

# Short-term Fluctuations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of Carbon Dioxide in the Gas Exchange of Norway Spruce Measured with a Tunable Diode Laser Absorption Spectrometer

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## I. Background

Understanding the role of terrestrial ecosystems in governing the isotopic composition of atmospheric  $\text{CO}_2$  requires knowledge of environmental controls of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of  $\text{CO}_2$  in biosphere-atmosphere  $\text{CO}_2$  exchange. Leaf-atmosphere  $\text{CO}_2$  exchange plays an important role in determining  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of ecosystem  $\text{CO}_2$ , as leaves are a  $\text{CO}_2$  sink due to photosynthetic assimilation with associated discrimination against the heavier C and O isotopes, but also a  $\text{CO}_2$  source due to dark and photorespiration as well as the backflow of non-assimilated  $\text{CO}_2$  out of the leaf after exchanging O isotopes with leaf water, which is usually significantly enriched in  $^{18}\text{O}$  compared to soil water due to isotopic fractionation during transpiration. The oxygen isotopic composition of  $\text{CO}_2$  is the pivotal factor for disentangling the  $\text{CO}_2$  component fluxes in ecosystem-atmosphere  $\text{CO}_2$  exchange. However, the disentangling will only succeed if spatial and temporal variability, especially short-term fluctuations, of  $\delta^{18}\text{O}$  of  $\text{CO}_2$  are known and understood. Tunable diode laser absorption spectroscopy (TDLAS) has recently led to great advances in the field of stable isotope research at the plant and ecosystem level, as it allows for measuring stable isotope ratios in trace gases and water with an unprecedented time resolution. Here we show data from laboratory experiments with Norway spruce saplings in closed chambers and a TDL instrument on short-term fluctuations of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of  $\text{CO}_2$  exchanged between needles, soil compartment and cuvette air. The data presented show on the one hand the feasibility of applying the TDLAS technique to leaf-level gas exchange measurements, on the other hand the relevance of short-term fluctuations of  $\delta^{18}\text{O}$  of  $\text{CO}_2$  in plant-atmosphere exchange for assessing the contribution of different sources and sinks to whole ecosystem  $\text{CO}_2$  fluxes.

## II. Experiment

**A. Plant material.** 4-year-old spruce saplings were dug out in a Norway spruce forest (Höglwald close to Augsburg, Germany) in April 2007 with the roots in the original soil, leaving the roots as intact possible. The plants were potted in plastic pots and transferred to the IMK-IFU. During the summer, the plants were kept outside and watered regularly.

**B. Experimental set-up.** The experiments were conducted in September 2007 in an air-conditioned laboratory ( $\sim 21^\circ\text{C}$ ). For each experiment, two spruce saplings were put in gas-tight perspex cuvettes, consisting of a bottom part enclosing the potted roots and a top part enclosing the shoot. Each cuvette was flushed with  $2 \text{ L min}^{-1}$  of purified air with a dewpoint (dp) of  $1^\circ\text{C}$  and with 380 ppm  $\text{CO}_2$  with a  $\delta^{13}\text{C}$  of  $-32\text{‰}$  vs. PDB. Soil temperature was measured with a PT100 sensor; needle temperature was measured with three fine-wire thermocouples attached to the needles. A global radiation pyranometer was placed between both shoot cuvettes. Light (Osram Halogen 60 W) was automatically turned on every day at 5:00 LT and turned off at 21:00 LT. The outlet of each cuvette was connected to the TDL instrument (TGA100A, Campbell Scientific, USA) and an IRGA for  $\text{H}_2\text{O}$  measurements.

**C. Measurements.** After a pre-run for 3–4 days to adapt plants to the new environment, a measurement sequence was started. On 5 consecutive days, environmental parameters were individually changed for a time period of 8 hours, and the response of shoots and roots was measured. During 9:00 and 17:00 LT the plants were exposed to (1) low air humidity (dp  $\approx -30^\circ\text{C}$ ), (2) low light intensity, (3) changing light intensity, (4) low  $\text{CO}_2$  concentration (280 ppm), (5) high  $\text{CO}_2$  concentration (700 ppm). The measurements were followed by a post-run of 3 to 4 days, in which the original conditions were maintained.

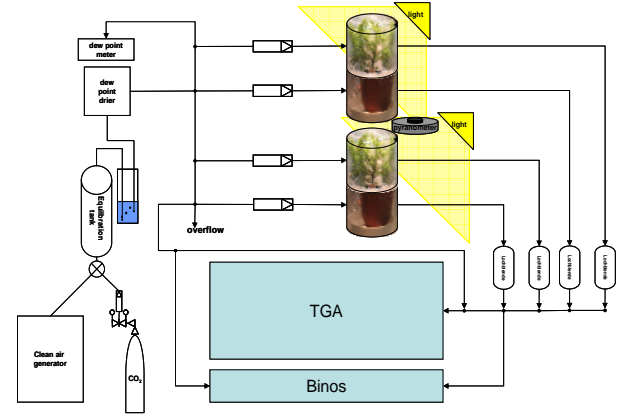


Fig. 1. Scheme of the experimental set-up

## III. Results



Fig. 2. Spruce sapling in the twin cuvette for separate measurements of above- and belowground compartment.

