Final Report

National Institute for Climatic Change Research

Project Title:
Carbon Isotopic Studies of Assimilated and Ecosystem Respired CO_2 in a Southeastern Pine Forest

Project Grant No (Prime/Subaward):
DE-FC02-06ER64156/06-SC-NICCR-1063

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Funding (Last Award Year):
9/2006 to 9/2007: $59,015

Executive Summary:

Carbon dioxide is the major "greenhouse" gas responsible for global warming. Southeastern pine forests appear to be among the largest terrestrial sinks of carbon dioxide in the US. This collaborative study specifically addressed the isotopic signatures of the large fluxes of carbon taken up by photosynthesis and given off by respiration in this ecosystem. By measuring these isotopic signatures at the ecosystem level, we have provided data that will help to more accurately quantify the magnitude of carbon fluxes on the regional scale and how these fluxes vary in response to climatic parameters such as rainfall and air temperature. The focus of the MBL subcontract was to evaluate how processes operating at the physiological and ecosystem scales affects the resultant isotopic signature of plant waxes that are emitted as aerosols into the convective boundary layer. These wax aerosols provide a large-spatial scale integrative signal of isotopic discrimination of atmospheric carbon dioxide by terrestrial photosynthesis (Conte and Weber 2002). The ecosystem studies have greatly expanded of knowledge of wax biosynthetic controls on their isootpic signature The wax aerosol data products produced under this grant are directly applicable as input for global carbon modeling studies that use variations in the concentration and carbon isotopic composition of atmospheric carbon dioxide to quantify the magnitude and spatial and temporal patterns of carbon uptake on the global scale.

Proposal Objectives:

- *To quantify the magnitude and responses of photosynthetic carbon isotopic discrimination (Δ) and isotopic composition of respired CO_2 (δCr) and its components, namely foliage respiration and soil respiration, to variations in climatic forcing.*
- *To directly link the magnitude and time-varying pattern of isotopic discrimination of terrestrial photosynthesis with the isotopic signature of higher plant derived leaf wax aerosols emitted into the continental boundary layer.*

Project Approach:

To address Objective #1, we measured the isotopic composition of foliage organic matter (δC_{OM}), leaf soluble carbohydrates (δCsc) and needleleaf waxes (δCw) to assess leaf level carbon isotopic discrimination, and the isotopic composition of CO_2 respired by soil- (δCs), foliage-(δCf), and at the ecosystem-level (δCr). The field sampling campaign was at the Ameriflux site at the Austin-Carey Memorial Forest near Gainesville FL. Foliage samples for analysis of the $\delta^{13}C$ of bulk leaf tissue, leaf waxes and leaf sugars were collected at two sites within the Forest: an open, fire-managed mature (~65 year old mean tree age) stand of slash pine (*P. elliotii*) and longleaf pine (*P. palustris*) and a young (~15 year old mean tree age), dense monoculture stand of slash pine (Figure 1). This sampling was done in conjunction with respiration measurements conducted by Chanton and Mortazavi. Collection frequency was approximately every 3-4 weeks. These data were used in conjunction with meteorological and forest data gathered by the Ameriflux program (e.g. soil moisture, canopy vapor pressure deficit, temperature) to evaluate the linkage between climatic parameters and the isotopic photosynthetic discrimination and the $\delta^{13}CO_2$ of ecosystem-respired carbon. These activities allowed us to determine the magnitude and controls on the variability of photosynthetic carbon isotopic discrimination of atmospheric CO_2, the isotopic composition of respired CO_2 in southern pine forest ecosystems, and the newly biosynthesized and second year needle waxes (principally C_{20} to C_{36} *n*-acids).

We also conducted a related field study to evaluate whether there is an effect of tree height on isotopic discrimination. We hypothesized that taller trees would show lower canopy discrimination due to an effect of hydraulic conductance on water availability in the tree crowns, as indicated by the studies of (Ryan and Yoder 1997). Sunlit needles at the top of the canopy were collected by shotgun or pruners along a kilometer long transect. The heights of the trees was randomly distributed along the transect.

To address Objective #2, we deployed a mid-volume aerosol collector on the tower at the Donaldson stand to continuously measure the wax aerosol composition just above the forest canopy (Figure 1). Each aerosol sample collected continuously for approximately a two week integration period. The aerosol sampling campaign ran for approximately one year, from Dec 2004 to Dec 2005. For each sample, trajectories were generated using the NOAA HYSPLIT model (Draxler and Hess 1997) and rain-truncated (waxes are efficiently removed by precipitation). The trajectory clusters statistically estimate the aerosol footprint in each sample.

