Does vapor pressure deficit drive the seasonality of $\delta^{13}C$ of the net land-atmosphere CO$_2$ exchange across the United States?

B. Raczka$^1$, S. C. Biraud$^2$, J. R. Ehleringer$^1$, C.-T. Lai$^3$, J. B. Miller$^4,5$, D. E. Pataki$^1$, S. R. Saleska$^6$, M. S. Torn$^7$, R. Wehr$^6$, and D. R. Bowling$^1$

Abstract

The seasonal pattern of the carbon isotope content ($\delta^{13}C$) of atmospheric CO$_2$ depends on local and nonlocal land-atmosphere exchange and atmospheric transport. Previous studies suggested that the $\delta^{13}C$ of the net land-atmosphere CO$_2$ flux ($\delta_{\text{source}}$) varies seasonally as stomatal conductance of plants responds to vapor pressure deficit of air (VPD). We studied the variation of $\delta_{\text{source}}$ at seven sites across the United States representing forests, grasslands, and an urban center. Using a two-part mixing model, we calculated the seasonal $\delta_{\text{source}}$ for each site after removing background influence and, when possible, removing $\delta^{13}C$ variation of nonlocal sources. Compared to previous analyses, we found a reduced seasonal (March–September) variation in $\delta_{\text{source}}$ at the forest sites (0.5‰ variation). We did not find a consistent seasonal relationship between VPD and $\delta_{\text{source}}$ across forest (or other) sites, providing evidence that stomatal response to VPD was not the cause of the global, coherent seasonal pattern in $\delta_{\text{source}}$. In contrast to the forest sites, grassland and urban sites had a larger seasonal variation in $\delta_{\text{source}}$ (5‰) dominated by seasonal transitions in C$_3$/C$_4$ grass productivity and in fossil fuel emissions, respectively. Our findings were sensitive to the location used to account for atmospheric background variation within the mixing model method that determined $\delta_{\text{source}}$. Special consideration should be given to background location depending on whether the intent is to understand site level dynamics or regional scale impacts of land-atmosphere exchange. The seasonal amplitude in $\delta^{13}C$ of land-atmosphere CO$_2$ exchange ($\delta_{\text{source}}$) varied across land cover types and was not driven by seasonal changes in vapor pressure deficit. The largest seasonal amplitudes of $\delta_{\text{source}}$ were at grassland and urban sites, driven by changes in C$_3$/C$_4$ grass productivity and fossil fuel emissions, respectively. Mixing model approaches may incorrectly calculate $\delta_{\text{source}}$ when background atmospheric observations are remote and/or prone to anthropogenic influence.

1. Introduction

The land-atmosphere exchange of carbon has an important influence on the magnitude and spatiotemporal pattern of both the mole fraction and $\delta^{13}C$ of atmospheric CO$_2$. The global average atmospheric CO$_2$ mole fraction increased by ~40% from 1850 to 2016 (from 280 to 400 ppm) primarily driven by fossil fuel emissions. Concurrently, the $\delta^{13}C$ of atmospheric CO$_2$ ($\delta_{\text{atm}}$) has decreased [Rubino et al., 2013] and continues to decrease at a rate of ~0.25‰ per decade in the northern midlatitudes [Bowling et al., 2014]. The $\delta_{\text{atm}}$ is also influenced by land and ocean processes [Randerson et al., 2002; Alden et al., 2010], predominantly through photosynthetic discrimination by land plants [Farquhar et al., 1989] (vegetation assimilates 12CO$_2$ at a higher rate than 13CO$_2$ and also because the $\delta^{13}C$ of the carbon absorbed and released by the land and ocean systems, respectively, are in isotopic disequilibrium. The terrestrial biosphere discriminates against 13CO$_2$ ($\delta^{13}C$ hereafter) relative to 12CO$_2$ ($\delta^{12}C$ hereafter) by 12–16‰ on average [Fung et al., 1997; Suits et al., 2005], which is much larger than the discrimination by the net ocean exchange (2.0‰). This difference in discrimination allows the use of observations of $\delta_{\text{atm}}$ to constrain the global carbon budget and partition the global carbon uptake between the land and ocean through atmospheric inversion modeling [Ciais et al., 1995; Battle et al., 2000; Alden et al., 2010]. Many of these modeling approaches, however, assume that the photosynthetic
discrimination by land plants is constant, despite evidence to the contrary [e.g., Randerson et al., 2002; Scholze et al., 2003; van der Velde et al., 2013]. Relatively small uncertainties in photosynthetic discrimination can introduce large uncertainties in inferred carbon uptake. For example, just a 1‰ decrease in photosynthetic discrimination results in a direct increase in the inferred land uptake of 0.2 Pg C yr⁻¹ [Still et al., 2003a]. Uncertainty in discrimination can also indirectly influence land-ocean carbon partitioning through the inferred land isotopic disequilibrium, which is important for balancing the global isotopic carbon budget. In this case, just a 0.1‰ decrease in photosynthetic discrimination can affect the inferred land uptake by 0.7 Pg C yr⁻¹ [Randerson, 2005]. These uncertainties in the inferred land uptake are as much as 27% of the total annual carbon uptake by the global land carbon sink [Le Quéré et al., 2015]. Therefore, the uncertainty of terrestrial $^{13}$C discrimination inhibits an accurate diagnosis of the atmospheric and land conditions that impact the global carbon budget.

The terrestrial $^{13}$C discrimination is primarily influenced through isotopic fractionation during $C_3$ photosynthesis [Farquhar et al., 1989]. Photosynthesis dominates global land-atmosphere exchange of carbon during the summer causing the troposphere to become enriched in $^{13}$C ($\delta_{\text{atm}}$ less negative) as a result of net carbon uptake by plants, followed by a decrease in $\delta_{\text{atm}}$ (more negative) during the winter due to a net release of depleted, plant-derived carbon. The $\delta^{13}$C of respiration ($\delta_{\text{resp}}$) is similar but not identical to photosynthetic uptake ($\delta_{\text{photo}}$) because of age-driven isotopic disequilibrium (Suess effect) and post-photosynthetic fractionation processes [Bowling et al., 2008; Brüggemann et al., 2011]. The magnitude of photosynthetic discrimination is controlled by the balance of CO₂ supply and demand in the chloroplast. The supply of CO₂ depends primarily on stomatal conductance, which responds to environmental conditions. In general, plants reduce their stomatal conductance during environmental conditions unfavorable for photosynthesis, and thus, $\delta_{\text{photo}}$ responds to atmospheric moisture deficit, soil water content, precipitation, and nutrient availability [Farquhar et al., 1989; Bowling et al., 2008; Cernusak et al., 2013].

An improved understanding of environmental conditions that influence stomatal conductance and $\delta_{\text{source}}$ (through $\delta_{\text{photo}}$) is important for the parameterization of terrestrial carbon models. For example, the coupling of the carbon and water cycles through plant stomata has been represented through the Ball-Berry [Ball et al., 1987] and Leuning [Leuning, 1995] models. Previous site-level studies have demonstrated that the Leuning model outperforms the Ball-Berry model due to the dependence upon vapor pressure deficit (VPD) and relative humidity of air for each model, respectively [e.g., Nijs et al., 1997; Way et al., 2011; Prentice et al., 2014]. In addition, global land surface modeling has suggested that the Leuning model better represents seasonal changes in $\delta_{\text{source}}$, as compared to the Ball-Berry [Ballantyne et al., 2011]. It was unclear, however, whether this improved performance was a result of the mechanistic linkage between stomatal conductance and VPD or from including more parameters within the model. This distinction can provide an important difference for carbon cycle projections given the diverging paths of VPD and relative humidity under future climate scenarios [Sato et al., 2015] and the impact on the strength of the terrestrial carbon sink [Arora et al., 2013]. Furthermore, terrestrial carbon models have been parameterized with stable carbon isotopes and have showed promise in calibrating parameters that influence stomatal conductance (e.g., stomatal slope) [Aranibar et al., 2006; Raczka et al., 2016]. Thus, the estimation of seasonal changes in $\delta_{\text{source}}$ has the potential to provide an important test and guidance for terrestrial carbon model development.

