Atmospheric Environment 152 (2017) 405–417

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Methanol emissions from maize: Ontogenetic dependence to varying light conditions and guttation as an additional factor constraining the flux

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HIGHLIGHTS

- Methanol emission from young leaves is complex and drivers are not well understood.
- Methanol production from mature maize leaves may be light dependent.
- Guttation is a potential source of nighttime emissions from young maize plants.
- Emission rates are considerably lower than those observed in previous maize studies.

ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form
20 December 2016
Accepted 22 December 2016
Available online 23 December 2016

Keywords:
Maize
Methanol
VOC
Guttation
Emission modelling

ABSTRACT

Because of its high abundance and long lifetime compared to other volatile organic compounds in the atmosphere, methanol (CH_3OH) plays an important role in atmospheric chemistry. Even though agricultural crops are believed to be a large source of methanol, emission inventories from those crop ecosystems are still scarce and little information is available concerning the driving mechanisms for methanol production and emission at different developmental stages of the plants/leaves. This study focuses on methanol emissions from *Zea mays* L. (maize), which is vastly cultivated throughout the world. Flux measurements have been performed on young plants, almost fully grown leaves and fully grown leaves, enclosed in dynamic flow-through enclosures in a temperature and light-controlled environmental chamber. Strong differences in the response of methanol emissions to variations in PPFD (Photosynthetic Photon Flux Density) were noticed between the young plants, almost fully grown and fully grown leaves. Moreover, young maize plants showed strong emission peaks following light/dark transitions, for which guttation can be put forward as a hypothetical pathway. Young plants' average daily methanol fluxes exceeded by a factor of 17 those of almost fully grown and fully grown leaves when expressed per leaf area. Absolute flux values were found to be smaller than those reported in the literature, but in fair agreement with recent ecosystem scale flux measurements above a maize field of the same variety as used in this study. The flux measurements in the current study were used to evaluate the dynamic biogenic volatile organic compound (BVOC) emission model of Niinemets and Reichstein. The modelled and measured fluxes from almost fully grown leaves were found to agree best when a temperature and light dependent methanol production function was applied. However, this production function turned out not to be suitable for modelling the observed emissions from the young plants, indicating that production must be influenced by (an) other parameter(s). This study clearly shows that methanol emission from maize is complex, especially for young plants. Additional studies at different

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http://dx.doi.org/10.1016/j.atmosenv.2016.12.041

developmental stages of other crop species will be required in order to develop accurate methanol emission algorithms for agricultural crops.

1. Introduction

Among all atmospheric hydrocarbons, methanol (CH_3OH) is the second most abundant volatile organic compound in the troposphere, with mixing ratios ranging up to several tens of parts per billion (Riemer et al., 1998; Singh et al., 2000; Schade and Goldstein, 2001; Jacob et al., 2005; Wohlfahrt et al., 2015). Since it is an important precursor of carbon monoxide, formaldehyde and tropospheric ozone, it plays an important role in the global tropospheric chemistry (Tie et al., 2003; Millet et al., 2006; Duncan et al., 2007; Choi et al., 2010; Hu et al., 2011). Field and laboratory measurements have been carried out to characterize methanol sources and sinks. By integrating this knowledge into global chemistry and transport models, global annual budgets have been constructed (Singh et al., 2000; Heikes et al., 2002; Galbally and Kirstine, 2002; Tie et al., 2003; von Kuhlmann et al., 2003; Jacob et al., 2005; Millet et al., 2008; Stavrakou et al., 2011). Terrestrial plants have been found to be a major source of atmospheric methanol, with an annual global emission ranging from 75 to 280 Tg y^{-1} and constituting 60–80% of the total source strength. Moreover, recent research has revealed bi-directional exchange of methanol between terrestrial ecosystems and the atmosphere. Deposition of methanol is likely to be favoured by the formation of wet layers from which it may be removed chemically or biologically (Wohlfahrt et al., 2015; Laffineur et al., 2012; Niinemets et al., 2014; Seco et al., 2007). In leaves, methanol is mainly produced by the demethylation of pectin (Fall and Benson, 1996). Consequently, changes in cell wall structure related to growth (MacDonald and Fall, 1993; Nemecek-Marshall et al., 1995; Galbally and Kirstine, 2002; Karl et al., 2003; Harley et al., 2007), leaf abscission, the ageing of leaf tissues (Harriman et al., 1991) and intercellular air space generation (Nemecek-Marshall et al., 1995) play an important role in methanol emission from leaves. Therefore, methanol fluxes are affected by the seasonality of the vegetation, i.e. by growth stages and phenological processes (Bracho-Nunez et al., 2011). Several studies already reported that methanol emission from young leaves of various plant species is several times higher than that from mature leaves (MacDonald and Fall, 1993; Nemecek-Marshall et al., 1995; Karl et al., 2003; Custer and Schade, 2007; Harley et al., 2007; Hüve et al., 2007; Bracho-Nunez et al., 2011; Hu et al., 2011; Wells et al., 2012). Furthermore, methanol emission was found to be correlated to stomatal conductance (MacDonald and Fall, 1993; Nemecek-Marshall et al., 1995; Niinemets and Reichstein, 2003a), temperature (Schade and Goldstein, 2001; Karl et al., 2003, 2004, 2005; Brunner et al., 2007; Custer and Schade, 2007; Hüve et al., 2007; Folkers et al., 2008) and light conditions (Harley et al., 2007; Hüve et al., 2007; Folkers et al., 2008).

