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 region's ecology and socioeconomics. Human disturbances, flooding from hurricanes, and runoff from industrial and wastewater treatment facilities and agricultural fields 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 zinc) concentrations at 8 sites on the Lower St. Johns River associated with a variety of anthropogenic sources from 2017 to 2019. Water chemistry and metal concentrations varied to some degree across sites. Seasonal variation and variation due to episodic storm events were much more pronounced than the spatial variability. For example, salinity was significantly different on every sampling date. This parameter, among others, can directly influence aquatic life, as well as the bioavailability and toxicity of metals to aquatic organisms. All metals tested except zinc fluctuated at levels above EPA class III water quality criterion values, thus raising concerns about the future health of flora and fauna. This research provides reference data to improve the understanding of spatial and temporal variability of water quality parameters in the Lower St. Johns River.

Introduction

The St. Johns River is the longest river in Florida, slowly flowing northward 499 km (310 mi) from central Florida to terminate at Jacksonville and the Atlantic Ocean (Fig. 1; DeMort 1990, Morris 1995). As a Florida Class III water body, this river has designated uses of recreation and the maintenance of well-balanced fish and wildlife populations (Fla. Admin. Code. 62-302.400). Along with its ecological and recreational importance, the St. Johns River has attracted thousands of businesses, schools, and other industries to northeast Florida and is therefore of vital socioeconomic importance to the area (Pinto et al. 2019).

The Lower St. Johns River (LSJR) basin covers 6700 km^2 in portions of Volusia, Flagler, Putnam, St. Johns, Clay, and Duval counties in northeast Florida (Fig. 1; SJRWMD 2008). The LSJR receives water from rainfall, stormwater runoff, aquifers, and naturally salty springs (Benke and Cushing 2005), and the salinity can vary from fresh- to full-strength seawater (Hendrickson and Konwinski 1998, Malecki et al. 2004). The extremely low gradient and flow velocity of the river limit drainage and increase retention time of pollutants (Benke and Cushing 2005, Durako et al. 1988).

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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;

