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VOC emissions from dry leaf litter and their dependence on temperature

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Abstract

Emissions of several volatile organic compounds (VOCs) from dry leaf litter at temperatures in the range 20–100 °C are reported for different plant species. The emission rates of ethane, ethene, propane, propene, *n*-pentane and methyl chloride increase exponentially with temperature and follow the Arrhenius relation. Emission rates up to 650 ng/gdw/h were observed for hydrocarbons at 70 °C, while for methyl chloride emission rates up to 18 µg/gdw/h were observed at this temperature. The emissions are of abiotic origin, which is indicated by activation energies higher than 50 kJ/mol. The emission of VOCs from dry leaf litter decreases in time, due to depletion of the precursor reservoirs. At low temperatures (20–30 °C) the decrease is very slow, but at higher temperatures (80–100 °C) it is noticeable on a timescale of hours. Our results show that hydrocarbons can be produced in the leaf, but the production requires oxygen. Emissions of methyl chloride from dry leaves can be significant for the global budget of methyl chloride.

1 Introduction

Living plants are an important source of volatile organic compounds (VOCs). Different plant species emit different types of VOCs, like isoprene, monoterpenes, acids, aldehydes, alcohols, and chlorinated compounds (e.g., König et al., 1995; Street et al., 1997; Kesselmeier and Staudt, 1999; Owen et al., 2001; Bouvier-Brown et al., 2009). The global annual emission of VOCs from living vegetation is estimated between 500 and 1500 Tg/yr and the bulk of these emissions consists of isoprene and monoterpenes (Fehsenfeld et al., 1992; Peñuelas and Llusiá, 2001). For numerous compounds, emissions from vegetation are a significant fraction of their global budget. The source of methyl chloride from living vegetation is estimated to be 0.91 Tg/yr, which is approximately 25% of the methyl chloride budget (Yokouchi et al., 2002; Keppler et al., 2005). Ethene emissions from vegetation are estimated to be 11.8 Tg C/yr, about one third of the global ethene source of 34.5 Tg C/yr (Poisson et al., 2000).

VOCs are emitted by living plants for different purposes. They are defense compounds against pathogens and herbivores, signaling compounds between plants and parts of plants, emitted in response to wounding and stress, or they are a byproduct of cell expansion. For example, the monoterpenes α- and β-pinene protect plants against insect attacks, while methanol is emitted during cell wall formation as a product of pectin demethylation (Hopkins, 1999). The factors that drive VOC emissions from living vegetation are therefore very complex and can be of biotic and abiotic origin. For example, emissions of VOCs can be temperature and light dependent, or can be influenced by the age of the plant, stage of growth, seasonal effects, wind, water availability, and stomatal conductance (e.g., Owen et al., 2002; Street et al., 1997; Peñuelas and Llusiá, 2001). Large differences exist between plant species, but differences within plant species are also observed (e.g., König et al., 1995; Nunes and Pio, 2001; Seco et al., 2007).

Emission rates of VOCs from living vegetation vary over several orders of magnitude. For isoprene and monoterpenes emission rates from close to zero up to several µg C/gdw/h are observed (e.g., Owen et al., 2002; Nunes and Pio, 2001), while for oxygenated compounds, the emission rates range up to 4.8 µg C/gdw/h (Seco et al., 2007). Emission rates of methanol from living vegetation are in the order of several 10s of µg/gdw/h, and are influenced by drought, temperature and light (MacDonald and Fall, 1993; Folkers et al., 2008). Methyl chloride and methyl bromide emissions are mainly observed for tropical vegetation. Emission rates up to 3.7 µg/gdw/h are observed for methyl chloride, although large differences exist between plant species (Yokouchi et al., 2002, 2007; Saito and Yokouchi, 2006).

VOCs emitted by living vegetation play a significant role in tropospheric chemistry, since most of the compounds are oxydized by ozone, OH and nitrate radicals, and therefore influence the cycles of these oxidizing species. The reaction products of the direct vegetation emissions can be involved in the formation of secondary organic aerosols (Cahill et al., 2006; Claeys et al., 2004; Holzinger et al., 2005).

When plants are under stress conditions, like high temperatures, drought or exposure to high concentrations of pollutants in the surrounding atmosphere, increased emission rates of several VOCs are observed. Holzinger et al. (2000) observed large emissions of acetaldehyde and ethanol from a Mediterranean holm oak species (Quercus ilex) when the root system was flooded. Stressed plants also emit VOCs that are not emitted under “normal”, unstressed conditions. For example, when stress is so severe that (part of) the plant is dying, ethane is emitted by the plant (e.g., Kimmerer and Kozlowski, 1982; Bressan et al., 1979; Peiser and Yang, 1979).

In contrast to living plants, emissions of VOCs from dry and degrading plant matter have only been measured for few compounds. Schade et al. (1999) studied carbon monoxide (CO) emissions from degrading plant matter in field and laboratory experiments. They found that CO emissions can be induced thermally, photochemically, or by visible light. Thermally induced CO emissions obeyed the Arrhenius relation, but the emission rates were lower than photochemically induced CO emissions.

Several oxygenated compounds are emitted by degrading plant matter. Warneke et al. (1999) measured emissions of acetone and methanol of 1×10^{-4} g/g and 3–5×10^{-4} g/g of plant matter, respectively. The global annual emission from degrading leaves was estimated to be 6–8 Tg for acetone and 18–40 Tg for methanol, which is a significant contribution to the global budget of these compounds. Polar compounds like acetone and methanol are not emitted directly, but stick to the cell material. In contact with water these VOCs are exchanged with water molecules and can be emitted into the atmosphere. Emissions rates were higher at high temperatures and in the presence of water, but the total emission was found to be independent of temperature and moisture (Warneke et al., 1999).

