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Ecosystem-scale biosphere-atmosphere interactions of a hemiboreal mixed forest stand at Järvelja, Estonia

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Abstract

During two measurement campaigns, from August to September 2008 and 2009, we quantified the major ecosystem fluxes in a hemiboreal forest ecosystem in Järvelja, Estonia. The main aim of this study was to separate the ecosystem flux components and gain insight into the performance of a multi-species multi-layered tree stand. Carbon dioxide and water vapor fluxes were measured using the eddy covariance method above and below the canopy in conjunction with the microclimate. Leaf and soil contributions were quantified separately by cuvette and chamber measurements, including fluxes of carbon dioxide, water vapor, nitrogen oxides, nitrous oxide, methane, ozone, sulfur dioxide, and biogenic volatile organic compounds (isoprene and monoterpenes). The latter have been as well characterized for monoterpenes in detail. Based on measured atmospheric trace gas concentrations, the flux tower site can be characterized as remote and rural with low anthropogenic disturbances. Our results presented here encourage future experimental efforts to be directed towards year round integrated biosphere-atmosphere measurements and development of process-oriented models of forest-atmosphere exchange taking the special case of a multi-layered and multi-species tree stand into account. As climate change likely leads to spatial extension of hemiboreal forest ecosystems a deep understanding of the processes and interactions therein is needed to foster management and mitigation strategies.

Keywords

Eddy-covariance; net ecosystem CO₂ exchange; monoterpene emission; soil trace gas fluxes; leaf photosynthesis

1 Introduction

Forest ecosystems are a major part of the biosphere and control as such land surface-atmosphere interactions. They influence atmospheric composition and climate significantly because of their importance as sources and sinks of trace gases and energy on both, local and regional scales (Höglberg, 2007; Magnani *et al.*, 2007; Misson *et al.*, 2007). To better understand both, how forest ecosystems will respond to changes in climate and how they

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will feed back to the atmosphere, we need to gain quantitative insight into the energy and matter fluxes between the biosphere and atmosphere.

Forests themselves form complex ecosystems, exhibiting a great variability in their composition and structure in horizontal and vertical directions. Major fluxes of carbon dioxide, methane and water vapor are exchanged between soil, plants and the atmosphere at several distinct layers. Those layers are characterized by very different functional properties and they also differ in their flux contributions (Baldocchi, 1997; Misson *et al.*, 2007). Reactive trace gases such as ozone or nitrogen oxides (NO_x) and sulfuric compounds for example represent abiotic stressors to the plants in the forest ecosystem, causing reductions in biomass production (Wallin *et al.*, 1990; Laurence *et al.*, 2001; Manning *et al.*, 2003). Together with biogenic volatile organic compounds (BVOC) that are emitted by many plant species to substantial amounts, these reactive trace gases determine the local, regional and global air quality. Their reaction products play a major role in the formation and growth of aerosol particles, ozone and organic acids (Atkinson and Arey, 2003; Bonn *et al.*, 2008; Hewitt *et al.*, 2009; Mentel *et al.*, 2009).

Hemiboreal forests, located in the transition zone between boreal and temperate forest biomes, are characterized by mixed stands of both coniferous and deciduous tree species, where deciduous species can dominate the initial stages of succession, being replaced by coniferous species at later stages of succession. Especially in mixed stands, the presence of deciduous tree species exerts a great variability on the forest microclimate, canopy shape and density by closing the canopy in spring and opening it up again in autumn when the leaves drop off.

Typically, the presence of multiple leaf layers in the canopy leads to gradients of environmental variables such as light, temperature, wind speed and turbulent mixing. These gradients in turn affect the magnitude of the ecosystem fluxes throughout the canopy. Furthermore, differences in energy availability and mixing properties of the air below and above canopy result in within-canopy variation in concentrations of carbon dioxide and reactive trace gases impacting on the growth and biomass production of the trees differently at different canopy layers.

So far, integrated forest ecosystem scale studies, covering leaf, soil and ecosystem fluxes of reactive and non-reactive trace gases have not yet been conducted for hemiboreal forest ecosystems in Estonia. Our goal was to assess a first overview on fluxes and concentrations of carbon dioxide, water vapor and reactive trace gases under the influence of a hemiboreal forest ecosystem. Specifically the occurrence of a major and suppressed tree layer and consequences thereof on the fluxes and concentrations are of particular interest. Therefore, we present below and above canopy eddy covariance fluxes, leaf level net photosynthesis rates, soil trace gas fluxes, within and above-canopy trace gas concentrations, and BVOC emissions measured during two field campaigns from August to September 2008 and 2009 at the Experimental Forestry Station in Järvselja, Estonia.

2 Materials and Methods

2.1 Site description

The measurements were carried out at a site located in Järvselja Experimental Forest of Estonian University of Life Sciences, located in southeastern Estonia (58° 25' N, 27° 46' E). Järvselja is situated in the hemiboreal forest zone with a moderately cool and moist climate. Mean annual temperature is 4–6 °C. Annual precipitation is 500–750 mm, about 40–80 mm of this total is snow. The length of the growing season (daily air temperature above 5 °C) averages between 170–180 days. A scaffolding tower of 20 m height was used for the flux

measurements above the forest canopy and the cumulative contribution (Horst and Weil, 1992) was 78% at a distance of 200 m upwind of the tower. The measurement cottage to house the sensors for the trace gas analysis and auxiliary equipment was established beside the base of the tower in 2008. For an overview of the location see Figure 1. Both campaigns were covering the time of late summer and in 2008 the measurements started from 6th of August and ended at 27th August while 2009 the measurement campaign started at 12th August and ended at 23rd September. Table 1 gives an overview on the measurements that have been conducted during those times.

To characterize the forest ecosystem structure five circular permanent sample plots with 30 m diameter were established in the vicinity of the flux tower. These were located along a virtual line to the south at distances ranging from 50–200 m which distributes them such that they are located within the footprint area of the tower according to the main wind direction. Within those permanent sample plots all trees with a diameter at breast height (dbh) more than 6 cm were recorded to account for tree number by species. Height measurements were conducted for 20% of trees per plot and as well the age was determined by counting the rings on increment cores for one average tree per major species. The stand characteristics were calculated separately for the dominant (Table 2) and suppressed tree layers. The forest around the flux tower site is secondary growth managed with clear cuts of various sizes (1–5 ha) resulting in quite fine mosaic of stands. The regeneration of this type of stands is usually a combined method with planted coniferous and naturally established hardwoods in mixture. The young stands are treated to reduce the proportion of hardwoods in favor of the economically more valuable coniferous species (both planted and advance regeneration). This type of management which employs a natural regeneration of the stand after replacing disturbances and following population control is the characteristic management according to medium intensity forestry (Metslaid *et al.*, 2007) and a common practice in Estonian forestry. The plots were dominated by Norway spruce (*Picea abies* (L.) Karst.) and the forest site type according to the Estonian classification is the *Oxalis-Myrtillus* (Lõhmus, 2004) type. We found as co-dominant species silver birch (*Betula pendula* Roth.) and black alder (*Alnus glutinosa* L.) and due to the presence of other species such as *Populus tremula* L., *Alnus incana* (L.) Moench, *Tilia cordata* Mill., and *Fraxinus excelsior* L. the stand mixture is fairly complex. Of particularly importance is the presence of a suppressed tree layer (mean height of 6.4 ± 0.6 m over the five plots) which affects turbulent air flows in the stand. The main components of ground vegetation are *Oxalis acetosella* (L.), *Vaccinium myrtillus* (L.), *Calamagrostis arundinacea* (L.), *Convallaria majalis* (L.), and *Melampyrum pratense* (L.). The moss layer consists of several species and partly at humid spots we found *Sphagnum* spp. The mean N concentration in the aboveground litter was 1.53 ± 0.10 %, and the mean C concentration 48.65 ± 0.72 %.

As the site is located in the Lake Peipsi depression (Arold, 2005) and bordered by wetland massifs the soils of the site are strongly groundwater influenced, and employed a high groundwater table due to the vicinity to Lake Peipsi and the low altitudes of forest grounds. The soil around the flux tower showed a thick raw humus horizon with an average thickness of 24 cm, and the underlying sediment material was characterized by blue gleyic spots. The soil type was Haplic Gleysol (eutric) (WRB, 2006). Due to high clay content of the soil, the soil hydraulic conductivity is low; implying that the soils will stay wet longer times after snowmelt in spring. If affected by drought, even heavy rainfalls poorly penetrate into the soil and much of the precipitation is lost as runoff (Niinemets *et al.*, 1999). To obtain data representing the area at larger scale, additional 4 sampling plots were established to the east direction of the flux tower. The soil types were Haplic Podsol and Haplic Stagnosol (WRB, 2006) and the forest site type *Oxalis-Myrtillus*.

