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Measuring ozone fluxes to terrestrial surfaces by eddy co-variance and aerodynamic methods

M. Coyle, E. Nemitz, and D. Fowler
NERC Centre for Ecology & Hydrology

Deposition of ozone to the Earth's surface represents a significant proportion of the ozone losses in the troposphere, accounting for 20% to 30% of the total. While important as a sink, the process is often greatly simplified in global models, yet these are generally used to assess the probable scale of effects on ecosystems and food security. This paper presents a comparison of the two main micrometeorological methods to measure ozone deposition and the analysis of fluxes to quantify stomatal and non-stomatal sinks at the surface.

The first measurements of deposition were made using the flux-gradient methodology ca 1978 and this method was the most commonly used until relatively recently, when economical and reliable fast sensors became more readily available for use in eddy-covariance (EC). The two methods can be summarised as:

- Gradient approach: the ozone concentration is measured at, at least, two heights using a standard ambient ozone analyser alongside turbulence (either from a sonic anemometer or gradient measurements of wind-speed and temperature). The ozone flux is then estimated from the flux-gradient relationship, using Monin-Obukhov similarity theory, where the sampling height is corrected to account for atmospheric stability.
- Eddy-covariance: The flux is calculated from direct measurements of the rapid changes in ozone concentration caused by the turbulent eddies along with the windspeed vector, sensible and latent heat fluxes using a fast ozone sensor, sonic anemometer and water vapour sensor (typically 10-20 Hz)

Both have their advantages and disadvantages but eddy-covariance is preferred on the principle that it is a direct measure of the flux, involving fewer assumptions and corrections. There has been limited development of fast ozone sensors to date and few are commercially available. The most commonly used are based on the chemiluminescence reaction of ozone with coumarin laser dyes (referred to as the Gusten method), although systems using luminol and NO titration have also been operated for some measurement campaigns. The main disadvantages of the Gusten type sensors are: the measurements only give the variations in ozone concentration relative to the average, not the absolute value, so a standard gas analyser has to be run alongside to calibrate the signal; the response is non-linear with an offset from zero and sensitivity decays (again non-linearly) with time adding uncertainly to the final flux estimates; the substrate coated with the ozone sensitive chemicals needs to be replaced, depending on the configuration of the sensor every 4-7 days or once a month.

Ozone fluxes have been measured almost continuously at a fieldsite to the south of Edinburgh since 1995, initially with a 3-height gradient which was upgraded to 5-heights in 2011 and replaced with an Gusten-EC setup in October 2015. The two systems ran in parallel for some time (November 2012 to October 2015), and in spring 2015 a suite of additional Gusten sensors were operated alongside them (25^{th} March – 8^{th} May 2015), providing a useful dataset for analysing the differences in results for each methodology. Errors in the final flux estimates are calculated using the standard methods to combine systematic and random errors in each parameter and the flux. In general, the two systems give similar results in terms of median deposition flux (EC = -0.246 μg m_{-2} s^{-1}; Gradient = -0.222 μg m_{-2} s^{-1} for November 2012 to September 2014) but can differ greatly from hour to hour. The relative error on the EC results tends to be slightly smaller and less variable than that for the gradient. The datasets will presented and the differences examined in detail, allowing us to make recommendations for the future development of ozone flux measurement systems.