Title: *Exploring critical zone structure and function in a tropical urban watershed through concentration-discharge relationships*

Introduction: Streams are recognized as integrators of the surrounding landscape. Stream water chemistry is thus an excellent indicator of broader critical zone (CZ) processes. The CZ is the space from the top of the vegetative canopy down to bedrock and lowest extent of freely circulating groundwater.[1] The CZ framework provides a holistic approach to develop predictive models that describe processes at the earth's surface, including the constraints on material export from the continents to fluvial networks.[2] Concentration-discharge (C-Q) relationships in streams provide an integrated signal of sources and transport processes to examine how solutes and sediment respond to changing patterns of runoff.[3] Studies of the CZ are mostly limited to pristine systems; however, C-Q relationships in urban streams may be more complex due to altered hydrology, impaired water quality and heterogenous subcatchments.[4] With increasing pressures on urban landscapes, there is an urgency to understand hydro-biogeochemical processes of the urban CZ that govern water quality and quantity. Research in urban systems will be highly valuable to cities and communities and can better inform management practices and help improve urban infrastructure.[4]

I propose to characterize and compare C-Q relationships across two stream networks with differing levels of urban development through a series of whole-network sampling efforts capturing baseflow to storm events. I also propose to study the impacts of hurricane disturbance on C-Q trends through analysis of long-term water chemistry records. I will test three hypotheses on variability in C-Q relationships across stream networks associated with watershed urbanization (H1-H3):

H1: Watershed urbanization drives greater variability in C-Q relationships across stream networks associated with increased impervious surface area.
H2: C-Q relationships during storm events are more variable in the urban network due to heterogenous hydrologic signals, and ultimately depend on storm intensity.
H3: Both urban and pristine stream networks show increased variability in C-Q relationships after hurricane disturbance, but the magnitude of variability is higher in urban watersheds.

Study sites: This work will be conducted in two watersheds: the urban Río Piedras in metropolitan San Juan, Puerto Rico and the mostly undeveloped Río Espíritu Santo in El Yunque National Forest in Río Grande, Puerto Rico, as a reference site. The Río Piedras flows through the metropolitan area with highly modified channels and significant impacts from failing sanitary infrastructure.[5] In contrast, the Río Espiritu Santo originates in the Luquillo Mountains and is mostly undeveloped except on its coastal plain with significant changes in water chemistry evident only after hurricane impacts.[6] The University of New Hampshire´s (UNH) Water Quality Analysis Lab (WQAL) group, including myself, has extensive experience working in these two stream networks. These watersheds are also a part of the Luquillo Long-Term Ecological Research (LTER) site and Luquillo Critical Zone Observatory (LCZO), which have generated multi-decadal records of stream chemistry and discharge. The lab also has ongoing collaborations with research groups at the University of Puerto Rico (UPR), who have worked in the Río Piedras: Jorge Ortiz-Zayas's Tropical Limnology Lab and Alonso Ramírez's Aquatic Ecology Lab.

Proposed approach: (H1) I will establish a synoptic sampling regime of 20 sites in each stream network, ranging from small headwater sites to larger mainstem and coastal sites. I will collect water samples as well as measure physicochemical parameters with a handheld multiparameter instrument at least 15 times in the span of 2 years. Samples will be analyzed for nitrate, ammonium, phosphate, dissolved organic carbon, anions, cations, dissolved greenhouse gases, and total suspended solids (TSS) at the UNH WQAL Lab. I will also take discharge measurements at each site and date either using dilution gauging or acoustic velocity measurements, depending on stream size. I will target sampling dates that capture a range of flow conditions by monitoring the US Geological Survey (USGS) gauging stations at two sites within each stream network. This sampling will allow me to characterize spatial and temporal variability in C-Q relationships across the stream network. **(H2)** I will conduct targeted storm sampling at one USGS gauged site in each stream network with ISCO automated samplers. These samples will be analyzed for the same solutes as in H1, with a focus on TSS to calculate sediment flux during storm events. Real-time discharge data for these events will be obtained online through the USGS´s National Water Information System Interface. I will capture events of different magnitude to explore effects of storm magnitude and intensity on C-Q relationships and solute and sediment transport. I will use these results to evaluate specific patterns of hysteresis, which characterize the rising and falling limbs of a storm event, providing additional insights into material reservoirs within watersheds. **(H3)** I will use long-term chemistry data from sites in the Río Piedras and the Río Espíritu Santo, which have been sampled weekly for approximately 10 years for multiple solutes and are USGS gauged sites. I will quantify C-Q relationships before and after Hurricane María in September of 2017 which will allow me to examine the resilience of these watersheds to a major perturbation.

Intellectual Merit: This work will provide insight into the interactions and mechanisms of sediment and nutrient production, pathways, and transport in a tropical urban watershed. Studying storm events and hurricanes is particularly important because they are "hot moments" of increased hydrological activity, which transport disproportionate amounts of solutes and sediments to streams and oceans compared to baseflow conditions.[7] Understanding high flow processes is crucial, as major storm events and hurricanes are expected to increase in intensity and frequency with climate change.[8] And though much C-Q work has been done on temperate systems, tropical streams supply disproportionate amount of sediments and solutes to the ocean and studying these systems in a global context is becoming increasingly important.[9] This work also leverages research done by the Luquillo LTER and LCZO research networks.

Broader Impacts: During this work, I will continue developing collaborations with local research groups in ways that will engage local underrepresented undergraduate students in fieldwork through my network and storm sampling efforts. I will work with UPR professors to offer independent research opportunities to students. This research will provide a useful framework for local government agencies to use in their nutrient and sediment management plans across the island, including restoration projects aimed to help reduce pollution and sedimentation and regain critical zone services in urban ecosystems.[7] For this, I will engage local researchers examining sediment and nutrient loading and the local Puerto Rico offices of the Department of Natural Resources. I will also collaborate with local organizations working in the Río Piedras such as the San Juan Bay Estuary and the ENLACE project of the Caño Martín Peña. These projects have longstanding efforts in the Río Piedras watershed and extensive connections with local communities. In collaboration with these organizations, I will use this opportunity to teach communities about water quality in their watershed through a series of roundtables and by providing educational resources to disadvantaged groups that have greater exposure to poor water quality.

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