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Novel applications of carbon isotopes in atmospheric CO₂: what can atmospheric measurements teach us about processes in the biosphere?

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Abstract

Conventionally, measurements of carbon isotopes in atmospheric CO₂ ($\delta^{13}\text{CO}_2$) have been used to partition fluxes between terrestrial and ocean carbon pools. However, novel analytical approaches combined with an increase in the spatial extent and frequency of $\delta^{13}\text{CO}_2$ measurements allow us to conduct a global analysis of $\delta^{13}\text{CO}_2$ variability to infer the isotopic composition of source CO₂ to the atmosphere (δ_s). This global analysis yields coherent seasonal patterns of isotopic enrichment. Our results indicate that seasonal values of δ_s are more highly correlated with vapor pressure deficit ($r = 0.404$) than relative humidity ($r = 0.149$). We then evaluate two widely used stomatal conductance models and determine that Leuning Model, which is primarily driven by vapor pressure deficit is more effective globally at predicting δ_s (RMSE = 1.7‰) than the Ball-Berry model, which is driven by relative humidity (RMSE = 2.8)‰. Thus stomatal conductance on a global scale may be more sensitive to changes in vapor pressure deficit than relative humidity. This approach highlights a new application of using $\delta^{13}\text{CO}_2$ measurements to test global models.

1 Introduction

The isotopic composition of atmospheric carbon dioxide ($\delta^{13}\text{CO}_2$) is a very powerful tool for inferring sources of CO₂ to the atmosphere as well as processes affecting the global carbon cycle. Conventionally, $\delta^{13}\text{CO}_2$ has been used for partitioning net global CO₂ uptake between the land and ocean. This application of $\delta^{13}\text{CO}_2$ is based on land plants preferential uptake of the lighter ¹²C isotope relative to the oceans. During photosynthesis in C₃ plants enzymes involved in carboxylation discriminate against the heavier isotope ¹³C ($\Delta \approx -18.0\text{‰}$) and diffusion in both C₃ and C₄ plants also discriminates against ¹³C ($\Delta \approx -4.4\text{‰}$), yielding a global flux-weighted estimate of discrimination by the terrestrial biosphere (Δ_{at}) between -14.8‰ and -16.5‰ (Fung et al., 1997; Suits et al., 2005). However, the degree of isotopic discrimination by

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the terrestrial biosphere may vary from year to year and is largely controlled by the response of stomatal conductance to climate variability (Randerson et al., 2001). In contrast, isotopic fractionation during air-sea gas exchange discriminates only slightly against ^{13}C ($\epsilon_{\text{a0}} = -2.0\text{‰}$) and thus is an order of magnitude less than isotopic discrimination by the terrestrial biosphere. Thus this differential isotopic fractionation has been used to partition carbon fluxes between the marine and terrestrial biosphere on global scales (Ciais et al., 1995; Battle et al., 2000). With the expansion of the global $\delta^{13}\text{CO}_2$ observation network (NOAA/ESRL), we are now capable of partitioning these fluxes at regional scales to assess the spatially heterogeneous response of the biosphere to climate variations (Bousquet et al., 2000). However, $\delta^{13}\text{CO}_2$ has largely been used in the inverse mode to solve for the partitioning of fluxes between the land and ocean. Here we outline a novel application for the use of $\delta^{13}\text{CO}_2$ in an entirely different mode of model testing.

The network of $\delta^{13}\text{CO}_2$ observations is continuously expanding, integrating much more detailed information about carbon cycle processes. The number of sites where regular flask measurements of atmospheric $\delta^{13}\text{CO}_2$ are being made has increased from 9 sites in 1990 to currently over 90 sites and 4 sites are currently using non-dispersive infrared analyzers to make continuous hourly in situ measurements of CO_2 . There has also been an increase in sampling from tall towers and aircraft, which allow us to better resolve vertical gradients of CO_2 and its isotopic composition in the atmosphere (Stephens et al., 2007). This increase in the frequency and density of $\delta^{13}\text{CO}_2$ observations has the potential to provide new insights into the global carbon cycle at finer spatial and temporal scales.

At the local scale $\delta^{13}\text{CO}_2$ observations are a useful diagnostic for inferring eco-physiological changes in response to environmental changes. Using the Keeling plot approach, researchers have been able to infer changes in the isotopic signature of respired CO_2 at the scale of individual forest-stands. This approach has revealed insights into the stomatal response of forests to changes in their environment over broad regional scales (Pataki et al., 2003). Using the $\delta^{13}\text{CO}_2$ composition of recently respired

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CO₂, researchers have been able to infer that stomates in some forests may respond to changes in atmospheric water vapor within weeks (Bowling et al., 2002). This approach has also been used at regional scales to determine that Δ_{al} is highly sensitive to total annual precipitation amount and to a lesser extent mean annual temperature (Pataki et al., 2003). Collectively, these observations from the Keeling plot approach confirm that stomatal conductance responds to water availability, as expected. However, these observations are restricted to the regional scale (i.e. primarily North America) and there are fundamental assumptions underlying the Keeling plot approach (see Sect. 2) that make it challenging to apply to the global scale.

Recent advances in isotopic theory have also taken place that allow us to gain insights into processes in the terrestrial biosphere from atmospheric observations at the global scale. An alternative approach to the Keeling plot has been used by Miller and Tans (2003) to account for changes in the background concentrations of atmospheric CO₂ and $\delta^{13}\text{CO}_2$. This approach makes use of the increased sampling effort of atmospheric $\delta^{13}\text{CO}_2$. Based on this approach it has been demonstrated that latitudinal gradients in Δ_{al} are not nearly as steep as previously predicted from models and a possible declining trend in Δ_{al} for the terrestrial biosphere of North America (Miller et al., 2003). Although these insights derived from atmospheric observations provide independent empirical evidence of spatial and temporal changes in isotopic fractionation, they do not provide detailed information about processes occurring on seasonal scales at individual sites.

Here we propose a new application of $\delta^{13}\text{CO}_2$ by analyzing the wealth of $\delta^{13}\text{CO}_2$ observations using the analytical framework proposed by Miller and Tans (2003). Using this approach, we are able to derive seasonal distributions of source $\delta^{13}\text{CO}_2$ to the atmosphere for a range of sites included in the NOAA/ESRL flask network (<http://www.esrl.noaa.gov/gmd/ccgg/>). Lastly, we use these seasonal distributions to evaluate two empirical models that are often used to predict stomatal conductance in response response to changes in atmospheric CO₂ and water content.

