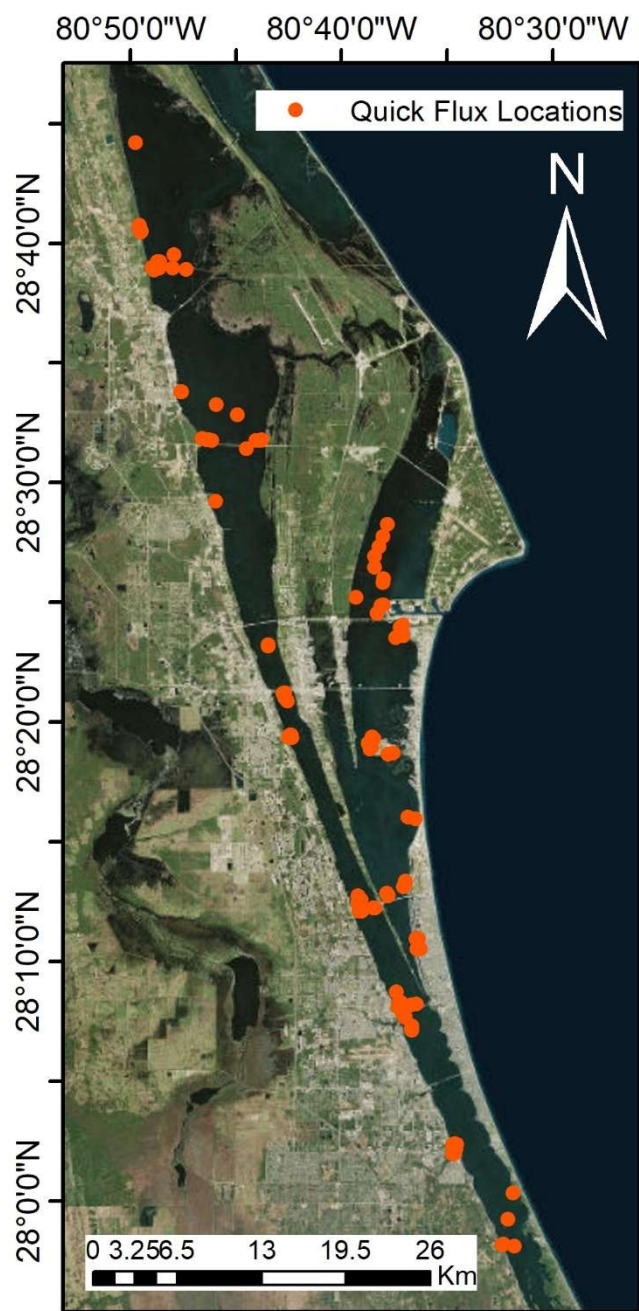


LAGOON-WIDE APPLICATION OF THE QUICK-FLUX TECHNIQUE TO DETERMINE SEDIMENT NITROGEN AND PHOSPHORUS FLUXES (SUBTASK 4)



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Impacts of Environmental Muck Dredging 2017-2018

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Executive Summary

Releases of dissolved nitrogen (N) and phosphorus (P) from Indian River Lagoon (IRL) muck to the overlying water contribute >30% of all nutrient inputs to the lagoon. Other major pathways for nutrient additions to the IRL include stormwater runoff, atmospheric deposition and groundwater/baseflow. Nutrients carried along these various pathways are predominantly introduced on land via fertilizers, wastewater, leaking septic systems, biomass burning, fossil-fuel combustion as well as agricultural and other human activities. To achieve the fundamental goal of decreasing N and P concentrations in the lagoon, adequate knowledge about each source is needed to implement effective remediation techniques. Muck is one of the less obvious and less understood sources of dissolved N and P to the IRL, largely due to insufficient data and an incomplete understanding of what controls these nutrient releases. This study was designed to (1) improve and validate a more rapid technique for estimating nutrient fluxes from muck and then (2) use that information to better understand and decrease N and P releases from muck.

The Quick-Flux technique was used to determine benthic fluxes of N and P from sediments collected at >400 stations in the IRL and Banana River Lagoon (BRL). This method was successfully validated by comparison with results using whole-core squeezers. Sediment samples also were analyzed for water content, Loss on Ignition (LOI) at 550°C, organic C and N, and other chemical and physical properties. The large Quick-Flux data set acquired was used as a valuable and planned component of reports for Muck Removal Efficiency plus Biological and Chemical Responses/Improvements after Muck Dredging, Johnson et al., 2019 and Optimizing Selection of Sites for Environmental Dredging in the Indian River Lagoon System, Trefry et al., 2019).