Methane is emitted by leaf litter at rates between 0.2 and 3 ng/gdw/h at 30 °C (Keppler et al., 2006). The emissions were of abiotic origin and depended strongly on temperature. In addition, exposure to natural sunlight also increased the emission rates. Vigano et al. (2008) also reported emissions of methane from dry and detached leaves irradiated with UV light. Emissions of methane, ethane and ethene from citrus pectin and tobacco leaves and their dependence on UV radiation have been studied by McLeod et al. (2008). Emissions of methane increased linearly with the intensity of the UV radiation. For ethane an emission rate of 125 ng/g/h was observed, while for ethene an emission rate of 271 ng/g/h was found at a total UV irradiance of 9.5 W/m^2 (280–400 nm).

Methyl bromide emissions have been studied in laboratory experiments for several plant species (Whiskerman et al., 2008). The emissions are of abiotic origin and the emission rate depends on both temperature (Arrhenius relation) and the bromine content of the plant material.

Emissions of methyl chloride from dead and senescent leaves (Hamilton et al., 2003; Keppler et al., 2000) show a clear temperature dependency between 30 and 50 °C. The emission rates are influenced by moisture and scale with the chlorine content of the leaves. Estimates of the global source of methyl chloride from dead and senescent leaves range up to 2.5 Tg/yr, which is significant for the global methyl chloride budget.

The goal of this study was to examine whether other VOCs are emitted from dry plant matter and whether these emissions are important for the global budgets of those VOCs. We focus on the emission of several hydrocarbons and methyl chloride from dry leaf litter and their dependence on temperature. Additional experiments were performed to determine whether the VOCs are formed by the leaves, or whether the emissions are only a result of deposition of atmospheric VOCs on the leaves. To get some insight in the precursors of the VOCs, the dependence of the emissions on oxygen is examined.

2 Experimental methods

For the experiments described here we used leaves of sequoia (*Sequoiadendron giganteum*), rice (*Oryza sativa*), maize (*Zea mays* spp.), cherry prinsepia (*Prinsepia sinenses*), and beech (*Fagus orientalis*). The plant material was collected in the botanical garden of the Johannes Gutenburg University in Mainz (Germany) and air-dried at

25 °C. After drying part of the plant material was grinded. Experiments were done both on whole leaves and on ground material. For cherry prinsepia and beech only ground material was available.

Dry plant material was inserted into a Suprasil quartz tube of 350 ml volume. The tube was continuously flushed with synthetic air or nitrogen gas at a flow rate of 50 ml/min. Air coming out of the quartz tube was inserted into the gas chromatograph via a nafion drier. Teflon lines were used to connect the different parts of the system. The temperature in the quartz tube can be varied via a heating wire wrapped around the tube and was measured in the quartz tube on the surface of the leaves. The quartz tube was covered with aluminum foil to exclude any influence of outside light or UV radiation.

A gas chromatograph (Varian star3600) equipped with a flame ionization detector was used to measure mixing ratios of different VOCs. Air from the quartz tube was cryotrapped at a flow rate of 33 ml/min in the sample pre-concentration trap (SPT) at −170 °C. Depending on the required sample size, the trapping time was 15 or 30 min. After trapping, the SPT was rapidly heated to 150 °C to release the sample to the column of the gas chromatograph. We used a 10 m CP-SIL 5CB column followed by a 50 m silicaPLOT column, both with an inner diameter of 0.53 mm. The temperature of the column was increased from 40 °C to 225 °C at a rate of 5 °C/min. The total run was completed in 40 min and the chromatograms were evaluated for ethane, ethene, ethyne, propane, propene, methyl chloride, *i*-butane, *n*-butane, *i*-pentane, and *n*-pentane mixing ratios. The gas chromatograph was regularly calibrated with reference gases with known mixing ratios of the mentioned compounds. An example of a measurement with our reference gas is shown in the top panel of Fig. 1. Only the first 20 min of the chromatogram are shown, since all reported compounds elute within this time. In the middle panel of Fig. 1 chromatograms of blank measurements at different temperatures with our analytical setup, but without plant material, are shown. The blank contributions of the different compounds we measure are generally small at all temperatures, except in the case of *n*-butane. At the elution time where *n*-butane is expected a large unidentified peak is observed. This compound is most likely released from the plant system and is a different compound than *n*-butane. There are also some additional, unidentified peaks that are not observed in the calibration measurement.

The mixing ratios are converted to emission rates according to Eq. (1).

$$\mathrm{ER}_x = \frac{C_x M_x F_{\mathrm{chamber}}}{V_{\mathrm{m}} m_{\mathrm{leafDW}}} \tag{1}$$

where ER_x is the emission rate of compound x in ng/gdw/h, C_x its mixing ratio in nmol/mol, M_x its molar mass in g/mol, V_{m} the molar volume in l/mol and F_{chamber} the flow rate through the quartz chamber in l/h.

In a typical experiment leaves were heated from 20 to 70 °C in steps of 10 °C. At each temperature level the emission rates were measured three times. If not stated otherwise we report the average of the three measurements, while we use the standard deviation of the three measurements as indication of the uncertainty.

3 Results and discussion

3.1 Investigated and emitted light hydrocarbons

The emission rates of several VOCs as function of temperature are measured for rice, maize, beech, cherry prinsepia and sequoia leaves. As example, chromatograms for whole maize leaves at 30, 50 and 70 °C are shown in the bottom panel of Fig. 1. Emissions of ethane, ethene, propane, propene, methyl chloride and *n*-pentane are clearly elevated compared to the blanks shown in the middle panel of Fig. 1. Emissions of ethane were detected at all temperature levels, but for some plant species the emission at low temperatures was too close to the detection limit to determine the mixing ratio accurately, so that no emission rate could be calculated. We do not see evidence for emission of ethyne, *i*-butane, *n*-butane and *i*-pentane from dry leaves. These compounds are either not formed or their emission rates are below the detection limit. For a few plant species very small emissions of ethyne were observed at the highest temperatures (70 °C). There were also emissions of additional VOCs that were not present in our reference gas and could therefore not be identified.

