Intro

* Streams link the terrestrial to the marine, actively transporting and transforming terrestrial carbon before it reaches the world’s oceans. Inland waters play a pivotal role in global energy cycling, acting as essential conduits where all substrates must pass through before reaching the ocean.
* Historically, streams were viewed as passive "pipes" merely transporting terrestrial debris downstream with minimal biogeochemical activity
* However, contemporary understanding characterizes streams as "active pipes" that actively transform carbon through processes like respiration and mineralization (reactor pathways), while also transporting global carbon through degassing and weathering (chimney pathways).
* Stream carbon is predominantly allochthonous, originating from terrestrial uplands and entering streams through lateral transport, either from soil carbon or via “pulse-shunting” during precipitation events. Once in the stream, carbon follows one of two pathways: the chimney or the reactor pathway. The chimney pathway involves the passive transport of externally sourced carbon (from soil, upland runoff, or groundwater), which largely exits the stream through CO2 degassing, with minimal downstream transport. In contrast, the reactor pathway involves the mineralization of organic carbon through respiration or anaerobic processes, producing CO2 as a byproduct.
* Most stream CO2 emissions come from the chimney pathway, with more CO2 degassing from inland waters than can be attributed to internal stream metabolism. However, the prominence of each pathway depends on spatial and temporal factors. Seasonal variations, such as temperature changes, enhances the rate of biogeochemical reactions, while seasonal flow regimes affect residence times, organic matter stocks, and redox potential, all of which dictate respiration rates and the reactor pathway's influence.
* Dually, spatial factors play a significant role in the chimney pathway, determining how the surrounding landscape influences external carbon contributions. Elements such as landscape slope, the presence of confined versus unconfined aquifers, soil permeability, and the extent of wetland areas impact lateral, surface, and subsurface carbon export to streams, thereby modulating the reactor pathway's influence.
* For example, Kirk and Cohen (2020) observed that net ecosystem productivity (NEP) contributed anywhere from 0% (chimney dominates) to 94% (reactor dominates) of stream CO2 and was dependent on whether the stream belong to an unconfined or confined aquifer basin.
* Despite current research into the role of inland waters in global carbon cycling, the dynamics of stream carbon input and output remain poorly understood. One major issue is the underrepresentation of low-order streams in global carbon cycle models. These headwater streams, which account for 75% of the terrestrial world's drainage network, are often remote and difficult to access, hindering comprehensive global studies. Consequently, there is limited research on how carbon dynamics in low-order streams influence higher-order receiving streams.
* Furthermore, although it is well acknowledged that streams are global carbon sources, the drivers of stream CO2 emissions remain largely speculative. Both spatial and temporal interactions are not fully resolved. Most studies on stream metabolism and carbon dynamics do not encompass multi-annual cycles or high-frequency data, leaving gaps in understanding the variations over time and space.
* However, the advent of high-frequency, durable sensors—many of which are cost-effective and efficient—presents an opportunity to observe carbon dynamics across seasonal fluctuations, rapid disturbances, and "hot moments." With the addition of long-range communication technologies that enable wireless internet connectivity, research in remote locations can become less resource-intensive.
* The objective of my first chapter is to investigate watershed-scale carbon dynamics, greenhouse gas emissions (GHG), and metabolism over a multi-annual timescale, focusing on the response of low-order streams to flow extremes and seasonal changes. To explore these dynamics, I have selected nine remote, flatwood streams within BEF and their higher-order receiving river, the Sampson River where I will deploy high-frequency, long-term sensor packages containing low-cost CO2 and methane sensors in these locations. Additionally, I will collect monthly samples for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and particulate organic carbon (POC).
* My research aims to parse seasonal and flow-induced fluctuations in stream carbon into the reactor and chimney pathways, a perspective rarely explored in current literature. Furthermore, I will use ternary diagrams to explore how carbon speciation (DIC, DOC, or POC) changes temporarily with flow and temperature.
* I hypothesize that (1) the chimney pathway dominates in flatwood streams, but the reactor pathway becomes more prominent during baseflow conditions when residence times are longer, and external contributions are minimal. Secondly, I hypothesize that (2) DIC, in the form of CO2, is the most prevalent carbon species, but DOC concentrations peak during high-flow periods. Lastly, I expect that (3) streams in basins with greater wetland areas predominantly source water from the chimney pathways, whereas streams in basins with less wetland area exhibit a more prominent reactor pathway.

Methods:

*Sites:*

The BEF is a contiguous pine flatwoods landscape situated above the substantial Hawthorne Formation clay bed, which confines the principal aquifer, the Upper Floridan Aquifer (UFA) (Hensley & Cohen, 2017). This area, characterized by low-relief topography, features numerous depressional basin wetlands typical of North Florida flatwoods. These wetlands, both isolated and riparian, support a shallow water table that serves as a buffer against drought and acts as a transport network for nutrients. The land is primarily managed for silviculture and is largely owned by the Rayonier Corporation, with only a few residential homes and businesses present.

