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SEASONAL AND DIURNAL VARIATIONS IN ATMOSPHERIC AND SOIL AIR ^{14}C IN A BOREAL SCOTS PINE FOREST

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ABSTRACT

We present a radiocarbon (^{14}C) dataset of tropospheric air CO_2 , forest soil air CO_2 , and soil CO_2 emissions over the course of one growing season in a Scots pine forest in southern Finland. The CO_2 collection for ^{14}C accelerator mass spectrometry (AMS) analysis was done with a portable, suitcase-sized system, using molecular sieve cartridges to selectively trap CO_2 . The piloting measurements aimed to quantify the spatial, seasonal and diurnal changes in the ^{14}C content of CO_2 in a northern forest site. The atmospheric samples collected above the canopy showed a large seasonal variation and an 11‰ difference between day and nighttime profiles in August. The higher $\Delta^{14}\text{C}$ values during night are partly explained by a higher contribution of ^{14}C -elevated soil CO_2 , accumulating in the nocturnal boundary layer when vertical mixing is weak. We observed significant seasonal trends in $\Delta^{14}\text{C}$ - CO_2 at different soil depths that reflected changes in the shares of autotrophic and heterotrophic respiration. Also the observed diurnal variation in the $\Delta^{14}\text{C}$ values in soil CO_2 highlighted the changes in the origin of CO_2 , with root activity decreasing more for the night than decomposition.

KEYWORDS: atmosphere, carbon dioxide, radiocarbon, soil.

1 INTRODUCTION

One of the most important research-aims concerning climate change is an accurate understanding of the global carbon cycle, down to the process level. CO_2 fluxes from northern forests show a strong seasonal cycle, acting as a net source during autumn and a net sink during spring and summer (Valentini et al. 2000; Kolari et al. 2004). The changes in carbon stocks are, however, not straightforward to determine from flux data only. It requires detailed knowledge of carbon dynamics between above-ground and below-ground compartments in these ecosystems.

Soil CO_2 efflux is one of the most dominating components in the ecosystem carbon balance and it may constitute more than half of ecosystem respiration in boreal forests

(Kolari et al. 2009). The two major processes contributing to soil CO₂ efflux are the heterotrophic soil respiration originating from decomposition of soil organic matter (R_d) by soil fauna and decomposing microbes as well as autotrophic root and rhizosphere respiration (R_r) which consists of the respiration of root tissue and plant-symbiotic mycorrhizal fungi utilizing root exudates, and other root-associated microbes. The proportion of R_r from total soil CO₂ efflux is highly variable and can range from 10 to 90% of total soil CO₂ efflux (Hanson et al. 2000), mostly varying between 30 and 70%. The great variability of these estimates reflects both the diversity in ecosystems but also the difficulties in accurately partitioning the different sources throughout the growing season due to their close interaction in nature. The most common method to partition soil respiration into its components is trenching, where the access of roots into soil is prevented (Epron et al. 1999; Kuzyakov 2006). Another method to restrain the flow of carbo-hydrates to the root system is to disrupt the phloem connection of the tree stems by girdling (Högberg et al. 2001). Both of these methods are destructive, have some potential biases, and cannot be repeated in the same measurement plot after the root system has been affected (Minkinen et al. 2007).

Allocation of assimilated carbon are also studied using pulse labeling experiments with stable ¹³C or radioactive ¹⁴C isotopes (Epron et al. 2012; JS Pumpanen et al. 2009; Heinonsalo et al. 2010) but these studies are most commonly used with seedlings outside field conditions because mature trees are difficult to label and their root systems are very extensive. In addition, these findings reveal only a momentary situation whereas in nature, the contribution of R_r is sea-sonally variable and depends on root growth and activity, the CO₂ uptake of trees and ground vegetation and their below-ground carbon allocation patterns (Boone et al. 1998; Pumpanen et al. 2015). In the spring, more carbon is allocated to above-ground parts than below-ground while the below-ground allocation becomes more dominating in late summer, mainly because most of the root growth occurs when shoot growth has ended (Konôpka et al. 2005). Since the soil CO₂ efflux and its components are very variable in time and space reliable separation of R_d and R_r is needed to estimate changes in the contribution of different parts of ecosystem C fluxes to total net ecosystem exchange.

¹⁴C measurements on CO₂ in canopy and soil air may help in deciphering the source of respiration within the ecosystem. The atmospheric bomb tests of the 1950s and 1960s have imprinted a strong artificial ¹⁴C signal in atmospheric CO₂, which was subsequently transferred into the carbon pools in oceans and in the terrestrial biosphere (Levin and Hesshaimer 2000; Naegler and Levin 2009b). The ¹⁴C bomb peak in the atmosphere can be used as an age tracer of carbon in other compartments (Trumbore 1993; Gaudinski et al. 2000). The terrestrial biosphere has been a net sink of bomb ¹⁴C until the 1980s, and it has stored this ¹⁴C in living and dead biomass, which is today slowly released back to the atmosphere (Naegler and Levin 2009a; He et al. 2016). The flux of bomb ¹⁴C from the biosphere to the atmosphere depends on season and on the age of the respiring biospheric reservoir. Levin et al. (2010) estimated the average contribution of this signal to the seasonal amplitude of atmospheric Δ¹⁴C-CO₂ to 2‰ (peak-to-peak) at mid-latitudes of the Northern Hemisphere. However, it may be larger in particular settings, e.g., if the difference between tropospheric Δ¹⁴C-CO₂ and ¹⁴C of respired CO₂ are large.

