Global methane emission estimates from ultraviolet irradiation of terrestrial plant foliage

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Summary

• Several studies have reported in situ methane (CH₄) emissions from vegetation foliage, but there remains considerable debate about its significance as a global source. Here, we report a study that evaluates the role of ultraviolet (UV) radiation-driven CH₄ emissions from foliar pectin as a global CH₄ source.
• We combine a relationship for spectrally weighted CH₄ production from pectin with a global UV irradiation climatology model, satellite-derived leaf area index (LAI) and air temperature data to estimate the potential global CH₄ emissions from vegetation foliage.
• Our results suggest that global foliar CH₄ emissions from UV-irradiated pectin could account for 0.2–1.0 Tg yr⁻¹, of which 60% is from tropical latitudes, corresponding to < 0.2% of total CH₄ sources.
• Our estimate is one to two orders of magnitude lower than previous estimates of global foliar CH₄ emissions. Recent studies have reported that pectin is not the only molecular source of UV-driven CH₄ emissions and that other environmental stresses may also generate CH₄. Consequently, further evaluation of such mechanisms of CH₄ generation is needed to confirm the contribution of foliage to the global CH₄ budget.

Introduction

Methane (CH₄) is a long-lived greenhouse gas with a 100 yr global warming potential 25 times that of CO₂, and its current atmospheric concentration of 1.8 ppm makes a significant contribution to climatic warming (Solomon et al., 2007). While the main components of the global CH₄ budget have been identified and the total global CH₄ source is relatively well known (Forster et al., 2007), the individual sources and sinks and the recent changes in the growth rate of atmospheric CH₄ concentration and its interannual variability are far from comprehensively understood (Bousquet et al., 2006; Solomon et al., 2007); recent findings have questioned both the identity and magnitude of several important source terms (Beerling et al., 2007). New estimates of marine CH₄ sources have recently been reported for deep-water geological seeps (Solomon et al., 2009) and for surface phytoplankton in oceanic waters (Karl et al., 2008), while a new and controversial terrestrial source of CH₄ was also proposed by Keppler et al. (2006), who observed emissions from vegetation foliage under aerobic experimental conditions.

Hitherto, terrestrial CH₄ emissions from biogenic sources were attributed solely to methanogenic microorganisms growing under anaerobic conditions in wetland soils, rice paddies, the gastrointestinal tract of ruminants and termites, and landfills (Keppler et al., 2006; Bloom et al., 2010). However, Keppler et al. (2006) observed CH₄ emissions into CH₄-free air from detached leaves, air-dried leaves, intact plants and the plant structural component pectin. They reported emission rates from air-dried leaves of C₃ and C₄ plants in the range 0.2–3 ng g⁻¹ leaf DW h⁻¹ at 30°C, but these increased to much higher rates of 12–370 ng g⁻¹ leaf DW h⁻¹ for intact plants. Their emission rates increased by a factor of 3–5 when experimental chambers were exposed to natural sunlight and they also
increase over the range 30–70°C. This suggested a nonenzymatic mechanism as they occurred above the threshold of 50–60°C at which plant enzymes are denatured (Berry & Raison, 1981), but they knew of no mechanism to explain their observations (Keppler et al., 2006). Although these rates of emission were small, Keppler et al. (2006) completed a rough extrapolation of the total annual global emission of CH₄ from live vegetation by using mean sunlit and dark emission rates for leaf biomass scaled by day length, duration of growing season, and total net primary productivity (NPP) in each biome. Their estimate of between 62 and 236 Tg (1 Tg = 10¹² g) CH₄ yr⁻¹, with the largest contribution of 46–169 Tg CH₄ yr⁻¹ from tropical forests and grassland, was observed to equate to 10–40% of the known annual CH₄ source strength. Plant litter was estimated to contribute 0.5–6.6 Tg CH₄ yr⁻¹. Consequently, these first observations of Keppler et al. (2006) caused intense interest, considerable debate and some scepticism among the scientific community and the media (Schiermeier, 2006a,b), leading to further experimental studies and a wider consideration of their implications for the global CH₄ budget and greenhouse gas mitigation options (Lowe, 2006; NIEPS, 2006).

