UV light induces CH_4 emission from plant biomass: Mechanisms and isotope studies

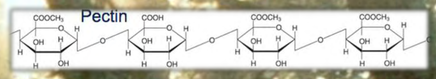
Universiteit Utrecht

IMAU Institute for Marine and Atmospheric research Utrecht

I.Vigano[1], T.Röckmann[1], R.Holzinger[1], A. van Dijk[2], F.Keppler[3], M. Greule[3], W.A. Brand[4], H. Geilmann[4] & H.van Weelden[5]

[1]Institute for Marine and Atmospheric Research, Utrecht University, The Netherlands; [2] Dept. of Earth Sciences, Utrecht University, The Netherlands;
[3]Max-Planck Institute for Chemistry Mainz, Germany; [4]Max-Planck Institute for Biogeochemistry, Jena, Germany; [5]Dept. of Dermatology and Allergology, Utrecht University Medical Center, Utrecht, The Netherlands

Ivan Vigano
i.vigano@uu.nl



Introduction

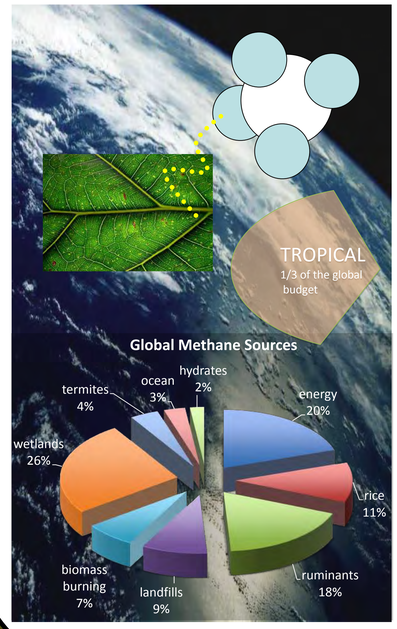
The recently reported finding that plant matter and living plants produce significant amounts of the important greenhouse gas methane under aerobic conditions (Keppler et al. 2006) has led to an intense scientific and public debate. The follow up studies performed (keppler et al. 2007, Vigano et al. 2008, Mc Leod et al. 2008), have been focused the attention on UV radiation and temperature effects . Here we show – using several independent experimental analysis techniques – that dry and detached fresh plant matter, as well as several structural plant components, emit significant amounts of methane upon irradiation with UV light and/or heating. **Emissions from UV irradiation are almost instantaneous, indicating a direct degradating photochemical process**.

The isotope source signature from different plant leaves and organic compounds has been derived, providing new $\delta^{13}C$ and δD values for atmospheric CH_4.

Isotopic analyses of bulk and potential precursors has been performed in order to better explain the reaction pathway of the CH_4 formation.

Additional experiments has been carried out with plants grown with water at different δD content where an isotopic relation with the methane emitted has been found.

Aerobic Methane Production - What's that?



According to established knowledge, CH_4 is produced primarily by anaerobic microbial activity in wetlands, rice fields, landfills and the gastrointestinal tract of ruminants, with non-bacterial emissions occurring at high temperature from fossil fuel usage and biomass burning (IPCC 2007). One third of the actual CH_4 budget has been recently asserted in tropical regions where vegetation plays a key role (Frankenberg et al. 2008).

Recently, Keppler et al. (2006) published results from laboratory experiments indicating that living plants, plant litter and structural plant components **emit methane to the atmosphere under aerobic conditions ($20\%O_2$)**. Our results (Vigano et al. 2008; Keppler et al. 2008, Vigano et al. 2009) report that **a mechanism indeed exists** with potential implications that need to be considered.

Methods and experimental set-up

Three different methods were used to quantify CH_4 levels:

1) An off-axis integrated cavity output spectrometer (Los Gatos Inc.) that allows real-time high-precision monitoring of CH_4 mixing ratios at a frequency up to 10 Hz and with a precision of ±2 ppb (Fig.3). No cross-sensitivities from other species are known for this instrument, and we verified this for the abundant plant emission methanol.

2)A GC-FID instrument for grab sample analysis (reproducibility ±10 ppb) for occasional cross-check for the optical technique and for the experiments with small static vials, where the small sample amount does not allow measurements with the optical system.

3) The isotope ratio mass spectrometry (IRMS) technique, also used by Keppler et al. 2006, to measure not only the concentration (reproducibility ±20 ppb at ambient concentration), but also the ^{13}C and D isotopic composition of the CH_4.

As light sources we used different types of lamps ranging from UVC (253nm) up to UVA (400nm) and visible (400-700nm).

