Uncertainties and Challenges in Long-term d13C Measurements of Atmospheric CO_2 at Canadian Baseline Stations: Can Human induced CO_2 Detected & Quantified at Regional Scale?

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Detecting and quantifying human induced Greenhouse Gases (GHGs) and air pollutants in ambient air are important to air quality and climate change research, particularly for addressing the issue of the continued increase of atmospheric CO_2. Isotope compositions are widely used as tracers in source identifications and attributions for atmospheric CO_2. Due to a long life-time ($\sim$ 200 years) of CO_2 and its exchanges in various processes with natural systems, the signal of human-induced CO_2 and its carbon isotopic compositions in the atmosphere is small. It is very challenging to quantify annual change rates and attribute those changes into human-induced and natural portions within an accepted range of uncertainty at global/regional scales. Thus, the requirements for the precision and accuracy in CO_2 and related tracers measurements, including δ^{13}C & δ^{18}O in CO_2, are very rigid (by WMO measurement community).

To conduct attribution studies, the annual mean changes in both CO_2 and δ^{13}C have to be determined precisely. It is known that the average annual global change rate of δ^{13}C is very small, $\sim$ 0.028 permil in δ^{13}C per year. To identify the small change accurately, it is required that the annual changes of isotope standards are much less than 0.028 permil. To anchor individual isotopic measurements of flask-air CO_2 to the primary VPDB scale (i.e. traceability), various forms of lab-standards can be used, such as pure CO_2, air CO_2 and CO_2 derived from pure carbonates. Usually, more than one level (e.g. primary, secondary and etc.) and more than one form of standards are used in individual labs. However, it is very challenging to ensure that the uncertainties of those standards over one year are less than 0.028 permil (i.e. the stability of the standard is within $\sim$ 0.02 permil) since ensuring that a lower level standard is stable/ or not drifting within $\sim$ 0.02 permil requires a higher level standard with a better stability than 0.02 permil. Ultimately, it is imperative to ensure that the primary standard, NBS19 is stable with an annual change rate less than 0.02 permil, in another words, to assess the uncertainty of NBS19 pure CO_2 productions.

How precise can the δ^{13}C of NBS19 pure CO_2 be produced? How well do we know the uncertainty anchoring each individual δ^{13}C measurement in atmospheric CO_2 to the primary standard? In this work, the long-term CO_2 isotope measurements ($\sim$ 10 years) at a Canadian baseline site (i.e., Alert/GAW station), the annual calibration records (i.e., secondary carbonate standards directly by NBS19CO_2) over 7 - 10 years and the measurements for air standards over 5 years will be presented. The annual changes/drifts for the related standards will be determined. The principle and a method for deriving the uncertainty for anchoring individual δ^{13}C measurements in flask-air CO_2 to the primary standard will be illustrated and discussed using those data. Even though taking account of the uncertainty of the traceability, it is likely that the annual mean changes of δ^{13}C measurements at Canadian baseline stations can be detected and attributed. An example using the detected annual mean changes (both CO_2 and δ^{13}C) to apportion the human-induced and natural contributions at a regional scale level will be discussed.