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Measuring the CO<sub>2</sub> isotopic composition in terrestrial ecosystems: studies in natural and controlled environments

#### Authors

Magda Mandic<sup>1\*</sup>, Nadine Ruehr<sup>2</sup>, Jelka Braden-Behrens<sup>3</sup>, Alexander Knohl<sup>3</sup>

<sup>1</sup>Thermo Fisher Scientific, Bremen, Germany

<sup>2</sup>Karlsruhe Institute of Technology (KIT), Institute of Meteorology and Climate Research - Atmospheric Environmental Research (IMK-IFU), Garmisch-Partenkirchen, Germany

<sup>3</sup>University of Goettingen, Bioclimatology, Faculty of Forest Sciences, Germany

\*magda.mandic@thermofisher.com

#### Introduction

The carbon cycle of plants is highly sensitive to changing environmental conditions. Responses of the two main fluxes, photosynthesis ( $CO_2$  uptake) and respiration ( $CO_2$  loss) including its isotopic signal, can be determined in high resolution by integrating the Thermo Scientific<sup>TM</sup> Delta Ray<sup>TM</sup> Isotope Ratio Infrared Spectrometer (IRIS) in a plant chamber gas exchange setup. This provides detailed information on plant stress responses and allows quantifying mesophyll conductance (i.e, the conductance for  $CO_2$  diffusion from intercellular airspaces to the chloroplast), an important process during photosynthesis (Warren 2006) that is quite challenging to measure.

#### Delta Ray Isotope Ratio Infrared Spectrometer

In the mid-infrared range, absorption lines are about 8000 times stronger than in the near-infrared. This enables a simple direct absorption approach requiring laser path length of 5 m. The raw spectrum is scanned 500 times a second, performing simultaneous measurement of all three isotopologues.



The gas is continuously flowing through the analyzer and has a gas exchange time of about 30 seconds. The Universal Reference Interface (URI) is an integral part of the Delta Ray IRIS solution which includes an internal calibration. In addition the URI can serve as a sample dilution device to match sample gas and reference gas concentrations for ultimate precision measurements using a sample/standard. A micro machined mixing and switching core (MITCH) together with a flow controller dilutes pure  $CO_2$  reference gases to match the sample concentration to minimize the effect of instrument nonlinearity.

The sample gas is dried in the URI to prevent matrix effects and interaction of water and  $CO_2$  (oxygen isotope exchange) with the added benefit of providing dry mole fraction concentration data.







Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer

# Application 1: natural environment (beech forest)

#### Setup and method for natural environment

We measured the  $CO_2$  concentration and its isotopic composition ( $\delta^{18}O$  and  $\delta^{13}C$ ) in nine heights during a three-month measurement campaign in autumn 2015. All nine inlets (in 0.1 m to 45 m height) were measured within 30 minutes and the observed data was used to calculate the isotopic composition of ecosystem  $CO_2$  efflux with a Keeling Plot approach. Our measurements were carried out at a meteorological tower in a managed beech forest in Central Germany (Figure 1).

#### Results for natural environment

The measured nighttime Keeling-Plot intercepts are interpretable as the isotopic composition of night time  $CO_2$  efflux ( $R_{eco}$ <sup>13</sup>C and  $R_{eco}$ <sup>18</sup>O) representing respiration in the case of <sup>13</sup>C and respired  $CO_2$  after the interaction with the ecosystem's water pools in case of <sup>18</sup>O (Figure 2). During our measurement period, the isotopic composition of nighttime  $CO_2$  efflux varied about 6‰ for <sup>13</sup>C and 42‰ for <sup>18</sup>O. In particular,  $R_{eco}$ <sup>18</sup>O decreased by 30‰ after the first snow/frost in autumn 2015 (Figure 3).



Figure 2. Simplified schematic of the monitoring setup in the beech forest



Figure 3. Time series of the isotopic composition of respiration in a managed beech forest<sup>1</sup>

#### Conclusion for natural environment

We captured the temporal variability of the isotopic composition of nighttime  $CO_2$  efflux ( $R_{eco}^{13}C$  and  $R_{eco}^{18}O$ ) over a period of three months, demonstrating the field applicability of the Delta Ray analyzer. Furthermore, the measured temporal variability of  $R_{eco}^{18}O$  indicates, that even short snow or frost events might strongly effect the <sup>18</sup>O composition of nighttime  $CO_2$  efflux at ecosystem scale.

#### **Application 2: controlled environment**

## Automated chamber measurements to quantify carbon isotope ratios during plant gas exchange

Transparent plant chambers (Figure 4) were supplied with air of known  $CO_2$  and  $H_2O$  concentrations at a constant flow rate (chamber in) and plant gas exchange measured (Figure 5). The Delta Ray analyzer was integrated into the measurement set-up using a 3/2 valve that switches between the air entering and leaving the chambers controlled via the Delta Ray Multiport. Because several plant chambers were measured in sequence, trigger signals allowed synchronizing the Delta Ray with the automated chamber program.

Figure 4. Transparent gasexchange chamber with pine seedling





Figure 5. Simplified schematic of the plant gas exchange set-up with the Delta Ray IRIS included. Measurements were conducted in a scientific greenhouse at KIT/IMK-IFU, Garmisch-Partenkirchen, Germany.

#### Results for controlled environment

During night, plants emit CO<sub>2</sub> to the atmosphere, which contains more <sup>12</sup>CO<sub>2</sub> and causes depletion of the  $\delta^{13}$ CO<sub>2</sub> signal in the air. Because the respiratory CO<sub>2</sub> flux of the measured seedlings was rather small, the corresponding change in the isotopic signal was not very distinct (Figure 6); this could be overcome by using smaller flow rates and chamber volumes. During the day, plant CO<sub>2</sub> uptake changes the isotopic signal in the other direction due to preferential uptake of <sup>12</sup>CO<sub>2</sub>, the sample air becomes enriched in <sup>13</sup>C (Figure 6). The photosynthetic discrimination ( $\Delta$ ) can be calculated from the change in the isotopic signal and [CO<sub>2</sub>] following Evans et al (1986).<sup>2</sup> In combination with simultaneously measured plant CO<sub>2</sub> and H<sub>2</sub>O gas exchange, this allows for example to calculate mesophyll conductance (Tazoe et al. 2011).<sup>3</sup>



Figure 6. Time series of averaged  $\delta^{13}CO_2$  for air entering (chamber IN) and air leaving (chamber OUT) a plant chamber. Photosynthetic discrimination is given during daytime, calculated from the differences in  $\delta^{13}CO_2$  and  $CO_2$  concentrations of chamber IN and chamber OUT.

#### Conclusion for controlled environment

The Delta Ray analyzer can be easily integrated into already existing gas exchange experiments to measure the  $\delta^{13}$ C and  $\delta^{18}$ O in CO<sub>2</sub> of several plant chambers sequentially. This results in a high-resolution dataset of plant gas exchange and its isotopic signature, which allows to identify short-term and long-term changes in plant metabolism.

#### References

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