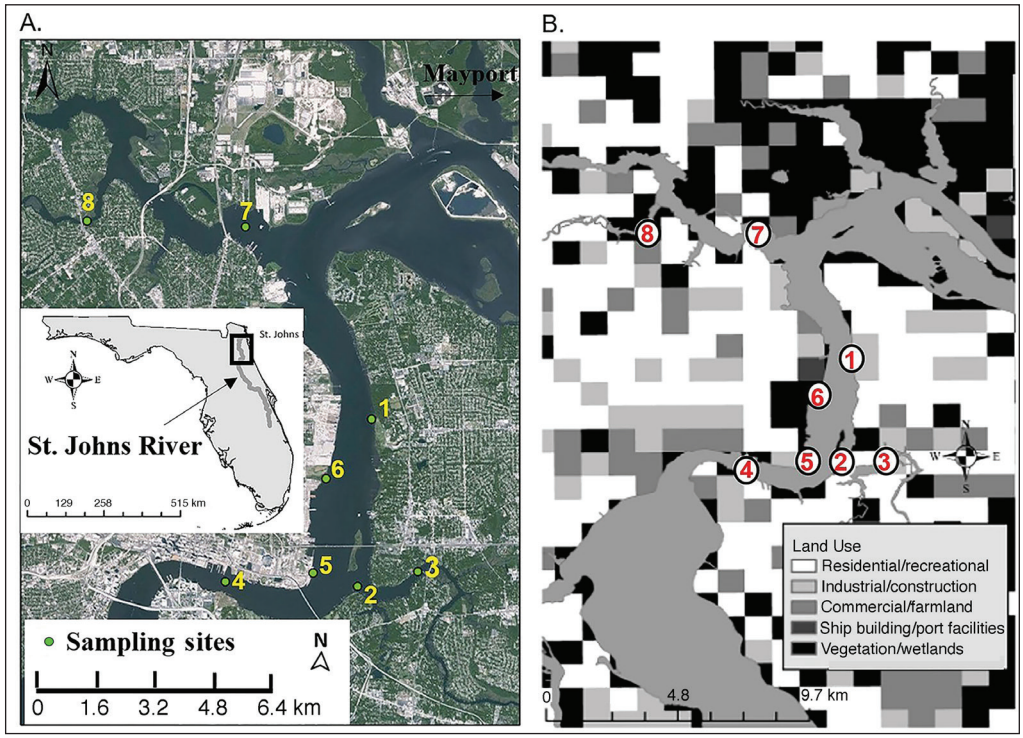

Figure. 1. GIS map containing (A) sampling site locations, with inset map of the State of Florida with the St. Johns River highlighted (the box indicates the area of interest), and (B) land-use designations in the Lower St. Johns River, FL. Site 1 = Jacksonville University dock, site 2 = Arlington River 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 [ORD]) is known to modify the toxicity of metals in various ways (Bielmyer et al. 2007, 2012b, 2013; Bielmyer-Fraser et al. 2018; Patel and Bielmyer-Fraser 2015; Mager et al. 2011). Therefore, metal toxicity may differ in different water bodies or along different sites of the same water body (Campbell 1995, DiToro et al. 2001). Additionally, there may be combined effects of multiple contaminants (e.g., metals and salinity) in the river ecosystem. Freshwater input from rainwater can change the salinity of the LSJR in a predictable manner, with the wet season extending from June to October (Rao et al. 1989). However, rapid changes in water quality (e.g., flooding from hurricanes, tropical storms, and nor'easters) can significantly affect biotic communities and reduce species biodiversity (Bielmyer and Grosell 2011, Cross and Williams 1981).

The overall goals of this study were to provide reference water chemistry and metal contaminant (cadmium, copper, lead, nickel, silver, and zinc) concentrations in the main stem and select tributaries of the LSJR and to document patterns and long-term temporal changes in these parameters.

Methods

Field sites

Criteria for selection of sampling sites included land use and impairments in the vicinity of the sites (e.g., near an Enivronmental Protection Agency [EPA]-designated Superfund site), and time and fuel constraints to reach the sites. We identified 8 sites along the LSJR in northeast Florida as having impairments, due to various land-use practices (Fig. 1). We visited the sites periodically (12 times) over a 2-year period (February 2017 to April 2019) between approximately 11:00

am and 4:00 pm, using Jacksonville University research vessels, the Seabatical and the RV Larkin. Due to time constraints or other obstacles, we did not sample sites 7 (sampled 10 times) and 8 (sampled 5 times) on every sampling date.

Site 1 is located near Jacksonville University, with cargo ship unloading occurring on the far shore (across the waterway). Sites 2 and 3 are located at the mouth and farther upstream in the Arlington River, respectively (Fig. 1). The Arlington River is tidally influenced and highly urbanized (65.8% of the total watershed area), receiving drainage from Pottsburg Creek, Little Pottsburg Creek, Strawberry Creek, and Silversmith Creek sub-basins (Magley 2009). Surface runoff, groundwater inflow, septic tanks, a wastewater treatment facility, as well as loading from upstream drainage areas (urban, agricultural, forest, wetland land uses) contribute nutrients (nitrogen and phosphorus) into the Arlington River (Magley 2009). Consequently, Arlington River has been identified as impaired for these nutrients. Site 4 is near the mouth of Hogan's Creek and is historically polluted with various contaminants including phosphorus (Wainright 2006). Additionally, this site contains hazardous, toxic, and radioactive waste, resulting in part from ash deposits dating back to the early 1900s (Pinto et al. 2019). Exceedances of metals in addition to other contaminants have been documented at this site (USACE 2012). Several factories are located along the shores of Hogan's Creek, with over 98% of the land use designated as residential, commercial and services, and institutional (49.3% high density) (USACE 2012). Site 5 is located near the North Florida Shipyard at Commodore Point. This facility has been operating in Jacksonville since 1977, and a few examples of the work there consists of blasting and coating, rudder and propeller repairs, as well as fabrication and installation of ship components (NFSY 2019). These processes may result in metals leaching into aquatic environments. Site 6 is located near Deer Creek and is an EPA-designated Superfund site (Kingon and Reich-Zeisher 2009, Patterson 2016). The land use is categorized as 33.4% high density residential, 14.5% light industrial, and 13.3% commercial and services (Kingon and Reich-Zeisher 2009). The Kerr–McGee Chemical Corp was placed on the EPA Superfund Program's National Priority list in 2010 due to contaminated soil and groundwater from the facility (EPA 2017). The company used 670 different chemicals in the manufacturing of pesticides and fertilizers (Patterson 2016). Site 7 is at the mouth of the Trout River, which is surrounded by land that is predominantly (72%) natural area (including wetlands), with about 28% impacted by humans (low-density residential areas) (Magley 2009, Wainwright and Hallas 2009). Excess nutrients from septic tanks and other nonpoint sources have been reported in the Trout River (Wainwright and Hallas 2009). A marina and welding school are also located close to the sampling site. Site 8, the Ribault River, is a shallow, highly urbanized area (38% high density residential) with about 78% of the watershed impacted by humans, including several companies with permits to discharge their effluent (Wainwright 2018). Elevated levels of phosphorus have been documented at this site (FDEP 2016).