2 Isotopic theory

Our ability to infer the isotopic signature source CO₂ to the atmosphere is based on the conservation of mass, such that the concentration of atmospheric CO₂ (c_a):

$$c_a = c_{bg} + c_s, \quad (1)$$

is equal to the sum of the background CO₂ concentration (c_{bg}) and the CO₂ contribution from recent sources, positive or negative (c_s). Because $\delta^{13}\text{CO}_2$ is also effectively conserved in the atmosphere Eq. (1) can be expanded to include the product of CO₂ and its isotopic composition,

$$\delta_a c_a = \delta_{bg} c_{bg} + \delta_s c_s, \quad (2)$$

where δ_a represents the $\delta^{13}\text{CO}_2$ composition of atmospheric CO₂, δ_{bg} represents the $\delta^{13}\text{CO}_2$ composition of background CO₂, and δ_s represents the $\delta^{13}\text{CO}_2$ composition of source CO₂. These equations were first combined by Keeling (1958), to derive the familiar Keeling plot:

$$\delta_a = c_{bg}(\delta_{bg} - \delta_s)/c_a + \delta_s, \quad (3)$$

whereby the y-intercept corresponds with source $\delta^{13}\text{CO}_2$. However, the most common application of this relationship is to infer the isotopic composition of respired CO₂ in relatively pristine forest environments, where δ_{bg} is assumed to be constant. This assumption is usually satisfied by sampling at night in the absence of photosynthesis when the canopy air space is stratified. However, with the greater abundance of $\delta^{13}\text{CO}_2$ observations we need not assume that δ_{bg} is constant, but rather we can rearrange Eqs. (1) and (2) to formulate the following equation:

$$\delta_a c_a - \delta_{bg} c_{bg} = \delta_s (c_a - c_{bg}), \quad (4)$$

based on this approach we can specify a slowly varying background concentration of CO₂ (i.e. c_{bg}) and its isotopic composition (i.e. δ_{bg}) to solve for the slope-term δ_s , which

corresponds to the isotopic composition of source CO₂ to the atmosphere. δ_s can then be used as a diagnostic tool for processes regulating the transfer of carbon between the biosphere and the atmosphere.

3 Methods

3.1 Site selection

For our analysis we only included terrestrial sites from the NOAA/ESRL network of atmospheric sampling sites with at least 5 years of data. These criteria yielded 18 sites all located within the Northern Hemisphere (Table 1). On average these sites had 13 years of data, which is more than sufficient for determining seasonal distributions of δ_s . There are several potential time series to specify as background isotopic concentrations for inferring δ_s , but previous analysis has indicated that observations at Niwot Ridge, CO, USA (NWR) are statistically indistinguishable from independent observations made from the free troposphere (2000 to 5000 m a.s.l.) making it an excellent background reference for the Northern Hemisphere (Ballantyne et al., 2010).

3.2 Data analysis

For each site a seasonal distribution of δ_s was calculated. A moving three month window was used for calculating δ_s values, such that January δ_s values were calculated from observations made during December, January, and February (DJF) and February δ_s values were calculated from JFM observations, etc. This approach has been shown to yield the most robust seasonal patterns with the smallest standard error estimates for any given month (Ballantyne et al., 2010). Values of δ_s were calculated by first subtracting the background reference curve from time series at each site and then using a linear least-squares regression that incorporates error terms in both the x- and y-axes (Miller and Tans, 2003) to calculate the slope (δ_s in Eq. 3). Although such a

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regression analysis with errors in both the x and y terms may lead to values of δ_s values that are biased (Zobitz et al., 2006), this is at ranges of CO₂ concentration below 10 ppm, which are much lower than those in our 3 month moving window of atmospheric observations. All atmospheric observations were screened for anomalous values that might contribute disproportionately to our regression. All atmospheric CO₂ and $\delta^{13}\text{CO}_2$ observations that exceeded 2σ from the mean of our 3 month moving window were excluded from our analysis. This screening of data only removed between 0 and 2 % of observations across all sites, but greatly reduced anomalous values that may have caused an over-amplification of the seasonal cycle in δ_s .

3.3 Model evaluation

To test models designed to simulate the isotopic fractionation occurring during stomatal conductance, we used the simple biosphere model SiB biosphere model (Sellers et al., 1996). The model was driven by National Centers for Environmental Prediction Reanalysis Data (Kanamitsu et al., 2002) interpolated to the model timestep for the years 1983–2006. Maps of plant functional types were derived from remote sensing products (DeFries and Townshend, 1994). Surface temperature and relative humidity (RH) values were calculated at the leaf-atmosphere interface, according to the most recent version SiB3 (Baker et al., 2010). Leaf surface temperature and RH were then used to calculate saturation vapor pressure and ultimately vapor pressure deficit (VPD). Values of R and D were then used as the primary variables driving 2 commonly used stomatal conductance models – the Ball-Berry Model (Ball, 1988):

$$g_c = m \frac{(A \times \text{RH})}{c_a} + b, \quad (5)$$

and the Leuning Model (Leuning, 1995):

$$g_c = g_o + m_L \frac{A}{(c_a - \Gamma) \left(1 + \frac{\text{VPD}}{D_o}\right)}. \quad (6)$$

The effects of these models on isotopic fractionation by the biosphere were evaluated based on the framework outlined by Katul et al. (2000), whereby the equation for assimilation (Farquhar and Sharkey, 1982):

$$A = g_c(c_a - c_i), \quad (7)$$

was substituted into the assimilation term (A) for both models which were then solved for ratio of intercellular to atmospheric CO_2 (c_i/c_a), the primary factor driving isotopic fractionation by the terrestrial biosphere, according to Farquhar et al. (1989):

$$\Delta_{\text{ai}} = a + (b - a)c_i/c_a, \quad (8)$$

where a is a constant representing fractionation during diffusion (-4.4‰) and b is a constant representing fractionation during carboxylation by Rubisco (-27‰). Model parameters and the values used for the various biomes considered in this study are reported in Table 2.