The aim of this study was to determine the temporal variation in Δ¹⁴C-CO₂ belowground, in the canopy, and in the atmosphere above the canopy in a boreal

middle-aged Scots pine forest. Emphasis was placed on the seasonal and diurnal changes in the $\Delta^{14}\text{C}$ -values. We compared the seasonal variation in atmospheric ^{14}C measured in a boreal forest ecosystem to that observed in free atmospheric air ^{14}C measured at a high altitude site at Jungfraujoch (Levin et al. 2013). We also investigated whether changes in auto- and heterotrophic respiration could be observed in the $\Delta^{14}\text{C}$ -values measured in the soil CO_2 efflux and in air measured above the soil and at different depths in soil profile, as well as the potential influence of free tropospheric air. Finally, we describe briefly the CO_2 sample collection method, present the measured data of atmosphere and soil $^{14}\text{CO}_2$ in detail, and discuss the possible mechanisms underlying the temporal and spatial variation in the measured $\Delta^{14}\text{C}$ - CO_2 values.

2 MATERIALS AND METHODS

2.1 MOLECULAR SIEVE SAMPLING SYSTEM

CO_2 samples were collected with a portable molecular sieve collection system, described in detail in Palonen (2015). A brief overview of the system is given here.

The target gas (ambient or soil air) is circulated through the collection system with an adjustable flowrate of 0.1 to 2 l/min. The gas is first taken through a Nafion dryer, which removes H_2O (below 1‰). A $\text{CO}_2/\text{H}_2\text{O}$ analyzer (Li-840A) is then used to measure the CO_2 concentration in the gas in order to make sure enough CO_2 is collected for ^{14}C AMS analysis (1 mg of carbon). For the soil chambers, the CO_2 measurement is also used to estimate the flux of CO_2 from the soil to the chamber. After the $\text{CO}_2/\text{H}_2\text{O}$ analyzer, the sample air is taken through the sample cartridge, which is a vacuum-tight quartz tube containing roughly one gram of molecular sieve material (13X), which traps all of the CO_2 and H_2O in the sample air. After CO_2 collection, the target gas is circulated back to the chamber headspace or to the atmosphere. For ^{14}C analysis in the laboratory, the collected CO_2 is released from the sample cartridges by heating under vacuum (Palonen 2013). The method does not introduce significant under-pressure to the target system (i.e. chamber headspace) because CO_2 is selectively removed from the target gas, while the sample air is returned to the chamber.

2.2 SITE AND SAMPLING

The CO_2 samples were collected in a boreal forest at the SMEAR II measurement station (61°51', 24°17', 181 m asl) (Hari and Kulmala 2005) that is dominated by ca. 50-yr-old Scots pine trees (*Pinus sylvestris* L.). Material and energy fluxes within the forest stand and between the forest and the atmosphere have been monitored intensively at the site since 1996 (Hari and Kulmala 2005). The average annual precipitation at the SMEAR II station is 697 mm and annual mean temperature +2.9°C (Ilvesniemi et al. 2010). The stand had been clear-cut in 1962 and was treated with prescribed burning and sown with Scots pine seeds. The soil above the homogeneous bedrock is Haplic podzol formed on a glacial till (FAO 1990), with an average depth of 0.5–0.7 m. The C content of the organic soil layer in the top of the mineral soil is 300 mg g⁻¹ and in the A-horizon it is 60 mg g⁻¹ which decreases to 3 mg g⁻¹ in the

lower part of the B-horizon. The biomass inventory (Ilvesniemi and Liu 2001) indicated the total surface area of the roots <2 mm to be generally about $3.5 \text{ m}^2 \text{ m}^{-2}$ in the organic soil layer, $1.8 \text{ m}^2 \text{ m}^{-2}$ in the A-horizon and about $0.8 \text{ m}^2 \text{ m}^{-2}$ in the B-horizon. The dominant species in the field-layer vegetation are *Vaccinium myrtillus* and *Vaccinium vitis-idaea*. The ground vegetation consists mainly of mosses *Dicranum polysetum*, *Hylocomium splendens* and *Pleurozium schreberi*, which overlie a 0.05 m layer of soil humus.

The atmospheric air CO_2 samples were collected from April 2012 to April 2013 at two-week to monthly intervals. Samples were collected from a measurement mast at the heights of 1.0, 16.8, 67.2, and 125 m using a flow rate of 1 L/min. The sample integration time was 10 min. The collection took place always between 10:00 and 12:00 AM (local time) for the daytime sampling, and between 1:00 and 2:00 AM for the nighttime samples.

Soil air CO_2 samples were collected from soil air collectors approximately monthly from April to late August 2012. The collectors were installed in the middle of the 5-cm organic layer (O-horizon on top of the mineral soil) and at 2 cm, 8 cm, 28 cm, 48 cm, and 69 cm depths in the mineral soil (PIT100 soil profile [Pihlatie et al. 2007]). The soil air collectors consisted of 10 cm long (outer diameter 12 mm) porous PTFE tubing (product code 110-05-1, International Polymer Engineering, Tempe, AZ) installed horizontally in the soil. Stainless steel tubes (10 mm outer diameter) were connected to both ends of the collector with Swagelok tube connectors, and directed to the soil surface and closed from both ends with rubber septa. During the air sampling, both steel tubes of the collector were connected to the portable CO_2 sampling system. The collectors were installed in summer 2011. Soil was excavated from the soil pits layer by layer and repacked into the same volume, minimizing the disturbance of the soil. The roots cut in the excavation will grow back to the excavated soil in a relatively short time. In natural forest soil, the fine root turnover is also relatively short. Thus, we can assume that the living fine root biomass had recovered sufficiently. The ground vegetation had fully recovered based on visual observation.

The CO_2 was first scrubbed from the collector and then allowed to accumulate for 20–30 min. After accumulation, the CO_2 sample was pumped through a molecular sieve cartridge at a constant flow rate of 0.3 L min^{-1} . Soil air samplings were usually conducted in the afternoon, except for 31 August, when the sampling took place during night at 2:00 AM. Samples of soil air were also taken by syringes some hours before the CO_2 collection for ^{14}C analysis and taken to a gas chromatograph for CO_2 concentration measurement.