One approach to understand land-atmosphere exchange of $\delta^{13}$C ($\delta_{\text{source}}$) takes advantage of site-level measurements of atmospheric CO₂ and $\delta_{\text{atm}}$. This approach estimates $\delta_{\text{source}}$ through a two-part mixing model that assumes that the local atmospheric CO₂ mole fraction and $\delta_{\text{atm}}$ are from a combination of background (nonlocal) and local sources. Several types of mixing models have been developed; however, the Miller-Tans plot [Miller and Tans, 2003] with background correction [Ballantyne et al., 2010] is generally the most robust method, capable of accounting for time-varying background influences. All mixing models have limited applicability to when there is a single, well-mixed local net source or sink [Vardag et al., 2016].

Mixing models have been used to identify several factors that contribute to variation in $\delta_{\text{resp}}$. First, short-term changes in environmental conditions have been linked to changes in $\delta_{\text{resp}}$. For example, stomatal response to VPD influences the $\delta^{13}$C of soil [Ekblad and Högborg, 2001] or whole-forest respiration, and in some conifer forests, there is a 10–15 day lag time for the highest correlation between VPD and $\delta_{\text{resp}}$ [Bowling et al., 2002]. Soil moisture has been found to be correlated with $\delta_{\text{resp}}$ at Howland and Wind River sites [Lai et al., 2005] and precipitation at sites across North and South America [Pataki et al., 2003b]. Linkages between
VPD and soil moisture with $\delta_{\text{resp}}$, however, are not universal [Schaeffer et al., 2008; Riveros-Iregui et al., 2011; Shim et al., 2011; Bowling et al., 2014]. The cause of seasonal variation of $\delta_{\text{source}}$ is less well understood, but it has been hypothesized that the coherent seasonal pattern in $\delta_{\text{source}}$ among midlatitude sites (coniferous forest, deciduous forest, and crops) inferred from an atmospheric mixing model is driven by stomatal response to seasonal variation in VPD [Ballantyne et al., 2010, 2011].

Second, strong seasonality in $\delta_{\text{source}}$ occurs in mixed C$_3$/C$_4$ grasslands, caused by a seasonal transition from primarily C$_3$ photosynthesis during spring/early summer to a varying mixture of C$_3$/C$_4$ photosynthesis during mid/late summer [Lai et al., 2003; Still et al., 2003b; Torn et al., 2011]. Grasslands are prevalent worldwide [Collatz et al., 1998] and thus an important contributor to the seasonality of global $\delta_{\text{atm}}$ [Fung et al., 1997; Conte and Weber, 2002; Still et al., 2003a]. Although natural mixtures of C$_3$/C$_4$ grasslands have become increasingly rare due to land-use change from agriculture [Torn et al., 2011], the regional planting of a combination of C$_3$/C$_4$ crops (corn (C$_4$), soybean (C$_3$), and wheat (C$_3$)) likely have similar impacts upon regional $\delta_{\text{source}}$ and $\delta_{\text{atm}}$ due to atmospheric mixing. For example, an analysis of tall tower observations taken over fields of mostly corn and soybeans in the upper Midwest found that $\delta_{\text{atm}}$ was dominated by C$_3$ discrimination during the spring and fall; however, C$_4$ species accounted for as much as 45% of the gross photosynthetic flux during summer [Griffis et al., 2010]. Third, urban areas can impose a local seasonal cycle in $\delta_{\text{source}}$ reflecting the type and emission rate of fossil fuels. For example, the seasonal cycle of $\delta_{\text{source}}$ in Salt Lake City is influenced by high emissions from natural gas combustion during winter (for heating), by plant and soil CO$_2$ exchange during summer, and by petroleum combustion (transportation) year-round [Pataki et al., 2003a, 2007]. In this case, the depleted $\delta^{13}$C signature of CO$_2$ from combustion of natural gas as compared to petroleum and biogenic respiration creates a seasonal $\delta_{\text{source}}$ that is relatively depleted in the winter and enriched during the summer. These three mechanisms—VPD influencing stomatal conductance and $\delta_{\text{photo}}$, C$_3$/C$_4$ grassland transition, and fossil fuel emission with seasonal changes in fuel type—each, alone, or in combination, contribute to observed seasonal changes in both $\delta_{\text{source}}$ and $\delta_{\text{atm}}$. The relative importance of these three mechanisms both locally and regionally remains unclear.

Here we analyze atmospheric observations from seven sites within the United States to determine the seasonality of $\delta_{\text{source}}$. Departing from previous studies, we account for nonlocal influences by choosing a background location that is nearly collocated with the site of interest to isolate the local (~1–10 km$^2$) $\delta_{\text{source}}$ signal. We examine to what extent the choice of background location and temporal resolution affect $\delta_{\text{source}}$. We choose sites that together provide over 50 site-years of atmospheric observations and include coniferous forest, deciduous forest, grassland, and an urban site to understand how land type influences $\delta_{\text{source}}$ and $\delta_{\text{atm}}$. Specifically, we test the hypothesis of Ballantyne et al. [2011] that the coherent seasonal cycle in $\delta_{\text{source}}$ among midlatitude sites is driven primarily by plant stomatal conductance responding to seasonal changes in VPD. Finally, we use the isoforcing, a function of the site-level $\delta_{\text{source}}$ and the net carbon exchange (NEE), to determine what factors are most responsible for the seasonal change in the $\delta^{13}$C of net land-atmosphere exchange of CO$_2$ and how this may impact $\delta_{\text{atm}}$.

2. Materials and Methods

This section describes the observation sites (section 2.1) and observation protocol (section 2.2) used for this analysis and a description of the methods used to calculate the $\delta_{\text{source}}$ (section 2.3) and isoforcing (section 2.4) for each site. This is followed by a description of the method used to diagnose the influence of VPD (section 2.5) and anthropogenic trace gases (section 2.6) on $\delta_{\text{source}}$. A complete list of variables is provided in Table 1.

2.1. Site Description

The sites (Table 2) represent a variety of land cover types including evergreen forests (US-NR1, Wind River, Howland), deciduous forests (Harvard), grasslands (SGP, Rannells), and an urban area (Salt Lake City). US-NR1 is a subalpine conifer forest located in the Rocky Mountains of Colorado. The site is a secondary growth forest and consists of lodgepole pine (Pinus contorta), Engelmann spruce (Picea engelmannii), and subalpine fir (Abies lasiocarpa) [Monson et al., 2002; Hu et al., 2010a]. The Wind River site is located within Gifford Pinchot National Forest, Washington, and is an old-growth temperate conifer forest dominated by Douglas fir (Pseudotsuga menziesii) and western hemlock (Tsuga heterophylla) [Shaw et al., 2004; Unsworth et al., 2004].
Table 1. List of Variables Used