4 Results

4.1 Analytical approach

Our approach to inferring the isotopic signature of source CO_2 to the atmosphere is contingent upon selecting a suitable background reference curve for calculating residuals. It has been demonstrated previously that the free-troposphere (2000 to 5000 m a.s.l.) represents the best background reference as it introduces the fewest artifacts when inferring a seasonal cycle in δ_s (Ballantyne et al., 2010). Ideally, we would use free troposphere observations immediately above each atmospheric sampling site as our background reference; however, this is only possible for a limited number of sites. Instead Niwot Ridge, CO (NWR, 3437 m a.s.l.) has been identified as a suitable mid-continental background site for observations in North America.

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To demonstrate how this analysis is performed, let us consider the isotopic variability of CO₂ observed at Wendover, UT (UTA). We see that there is considerably more variability in atmospheric CO₂ and $\delta^{13}\text{CO}_2$ observations at UTA than the more attenuated tropospheric reference curve at NWR (Fig. 1a). Atmospheric CO₂ levels at UTA are greater during winter months and lesser during summer months than those at NWR (Fig. 1a). Although the curves differ in seasonal amplitude, they tend to be in phase on seasonal timescales. Atmospheric $\delta^{13}\text{CO}_2$ values are a reflection of the CO₂ curves, with values more depleted at UTA than NWR during winter months and values more enriched at UTA than NWR during summer months (Fig. 1b). Essentially, surface observations show an amplification of the seasonal cycle in both CO₂ concentration and isotopic composition relative to the free troposphere.

If we take the residuals between CO₂ in the boundary layer and CO₂ in the free troposphere and we plot them against the residuals between the product of CO₂ and $\delta^{13}\text{CO}_2$ in the boundary layer and the product in the free troposphere, we can then determine the slope (Fig. 1c). This slope value corresponds to δ_s and it is evident that δ_s varies slightly according to season. If we solve for δ_s for each month, using our moving window approach, a distinct seasonal pattern emerges whereby winter months are characterized by more depleted δ_s values and summer months are characterized by more enriched δ_s values (Fig. 1d). The magnitude of the seasonal pattern (i.e. the signal) greatly exceeds the uncertainty in any given month (i.e. the noise), suggesting that this might be an effective tool for detecting isotopic signatures associated with processes in the biosphere.

4.2 Globally coherent patterns

The distribution of δ_s inferred from a network of atmospheric sampling sites reveals globally coherent seasonal patterns. The array of Northern Hemisphere sites shows a consistent pattern of enriched δ_s values during summer months and more depleted values during winter months (Fig. 2b). Most of the sites included in our analysis showed

maximum δ_s values between July and August (see supplemental Fig. 1); however, lower latitude sites appear to reach maximum δ_s values (July–August) prior to higher latitude sites (August–September). The seasonal amplitudes in δ_s values vary between 2 and 7.6‰, with arid low latitude desert sites, such as KZD, Kazakhstan and ASK, Algeria, experiencing much greater amplitudes in seasonal variations of δ_s , than mid-latitude mixed forest sites, such as BAL near the Baltic Sea and TAP in Korea (Table 1).

Values of δ_s inferred at most of our sites were highly correlated with metrics of atmospheric water vapor calculated at the leaf's surface (Table 1). Correlation coefficients for all sites ranged from 0.09 to 0.97, but mid-latitude and low-latitude sites with greater seasonal amplitude in δ_s tended to have higher correlations with both VPD and RH. Of the 19 sites included in our analysis 16 showed significant correlations with vapor pressure deficit and 14 showed significant correlations with relative humidity.

Although there was generally a strong relationship between seasonal δ_s values and metrics of atmospheric water vapor across sites, some sites showed a stronger response to VPD and some sites showed a stronger response to RH. Of the 16 sites that showed a significant response to VPD, 11 were more highly correlated with the natural log of VPD and of the 14 sites that showed a significant response to RH, only 5 were more highly correlated with the natural log of RH. These results indicate the possible saturation of isotopic fractionation by stomatal conductance, especially at the sites that were more responsive to VPD.

At individual sites δ_s may correlate better with RH or VPD; however, if we look at the global dataset of seasonal δ_s values for all sites there is a much stronger correlation with VPD than RH (Fig. 3). We found the optimal global fit to be between δ_s and the natural log of VPD ($r = -0.404$, $p\text{-value} = 2.2 \times 10^{-6}$, $DF = 226$), indicating an incrementally smaller amount of isotopic fractionation at higher VPD values. There was only a slight increase in this correlation when individual non-significant sites (see BRW, OXK, and TAP in Table 1) were removed from the analysis ($r = -0.408$, $p\text{-value} = 2.2 \times 10^{-6}$, $DF = 190$). Regional differences between sites also emerged from this analysis, such

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that high-latitude evergreen sites tended to have a much greater response in δ_s over a smaller range of VPD values, whereas δ_s was not nearly as sensitive to changes in VPD values at lower latitude desert sites (Fig. 3a). Although the global relationship between δ_s and RH was also significant, the relationship was not nearly as strong ($r = 0.149$, p -value = 0.023, $DF = 226$) and the optimal relationship was with a natural log transformation of RH. These global patterns suggest that if isotopic discrimination is indeed due to stomatal conductance, then the physical mechanism responsible for these patterns of isotopic discrimination is probably VPD.

4.3 Evaluation of models

Values of δ_s inferred from atmospheric measurements can also be used to test biosphere models created to simulate the exchange of mass at the biosphere-atmosphere interface. Assuming that stomatal conductance is the primary mechanism causing isotopic fractionation during photosynthesis (Farquhar et al., 1989) and that there is no net fractionation associated with autotrophic respiration (Lin and Ehleringer, 1997), we can then use values of δ_s to gain insight about factors controlling stomatal conductance. In most cases, the Leuning model performed better at predicting δ_s than the Ball-Berry model (Table 1). At almost all sites, root mean squared error (RMSE) estimates were less for the Leuning model than the Ball-Berry model. The exceptions were ASK, LEF, and NWF. Globally, RMSE values were significantly lower for the Leuning model, 1.8‰, than for the Ball-Berry model, 2.7‰ (two tailed t-test, p -value = 0.00106, $DF = 27$), suggesting that VPD may be more important in governing stomatal conductance than RH at global scales.