Samples for ^{14}C -determination from soil CO_2 efflux were collected from a closed chamber (Pumpanen et al. 2015) placed over the soil. The chamber (8.1 L, 20 cm diameter, 30 cm height, made from polycarbonate) was equipped with a small fan and covered with aluminum foil to exclude sunlight. During the sample collection, the chamber was mounted on a collar made of high density polyethylene (20.5 cm diameter and 5 cm height). The collection started by placing the chamber on top of the collar, and immediate scrubbing the CO_2 from the chamber headspace to remove the atmospheric CO_2 from the chamber. We used a flow rate of 2 L min^{-1} and the scrubbing lasted for approximately 20 min, after which the contribution from atmospheric CO_2 was deemed to be sufficiently low (less than 2%). The CO_2 was then allowed to

accumulate and the CO₂ concentration was monitored for 15–30 min to guarantee sufficient amount of CO₂ for further analysis. After this, the air in the chamber was circulated through the molecular sieve sampling cartridge, which traps all of the CO₂ from the gas flow. A flow rate of 1 L min⁻¹ was used during the CO₂ collection. The CO₂ fluxes were calculated from the CO₂ concentration increase in the chamber following the CO₂ removal with the HMR procedure (Pedersen et al. 2010). The HMR fit was performed on the CO₂ concentration values exceeding that of the free atmosphere.

The collected samples were graphitized with Fe/Zn reduction (Slota et al. 1987) in the Laboratory of Chronology, University of Helsinki, and measured at three AMS laboratories to the precision of 1.3–3.0‰, depending on the laboratory and the mass of the sample. The laboratories were the Vienna Environmental Research Accelerator (VERA), the Tandem Laboratory at the University of Uppsala, and Helsinki Accelerator Mass Spectrometry Facility (HAMS) at the University of Helsinki. The $\delta^{13}\text{C}$ values shown in the tables were measured with an Isotope Ratio Mass Spectrometer (ThermoQuest Finnigan) from CO₂ prior to graphitization, as these best describe the original $\delta^{13}\text{C}$ of the target (no effects from the AMS ion source). The fractionation correction for the radiocarbon results (see section below) were done with AMS-measured $\delta^{13}\text{C}$ for the VERA results, and with the MS-measured for the HAMS and Uppsala results. The uncertainties of the $\delta^{13}\text{C}$ values are 0.2‰ unless otherwise stated.

2.3 UNITS AND DEFINITIONS

All ¹⁴C results are given as $\Delta^{14}\text{C}$ values,

$$\Delta^{14}\text{C} = [F^{14}\text{C} \times e^{-\lambda(y-1950)} - 1] \times 1000 \quad (1)$$

where $F^{14}\text{C} = A_{\text{sample}} / (0.95 A_{\text{standard}})$ and denotes the ratio of measured and $\delta^{13}\text{C}$ -corrected ¹⁴C/C ratios of a sample and oxalic acid standard (Reimer et al. 2004), y is the year of measurement and $\lambda = 1/8267\text{y}^{-1}$ is the decay constant of radiocarbon. The $\delta^{13}\text{C}$ -correction for the samples was performed in the standard way given by (Stuiver and Polach 1977) to -25‰. It is used to correct for natural isotopic fractionation of the ¹⁴C/C ratios based on the measured ¹³C/¹²C ratios.

2.4 QUALITY CONTROL

The reliability of the sieve collection for CO₂ samples has been verified under laboratory conditions (Palonen 2013). The reliability of gas sample graphitization and AMS measurements was tested prior to sampling with several standards, the results of which were within 2 standard errors (1.9‰) from the reference value. To check the quality of the results for real field-collected samples, several 7-min sequential samples were taken from the same height (125 m) in the beginning of the measurement campaign. The results are given in Table 1. The duplicates give consistent ¹⁴C and $\delta^{13}\text{C}$ values within their uncertainties. For the subsequent figures and tables, average values

of individual measurements were used when sequentially sampled CO₂ samples were done.

For the later batches of samples, we noticed a slight carbon contribution (up to 0.4% of normal sample current, with ¹⁴C concentration of 0.12 fraction modern) coming from iron powder used in the graphitization step of sample preparation. Because the standard samples go through the same preparation process, the results from most samples are unaffected by the small amount of extra carbon. However, results from soil profile samples with small carbon mass had to be corrected for this extra carbon. Corrected values are shown in the figures, and both uncorrected and corrected values are given in Table 3. For the corrected values, the uncertainties are given as half of the difference between the original and corrected value.

Table 1. Results from multiple samples of the atmosphere on the same date. Some $\delta^{13}\text{C}$ values have been measured only once for two samples.

Date	Sample code	AMS	Mass (mg)	$\Delta^{14}\text{C}$ (‰)	$\delta^{13}\text{C}$ (‰)
18.4.2012	HU124	VERA	0.30	15.6 ± 2.4	From HU125
18.4.2012	HU125	VERA	1.00	21.5 ± 1.6	-9.17
18.4.2012	HU128	VERA	0.64	25.1 ± 1.7	-9.09
3.5.2012	HU180	VERA	1.32	23.4 ± 1.8	-9.17
3.5.2012	HU181	VERA	0.83	22.1 ± 1.9	From HU180
18.5.2012	HU187	VERA	1.00	29.7 ± 1.8	-9.25
18.5.2012	HU188	VERA	0.97	27.0 ± 1.8	From HU187
6.6.2012	HU229	VERA	1.60	27.4 ± 2.0	-8.98
6.6.2012	HU230	VERA	1.00	27.7 ± 2.1	-7.51
20.6.2012	HU241	VERA	1.39	29.0 ± 1.9	-8.84
20.6.2012	HU243	VERA	1.48	26.1 ± 2.0	-8.91
20.6.2012	HU244	VERA	0.91	33.0 ± 2.3	-8.92
20.6.2012	HU242	VERA	0.88	24.1 ± 2.3	-9.25
21.9.2012	HU317	VERA	1.47	28.1 ± 2.0	-8.52
21.9.2012	HU336	VERA	1.23	38.1 ± 3.0	-8.63