Each of the sites had different levels and types of contamination and a variety of sources of contamination. For example, some sites had more agricultural inputs (metal-containing pesticides, fertilizers, animal waste, etc.), others had more urbanization

(industrial effluent, wastewater effluent, 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, and salinity using a YSI Professional Plus meter with various probes (YSI®, Yellow Springs, OH); and pH using a pH meter (WTW 3310, Xylem Inc., Gloucester, MA) and probe. All probes were calibrated at the beginning of every field day. Additionally, we collected 1–2 L of water (for water chemistry analyses) via subsurface grab in 1-L polypropylene plastic bottles (pre-cleaned with detergent, thoroughly rinsed with tap water, and rinsed 3 times with ultra-pure Milli-Q® water [MilliporeSigma, Burlington, MA]). We kept the samples refrigerated at 3 °C until we analyzed them. On the day of sampling, we filtered (0.45 µm) 2 subsamples (15 ml; sample containers washed as specified above with addition of a 10% nitric acid rinse prior to rinsing with ultra-pure Milli-Q® water) of the water from each site and acidified them using trace-metal–grade nitric acid.

Laboratory analyses

We measured the stored water samples in duplicate for nitrite-N, nitrate-N, ammonia-N, and phosphate-P via a LaMotte® Colorimetric kit (Chestertown, MD). We quantified alkalinity and hardness in duplicate via titrimetric methods following standard methods (Greenberg 1985). We measured these parameters within 1 week of the field sampling date.

We analyzed filtered water samples in duplicate for cadmium, copper, lead, nickel, silver, and zinc using atomic absorption spectrophotometry (AAS; Perkin Elmer AAnalyst 800, Waltham, MA) with graphite furnace detection. The detection limits for each metal were: 0.1 µg/L cadmium, 0.7 µg/L copper, 0.7 µg/L lead, 1.2 µg/L nickel, 0.1 µg/L silver, and 0.4 µg/L zinc. Analysis of each metal included a blank (ultra-pure Milli-Q® water) and certified standards (Fisher Chemical, Fairlawn, NJ). We recalibrated every 40 samples, and analyzed quality control samples throughout each analysis.

Data analyses

We tested data for equality of variance and normality using a Levene test and Shapiro–Wilk test, respectively. The data were not normally distributed; therefore, we analyzed data for differences between sites and over time using Kruskal–Wallis one-way analysis of variance on ranks followed by Dunn's pairwise multiple comparison procedure ($\alpha < 0.05$). We determined correlations among the water quality data and among the metal data using Pearson's correlation test ($\alpha \leq 0.05$).

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 chloride concentration ≥ 1500 mg/L). The freshwater criterion for some metals, like cadmium, for example, is based on an equation which incorporates the hardness of the water body. For the purpose of this study, we used a water hardness of 100 mg $CaCO_3$/L for generating the freshwater criteria, as this was the average value in the freshwater portion of the LSJR.

Results

Metal concentrations in water samples collected from the 8 sites in the LSJR are shown in Figure 2. Site-specific differences were only observed for silver ($P < 0.001$). Specifically, silver concentration was significantly lower at site 5 than at sites 1 ($P < 0.001$), 4 ($P = 0.045$), and 7 ($P < 0.001$). Site 6 had significantly lower silver concentration than sites 1 ($P = 0.002$) and 7 ($P < 0.001$) (Fig. 2E). Significant differences over time were observed for all metals analyzed ($P < 0.001$). However, the patterns for each metal differed to some extent (Fig. 2). For example, concentrations of lead, nickel, and zinc increased over time with the highest concentrations observed in 2019, whereas cadmium and silver concentrations spiked in 2018 and then decreased in 2019 (Fig. 2). Significant positive correlations were observed between nickel and lead, nickel and zinc, and lead and zinc (Table 1). A significant negative correlation was observed between silver and nickel (Table 1).

Copper values in the LSJR frequently exceeded both fresh- and saltwater criteria; while Zn never exceeded the criterion values (Fig. 2B, F). Cadmium values exceeded the freshwater criterion, but not the saltwater criterion; Ni values exceeded the saltwater criterion, but not the freshwater criterion (Fig. 2A, D). Lead and silver concentrations in the LSJR exceeded both criteria during different sampling times (Fig. 2C, E).

The measured water chemistry variables collected from the 8 sites in the LSJR over a 2-year period are presented in Figures 3 and 4. We observed few site-specific differences, though temporal differences were pronounced (Figs. 3, 4) and we identified many correlations among variables (Table 2). During the sampling period in

Table 1. Pearson product-moment correlation coefficients for pair-wise correlations between the concentrations of 6 metals that were measured at each of 8 sites along the Lower St. Johns River, FL, on 12 sampling dates between December 2016 and June 2019. Sample sizes are given in parentheses after each coefficient and vary because not all variables were measured on each sampling day or site. * $P < 0.05$, ** $P < 0.0001$.