Although the Leuning model tends to outperform the Ball-Berry model, there are instances where the Leuning model deviates from observed δ_s values (Fig. 3). For instance, the Leuning model tends to be fairly accurate in its predictions of δ_s towards the mean of the distribution in observed δ_s values; however, it appears to be biased towards more enriched values at lower and higher observed δ_s values (Fig. 3c). In contrast, the Ball-Berry model systematically under-predicts the observed δ_s values in

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the atmosphere (Fig. 3d). Predicted values of δ_s from the Ball-Berry model tend to be ~ 2 to 4 per mil depleted relative to observed values, especially at the high end of the range of observed δ_s values. It is also apparent that the range of observed δ_s values exceeds the range of possible solutions for either model; this is evidenced by the flatline limit at $\sim 30\%$ evident in both model simulations (Fig. 3c and d).

5 Discussion

5.1 Analytical approach

The approach that we have presented here, relying solely on atmospheric observations is effective for extracting seasonal information regarding biosphere-atmosphere interactions on a global scale. By specifying background concentrations of CO_2 and $\delta^{13}\text{CO}_2$ we are able to generate seasonally coherent patterns of δ_s for most Northern Hemisphere sites included in this analysis. Here we have refined the original approach presented by Miller and Tans (2003) by resolving seasonal patterns on a global scale. Previous analyses of atmospheric observations and model simulations have identified the free troposphere as the most effective background reference curve for inferring δ_s values at regional scales and that the high elevation mid-continental site at NWR is an effective background reference, at least for North America (Ballantyne et al., 2010). Here we have extended this approach to a wider array of Northern Hemisphere sites and our analysis reveals coherent seasonal cycles of δ_s among these sites.

Although our more extensive analysis has revealed coherent seasonal patterns, there are subtle differences in these seasonal patterns that may be artifacts introduced during our analysis. For instance there appears to be a characteristic “stair-step” pattern in δ_s at higher northern latitudes. This is evidenced by the dark blue curves in Fig. 2b representing seasonal patterns in δ_s for Barrow, Alaska, USA (BRW); Baltic Sea, Poland (BAL), and Pallas-Sammaltunturi, Finland (PAL). Unlike lower-latitude sites that show a pronounced seasonal cycle of more enriched δ_s values during

summer months and more depleted values during winter months, these high-latitude sites show depleted δ_s values during winter months, more enriched values during summer months, but then δ_s values remain high into the fall months (Supplemental Fig. 1). This “stair-step” pattern may also be contributing to the reduced correlation coefficients between δ_s and VPD and RH, as well as the less optimal fit of stomatal conductance models at higher latitudes (Table 1). It is difficult to ascertain whether this is a circum-arctic phenomenon based on our analysis from only three sites, but it does deserve further investigation. The anomalous seasonal pattern observed at these sites may also be due to the mid-latitude background site (i.e. NWR) selected for our analysis. There may be lags introduced into the analysis as a result of the transport time of mid-latitude background air by Ferrel cells advecting air poleward. However, with increased aircraft sampling, background reference curves from higher latitudes are becoming increasingly available and more highly resolved.

Some low-latitude sites also showed deviations from the seasonal patterns characteristic of mid-latitude sites. Generally, lower-latitude sites had larger seasonal amplitudes in δ_s than higher-latitude sites. However, there is a clear anomaly to the seasonal pattern in Assekrem, Algeria (ASK) where the primary peak in δ_s values is observed in July, but a secondary peak in δ_s is observed in November (Supplemental Fig. 1). Although this anomalous pattern may be due to our specification of the very distant NWR background reference curve for this site, it may also be due to this site's proximity to the equator. In our original analysis we included two equatorial sites (Bukit Kototaband, Indonesia: BKT and Mt. Kenya: MKN) and two Southern Hemisphere sites (Cape Grim, Tasmania: CGO and Gobadeb, Namibia: NMB). However, seasonal patterns were not as clear and errors were much greater at these sites, leading to their ultimate removal from our analysis. Although the equivocal results in the Southern Hemisphere are most likely due to our Northern Hemisphere background reference curve, this approach may yield ambiguous results at equatorial sites due to the inter-hemispheric transport of air masses. According to SiB3, ASK is included within the “low-latitude” C4 desert of Northern Africa. Recently revised global maps of C4 vegetation, however, show

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most C4 vegetation to be restricted to the savannahs of sub-Saharan Africa (Still et al., 2003). Therefore it is also possible that ASK is influenced by air masses conveying both C3 and C4 vegetation signals that differ in their seasonal timing and δ_s signatures.

5.2 Globally coherent patterns

5 Our analysis of a network of sites in the Northern Hemisphere has revealed seasonally coherent patterns in the isotopic composition of source CO₂ to the atmosphere. These broad global patterns are consistent with previous analyses done on individual sites. For example, Bakwin et al. (1998), employing the Keeling plot approach at ITN and HUN identified a slight enrichment of δ_s during summer months compared to winter months. Bakwin et al. attributed the changes in δ_s at these two sites to isotopic sources that were dominated by fossil fuel sources during winter months and dominated by terrestrial uptake during the summer months. Our results are consistent at ITN and HUN; however, we are able to take advantage of additional data to resolve a clear seasonal cycle in δ_s at these two sites. Although there are numerous confounding factors that may influence δ_s on seasonal time scales, the globally coherent seasonal cycle in δ_s reported here indicates a common underlying physical mechanism rather than disparate local factors influencing δ_s .

At local to regional scales fossil fuel emissions may have a large impact on δ_s values inferred from atmospheric observations, especially near large urban areas. This has been clearly demonstrated in urban environments that experience strong inversions during winter months. For example in Salt Lake City, midday $\delta^{13}\text{CO}_2$ values may become depleted during winter months by as much as 5%, which has been attributed primarily to increased emissions from natural gas used for home heating (Pataki et al., 2006). Although fossil fuel emissions should be taken into account when evaluating δ_s values at individual sites, fossil fuel consumption and fossil fuel type show broad spatial and temporal variability. For instance, the Eastern US relies primarily on coal and the Western US relies primarily on natural gas for power generation (Pétron et

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al., 2008) and emissions from these sources have very different isotopic signatures. Furthermore, emissions tend to be higher during winter months in northern US states due to home heating, whereas emissions tend to be higher during summer months in southern US states due to home cooling (Gregg et al., 2010). Despite this regional variability in the timing and type of fossil fuel consumption our network of sites shows a clear and consistent seasonal cycle in δ_s , especially across the continental US. Therefore fossil fuels may help to explain the variability in seasonal δ_s between sites, but fossil fuel emissions cannot explain the global patterns of δ_s revealed by our analysis.