2.2 Eddy covariance system

Eddy covariance (Baldocchi *et al.*, 1988; Aubinet *et al.*, 2000) CO₂, H₂O and energy flux measurements were conducted above the forest canopy on a 20 m tall tower (referred to as overstory flux measurements) and below the canopy at 1.5 m height above the ground (referred to as understory flux measurements). The three wind components and the speed of sound were measured by three-dimensional sonic anemometers (2008: CSAT3, Campbell Scientific, Logan, UT, USA; 2009: Metek USA-1, Metek GmbH, Elmshorn, Germany), CO₂ and H₂O mole densities/fractions in 2008 (over- and understory) by an open-path infrared gas analyzer (IRGA) (Li-7500) and in 2009 (over- and understory, but not at the same time) by a closed-path IRGA (Li-7000, both Li-Cor, Lincoln, NE, USA). In the closed-path system air was sucked from the inlet, mounted 0.1 m below the centre of the sensor volume of the sonic anemometer, through a 35 m Teflon tube of 0.008 m inner diameter through a filter (Acro 50, Gelman, Ann Arbor, MI, USA) to the closed-path IRGA deployed in a measurement cottage at the base of the tower at a flow rate of 15.2 L min⁻¹ (KNF Laboport, KNF GmbH Freiburg, Germany). The closed-path IRGA was operated in the absolute mode, flushing the reference cell with dry N₂ from a gas cylinder at 0.1 L min⁻¹. The open-path IRGAs were mounted 0.2 m below the centre of the sensor volume of the sonic anemometer in a horizontal position. Sonic anemometers, the intake of the closed-path inlet tube, and the open-path IRGAs were oriented into the main wind direction to minimize flow distortion and longitudinal sensor separation to the sonic anemometers. In 2008, data from the sonic anemometers and the open-path IRGAs were acquired at 20 Hz and transferred via the SDM protocol to data loggers (CR3000, Campbell Scientific, Logan, UT, USA). In 2009, the data from the sonic anemometer was transferred by serial protocol with a frequency of 10 Hz to a computer and closed path IRGA data were transferred as analog signals with the same frequency and captured by a datalogger (Pico ADC20, Pico Technology, St Neots, UK) connected to the same computer. Half-hourly average eddy fluxes were calculated from quality controlled flux data as the covariance between the turbulent departures from the mean of the vertical wind speed and the CO₂ and H₂O mixing ratios as described in detail in (Haslwanter *et al.*, 2009) and will thus not be repeated here. Net CO₂ and H₂O fluxes were calculated as the sum of the corrected vertical eddy term and the storage fluxes, the latter being estimated from the time-rate-of-change in scalar density at the respective reference height. Negative fluxes represent transport from the atmosphere towards the surface, positive ones the reverse.

2.3 Leaf level photosynthesis

We used a portable infrared gas analyzer (IRGA) cuvette system (Walz, GFS3000, Walz GmbH, Effeltrich, Germany) for leaf level photosynthesis measurements. Broad leaved species were measured using a clamping cuvette with parameter settings: flow rate of 1 L min⁻¹, 380 μmol mol⁻¹ CO₂, 75–80% humidity and 25 °C. Conifers (*Picea abies*) were measured using the conifer chamber (provided by Walz for GFS3000), where small twigs can be fitted in. To avoid clamping stress, twigs were selected and prepared 3 days before the measurements by removing a portion of the needles and wrapping the site of needle removal airtight in Teflon tape. Trees in the top part of the canopy (*P. abies* and *B. pendula*) were accessed from the scaffoldings located at the measurement site (2 towers of 16 and 20 m height) and were measured at a height of 16 and 18 m (maximal canopy height about 20 m). To represent sun and shade conditions, we choose leaves that are exposed to south, west and north directions. Leaves of trees in the understory (*P. abies*, *Tilia cordata*, *B. pendula* and *B. pubescens*) were measured at a height between 0.1 and 1.5 m and are supposed to be all under shade condition during summer time where the canopy is densely closed by the leaves of the deciduous trees. Leaves of trees in forest gaps were measured at heights between 0.4 and 1.5 m and we choose mostly sun exposed leaves to assess if there is difference to the sun exposed leaves in the top canopy.

2.4 Trace gas analyses

The trace gas analyzers have been installed within the measurement cottage. We took their inlet airstreams from above canopy by a Teflon tube that reached to the top of the tower and a bypass inlet at 2 m height to allow sampling also below canopy. The ozone was detected using a Thermo (Model 49i) ozone analyzer and NO/NO₂/NO_x were detected with a Thermo (Model 42i), both Thermo Scientific, Waltham, MA, USA. During the campaign in 2008 we had additionally an air quality measurement transportable laboratory, equipped with instruments for NO_x (Horiba APNA-370), SO₂ (Horiba APSA-370) both from Horiba Jobin Yvon GmbH, Unterhaching, Germany and particulate matter (PM₁, PM_{2.5} and PM₁₀, Grimm EDM107, Grimm Aerosol Technik GmbH & Co. KG, Ainring, Germany) sensors, placed on the side of a small forest road 100 m west of the flux tower.

2.5 Manual soil chamber measurements of CH₄, N₂O and CO₂ soil fluxes

One plot was selected near to the understory eddy covariance system and two circular stainless steel collars were inserted about 6 cm into the top soil. The placement of the collars took place in the beginning of the campaign in 2008 and measurements conducted refer to the campaign in 2009 (Table 1). The effective chamber volume (23.8 L) of the cylindrical stainless steel chambers was calculated from the average height from the soil surface to the top of the chamber. The chamber atmosphere was mixed by a small built-in fan to prevent the formation of gradients (Frenzel and Karofeld, 2000) and sealed air tight with water. Pre-installed thermocouple sensors connected to a thermocouple reader (Comark KM330) registered the temperatures in soil (−0.1 m, −0.15 m, −0.25 m of depth), inside the chambers, and in the atmospheric air (0 m, 0.5 m, 2 m of height).

Samples were drawn into 100 mL gas-tight syringes from the top of the chamber via a capillary (diameter 2 mm). 30 seconds before each sampling, the capillary air was mixed for four times using the syringe. The samples were injected into 7 mL non-evacuated vials (Labco Exetainer 768W). The vials were flushed with 80 mL of sample air and over-pressurized with 20 mL of sample air. The chambers were operated in closed static mode and closed for a maximum of 30 min. Six to ten samples were collected during this time. These were stored in darkness at −18 °C and analyzed within two months after sampling by gas chromatography with a GC-FID/ECD (model HP 6890) and a GC-TCD (model HP 7890) as described by Syväsalö *et al.* (2004). All flux rates were calculated from the exponential change in gas concentrations in the chamber and temperature corrected (Appendix 1). Air temperature inside the chambers was taken each time a sampling was conducted.

2.6 Automatic chamber measurements of CO₂ soil flux

Within the five circular sampling plots and at four reference locations outside of the sample plots, two stainless steel collars were placed in each, 7 m north and 7 m south from the plot center or at similar distance if outside a plot. The placement of the collars took place in the beginning of the measurement campaign 2009. In total, 18 collars of the size of 230 mm in diameter and 80 mm in height were installed and inserted about 2–3 cm into the top soil in order to eliminate diffusion through the soil away from the measurement area.

Soil respiration was measured using an automatic CO₂ Exchange System ACE (ADC BioScientific Limited, UK) equipped with a soil chamber, an infra-red gas analyzer (IRGA), a sensor for detecting photosynthetic active radiation, a soil moisture sensor (SM200, Delta-T Devices Ltd, Cambridge, England) and two temperature sensors. The soil chamber was equipped with a small fan for mixing the air. Volume of the lid of the soil chamber was 2.6 L.

