemistry and Physics* **6**, 5315-5319
- Shao X, Wang W (2004) Adsorption of methane and hydrogen on mesocarbon microbeads by experiment and molecular simulation. *Journal of Physical Chemistry B* **108**, 2970-2978
- Smith KA, Dobbie KE, Ball BC, Bakken LR, Sitaula BK, Hansen S, Brumme R, Borken W, Christensen S, Prieme A, Fowler D, MacDonald JA, Skiba U, Klemmedtsson L, Kasimir-Klemmedtsson A, Degorska A, Orlanski P (2000) Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystems, and uncertainties in the global terrestrial sink. *Global Change Biology* **6**, 791-803
- Striegl RG (1993) Diffusional limits to the consumption of atmospheric methane by soils. *Chemosphere* **26**, 715-720
- Thammakhetta C, Thavarungkul P, Brukh R, Mitra S, Kanatharana P (2005) Microtrap modulated flame ionization detector for on-line monitoring of methane. *Journal of Chromatography A* **1072**, 243-248
- Zhang T, Krooss BM (2001) Experimental investigation on the carbon isotope fractionation of methane during gas migration by diffusion through sedimentary rocks at elevated temperature and pressure. *Geochimica et Cosmochimica Acta* **65**, 2723-2742