Metal	Cadmium	Copper	Nickel	Lead	Zinc
Silver	0.04 (82)	-0.05 (82)	-0.26* (78)	-0.13 (82)	-0.13 (82)
Cadmium		-0.14 (82)	-0.17 (78)	-0.06 (82)	0.06 (82)
Copper			0.17 (86)	-0.11 (82)	-0.09 (82)
Nickel				0.59** (78)	0.49** (78)
Lead					0.54** (82)

this study, salinity fluctuated from 1 to 25 ppt at the 8 sites in the LSJR (Fig. 3A). Across all the sampling times, salinity was not significantly different among sites; however, salinity was significantly different among sampling times ($P < 0.001$). Significant 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 fluctuated seasonally with the lowest temperatures in the winter and highest temperatures in the summer; DO was

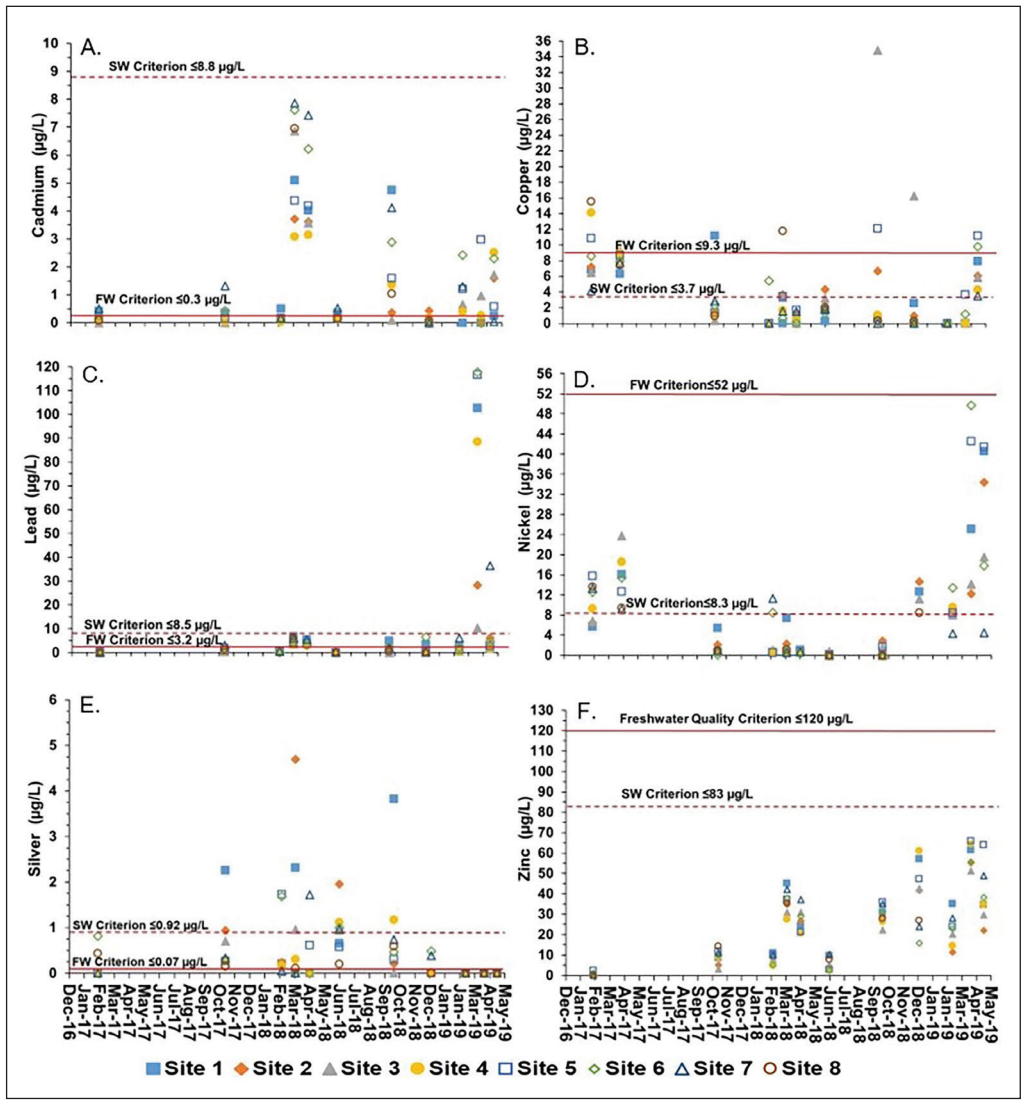

Figure. 2. Concentrations of (A) cadmium, (B) copper, (C) lead, (D) nickel, (E) silver, and (F) zinc in subsurface water samples collected at 8 sites (see Fig. 1) in the Lower St. Johns River, FL, from January 2017 to April 2019. Solid lines indicate the freshwater (FW) criterion, and dashed lines indicate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

inversely correlated with temperature (Fig. 3E, F; Table 2). Precipitation was greatest in the summer months (May–September; Fig. 5), and we observed significant changes in water chemistry (e.g., salinity and hardness; Fig. 3) following these periods, as well as after the significant flooding from Hurricane Irma (10–11 September 2017; Fig. 5; Cangialosi et al. 2018). Salinity decreased substantially (≤5 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-specific differences were observed among these variables even with the spikes in ammonia, particularly at site 1. Temporal differences only