Upon measurement the lid was automatically placed tightly on the collar. Tight closing of the soil chamber was guaranteed by a rubber ring-seal in the contact surface between the rims of the lower part of the chamber (collar inserted under a special rim of the frame of the station) and its upper (guided) counterpart. The height of the collars from the soil surface was measured at every occasion. The ACE station was operated in closed mode with zero option. In this mode the increase of CO₂ in the chamber from soil activity is measured. The zero measurement is made by passing CO₂-free air through the chamber. In that mode, the chamber is operated as a closed static chamber (Pumpanen *et al.*, 2004) and details about the data handling are given in Appendix 1. Continuous measurements were conducted in one collar using the interval of 15 minutes between each measurement cycle of 5 minutes. Single repeated measurements were conducted upon the time of collar installments, during the main campaign, and later in October and November 2009. Two to ten sequential measurements were conducted. Simultaneously with the soil flux measurements, soil temperature and moisture were measured at the depth of 5 cm, and air temperature on the ground level. Litter samples were collected in each plot. To distinguish the share of respiration originated from the fallen litter and from the soil, upon measurement the litter was removed in one collar (always the southern one) of each plot. The respiration from the decomposition of litter would result from the difference between the collars. The litter was taken to the lab, dry weight measured and analyzed for C and N contents.

2.7 BVOC sampling and analyses

We measured volatiles organic compounds (VOC) emitted from leaves in parallel with leaf physiological parameters by diverting a part of the Walz leaf and conifer cuvette outflow. The VOCs were adsorbed onto multibed stainless steel cartridges (10.5 cm length, 3 cm inner diameter, Supelco, Bellefonte, USA) filled with Carbotrap C 20/40 mesh (0.2 g), Carbopack C 40/60 mesh (0.1 g) and Carbotrap X 20/40 mesh (0.1 g) adsorbents (Supelco, Bellefonte, USA) at a flow rate of 250 ml min⁻¹ for 10 min. (altogether 2.5 L air). Background air samples were collected from the empty chamber before and after the measurements. Adsorbent cartridges were analyzed with a combined Shimadzu TD20 automated cartridge desorber and Shimadzu QP2010 plus GC-MS instrument (Shimadzu Corporation, Kyoto, Japan). The TD20 parameters, GC-MS conditions and compounds identification were presented in detail in (Copolovici *et al.*, 2009; Toome *et al.*, 2010). From the manually operated soil chambers VOC samples were taken analogously as from the leaves using the same flow rates of 250 mL min⁻¹ but sampling for 20 minutes. After sampling a background air sample, the chamber was closed for a period of 30 min and then the sample was taken onto the steel cartridge. To avoid underpressure in the water-sealed chamber, we allowed background air to enter via a small Teflon tube to the bottom of the chamber during sampling using a valve sealing that allows to open an inlet while sampling. That led to a change in the operation mode from a closed static chamber to an open dynamic chamber. The data handling is described in detail in Appendix 1. Subsequent GC-MS analysis of the VOC soil emissions have been conducted as described above.

3 Results and Discussion

3.1 Net ecosystem CO₂ exchange

The net ecosystem CO₂ exchange (NEE) above the canopy exhibited a clear diurnal cycle with net uptake during daytime and net loss of CO₂ during nighttime (Fig. 2, Table 3). These fluxes fall in between those observed for European deciduous (Granier *et al.*, 2003) and coniferous (Bernhofer *et al.*, 2003; Ceulemans *et al.*, 2003) forest ecosystems and likely reflect the mixed nature of the stand. In contrast, the NEE measured in the understory exhibited hardly any diurnal cycle and was positive for almost all of the time (Fig. 2, Table 3). Consistent positive daytime understory NEE for summertime conditions were also

reported by Misson *et al.* (2007) for 8 out of 11 study sites. The contribution of the storage flux to the NEE was negligible in the understory (Misson *et al.*, 2007), while an appreciable negative and positive storage flux (Fig. 2) in the morning and evening, respectively, was detected with the overstory system indicative of venting and accumulation of canopy air, respectively (Aubinet *et al.*, 2000). Flux divergence was observed during nighttime, when the respiration measured above the canopy was lower than in the understory (Fig. 2). This may reflect differences in the footprint between the over- and understory eddy covariance systems which generally differ greatly in extent (Baldocchi, 1997) and in addition sometimes differed in direction due to occasional decoupling of flow directions above and below the canopy (data not shown). The differences in nighttime over- and understory respiration may also be indicative of advection (Aubinet *et al.*, 2000), part of the CO₂ being respired by the soil and understory vegetation potentially being advected (horizontally and/or vertically). In order to confirm the latter hypothesis, however, detailed measurements of within-canopy horizontal and vertical gradients in CO₂ concentration and wind speed would be required (Feigenwinter *et al.*, 2008).

3.2 Reactive trace gases

3.2.1 Ozone and nitrogen oxides—The formation of tropospheric ozone is bound to the availability of sunlight and NO_x which provide the energy and the primary source of oxygen atoms, respectively. VOCs act as catalysts of this reaction (Atkinson, 2000; Atkinson and Arey, 2003). As seen in Fig. 3, ozone varied in a clear diurnal cycle above and below the canopy. Lowest values were found under nighttime conditions, while the highest values occurred during daytime. The peak in ozone concentrations above canopy was broader and somewhat skewed towards the afternoon, while below canopy ozone concentrations peaked around noon and reached nighttime levels about one hour earlier. Typical daily variations in ozone concentration above forest canopies have been reported to span the range from 10–70 nmol mol⁻¹ (Mikkelsen *et al.*, 2004), which is well represented by our findings as well.

NO and NO₂ concentrations showed as well diurnal cycles where NO ranged between 0.05–0.3 nmol mol⁻¹ and NO₂ between 0.2–1.5 nmol mol⁻¹ with lower values during nighttime. A slight canopy gradient with smaller values below was found. Nitrogen oxides, as originated from burning processes and soil efflux, were found to correlate with wind direction (Fig. 4). Westerly winds caused higher NO and NO₂ concentrations, while smallest concentrations were associated with easterly winds. Cities and settlements as well as an access road to the region are located to the West of the measurement station. Ozone concentrations followed that same pattern and were highest on days with West to South-West winds and lowest with winds from the East (Fig. 4).

Ozone uptake to forest canopies has been reported for temperate and boreal ecosystems (Mikkelsen *et al.*, 2004; Rannik *et al.*, 2009). That uptake is mostly reported to occur through stomata, surface deposition and also by reaction with emitted BVOC. While the difference in the ozone concentrations above and below the canopy are suggesting that there should be a net ozone uptake by the canopy the question remains to what extend the different environmental conditions above and below the canopy influence that flux.

3.2.2 Particulate matter and anthropogenic influences—In order to assess possible anthropogenic influences on the location of the flux tower we compared the measurements of the air quality measurement bus and the measurements within and above the canopy. Table 4 summarizes the results. If compared to the reported Estonian yearly background values (Pajuste *et al.*, 2004), the situation found in Järvelja is about 2–3 times lower. Sulfur

dioxide (SO₂) is predominantly of anthropogenic origin and plays a role in acid rain formation, which has a negative impact on forest ecosystems and tree growth.

The values found indicate, that the measurement site is not much influenced by SO₂ emissions. The same picture was found for NO_x. Especially the low NO values, direct tracers of nearby combustion, support the conclusion that Järvselja is located in an area with low human impact on air pollution.

Particulate matter concentrations (PM₁, PM_{2.5} and PM₁₀) also remained far below the national threshold (50 µg m⁻³, averaged over 24 hours for a period of 20 years) and characterize the site as between “remote” and “non-urban continental” (Seinfeld and Pandis, 2006). In conclusion, the measurement site at the flux tower in Järvselja can be graded as an atmospherically clean and low anthropogenic impacted site.

3.2.3 BVOC emissions—To assess the state of the atmosphere and the flux of carbon within the forest ecosystem at Järvselja, we also conducted measurements of leaf level and soil BVOC fluxes. These were focused on isoprene and monoterpenes. Largest monoterpene emission rates (sum of monoterpenes, 46 ± 9 nmol m⁻² s⁻¹) were found from *Betula* with α-pinene as the major monoterpene emitted. *P. abies* emitted a total monoterpene flux of 33 ± 11 nmol m⁻² s⁻¹, where Δ³-carene was the main contributing monoterpene followed by α-pinene and α-phellandrene (Fig. 5). The isoprene fluxes for *B. pendula* (1.2 ± 0.6 nmol m⁻² s⁻¹) and *P. abies* (1.02 ± 0.36 nmol m⁻² s⁻¹) showed no substantial differences. Compared to the total monoterpene emissions, isoprene emissions were about 45 times smaller.

