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Non-Microbial Methane Formation in Plants

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Abstract

The results of experimental studies aimed at determining methane formation mechanisms in the aerobic plant phyllosphere and the contribution of vegetation to global methane emission are reviewed and summarized. Until recently, methane formation and emission by biogenic sources had been associated exclusively with activities of methanogenic archaea growing under anaerobic conditions of water bodies and streams, swamps, rice fields, dumps, and the gastrointestinal tract of animals and termites. However, as demonstrated by modern data, methane formation is also possible via not only the microbial route, in the aerobic plant phyllosphere. Although the mechanism of anaerobic methane formation in plants is not clearly identified, the interconnection between the observed liberation of methane by plants and UV radiation impact and other physiological stresses (temperature change and plant physical trauma) recorded on the example of numerous experimental works demonstrates that this is a general process occurring in the presence of oxygen. It is considered that during UV radiation impact and other physiological stresses on plants, chemical reactions with the formation of oxygen active species start and consequently, some amount of methane is liberated from methoxyl groups of plant pectins (and according to some data, also from plant cellulose and lignin) as part of cell dissolution process. Using very diverse approaches, it is estimated that the most probable range of total methane emission by vegetation is 20–60 Tg/yr. Herewith, the fraction of foliar methane emission related to ultraviolet irradiation of pectin does not exceed 5 % of global methane emission by vegetation, ~60 % of which falls on tropical latitudes.

Keywords: plant phyllosphere, methane formation, mechanisms, emission

INTRODUCTION

It is common knowledge that during vital activity, plants affect the gas and chemical composition of the environment, enrich it with organic matter required for the lives of animal macro- and microorganisms [1]. Apart from the fact that plants after extinction provide an important source of organic substances, during decomposition of which significant amounts of methane may form [1, 2], living plants too have an impact on the rate of metagenesis, concentration level, and methane flow value.

Firstly, plants release solutions and readily accessible organic compounds into soils, on which they grow. Among organic matter, root secretions (so-called root exudates) prevail [3]. These organic compounds are regarded [4] as the main driving force of many microbial processes in the rhizosphere. in particular, root secretions are readily decomposed, are quickly recycled, and supply organic compounds to various microorganisms. The latter include precursor microorganisms of methanogenic archaea [5–9]. According to studies [10, 11], root exudates are responsible for more than half of seasonal methane emissions by some rice fields and swamps.

Secondly, plants mainly vascular wetland, provide methane transportation from grounds (soils, sediments, peat) (see *e.g.* [12–20] and the references given there for the original publications) to the atmosphere through aerenchyma forming a continuous air space within the plant. This route excludes oxidation of a significant part of methane in the ground – water system [21, 22]. For example, according to estimates [23–30], of 50 to 95 % of the total methane flow from swamp ecosystems is transported by plants from grounds through aerenchyma into the stems and leaves, and then into the atmosphere through the stomata of plants, as well as by diffusion through the surface of leaves and stems [31].

Aerenchyma of wetland plants acts as oxygen pipeline, by which it may diffuse through roots to the rhizosphere and adjacent grounds [12, 28, 32, 33], and as a result, stimulate methane-oxidizing bacteria in grounds. It is worth noting that methanotrophs also multiply and survive in the plant phyllosphere, despite their minor population [34–36]. In addition to breathing roots and microorganisms associated with roots, the partial pressure of oxygen in the rhizosphere may change due to the consumption of water by roots, as well as the penetration of roots into grounds, which loosens them and creates channels for pumping gas [37]. An increase in oxygen concentration in soil and bottom sediments leads to a rise in their redox potential and oxidation of such reduced compounds, as Fe^{2+}, Mn^{2+}, H_2S, and CH_4 [38]. Furthermore, the elevated redox potential would limit methane formation in grounds and consequently, reduce its emission into the atmosphere.

