Real-time measurements of atmospheric CO_2 isotope ratios (^{13}C, ^{18}O) using mid-IR QCL laser absorption spectroscopy

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The determination of the biogenic and anthropogenic contributions to atmospheric CO_2 levels is extremely important. Different physical and biological processes in the atmosphere enrich and deplete CO_2 isotopologues, for example the carbon isotopic composition of CO_2 produced by respiring organic matter is different to that taken up through photosynthesis. The accurate measurement of different isotopologues of atmospheric CO_2 therefore aids determination of its sources and sinks. While mass spectrometry is the conventional method for the determination of isotopic ratios and indeed provides high precision, it is labor intensive and does not allow real-time continuous measurements to be performed. We present a new method for the accurate measurement of carbon dioxide isotope ratios in real-time using a pulsed, room temperature quantum cascade (QC) laser operating around 4.3 microns to perform infrared absorption spectroscopy. We can measure both carbon and oxygen isotope ratios simultaneously using three closely spaced absorption lines around 2310 cm^{-1} corresponding to $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $C^{18}O^{16}O$. The instrument is also portable, does not require pre-concentration of samples, and can operate unattended. The response of the instrument is currently 10-20 seconds, and using the Allen variance technique we determine a precision of 0.04 and 0.01 per mil for 2 and 130 seconds averaging time respectively. The CO_2 ^{13}C and ^{18}O isotope ratios of sample and reference gases (400 and 440 ppm CO_2) were measured alternatively over 18 hours. Histograms of the replicate measurements indicated good instrument stability with FWHM of 0.1 per mil. Current improvements to the long term pressure and temperature control of the system will improve these values, especially the response of the instrument which should reach 1 second.

Preliminary measurements on ambient air in Higashiyama campus of Nagoya University over two days in October 2007 demonstrated the instruments ability to measure both ^{13}C and ^{18}O CO_2 isotope ratios of ambient air in real time, a diurnal variation in the CO_2 mixing ratio and isotope ratios was observed, with the possible effect of traffic emissions in the early morning and late afternoon.

New ambient CO_2 measurements will be presented along with instrument specifications. This instrument will be suitable to measure CO_2 isotope ratios for a number of applications including future eddy covariance flux measurements.