Total soil monoterpene fluxes were found to be 40 times smaller (1.22 ± 0.16 nmol m⁻² s⁻¹) than leaf emission rates. As isoprene is synthesized from recently fixed carbon by plants, the very small flux from the soil (0.05 ± 0.01 nmol m⁻² s⁻¹) may be caused by the enclosed small plants and mosses which are known to emit isoprene as well (Tiiva *et al.*, 2009). Another possibility is that soil bacteria are also involved in the isoprene fluxes - release and consumption of isoprene by soil bacteria has been reported (Cleveland and Yavitt, 1998; Scholler *et al.*, 2002). The composition of monoterpene soil fluxes (Fig. 5) shows some interesting patterns as compared to the monoterpene emissions from the leaves of the species mainly contributing to the leaf litter in the soil O-horizon. We found, that α-phellandrene is lacking completely and that the main contributing monoterpenes at the leaf level, α-pinene and Δ³-carene, are less abundant in the soil monoterpene fluxes. Instead, α-thujene and limonene, which have been found less abundant at the leaf level, are main contributors to the soil monoterpene fluxes. It is known, that monoterpene emission patterns are changing with the seasons and that stored monoterpenes, i.e. from resin ducts, exhibit different patterns than emission from newly synthesized monoterpenes (Hakola *et al.*, 2003; Vuorinen *et al.*, 2005; Holzke *et al.*, 2006; Räisänen *et al.*, 2008). Our result suggest, that α-thujene and limonene may be stored to greater amounts in the leaf tissues related to their synthesis when still attached to the branches and that α-phellandrene seems not to be stored in substantial amounts. Given the fact, that deciduous leaves mostly do not build specialized storage organs we can speculate that soil monoterpene emissions are caused by the coniferous litter. The contribution of the different litter parts, needles, leaves, cones etc. to the terpene fluxes remains to be investigated for our measurement site. As it is known that beside the leaf litter soil fungi and roots also emit different volatiles (Leff and Fierer, 2008) their contribution to the total emitted soil fluxes presented here have to be assessed in future.

3.3 Leaf level photosynthesis

Betula pendula is the most abundant, deciduous tree species present in both over- and understory of the experimental site. Leaf level net photosynthetic rates showed a clear dependency on and adaptation to light availability. *Betula* leaves at the top of the canopy

(about 16–18 m) showed highest net assimilation rates when exposed to light fluxes of 1000 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$. Leaves that exposed to south and west directions were found to exhibit twice as high net assimilation ($11.6 \pm 0.3 \mu\text{mol m}^{-2} \text{s}^{-1}$) as compared to north exposed leaves ($5.7 \pm 0.4 \mu\text{mol m}^{-2} \text{s}^{-1}$; Fig. 6). To simulate also shade conditions, the same leaves were measured with a light flux of 200 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$. In this case, lowest net assimilation rates were measured in west exposed ($3.5 \pm 0.6 \mu\text{mol m}^{-2} \text{s}^{-1}$) and highest in north exposed ($5.5 \pm 0.3 \mu\text{mol m}^{-2} \text{s}^{-1}$) leaves (Fig. 6). Photosynthetic photon flux density (PPFD) in the top of the canopy was between 130–1230 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ for south- and west-exposed leaves and between 261–77 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ for north-exposed leaves. Interestingly, the photosynthesis of north-exposed *Betula* leaves in the top of the canopy seemed to be light-saturated already at a rather low photon flux density of 200 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$. Increasing light to 1000 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ increased photosynthesis only marginally, while the photosynthesis rate of west- and south-exposed leaves was about doubled (Lichtenthaler *et al.*, 2007). Adaptations of the photosynthetic apparatus to light intensities are explaining that behavior (Niinemets *et al.*, 1998, 1999, 2004).

P. abies is the most abundant tree species in the overstory of the measuring site. Net assimilation rates measured at 16–18 m height and a light flux of 1000 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ were $7.9 \pm 1 \mu\text{mol m}^{-2} \text{s}^{-1}$. Although *P. abies* net assimilation rate is lower than that of *B. pendula* (as was to be expected), it is still appreciable and in the normal to high range (Wallin *et al.*, 1990; Marek *et al.*, 1997). The expositions of the branches measured have been West, South and North.

Net assimilation rates of *B. pendula* leaves in the understory (apparent light was between 6 and 69 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$) were about 2 $\mu\text{mol m}^{-2} \text{s}^{-1}$ when measured with a light flux of 200 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ (Table 5) and therefore much lower than overstory leaves measured under the same conditions (Fig. 6). For *B. pendula*, a light-requiring species, only small seedlings were found in the understory. Another typical pattern in forest ecosystems are gaps due to fallen or removed trees. We measured also in such gap situations. Light conditions there were much improved compared with the understory (apparent light was between 7 and 824 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$) and due to that we measured again with 1000 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$. The net assimilation rate of *Betula* leaves were very variable, ranging between 5.6 to 9.6 $\mu\text{mol m}^{-2} \text{s}^{-1}$, at average about 8 $\mu\text{mol m}^{-2} \text{s}^{-1}$, almost as high as in the overstory (Table 6). Of the species measured in the understory (3 species shown in Table 6), *Tilia* had higher net assimilation rates than the two *Betula* species. The gap offered a niche for those species, which were not found in the understory, like *Quercus robur* and *Populus tremula*. In general, the canopy discriminates the irradiative energy input strongly. In particular, the photosynthetic active radiation (PAR) input that is absorbed more strongly than near infra-red light can be even less than 1–2% of above-canopy value in these types of forests (Niinemets *et al.*, 1998).

3.4 Soil chambers

3.4.1 Soil CO₂ efflux—Manual chamber measurements resulted in a mean soil CO₂ efflux of $3.54 \pm 0.62 \mu\text{mol m}^{-2} \text{s}^{-1}$. Compared to boreal soil fluxes ranging between 2–6 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in summer (Rayment and Jarvis, 2000; Kolari *et al.*, 2006; Kolari *et al.*, 2009) and cool temperate forest ecosystem soil fluxes ranging between 2–8 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (Lee *et al.*, 2002; Yuste *et al.*, 2005) depending on the species contribution the values found in Järvselja fit into that picture. The average air temperature recorded on the soil surface was $17.7 \pm 1.3 ^\circ\text{C}$ and the average soil temperature at –0.1 m was $13.6 \pm 0.5 ^\circ\text{C}$. Mean soil CO₂ efflux was $4.29 \pm 0.11 \mu\text{mol m}^{-2} \text{s}^{-1}$ over the continuous measurement period of 72 hours with the automatic chamber system. Average volumetric soil moisture was 51.36% (max 56.97%, min 45.71%), the average air temperature $10.2 \pm 0.2 ^\circ\text{C}$, and the average soil temperature

11.7 ± 0.1 °C during the days of measurements. The average daytime temperature from 09-18 h was very stable at 11.9 ± 0.3 °C. Results of the additional single measurements are presented in Table 7. In both cases, manual and automatic chamber measurements, we found rather stable emissions over the course of the day which is in accordance with the stable soil temperature during the measurements. As the chambers have been operated under shade conditions in the understory, the average temperature change during measurements have been 0.9 ± 0.5 °C. The data, obtained on both plots, give hints about the plasticity which occurs through changes in soil type and canopy structure and may be reflected by substantial changes in soil CO₂ efflux. Even though soil respiration is known to correlate positive with soil temperature which is influenced by soil moisture and PAR (Lloyd and Taylor, 1994; Ruehr and Buchmann, 2010), we found only weak correlations which is mainly caused by the limited number of the measurements during the campaign in 2009.

Comparison of the two methods of continuous measurement cycles (Fig. 7) revealed that greater values of CO₂ efflux were recorded with the automatic chamber system. Even though, the mean daytime air temperature was by 5.8 °C lower and there was one week difference between the first conducted manual chamber measurements. Given the temperature dependency of soil respiration, this is a contradictory result, which may be reconciled based on differences in the sampling and analysis techniques employed. Among the technical explanations, site heterogeneity, different depth or the time of collar installation might have played a role as well.

Forest floor soil respiration measured may represent more than 75% of total ecosystem respiration (Solondz *et al.*, 2008). Compared with the results of the understory eddy covariance fluxes as given by Table 3 our chamber fluxes exceeded the daytime eddy fluxes as measured in 2 m height by about 20% for the manual chamber measurements and on the whole day basis about 19% as compared to the mean fluxes from the automatic chamber over the 24h period. Given the differences in footprint between both methods (Baldocchi, 1997), the random and systematic uncertainties associated with each method (Hollinger and Richardson, 2005), and finally the differing time frames during which these measurements were made, we consider these results as very encouraging.