An early indication that the upscaling approach of Keppler et al. (2006) contained methodological inconsistencies came from Kirschbaum et al. (2006), who used two different methods to estimate global CH₄ emissions based on leaf biomass (rather than NPP) and on photosynthesis. Both approaches suggested much lower global emissions from vegetation than originally proposed by Keppler et al. (2006). Subsequently, further analyses using a variety of methods (Houweling et al., 2006; Parsons et al., 2006; Butenhoff & Khalil, 2007; Ferretti et al., 2007; Megonigal & Guenther, 2008) also suggested substantially lower global emissions from a vegetation source (Table 1). Most recently, Rice et al. (2010) have estimated the global transfer of soil-derived CH₄ to the atmosphere by trees in flooded forest regions.

Several recent studies were unable to detect any CH₄ emissions from vegetation foliage (Beering et al., 2007; Ducek et al., 2007; Kirschbaum & Walcroft, 2008; Megonigal & Guenther, 2008; Nisbet et al., 2009), but other studies have reported CH₄ emissions (Cao et al., 2008; McLeod et al., 2008; Vigano et al., 2008; Wang et al., 2008; Bru¨ ggemann et al., 2009; Bruhn et al., 2009) and some have proposed that ultraviolet (UV) generation of reactive oxygen species (ROS) is a component of the mechanism for CH₄ formation (Messenger et al., 2009a,b). Following the suggestion by Keppler et al. (2006) that the methyl esters (methoxyl groups) of pectin were a potential source of CH₄, Vigano et al. (2008), McLeod et al. (2008) and Bruhn et al. (2009) all demonstrated that CH₄ emissions from the structural component pectin, as well as fresh and dried leaf tissue, depend on UV radiation. The studies of Dueck et al. (2007), Beering et al. (2008) and Kirschbaum & Walcroft (2008) did not include UV wavelengths, which might

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LAI, leaf area index; MODIS, Moderate Resolution Imaging Spectroradiometer; VOC, volatile organic compound.
explain the absence of CH4 emissions in their experiments. McLeod et al. (2008) and Bruhn et al. (2009) also demonstrated that prior removal of methyl esters from pectin stopped CH4 production under UV irradiation, while Keppler et al. (2008) used isotopically labelled pectin to demonstrate that pectin methyl esters are a source of the emitted CH4. These studies clearly demonstrate that pectin can be a source of CH4 under the influence of UV irradiation, including natural sunlight (McLeod et al., 2008). We therefore decided to estimate the potential global production of CH4 from plant pectin under appropriate spectrally weighted UV radiation. In this study we used the spectral weighting function for UV-driven CH4 emission from foliar pectin weighted UV radiation. In this study we used the spectral weighting function for UV-driven CH4 emission from foliar pectin (McLeod et al., 2008) to provide a first estimate of the potential global emission of CH4 from foliar pectin and we compare this with other published estimates of the contribution of vegetation to the global CH4 budget.

Materials and Methods

We estimate monthly CH4 emissions per unit ground area (FCH4) from the UV irradiation of terrestrial plant foliage using a CH4 emission rate per unit leaf DW (KLeaf) with a global distribution of leaf DW estimated from the mean biome specific leaf area (SLA) and the global distribution of leaf area index (LAI). We assume that where LAI > 1, the total incident UV radiation is intercepted by unit LAI and that all its foliar pectin is irradiated. We extrapolate short-term (2 h) experimental emission rates from McLeod et al. (2008) to a monthly timescale, thus providing an upper estimate of global emissions but with assumptions that are discussed later.

