Geophysical Research Abstracts
Vol. 19, EGU2017-10986, 2017
EGU General Assembly 2017

Real time, ambient air laser monitor and a novel preconcentrator for CO isotopologues

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As a key reactive species in oxidative pathways in the atmosphere, carbon monoxide (CO) has an important role in global atmospheric chemistry. Carbon monoxide has a relatively short lifetime (2 months) in the atmosphere and a number of sources, leading to spatial and temporal variations in CO concentration. Also, the reaction of OH with CO is the major sink for both OH and CO, thus the CO reaction with OH is crucial in determining the oxidative capacity of the atmosphere. Changes in CO levels therefore have a significant impact on other atmospheric gases, making it critical to better understand its sources and sinks.

Current estimates of the sources and sinks of CO can be improved by inclusion of high-frequency, high-precision global measurements of the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotopic ratios of atmospheric carbon monoxide, since the various sources and the OH sink have different isotopic signatures. A continuous monitor of CO isotopologue ratios will provide powerful constraints on the various sources and the atmospheric sink in both the short and long term.

We present a new field deployable dual laser isotope monitor based on Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) for the simultaneous, sensitive, real time measurement of isotopologues of carbon monoxide. Excellent precisions of 0.5 per mil for $\delta^{13}CO$ and 3.0 per mil for $\delta C^{18}O$ have been achieved with a few minutes averaging in ambient measurements without preconcentration. To achieve higher precision, we have developed a novel preconcentration method for separating CO from air without isotopic fractionation. This also enabled meaningful measurements of $C^{17}O$ in ambient air samples. This automated system was integrated with the dual laser instrument. The integrated instrument measured $\delta^{13}CO$, $\delta C^{17}O$ and $\delta C^{18}O$ with a measurement interval of 20 minutes. Variability of the isotopic ratios in ambient air was observed over several days in preliminary experiments sampling rooftop air at Aerodyne Research.