Streams within the BEF exhibit typical characteristics of blackwater systems: they are tannic, rich in dissolved organic carbon (DOC), have low pH levels, and contain high concentrations of carbon dioxide (CO2) (~20,000 ppm). These streams, both permanent and intermittent, drain the landscape before discharging into the Sampson River (at the southern extent) or Sampson Lake (at the northern extent). Nine streams (Stream IDs: 3, 5, 5a, 6, 6a, 7, 9, 13, and 15) across nine delineated basins were chosen for long-term observations and monthly sampling. Each stream displays distinct characteristics owing to each basin’s specific features, such as wetland area and groundwater influence. Each basin falls along a gradient of wetland area that dictates the stream’s hydroperiod. Streams 5a, 6a, and 15 are ephemeral, only wet after consecutive precipitation events. In contrast, Streams 5, 6, and 9 are rarely dry, likely due to the dense wetland coverage in basins 5, 6, and 9. Although groundwater seepage is uncommon in BEF, Stream 13 exhibits high specific conductivity, high DIC concentrations, and remarkably clear water for the landscape, indicating deeper groundwater influences.

*Long-term Observations:*

Each of the nine selected streams will be equipped with a sensor package that tracks hourly changes in water quality. This package includes sensors for dissolved oxygen (DO), pH, CO2, and specific conductivity (SpC), as well as a pressure transducer (PT). In streams 5 and 6a, located in the northern and southern regions respectively, a PT will be deployed in ambient conditions for accurate water depth calculations. Each sensor package will be serviced, and data offloaded once a month.

DO and temperature measurements will be used to assess stream metabolism, delineating reactor-pathway sourced carbon, while corresponding CO2 measurements will track total CO2 concentration from both pathways. Data on CO2, pH, and temperature will be used to interpolate continuous concentrations of HCO3 -and CO32-.

*Sampling:*

During the monthly sensor servicing, each stream will be sampled DIC, DOC, FDOM, and POC. Analyzing DIC is notoriously challenging due to its tendency to degas from the sample, potentially underestimating concentrations. To minimize error, acid-washed Shimadzu sample vials are used in the field to sample DIC, avoiding any potential degassing during decanting. In the field, vials are filled to maximum capacity to prevent head-space equilibration. After collection, all samples are stored in the fridge and analyzed within 48 hours.

Both DIC and DOC analyses will be conducted using the Shimadzu TOC-L analyzer, employing the total organic carbon (TOC) measurement method. Although FDOM is more stable than DIC, it can degrade if stored for extended periods, or denatured if frozen. Therefore, FDOM samples are stored in the fridge in opaque, dark bottles and analyzed on the Horiba Aqualog within three weeks of collection. POC samples are collected using 500mL to 1L Nalgene bottles, submerged midway in the water column and capped underwater. The samples are then filtered using 0.45-micron filters. These filters are then processed utilizing the ash-free dry weight method.

*Stream Metabolism:*

To estimate the significance of the reactor pathway in flatwood streams, stream metabolism—the rates of gross primary productivity (GPP) and ecosystem respiration (ER)—will be modeled. Stream metabolism serves as a holistic, in-situ measure of stream carbon cycling and organic carbon mineralization. ER represents the total respiration (oxygen consumption) and is the dominant pathway for internal CO2 generation, while GPP represents the total productivity (photosynthesis; oxygen production) within the ecosystem. Assuming a respiration ratio of 1:1 for CO2 and DO (where every mole of DO consumed results in the respiring of a mole of CO2), the difference between observed CO2, and CO2 estimated by ER, indicates allochthonous CO2 from the chimney pathway.

One-station stream metabolism estimates GPP and ER by tracking continuous fluctuations in dissolved oxygen (DO) concentrations (mg/L) over time (hr^-1) and depth (m^-3), calculating an oxygen flux (g O2 m^-3 hr^-1) where GPP indicates oxygen production and ER indicates consumption. Stream metabolism modeling will be performed using StreamMetabolizer (Appling et al. 2020), an open-source R package that integrates principles from Odum’s *Primary Production in Flowing Waters* and Bayesian modeling to estimate GPP and ER. DO fluxes will be interpolated using recorded data from our sensor packages.

*Estimating Gas Exchange*

To determine air-water exchange rates—an essential parameter for stream metabolism modeling—the reaeration coefficient (K600) will be field-estimated using gas dome methods. During each monthly field visit, K600 will be empirically estimated using a floating dome, an inverted plastic container with a headspace volume of 15.5 L. Within the dome, a high-frequency CO2 sensor will be placed in the headspace, sampling at 1 sample per 10 seconds for approximately 25 minutes. Given that stream CO2 concentrations often exceed 20,000 ppm, the diffusion of CO2 from the water column to the headspace will be monitored to calculate the rate of air-water equilibration.The gas exchange velocity, K (m d^-1), which represents diffusion between the water column and atmosphere (Hall and Ulseth, 2019), and subsequently the reaeration coefficient, k (d^-1) (calculated as K divided by stream depth), were predicted following methodologies outlined by Khadka et al. (2014) and McDowell & Johnson (2018).

Using the field-measured K600 values and discharge data, a rating curve will be developed to enable continuous estimation of K600. This rating curve will be integrated into *StreamMetabolizer* to refine K600 estimates as a function of discharge to improve accuracy. Discharge measurements will be obtained through periodic dilution gauging. During monthly field visits, streams with observable flow will undergo dilution gauging using salt dilution techniques and slug-injection methods. By correlating depth at the time of dilution gauging with discharge rates, a rating curve will be constructed to maintain continuous discharge estimates.

*DIC Interpolation*:

Using the Bjerrum equation, continuous bicarbonate (HCO3^-) concentrations will be interpolated from temperature, pressure (PT), pH, and CO2 sensor measurements. The R package seacarb facilitates estimation of the first and second dissociation constants of carbonic acid based on temperature and water pressure, streamlining data manipulation processes.