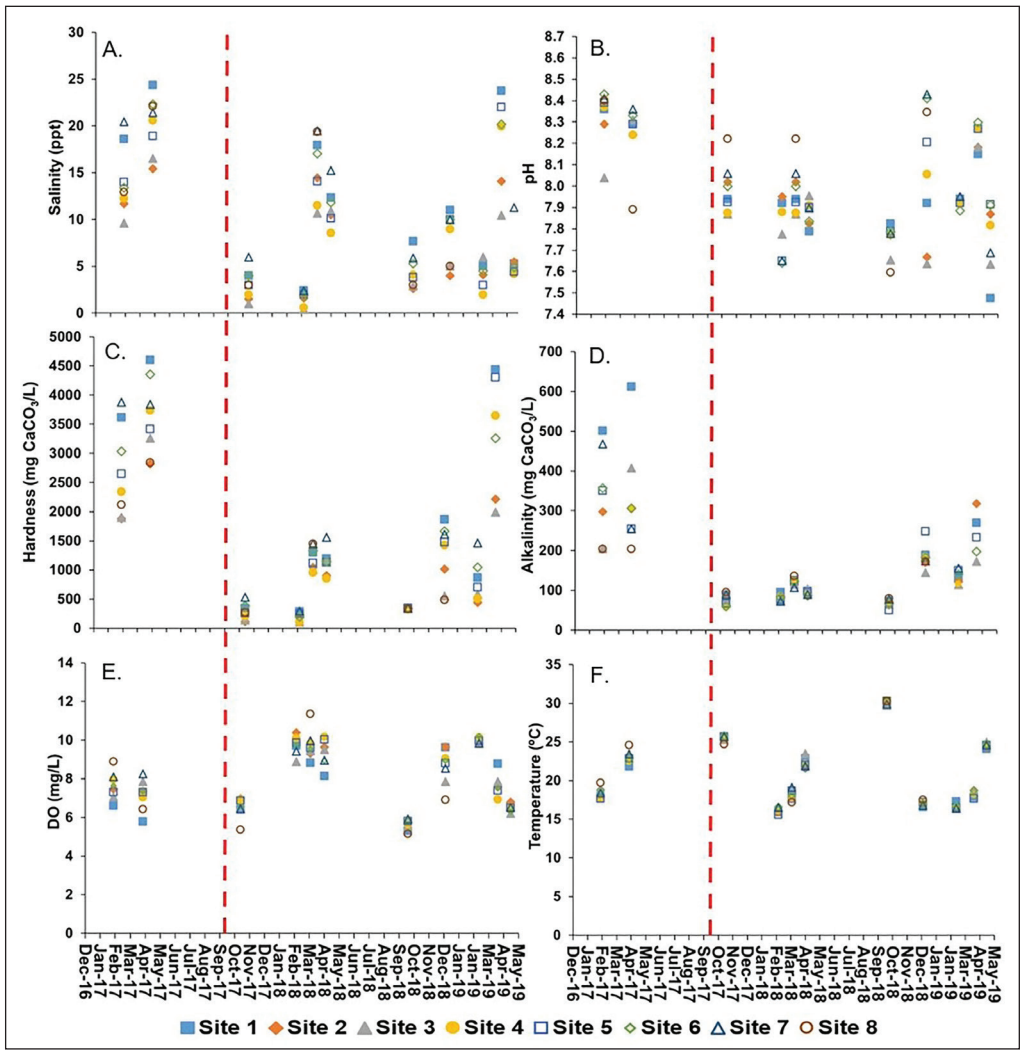

Figure. 3. (A) Salinity, (B) pH, (C) hardness, (D) alkalinity, (E) dissolved oxygen (DO), and (F) temperature in subsurface water samples collected at 8 sites (see Fig. 1 legend) in the Lower St. Johns River, FL, from January 2017 to April 2019. The dashed vertical line represents the occurrence of Hurricane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

were observed in ammonia concentration ($P < 0.001$; Fig. 4). Phosphate was positively correlated with nitrate and nitrite, and negatively correlated with ammonia, pH, salinity, alkalinity, and hardness (Table 2). Nitrate and nitrite had a strong positive correlation with each other and, like phosphate, were each negatively correlated to pH, salinity, alkalinity, and hardness. Ammonia was negatively correlated with nitrite and nitrate and positively correlated with pH, salinity, alkalinity, and hardness (Table 2).

