**Chapter 2: The River Corridor is a Significant Source of Stream Carbon.**

Wetlands are functionally unique inland waters, serving as global carbon sinks rather than carbon sources (Abril et al., 2014; Cole et al., 2007; Raymond et al., 2013). Wetland emergent vegetation is highly productive, sequestering and mineralizing CO2 while wetland soils—hydric and anoxic from the surficial aquifer—store litterfall, debris, and decaying organic matter (OM) for months to decades (Abril & Borges, 2019; Cole et al., 2007; Mitsch et al., 2013; Raymond et al., 2013; Wilcock et al., 1999). The long residence times allow substantial carbon processing (Leibowitz et al., 2018; Mitsch et al., 2013), with most wetland carbon fated for long-term burial and a minority being mineralized by anaerobic processes or exported downstream (Cole et al., 2007; Raymond et al., 2013; Solano et al., 2024). While wetland hydric soils are recorded to be substantial sources of greenhouse gases (GHGs), the carbon storage potential of wetlands (Leibowitz et al., 2018), coupled with the productivity of emergent vegetation, offsets these emissions. Often described as the intermediate between the terrestrial and the aquatic (Cole et al., 2007), wetlands possess the productivity of the terrestrial biosphere while maintaining inundated conditions.

Many wetlands have strong connectivity with streams, rivers, and lakes via subsurface or overland flow (Leibowitz et al., 2018; Raymond et al., 2013; Solano et al., 2024). Specifically, riparian wetlands bridge lotic and terrestrial environments, serving as the ecotone between terrestrial uplands and flowing waters (Kirk & Cohen, 2023; Ledesma et al., 2018). Unlike depression wetlands, all lateral exports from the catchment must bypass riparian wetlands before discharging to streams. Therefore, despite comprising only 7% of wetland area, riparian wetlands are hypothesized to have a disproportionate influence on the global carbon budget (Abril & Borges, 2019; Kirk & Cohen, 2023). Coined by Abril and Borge (2019) as “carbon pumps,” riparian wetlands possess significant potential for carbon storage and delivery, with riparian groundwater and soil water having higher DOC (Ledesma et al., 2015, 2018) and CO2 (Abril et al., 2014) concentrations than stream water. Additionally, riparian groundwater and the hyporheic zone have been observed to have higher CO2 concentrations than stream water and are predicted to have an inexhaustible pool of DOC at current export rates (Ledesma et al., 2015). Beyond carbon storage and export, riparian wetlands are hypothesized to regulate stream carbon export, transforming carbon in their hydric soils and facilitating carbon exchange between the stream, the hyporheic zone, and the riparian zone(Ledesma et al., 2018). Especially in headwater streams, riparian wetlands play a prominent role as carbon reactors.

The bidirectional exchange between a stream and its adjacent riparian wetland is termed the river corridor, which includes the stream, the hyporheic zone, and the riparian wetland from surficial aquifer to canopy (Harvey & Gooseff, 2015; Kirk & Cohen, 2023). Encompassing both the riparian wetlands and stream respiration, the river corridor is assumed to play a prominent role in stream carbon cycling (Abril & Borges, 2019; Kirk & Cohen, 2023; Ledesma et al., 2015, 2018). Yet, the contribution of the river corridor to the global carbon budget is largely unknown, poorly constrained, and often neglected in research. The river corridor is often excluded from global estimates because remotely distinguishing riparian wetlands from terrestrial uplands is challenging, making river corridor delineations subjective (Raymond et al., 2013). Regionally, in-situ measurements of river corridor groundwater and stream CO2 dynamics are scarce. Studies investigating wetland carbon fluxes to streams often overlook riparian wetlands, focusing instead on isolated or intermittently connected wetlands linked to streams by overland flow (Casson et al., 2019; Solano et al., 2024). Research on the riparian corridor has yet to compare riparian versus upland carbon, systematically capture carbon fluxes across terrestrial-wetland and wetland-stream boundaries, or consider the landscape hydrology. In-situ measurements of riparian groundwater and stream CO2 dynamics are scarce, leading to inflated global estimates of groundwater inputs to stream carbon while underestimating the significance of aquatic ecotones, potential global hotspots for carbon storage and exports. Kirk and Cohen (2023) found that 86% of CO2 in the lower Santa Fe River originated from its riparian wetlands, with only 14% sourced from groundwater seepage. Similarly, studies in boreal forests have shown that up to 90% of CO2 is derived from the river corridor (Ledesma et al., 2015, 2018).

For the second chapter of my dissertation, I will investigate the importance of the river corridor (RC) on stream carbon by estimating RC carbon fluxes to streams. In three streams, spanning a gradient of wetland coverage, I will estimate DIC, DOC, and CO2 fluxes from the RC to the stream using a combination of water samples and sensor readings. In addition to field measurements, I will synthesize information from the literature, the US Water Quality Portal (WQP), and the National Water Information System (NWIS) to explore RC carbon transport across both confined and unconfined watersheds, broadly elucidating the RC's role in global stream carbon fluxes. I hypothesize:

1. The RC delivers the majority of stream carbon and serves as a significant carbon stock in the flatwood landscape.
2. RCs within basins with greater wetland area will exhibit greater carbon-storage potential due to their raised water tables supporting lateral, subsurface transport.
3. Additionally, I expect RC carbon fluxes will be greatest during high discharge periods when the surficial aquifer is shallowest.

This chapter will develop a conceptual understanding of RC carbon contributions across different watershed types (confined and unconfined aquifer units) to broadly interrogate the significance of terrestrial-aquatic ecotones and lateral carbon transport.