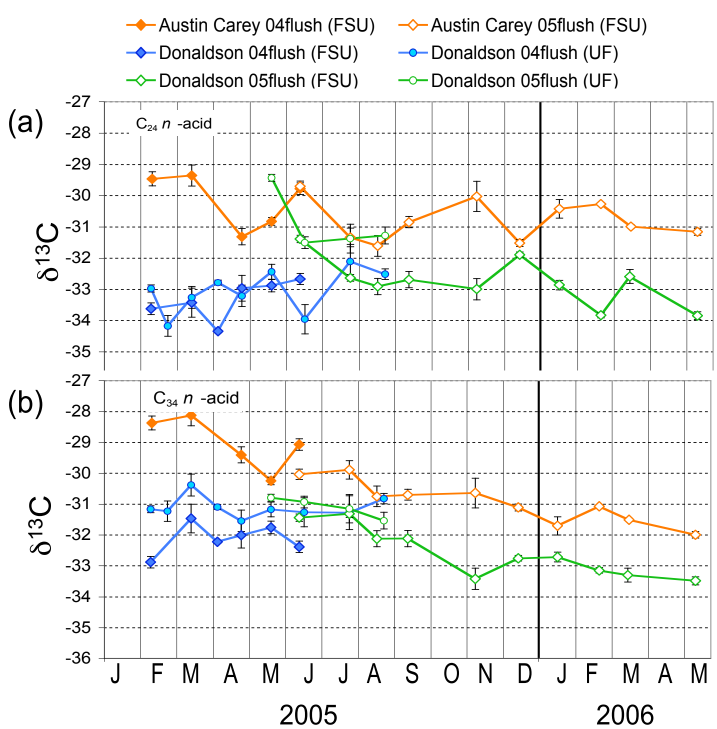
Figure 1. Above: The mature slash/longleaf pine stand at the Austin-Carey site. Right: The atmospheric sampling tower at the 15 year old slash pine stand at the Donaldson site. The aerosol collection apparatus (under round rain cover) can be seen at the top of the tower extending on a pole support positioned in direction of the prevailing winds.

Project Accomplishments:

(Please refer to report of collaborators Chanton and Mortazavi for discussion of respired carbon data)

(1) Temporal trends in plant wax isotopic composition and relationship to physiological and environmental parameters (Mortazavi et al., in prep., a; Conte et al. in prep.): Needle wax isotopic composition of slash pines (~15 yr mean age) and mature longleaf pines showed very little seasonality in this ecosystem (Figure 2). This finding concurred with analyses of bulk carbon, physiological data and isotopic data on CO_2 respiration that indicated little variation in photosynthetic discrimination over the sampling period. However, the mature longleaf trees at the Austin-Carey site were more enriched isotopically than the young slash pine plantation at Danaldson. The lower discrimination in longleaf pine appears to be related both its greater water use efficiency as well as its greater tree height (see below).

Although both canopy photosynthetic parameters and δCf did not show detectable trends over the two year sampling period, the $\delta^{13}C$ of canopy needle waxes in both the mature longleaf pines at the Austin Carey site and the 15-yr slash pine stand at the Donaldson site exhibited a small but statistically significant decreases over time. Interestingly, the rate of decrease in wax $\delta^{13}C$ was similar in both stands, leading us to speculate a similar physiological response to an environmental forcing. Our recent results of an isotopic labeling experiment have found that stored as well as recently fixed carbon pools contribute in the biosynthesis of leaf waxes, as well as other biosynthetic products (Crumsey *et al.* 2005, Mortazavi *et al.* 2008, Mortazavi *et al.* in prep, b). The contribution of stored carbon resources for biosynthetic processes leads to a temporal lag as well as damping of isotopic variation as old and newly fixed carbon is mixed in the biosynthetic products. Accordingly, a plausible explanation for the decreasing trend in wax $\delta^{13}C$ is a slow recovery from an environmental parameter such as drought that would lead to reduced discrimination in the past. The meteorological data collected by the Ameriflux team support of this hypothesis: extended spring droughts in both 2003 and 2004 resulted in a large precipitation deficit until autumn 2004 (Figure 3). Additionally, vapor pressure deficits during the spring flush period were higher and more pronounced in 2003 and 2004 than in 2005.



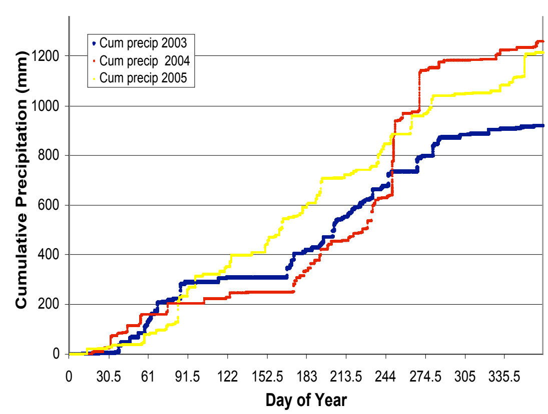


Fig. 2 (left). Time-series of wax n-alkanoic acids (a) C24 acid (b) C34 acid. The year of needle flush and the group collecting needles is indicated. FSU collected canopy vegetation by shotgun, whereas UF collected sunlit needles from canopy after physiological measurements were conducted. **Fig. 3 (above)** Cumulative precipitation 2003-2005 measured by the Ameriflux team.

A second unexpected finding was the influence of carbon chain length on the observed temporal trend (Figure 2). During the biosynthesis of waxes, the longer chain compounds are produced by chain elongation of shorter chain precursors, but the internal source(s) of the added carbons is not well known. Our results suggest that the added carbons may be more strongly sourced from recently-fixed photosynthate, and thus exhibit a stronger dependence on environmental conditions affecting fractionation. To evaluate this hypothesis, we used a simple mass balance equation to estimate the average $\delta^{13}C$ of the C_{32}-C_{36} acids, making a first order assumption that the average $\delta^{13}C$ of the C1 through C28 carbons in the C_{32}-C_{36} compounds is similar that measured for the C_{28} compound. If the presumed biosynthetic pathway of chain elongation of waxes is in fact correct, the results (Figure 4) indicate a ~10‰ decline in the $\delta^{13}C$ of carbons added during the chain elongation step over this period.