Figure 2 shows the measured emission rate (ng/gdw/h) as function of temperature for ethane, ethene, propane, propene, *n*-pentane and methyl chloride for selected plant species. For both hydrocarbons and methyl chloride, the emission rates increase exponentially with temperature between 20 and 70 °C. The emission rates of methyl chloride (up to 350 ng/gdw/h) are much higher than of the hydrocarbons (up to 25 ng/gdw/h), especially at high temperatures. Emission rates of alkenes are generally larger than emission rates of alkanes. The other plant species show a similar exponential increase of the emission rates with temperature. At the highest temperatures relatively large standard deviations are observed. The reason for the large standard deviation is that at such high temperatures the emission rates decrease during the three hours that are necessary to perform three measurements at the respective temperature level, indicating that the precursor reservoirs are being depleted.

At high temperatures the emission rates for whole leaves are generally much higher compared to ground leaves. At low temperatures, slightly higher emission rates are observed for the ground leaves, resulting in a weaker temperature dependence of the emission rates for ground leaves compared to whole leaves. In ground leaves the structure of the leaves, including the cells and cuticle, is destroyed during the grinding process and VOCs can be released relatively easy. It is likely that a fraction of the VOCs is lost during the grinding process, or during storage of the ground plant material. The emission rates of ethane and ethene from both ground and whole leaves are low compared to the UV induced emission of ethane and ethene that McLeod et al. (2008) found.

Emissions of hydrocarbons and methyl chloride differ by several orders of magnitude between plant species. An overview of the emission rates at 50 °C for all measured plant species is shown in Table 1. For example, 1.3 ng/dgw/h methyl chloride was emitted from whole maize at 50 °C, while whole rice emitted 1209 ng/gdw/h. Emissions from whole rice leaves are higher than from the other plant species of which the whole leaves were measured. For ground leaves, there is more variability among the plant species. For example, the highest propene emissions are observed from ground sequoia, while ground rice emits the largest amount of ethene. The highest hydrocarbon emission observed from any species investigated was from whole rice: 653 ng/gdw/h of ethene was measured at 70 °C. The highest methyl chloride emissions were also from whole rice leaves at 70 °C, corresponding to 18 µg/gdw/h.

The emission rates increased exponentially with temperature for all plant species used in these measurements over the full temperature range. This is an indication that the emission of hydrocarbons and methyl chloride from dry leaves is an abiotic process. If the process was of biotic origin, emission rates increasing with temperature would be expected until a maximum emission rate at 30–40 °C, followed by a sharp decline at higher temperatures due to denaturation of enzymes (Atkins and de Paula, 2002; Campbell and Reece, 2002).

In the rest of this paper the emission of hydrocarbons and methyl chloride will be discussed separately, because all measured hydrocarbons probably originate from the same precursor in the leaf (membrane fatty acids of the plant cells) and show similar behaviour, while methyl chloride originates from the methoxyl groups of pectin and shows a different behaviour (Hamilton et al., 2003; John and Curtis, 1977; Halliwell and Gutteridge, 2008; Keppler et al., 2004; Dumelin and Tappel, 1977).

3.1.1 Arrhenius plots

To quantify the temperature dependence of the emission rates, the measurements are analyzed with the Arrhenius equation (Eq. 2).

$$k = A\exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{2}$$

where k is the reaction rate constant, A the pre-exponential factor, E_a the activation energy, R the gas constant, and T the temperature. In case of a pseudo-first order reaction, i.e. when there is a very large amount of precursor, while only a very small fraction of this precursor reacts to a VOC, the reaction rate constant k is proportional to the emission rate ER. The activation energy can then be determined directly from measurements of the emission rate at different temperatures. The slope of a plot of ln(ER) as function of the inverse temperature (Arrhenius plot) is then equal to $-E_a/R$ (Atkins and de Paula, 2002).

Figure 3 shows Arrhenius plots for ground and whole leaves of selected plant species for ethene as example for the hydrocarbons and for methyl chloride. An overview of the activation energies for ethane, ethene, propane, propene, *n*-pentane and methyl chloride for all measured plant species is shown in Table 2. In the case of ground cherry prinsepia and ground rice, the emission rate of ethane was too close to the detection limit to determine its magnitude accurately, and the activation energy could therefore not be calculated. The activation energies are generally higher than 50 kJ/mol, which is another indication that the emissions are of abiotic origin (Schönknecht et al., 2008).

The Arrhenius plots are made with the assumption that the pseudo-first order approximation is valid. As discussed above, at high temperatures we observed decreasing emission rates over the course of a few hours, which was interpreted as an effect of emptying precursor reservoirs. Therefore we do not expect a linear behavior in the high temperature part of the Arrhenius plots. Indeed we observe in Fig. 3 that for hydrocarbon emissions from whole plant material the point at 70 °C is lower than expected from the Arrhenius fit. Not surprisingly, this effect is strong (also at 60 °C) for ethene emissions from sequoia, where we observed a strong decline in the three consecutive measurements of the ethene emission rate above 60 °C, as indicated by the error bar in Fig. 2. For maize the effect is weak, again in agreement with the error in Fig. 2. Therefore, activation energies calculated for the whole leaves from the slope of the linear fit are probably underestimated and should be regarded as lower limit. For hydrocarbon emissions from ground plant material we observe an upward bend in the region 40–50 °C. Clearly the points do not follow a pseudo-first order process here, however it cannot be explained by a reservoir exhaustion effect. We suggest that the relatively high emissions at low temperature are due to a different source of these compounds, i.e. adsorption of gas phase molecules on the surface of the leaf. Ground plant material offers a large surface area onto which VOCs from ambient air can adsorb. Heating of the plant material will result in desorption of the VOCs. The size of this reservoir however is relatively small and it becomes exhausted at temperatures of 40 °C. Therefore, we only used the measurements at temperatures from 50 to 70 °C for the Arrhenius fits of the hydrocarbon emissions from ground leaves. The surface:volume ratio of whole leaves is very small compared to ground leaves, so that only a small amount of VOC can be adsorbed on the leaf surface of whole leaves. Therefore, for hydrocarbon emissions from whole leaves this desorption effect is small and only sometimes visible at 20 °C.

The emission of hydrocarbons from whole leaves are higher than from ground leaves at the higher temperatures where the desorption effect for both whole and ground leaves. As for each species the whole leaves and the ground leaves originate from the same batch of leaves, part of the hydrocarbon precursor reservoir must be lost during the grinding process or during storage of the leaves.

