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Emissions of biogenic volatile organic compounds in a Salix biofuel plantation – field study in Grästorp (Sweden)

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Abstract

Biogenic volatile organic compounds (BVOCs) play an important role in the climate system by altering the oxidative capacity of the atmosphere, affecting the lifetime of methane and production of tropospheric ozone, and by contributing to formation of aerosols and clouds. Salix plants (willows) are well-documented emitters of BVOCs and this study aims to examine emissions in a Salix biofuel plantation for a better understanding of its total climate impact. Measurements of BVOC soil emissions from sewage sludge treated Salix were compared with control plots and additional branch level measurement were carried out. The average emission rate for soil emissions was estimated to 168 μg C m^{-2} h^{-1} for treatment plots and 111 μg C m^{-2} h^{-1} for control plots, with emissions dominated by the compound classes alkanes, alcohols, carbonyls and aromatics. Branch emissions contained compounds similar to soil emissions.

Measurements of BVOC soil emissions were additionally performed in a harvested area of the Salix plantation, with a comparison of emissions from stumps and from the bare soil (control). Average emission rates were slightly higher for control plots than the stumps, with emissions of 175 μg C m^{-2} h^{-1} for the control plots and 163 μg C m^{-2} h^{-1} for the stumps. This study gives a first insight to what types BVOC soil emission that occurs in Salix plantations. However, it remains unclear how the emissions change over the season and how those compounds might affect the atmospheric composition.

Keywords: biogenic volatile organic compounds, BVOC, Salix, willow, atmosphere

Sammanfattning

Biogeniska flyktiga organiska ämnen (BVOCs) spelar en viktig roll i vårt klimatsystem genom att påverka atmosfärens sammansättning, bland annat genom att ha en inverkan på livslängden av metan och produktion av marknära ozon, samt att bidra till formation av aerosoler och molnbildning. Salix planteringar (energiskog) är väldokumenterade utsläppskällor av BVOCs och denna studie ämnar undersöka emissioner från Salix för att ge en bättre förståelse och kunskap om dess totala klimatpåverkan. Mätningar av BVOC-emissioner från marken i områden behandlade med avloppsslam jämfördes med kontrollmätningar därutöver uppmättes grenemissioner. Den genomsnittliga markemissionen var 168 μg C m^{-2} h^{-1} för de behandlade ytorna samt 111 μg C m^{-2} h^{-1} för kontrollerna, mätningarna av grenemissioner visade att liknande ämnen emitteras från mark och grenar.

Markbaserade mätningar av BVOC-emissioner genomfördes även på en avverkad yta där emissioner från stubbar jämfördes med emissioner från bar mark (kontroll). De genomsnittliga emissionerna var något högre för kontrollerna än stubbarna, med emissioner av 175 μg C m^{-2} h^{-1} för kontrollerna och 163 μg C m^{-2} h^{-1} for stubbarna. Denna studie ger en första inblick i vilka typer av BVOCs som förekommer i markemissioner i ett Salix plantage. Likväl, kvarstår oklarheterna om hur BVOC emissionerna varierar över året och hur dessa ämnen skulle kunna påverka atmosfären.

Contents

1. Introduction

1.1 Biogenic volatile organic compounds (BVOCs) in the Earth system

It is widely known that terrestrial ecosystems have a significant impact on the atmosphere and the climate system. Most attention has been given to the processes involved in release and uptake of carbon dioxide (CO_2) and methane (CH_4), in order to estimate the current carbon (C) pools and their fluxes (Penuelas and Staudt 2010). However, CO_2 and CH_4 are not the only C-containing gases being exchanged between the biosphere and the atmosphere. In addition, terrestrial vegetation is a source of biogenic volatile organic compounds (BVOCs) (Laothawornkitkul et al. 2009; Penuelas and Staudt 2010). Compounds included in the group of BVOCs are terpenoids, alkenes, carbonyls, esters, ethers, alcohols, and acids (Laothawornkitkul et al. 2009; Liu et al. 2004). Quantitatively, terpenoids (isoprene C_5H_8, monoterpenes $C_{10}H_{16}$, sesquiterpenes $C_{15}H_{24}$) represent the largest BVOC fraction emitted to the global atmosphere, and of those it is isoprene that dominates with an estimated emission of about 0.4-0.6 Pg C $year^{-1}$ (Pacifico et al. 2009). This figure can be compared with the total global BVOC emission of 0.7-1.2 Pg C $year^{-1}$, which accounts for about 2% of the total assimilated C in the biosphere (Laothawornkitkul et al. 2009; Kulmala et al. 2004; Pacifico et al. 2009). The unsaturated, and therefore highly reactive BVOCs play an important role in the climate system, mainly by influencing the atmospheric oxidative capacity and by contributing to formation of secondary organic aerosols (SOA) and clouds (Kulmala et al. 2004). The high reactivity towards e.g. the hydroxyl (OH) radical influences the lifetime of methane and other greenhouse gases in the atmosphere and also affects the production of tropospheric ozone (Atkinson 2000).

1.2 Objectives and hypotheses

In order to reduce the use of fossil fuels as an energy source, renewable alternatives such as biofuels, have been developed during the last decades. In Sweden, Salix species (willows) is widely used for this purpose due to their high growing capacity and yield (Olofsson et al. 2005). However, Salix species are well-documented emitters of BVOCs (Copeland et al. 2012; Hakola et al. 1998; Olofsson et al. 2005; Behnke et al. 2012) and might consequently have a significant impact on atmospheric properties and local air quality (Copeland et al. 2012; Atkinson 2000). This study aims to examine BVOC emissions from a Salix biofuel plantation at a site in South West Sweden, with focus on soil emissions. Even though the leaves seems to be responsible for the greatest mass emission rates, BVOCs can also be emitted from belowground plant organs (Laothawornkitkul et al. 2009) and emissions could possibly occur even after harvest and outside the growing season. In addition, branch-level measurements were performed as well.

Salix plantations in Sweden are commonly used as cleansing agents for wastewater and sewage sludge. This biological purification removes nitrogen and phosphorous from the water and fertilizes the Salix plants at the same time (Melin et al. 2004), but addition of fertilizers could enhance the BVOC emission rates (Litvak et al. 1996). The plantations usually have a short rotation time with harvest every 2-5 years. After harvest, new shoots appear from the root system and the Salix plant have

a lifetime of about 25-30 years (Melin et al. 2004). This continuous disturbance could possibly trigger BVOC emissions due to wound sealing processes (Niinemets et al. 2010).

The specific objectives of the study were to investigate:

1) Soil emissions of BVOCs from a Salix biofuel plantation
   My particular aim was to compare emissions from fertilized versus non-fertilized areas, but also emissions from stumps at a harvested area versus control plots next to the stumps.
2) To carry out additional branch-level BVOC measurement and compare emissions from fertilized and non-fertilized plots. Only a qualitative study to examine the types of compounds emitted.

Objectives (1) and (2) will together give a first, unique estimate of above- and belowground BVOC emissions from Salix biofuel plantations in Sweden.

Based on the above objectives, the following hypotheses were put forward:

a) Soil emissions of BVOCs will occur due to root and microbial activity.
b) Higher BVOC emissions in fertilized areas.
c) Soil BVOC emissions are expected to occur after harvest due to root activity and wound sealing processes.

2. Background

2.1 Functions of BVOCs in the biosphere

Plants can put a significant part of their carbon budget into producing BVOCs; the rates of emissions are species specific and affected by both biotic and abiotic factors. BVOCs serve functions at several spatial scales, from cell to landscape and some suggested purposes of BVOCs are: communication (signaling and defense), thermo-protection, wound sealing, protection against herbivory and pathogens, protection against cell damage, and reproduction (attraction of pollinators) (Sharkey et al. 2008; Niinemets et al. 2010). The most discussed functions of BVOCs (isoprene in particular) are thermo-protection and ozone tolerance. Thermo-protection has been argued to be one of the most advantageous gains of isoprene. Several studies have also found that isoprene protects the plant cells against damage from ozone and other reactive oxygen species (ROS), which could prevent both visible damage and loss of photosynthetic capacity (Sharkey et al. 2008; Behnke et al. 2012). Some plants damaged by herbivory can release cis-jasmone, a volatile compound and a plant regulator that increases the plants resistance to aphids. The wound-sealing processes occurring after herbivory may also trigger the release of ethylene, which generally enhance the production and emission of BVOCs. Additionally jasmonic acids (such as cis-jasmone) and ethylene may interact to regulate the BVOC synthesis (Laothawornkitkul et al. 2009).