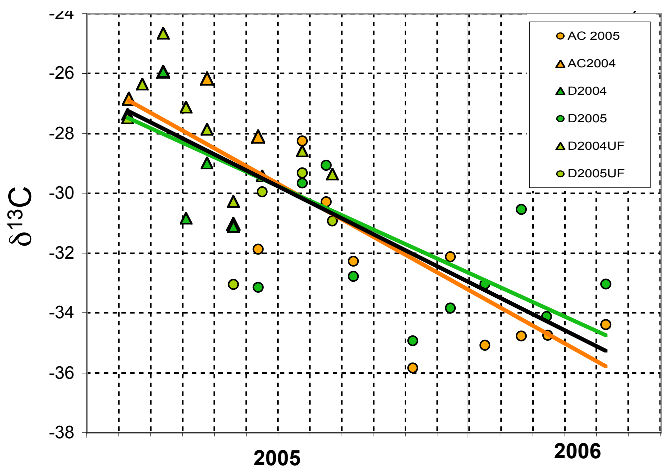


Fig. 4 Mass balance estimates of average $\delta^{13}C$ of the C_{32} to C_{36} carbons added during the chain elongation step in biosynthesis of long-chain needle waxes.

(2) Effect of tree height on carbon isotopic discrimination:

Studies (e.g. Ryan and Yoder 1997) suggest that leaf specific hydraulic conductance declines with tree height. Stomatal closure to conserve water would lead to a decline in assimilation and, in turn, isotopic discrimination. To evaluate this, we examined the relationship between tree height and photosynthetic parameters, leaf respiration δCf, organic matter δC_{OM} and needle wax δC_W. A weak or nonsignificant correlation was observed in photosynthetic parameters and δCf, but both bulk carbon and needle wax d13C was strongly correlated with height for trees between 15 and 25 m tall (Fig. 5). The regression was similar in all C_{24} to C_{36} wax *n*-acids, with an average of $\delta^{13}C_w = -35.42 + 0.25X$, where X is tree height in meters. These data confirm that waxes faithfully record plant discrimination.

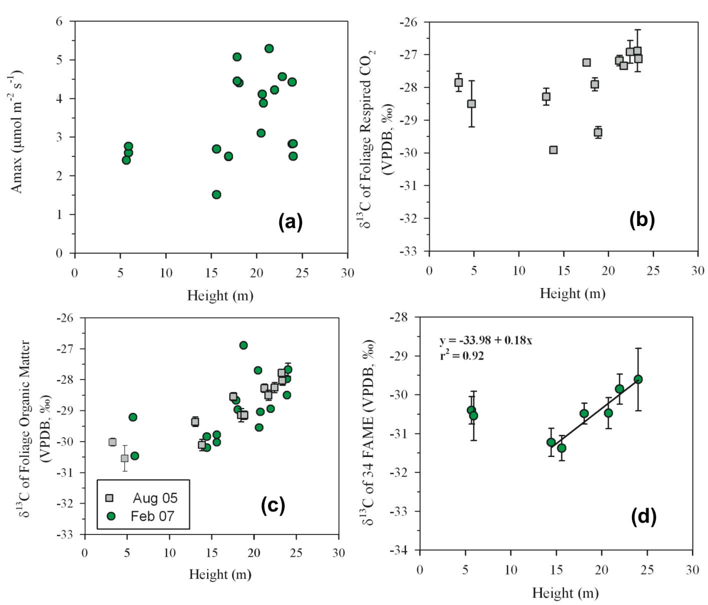


Fig. 5 Relationship between tree height and assimilation rate, A_{max} (a), and the d13C of leaf respired CO_2, δCf (b), bulk leaf carbon, δCp (c) and the C_{34} wax *n*-acid, δCp (d). The lack of any relationship for A_{max} and δCf is likely due to the short time period these measurements reflect.

(3) Temporal trends in above canopy wax aerosol molecular and isotopic composition:

Wax aerosol data previously collected as part of NIGEC-NERC funded research at the Ameriflux site at the Howland Experimental Forest, Maine indicates that the wax aerosol "footprint" is large regional in scale. Initial inspection of aerosol filters collected here also indicated the aerosol "footprint" was large, as the filters were noticeably loaded with charcoal when there was no local burning but controlled burns in the mid Florida region.

The time-series of wax aerosol molecular and isotopic composition confirms the very large spatial scale of the aerosol signal. A striking feature of the Florida data is the very large (~6 ‰) seasonal increase in $\delta^{13}C$ of the wax signal (Fig. 6left). This increase is consistent the increase in the contribution of C4 plants in the Northern Hemisphere (e.g. corn, sugar cane) as the growing season progresses, and also the greater contribution of easterlies transporting air masses African and Central American/Carribean regions in the summer. To illustrate this, in Fig. 6 (left) we have highlighted several large oscillations in wax aerosol $\delta^{13}C$. The ^{13}C enriched samples are marked by blue circles, and the ^{13}C depleted samples in red. Inspection of back air mass trajectories (Fig 6 right) shows that these oscillations were related to changes in the predominate wax aerosol source regions. Air masses transported by southerly flow corresponded to the more enriched aerosols, i.e. a greater contributions from C4 vegetation (or C3 vegetation with higher water use efficiencies), whereas North American air masses brought wax aerosols having a greater C3 plant signature. This pattern is also consistent with vegetation data and photosynthesis models that show a larger relative contribution of C4 plant photosynthesis at lower latitudes.

