



Extreme climatic events induce changes plant carbon allocation into BVOCs and primary metabolism

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Processes controlling plant carbon allocation into primary and secondary metabolism, such as assimilation, respiration and BVOC synthesis are still associated with high uncertainties, particularly in response to environmental stress. In the light of increased extreme climatic events, such as drought spells and heat waves, the plant's ability to rapidly adjust its metabolism and protect the photosynthetic machinery against these stresses will be decisive for its persistence. Plant species have evolved multiple structural and functional adaptations to withstand environmental stress. One mechanism to mitigate stress effects is through the production of volatile isoprenoids, which can enhance thermo-tolerance and protect against excessive radiation. However, extreme climatic events can expose plants to stress levels beyond their acclimation capacity, strongly restricting carbon uptake, with cascading effects on plant and ecosystem functioning. However, *de novo* synthesis of BVOC depends on the availability of carbon, as well as energy provided by primary metabolism. Thus, carbon allocation may compete between primary and secondary metabolism, which are linked via a number of interfaces including the central metabolite pyruvate, the main substrate fueling respiration. Notably, it is a known substrate in a large array of secondary pathways leading to the biosynthesis of BVOCs, such as volatile isoprenoids, oxygenated VOCs, aromatics, fatty acid oxidation products, which can be emitted by plants.

Here we investigate the linkage between BVOC emissions, CO₂ fluxes and associated isotope effects based on simultaneous real-time measurements of stable carbon isotope composition of branch respired CO₂ (CRDS) and VOC fluxes (PTR-MS) in an array of plant species subjected to extreme environment stresses (drought and heat waves). We utilized positionally specific ¹³C-labeled pyruvate branch feeding experiments to trace the partitioning of C1, C2, and C3 carbon atoms of pyruvate into BVOCs versus CO₂ emissions in the light and in the dark.

In the light, we found high emission rates of a large array of BVOC including volatile isoprenoids, oxygenated BVOCs, green leaf volatiles, aromatics, sulfides, and nitrogen containing BVOCs, which were species specific and revealed a high dynamics response towards the extent and duration of stress conditions. These observations suggest that in the light, most of the examined species 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 ¹³CO₂ decarboxylation from pyruvate-1-¹³C in the light, while mitochondrial respiration was markedly down-regulated. In the dark, VOC emissions dramatically declined while respiration was stimulated with ¹³CO₂ emissions under pyruvate-1-¹³C exceeding those under pyruvate-2-¹³C 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 CO₂ and VOCs.