3 RESULTS

3.1 $\Delta^{14}\text{C}$ -CO₂ VALUES IN THE ATMOSPHERE

$\Delta^{14}\text{C}$ -CO₂ in the atmosphere varied between 20 to 38‰ (Figure 1 and Table 2). There was no vertical gradient observed in the $\Delta^{14}\text{C}$ above the canopy (i.e. >16 m agl). The results from 16.8-, 67.2-, and 125-m heights were consistently within the uncertainty values of the measurements. The $\Delta^{14}\text{C}$ values at 1-m height were close to the values observed higher in the atmosphere but in some cases the 1-m value was shifted towards the higher $\Delta^{14}\text{C}$ values of soil-emitted CO₂ (arrows in Figure 1). There was a significant difference between the nighttime and daytime measurements in August, with the nighttime values being roughly 11‰ higher compared to the daytime values.

The average $\Delta^{14}\text{C}$ calculated from the 16.8-, 67.2-, and 125-m heights showed a $10 \pm 0.5\%$ seasonal variation with the highest $\Delta^{14}\text{C}$ values observed during late summer and autumn and the lowest values in the winter and spring (Figure 2).

Figure 1. $\Delta^{14}\text{C}$ -CO₂ values of atmospheric (top) and soil air (bottom) as a function of height. Symbols with arrows represent the $\Delta^{14}\text{C}$ values of soil emission. Asterisks represent corresponding $\Delta^{14}\text{C}$ values at Jungfraujoch, Swiss Alps.

Figure 2. Average atmospheric $\Delta^{14}\text{C}$ level in Finland compared to the measurements from the Swiss Alps (Levin and Hammer, n.d.). While the present data is only one year long, it seems to point to larger seasonal variation in the northern latitudes.

Table 2. Atmospheric results for different dates and heights. Some values represent averages of N measurements. Samples were measured at three AMS facilities; VERA = Vienna Environmental Research Accelerator, HAMS = Helsinki Accelerator Mass Spectrometry Facility, Uppsala = Tandem Laboratory, University of Uppsala. CO₂ concentrations were measured with Li-Cor LI-840 infrared light absorption analyzer and the air temperatures with Pt100 sensors at corresponding heights.

Date	Height	N	Sample Code	AMS	$\Delta^{14}\text{C}$ [‰]	$\delta^{13}\text{C}$ [‰]	CO ₂ [ppm]	Temp. [°C]
2012-04-18 15:17:00	1 m	1	HU126	VERA	20.2 ± 1.8	-9.27	400.1	-
2012-04-18 14:00:00	16.8 m	1	HU129	VERA	19.1 ± 1.7	-9.19	400.1	0.5
2012-04-18 13:30:00	67.2 m	1	HU127	VERA	22.3 ± 1.6	-9.16	400.4	-0.6
2012-04-18 14:13:20	125 m	3	several	VERA	20.7 ± 1.1	-9.14	-	-
2012-05-03 12:35:00	16.8 m	1	HU179	VERA	23.1 ± 1.9	-9.12	397.5	6.4
2012-05-03 12:10:00	67.2 m	1	HU182	VERA	22.7 ± 1.7	-9.21	398.0	5.3
2012-05-03 11:30:00	125 m	2	HU180,HU181	VERA	22.7 ± 1.3	-9.17	-	-
2012-05-18 11:53:30	16.8 m	2	HU184,HU185	VERA	28.8 ± 1.2	-9.09	393.1	9.5
2012-05-18 11:05:00	67.2 m	1	HU186	VERA	27.2 ± 1.8	-10.28	394.4	8.3
2012-05-18 10:53:30	125 m	2	HU187,HU188	VERA	28.3 ± 1.3	-9.25	-	-
2012-06-06 11:00:00	1 m	1	HU231	VERA	34.2 ± 2.1	-8.40	388.3	12.9
2012-06-06 10:00:00	16.8 m	1	HU227	VERA	27.3 ± 2.1	-9.32	389.0	11.9
2012-06-06 10:15:00	67.2 m	1	HU228	VERA	28.1 ± 2.1	-8.83	389.6	11.0
2012-06-06 10:40:00	125 m	2	HU229,HU230	VERA	27.5 ± 1.5	-8.24	-	-
2012-06-20 11:38:00	1 m	1	HU240	VERA	28.7 ± 2.0	-8.52	388.3	12.5
2012-06-20 10:20:00	16.8 m	1	HU238	VERA	26.8 ± 1.9	-8.98	389.8	11.0
2012-06-20 10:35:00	67.2 m	1	HU239	VERA	27.4 ± 1.4	-9.67	390.9	10.2
2012-06-20 11:02:30	125 m	4	several	VERA	28.0 ± 1.1	-8.98	-	-
2012-07-04 11:24:00	1 m	1	HU265	VERA	26.5 ± 1.6	-8.58	-	20.2
2012-07-04 10:35:00	16.8 m	1	HU246	VERA	32.6 ± 2.4	-8.07	-	19.5
2012-07-04 10:45:00	67.2 m	1	HU247	VERA	31.2 ± 1.5	-8.82	-	18.3
2012-07-04 11:00:00	125 m	1	HU264	VERA	36.1 ± 1.8	-8.82	-	-
2012-07-18 11:07:00	1 m	1	HU268	VERA	33.9 ± 1.9	-8.17	-	17.2
2012-07-18 10:21:00	16.8 m	1	HU266	VERA	29.2 ± 2.2	-8.38	-	16.3
2012-07-18 10:33:00	67.2 m	1	HU267	VERA	34.6 ± 2.1	-8.23	-	15.4
2012-07-18 10:45:00	125 m	1	HU269	VERA	27.6 ± 2.3	-8.40	-	-
2012-08-10 12:50:00	1 m	1	Hu281	HAMS	31.3 ± 2.9	-7.97	374.5	12.0
2012-08-10 12:05:00	16.8 m	1	Hu278	HAMS	29.7 ± 2.9	-7.82	374.6	11.6
2012-08-10 12:15:00	67.2 m	1	Hu279	HAMS	30.9 ± 3.3	-9.45	375.7	10.8
2012-08-10 12:25:00	125 m	1	HU280	VERA	28.2 ± 1.9	-8.53	-	-
2012-08-30 13:05:00	1 m	1	HU315	VERA	35.4 ± 2.3	-8.24	382.1	16.5