Maize (*Zea mays* L.) was chosen for this study because of its vast cultivation worldwide (13.7% of the global cropland area, (FAO, 2015)) and because it is a fast-growing crop species which is potentially characterized by large methanol emissions. As methanol emission is the result of Pectin Methyl Esterase (PME) activity (Fall and Benson, 1996), which is in turn dependent on both the rate of cell division and cell expansion (which in turn are under the control of the plant hormones cytokinins (Taiz and Zeiger, 2010)), its emission rate from young developing leaves of fast growing maize plants may be higher than from slower-growing plant species. The little data available in the literature on BVOC emissions from maize (MacDonald and Fall, 1993; Das et al., 2003; Graus et al., 2013) indeed indicate that it could be an important plant species for exchanging methanol with the environment. Those studies, however, only covered a very limited period of the growing season and were conducted in very similar weather conditions. Recently, a field study was conducted to measure methanol exchanges from maize under natural environmental conditions for a whole growing season (Bachy et al., 2016). These flux measurements were performed at ecosystem-scale using the eddy covariance technique, thereby encompassing both soil and plant exchanges. Consequently, knowledge about methanol exchanges by the maize plant itself and their underlying exchange mechanisms remains limited. The present study aims to fill this knowledge gap by 1) evaluating the impact of varying PPFD on methanol emissions at constant temperature conditions in the environmental chamber, 2) studying the effect of leaf age on the methanol emission pattern and magnitude and 3) by confronting our measurements with the dynamic BVOC emission model of Niinemets and Reichstein (Niinemets and Reichstein, 2003a, 2003b) using different methanol production functions.

2. Materials and methods

2.1. Plants and environmental conditions

Investigations were carried out on silage maize (*Zea mays* L., variety Prosil, Caussade Semences, France) at three different life stages: young, middle age and fully grown (5 replicates for each stage). In what follows, these stages will be referred to as stage 1, stage 2 and stage 3, respectively. At stage 1, measurements were carried out on plants from 4 up to 14 days old (age counting began with seed germination). Four-day-old plants were about 10 cm tall and had 2 small leaves (leaf numbering started from the base). Fourteen-day-old plants were about 35 cm tall and had 4 to 5 leaves. The whole plant was enclosed at this stage because it was not feasible to enclose a single leaf for a sufficiently long period without damaging it. This was due to the fast elongation rate of both leaves and stem. An almost fully grown 7th leaf (total length was about 80 cm) of a 30 to 40-day-old plant (about 120 cm tall) was partially enclosed (the top 55 cm) during the experiments on leaves of stage 2. At stage 3, a fully grown leaf (either the 7th, 8th or 9th) of a fully grown maize plant (about 180 cm tall) was partially enclosed (the top 55 cm as well). After enclosing, the measurements on leaves of stage 2 and 3 were performed for about 5 days. More details about the plants and the enclosed leaf/leaves at the different plant developmental stages at which the experiments were carried out can be found in Table 1.

When the seeds had germinated, the small seedlings were transplanted in cylindrical 20 l pots containing soil that consisted of a mixture of 75% silty clay loam and 25% sand (volume/volume). Plants were grown in the environmental chamber where the BVOC measurements were conducted. They were watered regularly to keep the soil moisture content around 35%.

The dimensions of the environmental chamber were 3 m × 2.6 m × 2.2 m (L × W × H). Light intensity and temperature were controlled automatically. Seven-hour-long dark periods were