Results from our one-year research effort with Quick-Flux include the following:

- Muck locations from acoustic surveys, LIDAR and past probing were confirmed via probing. Some sites identified as containing muck were found to have accumulated high-water-content sand and shell or abundant benthic algae, not muck. Twenty large muck areas were probed at multiple locations to determine water depths, muck thicknesses and the spatial distribution of these deposits.
- N and P fluxes determined using the Quick-Flux technique were strongly correlated with values determined from detailed interstitial water profiles ($r = 0.92$ for N and 0.77 for P).

- The best predictors of benthic N fluxes were water content by volume (porosity) and organic matter content as Loss on Ignition (LOI). Porosity and log[LOI] were strongly correlated ($r = 0.99$).
- Fluxes of nitrogen and phosphorus followed seasonal temperature fluctuations with a 2 to 25-fold increase in fluxes as sediment temperatures increased from 16 to $>30^{\circ}\text{C}$. Equations were developed to standardize benthic fluxes to a sediment temperature of 25°C .
- The molar N:P ratio for interstitial water varied temporally and spatially from <10 to >50 ; these variations were likely a response to redox conditions in sediments and overlying water.

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Introduction

One of many challenges associated with restoration of the Indian River Lagoon (IRL) is identifying metrics that quantify success. One metric listed in the Save Our Lagoon Project Plan (SOLPP) is decreasing internal loading of N and P by 25% (Tetra Tech, 2016). This metric can be directly calculated if (1) the surface area of muck and release rates of nitrogen (N) and phosphorus (P) are known throughout the lagoon and (2) care is taken to account for natural and seasonal variations in nutrient fluxes.

Globally, releases of N and P from estuarine sediments have been recognized as important internal sources of nutrients to shallow coastal waterbodies (e.g., Fisher et al., 1982; Kelly and Nixon, 1984; Brady et al., 2013; Harris et al., 2015). As ecosystem health declines, benthic fluxes become an increasingly greater source of N and P that can produce a positive feedback loop that helps sustain eutrophication (Kemp et al., 1990; Sondergard et al., 2001; Harris et al., 2015). Beyond some threshold, a multifaceted approach to ecosystem restoration must include remediation of internal sources of N and P. The IRL has likely entered this feedback loop because >30% of N and P inputs to the lagoon were estimated to come from internal sources (TetraTech, 2016; Fox and Trefry, 2018). Internal sources of nutrients have been attributed to non-linear restoration trajectories that break feedback loops (Kemp et al., 2005); these internal sources should be reduced in a multifaceted approach to lagoon restoration.

Fine-grained, organic-rich sediments from the IRL, often called IRL muck, have been identified as a major source of N and P to the overlying water (Tetra Tech, 2016). Benthic fluxes have been previously reported to provide a large fraction of the nutrients required to support phytoplankton blooms in other regions including Chesapeake Bay, the Potomac River Estuary and the Baltic Sea (e.g., Callender and Hammond, 1982; Fisher et al., 1982; Kelly and Nixon, 1984; Koop et al., 1990; Cowan and Boynton, 1996; Gao et al., 2012; Harris et al., 2015). The relative importance of muck as a source of N and P to an estuary depends on both the surface area of the deposit and release rates of N and P from decaying organic matter. At present, data for the distribution of IRL muck are incomplete. Maps by Riegl et al. (2009, 2014) have now been ground-truthed and refined by us for most areas of the central and northern IRL. An additional component of our investigation includes analysis of muck in the context of dredging and other remediation techniques. We have characterized muck composition and volume at numerous stations within each deposit based on LOI and minimum thicknesses of >30 cm that align with presently available dredging technologies (Matt Culver, personal communication, 2018).

Data for releases of N and P from muck within the IRL are limited (Trefry et al., 2015). Previously reported N fluxes from muck (essentially all as ammonium) ranged from ~5–30 metric tons N/km²/yr; and P fluxes (essentially all as phosphate) ranged from ~0.5–3 metric tons P/km²/yr (Trefry et al., 2015, 2016). Observed ranges in benthic flux are controlled by seasonal variations in temperature that affect bacterial metabolism and, to a lesser degree, diffusion coefficients (e.g.,

Forja et al., 1994; Fox and Trefry, 2018). Previous investigators have shown that N and P fluxes increase with increasing sediment temperature, following seasonal trends of temperature and OM deposition (Elderfield et al., 1981; Klump and Martens, 1989; Kemp 1984; Forja et al., 1994; Cowan and Boynton, 1996; Brady et al., 2013; Fox and Trefry, 2018). Studies from estuaries globally show a range of values for N and P releases from fine-grained, organic-rich sediments that span orders of magnitude (e.g., Bailey 2005; Sheibley and Paulson, 2014).