2012-08-30 12:00:00	16.8 m	1	HU312	VERA	27.9 ± 2.2	-8.89	383.6	15.7
2012-08-30 12:10:00	67.2 m	1	HU313	VERA	24.9 ± 2.0	-8.57	384.4	14.8
2012-08-30 12:25:00	125 m	1	HU314	VERA	26.7 ± 1.9	-8.37	-	-
2012-08-31 01:47:00	1 m	1	HU287	VERA	40.9 ± 2.4	-9.69	404.2	11.6
2012-08-31 01:30:00	16.8 m	1	HU285	VERA	37.4 ± 1.9	-10.18	401.3	11.7
2012-08-31 01:10:00	67.2 m	1	HU284	VERA	38.2 ± 1.9	-9.35	396.2	11.4
2012-08-31 01:00:00	125 m	1	HU286	VERA	36.9 ± 2.3	-8.46	-	-
2012-09-21 11:23:00	1 m	1	HU337	VERA	34.1 ± 3.0	-8.68	384.3	7.4
2012-09-21 10:55:00	16.8 m	1	HU335	VERA	29.2 ± 3.0	-8.68	386.6	7.3
2012-09-21 10:44:00	67.2 m	1	HU334	VERA	27.2 ± 3.0	-8.71	387.3	6.7
2012-09-21 10:50:00	125 m	2	HU317,HU336	VERA	33.1 ± 1.8	-8.57	-	6.9
2012-10-18 11:30:00	1 m	1	HU368	Uppsala	28.2 ± 3.0	-9.24	399.7	7.3
2012-10-18 10:41:00	16.8 m	1	HU338	Uppsala	24.2 ± 3.0	-9.01	400.3	7.1
2012-10-18 10:50:00	67.2 m	1	HU339	Uppsala	31.1 ± 3.0	-9.18	400.2	6.5
2012-10-18 11:03:00	125 m	1	HU367	Uppsala	37.1 ± 3.0	-9.27	-	6.9
2012-11-27 12:15:00	1 m	1	HU381	HAMS	21.5 ± 1.8	-10.05	411.6	-0.1
2012-11-27 11:25:00	16.8 m	1	HU370	Uppsala	11.3 ± 3.0	-11.11	411.4	-0.4
2012-11-27 11:35:00	67.2 m	1	HU369	Uppsala	27.1 ± 3.0	-9.57	411.2	-1.0
2012-11-27 11:45:00	125 m	1	HU380	Uppsala	26.2 ± 3.0	-9.52	-	-0.7
2012-12-27 12:15:00	1 m	1	HU385	HAMS	21.1 ± 1.8	-10.46	406.4	-1.0
2012-12-27 11:10:00	16.8 m	1	HU371	Uppsala	15.2 ± 3.0	-9.63	408.0	-1.6
2012-12-27 11:23:00	67.2 m	1	HU372	Uppsala	24.2 ± 3.0	-9.62	406.7	-1.6
2012-12-27 11:35:00	125 m	1	HU384	HAMS	20.1 ± 1.8	-10.47	-	-1.1
2013-01-25 11:00:00	16.8 m	1	HU386	HAMS	25.1 ± 2.6	-9.93	405.3	-7.0
2013-01-25 11:13:00	67.2 m	1	HU387	HAMS	26.4 ± 2.6	-10.03	404.7	-7.5
2013-01-25 11:26:00	125 m	1	HU390	HAMS	37.4 ± 3.2	-12.95	-	-7.0
2013-02-22 11:15:00	16.8 m	1	HU392	HAMS	18.4 ± 2.8	-10.64	409.2	-2.3
2013-03-26 11:20:00	16.8 m	1	HU394	HAMS	28.1 ± 2.6	-10.83	401.9	-1.2
2013-03-26 11:30:00	67.2 m	1	HU395	HAMS	16.5 ± 2.6	-9.31	401.8	-2.3
2013-03-26 11:44:00	125 m	1	HU396	HAMS	24.5 ± 2.7	-9.22	401.6	-1.9
2013-04-25 11:09:00	1 m	1	HU440	HAMS	19.0 ± 2.7	-10.20	400.8	8.5
2013-04-25 10:20:00	16.8 m	1	HU421	HAMS	16.9 ± 2.8	-9.80	400.9	7.8
2013-04-25 10:33:00	67.2 m	1	HU405	HAMS	29.2 ± 2.8	-12.04	401.4	6.7
2013-04-25 10:46:00	125 m	1	HU428	HAMS	24.4 ± 2.9	-10.32	401.5	6.8

3.2 $\Delta^{14}\text{C}$ -CO₂ VALUES IN SOIL AIR AND IN SOIL CO₂ EMISSIONS

The $\Delta^{14}\text{C}$ values measured in soil CO₂ ranged mostly from 37 to 65‰ (Figure 1 and Table 3). High soil water content prevented taking a representative sample in some of the tubes during late autumn and early spring. The $\Delta^{14}\text{C}$ values were highest in spring and decreased significantly in autumn (Figure 1). This seasonal change was most notable in the deep soil. The difference between the nighttime and daytime $\Delta^{14}\text{C}$ results (late August) was pronounced, the nighttime results having 10‰ larger values than the daytime ones.

