

Continuous *In Situ* Measurements of Atmospheric O₂ and CO₂ at Harvard Forest

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Poster #146

Presenter: Mark Battle

Motivation

We can determine the fate of carbon removed from the atmosphere by measuring the rates at which atmospheric O₂ and CO₂ are decreasing and increasing, respectively [e.g. Houghton et al., 2001]. Land and ocean fluxes of carbon can be determined from measured O₂ and CO₂ trends according to:

$$f_{land} = -(\beta/\alpha)f_{fuel} + (1/2.49) dO_2/dt$$

$$f_{ocean} = -d[(CO_2/0.471) + (O_2/2.49)]/dt - [(\alpha - \beta)/\alpha]f_{fuel} - f_{cement}$$

where the factor of β (currently 1.44) is the fossil fuel combustion stoichiometry and α (~1.1) is the stoichiometry of terrestrial photosynthesis/respiration [Battle *et al.*, 2000]. The stoichiometries for fossil fuel combustion are relatively well known [Keeling, 1988], but those associated with the land biota carry a larger uncertainty [Severinghaus, 1995]. Improved knowledge of the factor 1.1 will translate directly to more precise values of f_{land} and f_{ocean} .

In addition, we expect the terrestrial biotic stoichiometry to vary spatially and temporally. Time series measurements of the stoichiometry should provide insight into the functioning of the ecosystem and the role of external influences on plant physiology.

Approach

To determine the stoichiometry of terrestrial biotic activity, we use precise, continuous, concurrent measurements of O₂ and CO₂. The slope of a plot of multiple measurements of O₂ vs. CO₂ yields α .

We make our measurements at the Harvard Forest Environmental Measurement Site in central Massachusetts; a mature mixed hardwood and conifer forest (Fig. 1). Air is drawn alternately from intakes at ~8m and 30m, providing measurements within and above the canopy.

Measurements are performed using an instrument whose design (Fig. 2) closely follows that of Stephens *et al.* [2001]. O₂ measurements are made with an Sable Systems Oxzilla II fuel cell analyzer, while CO₂ is measured with a LiCor LI-7000 NDIR analyzer.



Figure 1: The O₂/CO₂ analyzer installed in the Harvard Forest EMS instrument shack.



Figure 3: The suite of standard gases installed in the Harvard Forest EMS instrument shack.

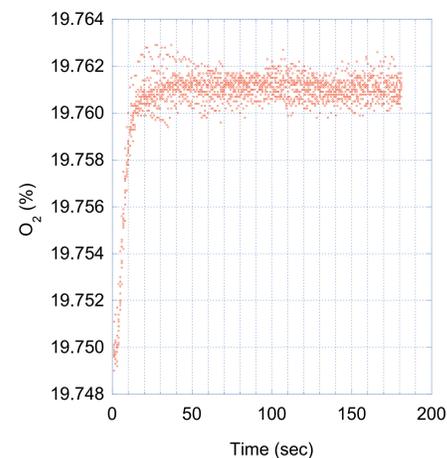


Figure 4: 10 records of the absolute O₂ concentration (uncalibrated) of tank air immediately following the de-energizing of the changeover valve. The plot shows a stabilization after ~40s, with a scatter about the mean of the remaining 140s of data of 0.004 permil (1 σ) for each of the 10 records.

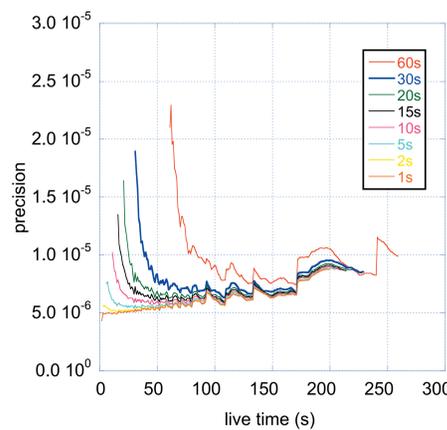


Figure 5: The drift-limited precision, derived from a representative, continuous analysis of unswitched tank air. For a given dead-time (see Fig 4), this plot shows the fractional precision that can be expected from one complete changeover cycle for any specified changeover period. Live time is defined as changeover period - deadtime [Keeling *et al.*, 2004].

Instrument Design

Fundamentally, the instrument is a pair of commercial analyzers, connected in series. All analyses are differential measurements, made against a working tank, which is itself periodically measured against a set of 4 standard tanks, independently calibrated on the WMO CO₂ scale, and the SIO O₂ scale (Fig. 3). All gas streams are cryogenically dried to a dew point of -80C prior to analysis. Flows of both sample and standard gases are maintained at 50scc/m using MKS mass-flow controllers. Pressures in the two gas streams are held within ~1% of each other, and a changeover valve alternately directs the sample and standard gases to the two cells of the O₂ analyzer (Fig. 2).

The instrument is controlled and monitored by a laptop computer running LabView™. The computer logs data, flow rates, temperatures, etc. and controls the choice of sample line (high/low), the changeover valve, and the Valco rotary valves that initiate instrument calibrations using the standard tanks. Remote control of the instrument is achieved using a DSL internet connection and PC Anywhere™.

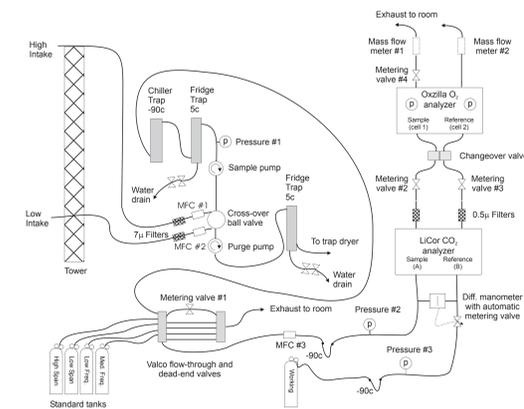


Figure 2: Schematic diagram of the O₂ & CO₂ analysis system currently installed at Harvard Forest. "MFC" indicates a mass flow controller.

Instrument Performance

The when calculating α , the limiting precision is that of the O₂ analyzer. We characterize the performance of our instrument by the deadtime following a changeover (~40s, Fig. 4), the scatter of measurements during live cycles (0.004 permil, Fig. 4) and the drift-limited precision of the instrument (Fig. 5).

Due to an unfortunate lightning strike, we do not yet have data from Harvard Forest.

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