Changes in climate may also affect the seasonal cycle in δ_s . In fact, a covariance between isotopic discrimination by the terrestrial biosphere and precipitation amount as mediated by El Niño events has been previously identified (Randerson et al., 2001). Although climate variability probably affects stomatal conductance and thus isotopic discrimination on inter-annual scales, this contributes to the error in our estimates of the seasonal cycle in δ_s . The fact that a strong seasonal signal in δ_s emerges despite the error associated with inter-annual climate variability suggests that temporal variability in δ_s is actually dominated by the seasonal cycle. However, our seasonal climatologies of δ_s could be used to estimate anomalies in any given year due to climate variability. For instance, if prolonged drought results in diminished stomatal conductance this could be diagnosed as an enriched departure from our seasonal climatology of δ_s due to decreased isotopic discrimination. Long term variability in isotopic discrimination may also arise from changes in atmospheric CO₂ concentration and/or climate change. Model simulations of the global carbon isotopic budget indicate a decrease in isotopic discrimination by the terrestrial biosphere of approximately 0.4‰, primarily due to an increase in water stress (Scholze et al., 2003). Such long term trends in isotopic discrimination should probably be considered, especially at some of the sites included in our analysis with more data (~20 years). However, this potential change in isotopic discrimination of 0.4‰ yr⁻¹, is dwarfed by the amplitude of the seasonal signal for sites included in our analysis (between 2 and 7‰).

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Changes in land use may also impact values of δ_s over time. It has been suggested that the intensification of agriculture and the proliferation of C4 crops has offset a fraction of CO₂ emissions (Burney et al., 2010). This has been demonstrated at the regional scale in the Amazon where the widespread conversion of tropical C3 forest to C4 pasture should lead to a decrease in isotopic discrimination and such a reduction in regional isotopic discrimination could lead to the spurious conclusion that terrestrial uptake in the tropics has decreased (Townsend et al., 2002). Unfortunately, there are very few tropical sites with continuous observations of $\delta^{13}\text{CO}_2$ making it impossible to extend this analytical approach into the tropics. However, there has been widespread land-use change at temperate latitudes as well, especially the proliferation of C4 corn to meet biofuel demands. Recent analyses of $\delta^{13}\text{CO}_2$ and CO₂ observations made from a tall tower in the Midwestern US have identified a strong isotopic signal from increased corn cultivation (Griffis et al., 2010). Griffis et al. (2010) suggest that increased corn cultivation for biofuels lead to an apparent decrease in isotopic discrimination from ~15‰ to ~12‰. Although most of this isotopic effect due to corn production was observed during the summer months the isotopic effect and its impact on $\delta^{13}\text{CO}_2$ seem to extend into the fall as well. These independent observations from Griffis et al. (2010) are a mere 300 km. from our LEF site and may actually help to explain some of the seasonal anomalies observed at LEF. Although LEF exhibits the same seasonal pattern in δ_s characteristic of most our Northern Hemisphere sites, there is a secondary peak in δ_s that occurs in the fall and may be due to decreased isotopic discrimination as a result of increased corn cultivation (Fig. 2). Furthermore, the leaf temperature estimates from SiB3 used in our model validation exercise consider the dominant plant functional type within this region to be “mixed C3 forest”. Although this is consistent for the most part with land use maps from the region (Griffis et al., 2010), the proportion and composition of crops in this region may change from year to year to meet market demands.

Although factors such as fossil fuels, climate variability, and land use may have an impact on the seasonal cycles in δ_s that we have inferred from the atmosphere. The

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fact that these seasonal cycles in δ_s are coherent across most sites in the Northern Hemisphere and that they are reproducible from year to year strongly suggests that they are driven by processes in the terrestrial biosphere.

5.3 Evaluation of models

5 Our results suggest that most of the seasonal variability in δ_s can be explained by changes in atmospheric water vapor. Both relative humidity and vapor pressure deficit calculated at the leaf's surface were highly correlated with δ_s (Table 1). Of the 19 sites investigated, 16 showed significant correlations with D and 14 showed significant correlations with R. Globally, δ_s was significantly correlated with both VPD and RH, but was more highly correlated with VPD. Conceptually, we would expect increases in relative humidity to lead to increases in stomatal conductance (i.e. increased c_i/c_a), resulting in greater isotopic discrimination against atmospheric $\delta^{13}\text{CO}_2$. In contrast, we would expect increases in vapor pressure deficit to lead to a decrease in stomatal conductance (i.e. decreased c_i/c_a), resulting in reduced isotopic discrimination against atmospheric $\delta^{13}\text{CO}_2$. Thus we would predict a negative relationship between δ_s and RH, in contrast to a positive relationship between δ_s and VPD. Where the sign of these predicted relationships is consistent with two stomatal conductance models evaluated here (Eqs. 5 and 6).

At every terrestrial site in the Northern Hemisphere that we evaluated D is positively correlated with δ_s , even at sites where the correlation is not significant (Table 1). Furthermore, the distribution of these correlation coefficients is normal ($W = 0.92$, p-value = 0.097), indicating that stomatal conductance responds to D according to our conceptual model (Fig. 4a). In contrast, the correlation coefficients between RH and δ_s are both positive and negative (Table 1). Moreover, the correlation coefficients between RH and δ_s are not normally distributed ($W = 0.82$, p-value = 0.0015), indicating that at some sites stomatal conductance is responding to RH as expected based on our conceptual model, but at other sites stomatal conductance contradicts our conceptual

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expectations. Lastly, many of the optimal correlation coefficients were based on the natural log of VPD or RH, which indicates a non-linear response of δ_s and thus stomatal conductance. In the Leuning model stomatal conductance responds non-linearly to VPD, whereas in the Ball-Berry model the response of stomatal conductance to RH is linear.