3.4.2 CH₄ and N₂O soil fluxes—Fluxes of methane and nitrous oxide were measured using the manual chamber system. We found negative methane fluxes during the campaign in 2009, which indicates a possible net consumption of CH₄ in soil (Chan and Parkin, 2001; Mori *et al.*, 2008) which was also reported for boreal forest ecosystems (Whalen *et al.*, 1992) or a possible atmospheric reaction of methane with hydroxyl radicals given sufficient high levels of NO_x (Wuebbles and Hayhoe, 2002) enclosed into the chamber. It is further known, that dry soils are sinks and wet soils act as sources for atmospheric methane as well as that tree species affect the source and sink properties of forest soils (Saari *et al.*, 1998; Borken and Beese, 2006). The daytime average CH₄ flux was -0.69 ± 0.36 nmol m⁻² s⁻¹. If compared to boreal soil methane fluxes in Hyytiälä, Finland (61° 84' N, 24° 29' E) of about -1.4 nmol m⁻² s⁻¹ (Pihlatie *et al.*, 2009a) we found a slightly lower sink flux. The inverse relationship between the CO₂ and CH₄ fluxes may support the idea of methane consumption by methanotrophic bacteria in the soil as a reason for the flux.

We found daytime nitrous oxide emissions that averaged 0.18 ± 0.09 nmol m⁻² s⁻¹ which are about the same compared to soil N₂O fluxes at Hyytiälä of 0.15 nmol m⁻² s⁻¹ (Pihlatie *et al.*, 2009b). N₂O is mainly produced by denitrification process in soils. In deeper layers, given wet and anaerobic conditions denitrification may occur frequently (Ball *et al.*, 1999; Yamulki and Jarvis, 2002). In our groundwater influenced study site, the soil temperature should positively correlate with the N₂O efflux (Schindlbacher *et al.*, 2004). Due to the limited number of measurements we observed only a weak positive correlation.

4. Conclusions and outlook

One might argue, and rightfully so, that the two measurement campaigns conducted at the Järvelja Experimental Forest station during the summers 2008 and 2009 only allowed us to take a snapshot of the multitude of trace gas fluxes which occur on a continuous basis between this forest and the atmosphere. While this is likely to be correct, we strongly believe that the two measurement campaigns already unearthed a number of encouraging results which may serve as building blocks upon which we aim to continue research at this site. We have characterized the structure and composition of the forest and the soil, we conducted above- and below-canopy eddy covariance CO₂ and H₂O flux measurements, quantified leaf photosynthesis, transpiration and isoprene/monoterpene emissions, soil CO₂, methane, nitrous oxide and monoterpene fluxes, as well as the above- and within-canopy concentrations of several reactive trace gases and particulate matter. Our major findings are that (i) in terms of the magnitude of the CO₂ exchange this mixed forest ranged in between boreal coniferous and temperate broad-leaved forests, that (ii) understory eddy covariance CO₂ fluxes and manual/automated soil respiration rates agreed reasonably, (iii) leaf and soil monoterpene emissions had contrasting signatures, (iv) soils were sinks for methane and sources for nitrous oxides, and (v) from an air quality point of view the study site was characterized as remote/rural. Future experimental efforts will be directed towards year-round flux measurements of a larger number of trace gases, of which some sources/sinks, such as of methane, nitrous oxide, isoprene and monoterpenes, were already characterized at the leaf and soil level. In a next step, these measurements both at the ecosystem and leaf/soil scale should be assimilated into process-oriented models of forest-atmosphere exchange in order to test our quantitative ability of simulating these processes. Combining these two lines of information, experimental field data and simulation analysis, will be critical in order to finally assess the role this and similar forests in this region are playing in modulating climate and how sensitive these ecosystems are to likely future climate.

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Appendix 1

We describe the concentration change in time by the flux from soil into a chamber by an exponential relation (Pedersen *et al.*, 2001; Pumpanen *et al.*, 2001; Pumpanen *et al.*, 2004):

$$C(t) = C_0 e^{kt} \quad (1)$$

where C_0 denotes the background concentration that is enclosed inside the chamber at the beginning of the closing period. In case of the manual chamber, the sampling procedure led to a series of data points $d = \{t_0, C_0, \dots, t_n, C_n\}$, which have been used to estimate the flux rate k by non-linear least-square fit of equation 1 to d . To calculate the molar flow F_c , we apply:

$$F_c = C(t_n) \frac{V}{A} \cdot \frac{1}{V_m} \quad (2)$$

with a given chamber volume V in m^3 , the covered area A in m^2 , and the molar volume V_m of 22.4 L mol^{-1} . We further assumed that the pressure stayed constant throughout the sampling period and corrected for the temperature changes by multiplying equation 2 with:

$$\xi(T) = \frac{T_0 - T}{T_0} \quad (3)$$

where T_0 is 273.15 K and T the temperature as measured from the chamber sensor in Kelvin. We conducted also the BVOC sampling by usage of the manual chamber system. In this case, it is only possible to apply a data set of two measurement points $d = \{t_0, C_0; t_1, C_1\}$, with the sample at t_0 given the background concentration and at t_1 the sample which is sucked onto the Carbotrap cartridge. Rearranging equation 1 and application of the logarithm led to:

$$\log(C(t_1) - C(t_0)) = k \quad (4)$$

and we applied again equations 1, 2 and 3 to achieve the temperature corrected molar flow of BVOC emitted from the top soil layer including leaf litter at the start of the BVOC sampling procedure. While the amounts of aliquot we took from the manual chambers volume (23 L) with the syringes are neglectable if compared to the total chamber volume that is not true in case of the BVOC measurements where we took an aliquot of five liters per sample over a period of 20 minutes. To prevent underpressure we let stream in background air to the bottom of the chamber with a small tube while sampling and by that changing instantaneously the concentration within the chamber. That resembles the open flow chamber system as described by Pumpanen *et al.* (2001) and can be described by a budget function assumed that there were no leak flows and the sample was taken with a flow q_1 :

$$\frac{dC_i}{dt} = Q + q_1 (C_0 - C_i) \quad (5)$$

where Q denoted the flow from the soil into the chamber while sampling and C_0 , the background air replacing the air drawn into the cartridge. Integration of equation 5 and rearranging with respect to Q leads to a timely description of the flux added while sampling:

$$Q(t) = q_1 (-C_0 + C_i - e^{-q_1 t}) \quad (6)$$

With that, we could account for the portion of soil efflux that have been generated during the 20 minutes sampling period and have been added to chamber.

The automatic chamber system measured the fluxes directly relative to a CO_2 free air standard and resembles in its operation therefore also a closed static system (Pumpanen *et al.*, 2004). The software of the automatic chamber system used the method as given by Pedersen *et al.* (2001) to calculate the chamber flows. Measurements that did not reach a stable fluxes have been discarded by the system.

References

Arold, I. Eesti maastikud (Estonian landscapes). Tartu Ülikooli Kirjastus; Tartu: 2005.