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit or Unit Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_a</td>
<td>Atmospheric mole fraction of CO₂ at site location</td>
<td>ppm</td>
</tr>
<tr>
<td>C_w</td>
<td>Atmospheric concentration of CO₂</td>
<td>μmol m⁻³</td>
</tr>
<tr>
<td>C_bg</td>
<td>Atmospheric mole fraction of CO₂ at background location</td>
<td>ppm</td>
</tr>
<tr>
<td>C_source</td>
<td>Local contribution (addition or removal) of atmospheric CO₂</td>
<td>ppm</td>
</tr>
<tr>
<td>C_smoothbg</td>
<td>Background CO₂ using smoothed method</td>
<td>ppm</td>
</tr>
<tr>
<td>C_nonsmoothbg</td>
<td>Background CO₂ using nonsmoothed method</td>
<td>ppm</td>
</tr>
<tr>
<td>δ³¹C</td>
<td>¹³C isotope composition (relative to VPDB)</td>
<td>‰</td>
</tr>
<tr>
<td>δ atm</td>
<td>¹³C of atmospheric CO₂ at site location</td>
<td>‰</td>
</tr>
<tr>
<td>δ a</td>
<td>¹³C of CO₂ at site location</td>
<td>‰</td>
</tr>
<tr>
<td>δ bg</td>
<td>¹³C of CO₂ at background location</td>
<td>‰</td>
</tr>
<tr>
<td>δ resp</td>
<td>¹³C of ecosystem respiration</td>
<td>‰</td>
</tr>
<tr>
<td>δ photo</td>
<td>¹³C of net photosynthetic assimilation</td>
<td>‰</td>
</tr>
<tr>
<td>δ smoothbg</td>
<td>Background δ³¹C (smoothed method)</td>
<td>‰</td>
</tr>
<tr>
<td>δ nonsmoothbg</td>
<td>Background δ³¹C (nonsmoothed method)</td>
<td>‰</td>
</tr>
<tr>
<td>δ nonsmoothsource</td>
<td>Local δ³¹C of land-atmosphere exchange of CO₂ (smoothed method)</td>
<td>‰</td>
</tr>
<tr>
<td>δ source</td>
<td>Local δ³¹C of land-atmosphere exchange of CO₂</td>
<td>‰</td>
</tr>
<tr>
<td>δ wood</td>
<td>δ³¹C of tree ring cellulose</td>
<td>‰</td>
</tr>
<tr>
<td>Isoforcing</td>
<td>Influence of net land carbon exchange upon δ atm</td>
<td>% per mol m⁻¹ s⁻¹</td>
</tr>
<tr>
<td>δ source</td>
<td>Uncertainty of δ source</td>
<td>%</td>
</tr>
<tr>
<td>NEE</td>
<td>Net ecosystem exchange of carbon</td>
<td>μmol m⁻² s⁻¹</td>
</tr>
<tr>
<td>GPP</td>
<td>Gross primary productivity (gross photosynthesis)</td>
<td>μmol m⁻² s⁻¹</td>
</tr>
<tr>
<td>VPD</td>
<td>Vapor pressure saturation deficit of air</td>
<td>kPa</td>
</tr>
<tr>
<td>VPD13C</td>
<td>Vienna Pee De Belemniten standard for δ³¹C</td>
<td>‰</td>
</tr>
</tbody>
</table>

The Howland site is located within a boreal-northern hardwood forest about 50 km north of Bangor, Maine. Land cover is dominated by conifers of red spruce (Picea rubens), eastern hemlock (Tsuga canadensis), and lesser amounts of red maple (Acer rubrum) and paper birch (Betula papyrifera) [Richardson et al., 2009]. The Harvard site is a temperate deciduous forest outside of Petersham, Massachusetts dominated by red oak (Quercus rubra) and red maple (Acer rubrum) with lesser coverage of hemlock (T. canadensis) and red pine (Pinus resinosa) [Urbanski et al., 2007]. The Southern Great Plains (SGP) site is located in Lamont, Oklahoma where land cover is a mixture of grassland (used for pasture and grazing) and annual crops, mainly winter wheat. In general, C₃ photosynthesis dominates during the early spring whereas both C₃ and C₄ grass species are active during summer. The Rannells site, near Manhattan, Kansas, is similar to SGP in that it is a mixture of C₃ and C₄ grasses [Lai et al., 2006]. There were no eddy covariance flux tower data available at Rannells; therefore, NEE from the nearby Konza prairie (US-Kon) was used to estimate δ¹³C isoforcing (section 2.4). US-Kon is located approximately 5 km from Rannells with similar vegetation and environmental conditions [Turner et al., 2003]. The Salt Lake City observations were made on the roof of a building at the University of Utah campus located 3.5 km east of downtown [Pataki et al., 2003a, 2007].

2.2. Site Sampling Protocol

The atmospheric CO₂ and δ¹³C of CO₂ data collected at the sites (Figure 1) were part of separate past studies; therefore, the instrumentation, sampling heights, sampling frequency, and time frame varied (Table 2, Figure 1). Most vegetation sites (Harvard, Howland, Wind River, and Rannells) had discrete, multihigh flask sampling that followed the sampling protocol described by Lai et al. [2005]. At those sites, 55 day and 145 night samples were collected per year on average. Separate flask sampling protocols were used at SGP [Tom et al., 2011], Salt Lake City [Pataki et al., 2003a, 2007], and the tundra site at Niwot Ridge (NWR). NWR sampling was part of the long-term effort conducted by NOAA and the Stable Isotope Laboratory at the University of Colorado [Dlugokencky et al., 2015; White et al., 2015] and is distinct from the forest site at Niwot Ridge (US-NR1). The NWR flask measurements were only used as a tool to identify periods of anthropogenic influence at US-NR1 (section 2.6), but not to calculate δsource at the site. Two sites also had continuous atmospheric δ¹³C observations (half-hourly resolution), taken by a tunable diode laser absorption spectrometer at Niwot Ridge forest (US-NR1) [Bowling et al., 2014] and by a quantum cascade laser spectrometer at Harvard Forest (growing season only) [Wehr et al., 2013]. The sampling heights varied among the sites (Table 2) but included subcanopy, canopy, and above-canopy air at all the vegetated sites.
The atmospheric flask data of CO2 and δ13C of CO2 for all sites is located within the Hydroshare repository [Ehleringer, 2017], with the exception of SGP (https://www.arm.gov/; DOI: 10.5439/1328127). The continuous data for Niwot Ridge (US-NR1) and Harvard are located at the Ameriflux website (http://ameriflux.lbl.gov/; DOI: 10.17190/AMF/1246088), and Harvard Forest Data Archive (http://harvardforest.fas.harvard.edu:8080/exist/apps/datasets/showData.html?id=hf209); respectively. The anthropogenic trace gas data for CH4, CO, and CO2 at the NWR tundra site is available at NOAA GMD (https://www.esrl.noaa.gov/gmd/dv/data/).

2.3. Calculating δsource

We used a mixing model [Miller and Tans, 2003] with background correction [Ballantyne et al., 2010] to calculate δ13C of the local net land-atmosphere carbon exchange (δsource). This approach assumes that the locally measured atmospheric CO2 (Cair) is the combination of background CO2 (Cbg) and local source CO2.

The atmospheric flask data of CO2 and δ13C of CO2 for all sites is located within the Hydroshare repository [Ehleringer, 2017], with the exception of SGP (https://www.arm.gov/; DOI: 10.5439/1328127). The continuous data for Niwot Ridge (US-NR1) and Harvard are located at the Ameriflux website (http://ameriflux.lbl.gov/; DOI: 10.17190/AMF/1246088), and Harvard Forest Data Archive (http://harvardforest.fas.harvard.edu:8080/ exist/apps/datasets/showData.html?id=hf209); respectively. The anthropogenic trace gas data for CH4, CO, and CO2 at the NWR tundra site is available at NOAA GMD (https://www.esrl.noaa.gov/gmd/dv/data/).

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Network (AmeriFlux, NOAA, DOE-ARM Site Codes)</th>
<th>Location (Degrees Lat. Long.)</th>
<th>Sampling Frequency</th>
<th>Sampling Method</th>
<th>Years</th>
<th>Sampling Heights (m)</th>
<th>Vegetation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niwot Ridge (forest: US-NR1)</td>
<td>NOAA (NWR)</td>
<td>(Forest: 40.03, – 105.55); (tundra: 40.05, – 105.63)</td>
<td>Continuous (forest) and flask (tundra)</td>
<td>Continuous: Bowling et al. [2014]; Flask</td>
<td>2006–2014; 2001–2014</td>
<td>0.1, 0.5, 1, 2, 5, 7, 9, 11, 21.5</td>
<td>Temperate evergreen forest</td>
</tr>
<tr>
<td>Rannells Flint Hills Prairie (Rannells)</td>
<td>N/A</td>
<td>(39.20, – 96.58)</td>
<td>Flask</td>
<td>Lai et al. [2006]</td>
<td>2001–2009</td>
<td>0.02, 0.38, 2.93</td>
<td>C3/C4 grassland</td>
</tr>
<tr>
<td>Salt Lake City</td>
<td>N/A</td>
<td>(40.76, – 111.89)</td>
<td>Flask</td>
<td>Pataki et al. [2003a]</td>
<td>2005–2012</td>
<td>18</td>
<td>Urban</td>
</tr>
<tr>
<td>Wind River</td>
<td>AmeriFlux (US-Wrc)</td>
<td>(45.82, – 121.95)</td>
<td>Flask</td>
<td>Lai et al. [2005]</td>
<td>2001–2009</td>
<td>0.1, 10, 2, 56</td>
<td>Temperate evergreen forest</td>
</tr>
</tbody>
</table>

Continuous sampling frequency was every 30 min.