2.2 Controls of BVOC emissions

Emissions of BVOCs are mainly affected by the environmental conditions connected to the photosynthesis, such as temperature, light availability, substrate availability (nutrients and water), and CO_2 concentration (Niinemets et al. 2010; Sharkey et al. 1996; Laothawornkitkul et al. 2009). The photosynthesis is essential for the substrate supply to the biosynthesis of BVOCs, and the leaf temperature also regulates the activity of enzymes involved in this process (Laothawornkitkul et al. 2009). Light availability is not only of importance for the photosynthetic rate, but light activation is also required as an enzymatic trigger for the synthesis of isoprene (Wildermuth and Fall 1996).

Moreover, emissions can also be species specific, age dependent, and change over the season (Sharkey et al. 2008). Accurate estimations and a correct understanding of emission controls are thus critical for reliable simulations of BVOCs and their possible impacts on the atmosphere (Arneth et al. 2011). In general, emissions of isoprene and most other BVOCs increase with both temperature and light. Temperature affects emissions of many BVOCs by regulating the diffusion rate between the leaf interior and the surrounding air, which is determined by Henry's law. The diffusion of gases is also controlled by the stomatal conductance, which is influenced by soil moisture, CO_2 concentration, O_3 and other environmental stressors (Niinemets et al. 2010). The effects of CO_2 are however ambiguous (Niinemets et al. 2010). CO_2 fertilization might increase total ecosystem BVOC emission due to increases in primary production that results in greater BVOC-producing biomass. When considering individual leaves, an increase in CO_2 could inhibit the biosynthesis of BVOCs and therefore give rise to decreased emissions on an areal basis (Niinemets et al. 2010; Sharkey et al. 2008).

2.3 Climate impacts of BVOCs

The magnitude of BVOC-induced climate impacts is rather uncertain. This is mainly because their high reactivity and thus rapid chemical transformations into new oxidation products, which may further be involved in atmospheric chemical reaction chains, are difficult to study. BVOCs in the atmosphere can initiate formation and growth of aerosol particles and potentials for both warming and cooling effects have been observed. They can also increase formation of tropospheric ozone and increase the atmospheric lifetime of methane, resulting in climate warming (Kulmala et al. 2004; Pacifico et al. 2009).

2.3.1 Aerosol formation and cloud properties

Several types of BVOCs react with oxidants (such as O_3, OH, and NO_3) in the atmosphere, resulting in low volatile products. Those products could take part in gas-to-particle conversion processes causing production of aerosols (Atkinson 2000; Sharkey et al. 2008). Aerosols directly affect the climate by scattering of incoming solar radiation, resulting in a negative radiative forcing which has a cooling effect on the climate (IPCC 2007). The aerosols could additionally act as cloud condensation nuclei (CCN) and thereby alter the cloud cover and the optical thickness of individual clouds (Kulmala et al. 2004). Changes in aerosol concentration and chemical composition will consequently have an impact on the cloud properties, and indirectly change the energy balance of the Earth by alterations in albedo and absorption of long wave radiation (Kulmala et al. 2004; IPCC 2007).

2.3.2 Impacts on tropospheric ozone and methane

BVOCs can alter the atmospheric concentrations of tropospheric ozone (O_3) as well as methane (CH_4), which both are strong greenhouse gases. With available solar radiation and NO_x, presence of BVOCs in the air can cause a net production of O_3 (Atkinson 2000; Sharkey et al. 2008). NO_x primarily origins from combustion of fossil fuels but could also be produced through denitrification processes in wetlands and agricultural land where nitrogen is abundant (Atkinson 2000; IPCC 2007). Apart from having detrimental effects on our respiratory system and causing decreased crop yields, the presence of O_3 in the troposphere is of importance for the production of OH radicals. Photolysis of O_3 in clean air (without NO_x) in the presence of water vapor is a major source of OH radicals in the troposphere (Atkinson 2000). Since OH radicals act as a cleansing, oxidation agent in the atmosphere and thus is a major sink for CH_4, this process significantly affects the atmospheric chemistry and radiation balance (Laothawornkitkul et al. 2009). BVOCs generally has a higher affinity for OH radicals than CH_4, and an increase in BVOC emission could indirectly lead to an increased concentration of CH_4 (Penuelas and Staudt 2010). Generally it is very difficult to model the impacts of BVOCs in the atmosphere due to the non-linear relationships of concentrations. For example, one molecule of isoprene could result in several molecules of O_3 (Sharkey et al. 2008).

2.3.3 Global change and BVOCs

Since BVOC emissions are generally controlled by the environmental conditions, they are subject to change with a global climate change and anthropogenic impacts. The

strong temperature dependence of BVOC emission supports the theory of increased emissions with a global warming of the climate. It has been suggested that emissions will increase with 30-45% with a temperature rise of 2-3°C, but it is possible that this response will be limited to high latitude biomes where temperature is the most regulating factor for plant growth (Penuelas and Staudt 2010; Filella et al. 2007). The temperature is mainly regulating the photosynthesis and the enzymatic pathways for BVOCs, but it could indirectly affect the emission rates by altering the species composition in a biome. Changes in vegetation community structure can additionally alter the amount of leaf litter, which is affecting the nutrient content in the soil that indirectly influences BVOC production (Harley et al. 1994; Penuelas and Staudt 2010). Correlation between nitrogen and isoprene emissions has been documented (Litvak et al. 1996) and anthropogenic N-deposition might thus have effects on emission rates. Moreover, changes in temperatures and precipitation will probably also affect the range and abundance of many insects (Musolin and Saulich 2012). Larger outbreaks could cause a significant increase of insects feeding on plants, which potentially could cause higher emission rates of BVOCs due to wound sealing and protection against herbivory (Niinemets et al. 2010).

However, land use change is probably the most significant and most rapid anthropogenic impact on BVOC emissions, due to the species-specific emission rates. Model-based estimations have suggested an increase of global isoprene emissions up to 37% due to conversion of natural vegetation to plantation (with temperatures at current levels) (Wiedinmyer et al. 2006). Movement of people and plants also causes dispersal of pathogens (Santini et al. 2013), which could be an environmental stress triggering production of BVOCs (Niinemets et al. 2010).

For some areas drought may increase with a warming climate and this environmental stress can potentially change emission rates of BVOCs. It is suggested that emissions might decrease significantly during severe droughts, but oppositely increase when droughts are mild (Niinemets et al. 2010; Penuelas and Staudt 2010). As mentioned in section 3.2, BVOC emissions might also response to changes in CO_2 concentration, which currently is changing. Similarly, concentrations of tropospheric O_3 is likely to change but both negative and positive effects of O_3 on BVOCs have been documented for different experimental conditions and species (Penuelas and Staudt 2010; Laothawornkitkul et al. 2009). Due to the fact that BVOCs themselves could cause a net production of O_3, possible feedback mechanisms have to be considered as well. Another potential feedback loop is the coupling between forest, aerosols, and climate. It is proposed that a warmer climate with higher CO_2 concentration will enhance emissions of BVOCs by the forests, which subsequently will cause an increase in aerosols and CCN that have a net cooling effect, resulting in a negative feedback loop (Kulmala et al. 2004).

2.4 Salix biofuel plantations

Biofuel from Salix is considered as a relatively clean source of energy with low net emissions of CO_2. In the early 1990's Salix plantations increased considerably in Sweden due to the need of renewable energy sources and generous subsidies from the European Union. With raised taxes on fossil fuels in 1991 biofuels became more competitive, and a biofuel market with a suitable infrastructure for the district-heating sector was established and growing by this time (Rosenqvist et al. 2000). More than 15 000 ha of Salix have been planted in Sweden during the last two decades,

accounting for 0.5% of the total arable land (Mola-Yudego and Pelkonen 2008; Melin et al. 2004).

2.4.1 Ecosystem services

Salix plantations could offer multiple ecosystem services such as biofuel production, treatment of wastewater and sewage sludge, and acting as a carbon sink. Because of the efficient carbon assimilation, Salix is a suitable short rotation crop for biofuel production. Yields are continuously increasing due to better land management and further development in breeding of new varieties of Salix species (Mola-Yudego 2011).