Previous efforts to quantify benthic fluxes of N and P in the IRL have been limited in spatial extent and temporal resolution by the time and cost associated with determining benthic fluxes using standard techniques. The Quick-Flux method was developed as part of this study, for use in fine-grained, organic-rich sediments to compliment data from detailed interstitial water profiles.

This study was designed to (1) verify existing data for muck distribution in the IRL system, (2) improve and validate our Quick-Flux method and (3) increase the temporal and spatial resolution of benthic flux data throughout the IRL. The Quick-Flux data are used in this study as well as in reports for Task 2, Muck Removal Efficiency (Johnson et al., 2019) and Task 5, Optimizing Selection of Sites for Environmental Dredging (Trefry et al., 2019). This report also uses data obtained from projects funded by (1) the State of Florida Department of Environmental Protection, projects managed by Brevard County, (2) St. Johns River Water Management District and (3) The Indian River Lagoon National Estuary Program. Data also were obtained via collaboration with the Muck Finders Program of the Marine Resources Council (MRC).

Approach

Sampling

Vertical profiles for salinity, temperature, pH and dissolved oxygen in the water column were obtained using a YSI ProDSS (Yellow Springs Instruments) for at least one station overlying each muck deposit. The Sonde was calibrated prior to sampling following the manufacturer's guidelines.

Muck surveys were carried out in the IRL and Banana River Lagoon (BRL) between Sebastian Inlet and the northern IRL near Mims (Figure 1) following methods from Trefry et al. (1990) using a 4-cm diameter, capped PVC pole that was marked at 1-cm intervals. The pole was lowered from a boat until the surface layer of sediments was struck. The pole was then pushed into the sediments until a firm bottom was encountered. If there was any uncertainty regarding the depth to the surface of the muck layer, a flat disk (~30 cm-diameter) attached to a measuring tape was lowered onto the sediment to verify this depth. Verification of muck deposits was accomplished by probing at the center of a previously identified deposit and at 100-m intervals to the north, south, east and

west of center. Additional probing locations (at 100-m intervals) were added until the edges of each deposit were identified. At every location, water depth (depth to the surface sediments), total depth (water + muck) and GPS coordinates were recorded. Field data sheets were scanned and data were entered into Microsoft Excel where the thickness of the muck layer was calculated (muck thickness = total depth - water depth). Contour maps were generated using ArcGIS (Version 10.5 Esri, Redlands, CA). Thicknesses of muck deposits are shown graphically in feet and inches, consistent with engineering literature. The surface area and volume of muck deposits were calculated using ArcGIS tools and a minimum thickness set to 1 foot (~30 cm), a value presently used for engineering design of dredge projects (Matt Culver, personal communication 2018).



Figure 1. Map of the study area from Sebastian Inlet to the northern Indian River Lagoon (IRL) and the adjacent Banana River Lagoon (BRL).

Sediment cores for interstitial water were obtained by (1) a SCUBA diver using push cores or (2) directly from our pontoon boat using a push corer with a check valve. Cores were returned to the Chemical Oceanography Lab at Florida Institute of Technology (FIT) for processing. Cores were transferred into whole core squeezers (Jahnke, 1988) and compressed from the bottom using hydraulic pressure. Samples were retrieved through 12–16 sample ports at depths in the sediments ranging from 0.5–32 cm. Interstitial water was separated through Porex rods with a nominal pore size of 32 μm . Interstitial water samples were further filtered through 0.45- μM polypropylene filters prior to chemical analysis.

Sediments for Quick-Flux analysis were obtained using a mini-piston corer made from a modified syringe (e.g., Fleege et al., 1988; McTigue et al., 2015). Sediment cores for Quick-Flux determination were subsampled from a 0.1-m² Ekman grab that was slowly lowered from an anchored boat. This process has been observed by SCUBA to verify that 10–15 cm of stratified sediment with overlying water were collected (Figure 2). This process has been used successfully to calculate nutrient fluxes in other studies (Sundby et al., 1992).

