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Spatial and Temporal Water Quality Assessment in the Lower St. Johns River, Florida

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Abstract - The St. Johns River is Florida's longest river and a valued resource. The river is important for the regionôs ecology and socioeconomics. Human disturbances, þooding from hurricanes, and runoff from industrial and wastewater treatment facilities and agricultural ýelds in recent years has prompted the need for an increased frequency in monitoring of the water quality conditions in the St. Johns River. The objective of this study was to measure various water chemistry parameters and metal (cadmium, copper, lead, nickel, silver, and

Land use surrounding the LSJR varies and includes agricultural, industrial, urban, suburban, and rural (Fig. 1); therefore, the pollutants and their loading also vary (Pinto et al. 2019, Pyati et al. 2012). Both point and nonpoint sources have contributed to the pollution in the LSJR over the years, including direct surface discharge, atmospheric emissions, and stormwater runoff (Pinto et al. 2018, Pyati et al. 2012). According to the Toxics Release Inventory, the main industries releasing chemicals in the LSJR basin include electric utilities, paper industries, the US Department of Defense (e.g., Army National Guard and US Naval stations), metals industries, and petroleum industries (EPA 2020). Nitrates, ammonia, and metals are among the chemicals released into the LSJR (EPA 2020).

In addition to the variety of industries discharging chemicals, stormwater runoff can carry pollutants from agricultural, silvicultural, urban, and rural areas into the river (Bielmyer-Fraser et al. 2017, Pinto et al. 2019). Nitrogen and phosphorus are important components of fertilizers and are therefore found in stormwater runoff (Correll 1983, Correll et al. 1992). In excess, those nutrients can cause eutrophic conditions in an aquatic system, resulting in stimulated growth of phytoplankton and bacteria, and depletion of dissolved oxygen (DO; Jordan et al. 1997a, b;

