

## **Compound-specific labelling: a tool to access the mechanisms underlying rapid dynamics in respired $\delta^{13}\text{CO}_2$**

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There is increasing evidence of marked diurnal dynamics in respired  $\delta^{13}\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{res}}$ ) of up to 10% in different plant organs (leaf, stem, roots), ecosystem compounds (foliage, trunk, heterotrophic and autotrophic soil respiration), and nocturnal ecosystem respiration ( $\delta^{13}\text{C}_{\text{R}}$ ). Nevertheless, the underlying mechanisms are still largely unknown. We combined compound specific labelling ( $^{13}\text{C}$ -pyruvate) with a rapid in-tube incubation technique and on-line gas exchange measurements to investigate the causes of diurnal patterns and short-term changes in  $\delta^{13}\text{C}_{\text{res}}$ . Positional labelled pyruvate revealed that apparent fractionation processes in respiratory pathways resulted in marked differences in  $\delta^{13}\text{C}_{\text{R}}$  dynamics between plant functional groups. Large diurnal enrichment of  $\delta^{13}\text{C}_{\text{res}}$  occurred in evergreen, slow growing and aromatic species due to increasing investment of pyruvate derived Acetyl-CoA into secondary metabolism (e.g. defence or aromatic compounds) while the Krebs-cycle activity remained constant. In contrast, fast growing herbs with a high respiratory energy demand exhibited no diurnal changes in  $\delta^{13}\text{C}_{\text{res}}$  or in the carbon flow through the respiratory pathways. Hence, allocation of carbon between respiratory pathways due to different metabolic demands for growth, maintenance or storage can induce large diurnal variations in  $\delta^{13}\text{C}_{\text{res}}$ . No distinct diurnal patterns were found in  $\delta^{13}\text{C}$  of water soluble organic matter in either leaves or roots. On a short-term scale (>30 min) very rapid post-illumination changes in  $\delta^{13}\text{C}_{\text{res}}$  ranging from 2 to 5‰ were not entirely attributable to partitioning between respiratory pathways. Theoretical calculations of potential fractionation effects revealed that a transient decarboxylation of an enriched substrate pool (e.g. malate) or, more probably, Rayleigh fractionation processes of enzymatic reactions in the respiratory pathways could explain these initial post-illumination  $\delta^{13}\text{C}_{\text{res}}$  dynamics. At the ecosystem scale, changes in environmental pattern such as increasing drought markedly influenced the diurnal dynamics of  $\delta^{13}\text{C}_{\text{res}}$  in different ecosystem components. Large variations in  $\delta^{13}\text{C}_{\text{res}}$  of foliage and roots were in accordance with the above described pattern of post-photosynthetic fractionation. Root  $\delta^{13}\text{C}_{\text{res}}$  reflected changes in allocation pattern with increasing. Marked diurnal dynamics in  $\delta^{13}\text{C}_{\text{res}}$  may therefore provide valuable information on both the physiological mechanisms and allocation patterns and may help to give further insights on species and ecosystem scale responses to changes in environmental conditions.