Intro

Introduce streams as drainage network:

* *Streams link terrestrial and marine environments, actively transporting, storing, and transforming terrestrial carbon before it reaches the world’s oceans.*
* *Terrestrial runoff flows into low-order, small streams, accumulates downstream in higher-order rivers before eventually discharging into the ocean.*
* *Within the ‘conventional carbon cycle’, streams were viewed as passive "pipes," merely transporting terrestrial debris downstream with minimal biogeochemical activity.*
* *Current knowledge understands streams as active players within the carbon cycle, or "active pipes," storing and transforming nutrients through respiration, mineralization, and anaerobic processes in addition to transporting “the ruins of continents”.*
* *All of terrestrial carbon eventually runoffs into stream but less than half is fated for the ocean. The rest mineralized or degassed to the atmosphere*
* *What enters the world’s oceans is the byproduct of numerous biogeochemical transformations and losses as water transitions from lower-order to higher-order streams and rivers.*
* *In fact, the sum of stream carbon is greater than in terrestrial inputs.* More than double of CO2 *emissions from streams is not accounted for by stream metabolism, and*
* *stream carbon fluxes are significantly greater per unit area than surrounding terrestrial uplands, impacting regional carbon balances, and in turn, global carbon budgeting.*
* *Streams, especially low-order, headwater streams, Are* *disproportionate active sites for c cycling relative the area they occupy however the detailed processes and mechanisms that allow higher activity to be sustained is unknown.*
* *Smalls streams cover more than 75% of the entire drainage basins and function as important elements in the global carbon cycle,* 
  + *Small headwater catchments have higher DOC concentrations and than downstream waters- have larger influence on the larger biogeochemical cycles*
  + *We do not have global co2are often remote and difficult to access, hindering comprehensive global studies.*
  + *Scaling has limitations. challenges for gas exchange rates, velocity, depth, and width assume steady state conditions and pose challenges for perenila ecosystems*
* Cole

Chimney-Reactor:

* Soil carbon pools often become mobilized when groundwater levels rise or soil waters exceed a critical moisture levels
* *What is understood but poorly constrained is stream carbon is fated for two pathways: the chimney pathway and 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.
* 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.*
  + *Low flows: residence time is similar to processing time*
  + *High: fast residence time. Disrupts the ecosystems ability to process carbon*
* *Dually, 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.*
* *Streams swing between pipe and reactor states (hypothesized from Zarnetske 2018) and are dictated by residence times*
* *The objective of my first chapter is to investigate carbon dynamics within low-order, flatwood streams over multi-annual timescales, focusing on the response to flow extremes, seasonal fluctuations, and landscape hydrology.*
* *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.*
* *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."*
* *Additionally,* *I will collect monthly samples for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and particulate organic carbon (POC).*
* *I aim to parse* *seasonal and flow-induced fluctuations in stream carbon* *into the reactor and chimney pathways, a perspective rarely explored in current literature.*
* *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:*

* *I need to add why I want to look at each*
* *POC: affects remain largely unknown because challenging to capture. Largely storm driven in so challenging to capture. Wide range of reports depedend on the catchmenst erosion potential*
* *DOC: derived from POC. Powers productivity. Linked to hydrology and carbon reservoirs related to flow regimes as well as*
* *DIC: CO2, but mentioned mineral weathering. We expect it to be low but Florida is essentially a limestone deposit so helpful to look*

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.