In a study by Grelle et al. (2007) the carbon exchange in a Salix plantation was examined to determine the net CO_2 sink strength. The study was carried out in a wastewater-irrigated plantation in central Sweden from 2002 to 2004. During 2003 the total carbon sink was about 8 tons C ha^{1}, whereof 5 tons C ha^{-1} allocated to aboveground vegetation and 3 tons C ha^{-1} to belowground. The addition of fertilizers from wastewater was assumed to attribute to about 50% of the total carbon uptake.

Salix plantations are commonly used as cleansing agents for wastewater and sewage sludge (Olofsson et al. 2005; Melin et al. 2004) that are rich in nutrients, nitrogen and phosphor in particular. According to Melin et al. (2004) wastewater treatment facilities in Sweden produce more than 200 000 tons dry solids of sludge per year, and about 10% of this is used to fertilize Salix. Some of the advantages of this method are: reduction of manufactured fertilizers, reduction of precipitation chemicals, and decrease in chemical sludge production. Salix plantations are often more efficient in nitrogen uptake from sludge compared with many traditional crops, resulting in less nitrogen leaching. It has also been debated whether to use sewage sludge for food production or not, due to possible risks of soil contamination. However, it has been more accepted for use in Salix plantations since it is not a food crop (Melin et al. 2004). It should also be noted that N-fertilization of Salix crops might increase emissions of both BVOCs (Litvak et al. 1996) and NO_x (Balasus et al. 2012), which could have impacts on the atmospheric chemistry (see section 2.3.2).

2.4.2 Policies for Salix plantations

The research question posed in this study is of relevance for Sweden's environmental quality objective 'Reduced Climate Impact' (Naturvårdsverket 2012). Energy use is one of the indicators applied to follow-up on this objective. A better understanding of the total climate impact of various energy sources is needed to provide a basis for sound policymaking and climate change mitigation strategies. BVOCs emitted from biofuel plantations and their climate impacts are currently not well understood, but this study contributes to the effort to fill the knowledge gap by providing emission measurements from both soils and branches in a cultivated Salix field. Due to the potential formation of tropospheric O_3 and aerosols, BVOC emissions from biofuel fields are also relevant for the environmental quality objective 'Clean air' (Naturvårdsverket 2011). In order to uphold the commitment of the 1997 Kyoto Protocol, short-rotation crops for biofuel give an opportunity to reduce greenhouse gas emissions, and potentially act as carbon sinks (Grelle et al. 2007). However, the whole life cycle of biofuel crops has to be considered to understand the total climate impact.

The policies for biofuels have been essential for the expansion of Salix plantations in Sweden. One of the main driving forces has been the generous planting

subsidies from the European Union starting in the early 1990's, giving farmers possibilities to invest in cultivation of Salix (Mola-Yudego and Pelkonen 2008). By the same time period, environmental and energy taxes were raised for fossil fuels, but excluding biofuels (Rosenqvist et al. 2000). The adoption rate of farmers have additionally been influenced by local factors such as farm type, soil type, interest from local agricultural co-ops and advisors. (Rosenqvist et al. 2000; Mola-Yudego and Pelkonen 2008). When subsidies were reduced to less than a third in 1997, the expansion of Salix plantation ceased (Mola-Yudego and Pelkonen 2008). A reduction in the adoption rate might also be due to the fact that many farmers were disappointed with the yields, which were lower than expected. However, the yield is strongly dependent on management and tends to increase with experience (Mola-Yudego and Aronsson 2008).

3. Material and method

3.1 Site description

This study was performed 24-25 of April 2013, in a Salix biofuel plantation located near Grästorp in the province of Västergötland, Sweden (58°20.85´N; 12°34.17´E). The plantation consisted of a few different clones of *Salix viminalis* and surrounded by open agricultural land. The study site was divided into two parts (see figure 1); one part harvested a few weeks before our measurements with no aboveground vegetation except for some stumps. The other part was harvested the previous year with a vegetation height reaching 2-2.5m. Furthermore this part was divided into 6 subplots (figure 3), 3 plots treated with sewage sludge the previous year (14-28 May 2012) and 3 control plots. For the first day of measurements (24 April) photosynthetic active radiation (PAR) was ranging from 132 to 413 µmol m^{-2} s^{-1} and during the second day (25 April) 904-1587 µmol m^{-2} s^{-1}. Soil temperature was measured to 4.6-5.6°C both days and air temperature 8-10°C for the first day and 10-12° for the second day. It should also be noted that foliation had not occurred when measurements were performed.

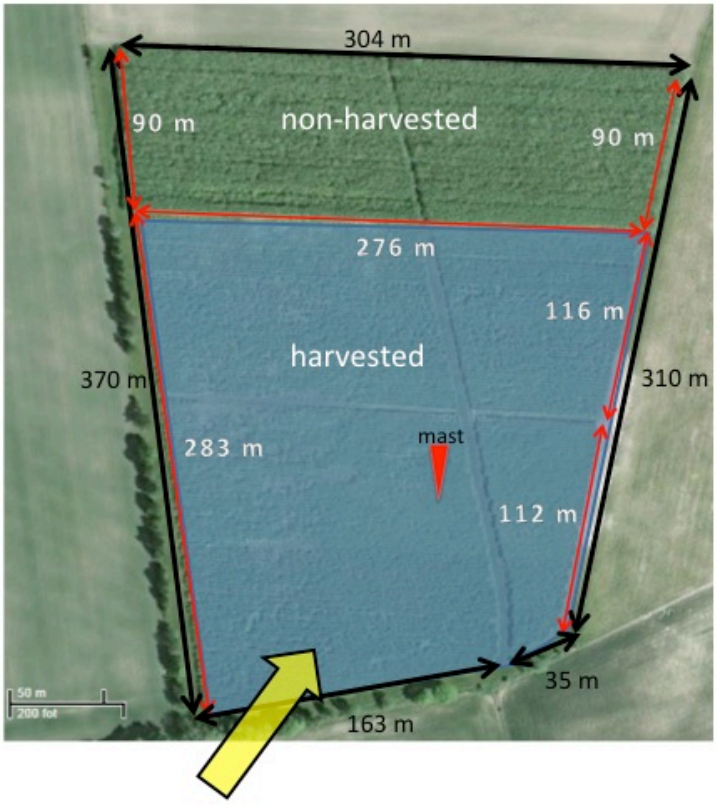

Figure 1: Aerial photo of the study area for overview and location of harvested and non-harvested area, yellow arrow gives the prevailing wind direction (used with permission from Leif Klemedtsson).

3.2 Data sampling

Sampling of soil emissions was carried out with transparent chambers (12 l) with closed system airflow (figure 2), and a flow set to 200 ml/min. BVOCs were collected on adsorbent tubes, for each sample 3 tubes were taken with a sampling time of 15 minutes per tube. At the non-harvested area one sample was taken from each plot and the chamber was placed next to the stems of a Salix plant. Two chambers were used for simultaneous sampling of one control plot (C1, C3 and C5 in figure 3) and one treatment plot (S2, S4 and S6 in figure 3). For the harvested area one chamber was placed on a stump (treatment plot; AS1, AS2 and AS3 in figure 3) and the other chamber placed close by on the bare soil (control plot; AC1, AC2 and AC3 in figure 3), this was repeated 3 times within the harvested plot with a few meters distance. Samples for control versus sludge were taken the 24th of April and data for the harvested area was collected the next day.