The chamber measurements showed an increase in the CO₂ emissions from May to late August (Figure 3a), while a high $\Delta^{14}\text{C}$ value in the emission was recorded in early

May, followed by a drop and a steady increase up to October (Figure 3b). In August, the $\Delta^{14}\text{C}$ in the CO_2 emission during nighttime was almost equal to the daytime value (Figure 3b) while the total CO_2 flux decreased (Figure 3a) and $\Delta^{14}\text{C}$ values increased in humus and 1 m above the soil surface (Figure 1) during the night.

Figure 3. The CO_2 flux (a) and $\Delta^{14}\text{C}$ in it (b). Error bars depict one standard error. Solid circles represent the nighttime values.

Table 3. Soil results for different dates and depths. Depths given in centimeters. For chamber-collected samples, the flux has been calculated with the HMR procedure for CO_2 values exceeding 390 ppm. Soil temperature was measured with Philips KTY81-110 temperature sensors at corresponding depths.

Date	Depth [cm]	Sample Code	Mass [mg]	AMS	$\Delta^{14}\text{C}$ [‰]	$\delta^{13}\text{C}$ [‰]	CO_2 [ppm]	Flux [$\text{mg s}^{-1} \text{m}^{-2}$]	Temp [$^{\circ}\text{C}$]
2012-05-03 15:31:00	-74	HU166	1.30	VERA	56.4 ± 2.3	-11.20	-	-	-
2012-05-03 16:42:00	-13	HU165	0.21	VERA	53.8 ± 1.6	-11.66	1923	-	2.9

2012-05-03 15:00:00	-2.5	HU145	0.19	VERA	41.1 ± 2.2	-15.99	635	-	4.2
2012-05-03 19:00:00	Surface	HU183	1.70	VERA	54.2 ± 1.8	-21.05	-	0.121	5.7
2012-06-06 14:15:00	-74	HU224	0.24	VERA	64.2 ± 2.8	-23.38	-	-	-
2012-06-06 16:05:00	-53	HU226	0.33	VERA	52.4 ± 2.7	-22.52	8630	-	6.0
2012-06-06 13:45:00	-13	HU211	0.33	VERA	48.3 ± 2.0	-22.83	3394	-	7.3
2012-06-06 14:45:00	-7	HU225	0.30	VERA	46.4 ± 2.7	-18.72	1850	-	8.4
2012-06-06 13:10:00	-2.5	HU210	0.16	VERA	42.1 ± 2.3	-19.06	1293	-	10.6
2012-06-06 12:45:00	Surface	HU232	2.00	VERA	48.4 ± 2.5	-20.09	-	0.162	14.0
2012-07-04 15:39:00	-74	HU237	0.65	VERA	53.4 ± 1.9	-25.70	-	-	-
2012-07-04 15:14:00	-53	HU236	0.69	VERA	54.7 ± 2.6	-25.06	10840	-	8.9
2012-07-04 14:21:00	-13	HU235	0.62	VERA	53.3 ± 2.1	-23.64	4496	-	11.1
2012-07-04 14:13:00	-7	HU234	0.37	VERA	49.1 ± 2.5	-22.77	2322	-	12.2
2012-07-04 13:40:00	-2.5	HU233	0.25	VERA	54.6 ± 1.4	-23.94	1729	-	15.0
2012-07-04 13:14:00	Surface	HU245	1.71	VERA	50.8 ± 1.5	-24.00	-	0.276	21.6
2012-08-30 16:20:00	-74	HU333	0.86	VERA	38.1 ± 3.0	-20.22	-	-	-
2012-08-30 15:43:00	-53	HU332	1.08	VERA	38.1 ± 3.0	-19.73	14503	-	11.0
2012-08-30 15:20:00	-13	HU331	1.01	VERA	40.1 ± 3.0	-18.76	6948	-	12.2
2012-08-30 14:57:00	-7	HU318	0.48	VERA	46.1 ± 2.2	-23.96	3204	-	12.7
2012-08-30 14:24:00	-2.5	HU316	0.36	VERA	43.1 ± 2.2	-27.61	2371	-	14.2
2012-08-30 14:01:00	Surface	HU283	1.93	VERA	53.6 ± 2.0	-26.26	-	0.412	17.0
2012-08-31 05:05:00	-74	HU311	0.91	VERA	47.5 ± 2.0	-25.24	-	-	-
2012-08-31 04:36:00	-53	HU310	1.03	VERA	50.1 ± 2.4	-24.38	13013	-	11.1
2012-08-31 04:10:00	-13	HU291	1.10	VERA	49.6 ± 2.1	-24.34	5766	-	12.3
2012-08-31 03:50:00	-7	HU290	0.75	VERA	52.8 ± 2.1	-25.95	3154	-	12.4
2012-08-31 03:20:00	-2.5	HU289	0.86	VERA	53.5 ± 2.0	-23.87	1764	-	12.6
2012-08-31 02:35:00	Surface	HU288	1.09	VERA	53.7 ± 2.2	-26.19	-	0.385	11.0
2012-10-18 13:15:00	Surface	HU373	1.86	Uppsala	56.9 ± 3.0	-24.58	-	0.171	7.5

4 DISCUSSION

4.1 ATMOSPHERIC RESULTS

While the vertical gradient in the atmospheric $\Delta^{14}\text{C}$ signal above the canopy was relatively constant from 16.7 m to 125 m height, the $\Delta^{14}\text{C}$ value in air collected close to the ground (1 m) in the forest canopy was obviously affected by the ^{14}C -elevated soil emission signal. This effect should be kept in mind when free tropospheric $^{14}\text{CO}_2$ levels shall be derived from air samples that are collected close to the ground. Depending on atmospheric mixing conditions, they may deviate from a real representative ^{14}C - CO_2 level, in our case of air sampled more than 100 m above the canopy by up to +10%. Consequently, as shrubs and other forest floor vegetation incorporate (via photosynthesis) the CO_2 close to the soil surface, they likely incorporate a higher $\Delta^{14}\text{C}$ value than from the free troposphere. This is important to keep in mind when dating recent materials with ^{14}C .