- Atkinson R. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*. 2000; 34:2063–2101.
- Atkinson R, Arey J. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmospheric Environment*. 2003; 37:S197–S219.
- Aubinet M, Grelle A, Ibrom A, Rannik Ü, Moncrieff J, Foken T, Kowalski AS, Martin PH, Berbigier P, Bernhofer C, Clement R, Elbers J, Granier A, Grünwald T, Morgenstern K, Pilegaard K, Rebmann C, Snijders W, Valentini R, Vesala T. Estimates of the annual net carbon and water exchange of European forests: the EUROFLUX methodology. *Adv. Ecol. Res.* 2000; 30:113–175.
- Baldocchi DD. Flux footprints under forest canopies. *Boundary-Layer Meteorology*. 1997; 85:273–292.
- Baldocchi DD, Hicks BB, Meyers TP. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. *Ecology*. 1988; 69:1331–1340.
- Ball BC, Scott A, Parker JP. Field N₂O, CO₂ and CH₄ fluxes in relation to tillage, compaction and soil quality in Scotland. *Soil Till. Res.* 1999; 53:29–39.
- Bernhofer, C.; Aubinet, M.; Clement, R.; Grelle, A.; Grünwald, T.; Ibrom, A.; Jarvis, P.; Rebmann, C.; Schulze, E-D.; Tenhunen, JD. Spruce forests (Norway and Sitka Spruce): Carbon and water fluxes, balances, ecological and ecophysiological determinants. In: Valentini, R., editor. *Fluxes of carbon, water and energy of European forests*, Ecological Studies. Vol. 163. Springer Verlag; Berlin: 2003. p. 99–123.
- Bonn, B.; Boy, M.; Maso, MD.; Hakola, H.; Hirsikko, A.; Kulmala, M.; Kurtén, T.; Laakso, L.; Mäkelä, J.; Riipinen, I.; Rannik, Ü.; Sihto, S-L.; Ruuskanen, TM. Nucleation and Atmospheric Aerosols. 2008. Biogenic Sesquiterpenes and Atmospheric New Particle Formation: A Boreal Forest Site Investigation; p. 344–349.
- Borken W, Beese F. Methane and nitrous oxide fluxes of soils in pure and mixed stands of European beech and Norway spruce. *European Journal of Soil Science*. 2006; 57:617–625.
- Ceulemans, R.; Kowalski, AS.; Berbigier, P.; Dolman, H.; Grelle, A.; Janssens, IA.; Lindroth, A.; Moors, E.; Rannik, Ü.; Vesala, T. Coniferous forests (Scots and Maritime Pine): Carbon and water fluxes, balances, ecological and ecophysiological determinants. In: Valentini, R., editor. *Fluxes of carbon, water and energy of European forests*, Ecological Studies. Vol. 163. Springer Verlag; Berlin: 2003. p. 71–97.
- Chan ASK, Parkin TB. Effect of Land Use on Methane Flux from Soil. *J. Environ. Qual.* 2001; 30:786–797. [PubMed: 11401268]
- Cleveland CC, Yavitt JB. Microbial consumption of atmospheric isoprene in a temperate forest soil. *Applied and Environmental Microbiology*. 1998; 64:172–177. [PubMed: 16349477]
- Copolovici L, Kännaste A, Niinemets Ü. Gas Chromatography-mass spectrometry method for determination of monoterpene and sesquiterpene emissions from stressed plants. *Studia Universitatis Babes-Bolyai, Chemia*. 2009; 54:329–339.
- Feigenwinter C, Bernhofer C, Eichelmann U, Heinesch B, Hertel M, Janous D, Kolle O, Lagergren F, Lindroth A, Minerbi S, Moderow U, Mölder M, Montagnani L, Queck R, Rebmann C, Vestin P, Yernaux M, Zeri M, Ziegler W, Aubinet M. Comparison of horizontal and vertical advective CO₂ fluxes at three forest sites. *Agricultural and Forest Meteorology*. 2008; 248:12–24.
- Frenzel P, Karofeld E. CH₄ emission from a hollow-ridge complex in a raised bog: The role of CH₄ production and oxidation. *Biogeochemistry*. 2000; 51:91–112.
- Granier, A.; Aubinet, M.; Epron, D.; Falge, E.; Umundsson, J.; Jensen, NO.; Köstner, B.; Matteucci, G.; Pilegaard, K.; Schmidt, M.; Tenhunen, JD. Deciduous forests (Beech): Carbon and water fluxes, balances, ecological and ecophysiological determinants. In: Valentini, R., editor. *Fluxes of carbon, water and energy of European forests*, Ecological Studies. Vol. 163. Springer Verlag; Berlin: 2003. p. 55–70.
- Hakola H, Tarvainen V, Laurila T, Hiltunen V, Hellén H, Keronen P. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmospheric Environment*. 2003; 37:1623–1634.
- Haslwanter A, Hammerle A, Wohlfahrt G. Open- vs. closed-path eddy covariance measurements of the net ecosystem carbon dioxide and water vapour exchange: a long-term perspective. *Agricultural and Forest Meteorology*. 2009; 149:291–302.

- Hewitt CN, MacKenzie AR, Di Carlo P, Di Marco CF, Dorsey JR, Evans M, Fowler D, Gallagher MW, Hopkins JR, Jones CE, Langford B, Lee JD, Lewis AC, Lim SF, McQuaid J, Misztal P, Moller SJ, Monks PS, Nemitz E, Oram DE, Owen SM, Phillips GJ, Pugh TAM, Pyle JA, Reeves CE, Ryder J, Siong J, Skiba U, Stewart DJ. Nitrogen management is essential to prevent tropical oil palm plantations from causing ground-level ozone pollution. *PNAS*. 2009; 106:18447–18451. [PubMed: 19841269]
- Högberg P. Environmental science: Nitrogen impacts on forest carbon. *Nature*. 2007; 447:781–782. [PubMed: 17568730]
- Hollinger DY, Richardson AD. Uncertainty in eddy covariance measurements and its application to physiological models. *Tree Physiology*. 2005; 25:873–885. [PubMed: 15870055]
- Horst TW, Weil JC. Footprint estimation for scalar flux measurements in the atmospheric surface layer. *Boundary-Layer Meteorology*. 1992; 59:279–296.
- Holzke C, Hoffmann T, Jaeger L, Koppmann R, Zimmer W. Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots pine (*Pinus sylvestris* L.). *Atmospheric Environment*. 2006; 40:3174–3185.
- Kolari P, Pumpanen J, Kulmala L, Ilvesniemi H, Nikinmaa E, Grönholm T, Hari P. Forest floor vegetation plays an important role in photosynthetic production of boreal forests. *Forest Ecology and Management*. 2006; 221:241–248.
- Kolari, P.; Pulkkinen, M.; Kulmala, L.; Pumpanen, J.; Nikinmaa, E.; Mäkelä, A.; Vesala, T.; Hari, P. Forest ecosystem CO₂ exchange. In: Hari, P.; Kulmala, L., editors. *Boreal forest and climate change*, *Advances in Global Change Research*. Vol. 34. Springer Verlag; New York: 2009. p. 351–382.
- Laurence JA, Retzlaff WA, Kern JS, Lee EH, Hogsett WE, Weinstein DA. Predicting the regional impact of ozone and precipitation on the growth of loblolly pine and yellow-poplar using linked TREGRO and ZELIG models. *Forest Ecology and Management*. 2001; 146:247–263.
- Leff JW, Fierer N. Volatile organic compound (VOC) emissions from soil and litter samples. *Soil Biology & Biochemistry*. 2008; 40:1629–1636.
- Lichtenthaler HK, Babani F, Langsdorf G. Chlorophyll fluorescence imaging of photosynthetic activity in sun and shade leaves of trees. *Photosynth. Res*. 2007; 93:235–244. [PubMed: 17486425]
- Lloyd J, Taylor JA. On the Temperature Dependence of Soil Respiration. *Functional Ecology*. 1994; 8:315–323.
- Lõhmus, E. Estonian: Eesti metsakasvukohatüübid. Eesti Loodusfoto; Tartu: 2004.
- Magnani F, Mencuccini M, Borghetti M, Berbigier P, Berninger F, Delzon S, Grelle A, Hari P, Jarvis PG, Kolari P, Kowalski AS, Lankreijer H, Law BE, Lindroth A, Loustau D, Manca G, Moncrieff JB, Rayment M, Tedeschi V, Valentini R, Grace J. The human footprint in the carbon cycle of temperate and boreal forests. *Nature*. 2007; 447:849–851.
- Manning WJ, Flagler RB, Frenkel MA. Assessing plant response to ambient ozone: growth of ozone-sensitive loblolly pine seedlings treated with ethylenediurea or sodium erythorbate. *Environmental Pollution*. 2003; 126:73–81. [PubMed: 12860104]
- Marek MV, Sprtová M, Kalina J. The photosynthetic irradiance-response of Norway spruce exposed to a long-term elevation of CO₂ concentration. *Photosynthetica*. 1997; 33:259–268.
- Mentel TF, Wildt J, Kiendler-Scharr A, Kleist E, Tillmann R, Dal Maso M, Fisseha R, Hohaus T, Spahn H, Uerlings R, Wegener R, Griffiths PT, Dinar E, Rudich Y, Wahner A. Photochemical production of aerosols from real plant emissions. *Atmos. Chem. Phys*. 2009; 9:4387–4406.
- Metslaid M, Jõgiste K, Nikinmaa E, Moser WK, Porcar-Castell A. Tree variables indicating the growth response and acclimation of advance regeneration of Norway spruce and other coniferous species after the release. *Forest Ecology and Management*. 2007; 250:56–63.
- Mikkelsen TN, Ro-Poulsen H, Hovmand MF, Jensen NO, Pilegaard K, Egeløf AH. Five years measurements of ozone fluxes to a Danish Norway Spruce canopy. *Atmospheric Environment*. 2004; 38:2361–2371.
- Mikkelsen TN, Ro-Poulsen H, Pilegaard K, Hovmand MF, Jensen NO, Christensen CS, Hummelshøj P. Ozone uptake by an evergreen forest canopy: temporal variation. *Environmental Pollution*. 2009; 119:423–429. [PubMed: 15092875]