The Arrhenius plot of methyl chloride (Fig. 3) for both ground and whole leaves generally shows a straight line over the temperature range used in the measurements (20–70 °C), although for some plant species, e.g. sequoia, depletion of the reservoir is observed at high temperatures. This is again indicated by the points at 60 and 70 °C falling below the Arrhenius fit. The activation energies for emissions from whole leaves are slightly higher than for the ground leaves. The desorption effect of atmospheric VOCs on the leaf surface that was observed for hydrocarbon emissions from ground leaves is of minor importance for the emission of methyl chloride from ground leaves and only visible at the lowest temperature, as indicated by the large error bar at 20 °C. Table 1 shows already that methyl chloride emissions are much higher than emissions of hydrocarbons. The contribution of atmospheric methyl chloride that is adsorped on the leaf surface is small compared to the amount of methyl chloride that is released from the leaf itself. Therefore, methyl chloride emissions from both ground and whole leaves seem to follow a pseudo-first order process. As for hydrocarbons, methyl chloride emissions are lower from ground leaves as compared to whole leaves.

Emissions of different hydrocarbons from dry, detached leaves likely all have the same precursor in the leaves, i.e. membrane fatty acids (e.g., Halliwell and Gutteridge, 2008; John and Curtis, 1977; Konze and Elstner, 1978; Dumelin and Tappel, 1977), while methyl chloride probably originates from the methoxyl groups of pectin (Hamilton et al., 2003; Keppler et al., 2004). The emission rate of methyl chloride from dry leaves is generally larger than the sum of all hydrocarbon emission rates. Therefore we conclude that the reservoir of methyl chloride precursor in the leaf is much larger than that of the hydrocarbon precursor.

3.2 Temporal evolution of VOC emission rates from dry leaf litter

As discussed above it was observed that at the highest temperatures used in the experiments the emission rates decrease in time already during the experiment, indicating that a reservoir of VOC or its precursor is being depleted (Fig. 2). This was further investigated in a temperature cycling experiment, where whole leaves of sequoia were heated from 20 to 80 °C in steps of 10 °C, cooled down to 20 °C and then heated again to 80 °C. The results are shown in Fig. 4 for ethene as an example for the hydrocarbons and for methyl chloride.

During both heating cycles the emission rates increase exponentially with temperature, but during the second heating cycle the emission rates are lower at each temperature than during the first heating cycle. This confirms the hypothesis that a reservoir of VOC or its precursor was depleted during the experiment, in agreement with the observations in the previous section where we observed that part of the precursor reservoir of the hydrocarbons and methyl chloride was lost during the grinding process or storage of the leaves. Depletion of the reservoirs is faster at high temperature. Like in Fig. 2, large error bars are also observed at 70 and 80 °C in this experiment, because the emission rates decreased in time already during the three hours required to perform three measurements at the respective temperature level.

To follow the temporal evolution of the emission rates, whole maize leaves were heated to 80 or 100 °C in an atmosphere of synthetic air and the emission rates of the different VOCs were measured over the course of several days. The results are shown in Fig. 5 for ethene as example for the hydrocarbons and for methyl chloride.

For the emission of both hydrocarbons and methyl chloride, the emission rates decrease to very low values after several hours, but complete emptying of the VOC reservoirs is not achieved within the duration of the experiment. The differences in the emission rates between 80 and 100 °C are larger for methyl chloride than for the hydrocarbons. This is expected since the activation energy of methyl chloride from whole maize is higher than the activation energy of the hydrocarbons, i.e. the temperature dependence is stronger for methyl chloride emissions. The integrated amounts of released VOC at 100 °C are larger than at 80 °C. Apparently, at 100 °C additional precursor reservoirs are accessible for longer periods of time compared to 80 °C. This is in contrast to our initial expectation that the total releasable VOC content of a leaf should be independent of temperature, and that the emptying of the VOC reservoirs in the leaf is only faster at high temperatures (like was observed for the emission of oxygenated VOCs by Warneke et al., 1999). However, it is not clear if this finding also holds for the range of ambient temperatures.

Emissions of VOCs from leaf litter can continue for a long period of time at ambient temperatures. For whole leaves of sequoia the emission rates as function of temperature were measured directly after the batch was collected. Approximately one year later sequoia leaves of the same batch were measured again. The emission rates still increased exponentially with temperature, but at all temperature levels the emission rates were approximately 90% lower than directly after collection of the leaf batch. The leaves were stored at room temperature, but apparently also at room temperature the degradation process in the leaves and the depletion of the VOC reservoirs continues, but at a much slower rate than at high temperature.

These observations have implications for estimates of the contribution of VOC emissions from leaf litter to the global budget of those VOCs. The total releasable VOC content per gram leaf material cannot be used for these estimates, because this quantity is strongly temperature dependent. To estimate the contribution to the global budget it is therefore more reasonable to assume that emissions at 20 or 30 °C continue for a long period of time. VOC emissions from degrading leaves can continue for at least a year at ambient temperature.

3.3 Formation of hydrocarbons requires oxygen

Hydrocarbons are thought to be generated in leaves via lipid peroxydation of the plant cell membranes, which is an oxygen requiring process (e.g., Konze and Elstner, 1978; Dumelin and Tappel, 1977). Methyl chloride is suggested to be formed from the methoxyl groups of pectin, and the formation does not require oxygen (Hamilton et al., 2003; Keppler et al., 2004). We investigated this difference with an experiment where we examined whether VOCs can be formed by the leaf itself, and whether the formation of VOCs from dry leaf litter requires oxygen.

Whole maize leaves were heated in ambient air to 80 °C for 10 days to remove as much VOCs as possible. After this treatment the emission rates of hydrocarbons and methyl chloride at 80 °C were measured. Afterwards, the leaves were divided into two fractions. Fraction 1 was stored in a quartz tube that was continuously flushed with nitrogen at a flow rate of 30 ml/min for 14 days. Fraction 2 was kept under equal conditions, but was flushed with synthetic air at 30 ml/min for 13 days. Both fractions were stored at room temperature. After the storage period, the emission rates were again measured as function of temperature. First the temperature was increased from 20 to 80 °C in steps of 20 °C, afterwards the temperature was decreased from 80 to 20 °C. In Figs. 6 and 7 the emission rate as function of temperature after the storage period is shown for ethene as example for the hydrocarbons and for methyl chloride, respectively. The emission rates at 80 °C before and after the storage period of the leaves are shown in Table 3.