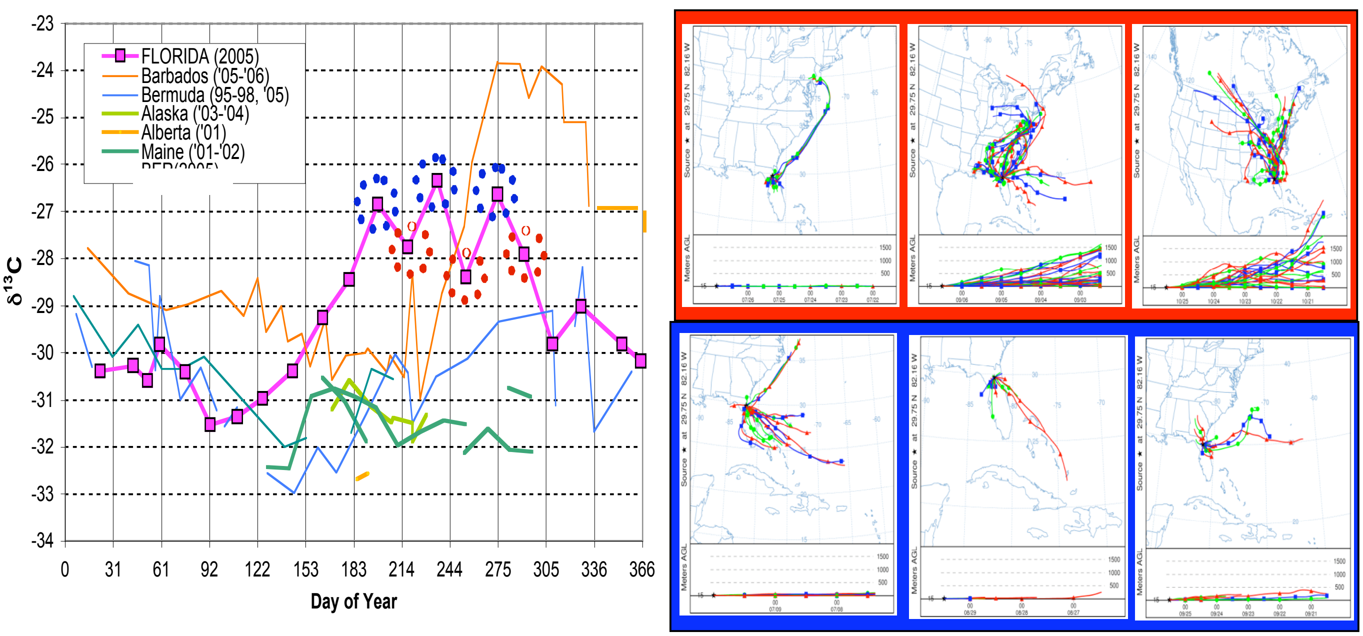


Fig. 6. (left) The $\delta^{13}C$ of the C_{24}-C_{34} wax *n*-alcohols (concentration-weighted averages) in aerosols collected just above the canopy at the Donaldson site (c.f. Fig. 1). Shown for comparison are our aerosol data from other sites. Barbados receives African air masses year round. Bermuda receives predominately North American air masses in winter/spring and both North American and African air masses in summer/fall. (right) The air mass trajectory footprints for the aerosol samples highlighted in blue and red.

Products developed under the award:

(1) Published abstracts (see addendum for copy):

Weber, J. C. and M. H. Conte. 2008. Large spatial-scale and temporal variability in carbon isotopic fractionation of atmospheric CO_2 by the terrestrial biosphere: A plant wax-aerosol proxy approach, *Geophys. Res. Abstracts,* 10, EGU2008-A-10062. European Geophysical Union General Assembly, Vienna, Austria, Apr 08.

Mortazavi, B., J. Chanton, M. Conte and T. Martin. 2008. Influence of tree height on the carbon isotopic discrimination of canopy photosynthesis in southeastern US pine forest ecosystems, *Geophys. Res. Abstracts*, 10, EGU2008-A-10062. European Geophysical Union, General Assembly, Vienna, Austria, Apr 08.

Mortazavi, B., M. Conte, M. Smith, J. Chanton, J.C. Weber, J. Crumsey and J. Barkman. 2008. Contribution of stored carbon pools to leaf level biosynthesis and respiration as revealed by ^{13}C labeling experiments. *Geophys. Res. Abstracts,* 10, EGU2008-A-09435. European Geophysical Union, General Assembly, Vienna, Austria, Apr 08.