Methods:

An ecosystem garnering increasing interest for its capacity to store carbon is the flatwoods of North Florida. Due to the flatwoods confined aquifer and dense wetland-area, deep groundwater seepage is negligible, and the flux of carbon to streams is primarily driven by lateral transport via the shallow water table. As a result, North Florida’s flatwood landscapes exhibit unique modes of carbon transport that are largely disconnected from deep groundwater upwelling. This hydrology fosters carbon storage and creates a transport network through which nutrients and particulates flow laterally downhill before ultimately discharging into tannic, blackwater streams.

For this chapter, I will observe three river corridors (RCs) from three streams (Stream: 5, 6, and 9) within the Bradford Experimental Forest (BEF), a contiguous pine flatwood situated above confining clay bed (Hawthorne Formation. Each of these streams belong to three distinct basins, each representing a gradient of wetland coverage (Ref. map).

*Sampling and sensor readings:*

Along with the high-frequency, long-term sensor packages from Chapter 1, groundwater wells will be strategically installed across each stream's river corridor (RC). RC wells will be deployed along the RC’s elevation gradient (stream bank, upland, and in-between) and in any significant micro-landscapes (intermittent flow paths and depressions, if present). Each well will be installed during the dry season to ensure the shallow water table can be reached even when the stream bed is dry, ensuring at least one well from each site has a viable volume of water present for sampling. Prior to sampling, at least triple the volume of the well water will be removed. If the well water is exhausted during this process, the well will be deemed dry.

Well water will be pumped directly into sample bottles for DIC and DOC analysis. For point readings, well water will be pumped into a chamber equipped with a CO2 sensor (K30 10%), a pH sensor, and inflow and outflow openings. The well-water will enter through the inflow opening and exit through the outflow opening, ensuring a continuous flow of well-water through the chamber. Readings will be monitored until the chamber reaches equilibrium. Equilibrium measurements will be recorded.

*Sample Processing:*

Both DIC and DOC analyses will follow the methods outlined in Chapter 1. For quality control, DIC will also be interpolated using the pH, temperature, and CO2 point readings, and select samples will be periodically analyzed for alkalinity.

FDOM samples will be analyzed following the protocols outlined in Chapter 1. FDOM results will infer how carbon quality changes as it travels across the river corridor.

*Discharge Estimates:*

The estimation of RC lateral fluxes will use methods adapted from Kirk and Cohen (2020) and will incorporate concepts from Kalbus et al. (2016) and Leopold & Maddock (1953). This approach involves first parsing stream discharge into baseflow and high discharge, the latter assumed to be surface runoff. In the second stage, Digital Elevation Models (DEMs) will be used for stream delineation analysis to estimate the upslope contributing area (UCA). The UCA represents the land area that contributes to the stream discharge. Finally, lateral discharge is interpolated by multiplying the UCA by the baseflow, referred to as qUCA. RC carbon fluxes are then calculated by dividing RC carbon concentrations by qUCA.

*Data Synthesis:*

By integrating water quality data from WQP and Digital Elevation Models (DEMs) from the USGS National Map, along with data from the nine streams in BEF, I will select approximately five additional streams from both confined and unconfined aquifer units to investigate RC carbon contributions across different watersheds. Assuming carbon concentrations are proportional to stream discharge and using methods outlined in *Discharge Estimates*, qUCA​ represents the volume of discharge generated by the surficial aquifer. Therefore, the difference between total discharge (Q) and qUCA is the discharge supplied by groundwater (Q−qUCA=qgw). Assuming carbon concentrations are proportional to stream discharge (and removing carbon sourced from stream respiration), stream carbon can be parsed into RC carbon and groundwater seepage using the ratios qUCA:Q and qgw:Q

Workflow:

1. Using sites from Appling et al. 2020I will screen the WQP corresponding CO2, DOC, TOC, and DIC data. If adequate carbon data is unavailable, I will screen for pH and temperature to interpolate either CO2.
2. Pair sites with adequate data to DEMs from the USGS National Map.
3. Subtract each site’s respiration carbon from total CO2.
4. Interpolate UCA using methods from Kirk and Cohen (2020), and filtering techniques from Kalbus et al. (2016) and Leopold & Maddock (1953).
5. Calculate qUCA ​and qgw
6. Interpolate carbon sources using the ratios qUCA:Q and qgw: Q.

*Statistical Analysis:*

To test Hypothesis 1, the RC delivers the majority of stream carbon, respiration-derived CO2 from Chapter 1 and estimated carbon from the RC will be subtracted from the total stream carbon. The remainder will be classified as "other," assumed to be sourced from groundwater seepage and overland flow. The proportions of carbon sourced from respiration, the RC, and "other" will be compared over time and across different basins.

For Hypothesis 2, basins with greater wetland areas will have larger RC exports, a linear regression model will be used to compare changes in RC fluxes with increasing basin-wetland coverage. Similarly, to assess whether RC carbon contributions vary with water table depths and stream discharge (Hypothesis 3), linear regression analysis will be employed between carbon concentrations, water table depth, and stream discharge. Furthermore, to assess the carbon quality as it travels through the RC, the humic index and fluorescence index from the FDOM analysis will be correlated with the wells' distance to the river. A linear regression will evaluate the RC’s biogeochemical influence on carbon quality.

By employing these statistical analyses, the study aims to investigate the factors influencing RC carbon-stream contributions and assess their significance in comparison to landscape hydrology.