3.3.1 Hydrocarbons

In case of the leaves stored in N_2 the emission rates of hydrocarbons were close to zero. The leaves flushed with N_2 were in fact further emptied during the two weeks storage period as shown by the lower emission rates after than before the N_2 treatment (Table 3). For the leaves that are stored in synthetic air the emission rates increase exponentially with temperature again after storage of the leaves. The emission rates at 80 °C were higher after the storage than before, so new VOCs were formed during the storage period. Because the leaves were stored in N_2 or synthetic air that did not contain VOCs, the difference between leaves stored in N_2 and synthetic air shows that (i) hydrocarbons can be produced in leaves and (ii) that their formation requires oxygen. The formation process is probably slow. After 14 days of storage at room temperature in synthetic air, an emission rate of 12.7 ng/gdw/h is observed for ethylene at 80 °C. To empty the largest part of this reservoir again, only a few hours are required at high temperature (Sect. 3.2).

3.3.2 Methyl chloride

When methyl chloride emission rates at 80 °C before and after storage of the leaves are compared, lower emission rates are observed after storage of the leaves in both N_2 and synthetic air, indicating that no new methyl chloride was formed by the leaf during the storage. The emission of methyl chloride is independent of the storage treatment. Once the reservoir of methyl chloride or its precursor is emptied, it cannot be refilled again. At 80 °C, lower emission rates are observed after storage of the leaves than before due to the continuous flushing of the quartz tubes.

When the reservoirs of hydrocarbons in dry leaf litter appear to be emptied, formation of VOCs can be initiated again when oxygen is present. When reservoirs of methyl chloride or its precursor are emptied, they cannot be refilled. This clearly confirms that methyl chloride and hydrocarbons have different precursors and production pathways in the plant. Our results are in agreement with the idea that the emissions of hydrocarbons from degrading leaves originate from the membrane fatty acids via the oxygen requiring lipid peroxydation process, while methyl chloride is suggested to originate from the methoxyl groups of pectin.

3.4 Relevance for the global budgets

In order to get a rough idea on the contribution of VOC emissions from leaf litter to the global budget of these VOCs, we apply a simple upscaling by assuming that at ambient temperatures the emission rates (ng/gdw/h) measured at 30 °C continue over one year at a constant rate (Eq. 3). The calculations for the ground leaves can be overestimated due to the desorbtion effect of atmospheric VOCs on the surface of the ground leaves at this temperature (Sect. 3.1).

$$\text{Total source} = \text{ER} \cdot \text{total decaying biomass} \cdot 365 \cdot 24 \qquad (3)$$

A total biomass decay rate of 7.0×10^{16} gr/yr is used in the calculations (Warneke et al., 1999). The results for the different VOCs are shown in Table 4 for ground and whole leaves together with estimates of their global annual budget. The estimated range of the VOC source from leaf litter is relatively large, because there are large variations in the emission rates of the measured plant species (Sect. 3.1).

Temperature induced emissions of hydrocarbons from degrading vegetation seem to be insignificant for the global hydrocarbon budgets. Emissions of methyl chloride are possibly significant, in agreement with earlier studies where contributions up to 2.5 Tg/yr were calculated (Keppler et al., 2004, 2005; Hamilton et al., 2003). Since this is only a very simplified estimate further investigation is needed. Also other factors, like moisture content of the leaves, UV radiation and humidity can have a significant influence on the emission rates. UV induced emissions of hydrocarbons and methyl chloride from leaf litter are currently under investigation. McLeod et al. (2008) has already measured emission rates of ethane and ethene from tobacco leaves induced by UV radiation that are much higher than the hydrocarbon emission rates observed in these experiments.

4 Conclusions

Ethane, ethene, propane, propene, *n*-pentane and methyl chloride are emitted from dry leaves at ambient temperatures, and the emission rates increase exponentially with temperature according to the Arrhenius relation. The emissions are of abiotic origin, as indicated by the continuous increase of the emission rate with temperature and the activation energies that are higher than 50 kJ/mol. No emissions of ethyne, *i*-butane, *n*-butane and *i*-pentane are observed. The comparison between ground and whole leaves suggests a desorption effect of atmospheric VOCs on the leaf surface. This effect is larger in ground leaves compared to whole leaves due to the large area:volume ratio of the ground leaves. The precursor reservoirs of both methyl chloride and the hydrocarbons can be depleted, most efficiently at higher temperatures. When the reservoir of hydrocarbon precursor appears to be emptied, it can be refilled again when the leaves are flushed with oxygen-containing air. Hydrocarbons are probably produced from the membrane fatty acids of the plant cells via an oxygen requiring process. Methyl chloride reservoirs cannot be refilled again once they are emptied and emissions of methyl chloride are independent of oxygen. Temperature induced emissions of hydrocarbons from dry leaves are probably insignificant for the global budgets, while emissions of methyl chloride from leaf litter may be a significant source for its global budget. More measurements on methyl chloride emission are required for a better estimate of the global source of methyl chloride from leaf litter.