We estimate FCH4 using the following relationship:

\[ F_{CH4}(t) = C(t)K_{LEAF}UV_{CH4}(t)M_{LEAF}(t), \]

Eqn 1

where \( t \) refers to a particular month; \( C(t) \) describes the temperature dependence of the emission rate on monthly timescales; \( K_{LEAF} \) is the CH4 production per unit leaf DW (kg CH4 kg\(^{-1}\) leaf DW) per unit of spectrally weighted UV irradiation (J m\(^{-2}\)); \( UV_{CH4} \) is the monthly total UV irradiation spectrally weighted for methanogenesis (J m\(^{-2}\)); and \( M_{LEAF} \) is the irradiated leaf DW calculated from the product of leaf area (with LAI ≤ 1) and mean biome SLA. We evaluate monthly \( F_{CH4} \) on a spatial scale of 1.25° longitude by 1.00° latitude resolution, from which we determine global mean annual \( F_{CH4} \). In the following sections we describe the details of all terms involved in calculating \( F_{CH4} \) along with their respective uncertainties.

Rate of foliar CH4 emission (KLeaf)

We calculate the foliar CH4 emission (KLeaf) from the leaf content of pectin, a structural component of plant cell walls, and a CH4 emission rate from pectin (KPECTIN) that was found in previous work to be linearly related to spectrally weighted UV irradiance (UVCH4) at 30°C (McLeod et al., 2008), where \( K_{PECTIN} = 3.09 \times 10^{-11} \) kg CH4 kg\(^{-1}\) pectin DW per unit of spectrally weighted UV irradiation (J m\(^{-2}\)). The spectral weighting, described later, was determined by finding the best-fit straight-line logarithmic relationship between weighted irradiance and CH4 emission using three types of polychromatic UV lamps and sunlight (McLeod et al., 2008). An independent study found a linear relationship between unweighted UV irradiance and CH4 emission from pectin and living leaves (Vigano et al., 2008) that extended up to five times ambient irradiance, and demonstrated persistent emissions over 35 d. Similar results were observed over a 1 wk period by Bruhn et al. (2009). We therefore apply laboratory measurements of \( K_{PECTIN} \) to larger spatial and temporal scales, as these measurements showed that UV-driven \( K_{PECTIN} \) was constant over long periods of time, and changed linearly with the UV irradiance. We assume a constant rate of \( 3.09 \times 10^{-11} \) kg CH4 kg\(^{-1}\) pectin per unit irradiation (J m\(^{-2}\)) for the UV-driven CH4 emission from pectin as an upper limit in our calculations and discuss the limitations of this approach later in the paper.

Published estimates of the pectin and cell wall content of vegetation vary between species and between plant organs, with the cell wall content averaging 15–20% of organ DW. Approximately 30% of the DW of the primary cell wall of dicots (flowering plants, angiosperms, with two cotyledons) is composed of pectins, while monocots (angiosperms with only one cotyledon) are generally thought to have very small amounts of pectin (McNeil et al., 1984; Voragen et al., 2009). However, Jarvis et al. (1988) found a large variability in pectin content between different monocot species, some containing similar amounts to the dicots. We therefore use a value for pectin content of 5% leaf DW as a representative upper value of the reported range. Assuming a foliar pectin content of 5% leaf DW provides a CH4 emission rate from UV irradiance of foliage, \( K_{LEAF} \), of \( 1.54 \times 10^{-12} \) kg CH4 kg\(^{-1}\) leaf DW per unit of spectrally weighted UV irradiation (J m\(^{-2}\)). This value for \( K_{LEAF} \) is similar to the value reported previously for spectrally weighted UV-driven CH4 emissions from tobacco (McLeod et al., 2008).

We describe the temperature dependence of \( K_{PECTIN} \), \( C \), as a power law:

\[ C = Q_{10}^{(T - T_0)/10}, \]

Eqn 2

where \( T \) is leaf temperature approximated using 2 m air temperature, \( T_0 \) is 30°C, and \( Q_{10} = 2 \) (i.e. a factor of 2 variation for a 10°C change in temperature), as suggested by Bruhn et al. (2009). We use monthly mean 2 m air temperature values from the 6-hourly analyses of NCEP/NCAR.
(National Centers for Environmental Prediction/National Center for Atmospheric Research) (Kalnay et al., 1996) to evaluate \( C \) and spatially interpolate 2 m air temperature onto a regular 1.25° longitude by 1.00° latitude grid. We fit a sine curve to the 6-hourly values and use the average temperature during the warmest 12 h as a proxy for daylight leaf temperature, which we use to determine monthly mean daylight leaf temperature.