Conte, M. H. and J. C. Weber. 2007. Biomass burning, long-range atmospheric transport and the sedimentary record of plant wax biomarkers", *Eos Trans. AGU, 88(52), Fall Meet. Suppl.*, Abstract PP51D-08, AGU Fall Mtg., San Francisco CA, Dec 07

Mortazavi, B., Chanton, J, Conte, M, Martin, T. 2007. Influence of tree height on the carbon isotopic discrimination of canopy photosynthesis in southeastern US pine forest ecosystems, *Eos Trans. AGU, 88(52), Fall Meet. Suppl.*, Abstract B13B-1197, AGU Fall Mtg., San Francisco CA, Dec 07

Conte, M. H. and J. C. Weber. 2006. Spatial and temporal patterns in $\delta^{13}C$ of leaf wax aerosols in continental air masses: Linkages with ecosystem discrimination, *Eos Trans. AGU, 87(52), Fall Meet. Suppl.*, Abstract B21-06, Fall AGU Mtg., San Francisco CA, Dec 06

Crumsey, J., M. Conte, J. C. Weber, B. Mortazavi, M. Smith and J. Chanton. Turnover of leaf waxes in florida slash pine: Results of an isotopic labeling experiment, *Eos Trans. AGU, 87(52), Fall Meet. Suppl.*, Abstract B22D-05, Fall AGU Mtg., San Francisco CA, Dec 06

Conte, M. H. and J. C. Weber. 2005. Quantification of isotopic fractionation of atmospheric carbon dioxide by terrestrial photosynthesis using the carbon isotopic composition of plant wax aerosols, *Eos Trans. AGU, 86(52), Fall Meet. Suppl.*, Abstract B13B-02. AGU Fall Mtg., San Francisco, CA, Dec 05

(3) Technology:

The grant provided opportunties to make improvements to our mid-volume aerosol collection system, to optimize it for future studies in more remote locations.

(4) Networking:

In addition to providing networking opportunities with Ameriflux researchers at the AC Memorial Forest, the grant provided travel funds for national and international conferences to present results, network and foster new collaborations for future research.

(5) *Sample collection and database:*

An archived vegetation sample collection is available for future study. The final database is available for future research endeavors (subject to a delayed release period as specified in the terms of the award agreement).

Contributions to education:

The grant provided support for several high school and undergraduate student assistants in the lab. In addition to providing direct experiences in research, the students have learned chemical analytical methods for analyses of bulk carbon/nitrogen, organic extraction methods and use of gas chromatographs and other analytical instrumentation. Additionally, some students were trained in use of the HYSPLIT model, providing them a solid introduction to the use of mathmatical models in environmental sciences.

Undergraduate and High School Students employed during the grant period.

Name	**University, City, State**	**% Time on Project**	**Degrees received during project, AY received**	**Congressional District**
Toltin, Abigail	Univ. Mass Dartmouth, MA	10%	sophomore	10
Clarkson, Rebecca	Brown Univ., Providence RI	30%	freshman	11
Gaylord, Andrew	Univ. Mass Amherst	25%	sophomore	10
Franzblau, Rachel	Ann Arbor Pioneer High School, Ann Arbor MI	25%	HS junior/senior	15

References:

Ciais P, Tans PP, Trolier M, White JWC, Francey RJ (1995) A large northern hemisphere terrestrial CO_2 sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO_2. Nature, 269: 1098-1102.

Conte MH, Weber JC (2002) Plant biomarkers in aerosols record isotopic discrimination of terrestrial photosynthesis. Nature, 417: 639-641.

Draxler RR., Hess GD (1997) Description of the Hysplit_4 modeling system. NOAA Tech Memo ERL ARL-224.

Fung I, *et al.* (1997) Carbon 13 exchanges between the atmosphere and biosphere. Global Biogeochem. Cycles, 11: 507-533.

Miller JB, Tans PP, White JWC, Conway TJ, Vaughn BW (2003) The atmospheric signal of terrestrial carbon isotopic discrimination and its implication for partitioning carbon fluxes. Tellus, 55B: 197-206.

Mortazavi B & Chanton JP (2002a) Carbon isotopic discrimination and control of nighttime canopy $\delta^{18}O\text{-}CO_2$ in a pine forest in the southeastern United States Global Biogeochemical Cycles, 10.1029/2000GB001390.

Ryan, M. G. and B. J. Yoder (1997) Hydraulic limits to tree heght and tree growth. Bioscience, 47: 235-242.

Yakir D & Sternberg L (2000) The use of stable isotopes to study ecosystem gas exchange. Oecologia, 123: 297-311.

Addendum
Abstracts of Conference Proceedings:

Weber, J. C. and M. H. Conte. 2008. Large spatial-scale and temporal variability in carbon isotopic fractionation of atmospheric CO_2 by the terrestrial biosphere: A plant wax-aerosol proxy approach, *Geophys. Res. Abstracts,* 10, EGU2008-A-10062. European Geophysical Union General Assembly, Vienna, Austria, Apr 08.

The carbon isotopic ratio ($\delta^{13}C$) of atmospheric CO_2 can help to partition land versus ocean fluxes because terrestrial photosynthesis strongly discriminates against $^{13}CO_2$ whereas ocean uptake does not. This approach requires precise knowledge of large regional scale patterns of carbon isotopic discrimination by terrestrial photosynthesis (Δ) but this has been problematic to quantify given the heterogeneity of terrestrial ecosystems. We are using a proxy approach based upon the $\delta^{13}C$ of higher plant-derived leaf wax aerosols in well-mixed continental air masses to scale up terrestrial photosynthetic discrimination (Δ) from the molecular to subcontinental scale. The approach combines the integrating power of atmospheric measurements with the specificity of organic biomarkers to isolate a large-spatially integrated signal of photosynthetic discrimination.