In all cases described, plants take direct or indirect part in regulating methane formation and emission processes, but the gas itself is generated outside plants. However, in 2006 it was found [39, 40] on the example of experiments with 30 different types of leaves and grasses from regions tropical and temperate climate, placed after cutting in special sealed chambers with the typical composition of air (but without methane) with all the live (green) and dead parts of plants (alive as torn and ripped already dried) released methane. According to [39], methane emission intensity by dry leaves varied in the 0.2–3 ng/g range of dry leaves an hour at 30 °C. The amount of methane released by leaving portions of plants (maximum of 12 370 ng/g of dry leaves an hour) usually exceeded by 10–100 times methane emission by dry parts. Methane emission rate increased in 3–5 times in the case, if experimental chambers turned out to be under the impact of natural sunlight, and also during increasing temperatures to 30–70 °C. Kepler *et al.* [39, 40] assumed that methane formation in plants was not related to activities of methanogenic archaea and proposed the nonenzymatic mechanism of methane formation at the expense of pectin *i.e.* a structural element of plant tissues of herbs and leaves that contributes to the maintenance of turgor in them. Although methane emission intensity in plants is minor, during deep extrapolation that was carried out by the authors of [39] and took into account the differences between day and night methane emission by leaves, the light day duration, vegetation period length, and pure primary products in each ecosystem, annual total methane emission value of methane emission value of methane emission by living vegetation turns out to be very significant – from 62 to 236 Tg/year, or 10–40 % of its annual global release into the atmosphere by well-known natural and anthropogenic sources. For instance, according to the data of [41], the global emission value is on average 588 Tg/year, which is consistent with other estimates, for example, [42] – 582 Tg/year. Tropical forests and pastures make the maximum contribution (over 70 %) into annual global methane emission by plants from 46 to 169 Tg of CH_4/year [40]. This is in agreement with satellite observations [43] that demonstrated methane clouds over tropical forests. Plant litter contribution was assessed as 0.5–6.6 Tg of CH_4/year [39]. Thus, Keppler *et al.* [39] demonstrated for the first time on the example of laboratory experiments that living plants and plant litter may emit methane into the atmosphere under aerobic conditions.

These assumptions aroused extraordinary interest, lengthy debate, and certain scepticism in the scientific community and mass media [44, 45], contributed to further experimental research, and the broader study of plants effect onto global methane balance and developments of reduction ways of its emission into the atmosphere [46, 47]. This response to the claim of the authors of [39] is driven by the following. Firstly, it is generally believed that methane is generated by methanogenic archaea during organic matter decomposition under anaerobic conditions or without the involvement of methanogens at high temperatures, for example during biomass combustion. And secondly, as demonstrated by extrapolation of laboratory measurements onto the global level [39], plant contribution into methane emission in relation to total global entrances into the atmosphere by natural and anthropogenic sources may be substantial.

The goal of the present work is a review and generalization of experimental research results aimed at determining methane formation mechanisms in plants and vegetation contribution to global methane emission performed after publishing [39]. It is worth noting that papers by Keppler *et al.* [39, 48] have remained virtually unnoticed in the domestic literature. There are only single publications on the subject to date [40, 49].

NON-MICROBIAL METHANE FORMATION IN PLANTS

Methane emission by leaves disconnected from plants has been confirmed by the example of a large number of papers ([49–60], *etc.*). Although aerobic methane formation mechanism has not been reliably identified, the relationship between the recorded amount of methane released by the plant and the effect of ultraviolet radiation and heat on the plant allowed suggesting that these physiological effects initiate chemical reactions with the formation of active oxygen forms, during which methane is generated from antioxidants produced in the mitochondria of living cells of plants [58, 59, 61, 62]. Similar anaerobic methane formation had been earlier demonstrated on the example of mitochondria of animal cells exposed to oxidative (oxidizing) stress [61, 63]. Under the influence of oxidative stress, the formation of reactive oxygen species such as hydrogen peroxide (H_2O_2) and hydroxyl radical (OH^-) may lead to the damage to vital cellular components. During the interaction with them, cells produce a number of antioxidant molecules that protect them by neutralizing active oxygen species. As demonstrated in [61, 63] methane may be obtained in a series of antioxidant molecules containing methyl ($-CH_3$) group by a reaction similar to its formation in mammalian cells.

The authors' assumption [39] of the fact that methyl esters (methoxyl group) in pectin molecules are potential sources of methane has been confirmed in subsequent experiments with isotopically labelled pectin [48]. As demonstrated in [51, 52, 56], all methane emissions at the expense of pectin of tissues in fresh and dry leaves depend on UV radiation. As shown in paper [59], active oxygen species contribute to methane release from methoxyl groups of plant pectins under UV radiation and other physiological stresses (*e.g.* changing temperature and pressure). Papers [51, 56] also showed that methane formation after UV radiation impact stopped after the removal of methyl esters from pectins. Thus, pectin can be a source of methane in case of UV radiation of plants including natural sunlight [51]. When carrying out research [64–68], plants were not exposed to UV radiation and other physiological impacts; probably because of that methane emission by leaves disconnected from plants was not found.