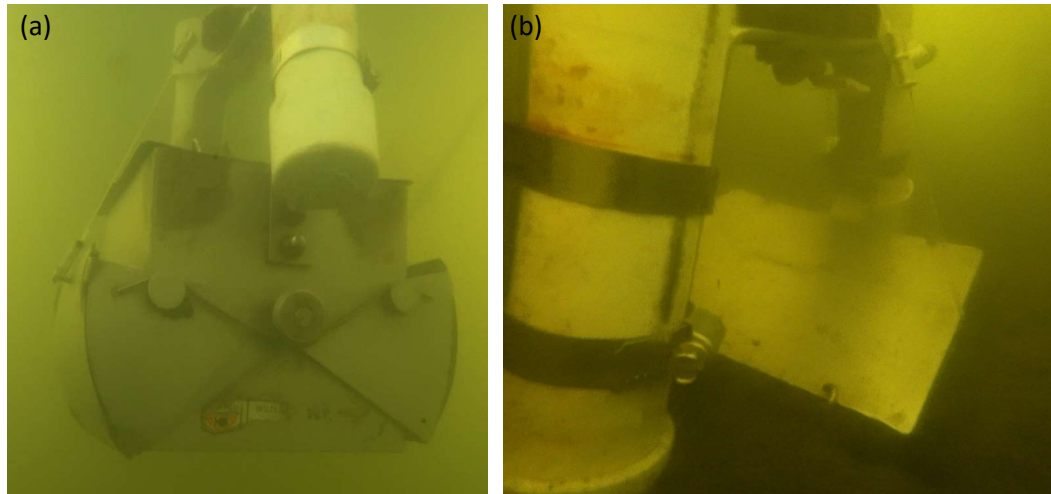


Figure 2. Ekman Grab photographed by scientist with SCUBA (a) descending through the water column and (b) settled in sediments with no visible disturbance to the sample.

Laboratory Analysis

Sediment for Quick-Flux analysis was obtained by extruding the top 3 cm of sediment from mini-piston cores into N₂-purged tubes. The sediment was then centrifuged at ~2,000 rpm for 5 minutes. The supernatant was filtered through 0.45- μM polypropylene filters into low-density polyethylene vials. This method has been successfully used by numerous investigators (e.g., Sundby et al., 1992; Clavero et al., 2000; Khalil and Rifaat, 2013). Sulfide analysis was carried out immediately (<10 seconds after filtration) following the Methylene Blue Method (Hach method 8131) using a Hach DR2800 spectrophotometer.

Ammonium concentrations were determined using standard methods (#4500-NH₃, Rice et al., 2012). Standards were prepared from stock solutions (RICCA Chemical Co.) and analyzed at least twice using UV-visible spectrometry with each batch of samples to ensure accuracy. Values for the SRM were within the 95% confidence interval for the prepared standard. Analytical precision (RSD) for lab duplicates was better than 3%.

Concentrations of ortho-phosphate were determined using a SEAL AA3 HR Continuous Segmented Flow AutoAnalyzer following manufacturer's method G-297-03. The NIST-traceable Dionex 5-Anion Standard was analyzed as a reference standard with each batch of samples to ensure accuracy; values were within the 95% confidence interval for this standard. Analytical precision (RSD) for lab duplicates averaged 3%.

All sediment samples were weighed, freeze dried using a Labconco FreeZone 6 system, and reweighed to determine water content. Freeze dried samples were then powdered using a SPEX Model 8000 Mixer/Mill. Loss on Ignition (LOI) at 550°C was determined following the method of Heiri et al. (2001). Values for LOI estimate the fraction of OM in the sample; these values are used in conjunction with concentrations of organic C, total N and total P to help characterize sediment composition. Concentrations of CaCO₃ were determined by heating the sediment treated for LOI at 550°C to 950°C following the method of Heiri et al. (2001).

Quality Assurance Plan

We submitted a revised detailed Quality Assurance plan (QA Plan) with responses to comments for the second year of this study during January 2017. This plan meets the minimum requirements for description of Research Field and Laboratory Procedures according to Rule 62-160.600, F.A.C. The 33-page document (plus a long list of standard operating procedures) covers all project plans, objective and analyses for the dredging component of the EMD study. As a continuation project, the January 2017 QA Plan covers the activities and analyses during this third year of study.

Results and Discussion

Overview

We begin with results from our muck surveys that were carried out to validate existing muck maps for the IRL. Then, we review data that support use of our Quick-Flux method to increase the spatial and temporal resolution for releases (fluxes) of N and P from IRL muck. Finally, we present results from Quick-Flux determinations to show the value of this approach to obtaining a large dataset for

benthic fluxes throughout the IRL. All this information is used to help accomplish the objectives of other environmental muck dredging work at FIT (Johnson et al., 2019 and Trefry et al., 2019).