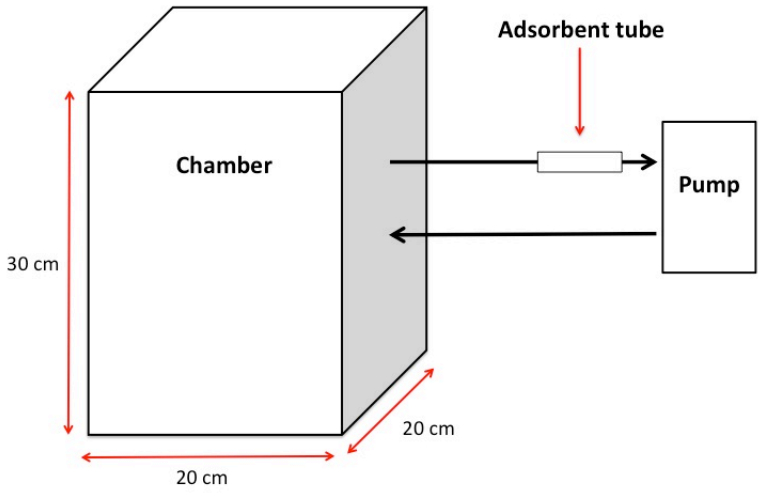

Figure 2: Chamber setup for measurement of soil emissions with pump and adsorbent tube, air moves within tubes in direction of the arrows with a flow of 200ml/minute. BVOCs are collected on the adsorbent tube for 15 minutes to estimate soil emissions.

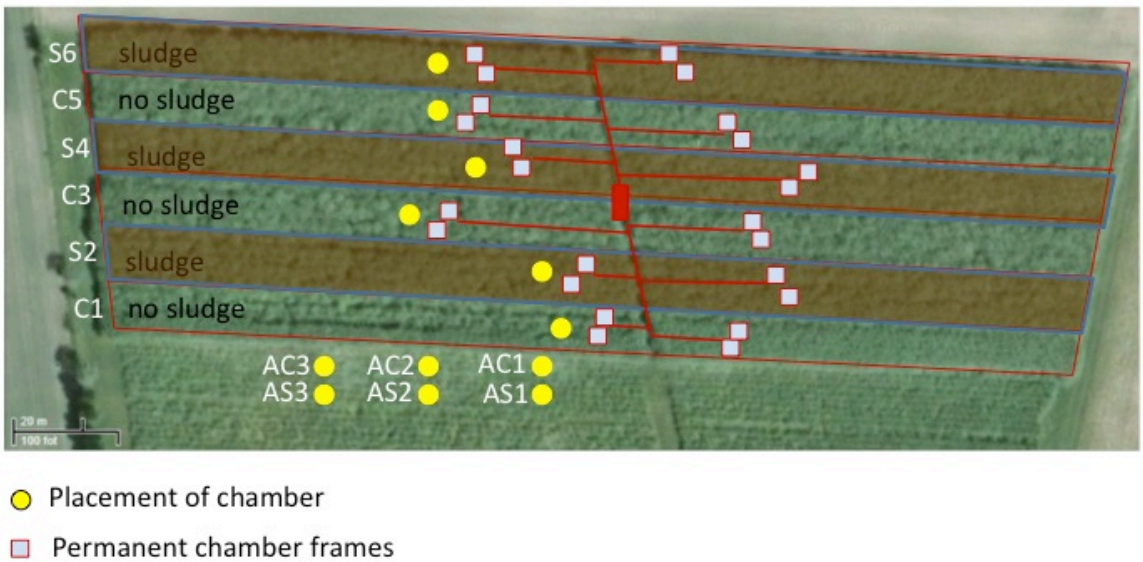

Figure 3: Aerial photo of the study area with an overview of the plots (used with permission from Leif Klemedtsson). In non-harvested area C=control and S=sewage sludge treatment, for harvested area C=control and S=stump. Permanent chamber frames are used as reference points.

Branch measurements were performed in two plots in the non-harvested area, one control plot (C1) and one treatment plot (S2). The measurements were carried out with a through flow system using Teflon bags as branch cuvettes. The flow rate of the ingoing air was approximately 5 l/min and a 220 ml/min subsample was collected from the outgoing air. BVOCs were collected on adsorbent tubes for 2x60 minutes per sample (total sample volumes ranged from 7 to 13 liters), with one sample per plot and day.

3.3 Data analysis

Data analysis was performed with gas chromatography-mass spectrometry (GC-MS). Samples collected onto the adsorbent tubes were thermally desorbed at 280˚C for 6 minutes and cryofocused at -30˚C on a Tenax TA coldtrap (Turbomatrix 650 ATD, PerkinElmer, Waltham, MA, USA). In a subsequent second desorption, the coldtrap was heated to 300˚C within 2 seconds and the sample transferred after a 3:1 split (25% of the sample to detection) via a heated transfer line (250˚C) for gas chromatographic separation and detection/identification by mass spectrometry (GC-MS, Shimadzu QP2010 Plus, Shimadzu Corporation, Japan). Helium was used as carrier and GC separation was performed in a Agilent EZ-Guard VF-5ms capillary column (30m*0.25mm, film thickness 0.25 µm) (Agilent Technologies, Santa Clara, USA) with the following temperature program: initial temperature 40˚C held for 1 min, 15˚C/min to 250˚C which was held for 2 min). The MS ion source (electron impact) was kept at 250˚C and the interface at 275˚C. Full scans for ion fragments m/z 47-350 were carried out and compound identification took place by comparison of mass spectra with the NIST 08 library. The average response factor and constant (linear integration) of the total ion counts (TIC) of pure standards of α-pinene, β-pinene, 3-carene, eucalyptol, limonene and caryophyllene were used for quantification.

With the TIC chromatogram from the GC-MS analysis, peak integration was carried out and 100 peaks were integrated for the analysis of each adsorbent tube. All peaks with a height less than 1% of the total height were excluded. For the remaining compounds a similarity search was performed in NIST 08 library for identification of compounds. The first choice of compound (the most similar) suggested in the NIST library was consistently chosen for all data. Calculations of fluxes were carried out for all compounds within each sample, on the condition that the same compound has to occur in two consecutive tubes for each sample and otherwise excluded. With the area of each individual peak in the TIC chromatogram compound mass could be calculated.

Equation 1 gives the relationships between TIC area (y) and compound mass (x) in ng.

$$y = Fx + k \quad (1)$$

F and k were determined from an average of measured standards and it was assumed that all compounds had a response factor of 1 relative to those standards.

F=23526.17
k=78317

With a flow set to 200ml/min and sampling time of 15 minutes the total collected volume for each tube was 3 l. This means that only ¼ of total chamber volume was collected on the tube and the remaining BVOCs stayed in the chamber. Masses of the remaining compounds (*sn*) are given by equation 2.

$$sn = \frac{BVOCs\ on\ tube}{collected\ air\ volume/chamber\ volume} - BVOC\ on\ tube \quad (2)$$

Estimation of total compound emission during the 15 minutes (*a*0) is given by equation 3.

$$a0 = \frac{sn}{q \times (q-1)/(q^{n-1})} \quad (3)$$

q=0.75, remaining volume fraction $(1 - (3/12) = 0.75)$
n=tube number (1, 2 or 3)

For comparison of emission rates, fluxes were converted from mass of compound per area and time unit (µg m^{-2} h^{-1}) into mass of carbon per area and time unit (µg C m^{-2} h^{-1}). All compounds found in the samples were then classified into following chemical classes: alkanes, alcohols, aromatics, carbonyls and 'others' (S-containing, Br-containing, terpenes, N-containing and ethers). An average carbon flux was calculated for each compound class and sample for a comparison between the control plots and treatment plots.

4. Results

4.1 Soil emissions

Figure 4 gives an overview of mean emission rates for each compound class for the control plots and the plots treated with sludge in the non-harvested area. Emissions in the treatment plots are dominated by alkanes, carbonyls and aromatics with average emission rates around 230 µg C m^{-2} h^{-1}. For the control plots carbonyl accounts for the highest emissions with an average rate of 160 µg C m^{-2} h^{-1}. Mean emission rate for all compound classes is higher for treatment plots than control plots, indicating a positive effect of the sludge treatment. However, alkane is the only compound class where emission rates for the treatment plot do not fall within the range of standard deviation for the control plot. If compound classes are disregarded, the overall average emission for control and treatment plots are 111 µg C m^{-2} h^{-1} and 168 µg C m^{-2} h^{-1}, respectively.

