Diurnal and Seasonal Variation of $\delta^{13}C$ and $\delta^{18}O$ of Carbon Dioxide in a Norway Spruce Forest 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 CO$_2$ requires knowledge of diurnal and seasonal variations of $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ in biosphere-atmosphere CO$_2$ exchange. Tunable diode laser absorption spectroscopy (TDLAS) has recently led to great advances in stable isotope ecosystem research, as it allows for measuring stable isotope ratios in trace gases and water with an unprecedented time resolution also in the field. Here we present several months of data on mixing ratios, $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ at different heights and on respiration rates and $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ from heterotrophic and total soil respiration in a Norway spruce forest (Högwaldl) close to Augsburg, Germany.

II. Method
CO$_2$ mixing ratios as well as $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ were measured with a TGA100A (Campbell Scientific, USA), equipped with sampling manifold, sample pump, flow controller and air dryers. Air was sampled within (2, 8, 15 m) and above the forest canopy (50 m), and total and heterotrophic soil respiration was measured close to the tower with three custom-made stainless steel chambers each, equipped with an inlet, an outlet and a vent to avoid pressure differences between inside and outside (see image at the right). Total and heterotrophic soil respiration chambers were placed on stainless steel rings of 2 and 30 cm depth, respectively, to include or to exclude roots. Rainwater was collected with a funnel and led into the chambers through a small PTFE tube. Inlet air for the chambers was provided from a 50 L buffer tank that was continuously filled by a pump with ambient air taken at 1 m height. Each height and each soil respiration chamber was sampled once within 30 min for 100 sec, of which the last 45 sec were taken as averaging period. Two reference gases (325 and 552 ppm CO$_2$ in air) were sampled every 15 min to monitor instrument drift.

III. Seasonal variation of mixing ratios, $\delta^{13}C$ and $\delta^{18}O$ of ecosystem CO$_2$
Fig. 1. Daily mean values of meteorological parameters (precipitation = daily sum), of CO$_2$ mixing ratios and $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ in and above the canopy of a Norway spruce forest (Högwaldl, Southern Germany) (n = 48, ± s.e.).

Fig. 2. 3-D-fit (Loess) of the dependencies of $\delta^{13}C$ (a) and $\delta^{18}O$ (b) of ecosystem CO$_2$ on global radiation and air temperature at 2 m height.

IV. Seasonal variation of release, $\delta^{13}C$ and $\delta^{18}O$ of soil-respired CO$_2$
Fig. 4. Daily mean values of meteorological parameters (precipitation = daily sum), of total and heterotrophic soil respiration rates and of $\delta^{13}C$ and $\delta^{18}O$ of soil-respired CO$_2$ (n = 48, ± s.e.).

Fig. 5. 3-D-fit (Loess) of the dependencies of $\delta^{13}C$ (a, b) and $\delta^{18}O$ (c, d) of CO$_2$ from total (a, c) and heterotrophic (b, d) respiration on global radiation and air temperature at 2 m height.

V. Diurnal variation of $\delta^{13}C$ and $\delta^{18}O$ of ecosystem CO$_2$
Fig. 6. Mean diurnal variation of mixing ratio, $\delta^{13}C$ and $\delta^{18}O$ of ecosystem CO$_2$ during winter, spring and summer at different heights of the forests (n = 122-184, ± s.e.).

VI. Diurnal variation of $\delta^{13}C$ and $\delta^{18}O$ of soil-respired CO$_2$
Fig. 7. Mean diurnal variation of respiration rate, $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ released from total and heterotrophic soil respiration during spring and summer (n = 122, ± s.e.).

VII. Summary
Ecosystem CO$_2$:
- Mean CO$_2$ mixing ratios were highest in winter and lowest in summer, $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ were lowest in winter and highest in summer
- Winter: $\delta^{13}C$ and $\delta^{18}O$ mirrored well the temporal variation in CO$_2$ mixing ratios and were closely correlated. Diurnal variation of all three variables was low.
- Spring/Summer: decoupling of $\delta^{13}C$ and $\delta^{18}O$, with $\delta^{18}O$ following more closely changes in air temperature and global radiation than $\delta^{13}C$. Diurnal variation was more pronounced, in summer even more than in spring.

Soil respiration:
- The daily maximum of total soil respiration occurred around 7 pm CET, the daily maximum of heterotrophic soil respiration around 4 pm CET
- Spring: Total respiration rates were on average only slightly higher than heterotrophic respiration rates. The $\delta^{13}C_{\text{heterotrophic}}$ was on average c. 1 % higher than the $\delta^{13}C_{\text{total}}$. The $\delta^{18}O_{\text{heterotrophic}}$ was on average c. 3 % lower than the $\delta^{18}O_{\text{total}}$.
- Summer: Total respiration rates were on average almost twice as high as heterotrophic respiration rates. The difference between $\delta^{13}C_{\text{heterotrophic}}$ and $\delta^{13}C_{\text{total}}$ had almost vanished. The difference between $\delta^{18}O_{\text{heterotrophic}}$ and $\delta^{18}O_{\text{total}}$ was reversed, with $\delta^{18}O_{\text{total}}$ being more positive.

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