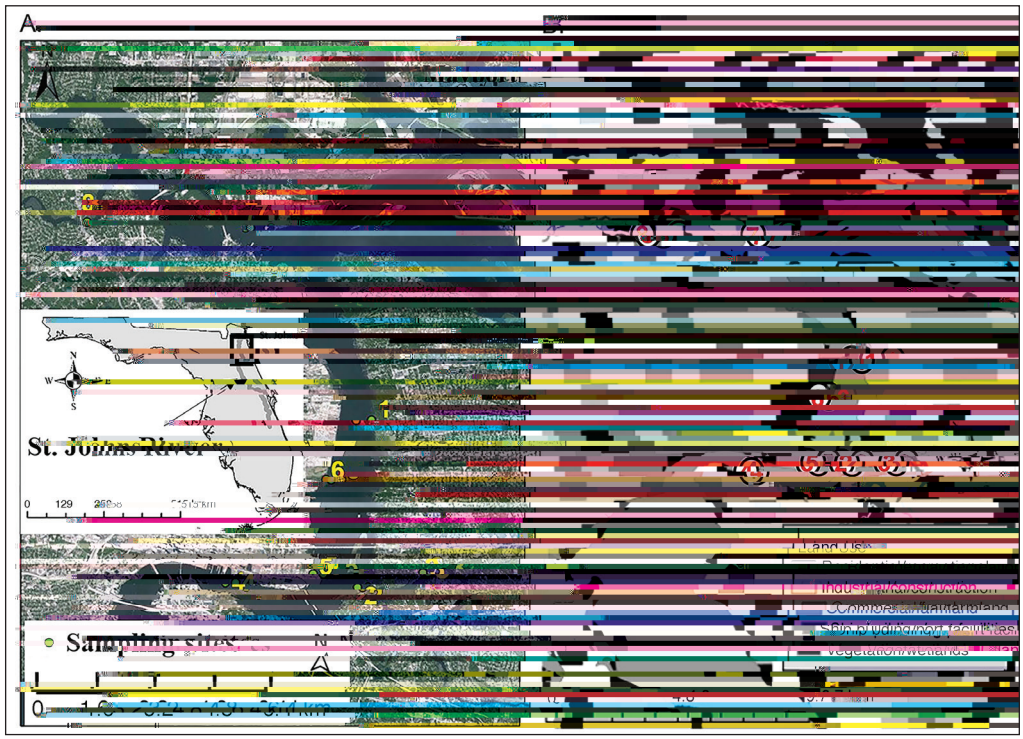

Figure. 1. GIS map containing (A) sampling site locations, with inset map of the State of Florida with the St. Johns River highlighted (the box indicates the area of interest), and (B) land-use designations in the Lower St. Johns River, FL. Site 1 = Jacksonville University dock, site 2 = Arlington River mouth, site 3 = Arlington River, site 4 = Hogan's Creek, site 5 = Downtown Dry Dock (south of Mathew's Bridge), site 6 = Superfund site (north of Mathew's Bridge), site 7 = Trout River Bridge, and site 8 = Ribault River Bridge.

Naumann 1929; Nixon 1995). Additionally, metals have been found in stormwater entering the LSJR and in the sediments from past contamination (Pinto et al. 2019). A variety of pollutants have been reported to exceed acceptable limits in the LSJR. For example, the US Naval Station at Mayport (Fig. 1) has had 12 exceedances of various pollutants including nickel and copper at levels above EPA class III water quality criteria between January 2016 and September 2017 (Berg et al. 2018).

Metal contaminants have been a growing problem in aquatic systems due to their many uses in modern society (Bielmyer-Fraser et al. 2017, Klein 1979, Pinto et al. 2019). Metals naturally enter aquatic systems through the weathering and physical break down of rock and sediment (Nriagu 1989). However, anthropogenic contributions of metals in aquatic environments are generally much greater than natural contributions and can often disrupt the natural cycles of elements (Eisler 1988a, 1988b, 1993, 1996; Klee and Graedel 2004; Nriagu 1996). Anthropogenic inputs of metals from nonpoint sources into rivers occur via agricultural and stormwater runoff and leachates from metal-based antifouling paints (Bielmyer et al. 2012a, Nriagu 1996, Pratt et al. 1981, Voulvoulis et al. 2000). Metals can accumulate in both plant and animal tissues, cause toxicity, and move through the food chain (Bielmyer et al. 2005, 2006; Bielmyer-Fraser et al. 2017; Jarvis et al. 2015; Mager and Grosell 2011), potentially impacting humans through consumption of aquatic species.

Water chemistry (i.e., salinity, hardness, DO, pH, oxidation–reduction potential
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(industrial efþuent, wastewater efþuent, nonpoint-source contaminants), and others had pollutant exposure from shipyards (metal structures and anti-foulant paints) and contamination issues (EPA Superfund site). Additionally, at many of these sites, metal concentrations have not been routinely measured by government agencies since 2016. Although we did not identify a reference or control site, we hypothesized that the degree and types of contamination at each site would vary.

Field sampling

At each site, we recorded GPS latitude and longitude coordinates. The sampling at each site occurred as close to the shore as possible, but it was not a consistent distance at every site because of varying depth. We measured DO, temperature,

To assess the health of the LSJR, we compared metal data to the Florida ambient water quality standards, including EPA class III water quality criterion values for both freshwater and saltwater/marine (haline; surface

this study, salinity þuctuated from 1 to 25 ppt at the 8 sites in the LSJR (Fig. 3A). Across all the sampling times, salinity was not signiýcantly different among sites; however, salinity was signiýcantly different among sampling times ($P < 0.001$). Signiýcant differences among sampling times were also observed for hardness (varying from 108 to 4360 mg $CaCO_3$/L; $P < 0.001$), alkalinity (varying from 60 to 500 mg $CaCO_3$/L; $P < 0.001$) and pH (varying from 7.48 to 8.43; $P < 0.001$) at the 8 sites in the LSJR (Fig. 3). Salinity, pH, hardness, and alkalinity all had strong positive correlations (Table 2). Temperature þuctuated seasonally with the lowest temperatures in the winter and highest temperatures in the summer; DO was