Discussion

The metal concentrations measured in this study reflect historical environmental levels and are typical of other blackwater rivers surrounded by highly urbanized land (Bielmyer-Fraser et al. 2017, Pinto et al. 2019, Pyati et al. 2012). Bielmyer-Fraser et al. (2017) reported differences in metal concentration in 4 streams in southern Georgia, USA, that were correlated with differences in land use and degrees of development surrounding the streams. Alternatively, the Alapahoochee River does not have a direct urban influence, and metal concentrations in this river were near detection, except following rain events where elevated levels were detected (Barnett et al. 2007). In the present study, flooding due to storm events in the

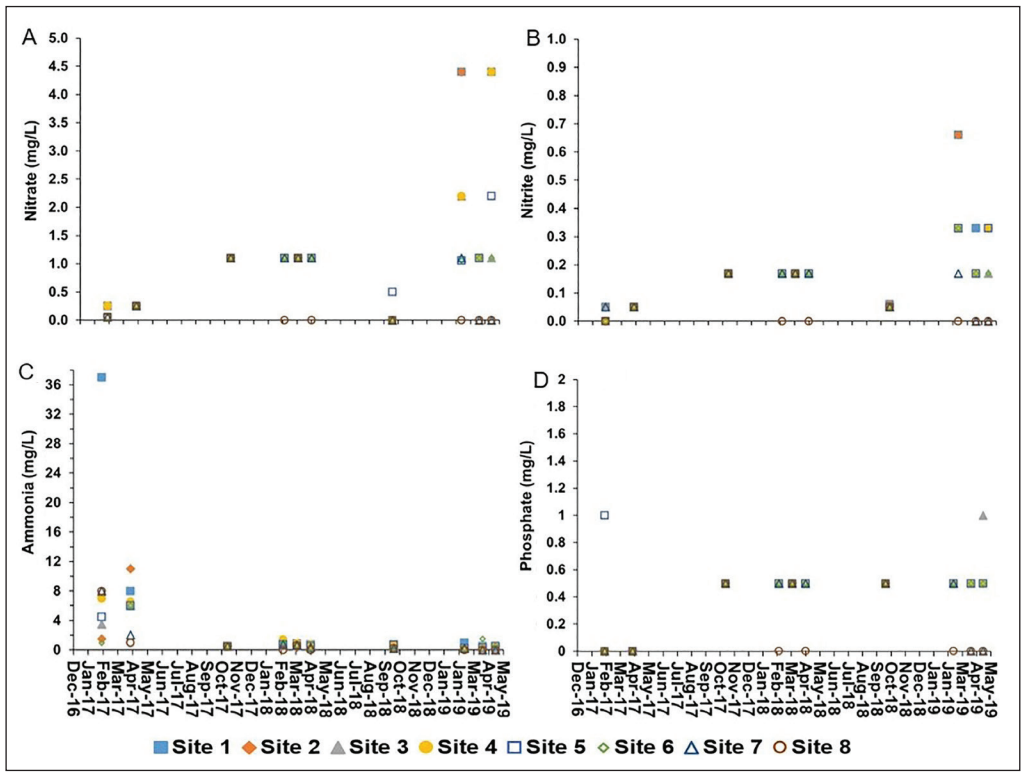

Figure. 4. (A) Nitrate, (B) nitrite, (C) ammonia, and (D) phosphate in subsurface water samples collected at 8 sites (see Fig. 1 legend) in the Lower St. Johns River, FL, from January 2017 to April 2019.

LSJR could have confounded detection of site-specific 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 influenced 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 in toxicity to phytoplankton and autotrophic bacteria in mesocosm studies. In the

Table 2. Pearson product-moment correlation coefficients for pair-wise correlations between the 10 water quality variables that were measured at each of 8 sites along the Lower St. Johns River, FL, on 12 sampling dates between December 2016 and June 2019. Sample sizes are given below each coefficient and vary because not all variables were measured on each sampling day or site. $^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$, $^{****}P < 0.0001$.

	Nitrogen								
Variable	Ammonia	Nitrate	Nitrite	pH	Dissolved oxygen	Salinity	Temp.	Alkalinity	Hardness
Phosphate	-0.52**** 73	0.41*** 66	0.41*** 73	-0.58**** 73	0.11 73	-0.49**** 72	0.05 73	-0.66**** 65	-0.61**** 67
Ammonia		-0.31** 66	-0.31** 73	0.46**** 73	-0.14 73	0.35** 72	-0.11 73	0.64**** 65	0.46**** 67
Nitrate			0.86**** 66	-0.50**** 66	0.1 66	-0.42*** 65	0.01 66	-0.46*** 58	-0.47**** 60
Nitrite				-0.31** 73	0.40*** 73	-0.31** 72	-0.31** 73	-0.30* 65	-0.29* 67
pH					0.01 82	0.62**** 81	-0.31** 82	0.72**** 73	0.72**** 75
DO						0.05 81	-0.77**** 82	-0.15 73	-0.11 75
Salinity							-0.19 81	0.68**** 72	0.89**** 74
Temp.								-0.24* 73	-0.19 75
Alkalinity									0.85**** 73

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-based sources of pollution than several of the other metals tested (e.g., cadmium and lead), and changes in waterborne concentrations would, therefore, be more difficult to detect due to sediment disturbance alone.