Flask collections from Niwot Ridge were taken at the tundra site (NWR) [Dlugokencky et al., 2015; White et al., 2015], including observations of CH4 and CO used to diagnose anthropogenic contributions to the US-NR1 forest site.

Figure 1. Time series of atmospheric CO2 (black symbols, left axes) and δ13C of atmospheric CO2 (gray symbols, right axes) for all sites. For Niwot Ridge and Harvard, the solid dots represent continuous, high-resolution observations whereas the open circles represent flask observations.
(\(C_{\text{source}}\); which can be positive or negative based on whether there is a net emission or uptake of carbon to land) following conservation of mass:

\[
C_a = C_{\text{bg}} + C_{\text{source}}.
\] (1)

Similarly, the product of CO\(_2\) and its isotopic composition (\(\delta\)) is conserved \([\text{Tans}, 1980]\), and following the conservation of mass of \(^{13}\text{C}\), the product of measured \(\delta\) and CO\(_2\) (\(\delta_a C_a\)) is the sum of the time varying background product (\(\delta_{\text{bg}} C_{\text{bg}}\)) and the local source product (\(\delta_{\text{source}} C_{\text{source}}\)) as

\[
\delta_a C_a = \delta_{\text{bg}} C_{\text{bg}} + \delta_{\text{source}} C_{\text{source}}.
\] (2)

Rearranging equations (1) and (2) yields the Miller-Tans relationship, with a variable background specified \([\text{Ballantyne et al.}, 2010]\) as

\[
\delta_a C_a - \delta_{\text{bg}} C_{\text{bg}} = \delta_{\text{source}} (C_a - C_{\text{bg}}).
\] (3)

The \(\delta_{\text{source}}\) value was calculated by linear regression of \(\delta_a C_a - \delta_{\text{bg}} C_{\text{bg}}\) against \(C_a - C_{\text{bg}}\). A major advantage of this approach is that the \(\delta_{\text{source}}\) signal is isolated from time-varying changes in the background atmospheric composition, allowing one to distinguish local changes from regional changes.

An established approach \([\text{e.g., Ballantyne et al.}, 2010]\) to specify the background terms within equation (3) is to fit a function to a set of discrete observations and use that fitted function to account for shifts in background mole fraction (illustrated in Figure 2). We refer to this variant as the \(\text{smoothed}\) approach where \(C_{\text{smooth bg}}\) and \(\delta_{\text{smooth bg}}\) are interpolated from a smoothed background function as defined as

\[
\delta_a C_a - \delta_{\text{smooth bg}} C_{\text{smooth bg}} = \delta_{\text{smooth source}} (C_a - C_{\text{smooth bg}}).
\] (4)

We used a curve-fitting technique to create the background function required for equation (4) that is provided by NOAA (http://www.esrl.noaa.gov/gmd/ccgg/mlb/crvfit/crvfit.html) which is based on a harmonic curve fitting method \([\text{Thoning et al.}, 1989]\) with an 80 day short-term cutoff filter. We fit curves independently to the discrete observations from the tallest inlet height (Figure 2) to create \(C_{\text{smooth bg}}\) and \(\delta_{\text{smooth bg}}\) for each site. To resolve the seasonal change in \(\delta_{\text{source}}\), we applied the regression in a 3 month window of data (centered in each of 12 months) grouped across all years (Figure 3), as in \text{Ballantyne et al.} \[2010\]. This approach maximized the number of samples for the regressions. This provided a more stable and
consistent seasonal cycle as compared to using only a 1 month moving window. First, we performed the
regression on a 3 month moving window for all the observations and created a preliminary
$\delta_{\text{source}}$. Next, we calculated the residuals between the preliminary regression and the observations. We then
filtered the data by removing observations that most poorly fit the preliminary regression—those with residuals greater
than the 95th percentile were removed (Figure 3, in gray). The filtering step removed outliers that could
have a large impact on the regression slope. Next, we performed the regression on the remaining data to
calculate the final $\delta_{\text{source}}$ (Figure 3, in black). We used Model 1 ordinary least squares regression [Zobitz
et al., 2006]. We considered regressions with an $R^2 < 0.90$ a poor fit, and these were not used in our analysis.
Second, we used a variation of the above approach to account for shifts in background by utilizing concur-
tent (in time) background and local site observations without curve
fitting (e.g., US-NR1; Figure 2 and
Figures S1 and S2 in the supporting information). We refer to this method as the
nonsmoothed approach where the
nonsmoothed background CO$_2$ ($C_{\text{nonsmoothbg}}$) and $\delta_{\text{C}}$($\delta_{\text{nonsmoothbg}}$) were directly measured from
the tallest inlet height at each site and defined similarly to equation (4). The advantage of the nonsmoothed
approach is that it accounts for high-frequency, short-duration changes in background mole fraction and iso-
otope composition that are missed by the smoothed approach. In this analysis, however, only US-NR1 and SGP
had sufficient data to perform the nonsmoothed approach in which to quantify the difference in
$\delta_{\text{source}}$ between methods (section 2.6). The $\delta_{\text{source}}$ was calculated using the nonsmoothed approach identically to the
smoothed approach as described in section 2.3 (Figures S1 and S2). Similar plots to Figures S1 and S2 were
created for SGP for the smoothed approach (Figure S3), nonsmoothed approach (Figure S4), and regression
statistics (Figure S5) and are included in the supporting information.

2.4. Calculating the Site-Level $^{13}$C Isoforcing
We calculated the site-level isoforcing to quantify and compare the impact of net land-atmosphere exchange
of $^{13}$CO$_2$ of different land surface types upon $\delta_{\text{atm}}$. Following Lee et al. [2009], isoforcing is defined as

$$\text{isoforcing} = \frac{\text{NEE}}{C_{av}}(\delta_{\text{smoothsource}} - \delta_{\text{atm}}).$$

(5)

For AmeriFlux sites, we calculated monthly average isoforcing with the monthly average NEE calculated from
and the monthly $\delta_{\text{smoothsource}}$ (equation (4)), with the exception of US-Wrc where we used NEE provided
directly from the site PI [Wharton et al., 2012]. The carbon balance at Salt Lake City is primarily controlled by anthropogenic emissions [Strong et al., 2011]; therefore, we calculated the isoforcing from anthropogenic emissions of natural gas, petroleum, and coal for 2014 within Salt Lake County (Hestia model [Patarasuk et al., 2016], provided by Daniel Mendoza and included in the supporting information) combined with the δ\(^{13}\)C of combustion of petroleum [Bush et al., 2007], natural gas [Pataki et al., 2003a, 2007], and coal. To provide a consistent comparison of isoforcing across sites, we used observations from NWR to define the atmospheric concentration of CO\(_2\) (\(C_{atm}\)) and δ\(_{atm}\). The same data years were used for each site to obtain site-level NEE (AmeriFlux) and δ\(_{smooth-source}\) (Table 2) to calculate the isoforcing (equation (5)) with the exception of Salt Lake City.

Cropland such as corn and soybean were not explicitly included in our analysis, yet they significantly impact the regional carbon (and \(^{13}\)C) budget within the United States as estimated by land surface models [Huntzinger et al., 2012] and atmospheric inversions [e.g., Lauvaux et al., 2012]. Considering the importance of these cropland species in influencing the carbon budget, we estimated the isoforcing of corn and soybean sites (Figure S6) through carbon uptake [Lokupitiya et al., 2009] and δ\(_{photo}\) values for these species [Dercon et al., 2006].

