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Water drives the deuterium content of the methane emitted from plants

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The spatial distribution of the deuterium content of precipitation has a well-established latitudinal variation that is reflected in organic molecules in plants growing at different locations. Some laboratory and field studies have already shown that the deuterium content of methane emitted from methanogens can be partially related to dD variations of the water in the surrounding environment. Here we present a similar relation for the methane emitted from plant biomass under UV radiation. To show this relation, we determined the hydrogen isotopic composition of methane released from leaves of a range of plants grown with water of different deuterium content. The plant leaves were irradiated with UV light and the CH4 isotopic composition was measured by continuous flow isotope ratio mass spectrometry (CF-IRMS). Furthermore, the deuterium content of bulk biomass and of the methoxyl groups of the biomass was measured. The D/H ratio successively decreases from the source water via bulk biomass and methoxyl groups to the CH4 emitted. The latter has only about half of the deuterium of the source water. The range of isotope ratios in bulk biomass and OCH3 groups is smaller than in the water used to grow the plants. OCH3 groups, which contain only non-exchangeable water, can be used to assess the fraction of external water that was incorporated before OCH3 groups were formed. Surprisingly, the CH4 formed from UV irradiation has a wider isotopic range than the OCH3 groups. These results are supported by analysis of the fractionation factors. Although the precise production pathway cannot be fully determined, the presented experiments indicate that methoxyl groups are not the only source substrate for CH4, but that other sources, including very depleted ones, must contribute. The results imply that the deuterium content of the methane generated from plants under UV irradiation is closely linked to dD in precipitation, and this dependency should be included in global isotope models.