For the LSJR, the predominant reference to determine if the metal concentrations detected in this study would cause toxicity to the aquatic biota are the fresh- and saltwater criteria, which consider a variety of organisms and water quality conditions. However, metal toxicity to some select organisms is discussed below. Bielmyer et al. (2008) reported lethal concentration values for 50% of the organisms (LC50s) in soft, freshwater of 3.88, 10.3, and 2.32 µg/L silver for the fish species *Fundulus heteroclitus* (L.) (Mummichog), *Danio rerio* (Hamilton) (Zebra Danio), and *Pimephales promelas* Rafinesque (Fathead Minnow), respectively. Water chemistry was also reported to greatly affect silver accumulation at the fish gill (Bielmyer et al. 2008). Silver LC50 values for an aquatic invertebrate, the water flea *Ceriodaphnia dubia* Richard, and a fish, Fathead Minnow, varied from 0.34 to 9.52 µg/L and 1.99 to 44.1 µg/L, respectively, in 9 different natural waters from North America (Bielmyer et al. 2007). These values are similar to those detected in this study. Likewise, cadmium LC50s varying from 3 µg/L in freshwater to 23,000 µg/L in saltwater for 2 fish species, Mummichog and *Kryptolebias marmoratus*

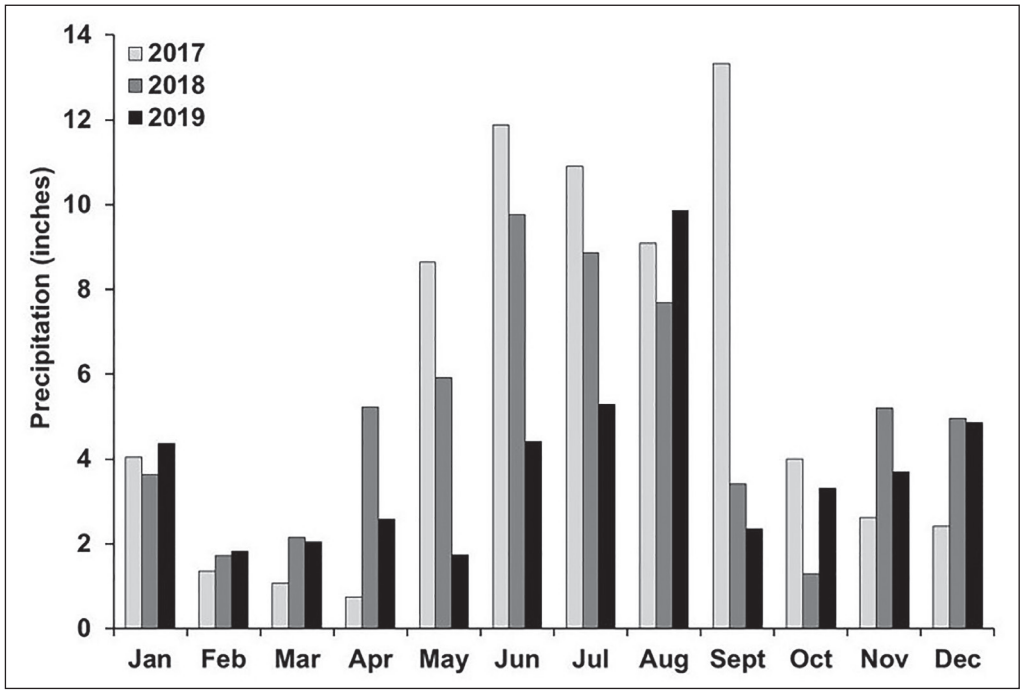

Figure. 5. Total monthly precipitation for Jacksonville, FL. Data were obtained from National Oceanic and Atmospheric Administration.

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 µg/L lead in waters of varying water chemistry. The highest lead concentrations detected in the LSJR in our study were 116–118 µg/L lead, detected at sites 5 and 6, respectively, in March 2019. These elevated lead concentrations could have been a result of the activities in the area and/or disturbance of the sediment. The lead concentrations detected far exceeded the acceptable limit, and aquatic species could have been susceptible to lead toxicity during that time. Alternatively, nickel and zinc LC50s for Mummichog and Mangrove Rivulus varied from 2000 µg/L nickel in freshwater to 66,600 µg/L nickel in saltwater (Bielmyer et al. 2013) and 130 µg/L zinc in freshwater to 34,500 µg/L zinc in saltwater (Bielmyer et al. 2012b), and were above the concentrations detected in this study. Metal toxicity in aquatic biota can vary greatly among species affected, and in waters of varying water chemistry (Bielmyer et al. 2006).