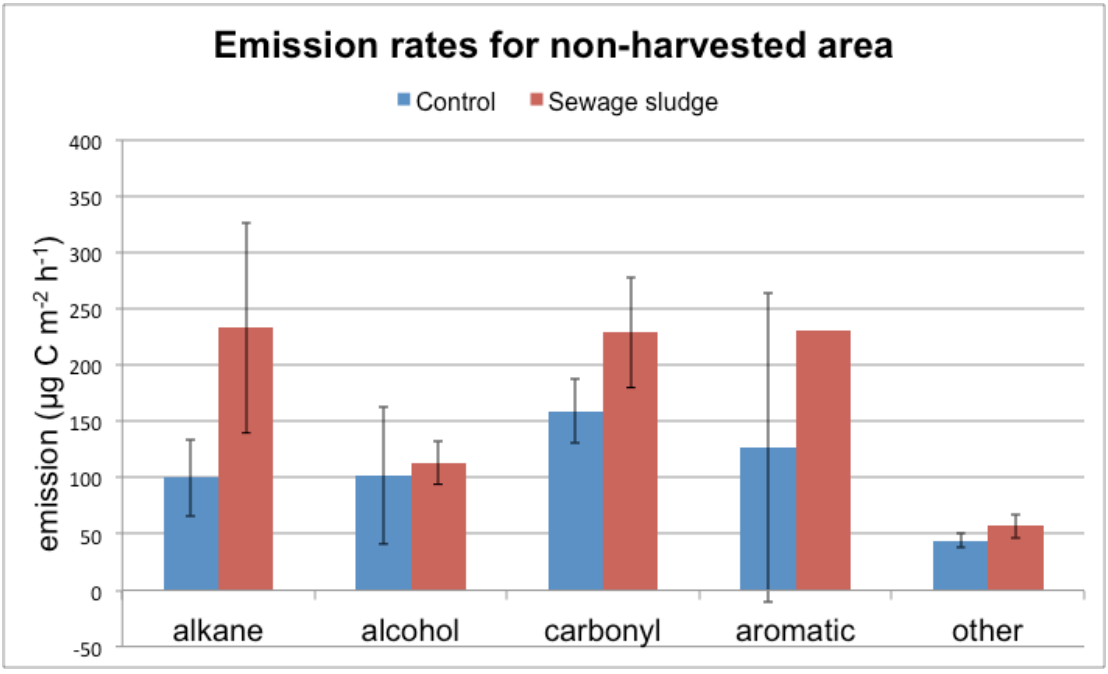

Figure 4: Carbon emission rates (µg C m^{-2} h^{-1}) for each compound class for control plots versus sewage sludge treatment plots in non-harvested area, error bars are standard deviations (no error bar for aromatics in the treatment plots since it was only found in one sample).

Emission rates in the harvested area are found in figure 5. For the classes alcohol, carbonyl and aromatic there are no clear differences between stump and control plots. The emissions rate for alkane is somewhat higher for the control plots, with an average emission of 233 µg C m^{-2} h^{-1} for the control and 163 µg C m^{-2} h^{-1} for the stump. Looking at the compound class 'other' there is a clear difference, this class is not found at all within the control plots but for the stumps emissions are about 115 µg C m^{-2} h^{-1}. The overall average emission rate, not considering compound class is 175 µg C m^{-2} h^{-1} for the control plots and 163 µg C m^{-2} h^{-1} for the stump plots. Complete tables of all compounds within the samples can be found table 2-5 in appendix 8.1.

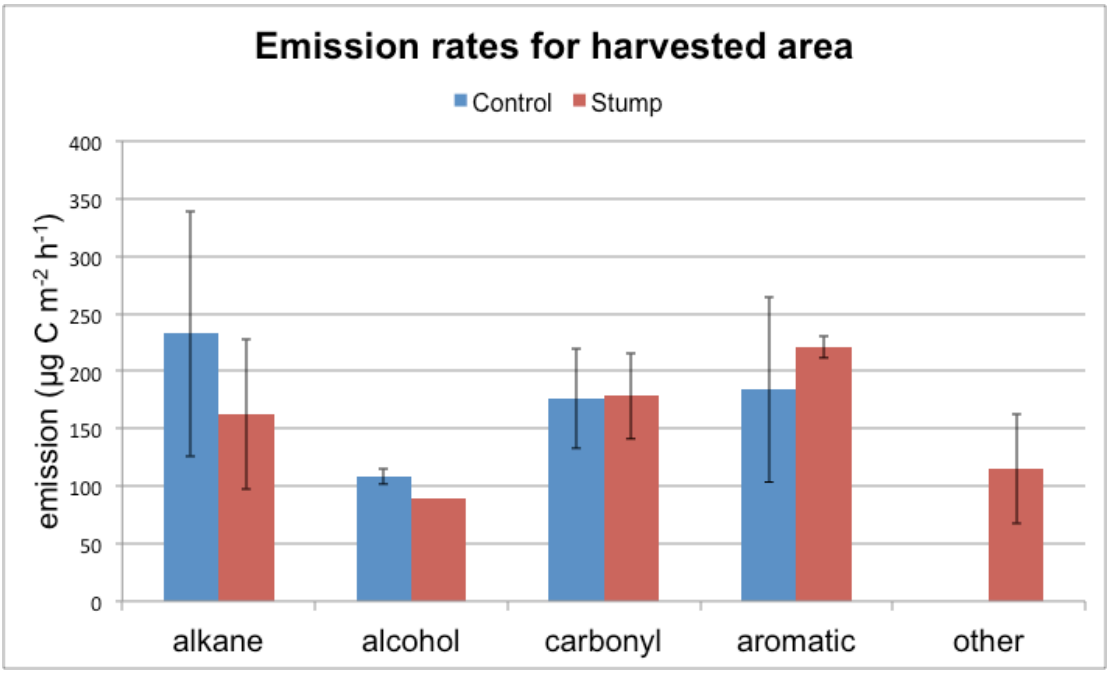

Figure 5: Carbon emission rates (µg C m^{-2} h^{-1}) for each compound class for control plot and stumps in the harvested area, error bars are standard deviations.

4.2 Branch emissions

Branch level emissions were analyzed qualitatively to compare if the type of compounds emitted differed between branches and the soil. Number of compound types within each class can be found in table 1. Overall, the most common compound types are alkanes, carbonyls and 'others'. Types of compounds are quite similar for the different samples except for plot S2 day 2, where many unique compounds are found. For this sample also many also many types of aromatics are detected which are rare in the other branch samples. Complete table of all compounds found within the samples from branch measurements can be found in table 6-9 in appendix 8.2.

Table 1: Occurrence of compounds in branch level measurements with number of compound types found within each class.

	plot C1		plot S2	
	day 1	day 2	day 1	day 2
alcohol	6	5	8	5
alkane	10	7	10	11
aromatic	2	1	1	7
carbonyl	10	11	9	11
other	5	9	9	10

5. Discussion

This study gives a first insight to what types of BVOCs that could be emitted from the soil in a Salix plantation. Even though the number of samples is low it gives an indication that BVOC emissions do occur even before the growing season has started.

5.1 Method

Regarding the sampling method and data collection there are possibilities for further improvements. First of all is the number of replicates, as mentioned before there is only one sample taken from each plot due to the limited time available for this project. Samples were quite spread out over the non-harvested area but the number of replicates is too low to statistically test the difference between control and treatment plots. For the harvested area all six samples were taken within a smaller part of the area, which makes it less representative even though the field looks quite homogenous. Another shortcoming is the uncertainties within the sampling method. It is assumed that the chamber is airtight and that the air stays within the system during each sample session, which probably is not entirely true. Fixed frames for the chambers could be a solution to avoid air leakage.

The fact that the measurements were performed early in the season, when foliation had not occurred, can be seen both as an advantage and shortcoming. First of all it shows the potential of BVOC emissions taking place before photosynthesis is active and temperatures are relatively low. On the other hand, emission rates are expected to change over the growing season, due to the light and temperature dependence, and soil emissions should therefore also be examined later on in the season to give the whole picture. With developed leaves on the branches it would also be easier to see differences between soil and branches, both when it comes to rates of carbon flux and types of compounds emitted.