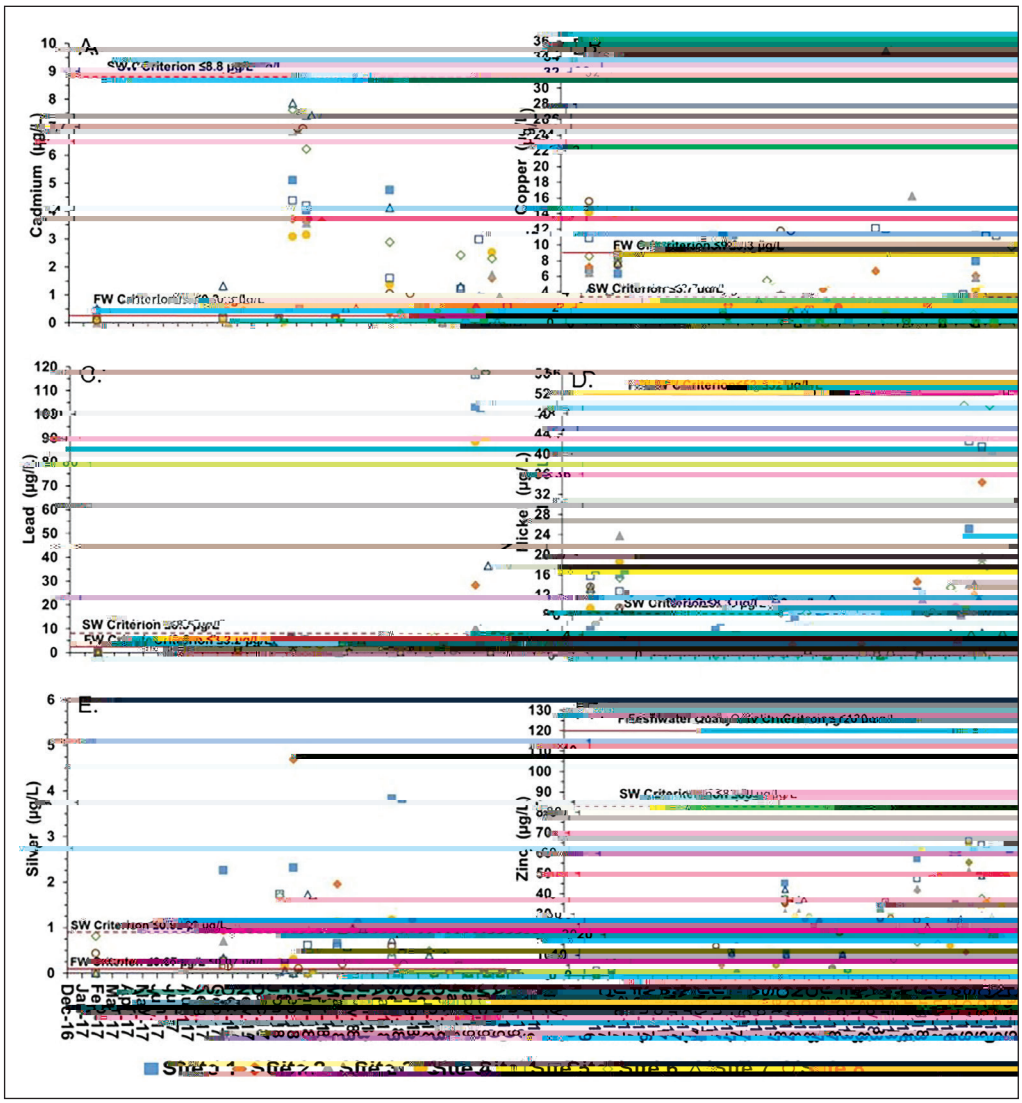

Figure. 2. Concentrations of (A) cadmium, (B) copper, (C) lead, (D) nickel, (E) silver, and (F) zinc in subsurface water samples collected at 8 sites (see Fig. 1) in the Lower St. Johns River, FL, from January 2017 to April 2019. Solid lines indicate the freshwater (FW) criterion, and dashed lines indicate saltwater (SW) criterion values for each metal.

inversely correlated with temperature (Fig. 3E, F; Table 2). Precipitation was greatest in the summer months (MayïSeptember; Fig. 5), and we observed signiýcant changes in water chemistry (e.g., salinity and hardness; Fig. 3) following these periods, as well as after the signiýcant þooding from Hurricane Irma (10ï11 September 2017; Fig. 5; Cangialosi et al. 2018). Salinity decreased substantially (Ò5 ppt) in the weeks following Hurricane Irma (October 2017 sampling date; Fig. 3).