As believed by the authors of [69], foliar methane emission (*i. e.* liberation not related to methane transportation from soils and bottom sediments through roots, stems, and leaves) at the expense of pectin would be proportional to the amount of UV radiation. Apart from this, methane emission by plants would depend on the leaf structure, pectin distribution therein, photosensitizing compounds, and also on chemical and biochemical processes of generating active oxygen species [51, 59]. These factors vary in different plant species.

During the experiment with variation in the duration of UV radiation [52], methane was generated from not only pectin but also from plant cellulose and lignin. Further research [70] using stable isotopes confirmed that only some of the recorded methane emissions from plants were related to methyl groups in pectin.

The experiment [52], in which the response time of dry grass (*Lolium perenne*) was determined by three short and strong impulses of Vitalux UV lamp as methane emission demonstrated that the response proceeded almost instantly and also immediately stopped with the disconnection of UV sources. Furthermore, the volume of methane emitted correlates with the radiation duration. The almost sudden response is clear evidence of the fact that methane emission source is the photochemical process and it is not related to bacteria. The peculiarity of the experiment formulation excludes the process of physical adsorption-desorption or gas release from other sources as a possible explanation of the observed methane emissions during UV irradiation under laboratory conditions. Methane emission begins immediately after irradiation of the plant, but the maximum intensity is reached in 1–2 min at the beginning of irradiation. Methane emission intensity by dry matter during UV radiation is by two orders higher than that upon its lack, which, as a whole, is in agreement with the results of [39].

In general, as experimentally shown [52], UV mediated methane formation is the general process that proceeds in the presence of oxygen. In addition, there was an opinion [58, 59, 71] that during other environmental stresses, both biological and abiotic, and also in processes, in the course of which active oxygen species were also produced in cells, some amount of methane might be generated from plant tissues because of cell dissolution. In particular, dramatic water temperature variations (temperature stress) led to [72] an increase in methane emissions by plants; plant physical injury also initiated dramatic methane emission [54].

Kirschbaum *et al.* [73] were among the first who pointed out at methodological discrepancies in the approach of Kepler *et al.* [39] during evaluating global methane emission by vegetation. Using different approaches for assessment (for example, leaf biomass, and not the value of pure primary products as in [39] was taken as the base), they acquired significantly lower global methane emissions by vegetation, than those calculated in [39]. Subsequent analysis using the most diverse approaches [60, 68, 74–77] also demonstrated lower global methane emission by vegetation.

According to the model [74], plants emit up to 125 Tg of methane per year, but other studies [60, 69, 73–76, 78–80] show that the global total methane emission by vegetation ranges from 4 to 69 Tg/year (the range of the greatest agreement between these estimates is 20–60 Tg/year), *i. e.* 1–12 % of its annual global release into the atmosphere by known natural and anthropogenic sources. Although estimates of global methane emissions by vegetation are significantly lower than the previously calculated values (236 Tg/year, [39]), they reflect the significant role of plants in the global methane cycle. Herewith according to [69], foliar global methane emissions related to UV irradiation of pectin may be 0.2–1.0 Tg/year (or 0.3–5 % of global methane emission by vegetation), of which about 60 % falls on tropical latitudes.

CONCLUSION

Until recently, methane formation and emission by biogenic sources were associated exclusively with activities of methanogenic archaea growing under anaerobic conditions of water bodies and streams, swamps, rice fields and dumps, the gastrointestinal tract of animals, and termites. However, as demonstrated by the current data, methane formation processes may proceed *via* not only the microbiological route in the aerobic plant phyllosphere. Although the mechanism of anaerobic methane formation in plants is not clearly identified, the interconnection between the observed liberation of methane by plants and UV radiation impact and other physiological stresses (*e. g.* dramatic temperature and pressure change and plant physical trauma) recorded on the example of numerous experimental works demonstrates that this is a general process occurring in the presence of oxygen. It is considered that the impact of UV radiation and other physiological stresses on plants activate chemical reactions therein with the formation of oxygen active species, resulting from which some amount of methane is liberated from methoxyl groups of plant pectins (and according to some data, also from plant cellulose and lignin) as a consequence cell dissolution process.

According to assessments using the most diverse approaches, the most probable range of global total methane emission by vegetation is 20–60 Tg/year. Herewith, foliar methane emission portion related to UV radiation of pectin does not exceed 5 % of global methane emission by vegetation.

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