One challenge to determining the extent of muck coverage is defining the fine-grained, organic-rich sediments that are being called IRL muck. Previous studies have described IRL muck as black sediments with high water content composed of organic matter mixed with silt and clay (Trefry et al., 1987). This broad description was later defined using empirical values set at >50% water by weight, >10% organic matter and >60% silt + clay (Trefry et al., 1990). These three key characteristics of muck have previously been shown to be strongly correlated (Trefry et al., 1990).

More recently, other working definitions of IRL muck have been used to facilitate broad-scale surveys. For example, penetration of sediments by a probe (i.e., pipe or pole) has been used to identify the presence of muck and to determine the area and volume of muck deposits. This method has been validated by collecting sediments to determine organic matter content for a subset of the probing sites and using sediment cores to validate muck thicknesses. The operational definitions of muck have been implemented to survey large areas; however, it often is necessary to collect sediments for chemical analysis to verify that these definitions accurately characterize the muck sampled.

Muck Survey Results

Data from muck probing surveys carried out from 2014–2018 have been compiled into ArcGIS to geospatially show muck deposits throughout the IRL system (Figures 3, 4 and 5). The probing surveys were initiated to ground-truth high-resolution maps generated using acoustics (Riegl et al., 2009, 2014) as well as to verify the presence of previously identified muck deposits (e.g., Trefry et al., 1990; Trefry and Trocine 2011). In many cases, areas containing muck identified by probing matched results from acoustic surveys. However, there were numerous areas where acoustic surveys identified false positives for muck because the sediment contained (1) high-water content, shell hash and/or (2) abundant drift algae. During 2018, large areas of muck at locations not identified by acoustic surveys (Figure 3) were located using bathymetry (LIDAR) data from the National Oceanographic and Atmospheric Administration and verified by probing (Figure 3).

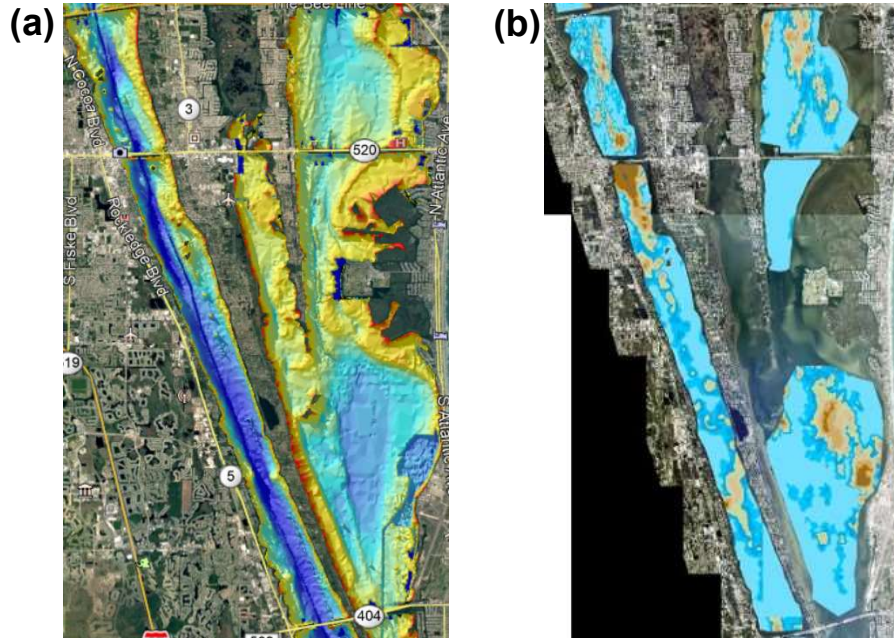


Figure 3. Maps of the Indian River Lagoon between Highways 404 and 520 showing (a) bathymetry, with water depths ranging from 0 (red) to 3.5 m (dark blue) (NOAA, 2017) and (b) muck deposits identified using dual frequency sonar, with thicknesses ranging from 0 (blue) to >1m (dark brown) (Riegl et al., 2014).

Additional data were obtained through collaboration with the MRC Muck Finders Program. These results have been incorporated into our growing muck database. The resulting map (Figure 4) provides a spatial perspective on results for muck thickness showing individual probe locations. Extensive overlap of points in many areas obscure the detail present. One goal of our initial survey and data synthesis was to identify sites that would be further investigated as part of a separate project to prioritize dredging locations. Based on the growing muck database, 20 deposits with the largest surface areas were identified for further investigation (Table 1, Figure 5).