The concentrations of nutrients (nitrate, nitrite, ammonia, and phosphate) were generally low, with exception of ammonia in 2017, where higher levels were observed (Fig. 4). No site-speciýc differences were observed among these variables even with the spikes in ammonia, particularly at site 1. Temporal differences only

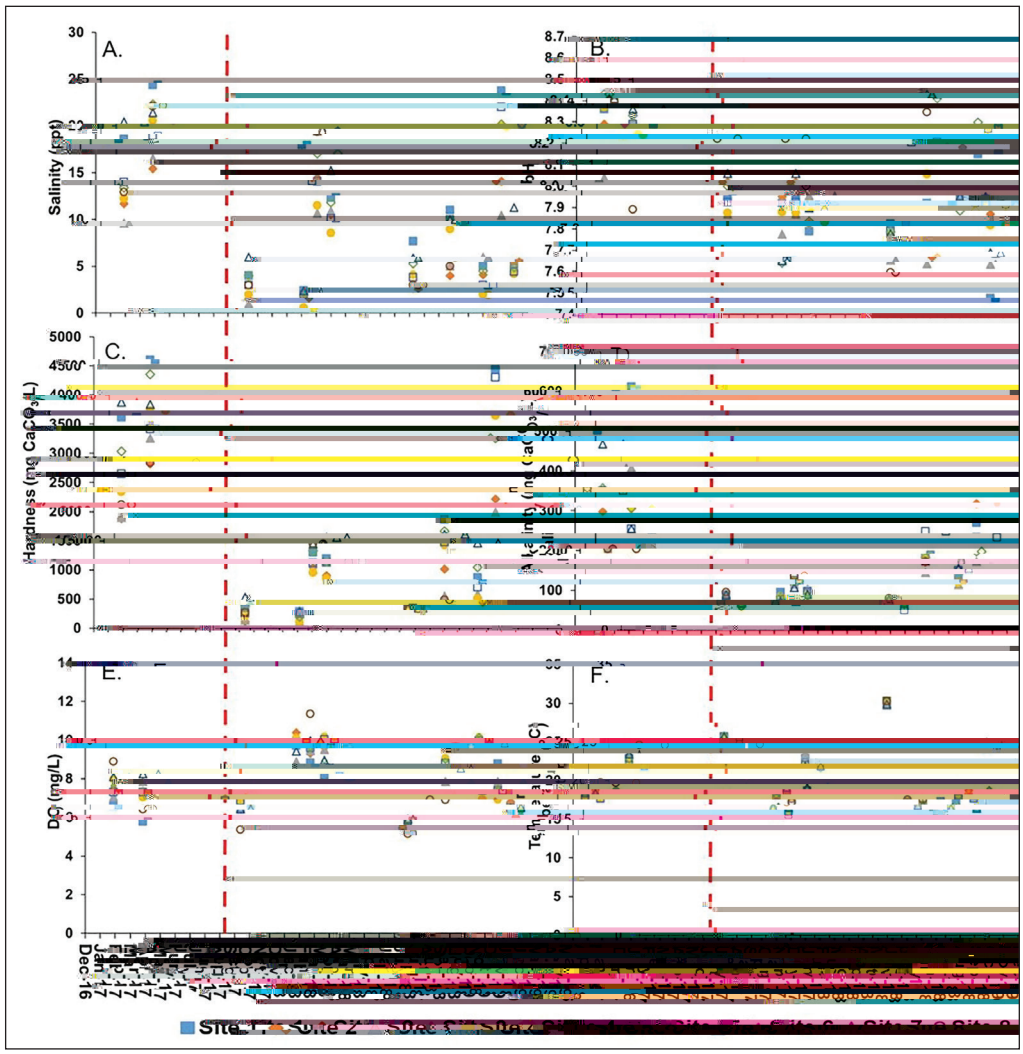

Figure. 3. (A) Salinity, (B) pH, (C) hardness, (D) alkalinity, (E) dissolved oxygen (DO), and (F) temperature in subsurface water samples collected at 8 sites (see Fig. 1 legend) in the Lower St. Johns River, FL, from January 2017 to April 2019. The dashed vertical line represents the occurrence of Hurricane Irma.

were observed in ammonia concentration ($P < 0.001$; Fig. 4). Phosphate was posi-

LSJR could have confounded detection of site-speciýc differences. More research is needed to elucidate this issue.