The more significant correlations observed between δ_s and VPD than δ_s and RH are consistent with our model evaluations indicating that the Leuning model is more accurate at predicting δ_s than the Ball-Berry model. RMSE values were significantly lower for the Leuning model than the Ball-Berry model (p -value = 0.001, DF = 27). Thus, if the global seasonal cycles observed in δ_s are in fact due to stomatal response to the environment, than the Leuning Model appears to be more effective at capturing this stomatal response on seasonal timescales. Although both models showed a significant relationship with δ_s globally (Table 1), both models failed to predict the extremely depleted values of δ_s observed at some sites (Fig. 3). Values of δ_s well below -30% were observed for many sites during winter months (Supplemental Fig. 1). However, there was not enough parameter space allowed by either model to account for these highly depleted values during winter months. In fact, in order to obtain reasonable predictions for δ_s we had to set the slope term in both models (i.e. m and m_L) to 25.0, which greatly exceeds any values from the literature (Sellers et al., 1996; Leuning, 1995). This mis-match between observations and predictions could be due to extreme physiological conditions that are not well simulated by the models, or else a depletion bias in inferred values of δ_s at some of our sites. The site at which this mis-match was the most pronounced was at ASK in Algeria. Although seasonal values of VPD range from 0.5 to 3.0 KPa and values of RH range from 35 to 50%, this site does not seem to experience climatic conditions that are any more extreme than other sites evaluated such as UTA or WIS. It is also possible that the extremely depleted values of δ_s observed during the winter months at ASK are an artifact of this site being very distant from the tropospheric background site specified (i.e. NWR) when calculating δ_s . Therefore, is more likely that the extremely depleted values of δ_s are due to possible

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biases introduced during this analysis and not necessarily a deficiency of the models.

Both of these stomatal conductance models have been derived from empirical observations at the laboratory scale and have subsequently been validated using field observations. However, they were not explicitly designed for global applications and yet they are now being used to evaluate how the Earth's biosphere will respond to future changes in atmospheric CO₂ and concomitant climate change (Friedlingstein et al., 2006). Our results suggest that the Leuning model of stomatal conductance may be more suitable for simulating stomatal conductance over a wider variety of biomes under a wider variety of climatic conditions. However, this is not so surprising as the Leuning model includes more parameters and thus has more degrees of freedom for simulating actual observations. In contrast the Ball-Berry model is elegant in its simplicity and actually performs reasonably well over a range of biomes and climatic conditions. Because of its simplicity it is not surprising that it has become the default stomatal conductance parameterization for many of the next generation Earth System Models. Although the terms driving these respective models (VPD and RH) are used almost interchangeably in the ecophysiological literature, they are very different metrics of atmospheric water vapor and thus may respond very differently to future warming scenarios.

6 Conclusion

Isotopic measurements in atmospheric CO₂ have greatly enhanced our understanding of the global carbon cycle. However, the increased sampling frequency of $\delta^{13}\text{CO}_2$ (both in space and time) combined with new analytical techniques, now make it possible to address research questions that were previously intractable using isotopes. Here we have presented a novel application of $\delta^{13}\text{CO}_2$, by which we are able to infer broad seasonal patterns of source CO₂ to the atmosphere. We have used this approach to yield a seasonal cycle of δ_s that is coherent across an array of N. Hemisphere atmospheric sampling sites. The resulting pattern can be thought of as a seasonal “Keeling Plot” for

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the Earth. The broad seasonal coherence observed across all sites suggests a single underlying physical mechanism driving this variability. To explain this variability we test two stomatal conductance models, which both suggest that changes in atmospheric water vapor drive changes in δ_s on seasonal timescales. The analytical approach here can be improved by specifying more regional background reference curves essential for calculating δ_s values. This analytical approach could also be extended to the tropics and the Southern Hemisphere as atmospheric observations of $\delta^{13}\text{CO}_2$ become increasingly available.

Supplementary material related to this article is available online at:

<http://www.biogeosciences-discuss.net/8/4603/2011/bgd-8-4603-2011-supplement.pdf>

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Table 1. Seasonal correlations between δ_s and metrics of atmospheric water vapor for terrestrial sites from the NOAA/ESRL network included in this analysis. For each site the corresponding station code from the NOAA/ESRL flask network and the biome according to SiB3 are reported in addition to the duration of the dataset included in the analysis. Correlation coefficients (r) are reported for seasonal distributions of δ_s (DF = 10) and vapor pressure deficit (VPD) and relative humidity (RH), respectively (see Fig. 2). The sign of the correlation coefficient indicates the sign of the relationship. Significant correlation coefficients appear in bold italics. Root mean squared error (RMSE) are reported for seasonal predictions of δ_s from the Leuning and Ball-Berry stomatal conductance models compared with δ_s values inferred from the atmosphere. Mean RMSE values across all sites are also reported.

Station				Duration (yrs)	Seasonal amplitude Source del ¹³ C per mil	Correlation coefficients		Seasonal		RMSE	
Code	Latitude	Longitude	Biomes			VPD	RH	Minimum	Maximum	Leuning	Ball-Berry
BRW	71.32	-156.61	tundra (C3)	19	5.7	0.464 ^a	0.673^a	Jan	Sep	2.0	2.5
PAL	67.97	24.12	needleleaf (C3)	8	3.2	0.565^b	-0.456 ^a	Jan	Aug	1.1	2.0
BAL	55.35	17.22	mixed forest (C3)	17	2.7	0.762^a	-0.694^b	Jan	Aug	1.4	2.8
OXX	50.03	11.8	generic crop (C3)	6	3.8	0.259 ^a	-0.090 ^b	Jun	Sep	1.5	2.6
HUN	46.95	16.65	generic crop (C3)	16	6	0.780^b	0.824^b	Mar	Aug	2.4	3.7
LEF	45.95	-90.27	mixed forest (C3)	15	3.8	0.721^b	-0.408 ^b	Apr	Jul	1.9	1.9
AMT	45.03	-68.68	mixed forest (C3)	6	4.9	0.717^a	-0.601^a	Jan	Aug	1.8	3.1
UUM	44.45	111.1	generic crop (C3)	17	3.6	0.678^a	-0.637^b	Feb	Jun	1.0	1.2
BSC	44.17	28.68	generic crop (C3)	15	3.3	0.711^a	0.819^b	Apr	Aug	2	3.8
KZD	44.08	76.87	generic crop (C3)	12	7.6	0.910^a	-0.882^b	Jan	Jun	1.5	2.2
NWF	40.05	-105.58	generic crop (C3)	19	5.2	0.861^a	-0.895^a	Mar	Aug	1.6	1.6
UTA	39.9	-113.72	low-latitude desert (C4)	16	6.6	0.872^a	0.916^a	Feb	Aug	1.3	1.4
SGP	36.8	-97.5	generic crop (C3)	7	5.2	0.915^a	-0.875^b	Feb	Aug	2.3	4.9
TAP	36.73	126.13	generic crop (C3)	19	2	0.375 ^b	0.439 ^b	May	Aug	3.0	4.6
WLG	36.29	100.9	generic crop (C3)	19	5.6	0.584^a	-0.335 ^b	Jan	Oct	1.4	3.4
ITN	35.35	-77.38	mixed forest (C3)	7	3.7	0.858^b	-0.725^b	Jan	Aug	1.0	2.3
WKT	31.32	-97.33	generic crop (C3)	8	7.1	0.967^a	-0.916^b	Dec	Jul	1.4	2.4
WIS	31.13	34.88	generic crop (C3)	14	3.5	0.910^b	-0.794^b	Jan	Sep	0.6	1.4
ASK	23.18	5.42	low-latitude desert (C4)	14	7.2	0.730^a	-0.753^a	Feb	Jul	4.9	3.7
Global						0.404^a	0.149^a			1.8	2.7