2.5. Diagnosing the Impact of VPD on δ\(_{source}\)

We calculated the correlation between monthly VPD and monthly δ\(_{source}\) (section 2.3) to identify if δ\(_{photo}\) drives seasonal changes in δ\(_{source}\) through stomatal conductance responding to VPD. We calculated a monthly average VPD from the daytime site-level VPD data obtained from AmeriFlux (http://ameriflux.lbl.gov); same site DOIs as section 2.4). We tested for correlation with the Pearson correlation coefficient (r) and determined significance when \(p < 0.05\).

2.6. Diagnosing the Impact of Anthropogenic Trace Gases on δ\(_{source}\)

A previous analysis at US-NR1 found that the sporadic influence of anthropogenic gases on local atmospheric measurements, particularly during winter, may have led to an erroneously high seasonal amplitude of δ\(_{source}\) [Bowling et al., 2014]. This finding was reached because the relatively depleted winter δ\(_{source}\) using the smoothed approach could not have resulted from the influence of biogenic sources alone. Here we diagnosed to what extent the smooth and nonsmoothed approaches removed the background anthropogenic influence from the local δ\(_{source}\). First, we leveraged a wide range of flask measurements at NWR that have been analyzed for CH\(_4\) and CO—both trace gases that indicate anthropogenic influence. We identified periods of anthropogenic influence at NWR when mole fractions of CH\(_4\) and CO were anomalously high as compared to their background values. These anomalies were calculated as the difference between the discrete flask measurement taken at the tundra site at Niwot Ridge and a harmonic fit [Thoning et al., 1989] to the flask time series. As shown later, sporadic anthropogenic anomalies of CH\(_4\) and CO during the winter were strongly linked to CO\(_2\) anomalies, and we assumed that these events also affected nearby Niwot Ridge forest (US-NR1).

3. Results

3.1. Seasonality of Smoothed δ\(_{source}\)

The average annual δ\(_{source}\) for a 3 month moving window was the most enriched for grassland sites (−19.0 ± 4.4‰ across-year standard deviation), most depleted for the urban site (−29.7 ± 2.2‰), and the forested sites were in between (−27.0 ± 1.5‰). Within the forested sites, the δ\(_{source}\) of conifer stands (−26.8 ± 1.1‰) was indistinguishable from the deciduous stand (−26.5 ± 0.2‰; Figure 4). The annual averages of δ\(_{source}\) for the 1 and 3 month moving windows were similar; however, there was more variability for the 1 month δ\(_{source}\). The seasonal amplitudes of δ\(_{source}\) for the 3-month moving window were largest for Salt Lake City and SGP (5.9‰ and 4.7‰, respectively), whereas the seasonal amplitude was smallest for the forested sites (excluding Harvard) with average amplitude of 4.1‰ (Figure 4).

3.2. Impact of Smoothed Versus Nonsmoothed Background on δ\(_{source}\)

The choice of background method had no significant impact upon the seasonal amplitude of δ\(_{source}\) for SGP, but the peak in δ\(_{source}\) shifted 1 month later for the nonsmoothed approach. The seasonal variation of δ\(_{source}\) for US-NR1, however, was eliminated with the nonsmoothed approach (Figure 5). The seasonal amplitude in δ\(_{source}\) remained about the same for SGP whether using the smooth or nonsmoothed approach as the
amplitudes were 4.7‰ and 5.0‰, respectively. The US-NR1 δ13C source, on the other hand, reduced from a seasonal amplitude of 2.6‰ to 0.6‰ from the smoothed to nonsmoothed approach, respectively (Figure 5).

3.3. Impact of Anthropogenic Trace Gases at Niwot Ridge on δ13C source

High CO2 events (C∞) at the NWR in winter were often associated with large contributions of anthropogenic trace gases. Flask observations revealed strong correlations between anomalies of CO2 and anomalies of anthropogenic trace gases with R² values of 0.72 and 0.51 for CH4 and CO, respectively (Figure 6). This finding suggests that the highest CO2 anomalies at the nearby Niwot Ridge forest site (US-NR1) were also related to anthropogenic influence given the two sites are less than ~5 km apart. Therefore, we examined the highest CO2 anomaly data periods at US-NR1 to diagnose the impact of anthropogenic influence upon δ13C source for US-NR1 only.

Time periods associated with the highest CO2 anomaly events at US-NR1 led to lower (more negative) δ13C source when calculated with the smoothed approach, but not for the nonsmoothed approach where δ13C source was more enriched and nearly identical regardless of time period (Figure 7). The δ13C source from December through February calculated with the smoothed approach had a monthly average of −28.8 ± 1.5‰ and −28.2 ± 1.1‰ for the highest (>95% and >90%) CO2 anomalies, respectively, and −27.2 ± 0.4‰ and −27.2 ± 0.4‰ for when these anomalous periods were removed. Likewise, the December through February annual averages of δ13C source calculated with the nonsmoothed approach were −25.5 ± 0.2‰ and −25.6 ± 0.2‰ for only the highest >95% and >90% CO2 anomalies and −25.8 ± 0.1‰ and −25.7 ± 0.2‰ when these periods were removed.

3.4. Influence of VPD on Seasonality of δ13C source

There were no significant correlations between the growing season (April–September) monthly mean values of δ13C source and VPD, with the exception of Wind River and SGP (Figure 8). Three out of four forested sites...
showed no correlation between $\delta_{source}$ and VPD (forest average $r = 0.15$), whereas the grassland sites of SGP and Rannells were more highly correlated (average $r = 0.82$). VPD values increased at each site from spring (April–June) through peak summer (July), followed by a decrease in late summer (August–September). On the other hand, the monthly $\delta_{source}$ for all sites but Harvard increased slightly during this period (April–September) on average of 1.1‰.

3.5. Impact of Land Surface Type on $\delta_{atm}$

The isoforcing is an indicator of the influence of land cover type on $\delta_{atm}$. Harvard Forest had the largest positive $^{13}$C isoforcing (making $\delta_{atm}$ more enriched from net carbon uptake by photosynthesis), whereas Salt Lake City had the most negative $^{13}$C isoforcing (making $\delta_{atm}$ more depleted from net release of carbon from fossil fuel combustion) with annual averages of $+1.0 \times 10^{-3}$ and $-7.0 \times 10^{-3}$‰ μmol m s$^{-1}$, respectively (Figure 9). Similar to Harvard Forest, the conifer forest and grassland sites also showed positive but smaller annual average isoforcing of $0.5 \times 10^{-3}$ and $0.3 \times 10^{-3}$‰ μmol m s$^{-1}$ respectively. Whereas a negative isoforcing persisted in Salt Lake City throughout the year, the sites dominated by vegetation switched sign in isoforcing during the year reflecting the change in sign in NEE (carbon sink summer, carbon source winter).

The deciduous Harvard Forest imparted the largest seasonal peak-to-peak magnitude of isoforcing ($9.6 \times 10^{-3}$‰ μmol m s$^{-1}$), and all other sites averaged a smaller seasonal change ($3.3 \times 10^{-3}$‰ μmol m s$^{-1}$). Although Salt Lake City imparted the largest absolute value of isoforcing overall, the seasonal change was similar to most of the nonurban-dominated sites at $4.0 \times 10^{-3}$‰ μmol m s$^{-1}$. The timing of peak isoforcing

![Figure 5](image-url)

Figure 5. The impact of both approaches on the mean seasonal pattern of $\delta_{source}$ between US-NR1 and Southern Great Plains (SGP). The annual mean $\delta_{source}$ was subtracted for each site/method for improved comparison of their seasonal pattern.