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Table 1. Overview of the emission rates (ng/gdw/h) at 50 °C for the for the examined plant species. Ethane emissions from ground rice and ground cherry prinsepia were not observed.

plant	ethane	ethene	propane	propene	*n*-pentane	methyl chl.
ground sequoia	0.03±0.05	0.54±0.06	0.15 ± 0.02	1.14±0.15	0.10±0.01	5.79±1.05
ground maize	0.04±0.03	0.24±0.02	0.08±0.04	0.14±0.02	0.08±0.04	2.21±0.29
ground rice		2.07±0.02	0.21±0.09	0.25±0.02	0.14±0.02	12.4±0.2
ground cherry prinsepia		0.17±0.04	0.25±0.02	0.33±0.02	0.18±0.05	11.9±0.3
ground beech	0.06±0.01	0.25±0.03	0.09±0.05	0.19±0.07	0.20±0.05	5.54±0.82
whole sequoia	0.04±0.01	2.49±0.34	0.47±0.04	3.27±0.22	0.20±0.19	49.2±13.0
whole maize	0.23±0.02	1.48±0.11	0.24±0.06	0.24±0.08	0.53±0.03	1.26±0.14
whole rice	1.48±0.42	322±133	10.2±2.9	17.6±5.3	3.18±0.92	1209±418

Table 2. Activation energies (kJ/mol) for different VOCs for several plant species. For hydrocarbon emissions from ground leaves the calculations are based on the measurements at temperatures from 50 to 70 °C. Activation energies for emissions of methyl chloride from both ground and whole leaves and for emission of hydrocarbons from whole leaves are calculated from measurements in the full temperature range.

plant species	ethane	ethene	propane	propene	*n*-pentane	methyl chl.
ground sequoia	37.6±27.8	92.9 ± 10.0	36.2±20.4	91.9±8.0	41.2±17.9	92.8±3.8
ground maize	55.4±22.9	118.3±8.1	88.2±12.7	93.9±13.0	70.5±21.4	89.3±5.3
ground rice		112.0±4.5	89.0±19.6	95.5±5.9	68.3±9.0	78.5±0.9
ground cherry prinsepia		82.1±11.2	105.6±6.7	85.6±4.5	53.5±12.0	99.6±2.6
ground beech	92.3±11.5	125.4±7.3	80.3±16.6	84.5±10.0	81.7±8.5	96.4±3.8
whole sequoia	85.5±8.5	151.6±5.0	100.1±4.8	113.3±2.8	30.1±3.2	118.9±4.2
whole maize	84.7±3.8	109.7±2.5	116.7±6.7	91.4±2.5	70.4±2.2	123.3±1.6
whole rice	78.0±12.6	191.6±8.6	102.8±7.6	120.4±8.4	83.8±5.8	191.8±3.8

Table 3. Emission rates at 80 °C (ng/gdw/h) before and after storage of the leaves in N_2 or synthetic air.

experiment	ethane	ethene	propane	propene	*n*-pentane	methyl chl.
N_2: before	0.18±0.05	0.64±0.13	1.04±0.19	0.24±0.04	0.68±0.25	1.96±0.29
N_2: after	0.11±0.03	0.22±0.04	0.45±0.08	0.07 ±0.01	0.33±0.12	0.92±0.13
synthetic air: before	0.25±0.06	0.54±0.11	1.14±0.21	0.42±0.06	0.96±0.35	4.98±0.72
synthetic air: after	0.45±0.12	12.7±2.6	3.85 ±0.71	3.66 ±0.56	5.31±1.95	3.56±0.52

Table 4. Estimates for the annual source strength of VOCs from dry leaf litter based on measurements at 30 °C and total global budget (Tg/yr).

leaf type	ethane	ethylene	propane	propylene	*n*-pentane	methyl chl.
ground leaves	0–2.05E-2	0.23–1.72E-1	0–8.13E-2	0.81–5.24E-1	0.26–1.54E-1	0.17–1.15
whole leaves	0–1.44E-2	0.11–4.16E-1	0–4.71E-2	3.84–9.13E-2	4.99–9.62E-2	0.03–4.48
global budget	8.8; 10.3[a]	35.7[b]	8.7[c]	19.7[d]		5.4[e]

[a] Stein and Rudolph (2007); Poisson et al. (2000)
[b] Poisson et al. (2000)
[c] Poisson et al. (2000)
[d] Poisson et al. (2000)
[e] Keppler et al. (2005)

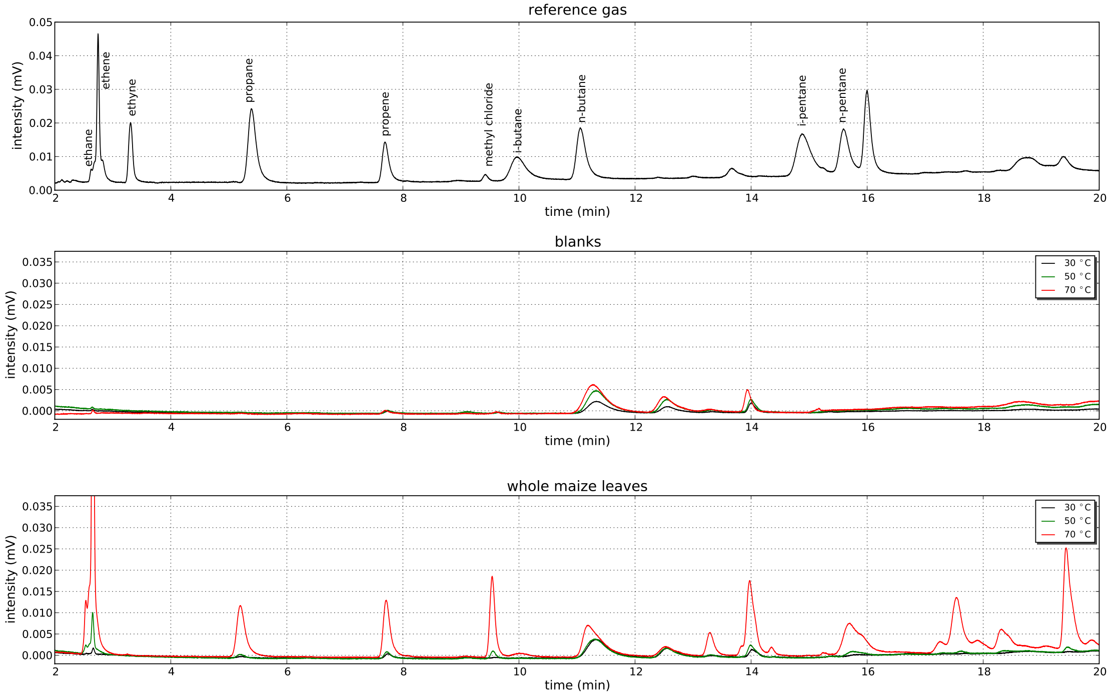

Fig. 1. Top panel: example of a measurement of the reference gas in which the target compounds are labelled. Middle panel: blank measurements at 30, 50, and 70 °C. Bottom panel: chromatograms of whole maize leaves at three temperatures as example of a plant measurement.