- Misson L, Baldocchi DD, Black TA, Blanken PD, Brunet Y, Curiel Yuste J, Dorsey JR, Falk M, Granier A, Irvine MR, Jarosz N, Lamaud E, Launiainen S, Law BE, Longdoz B, Loustau D, McKay M, Paw U, KT, Vesala T, Vickers D, Wilson KB, Goldstein AH. Partitioning forest carbon fluxes with overstory and understory eddy-covariance measurements: A synthesis based on FLUXNET data. *Agricultural and Forest Meteorology*. 2007; 144:14–31.
- Mori A, Hojito M, Shimizu M, Matsuura S, Miyaji T, Hatano R. N₂O and CH₄ fluxes from a volcanic grassland soil in Nasu, Japan: Comparison between manure plus fertilizer plot and fertilizer-only plot. *Soil Science and Plant Nutrition*. 2008; 54:606–617.
- Niinemets Ü, Bilger W, Kull O, Tenhunen JD. Acclimation to high irradiance in temperate deciduous trees in the field: changes in xanthophyll cycle pool size and in photosynthetic capacity along a canopy light gradient. *Plant Cell Environ*. 1998; 21:1205–1218.
- Niinemets Ü, Söber A, Kull O, Hartung W, Tenhunen JD. Apparent controls on leaf conductance by soil water availability and via light-acclimation of foliage structural and physiological properties in a mixed deciduous, temperate forest. *Int. J. Plant Sci*. 1999; 160:707–721.
- Niinemets Ü, Kull O, Tenhunen JD. Within-canopy variation in the rate of development of photosynthetic capacity is proportional to integrated quantum flux density in temperate deciduous trees. *Plant, Cell and Environment*. 2004; 27:293–313.
- Pajuste, K.; Kimmel, V.; Kohv, N.; Truuts, T. Estonian EMEP Assessment Report. In: Bartnicki, J.; Lövblad, G., editors. EMEP Assessment Part II National Contributions. Norwegian Meteorological Institute; Oslo: 2004. p. 63-70.
- Pedersen AR, Petersen SO, Vinther FP. Stochastic diffusion model for estimating trace gas emissions with static chambers. *Soil Sci. Soc. Am. J*. 2001; 65:49–58.
- Pihlatie, M.; Simojoki, A.; Pumpanen, J.; Hari, P. Methane fluxes in boreal forest soil. In: Hari, P.; Kulmala, L., editors. Boreal forest and climate change, *Advances in Global Change Research*. Vol. 34. Springer Verlag; New York: 2009a. p. 387-392.
- Pihlatie, M.; Pumpanen, J.; Simojoki, A.; Hari, P. Fluxes and concentrations of N₂O in boreal forest soil. In: Hari, P.; Kulmala, L., editors. Boreal forest and climate change, *Advances in Global Change Research*. Vol. 34. Springer Verlag; New York: 2009b. p. 387-392.
- Pumpanen J, Ilvesniemi H, Keronen P, Nissinen A, Pohja T, Vesala T, Hari P. An open chamber system for measuring soil surface CO₂ efflux: Analysis of error sources related to the chamber system. *J. Geophys. Res*. 2001; 106(D8):7985–7992.
- Pumpanen J, Kolari P, Ilvesniemi H, Minkkinen K, Vesala T, Niinistö S, Lohila A, Larmola T, Morero M, Pihlatie M, Janssens I, Yuste JC, Grünzweig JM, Reth S, Subke J-S, Savage K, Kutsch W, Østreng G, Ziegler W, Anthoni P, Lindroth A, Hari P. Comparison of different chamber techniques measuring soil CO₂ efflux. *Agricultural Forest Meteorology*. 2004; 123:159–176.
- Räisänen T, Ryyppö A, Kellomäki S. Effects of elevated CO₂ and temperature on monoterpene emission of Scots pine (*Pinus sylvestris* L.). *Atmospheric Environment*. 2008; 42:4160–4171.
- Rannik Ü, Mammarella I, Keronen P, Vesala T. Vertical advection and nocturnal deposition of ozone over a boreal pine forest. *Atmos. Chem. Phys*. 2009; 9:2089–2095.
- Rayment MB, Jarvis PG. Temporal and spatial variation of soil CO₂ efflux in a Canadian boreal forest. *Soil Biology & Biochemistry*. 2000; 32:35–45.
- Ruehr NK, Buchmann N. Soil respiration fluxes in a temperate mixed forest: seasonality and temperature sensitivities differ among microbial and root-rhizosphere respiration. *Tree Physiology*. 2010; 30:165–176. [PubMed: 20008837]
- Saari A, Heiskanen J, Martikainen PJ. Effect of the organic horizon on methane oxidation and uptake in soil of a boreal Scots pine forest. *FEMS Microbiology Ecology*. 1998; 26:245–255.
- Schindlbacher A, Zechmeister-Boltenstern S, Butterbach-Bahl K. Effects of soil moisture and temperature on NO, NO₂, and N₂O emissions from European forest soils. *J. Geophys. Res*. 2004; 109:D17302.
- Scholler CEG, Gurtler H, Pedersen R, Molin S, Wilkins K. Volatile Metabolites from Actinomycetes. *Journal of Agricultural and Food Chemistry*. 2002; 50:2615–2621. [PubMed: 11958631]
- Seinfeld, JH.; Pandis, SN. *Atmospheric Chemistry and Physics: from air pollution to climate change*. John Wiley & Sons; Hoboken, New Jersey: 2006.

- Solondz DS, Petrone RM, Devito KJ. Forest floor carbon dioxide fluxes within an upland-peatland complex in the Western Boreal Plain, Canada. *Ecohydrology*. 2008; 1:361–376.
- Syväsalo E, Regina K, Pihlatie M, Esala M. Emissions of nitrous oxide from boreal agricultural clay and loamy sand soils. *Nutr. Cycl. Agroecosyst*. 2004; 69:155–165.
- Tiiva P, Faubert P, Rätty S, Holopainen JK, Holopainen T, Rinnan R. Contribution of vegetation and water table on isoprene emission from boreal peatland microcosms. *Atmospheric Environment*. 2009; 43:5469–5475.
- Toome M, Randjärv P, Copolovici L, Niinemets Ü, Heinsoo K, Luik A, Noe SM. Leaf rust induced volatile organic compounds signalling in willow during the infection. *Planta*. 2010 (in press).
- Vuorinen T, Nerg A-M, Vapaavuori E, Holopainen JK. Emission of volatile organic compounds from two silver birch (*Betula pendula* Roth) clones grown under ambient and elevated CO₂ and different O₃ concentrations. *Atmospheric Environment*. 2005; 39:1185–1197.
- Wallin G, Skärby L, Selldén G. Long-Term Exposure of Norway Spruce, *Picea abies* (L.) Karst., to Ozone in Open-Top Chambers. I. Effects on the Capacity of Net Photosynthesis, Dark Respiration and Leaf Conductance of Shoots of Different Ages. *New Phytologist*. 1990; 115:335–344.
- Whalen SC, Reeburgh WS, Barber VA. Oxidation of methane in boreal forest soils: a comparison of seven measures. *Biogeochemistry*. 1992; 16:181–211.
- WRB. WRB - World reference base for soil resources. Food and Agriculture Organization of the United Nations; Rome: 2006. World Soil Resources Report; p. 145
- Wuebbles DJ, Hayhoe K. Atmospheric methane and global change. *Earth-Science Review*. 2002; 57:177–210.
- Yamulki S, Jarvis SC. Short-term effects of tillage and compaction on nitrous oxide, nitric oxide, nitrogen dioxide, methane and carbon dioxide fluxes from grasslands. *Biol. Fert. Soils*. 2002; 36:224–231.

Figure 1. Flux tower site at Järvelja.

The blue dot marks the location of the tower and the numbered circles represent the five permanent sample plots. The broken lines denote the flux footprint in southern direction. The measurement cottage is located two meters in western direction at the base of the tower.