Concerning the analytical method there are several possible ways to go for estimation of emission rates and their possible impact. Even though BVOCs contribute significantly to the global carbon budget, the impacts on atmospheric composition might be of higher importance when it comes to future changes of the climate, due to the indirect effects on greenhouse gases and aerosols. For this study emissions have been compared in units of carbon and the compounds have been classified by chemical classes. Compounds within the same class are expected to have similar properties due to their functional groups but the relative reactivity of the functional groups might be altered by other functional groups within the molecule. An alternative could be to look into how reactive the different individual compounds are and their potential effects on atmospheric properties, maybe in terms of indirect global warming potential or radiative forcing. Nevertheless, this would be quite complex since the atmospheric pathways for different BVOCs are dependent on the presence of other compounds, but also light and temperature conditions. In order to estimate the possible climate impacts by BVOCs, other factors than just plant emissions have to be considered. When it comes to the interaction between BVOCs and NO_x, which is causing net production of tropospheric O_3, estimates of both gas types have to be taken into account. Since many Salix plantations are treated with nitrogen-rich wastewater and sewage sludge, there are possibilities for NO_x emissions to occur. This means that the total net effect of those plantations could be an increase in emissions of BVOCs, NOx and tropospheric O_3 causing climate warming.

Currently most attention has been put to examine emissions and impacts of terpenoids (isoprene in particular), since they account for the largest fraction of emitted BVOCs. Together with other findings (Arneth et al. 2010), this study shows that emissions of many oxygenated compounds do occur but very little is known about the sources and magnitudes of these types of BVOCs. Modeling has estimated global plant emission of methanol to a rate of 0.1 Pg y^{-1} (equals to 0.0375 Pg C y^{-1}) (Galbally and Kirstine 2002). There is also a big knowledge gap when it comes to the chemical reactivity of these compounds and how they might affect the atmospheric composition in terms of greenhouse gas concentrations and particle formation. A complete understanding of those processes is critical for simulation of the interaction between the atmosphere and biosphere. As mentioned by Arneth et al. (2010) BVOCs play an important role in the global climate system and should therefore be included in dynamic global vegetation models (DGVMs). But the problem is that those models are mainly based on the interactions of plant functional types (PFTs) and BVOC emissions tend to be very species specific.

5.2 Emissions

Going back to the hypotheses posed in the introduction; can they be accepted or rejected?

a) Soil emissions of BVOCs will occur due to root and microbial activity.
b) Higher BVOC emissions in fertilized areas.
c) Soil BVOC emissions are expected to occur after harvest due to root activity and wound sealing processes.

For hypothesis a) results show that this cannot be rejected since emission have been found in all plots. Nevertheless, it could be discussed whether BVOC soil emissions originates from the roots system of Salix plants or from microbial activity. Other studies have shown that there are bacteria producing isoprene (Kuzma et al. 1995), but also microbial consumption of isoprene has been documented (Cleveland and Yavitt 1998). However, isoprene was not found within any of the plots in this study and further knowledge is needed to determine the importance of microbial activity and their possible BVOC production. Laboratory studies could maybe be suitable to examine BVOC emissions from the root system of Salix plants with exclusion of microbes.

When it comes to hypothesis b) the sample size is too small to prove this statement to be true. Results indicate that the average emission for most compound classes is slightly higher in the sludge treated areas but the variation between and within the samples is quite large (see complete tables of emissions in appendix 8.1) and this hypothesis cannot yet be accepted. Further studies with more samples and data over the whole season might give better knowledge and evidence to support or discard this hypothesis.

For hypothesis c) it is rather uncertain whether to accept or reject. As mentioned previously, soil emissions do occur also in the harvested area but this study gives no knowledge about the origin of those BVOC emissions. Regarding the comparison between emissions from stumps (treatment) and the bare soil (control), no clear differences could be seen except for the lack of compound class ‘others’ in the control plots. When comparing the overall emission rates for harvested and non-harvested areas, they are of the same magnitude except for the control plots in non-harvested area. However, it has to be taken into account that those measurements were performed on two different days with varying weather conditions, but with

constant soil temperature. Furthermore, the results can be compared with a study performed by Olofsson et al. (2005), a few years earlier at the same experimental site, where isoprene emission were measured at canopy level. Their study showed maximum isoprene fluxes of 0.23 μg m^{-2} s^{-1}, which is equal to 146 μg C m^{-2} h^{-1} and being in the same range as the emissions found in this study.

Considering the branch measurements it can be concluded that branch level emissions are similar to soil emissions when it comes to BVOC type, which supports the theory that some soil emissions origin from the Salix plant. The main difference is the low number of aromatics found in branch samples but being quite common in the soil emissions. Looking at the individual samples of branch emissions it can be concluded that they are fairly similar except for the sample from treatment plot (S2) the second day where many unique compounds are detected and the number of aromatics is higher. A reason for this could be the fact that the second day was slightly warmer and PAR was significantly higher than the first day (132-413 μmol m^{-2} s^{-1} for day 1 and 904-1587 μmol m^{-2} s^{-1} for day 2). By time of measurements there were quite many developing buds on the branches, and some of the unique compounds found could possibly be involved in the bud burst.

5.3 Biofuel policies

Due to the lack of understanding of the total climate impact by Salix plantations it remains unclear whether to promote this as a suitable source of renewable energy. The complexity of BVOC emissions and their affect on the atmospheric properties makes it hard to fully understand and to make future predictions about the effects. Maybe it would be better to find other alternatives for biofuel crops, which are not know to emit substantial amounts of BVOCs. Experiments have been made with genetic modification to inhibit isoprene emissions from poplar (*Populus canescens*) (Behnke et al. 2012). During two growing season under outdoor conditions, growing capacity and fitness was tested to examine if the isoprene had a substantial role for the plants. The result showed an enhanced growth by 6.9% of the isoprene-inhibited plants, but they also had a reduced susceptibility to fungal infections attracting more herbivores.

In a study performed in the UK by Copeland et al. (2012) isoprene emissions from Salix was compared with emissions from another short rotation bioenergy crop, elephant grass (*Miscanthus gigantus*). The results shown that the Salix plants had emissions rate of 1 mg m^{-2} h^{-1} but no measureable fluxes could be detected from the elephant grass. However, growing capacity of the two plant species was not taken into consideration. A study by Crespo et al. (2013), comparing BVOC emissions from elephant grass and black bamboo (*Phyllostachys nigra*), showed that black bamboo had significantly higher emission rates than the elephant grass. Emissions mainly consisted of isoprene and BVOCs associated with wounding (compounds from the hexanal and hexenal families) and it is suggested that emission rates are lower for perennial grasses than woody species. Regardless of BVOC emissions, Salix is probably a better solution than fossil fuels since it is CO_2 neutral and sometimes even a carbon sink. Nonetheless, it would be better to find an alternative crop with lower or no emissions, such as elephant grass, to limit climate impacts as much as possible. So far most attention regarding biofuel crops has been given to find suitable crops for different growing conditions and with high growing capacity, but it is also important to consider the whole life cycle of the crops.

6. Conclusions

The results of this study imply that BVOC soil emissions do occur in both harvested and non-harvested Salix plantations. The most common compound classes found within the samples are alkanes, alcohols, carbonyls and aromatics with emissions in the range of 100-230 μg C m^{-2} h^{-1}. Treatment of sewage sludge in the non-harvested area tends to increase emissions somewhat, but the number of replicates is too low for statistical evidence. Comparing emissions from stumps and bare soil in the harvested area showed no clear differences and the overall emissions, regardless of compound class, were in the same range for control and stumps, 163 μg C m^{-2} h^{-1} respectively 175 μg C m^{-2} h^{-1}. The qualitative study of branch emissions showed that similar compounds are emitted from soil and branches.

Even though soil emission of BVOCs have been found it remains uncertain whether they origin from the root system of Salix plants, microbial activity, or both. Further studies, with more samples over the whole growing season, are required to better capture the whole picture of the dynamics behind the production and emission of BVOCs in the soil. The potential atmospheric impacts of the compound classes found in this study are currently not well understood. Possible chemical pathways and reactions with other atmospheric compounds have to be studied for better estimates of future impacts on the atmospheric composition and its properties.

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8. Appendix

8.1 Complete tables for soil emissions

Table 2: Average carbon emission rates for all compounds found within samples from control plots in the non-harvested area.