![Figure 6](image-url)

Figure 6. A demonstration of anthropogenic trace gases at Niwot Ridge that likely impacted the smoothed analysis during the winter. The data are from the winter (November–March) flask observations for the Niwot Ridge tundra site (NWR). The anomalies of CO$_2$, $\delta^{13}$C, CH$_4$, and CO are the residuals between the raw data and the harmonic fit of the raw data.
varied between sites with Wind River and the SGP peaking the earliest (April), followed by Howland (May), US-NR1 and Rannells (June), and finally Harvard (July). Among all sites, the peak isoforcing at Harvard Forest coincided most closely with the seasonal peak of $\delta_{\text{atm}}$ at NWR (Figure S6). Specifically, the seasonal pattern of the Harvard Forest isoforcing preceded the seasonal pattern of the troposphere at this latitude ($\delta_{\text{atm}}$ at NWR) by 1–2 months throughout the year.

The main driver of seasonal variation in $^{13}$C isoforcing for all sites was the NEE, which is dominated by fossil fuel emissions in Salt Lake City. This is demonstrated by the strong anticorrelation between monthly NEE and isoforcing for each site based on the Pearson correlation coefficient (Figure 9). The seasonal variation in $\delta_{\text{source}}$ played only a minor role in influencing the seasonal isoforcing (Figure 4).

4. Discussion

4.1. Impact of VPD on Seasonal $\delta_{\text{source}}$

Using the Miller-Tans mixing model and atmospheric observations of CO$_2$ and $\delta_{\text{atm}}$, we detected a seasonal pattern in $\delta_{\text{source}}$ for all sites; however, this seasonal pattern was not driven by VPD. We arrive at this conclusion based both on the overall lack of strong correlation between seasonal changes in VPD and $\delta_{\text{source}}$ and on the inconsistent relationship between VPD and $\delta_{\text{source}}$ across sites (Figure 8; section 3.4). Atmospheric water vapor can influence leaf stomatal conductance [Farquhar et al., 1982], thereby reducing the ratio of leaf intracellular to atmospheric CO$_2$ that subsequently reduces the magnitude of photosynthetic discrimination [Farquhar et al., 1989]. Given this physiological relationship, it is possible for VPD to correlate with the magnitude of photosynthetic discrimination and $\delta_{\text{source}}$; however, we found no evidence of this for three of the four forested sites in this analysis (Figure 8). There are several explanations for why there was not a seasonal relationship between VPD and $\delta_{\text{source}}$. First, although environmental variables such as VPD, $T_{\text{air}}$, and PAR are known to impact $\delta_{\text{photo}}$ [Farquhar et al., 1982; Aistad et al., 2007], this signal may not propagate to $\delta_{\text{source}}$ given that it is a combination of isotopic signals from both photosynthesis and ecosystem respiration—the respiration flux itself comprising a relatively fast response autotrophic and slow response heterotrophic contributions [Bowling et al., 2008; Brüggemann et al., 2011]. Second, seasonal variation in soil moisture, VPD, and
photosynthetic capacity (influenced by air temperature and PAR) can covary and make it difficult to disentangle the effects. The lack of correlation between VPD and \( \delta_{\text{source}} \) is consistent with a modeling study [Raczka et al., 2016] performed at US-NR1 that demonstrates that VPD does not have a major influence upon photosynthetic discrimination on seasonal timescales at that location. There was a significant correlation between VPD and \( \delta_{\text{source}} \) at Wind River, but part of this correlation was likely from soil moisture stress during summer. Wind River experiences an exceptionally strong seasonal gradient in precipitation with only 5% falling during June, July, and August [Shaw et al., 2004]. Previous studies at Wind River have demonstrated that soil moisture content is correlated with \( \delta_{\text{resp}} \) [Lai et al., 2005] and that soil moisture stress, in addition to VPD, impacts the stomatal conductance [Wharton et al., 2009; Duarte et al., 2016] and thus \( \delta_{\text{source}} \). Furthermore, the old growth forest at Wind River (450–500 years old) has a stronger reduction in canopy conductance as compared to younger trees near the same location in response to dry conditions [Fessenden and Ehleringer, 2002; Wharton et al., 2009]. This increased response by old growth forest to dry conditions is attributed to hydraulic constraints on stomata due to stand-age effects [Ryan and Yoder, 1997; Woodruff et al., 2007] which contribute to the difference in correlation between VPD and \( \delta_{\text{source}} \) at US-Wrc, compared to younger forests (US-NR1, Howland, Harvard).

At the grassland sites, VPD and \( \delta_{\text{source}} \) were highly correlated (Figure 8); however, the correlation is likely unrelated to the physiological influence of VPD on stomatal conductance. The variation of seasonal productivity of C\(_3\) and C\(_4\) grasses has been attributed to optimum photosynthetic temperature [e.g., Kemp and Williams, 1980] and water availability [e.g., Paruelo and Lauenroth, 1996]. C\(_3\) grasses discriminate much less against \( ^{13}\text{C} \) as compared to C\(_4\) grasses, and this can lead to the seasonal rise and fall of \( \delta_{\text{source}} \) as demonstrated by a C\(_3/C_4\) end member mixing model at SGP [Torn et al., 2011] and other grassland sites [Lai et al., 2003; Still et al., 2003b]. Other factors besides the relative contribution of C\(_3/C_4\) productivity may have contributed to the seasonal variation in \( \delta_{\text{source}} \). For example, the change in seasonal VPD likely impacted the stomatal conductance and photosynthetic discrimination of the C\(_3\) grasses, although the impact of stomatal conductance on seasonal discrimination is known to be small (1–2‰) [Mole et al., 1994; Still et al., 2003b]. In addition the observation tower height at SGP (60 m) led to a large vegetation “footprint” capable of influencing the tower observations. It is likely the atmospheric measurements at the tower were influenced by cropland (primarily winter wheat) outside of the immediate mixed C\(_3/C_4\) natural grass area. The influence

Figure 8. The monthly average \( \delta_{\text{source}} \) (left axes) as calculated by the smoothed approach (3 month window; Figure 4) superimposed on monthly mean VPD (right axes). The uncertainty bars for \( \delta_{\text{source}} \) are the 95% confidence interval for the regression fits, and the uncertainty bars for the VPD are the standard error of the interannual variation. Each panel includes the Pearson correlation coefficient (\( r \)) between the monthly VPD and \( \delta_{\text{source}} \), where * indicates a significant correlation (\( p \) value < 0.05).
of winter wheat (C₃ photosynthesis) at SGP is consistent with a δsource that is 5‰ more depleted than Rannells Prairie (Figure 4). The relatively large size of the vegetation footprint combined with a possible seasonal shift in area and extent of the footprint may have played a role in the seasonal δsource [Griffis et al., 2010; Torn et al., 2011]. Nevertheless, the similarity of the seasonal pattern in δsource found at the Rannells grassland site (Figure 4), which has a smaller footprint than SGP (~3 m height), suggests that the effect of a shifting footprint at SGP was relatively small.

