



## Tracing the link between plant volatile organic compound emissions and CO<sub>2</sub> fluxes and by stable isotopes

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The vegetation exerts a large influence on the atmosphere through the emission of volatile organic compounds (VOCs) and the emission and uptake of the greenhouse gas CO<sub>2</sub>. Despite the enormous importance, processes controlling plant carbon allocation into primary and secondary metabolism, such as photosynthetic carbon uptake, respiratory CO<sub>2</sub> emission and VOC synthesis, remains unclear. Moreover, vegetation-atmosphere CO<sub>2</sub> exchange is associated with a large isotopic imprint due to photosynthetic carbon isotope discrimination and <sup>13</sup>C-fractionation during respiratory CO<sub>2</sub> release. The latter has 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. 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 the linkage between VOC emissions, CO<sub>2</sub> fluxes and associated isotope effects based on simultaneous real-time measurements of stable carbon isotope composition of branch respired CO<sub>2</sub> (CRDS) and VOC fluxes (PTR-MS). We utilized positionally specific <sup>13</sup>C-labeled pyruvate branch feeding experiments in the mediterranean shrub (*Halimium halimifolium*) to trace the partitioning of C1, C2, and C3 carbon atoms of pyruvate into VOCs versus CO<sub>2</sub> emissions in the light and in the dark.

In the light, we found high emission rates of a large array of VOC including volatile isoprenoids, oxygenated VOCs, green leaf volatiles, aromatics, sulfides, and nitrogen containing VOCs. These observations suggest that in the light, *H. halimifolium* dedicates a high carbon flux through secondary biosynthetic pathways including the pyruvate dehydrogenase bypass, mevalonic acid, MEP/DOXP, shikimic acid, and fatty acid pathways. Moreover, we found that high VOC emissions were closely related to <sup>13</sup>CO<sub>2</sub> decarboxylation from pyruvate-1-<sup>13</sup>C in the light, while mitochondrial respiration was markedly down-regulated. Moreover, we found that in the dark, VOC emissions dramatically declined while respiration was stimulated with <sup>13</sup>CO<sub>2</sub> emissions under pyruvate-1-<sup>13</sup>C exceeding those under pyruvate-2-<sup>13</sup>C and pyruvate-2,3-<sup>13</sup>C during light-dark transitions. Our observations suggest VOC emissions are associated with significant pyruvate C1 decarboxylation. Moreover, the data suggests that light fundamentally controls the partitioning of assimilated carbon in leaves by regulating the competition for pyruvate between secondary biosynthetic reactions (e.g. VOC production) and mitochondrial respiration. Our investigation provides novel tool to better understand the mechanistic links between primary and secondary carbon metabolism in plants with important implications for a better understanding biosphere-atmosphere exchange of CO<sub>2</sub> and VOCs.

### References

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