**Monthly spectrally weighted UV irradiance (UV\(_{\text{CH}_4}\))**

We calculate the CH\(_4\)-effective irradiance for pectin (UV\(_{\text{CH}_4}\)) by combining an annual climatology of UV spectral irradiance \( I(\lambda) \) at the Earth’s surface with a spectral sensitivity function for UV production of CH\(_4\) from pectin \( B(\lambda) \) (McLeod et al., 2008):

\[
UV_{\text{CH}_4} = \int_{280 \text{ nm}}^{400 \text{ nm}} I(\lambda) B(\lambda) d\lambda dt. \quad \text{Eqn 3}
\]

We evaluate UV\(_{\text{CH}_4}\) every 30 min in 1 nm steps from 280 to 400 nm using the NCAR radiative transfer TUV (tropospheric ultraviolet–visible) model (Madronich, 1993; Madronich & Flocke, 1997), and determine the monthly total irradiation on a geographical resolution of 1.25° longitude by 1.00° latitude.

We use the TUV model with satellite-based (Nimbus-7, Meteor-3 and Earth Probe) total ozone mapping spectrometer (TOMS) observations of column O\(_3\) (Herman et al., 1996; McPeters et al., 1996, 1998) averaged over 11 yr (1990–2000) to calculate \( I(\lambda) \). We account for scattering from aerosols and clouds by using TOMS reflectivity measurements at 380 nm and a cloud adjustment factor following the method of Lee-Taylor et al. (2010).

The spectral weighting function for UV production of CH\(_4\) from pectin, \( B(\lambda) \), determined by McLeod et al. (2008), which decays by a factor of 10 every 80 nm and is normalized to unity at 300 nm, is given by

\[
B(\lambda) = 10^{(300-\lambda)/80}. \quad \text{Eqn 4}
\]

Notably, this function is similar to that determined for CO emissions from plant leaves by Schade et al. (1999). Fig. 1 shows the monthly distribution of UV\(_{\text{CH}_4}\) for January and July, accounting for mean column O\(_3\) and cloud cover between 1990 and 2000. We also calculate the UV climatology without correction for cloud cover (data not shown) for comparative calculations (described later).

**Dry weight of UV-irradiated leaves (\( M_{\text{LEAF}} \))**

We estimate the biomass of UV-irradiated leaves, \( M_{\text{LEAF}} \) (kg m\(^{-2}\)), by

\[
\begin{align*}
\text{Table 2} & \quad \text{Specific leaf area (SLA) of biomes (from Parsons et al., 2006) and corresponding Global Land Cover 2000 categories (GLC, 2003) for each biome} \\
\hline
\text{Biome} & \text{SLA (m}^2\text{ kg}^{-1}\text{)} & \text{GLC2000 land cover groups} \\
\hline
\text{Tropical forests} & 12.0 & \text{All forests between 23.5°N and 23.5°S} \\
\text{Temperate forests} & 8.5 & \text{All forests between 23.5–50°N and 23.5–60°S} \\
\text{Boreal forests} & 7.7 & \text{All forests between 50–90°N and 50–90°S} \\
\text{Mediterranean shrublands} & 6.9 & \text{All shrub mosaics between 23.5–45°N and 23.5–45°S} \\
\text{Tropical savannas and grassland} & 16.9 & \text{All grass cover and shrub mosaics between 23.5°N and 23.5°S} \\
\text{Temperate grasslands} & 16.9 & \text{All grass cover outside 23.5°N–23.5°S and all shrub mosaics outside 45°S–45°N} \\
\text{Deserts} & 6.9 & \text{Deserts} \\
\text{Crops} & 24.5 & \text{All cultivated/managed areas and cropland mosaics} \\
\hline
\end{align*}
\]
where \( L_w \) is the leaf DW per unit area (kg m\(^{-2}\)). The monthly mean LAI is determined from the Moderate Resolution Image Spectroradiometer (MODIS) Terra 0.25° × 0.25° LAI product (Knyazikhin et al., 1999). We interpolate LAI to the regular 1.25° longitude by 1.00° latitude grid. Then, as UV transmittance of leaves and complete leaf canopies is generally very low (McLeod & Newsham, 1997), with most UV radiation absorbed by the top 25% of forest canopies (Brown et al., 1994), we assume a maximum LAI value of 1 with total absorbance of incident UV.