4.2. Drivers of Seasonal Amplitude of δsource and Isoforcing

The largest seasonal amplitudes in δsource were found at the grassland and urban sites, driven by the transition in productivity between C₃ and C₄ grasses and the intensity and timing of fossil fuel emissions, respectively. This finding is consistent with separate analyses at SGP [Torn et al., 2011] and at Salt Lake City [Pataki et al., 2003a]. Similar flask data were analyzed by different methods for SGP between this analysis (2002–2012) and Torn et al. [2011] (2002–2010). Torn et al. used the Keeling plot approach [Pataki et al., 2003b], subset the flask data into day and night, and grouped the data by months from separate years. This analysis, however, used the smoothed and nonsmoothed approaches and grouped all the data into a single seasonal cycle. Regardless of the regression approach and flask data grouping between these separate analyses, the seasonal δsource ranged from −25‰ during the winter to −20‰ during the summer (Figures 4 and 5). The consistency in the pattern and amplitude in δsource is an indication that the background δsource or CO₂ mole fraction does not change significantly at SGP within the months that the regression is performed. A relatively constant background signal within a single month seems feasible, given the seasonal atmospheric change of δatm in the Northern Hemisphere is <0.4‰ (Figure S6).
The seasonal change of $\delta_{\text{source}}$ at Salt Lake City ranged from $-35\%$ in the winter to $-28\%$ in the summer for 2002 [Pataki et al., 2003a] and $-33\%$ to $-27\%$ (2005–2012) for this analysis. The $\delta_{\text{source}}$ seasonal amplitude was nearly identical despite the differences in the methods: the Keeling plot [Pataki et al., 2003a] and smoothed approach (this analysis). The similarity of the $\delta_{\text{source}}$ seasonal cycle between 2002 and 2005–2012 suggests that the timing and contribution of emissions in Salt Lake City were similar with a higher proportion of natural gas emissions during the winter for home heating ($-37.7\%$) and a higher proportion of gasoline combustion ($-28.3\%$) during the summer [Bush et al., 2007]. These seasonal ranges of values found for Salt Lake City were similar but more depleted than those calculated in the urban area of Heidelberg, Germany (summer: $-25.0\%$, winter: $-32.5\%$) [Vardag et al., 2016]. In general, the seasonal pattern and amplitude of $\delta_{\text{source}}$ at Salt Lake City reflect the dominance of natural gas combustion for heating in winter and transportation in summer [Pataki et al., 2003a]. Whether this seasonal pattern applies to other urban areas depends upon the dominant local energy sources (natural gas versus petroleum, wood, coal, heating oil, etc.) and their seasonal demands.

Compared to previous analyses, we found relatively small seasonal variation in $\delta_{\text{source}}$ at the forest sites. The average seasonal amplitude of $\delta_{\text{source}}$ for forest sites found here ($2.3\%$) is smaller than forest sites determined by similar methods including a conifer forest in North Carolina ($3.7\%$) [Ballantyne et al., 2010] and the average of five midlatitude forest sites within the United States and Europe ($3.7\%$) [Ballantyne et al., 2011]. The methods employed by Ballantyne et al. and in our analysis are identical with the important exception of the proximity of the background location to the site observations. Ballantyne et al. chose a remote, upwind, high-altitude alpine tundra site (NWR) to remove regional land and anthropogenic influences. We, on the other hand, used a background nearly collocated with the site itself, which isolated the influence on $\delta_{\text{source}}$ to the region immediately surrounding the site (~1–10 km²). Therefore, the difference in $\delta_{\text{source}}$ between the remote [Ballantyne et al., 2010] and near (our analysis) background corrections likely results from the difference in land “footprint.” Our analysis suggests that when the local forest signal is isolated to the area within the tower footprint, the seasonal change in growing season $\delta_{\text{source}}$ is relatively small, whereas using a remote background will include upwind fluxes from both ecosystem and anthropogenic sources [Turnbull et al., 2015]. This can lead to a large seasonal cycle in $\delta_{\text{source}}$ that may be representative of larger scale processes (>100 km²) and susceptible to nonlocal fossil fuel emissions. The use of a nearly collocated background provided a seasonal pattern of $\delta_{\text{source}}$ that was generally robust to small changes in background location relative to the site observations. For example, the seasonal pattern of $\delta_{\text{source}}$ at SGP and Rannells (both mixed C3/C4) was similar, yet the background location for SGP was much more separated from the site observations than Rannells Prairie (Table 2, Figure 4). Furthermore, the pattern of smoothed $\delta_{\text{source}}$ at US-NR1 was similar when calculated from the data taken from each of the nine tower inlet heights separately (Figure S7).

The seasonal amplitude in isoforcing at the sites was driven primarily by seasonal changes in land-atmosphere net carbon exchange (e.g., net carbon uptake to land in the summer, net carbon release to atmosphere in the winter) and not from seasonal changes in $\delta_{\text{source}}$ (Figure 9, section 3.5). Therefore, NEE was more important than $\delta_{\text{source}}$ in shaping seasonal patterns in local $\delta_{\text{atm}}$ at our sites. Fossil fuel emissions in Salt Lake City had the largest multiyear impact upon local $\delta_{\text{atm}}$ because of the most negative isoforcing ($^{13}$C depleted CO₂ to the atmosphere) of any site. Negative isoforcing from urban centers contributes to long-term global decrease in $\delta_{\text{atm}}$ (Suess effect). Our estimate of seasonal isoforcing in Salt Lake City did not account for biogenic influence although it has a small but nonnegligible influence on local $\delta_{\text{atm}}$ [Pataki et al., 2003a]. As a result, the isoforcing (Figure 9) is likely underestimated during the summer (net carbon biogenic uptake) and overestimated in the fall (net carbon biogenic release). On a seasonal basis, the vegetated sites (especially Harvard) had the largest change in isoforcing. This large change in seasonal isoforcing, combined with a range of timing in peak isoforcing among the plant functional types represented by the sites (Figure S6), suggests a linkage between the generation of $^{13}$C enriched CO₂ (positive isoforcing) and delayed response of $\delta_{\text{atm}}$ due to mixing time. We caution that this suggestion of cause and effect is based on a subset of sites within the midlatitudes and does not include any quantification of the seasonal isoforcing impact from the ocean or land-atmosphere disequilibrium, which are important in closing the annual atmospheric $^{13}$C budget [Randerson et al., 2002; Bowling et al., 2014] and explaining interannual variation in $\delta_{\text{atm}}$ [Alden et al., 2010; van der Velde et al., 2013]. However, on seasonal timescales, the land carbon exchange in the Northern Hemisphere drives the seasonal pattern in atmospheric CO₂ [Keeling et al., 1996] and $\delta_{\text{atm}}$. 
4.3. Comparison With Discrimination Derived From Tree Ring Analysis

Similar to Ballantyne et al. (2010), we used tree ring measurements as an independent way to verify the seasonal changes of \( \delta_{\text{source}} \) derived from atmospheric mixing models (e.g., Figure 4). Our results for seasonality of \( \delta_{\text{source}} \) for forest sites are generally consistent with discrimination estimates derived from \( ^{13}\text{C} \) of cellulose in the wood of tree rings (\( \delta_{\text{wood}} \)) at other midlatitude forested sites similar to the ones studied here. The amplitudes of \( \delta_{\text{wood}} \) and \( \delta_{\text{source}} \) should be proportional, although not equivalent to each other for two reasons. First, \( \delta_{\text{source}} \) is influenced by photosynthetic fractionation \( (\delta_{\text{photo}}) \) and a variety of post-photosynthetic fractionation processes [Bowling et al., 2008; Brüggemann et al., 2011]. The \( \delta_{\text{wood}} \) signature, on the other hand, is influenced by photosynthetic fractionation and fractionation during wood growth.

Second, the carbon allocated to tree rings is not only the transfer of recent carbon assimilated from photosynthesis but a combination of both recent assimilate and stored carbon [Gessler et al., 2014]. Therefore, the seasonal amplitude of \( \delta_{\text{source}} \) should be larger than that of \( \delta_{\text{wood}} \). For example, a single substrate model [Ogée et al., 2009] suggests a \(~30\%\) reduction in amplitude between the seasonal range of \( \delta_{\text{source}} \) and \( \delta_{\text{wood}} \). Observations support the idea that there is a reduction in the seasonal ranges of \( \delta_{\text{source}} \) to \( \delta_{\text{wood}} \) of about 50\% for deciduous species [Helle and Schleser, 2004; Offermann et al., 2011] and 30\% for conifer [Gessler et al., 2009]. The closer match between the seasonal range of \( \delta_{\text{source}} \) to \( \delta_{\text{wood}} \) of coniferous species is consistent with the finding that the dynamics of storage and remobilization of carbon are less pronounced for these species [Gessler et al., 2014]. Thus, seasonal changes in the \( ^{13}\text{C} \) of assimilated carbon (driven by photosynthetic fractionation) are more likely to directly imprint on seasonal changes in \( \delta_{\text{wood}} \). Observations of the seasonal amplitude of \( \delta_{\text{wood}} \) include the species Pinus taeda (1–2\%) [Ballantyne et al., 2010], Pinus ponderosa (1\%) [Leavitt et al., 2002], Pinus radiata (4\%) [Barbour et al., 2002], Pinus sylvestris (1.5\%) [Gessler et al., 2009], Fagus sylvatica (1.3\%) [Offermann et al., 2011], Populus nigra (2.5\%), and Quercus petraea (1.3\%) [Helle and Schleser, 2004]. Assuming a 30\% reduction in amplitude between \( \delta_{\text{source}} \) to \( \delta_{\text{wood}} \), the relatively small growing season amplitude in \( \delta_{\text{source}} \) (2.3\%) in our analysis is consistent with the observed seasonal amplitude of \( \delta_{\text{wood}} \) (1.6\%). Furthermore, the mismatch between the amplitude of seasonal cycle of \( \delta_{\text{source}} \) (3\%) and \( \delta_{\text{wood}} \) (1\%) at a pine forest in North Carolina [Ballantyne et al., 2010] is consistent with an overestimation of \( \delta_{\text{source}} \) using remote-background mixing model methodology (see section 4.4).