As metals enter the water column, they may remain suspended for varying lengths of time and accumulate in biota (DiToro et al. 2001). Metals ultimately bind to the sediment layer and the timeframe of this process is inþuenced by the abiotic and biotic factors at the site. Resuspension of metals into interstitial water may also occur with disturbance of the sediment through activities such as dredging (Hall 1989, Nayar et al. 2004, Reichert and Jones 1994). The most recent dredging project in the LSJR began in February 2018 by JaxPort, and a marked increase in metal concentrations was observed for several of the metals tested (e.g., cadmium, zinc, nickel, lead) at the 8 sampling sites in this study. For more than 20 years, metals in the sediments of the LSJR have been elevated above background levels (Pinto et al. 2019). NOAA (2008) reported elevated concentrations of chromium, zinc, cadmium, lead, and mercury in many of the LSJR sediment samples analyzed since 2000. Other studies have reported differences in metal concentrations in water and sediment due to dredging activities (Hall 1989, Nayar et al. 2004). Nayar et al. (2004) reported resuspension of metals during intensive dredging which resulted

LSJR, concentrations of commonly used metals such as copper (Bielmyer et al. 2012a) exceeded acceptable limits (water quality criteria) more frequently than some other metals tested, and no correlations with rainfall or dredging activities were observed. Copper enters the LSJR more frequently from land-base Ĩ

Poey (Mangrove Rivulus; Bielmyer-Fraser et al. 2018), were also similar to those detected in this study. Grosell et al. (2006) reported LC50 values for Fathead Minnow of 4.5 to 1903 Õg/L lead in waters of varying water chemistry. The highest lead concentrations detected in the LSJR in our study were 116ï118 Õg/L lead, detected

example, in laboratory studies, decreasing salinity and hardness increased the toxicity of zinc, nickel, and cadmium to 2 estuarine fish species, Mummichog and Mangrove Rivulus (Bielmyer et al. 2012b, 2013; Bielmyer-Fraser et al. 2018). Likewise, Blanchard and Grosell (2006) reported altered copper toxicity to Mummichogs with changing salinity. Following Hurricane Irma, salinity decreased while copper and silver concentrations increased above EPA Class III water quality criteria at site 1; therefore, aquatic organisms may have been more susceptible to toxicity during that time.

In addition to metals, excess levels of nitrogen and phosphorus can cause harmful effects in aquatic systems, including eutrophication and increased occurrence of algal blooms (Anderson et al. 2002). In the present study, nitrate, nitrite, and to some extent ammonia (except for a couple values) were relatively low. These forms of nitrogen are commonly found in the environment and interconvert to each other with microbial actions and different conditions such as oxygen availability and pH (Wright and Nebel 2008). Ammonia is a naturally occurring waste product of aquatic organisms and can be toxic to salini گ T خ خ خ خ Ä φ ę f , nitr

were above these limits and should therefore be protective. It should be noted that sampling during different times of the day could affect the DO concentration. In addition to sampling time, temperature, salinity, organic matter, nutrients, biological activity (e.g., photosynthesis, respiration) and other parameters can affect the DO concentration in a water body (Wetzel 2001).

In summary, this study provided reference values for various water quality variables and metal contaminants in the main stem and select tributaries of the LSJR over several years, which may be used for future research. To date, temporal differences, resulting from seasonal changes and episodic storm events, have been more signiýcant than site-speciýc differences. We hypothesized that there would be signiýcant differences in these parameters among sites, even though all the sites were affected to some degree by anthropogenic inputs, yet few differences were detected. It is important to note that site-speciýc differences could have been confounded in part by the occurrence of storms and þooding in the LSJR, therefore additional research is needed in dryer years to determine these impacts. All metals analyzed, except zinc, þuctuated above freshwater and saltwater quality criteria, indicating potential threats to aquatic biota. More research is needed to assess the effects of metal pollutants and changing water chemistry on the health of the þora and fauna in the LSJR. We hope to continue to research these issues and assess correlations between water quality and phytoplankton distribution.

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