PRELIMINARY CONSTRAINTS ON FOSSIL-FUEL CO_2: COMPARISON OF TRACERS $^{14}CO_2$, CO AND SF_6

J.C. Turnbull[1], J.B. Miller[2,3], S.J. Lehman[1], R.J. Sparks[4], J. Southon[5], and P.P. Tans[3]

[1]*INSTAAR, University of Colorado, Boulder, CO 80309-0450; jocelyn.turnbull@colorado.edu*
[2]*Cooperative Institute for Research in Environmental Sciences, Univ. of Colorado, Boulder, CO 80309*
[3]*NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO 80305*
[4]*Rafter Radiocarbon Laboratory, Lower Hutt, New Zealand*
[5]*University of California at Irvine, Irvine, CA 92697*

ABSTRACT

We use the theoretically ideal tracer $^{14}CO_2$ to estimate the fossil fuel CO_2 enhancement in boundary layer air at two sites in New England and Colorado. Improved $\Delta^{14}C$ measurement precision of 1.6-2.6‰ provides fossil fuel CO_2detection capability of 0.8-1.5 ppm. Using the tracers CO and SF_6, we obtain two additional independent estimates of the fossil fuel CO_2 component, and we assess the biases in these methods by comparison with the $^{14}CO_2$-based estimates. Large differences are observed between the SF_6-based estimates and those from the $^{14}CO_2$ and CO methods. The CO-based estimates show seasonally coherent biases, underestimating fossil fuel CO_2 in winter and overestimating in summer.

INTRODUCTION

Precise measurement of atmospheric CO_2 concentrations can be used to estimate the net surface exchange flux of carbon, but cannot distinguish CO_2 contributions from net biological exchange and combustion of fossil fuels. Separation of the two fluxes can be obtained by estimating the (relatively large) fossil fuel component from economic emissions inventories. Any uncertainty in these inventories, which can be expected to increase with decreasing temporal and spatial scales of analysis, will translate directly to a bias in the magnitude (and, possibly, sign) of the biological exchange signal. Independent estimates of fossil fuel CO_2 emissions with quantifiable uncertainties are therefore needed.

$^{14}CO_2$ provides a theoretically ideal tracer for fossil fuel derived CO_2 (C_{ff}) because ^{14}C is entirely lost to radioactive decay in fossil fuels, whereas all other CO_2 sources contain ^{14}C in concentrations close to that of ambient air [*Levin et al., 2003; Meijer et al., 1996*]. The indirect tracers CO and SF_6 can also provide estimates of C_{ff}, by assuming a correlation (R_T) between emissions of the tracer CO or SF_6 and C_{ff} [*Potosnak et al., 1999; Bakwin et al., 1998*]. While measurements of these tracers may be more precise than for $^{14}CO_2$, uncertainty and variability in R_T may reduce the accuracy of the C_{ff} estimate. In the case of CO, other sources and sinks may also bias the results. We assess the biases in these methods by comparison with the $^{14}CO_2$-based C_{ff} estimates.

RESULTS

We estimate the C_{ff} contribution during winter pollution events at Niwot Ridge, Colorado using the $^{14}CO_2$, CO and SF_6 methods. The $^{14}CO_2$ method appears to accurately detect C_{ff}, whereas both the CO and SF_6 methods underestimate C_{ff} by several ppm.

We calculate the boundary layer C_{ff} using the $^{14}CO_2$, CO and SF_6 methods in 17 samples collected over New England from January to December 2004 (Fig. 1a). SF_6-based results are significantly more variable and at times imply implausibly large boundary layer enrichments. Although broadly consistent, differences between the $^{14}CO_2$- and CO- based results are significant with respect to the magnitude of the seasonal variation in the biological exchange of carbon. We infer the biological enrichment or depletion of CO_2 in the boundary layer (C_{bio}) as:

$$C_{bio} = C_{obs} - C_{bg} - C_{ff}$$

where C_{bl} and C_{ft} are the measured boundary layer and free troposphere CO_2 concentrations. When C_{ff} is assumed to be zero (black squares in fig. 1b), we obtain a reasonable seasonal cycle in C_{bio}, but there is considerable scatter, possibly because known variability from the fossil fuel component has not been accounted for.

Using $^{14}CO_2$ to determine and remove C_{ff} yields a seasonal cycle in C_{bio} that is reasonable, with small winter respiration release and strong summer uptake of CO_2. For some spring and fall sampling dates, the $^{14}CO_2$ method allows us to identify net uptake of CO_2, whereas net release would have been assumed without correcting for the C_{ff} estimate from $^{14}CO_2$. Correcting for C_{ff} using the CO method also gives a reasonable seasonal cycle in C_{bio}, but displays coherent seasonal bias relative to the $^{14}CO_2$ method (Fig. 1c). The summertime bias is likely related to summertime production of CO by hydrocarbon oxidation and forest fires.

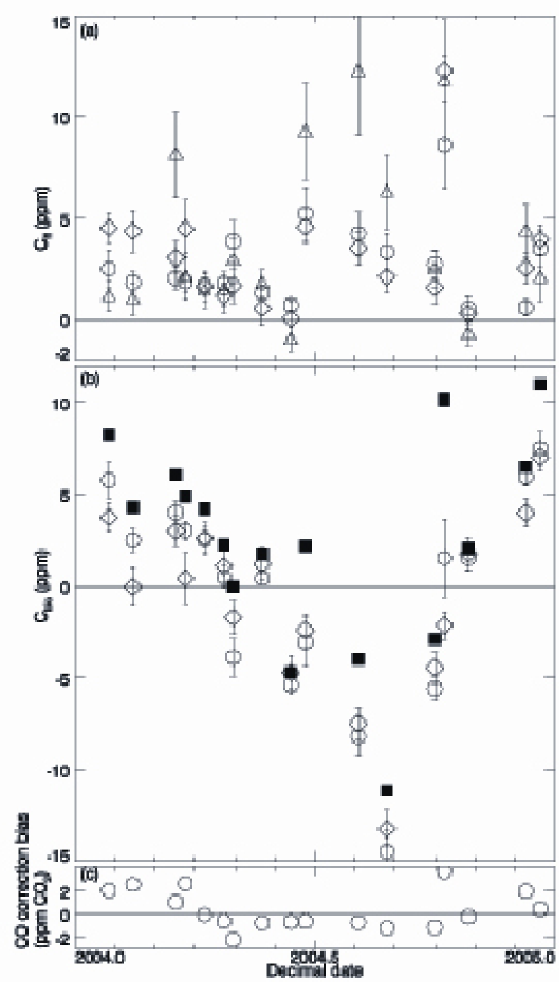

Fig. 1. Boundary layer measurements over New England at either HFM (42°32'N, 72°10'W) or NHA (42°57'N, 72°37'W): (a) C_{ff} determined using the $^{14}CO_2$ method (diamonds), CO method (circles) and SF_6 method (triangles); (b) C_{bio} calculated using the $^{14}CO_2$ method, CO method, and assuming no fossil fuel component (black squares); (c) The bias in the CO method relative to the $^{14}CO_2$ method. Error bars are 1σ errors including measurement precision and 25% uncertainty in R_T for the CO and SF_6 methods.

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