Continuous bulk aerosol measurements (2-week integration period) of wax aerosol molecular and isotopic composition have been made at strategically located sites that receive well-mixed air masses downwind of major ecosystems. High-volume samplers (ocean sectored to prevent local contamination) are used at towers in Bermuda and Barbados. A portable mid-volume unit with an aerosol sampler positioned above the canopy has been used at continental sites (Maine, Alaska, Alberta, Florida, French Guiana). Seasonality in the $\delta^{13}C$ of leaf wax aerosols (concentration-weighted $C_{24\text{-}34}$ *n*-alcohols) in the sampled air masses ranges from <2 per mil at Alaska and Maine sites to approximately 6 per mil at Barbados and Florida. Short-term variability in wax aerosol $\delta^{13}C$ can be attributed to shifting air mass trajectories, for example as observed at the Florida site when north westerlies bringing air masses from mid-latitudes of North America shift to south easterlies bringing subtropical air masses from the Caribbean and North Africa. At Barbados, extremely ^{13}C-enriched wax aerosols are sampled in Oct-Dec during the peak season of C_4 crop harvest/burning in the sub Saharan Africa. The wax aerosol-derived Δ of the air mass “footprints” we have sampled ranges over 10 per mil, from a nearly pure C_4 plant signal of 9 per mil in wintertime air masses arriving at Barbados from North Africa to a nearly pure C_3 plant signal of >19 per mil in air masses sampling north temperate ecosystems of North America in late spring. The magnitude and seasonality of the large-scale signal of Δ as estimated by wax aerosol $\delta^{13}C$ compares well with the model estimates of the global distribution of Δ and in seasonality in the relative contributions of C_3 and C_4 plant productivity and in the discrimination of C_3 plant ecosystems.

Mortazavi, B., J. Chanton, M. Conte and T. Martin. 2008. Influence of tree height on the carbon isotopic discrimination of canopy photosynthesis in southeastern US pine forest ecosystems, *Geophys. Res. Abstracts*, 10, EGU2008-A-10062. European Geophysical Union, General Assembly, Vienna, Austria, Apr 08.

Intensive investigations of carbon and water exchange in highly productive pine forests in the Southeastern US are restricted to a limited numbers of locations that are equipped with eddy covariance towers. These towers are mostly located within homogenous stands. However, the southeastern pine forests are composed of plantations of different ages/heights that are interlaced with hardwood forests. We have measured variability in photosynthetic parameters, and the 13C of ecosystem, foliage and soil respired CO2 over a 3-yr period at the Ameriflux tower site in Gainesville, FL, a slash pine ecosystem.

Additionally we examined trends in canopy foliage bulk organic matter 13C, leaf wax 13C and the 13C of foliage respired CO2 as a function of tree height. Sampled tree heights ranged from 5 to 25 meters along the transect, characteristic of pine plantations within this region. A highly significant positive correlation was observed between tree height and the 13C of foliage bulk organic matter. Leaf wax 13C mirrored the trend observed in foliage respired CO2 and bulk organic matter, with approximately a –3 ‰ offset from foliage respired CO2. Point measurements of upper-crown light-saturated net photosynthesis rate were not correlated with height, but were likely confounded by water stress effects. Research in other forest ecosystems has demonstrated tree height effects on hydraulics and leaf gas exchange, but these effects have not been explored in southern pines. These data suggest that southern pine hydraulics and leaf gas exchange may be influenced by tree height, and that scaling of isotopic data in these forests will require careful consideration of age and height variation.

Mortazavi, B., M. Conte, M. Smith, J. Chanton, J.C. Weber, J. Crumsey and J. Barkman. 2008. Contribution of stored carbon pools to leaf level biosynthesis and respiration as revealed by ^{13}C labeling experiments. *Geophys. Res. Abstracts,* 10, EGU2008-A-09435. European Geophysical Union, General Assembly, Vienna, Austria, Apr 08.

To assess how turnover rates of plant carbon pools affect the temporal coupling between photosynthesis and the isotopic signatures of respiration and biosynthetic products (leaf soluble carbohydrates and waxes), we grew slash pine (*Pinus elliottii*), sweetgum (*Liquidambar styraciflua*) and corn (*Zea mays*) plants in isotopically enriched $^{13}CO_2$ environments to label the plants, and then removed them to ambient conditions where we monitored the loss of ^{13}C label in night-time respiration (δC_F), leaf bulk organic matter (δC_{OM}), soluble carbohydrates (δC_{SC}) and waxes (dC_{LW}) over a several month period. Pine saplings were grown under label ($\delta^{13}CO2$ ~26 +/- 2 per mil) for an entire year before the start of the experiment. Small sweetgum trees were placed under label just prior to leaf out and for three months afterwards. Corn was grown from seed under label for three months. Controls were subject to similar conditions without the CO_2 treatment.