\( L_w \) is the reciprocal of SLA (m\(^2\) kg\(^{-1}\)). In order to determine biome SLA values (Parsons et al., 2006) for each grid square, we use the Global Land Cover 2000 product (GLC, 2003) by matching biome categorizations (Table 2).

**Results and Discussion**

Our estimates of methane emissions based on leaf DW are shown in Fig. 2 as the magnitude and distribution of the total annual \( F_{CH4} \) (a), the maximum monthly emission (b) and the minimum monthly emission (c). \( F_{CH4} \) is larger over the tropics, where temperature and UV irradiance are highest. We find the largest values (15 mg m\(^{-2}\) yr\(^{-1}\)) over the equatorial African rainforest belt and over northern Australia. Values over the Amazon and Southeast Asia are more diffuse, with a magnitude of, typically, 10 mg m\(^{-2}\) yr\(^{-1}\) as a result of lower UV radiation (see Fig. 1).

We determine uncertainties associated with \( F_{CH4} \) by propagating the uncertainties associated with \( C, K_{LEAF}, UV_{CH4}, \) and \( M_{LEAF} \). Errors associated with the gridded 2 m air temperature analyses were assumed to be spatially uncorrelated, and were attributed an uncertainty of 0.5°C, resulting in a 3% average uncertainty for \( C, K_{PECTIN} \), and pectin content errors are globally correlated. \( K_{PECTIN} \) has an associated uncertainty of 3.7%, as determined from the uncertainty of the gradient between the empirical relationship between UV irradiance and \( CH_4 \) emissions (McLeod et al., 2008). We assign an uncertainty of 50% for pectin content, reflecting sparse information about variations within the full range of species and ecosystems. As a result, the uncertainty of \( K_{LEAF} \) (51%) is dominated by the pectin uncertainty. We attribute a random error of 5% to \( UV_{CH4} \) (Lee-Taylor & Madronich, 2007). Systematic error associated with \( UV_{CH4} \) data can be up to 25%, being largest where absorbing aerosols are present, such as industrial or heavily urbanized areas: these are significant but within the uncertainty range for \( F_{CH4} \) (see later discussion). Although a positive snow-related \( UV_{CH4} \) bias is also expected, we anticipate negligible effects on \( F_{CH4} \) as a result of low coinciding air temperature.

The use of an action spectrum and spectral weighting function can have important effects on the experimental determination of UV effects. However, uncertainties in \( CH_4 \) emissions resulting from our choice of weighting function are not expected to be large, because the same function is used to quantify determination of \( K_{PECTIN} \) and to compute the global climatology of weighted UV radiation. Using data from McLeod et al. (2008), we estimate the uncertainty in \( F_{CH4} \) resulting from our choice of \( B(\lambda) \) by using a range of slopes for \( B(\lambda) \), within 90% of the maximum correlation of the experimental relationship between weighted irradiance and \( CH_4 \) emission (i.e. \( 10^{500–\lambda}/\lambda^{2} > B(\lambda) > 10^{300–\lambda}/\lambda^{2} \)). We estimate an uncertainty of 9.5% for the product \( UV_{CH4} \times K_{PECTIN} \) by integrating the range of \( B(\lambda) \) in \( K_{PECTIN} \) using an example solar spectrum from McLeod et al. (2008) representative of \( UV_{CH4} \).

