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Tracing CO_2 fluxes and plant volatile organic compound emissions by stable isotopes

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Plant metabolic processes exert a large influence on global climate and air quality through the emission of the greenhouse gas CO_2 and volatile organic compounds (VOCs). Despite the enormous importance, processes controlling plant carbon allocation into primary and secondary metabolism, such as respiratory CO_2 emission and VOC synthesis, remains unclear.

The vegetation exerts a large isotopic imprint on the atmosphere through both, photosynthetic carbon isotope discrimination and fractionation during respiratory CO_2 release ($\delta^{13}C_{res}$). While the former is well understood, many processes driving carbon isotope fractionation during respiration are unknown[1]. There are striking differences in variations of $\delta^{13}C_{res}$ between plant functional groups, which have been proposed to be related to carbon partitioning in the metabolic branching points of the respiratory pathways and secondary metabolism, which are linked via a number of interfaces including the central metabolite pyruvate[2]. Notably, it is a known substrate in a large array of secondary pathways leading to the biosynthesis of many volatile organic compounds (VOCs), such as volatile isoprenoids, oxygenated VOCs, aromatics, fatty acid oxidation products, which can be emitted by plants.

Here we investigate if carbon isotope fractionation in light and dark respired CO_2 is associated with VOC emissions in the atmosphere. Specifically, we hypothesize that a high carbon flux through the pyruvate into various VOC synthesis pathways is associated with a pronounced ^{13}C-enrichment of respired CO_2 above the putative substrate, as it involves the decarboxylation of the ^{13}C-enriched C-1 from pyruvate.

Based on simultaneous real-time measurements of stable carbon isotope composition of branch respired CO_2 (CRDS) and VOC fluxes (PTR-MS) we traced carbon flow into these pathways by pyruvate positional labeling.

We demonstrated that in a Mediterranean shrub the ^{13}C-enriched C-1 from pyruvate is released in substantial amounts as CO_2 in the light. Simultaneously, naturally ^{13}C depleted C-2 and C-3 carbon atoms of the acetyl-moiety are emitted as a variety of VOCs. Moreover, during light-dark transitions leaf emission bursts of the oxygenated metabolite acetaldehyde were observed as part of the PDH bypass pathway in the cytosol[2]. This may be a new piece of evidence for the origin of ^{13}C-enriched $\delta^{13}CO_2$ which is released during Light-Enhanced Dark Respiration (LEDR).

Our study provides the first evidence that the isotopic signature of respired CO_2 is closely linked to carbon partitioning between anabolic and catabolic pathways and plants strategies of carbon investment into secondary compound synthesis.

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