Plant ecophysiology over timescale of decades: Lab experiments, tree rings and isotopes

The IPCC considers the size of the CO_2 fertilization effect as a central uncertainty in Earth system models. Although plant CO_2 responses have been studied in chamber and free-air-CO_2 enrichment experiments, all manipulation experiments suffer from fundamental shortcomings: First, they are limited in time to at most years. Second, they impose a step increase in CO_2, instead of gradual. As a consequence, it is not clear if responses seen in these experiments hold for plants in the field, over decades, and in the presence of acclimation.

Conventional isotope applications – e.g. $\delta^{13}C$ measurements – record how diffusion through stomates versus Rubisco activity fractionate CO_2 with the ^{12}C isotope vs. the ^{13}C isotope. However, it has long been known that ^{13}C abundance varies among individual C positions within metabolites, and the same holds for the hydrogen isotope deuterium (D). Such intramolecular variation reflects other enzyme isotope fractionations and hence carries new information on metabolic regulation. This information can now be accessed since intramolecular isotope variation can be measured by NMR spectroscopy.

Isotope variation at a specific intramolecular site can be traced to branching of metabolic fluxes into different pathways at a particular enzyme. In our research approach, we use manipulation experiments to shift carbon allocation between pathways and relate this to intramolecular isotope shifts. Using material from plant archives such as tree-ring series or herbarium samples, we then detect intramolecular isotope shifts, which can via the established relations be translated into shifts in metabolism. In this way, shifts in metabolism over decades or centuries can be detected. Furthermore, correlations of the shifts with climate variables can indicate plant-climate interactions.

As first example, we observed that an intramolecular D ratio of photosynthetic glucose reflects the ratio of photorespiration to photosynthesis at Rubisco. This dependence was used to reconstruct trends in the photorespiration : photosynthesis ratio over the 20^{th} century. In several C3 plants, the CO_2 increase during the 20^{th} century suppressed photorespiration as quantitatively expected from CO_2 enrichment experiments, without evidence for plant acclimation.

Second, we observed large intramolecular ^{13}C variation in an annually resolved *Pinus nigra* tree ring series. Cluster analysis shows that tree-ring glucose exhibits several independent intramolecular ^{13}C signals, which constitute distinct ecophysiological information channels. The conventional ^{13}C signal - caused by ^{13}C fractionation by stomata/Rubisco and observed in $\delta^{13}C$ - represents just one of these signals. The other signals reflect C allocation downstream of Rubisco, indicating that intramolecular isotope variation: 1) gives insights in metabolic regulation 2) creates records of shifts in metabolism caused by past environmental changes.