The δC_F label was rapidly lost within the first week with the rate (corn>pine>sweetgum) inversely correlated with the total plant carbon stock. The label then slowly approached the control value, but after two months labeled sweetgum and pine δC_F still remained depleted by ~5‰, indicating continuing respiration of unlabelled, stored carbon pool(s). In contrast, δC_F of labeled corn reached that of the control after one month, indicating complete turnover of pools. For δC_{SC}, <5% of the pine and <35% of the sweetgum label was lost after two and three months, respectively. In labeled corn, dC_{SC} returned to control values within two weeks. For δC_{LW} and δC_{OM}, <5% of the pine and sweetgum labels were lost after two and three months, respectively. In labeled corn, $\delta C_{LW}$and δC_{OM} slowly approached control values although both remained depleted by 5‰ even after one month. These results indicate a strong, continuing influence of plant stored carbon pools on the isotopic composition of respiration and biosynthetic products. Signal damping and temporal offset arising from the influence of stored carbon pools requires consideration when relating plant respired $^{13}CO_2$ and the ^{13}C of foliage products to environmental variables.

Conte, M. H. and J. C. Weber. 2007. Biomass burning, long-range atmospheric transport and the sedimentary record of plant wax biomarkers", *Eos Trans. AGU, 88(52), Fall Meet. Suppl.*, Abstract PP51D-08, AGU Fall Mtg., San Francisco CA, Dec 07

Sedimentary distributions of plant leaf wax molecular and isotopic composition can provide detailed information about past terrestrial ecosystem structure and its variability in response to climatic forcing. However, in many locales (e.g. marine sediments, high elevation lakes), sedimentary plant waxes are derived primarily from atmospheric deposition rather than from local fluvial input or direct runoff. Thus, an understanding of wax atmospheric transport and deposition is essential for accurate interpretation of the sedimentary signal. In this talk we synthesize results from our studies of wax aerosol composition and atmospheric transport at strategically located sites (Northern Alaska, Maine, Florida, Bermuda, Barbados, French Guiana) that sample continental air masses passing over major terrestrial ecosystems (tundra, North American boreal, temperate and southern pine forests, North African desert grasslands, Amazon rain forest). Wax aerosols in boundary layer air masses reflect a large regionally integrated source signal. Over the North Atlantic, the long-range atmospheric transport of plant waxes is essentially uncorrelated with episodes of high African dust transport. Rather, the highest plant wax aerosol concentrations are clearly associated with continental air masses that are laden with smoke from biomass burning, which enhances long-range transport both by the process of steam distillation of wax and other easily volatilized compounds off living (moisture-rich) vegetation in the advancing front of the fire and by deep atmospheric convection, which efficiently injects re- condensed particles into the lower troposphere where they can be most efficiently transported by high altitude winds. The direct linkage between enhanced long-range atmospheric transport of plant waxes and biomass burning suggests that the wax sedimentary record in localities dominated by atmospheric input strongly co-varies with climate-driven changes in fire frequency and is compositionally biased towards the ecosystem structure of the burned source regions.

Mortazavi, B., Chanton, J, Conte, M, Martin, T. 2007. Influence of tree height on the carbon isotopic discrimination of canopy photosynthesis in southeastern US pine forest ecosystems, *Eos Trans. AGU, 88(52), Fall Meet. Suppl.*, Abstract B13B-1197, AGU Fall Mtg., San Francisco CA, Dec 07

Intensive investigations of carbon and water exchange in highly productive pine forests in the Southeastern US are restricted to a limited numbers of locations that are equipped with eddy covariance towers. These towers are mostly located within homogenous stands. However, the southeastern pine forests are composed of plantations of different ages/heights that are interlaced with hardwood forests. We have measured variability in photosynthetic parameters, and the 13C of ecosystem, foliage and soil respired CO2 over a 3-yr period at the Ameriflux tower site in Gainesville, FL, a slash pine ecosystem. Additionally we examined trends in canopy foliage bulk organic matter 13C, leaf wax 13C and the 13C of foliage respired CO2 as a function of tree height. Sampled tree heights ranged from 5 to 25 meters along the transect, characteristic of pine plantations within this region. A highly significant positive correlation was observed between tree height and the 13C of foliage bulk organic matter. Leaf wax 13C mirrored the trend observed in foliage respired CO2 and bulk organic matter, with approximately a –3 ‰ offset from foliage respired CO2. Point measurements of upper-crown light-saturated net photosynthesis rate were not correlated with height, but were likely confounded by water stress effects. Research in other forest ecosystems has demonstrated tree height effects on hydraulics and leaf gas exchange, but these effects have not been explored in southern pines. These data suggest that southern pine hydraulics and leaf gas exchange may be influenced by tree height, and that scaling of isotopic data in these forests will require careful consideration of age and height variation.

Crumsey, J., M. Conte, J. C. Weber, B. Mortazavi, M. Smith and J. Chanton. Turnover of leaf waxes in florida slash pine: Results of an isotopic labeling experiment, *Eos Trans. AGU, 87(52), Fall Meet. Suppl.*, Abstract B22D-05, Fall AGU Mtg., San Francisco CA, Dec 06

