Processes controlling the isotopic composition of CO_2 and O_2 in canopy air: A theoretical analysis with some observations in a Sitka spruce plantation

Abstract

This thesis combines a theoretical analysis of processes controlling the isotopic composition of CO_2 and O_2 and observations from a field study with the aim to better understand the mechanisms and coupling of isotopic gas exchange in terrestrial ecosystems. Measurements of photosynthetic discrimination against ^{13}C and ^{18}O during field campaigns in spring and summer 2001 form the experimental basis of this study. Diurnal variations in the isotopic composition of CO_2 in canopy air and the isotopic signatures of foliage and soil respiration were also investigated.

Branch bag measurements revealed pronounced diurnal cycles in photosynthetic discrimination against ^{13}C and ^{18}O, with highest values of $^{13}\Delta$ and $^{18}\Delta$ at dawn and dusk. Predictions of $^{13}\Delta$ and $^{18}\Delta$ were derived using parameters calculated from micro-climate, CO_2 and water flux measurements. Predictions from the commonly applied simple equation underestimated diurnal variations and overestimated diurnal integrals of $^{13}\Delta$. Good agreement of predicted with observed $^{13}\Delta$ values was achieved by combining influences of photosynthesis on the isotopic composition of ambient CO_2 with those of concurrent dark respiration, photorespiration and mesophyll conductance. This required non-steady state modifications to the existing theory of ^{13}C discrimination, including an "apparent fractionation" during day-time dark respiration.

The comparison of predicted values of $^{18}\Delta$ with observations was useful for evaluating different formulations of the ^{18}O enrichment of foliage water at evaporating sites, i.e. the ^{18}O signal that is transferred to atmospheric CO_2. Discrepancies were found between observed $^{18}\Delta$ values and those predicted based on the assumption of evaporating site water at an (instantaneous) isotopic steady state. Better agreement was achieved with the non steady state formulation accounting for a gradual approach towards the isotopic steady state for evaporating site foliage water under natural conditions. These results highlight the limitations of the steady state equation widely used in numerical models.

The oxygen isotopic composition of soil respired CO_2 was found to vary diurnally. This could be explained by a concurrent flux of atmospheric invasion of CO_2 entering and leaving the soil with intermittent equilibration with soil water. When the diurnally variable ratio of the two fluxes was taken into consideration, predicted oxygen isotopic signatures of soil respired CO_2 were in good agreement with measurements.

Stoichiometric ratios of O_2 : CO_2 exchange of photosynthesis and foliage respiration were found to range from 1.1 to 1.2. On the other hand, apparent stoichiometric ratios of canopy gas exchange derived from O_2 and CO_2 abundance changes were virtually indistinguishable from 1.0. This discrepancy indicates that measurements of concurrent changes of O_2 and CO_2 mole fractions in canopy air are not the appropriate method to determine the stoichiometric ratio of the ecosystem gas exchange. Attempts to measure changes in the isotopic signature of O_2 during canopy gas exchange processes showed that experimental uncertainties are currently too large to allow determination of isotopic signatures of O_2 fluxes. The analytical precision required to resolve changes in the isotopic composition of O_2 in canopy air and during chamber experiments was derived from estimates of the expected magnitude of signals.

Scaling the assimilation and respiration fluxes to the canopy level yielded magnitudes and diurnal variations of the net ecosystem exchange of CO_2. Estimates of ecosystem isotopic exchange (isofluxes) were then derived by multiplying the CO_2 fluxes with their respective isotopic signatures. Following this, the reliability of partitioning methods to estimate assimilation rates from canopy fluxes of turbulent CO_2 exchange was assessed. Advantages and disadvantages of three different formulations of partitioning equations were analysed, with two methods relying on canopy integrated values of stomatal conductance and one taking advantage of the coupling of carbon and oxygen isotopic discrimination during photosynthesis. The partitioning study revealed that of the less well known parameters, mesophyll conductance appeared to be crucial for reliable partitioning of the net ecosystem CO_2 exchange. Neglecting the influence of mesophyll conductance on ^{13}C discrimination resulted in overestimation of assimilation rates by up to 30 %.