^a Indicates regressions where the atmospheric vapor pressure term (i.e. VPD or RH) have been transformed by the natural logarithm and correlated with δ_s .

^b Indicates linear regressions between the atmospheric vapor pressure term (i.e. VPD or RH) and δ_s .

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Table 2. Model parameters according to C3 and C4 vegetation types. Models introduced in the text include the Ball-Berry and Leuning models of stomatal conductance (Eqs. 5 and 6) and the Farquhar model of isotopic discrimination during photosynthesis (Eq. 8).

Vegetation type	Ball-Berry ^a		Leuning ^b		Farquhar	
	<i>m</i>	<i>D_o</i>	<i>m_L</i>	Γ^c	<i>a</i> (‰)	<i>b</i> (‰)
C3 vegetation	9.0	1.0	6.4	$3.69 + 0.188(T - 25) + 0.0036(T - 25)^2$	4.4	27.3
C4 vegetation	4.0	3.0	4.0	$3.69 + 0.188(T - 25) + 0.0036(T - 25)^2$	4.4	–

^a The intercept term in the original Ball-Berry model “*b*” (Eq. 5) can be neglected when solving for isotopic discrimination (Katul et al., 2000).

^b Similarly the intercept term in the Leuning model “*g_o*” can be neglected when solving for isotopic discrimination (Katul et al., 2000).

^c Γ represents the CO₂ compensation point and varies as function of leaf surface temperature (*T* °C), according Brooks and Farquhar (1985).



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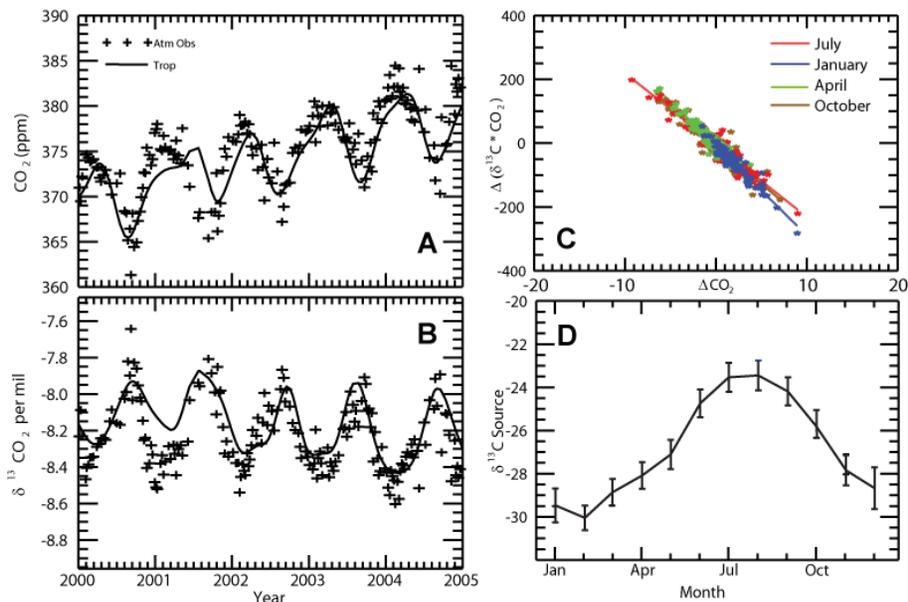


Fig. 1. Analytical approach to inferring $\delta^{13}\text{C}$ CO_2 source to the atmosphere. Panel (A) shows the seasonal cycle of atmospheric CO_2 observations at Wendover, Utah (UTA) compared with free troposphere observations of CO_2 at Niwot Ridge, Colorado (NWR). Panel (B) shows atmospheric $\delta^{13}\text{C}$ CO_2 observations at UTA compared to free troposphere observations of $\delta^{13}\text{C}$ CO_2 at NWR. Panel (C) shows the residual technique used for inferring changes in $\delta^{13}\text{C}$ CO_2 source (δ_s) to the atmosphere, where δ_s is estimated as the slope. Lastly, Panel (D) shows the resultant seasonal pattern in δ_s generated from monthly estimates and their associated uncertainties (1σ).

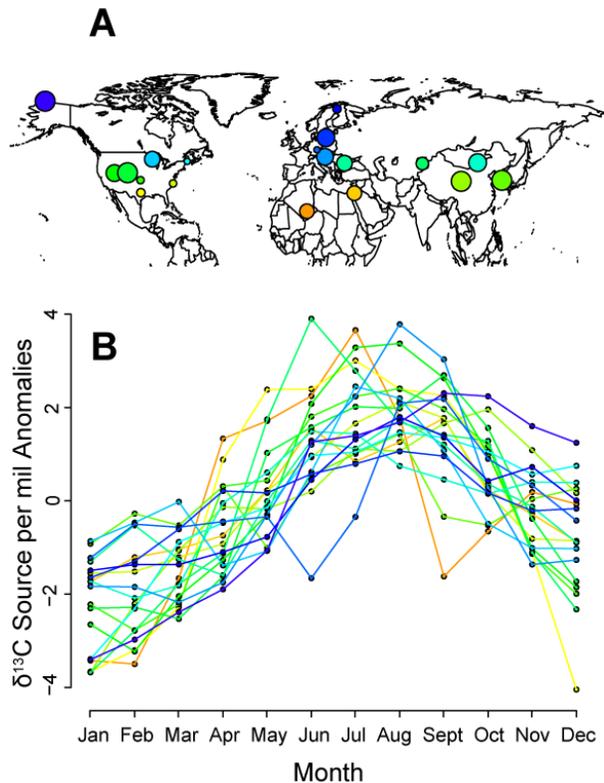


Fig. 2. Global coherence of $\delta^{13}\text{CO}_2$ source (δ_s) anomalies to the atmosphere. The network of sites included in our analysis (**A**), where the size of points corresponds with length of the dataset (see Table 1) and the color of the point corresponds with latitude and also the seasonal distribution of points in panel (**B**). The seasonal distribution of δ_s for all sites included in our analysis (**B**).