4.4. Impact of Mixing Model Methodology on \( \delta_{\text{source}} \)

Previous analyses [e.g., Ballantyne et al., 2010, 2011] may have overestimated the seasonal amplitude of \( \delta_{\text{source}} \) by not accounting for either regional changes in background air, or for short duration, high frequency fossil fuel contamination events. At US-NR1, for example, we suspected that the seasonal amplitude of \( \delta_{\text{source}} \) was overestimated due to the influence from urban emissions [Bowling et al., 2014]. Two lines of evidence support this. First, we found a large seasonal amplitude of \( \delta_{\text{source}} \) at US-NR1 when using the smoothed approach, but the seasonal amplitude was negligible when using the nonsmoothed approach (Figure 5; section 3.2). Second, when time periods with urban influence were removed (based on analysis of anthropogenic trace gases; Figure 6; section 3.3), the resulting \( \delta_{\text{source}} \) was more enriched (Figure 7). Inclusion of only the urban-influenced periods led to a \( \delta_{\text{source}} \) that was too depleted (\(~32\%\) thru ~30\%) to be biogenic in origin [Schaeffer et al., 2008; Hu et al., 2010b] and was characteristic of \( ^{13}\text{C} \) of fossil fuel combustion (natural gas: \( ~38\); petroleum: \( ~28\)) [Bush et al., 2007]. Niwot Ridge likely experiences urban contamination from the Denver-Boulder metropolitan area [Roberts et al., 1985; Parrish et al., 1991]. SGP, however, was not susceptible to winter underestimation of \( \delta_{\text{source}} \) when using the smoothed approach (Figure 5) for two possible reasons. First, anthropogenic emissions may not be as prevalent near SGP. Whereas US-NR1 is only \(~30\) km to the west of Boulder and \(~60\) km to the northwest of downtown Denver, the closest major urban centers to SGP (Oklahoma City, Tulsa) are approximately 170 km to the south and southeast of SGP which may allow for more mixing and dilution of the urban air. Second, during the winter months, SGP provides a greater biological signal (land sink of carbon: 0.54 \( \mu\text{mol m}^{-2} \text{s}^{-1} \)) than US-NR1 (land source of carbon: 0.33 \( \mu\text{mol m}^{-2} \text{s}^{-1} \); Figure 9) that may help constrain the \( \delta_{\text{source}} \) regression. The increased carbon sink at SGP is likely from a combination of a warmer winter climate as compared to US-NR1 and the planting and fertilization of winter wheat (October to May) during most years between 2003 and 2012 [Raz-Yaseef et al., 2015]. On average, there is no photosynthesis at US-NR1 between mid-November and late March [Raczka et al., 2016].
We note that mixing models can provide spurious \( \delta_{\text{source}} \) when atmospheric measurements are influenced by multiple CO\(_2\) sources with distinct \( \delta^{13}C \) signatures [Vardag et al., 2016]. We combined all day and night flask data into a single regression in an effort to maximize the sample size in an effort to best constrain the regression used to calculate \( \delta_{\text{source}} \). Strictly speaking, using daytime flask observations combines two separate CO\(_2\) sources/sinks (photosynthesis, ecosystem respiration) with distinct but similar \( \delta^{13}C \) \( (\delta_{\text{photo}}, \delta_{\text{resp}}) \). The difference between \( \delta_{\text{photo}} \) and \( \delta_{\text{resp}} \) is estimated to be \(-1\%\) at US-NR1 [Bowling et al., 2014] and 0.5\% at Harvard [Wehr and Saleska, 2015]. We found that using all the atmospheric data was justified because calculating the \( \delta_{\text{source}} \) for the day and night observations separately did not provide a significant difference in the seasonal amplitude for US-NR1 [Bowling et al., 2014], Harvard, and SGP [Torn et al., 2011]. At US-NR1, day-only data led to poorer monthly regressions as compared to night-only data, but for most months, the difference was small \( (R^2 < 0.1) \) [Bowling et al., 2014]. The strongest indicator of regression quality for US-NR1 was season. With little biological activity and only minimal temporal variation in CO\(_2\) and \( \delta^{13}C \), monthly regressions during the winter (October–March) were relatively poor \( (R^2 < 0.85) \); however, the months most relevant for comparison between VPD and \( \delta_{\text{source}} \) (April–September; Figure 8) had \( R^2 > 0.85 \) [Bowling et al., 2014].

5. Conclusions

We used atmospheric measurements of CO\(_2\) and \( \delta^{13}C \) at a variety of sites across the United States representing major vegetation types and an urban area to examine what drives the seasonal pattern of the \( \delta^{13}C \) of land-atmosphere exchange \( (\delta_{\text{source}}) \). We found that seasonal changes in VPD at the forest sites were not responsible for the seasonal changes in \( \delta_{\text{source}} \), with the exception of Wind River, where a unique combination of seasonal drought and stand-age effects likely played a role. Although the grassland sites showed a correlation between \( \delta_{\text{source}} \) and VPD, this was more likely driven by a shift in relative productivity between the C\(_3\)/C\(_4\) species during the summer. The grassland and urban sites showed the largest seasonal change in \( \delta_{\text{source}} \) due to the C\(_3\)/C\(_4\) grass growth transition and the type/intensity of fossil fuel emissions, respectively. The largest driver of seasonal patterns in local \( \delta_{\text{atm}} \) was the seasonal change of net carbon uptake, especially for forest sites, and not the relatively small seasonal variation in \( \delta_{\text{source}} \) (0.5\%). Overall, the lack of correlation between VPD and \( \delta_{\text{source}} \) suggests that stomatal response to VPD is not the main cause of the coherent global seasonal cycle of \( \delta_{\text{source}} \) and that C\(_3\)/C\(_4\) grasslands are more likely to play a dominant role within the midlatitudes. Although natural mixtures of C\(_3\)/C\(_4\) grasslands as analyzed here are increasingly rare due to agricultural conversion, the impact upon the atmosphere of regional patchwork of C\(_3\) and C\(_4\) croplands is likely similar due to atmospheric mixing. This site-specific information on \( \delta_{\text{source}} \) can help formulate and calibrate the relationship between atmospheric moisture, stomatal conductance, and \( \delta^{13}C \) discrimination within terrestrial carbon models by excluding regional and continental scale influence from local analyses. Such models can be used to better quantify the contributions of the three key mechanisms (stomatal response to VPD, variation in C\(_3\)/C\(_4\) productivity, and fossil fuel emissions) that influence the seasonal variation in \( \delta_{\text{source}} \).

These findings demonstrate that the location used to account for atmospheric background variation plays a critical role in the estimation of \( \delta_{\text{source}} \) and what it represents. The choice of background location should depend on whether the intent is to understand localized site-level mechanisms or the regional, integrated, impact of the landscape on \( \delta_{\text{source}} \). More studies are required to understand the difference between regional and local estimations of \( \delta_{\text{source}} \), and to determine whether this difference is caused by the spatial scale of the vegetated landscape or the influence of anthropogenic emissions.

References


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