We assume spatially uncorrelated errors associated with MODIS LAI and attribute an uncertainty of 5% to LAI values ≤1. Errors in SLA are correlated within each biome and uncorrelated between different biomes: we attribute an
uncertainty of 20% for each SLA. The overall uncertainty of $M_{\text{LEAF}}$ is 55%. We find an average grid-scale emission uncertainty of 56.5% by summing the uncertainties of all terms in quadrature. Uncertainties associated with pectin content and biome SLA make the largest contributions to the overall uncertainty of $F_{\text{CH}_4}$.

Fig. 3 shows the contributions and uncertainties of $F_{\text{CH}_4}$ from the eight biomes used (Table 2). The global annual total for $F_{\text{CH}_4}$, using corrections for cloud cover and air temperature, was estimated to be $0.49 \pm 0.27$ Tg yr$^{-1}$. Emissions from tropical latitudes account for 63% of the total values, with tropical forests representing the single largest contribution to $F_{\text{CH}_4}$, as expected. Crops (20%), tropical savannas and grassland (14%) and temperate forests (10%) also represent significant contributions to $F_{\text{CH}_4}$.

Fig. 3 also shows the sensitivity of these results to the UV$_{\text{CH}_4}$ fields if the effects of clouds and temperature are included separately and in combination. The largest effect for many of the biomes results from the temperature correction $C$, particularly extra-tropical biomes where there is a large seasonal cycle in surface air temperature, resulting in a 37% decrease in global emissions compared with uncorrected values (data not shown) and a 50% decrease over extra-tropical biomes. Neglecting the cloud correction of UV irradiance would result in a 29–34% increase in emissions.

Leaf structure and its internal distribution of pectin (plus other factors described later) will affect the emission of CH$_4$, so that resulting emission may be more related to leaf surface area than to leaf DW. We therefore perform a second CH$_4$ emission calculation based on leaf area, instead of leaf DW, assuming that the experimental pectin sheets used to generate $K_{\text{PECTIN}}$ (McLeod et al., 2008) are representative of all foliage. This method of calculation assumes that the density of pectin and its UV absorbance on experimental sheets is representative of pectin in foliage and has its own caveats. However, assuming a pectin content of 5% DW for leaves, the pectin sheets (20.3 cm$^2$) containing 250 mg pectin would have an equivalent leaf SLA value of 10.3 m$^2$ kg$^{-1}$, which is within the range of average values for biome SLA (Table 2). We therefore apply the equivalent CH$_4$ emission rate per unit leaf area to $K_{\text{LEAF}}$, which we redefine as $K_{\text{LFAREA}}$ (kg CH$_4$ m$^{-2}$ leaf area) per unit spectrally weighted UV irradiance (J m$^{-2}$), and recalculate $F_{\text{CH}_4}$ using the formula:

$$F_{\text{CH}_4}(t) = C(t)K_{\text{LFAREA}}\text{UV}_{\text{CH}_4}(t)\text{LAI}(t),$$  
Eqn 6

where LAI $\leq 1$ and assuming a constant SLA value of 10.3 m$^2$ kg$^{-1}$ for all biomes. Estimating the value of $F_{\text{CH}_4}$ by scaling with leaf area yields a total CH$_4$ source of 0.65 ± 0.34 Tg, which is also shown in Fig. 3 as global and individual biome contributions. Although this method gives a global CH$_4$ source 37% higher than the value scaled using leaf DW and biome specific SLA, the spatial distributions of CH$_4$ emissions remain relatively unchanged.

Assuming global CH$_4$ sources of 550 Tg yr$^{-1}$, we find that $F_{\text{CH}_4}$ emissions scaled by leaf DW account for 0.04–0.15% of the global source. Table 1 shows our estimate to be at least one to two orders of magnitude smaller than previously reported $F_{\text{CH}_4}$ emissions. Our analysis explicitly accounts for the part of the UV spectrum where pectin emission is most responsive; accounts for the temperature dependence of $F_{\text{CH}_4}$ emissions; uses the most up-to-date global datasets to account for spatial and temporal changes in LAI, and spatial distributions of biomes; and provides an uncertainty for the $F_{\text{CH}_4}$ emission estimate related to the input datasets.