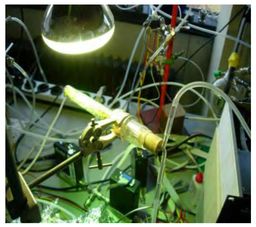


Fig.1- The setup with a UV-lamp irradiating the sample

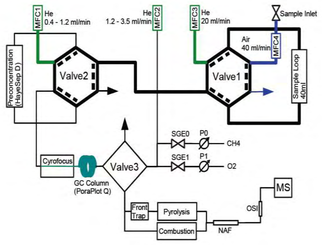


Fig.2- GC-IRMS system (M.Brass & T.Röckmann)

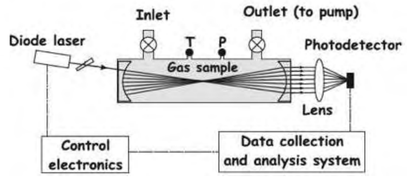
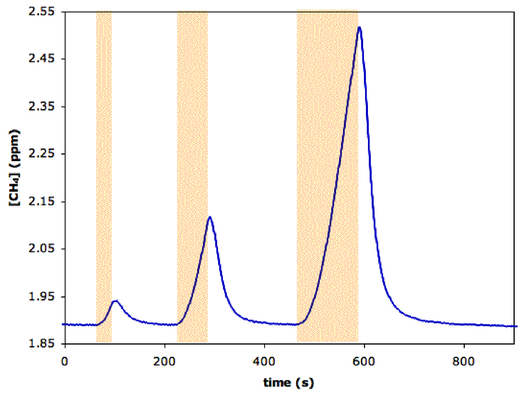


Fig.3- The Cavity Ring-down spectrometer (D.Baer)

Results



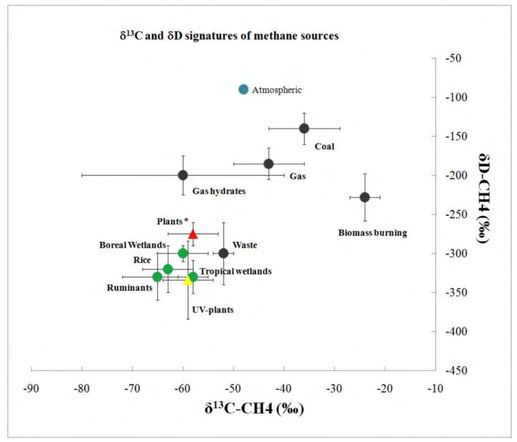


Fig.4 Response of a grass sample (*Lolium Perenne)* to strong UV irradiation (189W/m² UVA and 27W/m² UVB irradiance, Vitalux lamp). The shaded areas mark the times of illumination with the UV light source for 30, 60 and 120 sec., corrected for the flushing time of the vial and connecting lines. This flushing time was determined by adding a spike of CH_4 at the inlet. It is about one minute, in agreement with the size of the vial (100 ml) and the flow rate (100 ml/min). Taking this delay into account the response of the plant matter to light is almost instantaneous.

*$\delta^{13}C$ data are from Keppler et al. 2006 while the δD is in the range of the projections made by Whiticar et al.2007 and Fisher et al. 2008.

Fig.5 Data are from Quay et al. 1999 and Whiticar M.J. 1993. Mainly non microbial sources are indicated by grey dots, mainly bacterial sources by green dots. Plants signatures are indicated with triangles: red for the old evaluations, yellow for the new UV signatures here described.
The error bars indicate the spread of reported values. Actual atmospheric δ values are indicated with a blue dot.

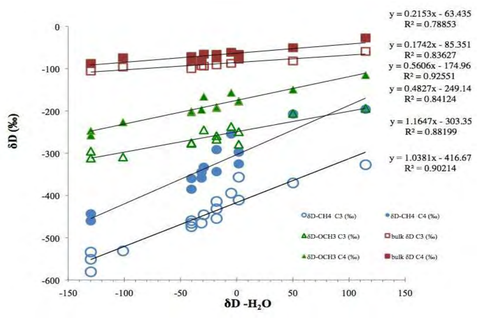


Fig.6 Relation between δD-H_2O with the δD of methane and other chemical plant moieties

The role of light in aerobic methane production was mentioned already by Keppler et al. (2006). Our experiments imply that UV light (280-400nm), when irradiating plant compounds, initiates a fast photochemical reaction releasing methane (Fig.4). Keppler et al (2008) showed that methoxyl groups (O-CH_3) are precursors of this aerobic methane production. Our new isotopic results support some of the previous findings (Vigano et al. 2009) and the isotope source signatures of CH_4 provide a new scenario (Fig.5).

New unpublished experiments showed how the δD content of the water provided to different plant species is distributed with diverse isotopic fractionation in the different plant compounds and the methane emitted reflect, as well, the deuterium strength (Fig.6).

We want to demonstrate how precipitations can affect the deuterium isotopic balance in plants an in the methane emitted from the organic moieties decomposed by UV radiation.

The role of the vegetation as a source and sink of this green house gas is yet not defined but certainly the effect is evident from lab and field experiments.

References:

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