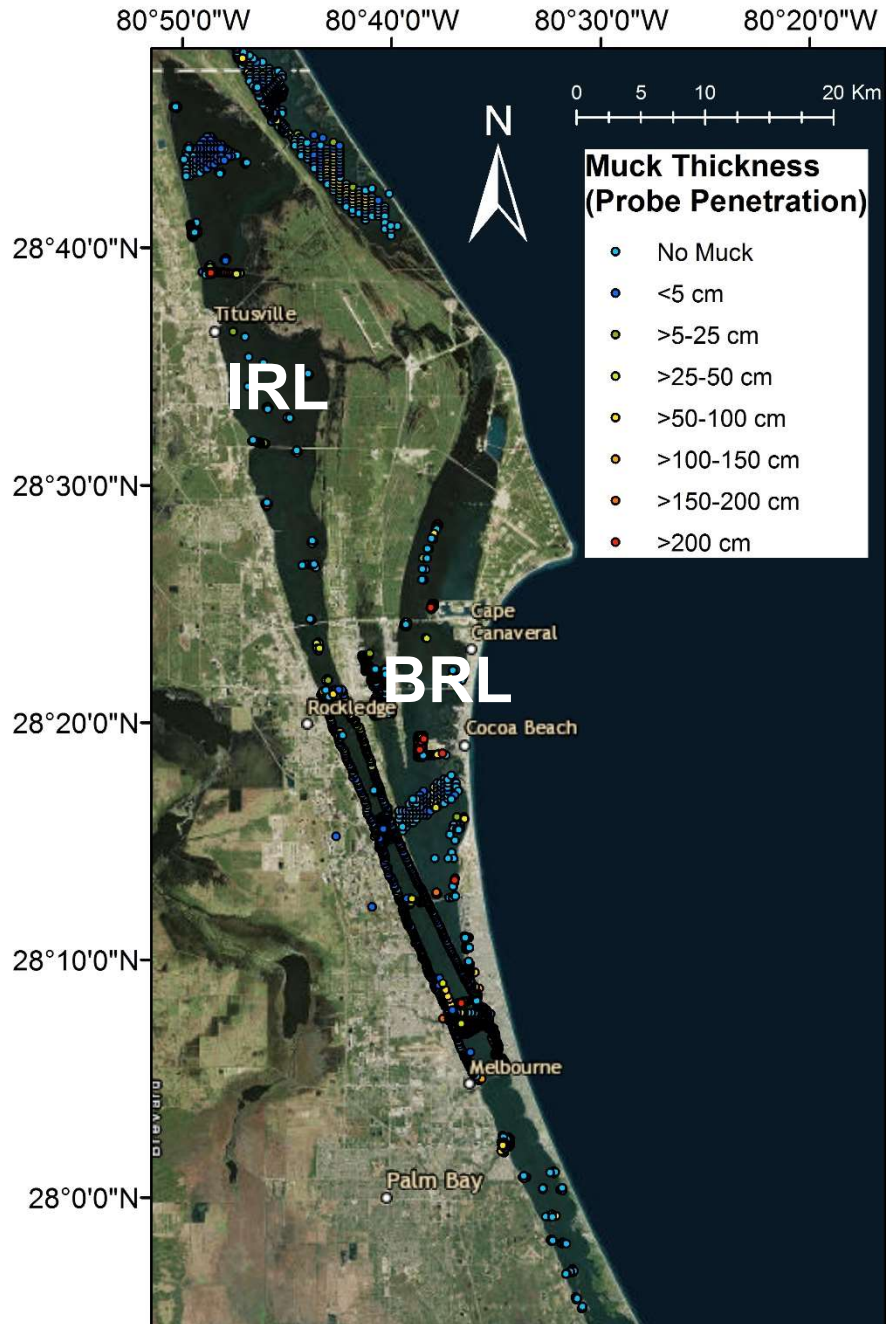


Figure 4 Map showing muck thicknesses from Sebastian Inlet to the northern Indian River Lagoon (IRL) and the adjacent Banana River Lagoon (BRL). Extensive overlap of points in many areas obscure the detail present.

Table 1. Site number, surface area, volume, latitude, longitude and description for each of the 20 largest muck sites identified during this study. Locations on Figure 5. Surface area and volume calculations are based on a minimum muck thickness of 30 cm (1 foot).