Isotopic discrimination of terrestrial photosynthesis, atmospheric CO2 concentration, and δ^{13}CO2 are important parameters in global carbon models that are employed to estimate global carbon sources and sinks. Yet, terrestrial isotopic discrimination can be highly variable over space and time, yielding large uncertainties of terrestrial fluxes. The isotopic composition of plant wax aerosols in continental air masses can be used as an indirect measure of the spatial and temporal patterns of photosynthetic discrimination integrated over large (subcontinental) spatial scales. However, the temporal offset between wax biosynthesis and the wax aerosol isotopic signal of photosynthetic discrimination is not well constrained. To further our understanding of this temporal lag, this study sought to determine the turnover time of conifer leaf waxes by performing an isotopic labeling experiment. Four clonal pine saplings were placed in a tent and labeled with enriched $^{13}CO_2$ for one year, while another four control saplings were grown under ambient CO2. At the end of the year long enrichment, the labeled saplings were removed from the tent and placed in ambient air, such that the wax turnover rate could be determined by analyzing the resultant isotopic and molecular changes. The results of this experiment indicated that after 80 days of sequestering ambient CO2, the wax (and soluble sugar) isotopic composition of the labeled saplings varied minimally. The molecular composition of the waxes, however, did change over time. From these results we concluded that waxes are turning over, but rather than being synthesized de novo from recently fixed carbon precursors they are synthesized using carbon from stored (labeled) carbon pools. Therefore, the $\delta^{13}C$ of conifer leaf waxes in aerosols may not reflect recent photosynthetic discrimination, but instead represents photosynthetic discrimination integrated over a longer period of time. The implications of these findings are focused on interpreting the wax aerosol $\delta^{13}C$ as an integrative measure of past photosynthetic discrimination in global carbon cycling models, and also provide new insights on internal cycling among plant carbon pools.

Conte, M. H. and J. C. Weber. 2006. Spatial and temporal patterns in $\delta^{13}C$ of leaf wax aerosols in continental air masses: Linkages with ecosystem discrimination, *Eos Trans. AGU, 87(52), Fall Meet. Suppl.*, Abstract B21-06, Fall AGU Mtg., San Francisco CA, Dec 06

Temporal and spatial variations in the concentration and isotopic composition of atmospheric carbon dioxide can be used to estimate the relative magnitudes of the terrestrial and oceanic carbon sinks. An important model parameter is the terrestrial photosynthetic carbon isotopic fractionation of CO2 (Δ), yet estimating Δ over the large spatial scales required by models remains problematic. Epiculticular leaf waxes appear to closely reflect the plant's carbon isotopic discrimination; therefore, the ablated wax aerosols present in well-mixed continental air masses may be used as a proxy to estimate the magnitude of Δ integrated over large (subcontinental) spatial scales. Over the last several years, we have been conducting time-series studies of wax aerosol molecular and isotopic composition at strategically located sites (Maine, northern Alaska, Florida, Bermuda, Barbados) which receive continental air masses passing over major terrestrial biomes (northern temperate/ecotonal boreal forests, tundra, southern US pine/hardwood forests, North American and north African). In this presentation, we describe and contrast patterns of wax aerosol-derived estimates of Δ at these sites. In North American air masses, estimates of Δ range from 14.5-20.5 using the concentration-weighted average $\delta^{13}C$ of wax n-acids and from 13.5-19.5 for the wax n-alcohols. Seasonal trends observed in the Florida (southern US) and Bermuda samples (mixed North American air masses) indicate maximum discrimination in early spring and minimum discrimination during the summer dry season. In northern US and high latitude air masses, seasonal trends are less pronounced but in general temporally offset with highest discrimination occurring during late summer. At Barbados, which is dominated by north African air masses passing over regions largely comprised of arid C4 grasslands, estimated Δ for the wax n-acids is significantly lower (14.0-15.5 per mil), consistent with a higher predominance of C4 plants in the aerosol source regions; however, the estimated Δ for the wax n-alcohols is roughly 2 per mil higher indicative of possible different weighting of vegetation sources. Interannual variability is also observed to some extent signifying that the wax aerosol signal of Δ is sensitive to year-to-year differences in environmental forcing (e.g. drought).

Conte, M. H. and J. C. Weber. 2005. Quantification of isotopic fractionation of atmospheric carbon dioxide by terrestrial photosynthesis using the carbon isotopic composition of plant wax aerosols, *Eos Trans. AGU, 86(52), Fall Meet. Suppl.*, Abstract B13B-02. AGU Fall Mtg., San Francisco, CA, Dec 05

The concentration and carbon isotopic composition of atmospheric CO_2 can be used to partition terrestrial and ocean carbon sinks because terrestrial photosynthesis strongly discriminates against ^{13}C whereas discrimination during ocean uptake is negligible. This approach, though powerful, depends upon the accurate knowledge of the temporal and large spatial scale variation in terrestrial photosynthetic discrimination (Δ), a formidable challenge due to heterogeneity of terrestrial ecosystems. Previous studies have indicated that the isotopic composition of plant leaf wax aerosols record Δ over large regional spatial scales and at ~monthly resolution. Recent studies have focused upon the processes that link carbon isotopic discrimination at the ecosystem scale with the isotopic composition of plant wax aerosols in the atmospheric boundary layer. In this presentation we will synthesize results from "groundtruthing" studies of terrestrial ecosystems [Alaska (tundra), Italy (hardwood beech forest), Florida (slash pine forest), Maine (transitional boreal forest), and Alberta (northern prairie)] and from sampling continental air masses at remote island stations (Bermuda, Barbados). These data provide further evidence that wax isotopic composition faithfully tracks changes in plant discrimination and that ablated waxes in continental air masses reflect the weighted Δ of the source ecosystems.