The nighttime atmospheric $\Delta^{14}\text{C}$ -CO₂ profile in August 2012 was on average consistently 11‰ higher than the daytime profile. This result may have been caused by the diurnal changes in the atmospheric boundary layer (ABL) height (Garratt 1992). During the day, the atmosphere is heated from below by the absorption of sunlight, resulting in convective mixing of the air masses up to the height 1 or 2 km. During the night, the absence of sunlight and hence convection results in a shallow nocturnal boundary layer (NBL), in which mixing is mainly caused by wind friction. This layer is usually between 100 and 300 m thick. Within the NBL, CO₂ from soil respiration with higher $\Delta^{14}\text{C}$ values is mixed with atmospheric air. Indeed, effects of soil respiration are observed up to the 125 m height based on the $\Delta^{14}\text{C}$ signature for the night. This is in line with similar results from other studies (Phillips et al. 2015; LaFranchi et al. 2016).

However, a simple mass balance, calculating the amount of soil CO₂ required explaining the observed $\Delta^{14}\text{C}$ increase during night in an air column up to 125 m height yields approximately 100 g. Comparing this to the amount of CO₂ from soil emission (Figure 3, i.e. 14 g over 10 hr), the direct contribution from soil emission cannot be solely responsible for the ^{14}C shift. We therefore conclude that the system is more complex. Also, the present study has only one set of nighttime measurements, therefore, it would be premature to draw further conclusions. Indeed, a full quantitative explanation for the high atmospheric nighttime $\Delta^{14}\text{C}$ values will likely require detailed micrometeorological and ecosystem-level modeling and further experimental work targeting this particular question.

The $10 \pm 0.5\text{‰}$ seasonal variation in $\Delta^{14}\text{C}$ in the present atmospheric data is significantly larger than the average 4‰ at Jungfraujoch (Levin et al. 2013). The larger seasonal variation at this higher-latitude lower tropospheric site may be caused by the strong seasonality of soil respiration in higher latitudes, which has an elevated ^{14}C signal (see Figure 1; LaFranchi et al. 2016). Alternatively, it may reflect the fact that, due to the deflection of cosmic rays by the earth's magnetic field, roughly four times more ^{14}C is produced in the stratosphere and the troposphere near the geomagnetic poles compared to the equator (Lingenfelter 1963).

4.2 SOIL RESULTS

Root and rhizosphere respiration arises from the growth and maintenance of plant roots and microbial utilization of labile root exudates. It can be assumed to have the $\Delta^{14}\text{C}$ signature close to that of the atmosphere since it is mainly originating from the recently assimilated carbon (Högberg and Read 2006) having an average $\Delta^{14}\text{C}$ value of 27‰ in our study. The ^{14}C of the Rd depends mainly on the age of soil organic matter (SOM), which is variable but can be hundreds or up to some thousands of years old especially in the lower mineral soil horizons (Liski et al. 1998). In another project, $\Delta^{14}\text{C}$ in the SOM collected from a similar site 5 km away from the site used in this study indicated that the C in the upper organic soil horizon was on average approximately 30 yr old (Lindén et al. 2014). This means that SOM mainly originates from the post-bomb period of over-modern but with decreasing $\Delta^{14}\text{C}$ in the atmosphere. Based on trenching experiments performed at the current site (unpublished data), we can estimate by a linear extrapolation from measurements carried out in 2013–2015 that the $\Delta^{14}\text{C}$ value of R_d would be around $(70 \pm 10)\text{‰}$ in the year 2012.

We expected that the $\Delta^{14}\text{C}$ values in soil air CO_2 and soil CO_2 efflux would be different in early summer compared to late summer. The $\Delta^{14}\text{C}$ values especially in the deeper soil layers decreased towards the end of the autumn by up to 15‰ units relative to the values measured in spring i.e. they approached atmospheric values. This could be an indication of changes in the origin of CO_2 suggesting an increase in tree root activity and a larger share of autotrophic respiration (including rhizosphere respiration) in total soil CO_2 emissions. This is in line with (Pumpanen et al. 2015) who determined the autotrophic respiration at the same site to be highest in late July and early August when also the highest fine root biomass occurs. Also Phillips et al. (2013) measured $\Delta^{14}\text{C}$ - CO_2 soil profiles in a hardwood forest in Wisconsin, USA, and found respired $\Delta^{14}\text{C}$ - CO_2 to decline throughout the summer in intact plots, shifting from an older C composition to younger one. At the same time, respired $\Delta^{14}\text{C}$ - CO_2 from plots excluding living tree roots remained comparatively higher than that in intact plots and thus, we can expect that the decline in the intact plots was caused by the increase in autotrophic respiration having $\Delta^{14}\text{C}$ - CO_2 levels close to ambient. In addition, microbes likely shift sources from older SOM in early summer and spring toward more recently fixed carbon in summer when plants and plant roots are more active. This would influence particularly the lower depths of the profile, where autotrophic respiration is not as large.