Plot	Name	Compound class	Average emission $\mu g\ C\ m^{-2}\ h^{-1}$
C1	1-Hexanol, 2-ethyl	alcohol	27
	Ethanol, 2-[4-(1,1-dimethylethyl)phenoxy]	alcohol	77
	Decane, 2,2-dimethyl	alkane	134
	Benzene	aromatic	19
	Acetophenone	carbonyl	157
	Nonanal	carbonyl	25
C3	.beta.-Phenylpropiolophenone	carbonyl	79
	Acetophenone	carbonyl	326
	Decane, 2,2-dimethyl	alkane	208
	Decane, 4-methyl	alkane	60
	Dodecane, 2,6,11-trimethyl	alkane	137
	Furan-3-carboxaldehyde, 2-methoxy-2,3-dihydro-	carbonyl	45
	Methanesulfonic anhydride	other	49
	Nonane, 2,6-dimethyl	alkane	85
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	172
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	136
	Phenylmaleic anhydride	carbonyl	114
	Toluene $$ Benzene, methyl	aromatic	55
C5	Phenol, 4-(1,1-dimethylpropyl)	alcohol	124
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	108
	Decane, 2,2-dimethyl	alkane	113
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	434
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	441
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	381
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	223
	Benzene	aromatic	111
	Phenol	aromatic	42
	4H-Pyran-4-one, 2,6-diphenyl	carbonyl	286
	Acetic acid	carbonyl	13
	Acetophenone	carbonyl	234
	Benzoic acid, 2-methoxy-, 2-oxo-2-phenylethyl ester	carbonyl	578
	Ethanone, 2-(acetyloxy)-1-phenyl-	carbonyl	155
	Furan-3-carboxaldehyde, 2-methoxy-2,3-dihydro-	carbonyl	89
	Nonanal	carbonyl	58
	Nonanoic acid	carbonyl	61
	Phenylmaleic anhydride	carbonyl	163
	Methanesulfonic anhydride	other	32
	Methyl octyl ether	other	47

Table 3: Average carbon emission rates for all compounds found within samples from treatment plots in the non-harvested area.

Plot	Name	Compound class	Average emission $\mu g\ C\ m^{-2}\ h^{-1}$
S2	1-Hexanol, 2-ethyl	alcohol	100
	Acetophenone	carbonyl	265
	Decane, 2,2-dimethyl	alkane	340
	Methanesulfonic anhydride	other	52
S4	Phenol, 4-(1,1-dimethylpropyl)	alcohol	127
	Nonane, 5-(2-methylpropyl)	alkane	190
	Acetic acid	carbonyl	46
	Acetophenone	carbonyl	501
	Benzoic acid, 2-methoxy-, 2-oxo-2-phenylethyl ester	carbonyl	189
	Ethanone, 2-(acetyloxy)-1-phenyl-	carbonyl	55
	Nonanal	carbonyl	52
	Phenylmaleic anhydride	carbonyl	202
	.beta.-Pinene	other	69
	Methanesulfonic anhydride	other	31
S6	Decane, 2,2-dimethyl	alkane	112
	Dodecane, 2,6,11-trimethyl	alkane	237
	Dodecane, 2,6,11-trimethyl	alkane	66
	Octane, 6-ethyl-2-methyl	alkane	255
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	347
	Benzene	aromatic	181
	Toluene	aromatic	164
	4H-Pyran-4-one, 2,6-diphenyl	carbonyl	224
	Acetic acid	carbonyl	52
	Acetophenone	carbonyl	542
	Nonanal	carbonyl	69
	Phenylmaleic anhydride	carbonyl	289
	Piperidine, 3-isopropyl	other	69

Table 4: Average carbon emission rates for all compounds found within samples from control plots in the harvested area.

Plot	Name	Compound class	Average emission $\mu g\ C\ m^{-2}\ h^{-1}$
AC1	1-Hexanol, 2-ethyl	alcohol	78
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	183
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	72
	Decane, 2,2-dimethyl	alkane	143
	Dodecane, 2,6,11-trimethyl	alkane	193
	Dodecane, 2,6,11-trimethyl	alkane	122
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	23
	Benzene	aromatic	162
	Toluene	aromatic	196
	Acetophenone	carbonyl	411
	Nonanal	carbonyl	60
	Nonanoic acid	carbonyl	73
	Oxalic acid, ethyl 2-isopropylphenyl ester	carbonyl	94
	Phenylmaleic anhydride	carbonyl	253
AC2	1-Hexanol, 2-ethyl	alcohol	104
	Decane $$ n-Decane $$ n-C10H22 $$ UN 2247 $$	alkane	97
	Decane, 2,2-dimethyl-	alkane	355
	E,Z-4-Ethylidenecyclohexene	alkene	609
	3-Octanone $$ n-Octanone-3	carbonyl	109
	4H-Pyran-4-one, 2,6-diphenyl	carbonyl	282
	Acetophenone	carbonyl	573
	Ethanone, 2-(acetyloxy)-1-phenyl	carbonyl	74
	Nonanal	carbonyl	85
	Phenylmaleic anhydride	carbonyl	222
AC3	1-Hexanol, 2-ethyl	alcohol	76
	3-Hexen-1-ol	alcohol	111
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	142
	Decane, 2,2-dimethyl	alkane	332
	Tetradecane $$ n-Tetradecane $$	alkane	77
	E,Z-4-Ethylidenecyclohexene	alkene	95
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	265
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	229
	Benzene	aromatic	145
	Toluene	aromatic	324
	4H-Pyran-4-one, 2,6-diphenyl	carbonyl	247
	Nonanal	carbonyl	37
	Phenylmaleic anhydride	carbonyl	132

Table 5: Average carbon emission rates for all compounds found within samples from stump plots in the harvested area.

Plot	Name	Compound class	Average emission $\mu g\ C\ m^{-2}\ h^{-1}$
AS1	1-Heptanol, 2-propyl	alcohol	93
	Phenol, 4-(1,1-dimethylpropyl)	alcohol	86
	Decane, 2,2-dimethyl	alkane	174
	Decane, 4-methyl	alkane	102
	Nonane, 2,6-dimethyl	alkane	106
	Octane, 2,3,6,7-tetramethyl	alkane	68
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	231
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	252
	Benzene	aromatic	164
	4H-Pyran-4-one, 2,6-diphenyl	carbonyl	221
	Nonanal	carbonyl	51
	Phenylmaleic anhydride	carbonyl	135
	Phenol, 4,4'-(1,2-diethyl-1,2-ethanediyl)bis-, (R*,S*)	other	122
AS2	Decane, 2,2-dimethyl-	alkane	181
	Dodecane, 2,6,11-trimethyl	alkane	148
	Dodecane, 2,6,11-trimethyl	alkane	70
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	236
	2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic	251
	Benzene	aromatic	160
	4-Cyclopentene-1,3-dione, 2,4-diphenyl-	carbonyl	244
	4H-Pyran-4-one, 2,6-diphenyl	carbonyl	308
	Acetophenone $$ Ethanone, 1-phenyl	carbonyl	418
	Nonanal	carbonyl	64
	Nonanoic acid	carbonyl	65
	Phenylmaleic anhydride	carbonyl	163
	Benzene, 1-(1,3-dimethyl-3-butenyl)-4-methoxy	other	159
AC3	Decane, 2,2-dimethyl	alkane	312
	Dodecane, 2,6,11-trimethyl	alkane	308
	Nonane, 2,6-dimethyl	alkane	51
	Benzene	aromatic	200
	Toluene	aromatic	265
	5(4H)-Isoxazolone, 3-phenyl-4-(phenylmethylene)-, (Z)	carbonyl	203
	Phenylmaleic anhydride	carbonyl	191
	Nonanal	other	65

8.2 Complete tables for branch measurements

Table 6: All compounds found in sample from plot C1 day 1, compounds found in 2 adsorbent tubes is highlighted in yellow.

