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$_2$ detection 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.

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:
\[ C_{\text{bio}} = C_{\text{obs}} - C_{bg} - C_{ff} \]

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 \(^{14}\text{CO}_2\) 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 \(^{14}\text{CO}_2\) 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 \(^{14}\text{CO}_2\). 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 \(^{14}\text{CO}_2\) method (Fig. 1c). The summertime bias is likely related to summertime production of CO by hydrocarbon oxidation and forest fires.

REFERENCES


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 \(^{14}\text{CO}_2\) method (diamonds), CO method (circles) and SF\(_6\) method (triangles); (b) \( C_{bio} \) calculated using the \(^{14}\text{CO}_2\) method, CO method and assuming no fossil fuel component (black squares); (c) The bias in the CO method relative to the \(^{14}\text{CO}_2\) method. Error bars are 1σ errors including measurement precision and 25% uncertainty in \( R_{T}\) for the CO and SF\(_6\) methods.