On the other hand, we observed an increase in the $\Delta^{14}\text{C}$ values in the surface soil, i.e. in the measured soil emissions towards the end of the summer. This may be partly explained also by root zone and rhizosphere activity. Most of the biologically active organic matter in this forest stand is accumulated in the topsoil, organic soil layers and upper centimeters of the mineral soils, and a large part of the material in the organic layer has accumulated only after the forest stand was regenerated and exposed to prescribed burning in 1962. However, SOM also contains older carbon in recalcitrant fractions, which are resistant to decomposition. This material also contains large amounts of nitrogen, which is bound in SOM matrix and not easily available for the use of living vegetation (Korhonen et al. 2013). In most boreal forests, nitrogen is a growth limiting factor and for acquiring nutrients, trees need to allocate large amounts of carbo-hydrates belowground to microbes e.g. ectomycorrhizal fungi, which are using it for producing extracellular enzymes to degrade SOM (Heinonsalo et al. 2015; Kieloaho et al. 2016). In addition, we showed recently in a microcosm experiment that the mineralization of old SOM was significantly increased in the presence of living root system having active ectomycorrhizal fungi (Lindén et al. 2014). This was observed as increasing age in soil respiration measured with $\Delta^{14}\text{C}$. Thus, it seems evident that the root activity induces decomposition of older SOM fraction in the topmost soil layers that is seen in this study as an increase in $\Delta^{14}\text{C}$ in soil CO_2 emissions even if the root activity in deep soil decreased $\Delta^{14}\text{C}$ throughout the season.

The $\Delta^{14}\text{C}$ values near the soil surface were closer to the atmospheric values than those measured in the chamber i.e. CO_2 emissions. This remains unsolved but may be due to high spatial variation in root biomass and amount of SOM and its quality. Even if the chamber measured the emissions nearby the profile, the CO_2 production rates and the origin might have differed. Another possibility is that atmospheric air entered the profile tube, although the $\delta^{13}\text{C}$ values measured from the tubes (Table 3) do not seem to support this. In addition, the estimated sampling volume of soil air after the CO_2

removal roughly corresponds to a cylinder with 3.3 cm radius around the profile tubes, thus the air collected from the tubes was mostly originating from the organic layer.

The difference in the $\Delta^{14}\text{C}$ values in soil CO_2 in August was significant between day and night. This is likely the result of changes in the shares of R_d and R_r . Savage et al. (2013) showed that autotrophic respiration has a diurnal cycle in a middle aged hardwood forest in Massachusetts, USA, and Kodama et al. (2008) found diurnal changes in the relative share of autotrophic and heterotrophic respiration in a temperate Scots pine forest in Germany. Also, in our study, the decrease in the amount of photosynthates entering the roots, root zone, and rhizosphere activity decreases during night more than the decomposition of SOM. The time delay between photo-synthesis and soil CO_2 efflux depends on the transfer time of carbohydrates in the phloem and most studies conducted by pulse labeling with isotopes have shown time lags from few hours to 5 days between photosynthesis and soil respiration (Mencuccini and Hölttä 2010). However, those results describe the transfer time of actually assimilated C molecules while the changes in photosynthesis rate may also be reflected to R_r through pressure propagation in the phloem with a much shorter time delay (Mencuccini and Hölttä 2010). Also, the size of carbohydrate pool within the plants may affect the magnitude and time delay of changes in soil CO_2 efflux following changes in photosynthesis. Big plants such as trees having larger carbohydrate pools have longer time delay between photosynthesis and belowground respiration while shrub and herbaceous vegetation with smaller structural C pools have shorter time delay. In a recent study (Kulmala L, unpublished results) it was shown that for underground vegetation plants, mainly ericoid dwarf shrubs, the day-night difference in the autotrophic respiration was significant, even after some minutes in darkness the belowground respiration was significantly decreased. This could mean that in our case, ericoid plant species could have an influence on the observed differences in the $\Delta^{14}\text{C}$ values in soil CO_2 in August between day and night. There was also a notable difference in the soil temperature, which likely affects heterotrophic and autotrophic soil respiration differently (Ekblad et al. 2005; Heinemeyer et al. 2007). However, the diurnal cycle of respiration components in boreal Scots pine forest soil still requires further study.

5 CONCLUSIONS

We collected CO_2 from different parts of a forest ecosystem with a portable sampling system using molecular sieve cartridges to selectively trap the CO_2 in the target gas. The results represent the first larger ecosystem-level $\Delta^{14}\text{C}$ dataset from northern Europe.

The atmospheric samples of the present study show a large seasonality in the $\Delta^{14}\text{C}$ - CO_2 in northern Europe. The consistently higher $\Delta^{14}\text{C}$ values at night suggest a significant contribution of ^{14}C -enriched CO_2 that could be observed up to 125 m height. A partial explanation for this is the increased proportion of CO_2 from soil emission due to reduced vertical mixing of air during night, but this alone seems not to be able to explain the large difference compared to daytime values. Further research is needed to explain the observed large diurnal variation in detail.

With the soil air and soil CO₂ efflux $\Delta^{14}\text{C}$ -CO₂ measurements, we observed an increase in the $\Delta^{14}\text{C}$ values in the surface soil CO₂ towards the end of the summer. We attribute this to increasing root activity, which then induces decomposition of older SOM fraction at the site, the conclusion being supported by other studies performed at the site. On the other hand, a decreasing seasonal trend was observed in $\Delta^{14}\text{C}$ for the lower depths in the forest soil, likely caused by an increase in autotrophic respiration up to August.

We also observed a large diurnal variation in soil-air $\Delta^{14}\text{C}$ -CO₂. Here, the $\Delta^{14}\text{C}$ values reflect the changes in the shares of autotrophic and heterotrophic respiration, with the root activity decreasing during the night more than the decomposition of soil organic matter. However, the proportions of $\Delta^{14}\text{C}$ signals from autotrophic or heterotrophic CO₂ sources at the different soil depths are presently unknown. This deserves further research as more knowledge on the priming of SOM and changes in boreal forest soil C pools is necessary for reliable soil C modeling.

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