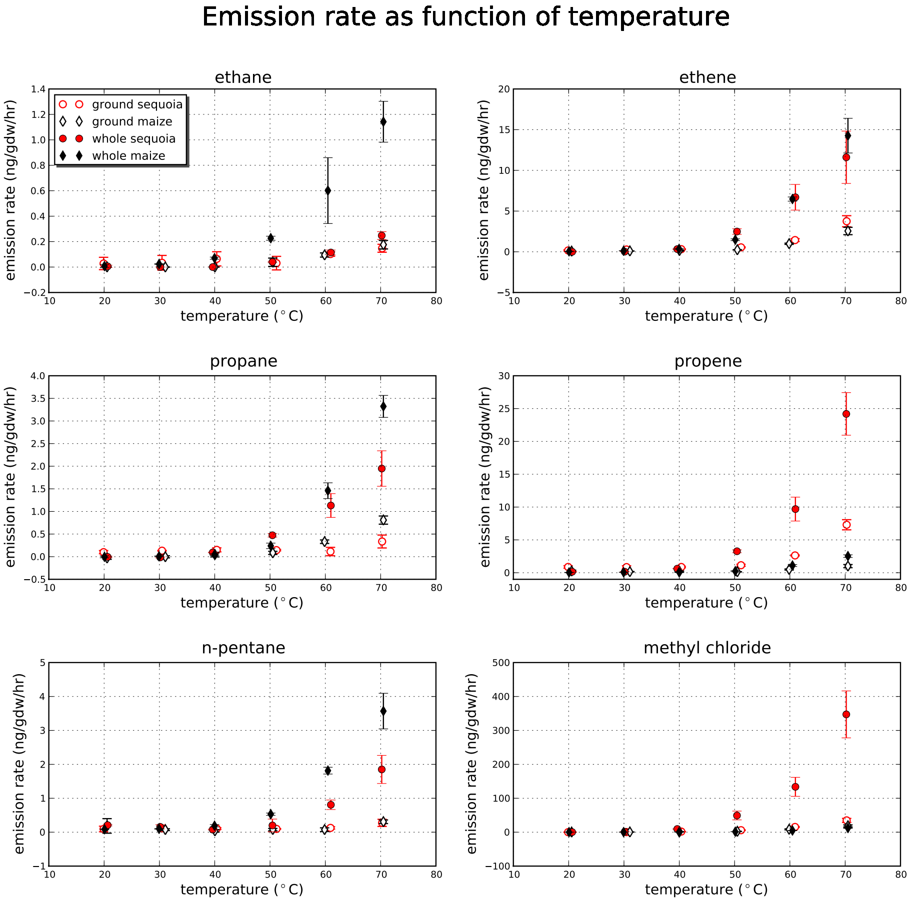

Fig. 2. Emission rate as function of temperature for different VOCs from selected plant species. Note the different scales of the emission rates for the different compounds.

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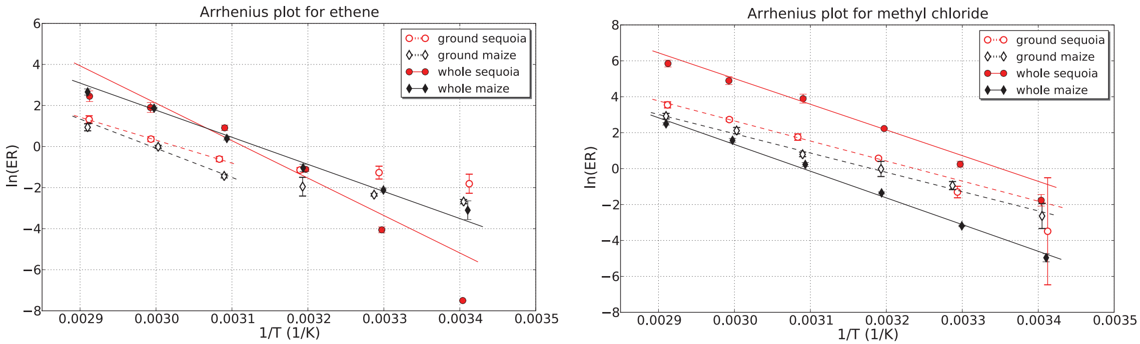


Fig. 3. Arrhenius plot for ethene and methyl chloride emissions from selected plant species for measurements between 20 and 70 °C.

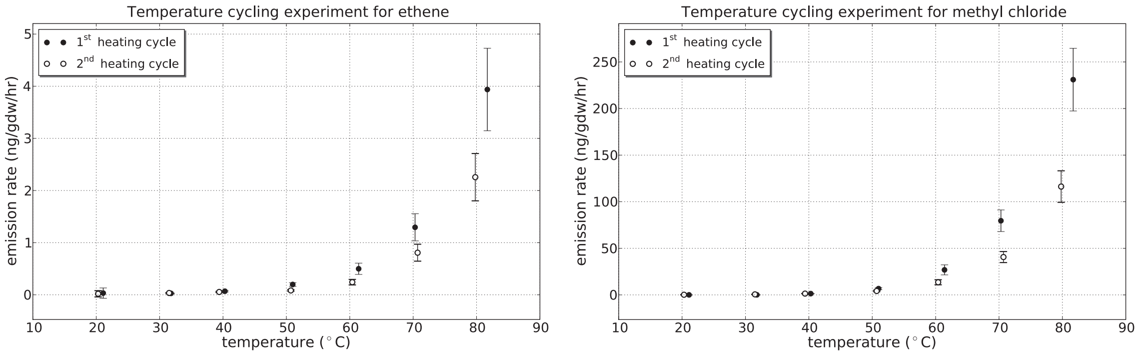
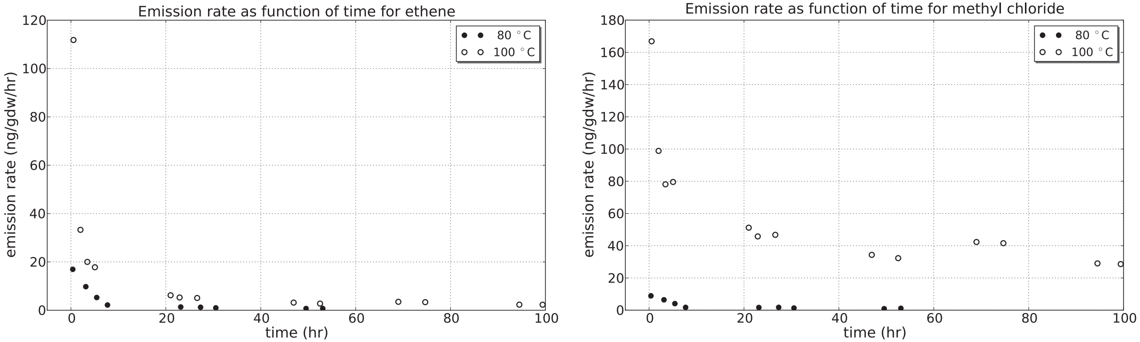