Our estimates of $F_{\text{CH}_4}$ make several assumptions that require further discussion. We extrapolate CH$_4$ emissions from plant pectin measured over 2 h to calculate monthly means and we assume that the rates of emission do not saturate at high irradiance or decline through time. We justify
this because independently determined experimental rates of UV-driven CH₄ emission were linear, with UV irradiance up to five times ambient values of unweighted UV, and persisted over 35 d (Vigano et al., 2008). The emission rate of CH₄ from irradiating experimental pectin sheets (McLeod et al., 2008) at the global maximum irradiation of \(1.27 \times 10^8\) J yr\(^{-1}\) m\(^{-2}\) from our spectrally weighted UV climatology (including cloud correction) corresponds to yearly conversion of only c. 9.6% of the pectic methyl groups on the pectin. However, it is likely that CH₄ emission rates would fall through time and our calculations should therefore be regarded as upper estimates.

We expect that the CH₄ emissions from foliar pectin will be proportional to the UV radiation absorbed but will also be influenced by leaf structure, pectin distribution, UV-photosensitizing compounds, UV-screening compounds, and chemical and biochemical processes for quenching ROS (McLeod et al., 2008; Messenger et al., 2009b). These factors will vary between plant species and influence both the spectral response and magnitude of \(k_{\text{LEAF}}\). While our calculations may provide an upper estimate for the potential global emission of CH₄ from UV irradiation of foliar pectin, there remain additional questions arising from published experimental work and potential refinements to the calculations. For instance, it would be possible to estimate UV irradiation within a leaf canopy using a model with a detailed canopy environment component (e.g. MEGAN: Model of Emissions of Gases and Aerosols from Nature as described by Mégonigal & Guenther, 2008) and to refine the calculation of \(\bar{F}_{\text{CH}_4}\) based upon canopy architecture and UV-irradiated leaf area. We omit night-time emissions from our global estimate of \(\bar{F}_{\text{CH}_4}\) as negligible emissions were observed in the absence of UV (McLeod et al., 2008). We do not include potential CH₄ emissions derived from nonleafy biomass and other plant structural compounds in foliage. Vigano et al. (2008) observed UV-driven CH₄ emissions from plant cellulose and lignin in addition to pectin and the significance of these emissions remains unquantified. Most recently, Vigano et al. (2009) reported that studies using stable isotopes revealed that only some of the CH₄ emissions detected from plants originated from pectin methyl groups. Additionally, it has been suggested that other environmental stresses (both biotic and abiotic) and cellular signalling processes that produce ROS may all generate some CH₄ from plant material (Keppler et al., 2009; Messenger et al., 2009a,b). Qaderi & Reid (2009) reported that temperature and water stress increased a subsequent CH₄ emission using six plant species, and Z. P. Wang et al. (2009) showed that physical injury also elicits CH₄ emissions.

The transport of CH₄ from anaerobic processes in soil to the atmosphere via internal plant tissues, such as aerenchyma, is well known in aquatic vascular plants (especially grasses and sedges) of wetlands and rice paddies (Schütz et al., 1991). However, several studies have suggested that soil-derived CH₄ can be transferred to the atmosphere via the transpiration stream of vegetation (Nisbet et al., 2009) or via internal tissues of trees (Rusch & Rennenberg, 1998; Terazawa et al., 2007; Rice et al., 2010), and several field observations of vegetation emissions (do Carmo et al., 2006; Crutzen et al., 2006; Sanhueza & Donoso, 2006; Sinha et al., 2007; Cao et al., 2008; Wang et al., 2008; S. Wang et al., 2009) have an unexplained CH₄ source. Consequently, further studies are still required to complete the understanding of the mechanisms and magnitude of plant CH₄ emissions.

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