Figure 2. Eddy fluxes (upper panel) and storage fluxes (lower panel). Overstory fluxes are black dots and understory fluxes gray squares. Median daily fluxes were compiled from the measurements in 2008 and error bars denote standard errors.

Figure 3. Comparison between the ozone mixing ratios above and below the canopy. The data sets have been combined from both measurement campaigns. Ozone data was acquired with 1 s intervals, and half hourly averaged. From the combined data sets, medians have been calculated and error bars denote standard errors.

Figure 4. Relationship between the wind direction and the mixing ratios of nitrogen oxides (NO and NO₂) and ozone during the measurement campaign in 2009. Darker color refers to higher mixing ratios.

Figure 5. Monoterpene emissions from the main tree species *B. pendula* and *P. abies*, averaged over leaves and branches differently exposed to sunlight.

We used in both cases West, South and North exposed leaves or branches. The lower panel shows monoterpene emissions from soil and leaf litter. Error bars indicate standard errors.

Figure 6. Photosynthetic net assimilation rate of *B. pendula* on leaf level, averaged over 3-5 leaves.

To simulate high light conditions (denoted sun condition) the measurement was conducted with a quantum flux of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and shade conditions were simulated by a quantum flux of $200 \mu\text{mol m}^{-2} \text{s}^{-1}$. Directions given in the bars refer to the direction in which the leaves measured have been exposed. Error bars denote standard errors.

Figure 7. Daily mean soil respiration measured over 3 days during the 2009 campaign by the automatic chamber system.
 Error bars denote standard errors of hourly measurements ($N = 2-9$). The inset shows a one day data set of soil respiration fluxes measured with the manual chamber system.

Table 1
Overview on the measurement series conducted throughout both campaigns.

In 2008 we conducted already several measurements, denoted by “preview”, which have been used to set up the measurements in 2009.

	2008		2009	
	time	height over ground	time	height over ground
Flux measurements ^a	6 th - 21 st Aug.	20 m and 2 m	12 th - 19 th Aug.	20 m
			19 th - 25 th Aug.	2 m
			25 th Aug. - 9 th Sept.	20 m
			9 th - 21 st Sept.	2 m
Trace gases	6 th - 21 st Aug.	20 m and 2 m	12 th Aug. - 21 st Sept.	20 m and 2 m
Particles	6 th - 20 th Aug.	3 m	-	-
Leaf level BVOC and photosynthesis	11 th - 17 th Aug.	16 m <i>B. pendula</i>	24 th - 27 th Aug.	16 m <i>B. pendula</i>
		18-16 m <i>P. abies</i>		0.5 m <i>T. cordata</i>
		0-2 m understory preview	2 nd - 5 th Sept.	16-18 m <i>P. abies</i>
				2 m <i>Q. robur</i>
				1 m <i>B. pubescens</i>
				1.5 m <i>P. tremula</i>
Soil fluxes CO ₂	-	-	14 th - 16 th Sept.	0 m
			7 th Oct. / 23 rd Nov.	0 m
manual chamber	14 th - 15 th Aug.	preview	7 th - 11 th Sept.	0 m
Soil BVOC	-	-	25 th , 27 th - 29 th Aug.	0 m
			7 th - 8 th Sept.	0 m
auxiliary ^b	6 th - 21 st Aug.	20 m and 2 m	12 th Aug. - 21 st Sept.	20 m and 2 m

^aData of the year 2009 have been measured with one Eddy system on timely separated heights and were therefore not included into Figure 1.

^bAuxiliary measurements are air temperature, pressure, relative humidity, and global solar radiation.

Table 2
Description of the dominant canopy layer of sample plots at the atmosphere - forest measurement campaign site.

The proportion of the tree species is calculated on volume basis of stand total wood volume.

Plot number	Stand volume $\text{m}^3 \text{ha}^{-1}$	Number of trees ha^{-1}	Proportion (%)				Age	Height
			<i>Picea abies</i>	<i>Betula pendula</i>	<i>Alnus glutinosa</i>	Other		
1	171.4	1789	46.6	46.0	0.6	7.4	28	14.3
2	72.8	2395	39.8	34.5	25.3	0.4	21	10.0
3	54.2	2621	46.7	41.1	12.0	0.2	29	8.9
4	116.7	2621	43.9	28.7	–	27.4	23	10.2
5	210.8	2015	57.6	39.6	1.7	1.1	27	14.4

Table 3
Mean values and standard errors of the ecosystem CO₂ fluxes (August 2008).

All fluxes are expressed in $\mu\text{mol m}^{-2} \text{s}^{-1}$.

		Overstory		Understory			
			min	max		min	max
daily total	f_{cn}	-4.59 ± 1.01	-19.83	4.56	3.60 ± 0.23	1.19	7.15
	f_{sn}	0.1 ± 0.3	-4.97	6.26	0.03 ± 0.03	-0.35	0.66
daytime	f_{cn}	-10.28 ± 0.99			2.93 ± 0.99		
	f_{sn}	-0.5 ± 0.3			-0.04 ± 0.03		
nighttime	f_{cn}	2.92 ± 0.25			4.34 ± 0.34		
	f_{sn}	0.74 ± 0.41			0.09 ± 0.04		

f_{cn} , net CO₂ flux; f_{sn} , net storage flux.

Table 4
Comparison of trace gases and particles ($\mu\text{g m}^{-3}$) measured at the roadside (bus) and the flux tower in the forest (cottage).

	NO	NO ₂	SO ₂	O ₃	PM1	PM2,5	PM10
location	bus	cottage	bus	cottage	bus		
instrument	APNA 370	TEI 42i	ASNA 370	TEI 49/i	Grimm monitor N 180		
Median	0.1 – 0.7	0.2 – 0.9	0	43.33	4	6	14.50
95%	1.2 – 1.5	1.2 – 2.3	0.4	78.2	12	20.0	75.0
5%	0 – 0.2	0 – 0.2	0	5.71	2	2.90	5.50

Table 5
CO₂ assimilation and transpiration from tree leaves in the understory at a photon flux density of 200 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$.

Values shown are mean $\pm$ standard error of 3 different trees (3–7 measurements per tree).

Species	CO ₂ assimilation ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	Transpiration ($\text{mmol m}^{-2} \text{s}^{-1}$)	N
<i>Betula pendula</i> ^a	2.18 $\pm$ 0.13	0.78 $\pm$ 0.10	7
<i>Betula pubescens</i>	1.97 $\pm$ 0.14	1.03 $\pm$ 0.10	5
<i>Tilia cordata</i>	3.79 $\pm$ 0.27	1.12 $\pm$ 0.10	3

^a Overstory assimilation values measured under 200 $\mu\text{mol Quanta m}^{-2} \text{s}^{-1}$ (shade condition) are inserted from data given in Figure 5 for comparison.

Table 6
CO₂ assimilation and transpiration from tree leaves in a forest gap at a photon flux density of 1000 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$.

Values shown are mean $\pm$ standard error of 3 different trees (4–8 measurements per tree).

Species	CO ₂ assimilation ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	Transpiration ($\text{mmol m}^{-2} \text{s}^{-1}$)	N
<i>Quercus robur</i>	5.14 $\pm$ 1.22	1.46 $\pm$ 0.32	4
<i>Populus tremula</i>	8.24 $\pm$ 0.88	2.97 $\pm$ 0.09	5
<i>Betula pendula</i>	8.03 $\pm$ 1.23	2.29 $\pm$ 0.25	8

Table 7
Mean soil CO₂ effluxes and key environmental variables at Järvelja, measured with the automatic chamber system during the campaign in 2009.

Time of measuring was between 12–17 h. Data given as mean (of 2 – 10 measurements) $\pm$ standard error.

Date	16 Sep	7 Oct	23 Nov
Soil efflux, $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$	8.40 ± 0.82	9.60 ± 0.04	5.45 ± 0.53
T _{air} , °C	13.3 ± 0.3	8.4 ± 0.0	6.3 ± 0.1
T _{soil} , °C	12.6 ± 0.1	8.4 ± 0.1	5.7 ± 0.0
PPFD, $\mu\text{mol m}^{-2} \text{ s}^{-1}$	5.30 ± 1.14	21.50 ± 1.50	5.00 ± 1.10
Soil moisture % (v/v)	67.0 ± 5.8	69.1 ± 0.5	81.9 ± 10.9
Number of collars used	3	1	3