Fig. 4. Temperature cycling experiment for ethene and methyl chloride emissions from dry sequoia leaves.


Emission rate as function of time for ethene

Emission rate as function of time for methyl chloride

Fig. 5. Ethene and methyl chloride emission rate as function time for whole maize leaves in synthetic air at 80 and 100 °C.

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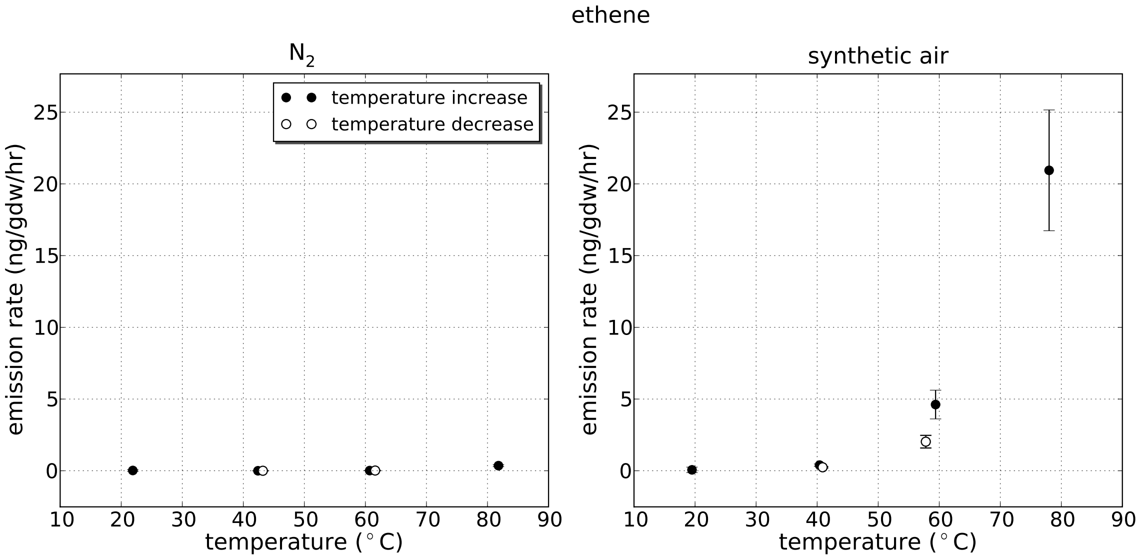

Fig. 6. Emission rates as function of temperature after the leaves were stored in N_2 or synthetic air for ethene.

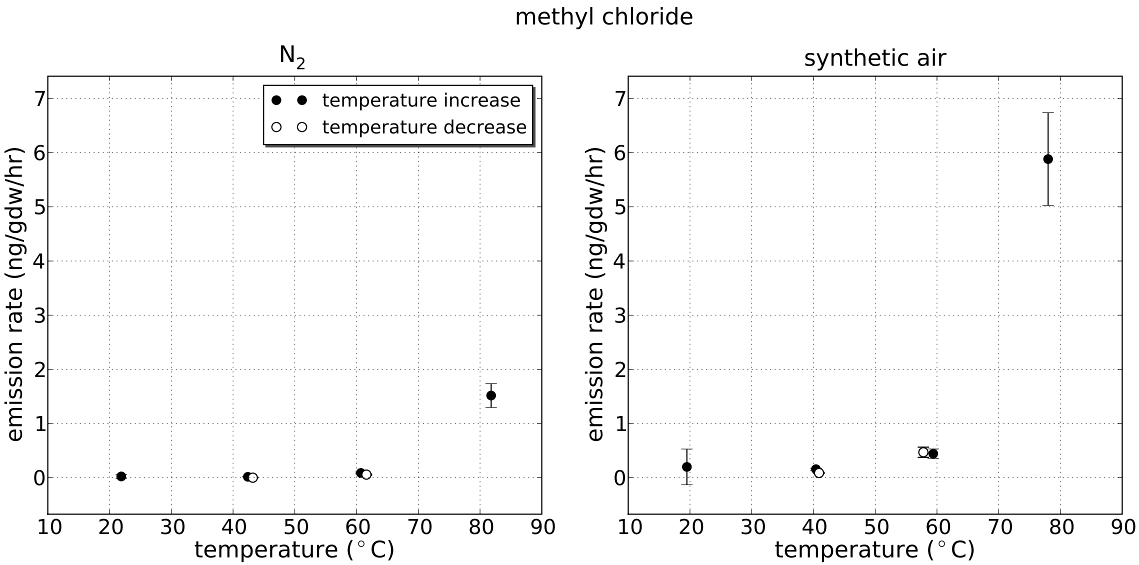

Fig. 7. Emission rates as function of temperature after the leaves were stored in N_2 or synthetic air for methyl chloride.