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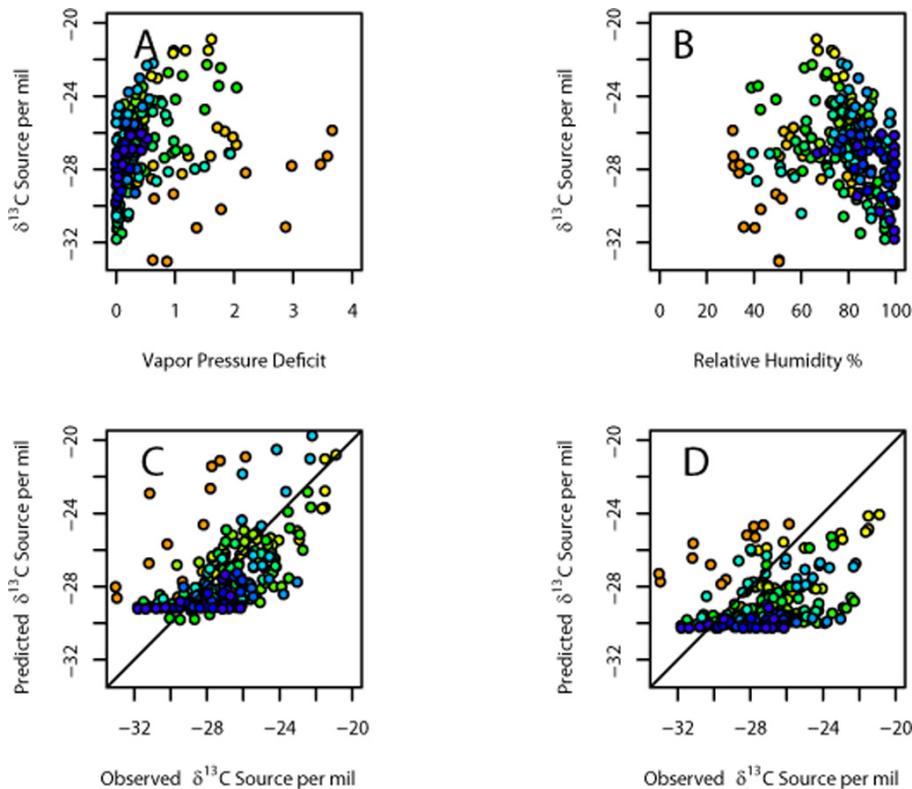


Fig. 3. Correlation analysis $\delta^{13}\text{CO}_2$ source (δ_s) and metrics of atmospheric water vapor. The color of points corresponds with the color code for individual sites denoted in Fig. 1. Global correlations for seasonal vapor pressure deficit and δ_s (**A**). Global Correlations for seasonal Fractional Humidity and δ_s (**B**). Comparisons between observed δ_s and predicted δ_s values for the Leuning Model driven by vapor pressure deficit (**C**) and for the Ball-Berry Model driven by fractional humidity (**D**). See Table 1 for global and local statistics and see Table 2 for model parameters.

Novel applications of carbon isotopes in atmospheric CO₂

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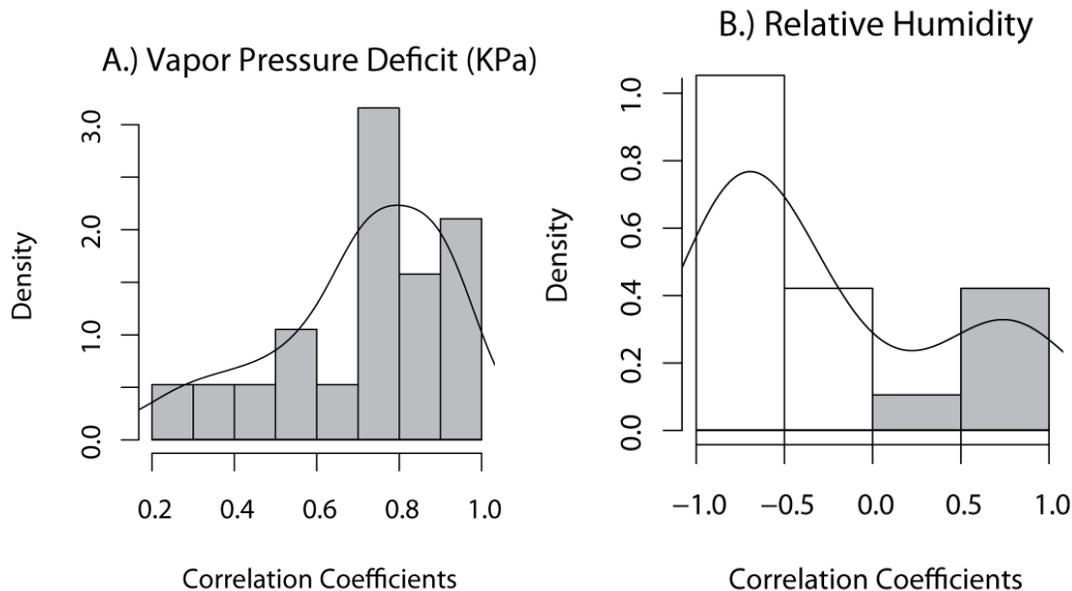


Fig. 4. Probability density functions for Pearson correlation coefficients. Correlation coefficients are reported for relationships between δ_s and vapor pressure deficit **(A)** as well as relative humidity **(B)**. Positive relationships are indicated by positive correlation coefficients (grey bars) and negative relationships are indicated by negative correlation coefficients (white bars). See Table 1 for actual values.

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