



## New methodology to measure continuously the $\delta^{13}\text{C}$ of soil CO<sub>2</sub> efflux and concentration at different depths by laser spectrometry

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The use of the carbon isotopic composition of CO<sub>2</sub> ( $\delta^{13}\text{C}$ -CO<sub>2</sub>) is a promising tool to improve our knowledge about the mechanisms of CO<sub>2</sub> production within soil. Temporal fluctuations of  $\delta^{13}\text{C}$ -CO<sub>2</sub> soil efflux reflect the influence of climatic and edaphic conditions on (i) partitioning between the respiration sources, (ii) CO<sub>2</sub> production intensity and (iii) CO<sub>2</sub> transport from soil layers to surface. A better understanding of fractionation processes affecting CO<sub>2</sub> during this transport is required to obtain quantitative information about the CO<sub>2</sub> production.

The differences in transport (diffusion, advection) properties between <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub> cause a fractionation during CO<sub>2</sub> transfer from sources to the surface, creating a decrease of  $\delta^{13}\text{C}$ -CO<sub>2</sub> at surface compared to air contained in soil pores. Short-term fluctuations of this apparent fractionation is expected in case of (i) changes in diffusive properties of the soil (soil water content, temperature) and/or (ii) air pressure variations created by turbulence. As a consequence, at this time scale, the difference between  $\delta^{13}\text{C}$ -CO<sub>2</sub> of soil atmosphere and  $\delta^{13}\text{C}$ -CO<sub>2</sub> of soil CO<sub>2</sub> efflux is very variable and difficult to interpret. With tunable diode laser spectrometer (TDLS) it is now possible to measure  $\delta^{13}\text{C}$ -CO<sub>2</sub> with high frequency. TDLS offers then the possibility to quantify  $\delta^{13}\text{C}$ -CO<sub>2</sub> of soil efflux (by coupling with soil chamber, Marron et al. 2009) and soil atmosphere if (i) soil air sampling doesn't disturb the natural environment and (ii) soil air collected is diluted to reduce the high soil CO<sub>2</sub> concentrations (several thousand ppmv) to values measurable by the TDLS (inferior to 1000 ppmv). To solve these limitations, we have adapted a method (Gut et al. 1998) based on the diffusion of soil pore air within a tube through a membrane having a high permeability to gases and being hydrophobic. These tubes have been placed horizontally at different depths in the soil. An air flowing in tubes allows CO<sub>2</sub> circulation up to a diluting system composed by mass flow controllers and free CO<sub>2</sub> injection. The output of this diluting system is coupled to the TDLS and measurements permit then to establish a vertical profile of the isotopic signature of soil CO<sub>2</sub> concentration at hourly scale.

Laboratory tests were performed to prove the absence of membrane influence on the  $\delta^{13}\text{C}$ -CO<sub>2</sub>. The membrane tube has been placed in a chamber where gases with different CO<sub>2</sub> concentration and  $\delta^{13}\text{C}$  were introduced. Results didn't show any fractionation for <sup>13</sup>C during diffusion through the membrane. The  $\delta^{13}\text{C}$  difference between gas inside and gas outside the tube was always inferior to the TDLS precision ( 0.2 ‰ ). In addition, some tests in the field have proved (i) that soil CO<sub>2</sub> concentrations and  $\delta^{13}\text{C}$  are not significantly affected by our system functioning (observation of natural evolution) and (ii) that the values obtained are coherent with results from IRMS ( $R^2=0.98$ ) and with efflux measurements.

This new methodology seems to be a very effective technique for measuring the  $\delta^{13}\text{C}$ -CO<sub>2</sub> vertical profile of soil atmosphere and to understand fractionation processes that occur during this transfer. Moreover, incorporation of data collected using our methodology in mechanistic models of CO<sub>2</sub> transport processes will permit to assess the vertical profile of sources contributions to CO<sub>2</sub> efflux and will provide new insights into soil carbon dynamics.