Site	Surface Area (m ²)	Volume (m ³)	Lat. (°N)	Long. (°W)	Description
Indian River Lagoon					
1	100,000	106,000	28.037	80.581	Tributary
2	301,000	129,000	28.129	80.612	Open Lagoon, near ICW
3	235,000	265,000	28.133	80.622	Borrow Pit
4	294,000	130,000	28.137	80.612	Borrow Pit
5	149,000	114,000	28.209	80.654	Open Lagoon, near Borrow Pit
6	572,000	309,000	28.247	80.676	Open Lagoon
7	152,000	96,000	28.264	80.671	Open Lagoon, outside canal
8	106,000	86,000	28.324	80.709	Open Lagoon
9	460,000	358,000	28.353	80.714	Open Lagoon, near ICW
10	78,000	35,000	28.388	80.726	Open Lagoon
11	101,000	118,000	28.530	80.775	Borrow Pit
12	138,000	217,000	28.529	80.736	Borrow Pit
13	147,000	293,000	28.649	80.816	Borrow Pit
14	283,000	446,000	28.649	80.791	Borrow Pit
15	26,000	22,000	28.675	80.825	Borrow Pit
Banana River Lagoon					
16	99,000	204,000	28.414	80.636	Borrow Pit
17	223,000	320,000	28.399	80.621	Borrow Pit
18	566,000	746,000	28.317	80.644	Borrow Pit
19	103,000	158,000	28.221	80.618	Borrow Pit
20	113,000	149,000	28.213	80.632	Borrow Pit

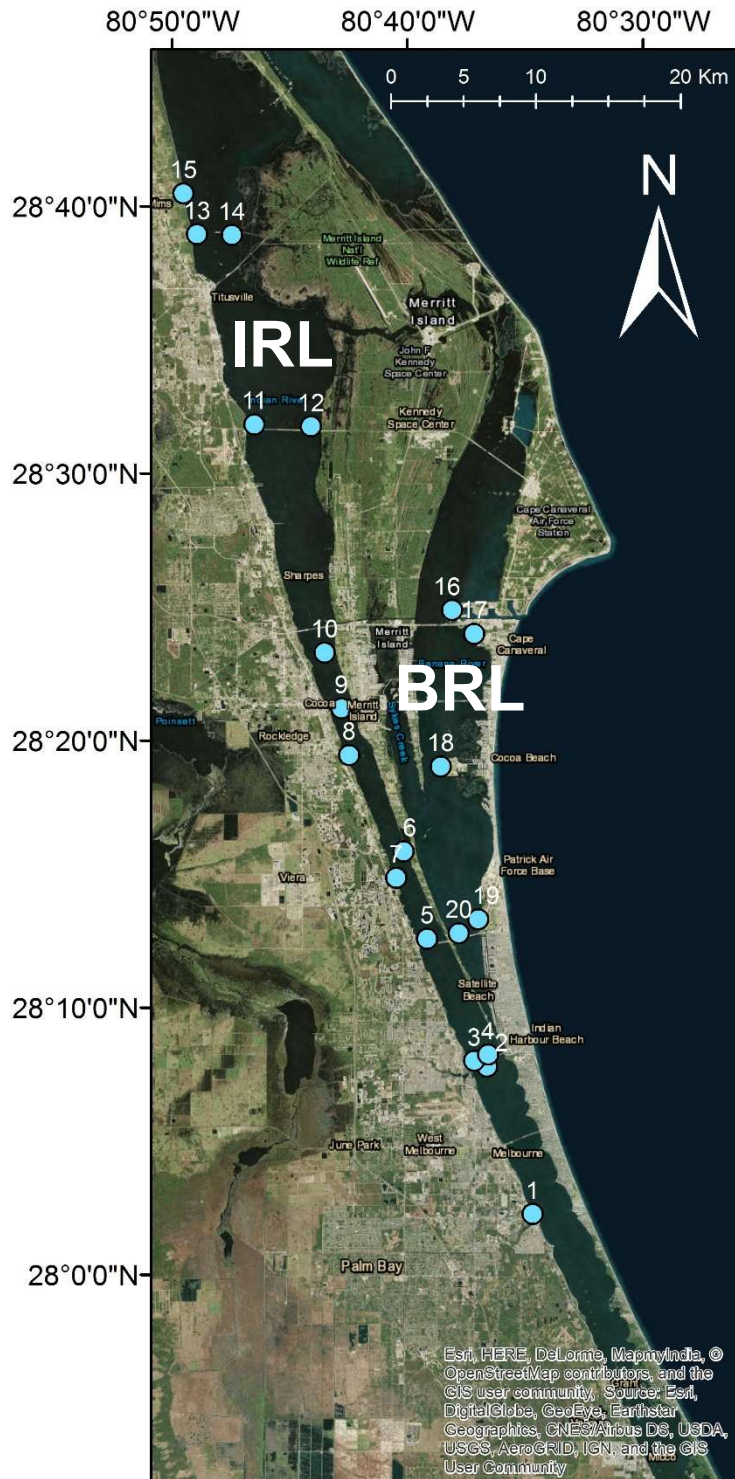


Figure 5. Map of the study area from Sebastian Inlet to the northern Indian River Lagoon (IRL) and the adjacent Banana River Lagoon (BRL) showing the top 20 optimal muck sites for dredging as selected for Trefry et al., 2019. Site numbers correspond to values in Table 1 and do not represent any attributes of the deposit.