Tab. 1. Time table for the different treatments in the two experiments.

Treatment	Exp. 1	Exp. 2
Pre-run	30 Aug-2 Sep	13-16 Sep
Low $\text{H}_2\text{O}$	3 Sep	17 Sep
Low light	4 Sep	18 Sep
Variable light	5 Sep	19 Sep
Low $\text{CO}_2$	6 Sep	20 Sep
High $\text{CO}_2$	7 Sep	21 Sep
Post-run	8-11 Sep	22-24 Sep

Fig. 3. Time courses of  $\text{CO}_2$  isotopic and  $\text{H}_2\text{O}$  fluxes, of environmental variables and of  $\Delta\delta^{13}\text{C}$  and  $\Delta\delta^{18}\text{O}$  of  $\text{CO}_2$  (= difference between cuvette inlet and outlet) in experiment 1 for shoots (A-E) and roots/soil (F-H).

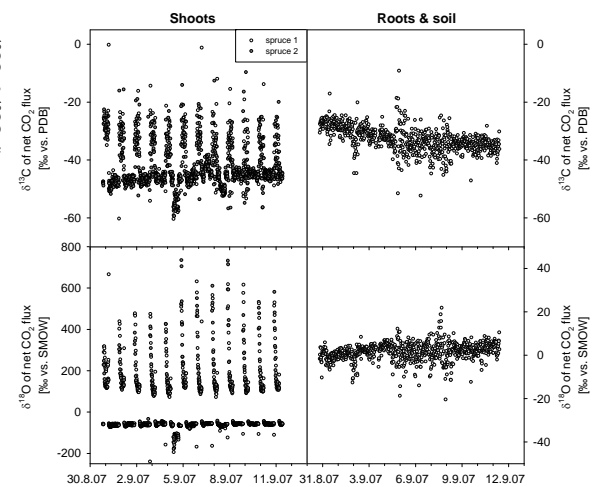
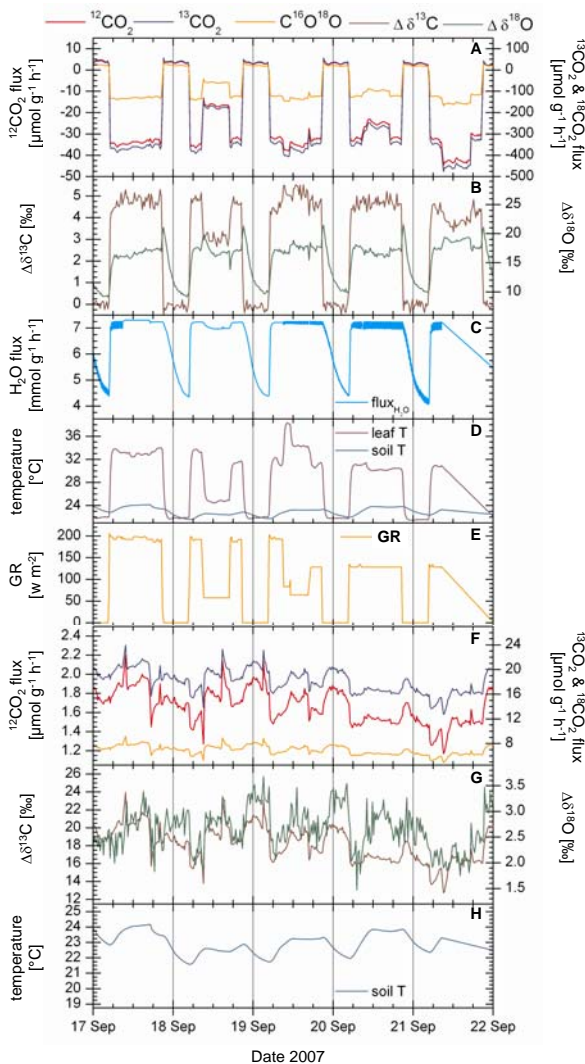


Fig. 4. Calculated  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for the net  $\text{CO}_2$  flux into/out of shoots and roots/soil of the two Norway spruce saplings of experiment 1. In the roots/soil graphs only data for spruce 1 are shown as the soil cuvette became leaky after some days.

## IV. Summary

During steady-state photosynthesis, which was reached one hour after exposing the spruce saplings to full light, isotopic  $^{13}\text{C}$  fractionation during  $\text{CO}_2$  uptake was in the range of 20‰, whereas  $^{18}\text{O}$  fractionation was in the range of 45‰. At night,  $^{13}\text{C}$  fractionation disappeared. In contrast, rapid changes from light to darkness caused a huge increase in  $\delta^{18}\text{O}$  in  $\text{CO}_2$  released by the above-ground plant material of up to 700‰ within a few minutes. In the following eight hours of darkness the  $\delta^{18}\text{O}$  values decreased quickly at first, then more gradually to approx. 50-100‰ enrichment. The only significant treatment effect on both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  was observed during low light intensity, when C and O isotopic fractionation was enhanced (4 Sep in Fig. 4). Elevated  $\text{CO}_2$  treatment had an increasing effect on  $^{13}\text{C}$  discrimination only (7 Sep in Fig. 4). The roots/soil compartment did not show any significant treatment effect nor a visible diurnal cycle in isotopic fluxes.