Changes in water quality in streams and rivers due to various reasons including urbanization, changing land use, and climate change (e.g., episodic storm events), can have long-term effects on biotic communities and ecosystem health (Behnke 1990, Khuhawar et al. 2018, Mason 1998, Peierls et al. 1991, Woldeab et al. 2019). Time-series studies enable the observation and documentation of a variety of complex water chemistry variables and can help to assess the state of a water body (Bielmyer-Fraser et al. 2017). In the present study, seasonal changes and episodic rain events modified water chemistry to a greater extent than site-specific differences. However, all the sampling sites were impacted to some degree by anthropogenic processes.

Abrupt changes in salinity, in particular, can have drastic effects on biota in aquatic systems (Bachman and Rand 2008, Bielmyer and Grosell 2011, Cross and Williams 1981, Livingston 2008). Bachman and Rand (2008) reported adverse effects of acute, abrupt salinity changes on the survival and development of fish in Florida Bay, FL. In the LSJR, the abundance and distribution of a variety of fish species, macroinvertebrates like *Callinectes sapidus* M.J. Rathbun (Blue Crab), shrimp, and oysters, as well as submerged aquatic vegetation (SAV) and other important plant species could be substantially changed by the inflow of freshwater and changes in salinity (Montagna et al. 2011, Mulamba et al. 2019). SAV provides habitat for many organisms and is an integral part of the diet of *Trichechus manatus latirostris* (Harlan) (Florida Manatee) in the LSJR (Best 1981, White et al. 2002). SAV in some parts of the LSJR has declined considerably since 2000, and SAV were particularly impacted by the hurricanes and storms in 2017 and 2018 (Pinto et al. 2019).

Temporal changes in water hardness reflected salinity changes. In freshwater, abrupt changes in water hardness can affect the abundance and distribution of flora and fauna (Venkat et al. 2016). Increased precipitation corresponded with decreased alkalinity and pH, which reduce the buffering capacity of aquatic systems (Schuurkes et al. 1986). Additionally, these water chemistry parameters can affect the bioavailability and toxicity of metals and other toxicants to aquatic organisms (Bielmyer et al. 2007, 2008; DiToro et al. 2001; Shyn et al. 2012). For

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 aquatic organisms at elevated concentrations (Tomasso 1994). Nitrate enters aquatic systems via atmospheric deposition, stormwater runoff containing fertilizers, inadequately treated wastewater, septic tank leachate, and atmospheric deposition from fossil fuel combustion (Harrington et al. 2010). Nitrate and nitrite can interconvert with oxidation–reduction reactions, and nitrite can be quite toxic to some fish species (Tomasso and Grosell 2005). The source of nitrogen is not always easily identified due to the various biotic and abiotic processes occurring in waterbodies. However, the form of nitrogen can help to indicate the source. Other methods (e.g., measuring the nitrogen isotope N^{15}) than those used in the present study could also assist in the process. Like the nitrogen species measured, phosphate levels were also relatively low in the LSJR. Phosphorus enters aquatic systems from its use in fertilizers, detergents, and commercial cleaners, and via wastewater and agricultural runoff (Wright and Nebel 2008). Organically bound phosphate and orthophosphate are the main phosphorus species found in natural waters (Wetzel 2001). It should be noted that we did not measure total nitrogen and total phosphorus, though algal blooms were documented in the LSJR during the time span of this study, indicating elevated nutrient loads (FDEP 2013a, Pinto et al. 2019).

Increased nutrients and occurrence of algal blooms can cause decreased DO levels, due to the breakdown of organic matter via respiration. In this study, DO levels fluctuated seasonally throughout the collection period. However, DO levels were within acceptable limits. The class III freshwater quality criterion in predominantly freshwaters of the SJR in the Peninsula bioregion for DO requires that normal daily and seasonal fluctuations must be maintained above 38 percent saturation, which is equivalent to approximately 2.9 mg/L at 30 °C and 3.5 mg/L at 20 °C, to protect aquatic life (FDEP 2013b). However, the areas of the LSJR inhabited by *Acipenser brevirostrum* Lesueur (Shortnose Sturgeon) and *Acipenser oxyrhynchus* Mitchill (Atlantic Sturgeon) should maintain DO levels above 5.0 mg/L during spawning season (February–March; FDEP 2013b). The DO concentrations measured

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 significant than site-specific differences. We hypothesized that there would be significant 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-specific differences could have been confounded in part by the occurrence of storms and flooding in the LSJR, therefore additional research is needed in dryer years to determine these impacts. All metals analyzed, except zinc, fluctuated 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 flora 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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