Branch measurements: plot C1

(yellow=occurs in both tubes)

Day 1: 2013-04-24

Compound name	Compound class
1-Hexanol, 2-ethyl-	alcohol
4-Methyl-2-tert-octylphenol	alcohol
Ethanol, 2-[2-(4-nonylphenoxy)ethoxy]-	alcohol
Hexestrol	alcohol
Phenol, 4-(1,1-dimethylpropyl)-	alcohol
Phenol, 4,4'-(1,2-diethyl-1,2-ethanediyl)bis-, (R*,S*)-	alcohol
Decane, 2,2-dimethyl-	alkane
Dodecane, 2,6,11-trimethyl-	alkane
Eicosane	alkane
Heptadecane	alkane
Nonane, 5-(2-methylpropyl)-	alkane
Nonane, 5-butyl-	alkane
Octanal	alkane
Octane, 6-ethyl-2-methyl-	alkane
Pentadecane	alkane
Tetradecane	alkane
Benzene	aromatic
2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic
1-Adamantanecarboxylic acid, 2-propenyl ester	carbonyl
4H-Pyran-4-one, 2,6-diphenyl-	carbonyl
5(4H)-Isoxazolone, 3-phenyl-4-(phenylmethylene)-, (Z)-	carbonyl
Acetic acid	carbonyl
Acetophenone	carbonyl
Benzoic acid, 2-methoxy-, 2-oxo-2-phenylethyl ester	carbonyl
Decanal	carbonyl
Nonanal	carbonyl
Nonanoic acid	carbonyl
Phenylmaleic anhydride	carbonyl
Methanesulfonic anhydride	other
4-Phenyl-3,4-dihydroisoquinoline	other
Allantoic acid	other
Benzene, 1-(1,3-dimethyl-3-butenyl)-4-methoxy-	other
Spiro-1-(cyclohex-2-ene)-2'-(5'-oxabicyclo[2.1.0]pentane), 1',4',2,6,6-pentamethyl-	other

Table 7: All compounds found in sample from plot C1 day 2, compounds found in 2 adsorbent tubes is highlighted in yellow.

Branch measurements: plot C1

(yellow=occurs in both tubes)

Day 2: 2013-04-25

Compound name	Compound class
1-Hexanol, 2-ethyl-	alcohol
4-Methyl-2-tert-octylphenol	alcohol
Benzestrol	alcohol
Hexestrol	alcohol
Phenol, 4-(1,1-dimethylpropyl)-	alcohol
Decane, 4-methyl-	alkane
Decane, 2,2-dimethyl-	alkane
Dodecane, 2,6,11-trimethyl-	alkane
Eicosane	alkane
Heptadecane	alkane
Nonane, 2,6-dimethyl-	alkane
Tetratetracontane $$ n-Tetratetracontane $$	alkane
Benzene	aromatic
1-Adamantanecarboxylic acid, 2-propenyl ester	carbonyl
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	carbonyl
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	carbonyl
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	carbonyl
Butanoic acid, 2,2-diethyl-	carbonyl
Decanal	carbonyl
Nonanal	carbonyl
Nonanoic acid	carbonyl
Oxalic acid, ethyl 2-isopropylphenyl ester	carbonyl
Phenylmaleic anhydride	carbonyl
Propanoic acid, 2-(benzoylthio)-, ethyl ester	carbonyl
.beta.-Phenylpropiolophenone	other
2-Butene-1,4-dione, 1,4-diphenyl-	other
5(4H)-Isoxazolone, 3-phenyl-4-(phenylmethylene)-, (Z)-	other
Acetophenone	other
Benzene, 1-(1,3-dimethyl-3-butenyl)-4-methoxy-	other
Methyl octyl ether	other
N-(1-Methylethyl)-2-phenyl-4-quinolinamine	other
Propiophenone, 2'-(trimethylsiloxy)-	other
Spiro-1-(cyclohex-2-ene)-2'-(5'-oxabicyclo[2.1.0]pentane), 1',4',2,6,6-pentamethyl-	other

Table 8: All compounds found in sample from plot S2 day 1, compounds found in 2 adsorbent tubes is highlighted in yellow.

Branch measurements: plot S2

(yellow=occurs in both tubes)

Day 1: 2013-04-24

Compound name	Compound class
1-Hexanol, 2-ethyl-	acohol
2-(p-Nitrophenyl)-1,3-propanediol	alcohol
4,4-Dimethyl-cyclohex-2-en-1-ol	alcohol
Benzestrol	alcohol
Ethanol, 2-[2-(4-nonylphenoxy)ethoxy]-	alcohol
Hexestrol	alcohol
Phenol, 4-(1,1-dimethylpropyl)-	alcohol
Phenol, 4,4'-(1,2-diethyl-1,2-ethanediyl)bis-, (R*,S*)-	alcohol
1,3-Dimethyl-(3,7-dimethyloctyl)cyclohexane	alkane
Decane, 3,7-dimethyl-	alkane
Eicosane	alkane
Heptadecane	alkane
Heptadecane	alkane
Nonane, 5-(2-methylpropyl)-	alkane
Nonane, 5-(2-methylpropyl)-	alkane
Nonane, 5-butyl-	alkane
Tetradecane	alkane
Undecane, 2-methyl-	alkane
2,2'-Binaphthalene, 5,5',6,6',7,7',8,8'-octahydro-	aromatic
1-Adamantanecarboxylic acid, 2-propenyl ester	carbonyl
2-Benzoylaminomalonic acid, monomethyl ester	carbonyl
4H-Pyran-4-one, 2,6-diphenyl-	carbonyl
5(4H)-Isoxazolone, 3-phenyl-4-(phenylmethylene)-, (Z)-	carbonyl
Benzaldehyde, 2-hydroxy-	carbonyl
Decanal	carbonyl
Nonanal	carbonyl
Oxalic acid, ethyl 2-isopropylphenyl ester	carbonyl
Phenylmaleic anhydride	carbonyl
Methanesulfonic anhydride	other
.beta.-Phenylpropiolophenone	other
(N-(-2-Acetamido))-2-aminoethanesulfonic acid	other
4-Cyclopentene-1,3-dione, 2,4-diphenyl-	other
Acetophenone	other
Benzene, 1-(1,3-dimethyl-3-butenyl)-4-methoxy-	other
Hydrazine, 1,2-dimethyl-	other
Spiro-1-(cyclohex-2-ene)-2'-(5'-oxabicyclo[2.1.0]pentane), 1',4',2,6,6-pentamethyl-	other
Sulfur dioxide	other

Table 9: All compounds found in sample from plot S2 day 2, compounds found in 2 adsorbent tubes is highlighted in yellow.

Branch measurements: plot S2

(yellow=occurs in both tubes)

Day 2: 2013-04-25

Compound name	Compound class
Phenol, 4-(1,1-dimethylpropyl)-	acohol
2-Octanol	alcohol
3-(Benzyloxymethyl)hex-5-ene-1,2-diol	alcohol
Benzestrol	alcohol
Ethanol, 2-butoxy-	alcohol
2,3-Dimethyldecane	alkane
Cyclohexane, 1,2,4-trimethyl-	alkane
Cycloundecane, (1-methylethyl)-	alkane
Decane, 2,2-dimethyl-	alkane
Dodecane, 2,6,11-trimethyl-	alkane
Heptadecane	alkane
Heptane	alkane
Heptane, 4-methyl-	alkane
Octane, 4-methyl-	alkane
Octane, 6-ethyl-2-methyl-	alkane
2,4-Dimethyl-1-heptene	alkene
Benzene	aromatic
Benzene, 1-ethyl-2,3-dimethyl-	aromatic
Benzene, 1,2,3-trimethyl-	aromatic
Benzene, 1,3-dimethyl-	aromatic
Ethylbenzene	aromatic
p-Xylene	aromatic
Toluene	aromatic
1-Adamantanecarboxylic acid, 2-propenyl ester	carbonyl
2-Isopropyl-5-oxohexanal	carbonyl
Butanoic acid, 2-methyl-, pentyl ester	carbonyl
Furan-3-carboxaldehyde, 2-methoxy-2,3-dihydro-	carbonyl
Hydrazine, ethyl-	carbonyl
Nonanal	carbonyl
Nonane, 2,6-dimethyl-	carbonyl
Nonane, 5-(2-methylpropyl)-	carbonyl
Nonanoic acid	carbonyl
Oxalic acid, ethyl 2-isopropylphenyl ester	carbonyl
Phenylmaleic anhydride	carbonyl
.alpha.-Pinene	other
1H-Cyclopento[c]pyrrole-1,3-dione, hexahydro, 5-isopropylidene-2-methyl-	other
2-Benzylpiperazine	other
3,5-Octanedione, 2,2,4,7-tetramethyl-	other
4-Cyclopentene-1,3-dione, 2,4-diphenyl-	other
6-Hepten-3-one, 5-hydroxy-4-methyl-	other
Acetophenone	other
Benzene, 1-(1,3-dimethyl-3-butenyl)-4-methoxy-	other
D-Limonene	other
Pyridine, 2-nitro-	other

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