The large ground-truthing effort was carried out based on targets identified using acoustics, bathymetry (NOAA), and historic muck deposits (Trefry et al., 1990; and Trefry and Trocine 2011). Preliminary data from each target were obtained by probing at the center and at 100-m intervals to the north, south, east and west of center. This initial survey identified numerous false positives where muck was absent (Figure 4). The largest deposits were revisited and probed in a gridded pattern with ~100 m intervals following lines of latitude and longitude. Resulting data were processed using ArcGIS to generate contour plots and to calculate the surface area and minimum volume of each major deposit (e.g., Figure 6 and Table 1). Further discussion of the major deposits is available in Trefry et al. (2019), “Optimizing Selection of Sites for Environmental Dredging in the IRL System”.

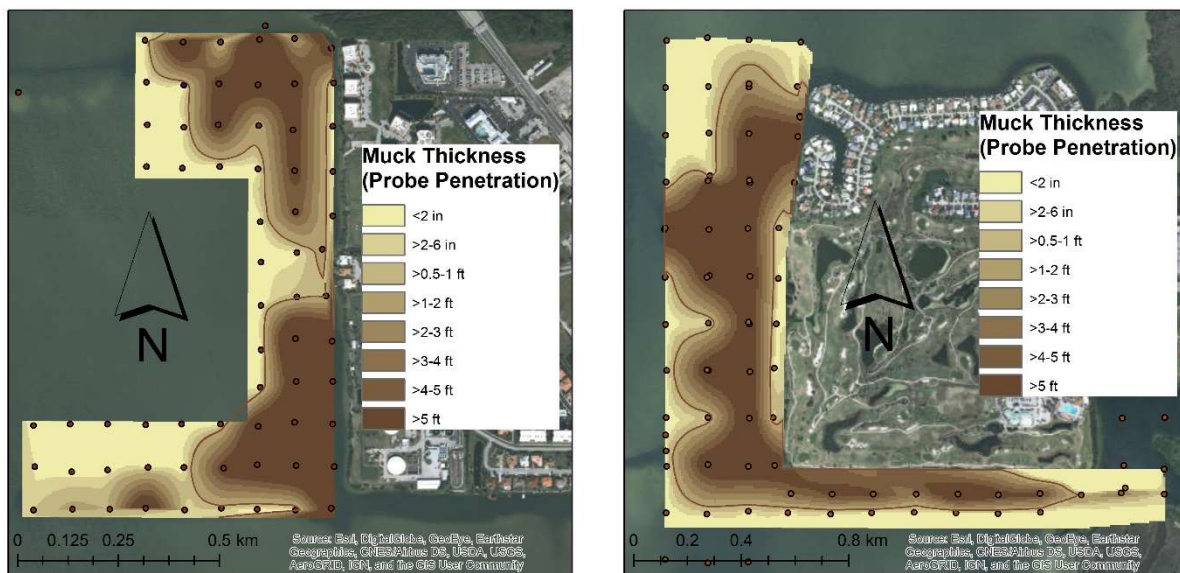


Figure 6. Figures showing muck thicknesses at sites 17 (left) and 18 (right). Station locations correspond to numbers in Figure 5.

Quick-Flux: Development and Validation

More than 5 million cubic yards of muck are distributed throughout the IRL (Fox and Trefry, 2018). Benthic fluxes from this muck contribute >30% of the total inputs of N and P to this system (TetraTech 2016). Recent studies identified large differences in the composition of IRL muck and benthic fluxes of N and P (Fox and Trefry, 2018); however, presently accepted methods for identifying variations in muck flux are time consuming and expensive. The Quick-Flux technique was developed to obtain a large dataset for benthic fluxes of N and P in the IRL. Therefore, adequate validation of this technique was essential.

The Quick-Flux technique is based on the same principles used to calculate fluxes from interstitial water profiles (e.g., Presley and Trefry, 1980; Fox and Trefry, 2018). Diffusive fluxes (F) in both

cases are calculated using (1) the linear portion of the concentration gradients (dc/dz) for dissolved species in interstitial water, (2) site-specific sediment diffusion coefficients (D_s) (e.g., Li and Gregory, 1974) and (3) the equation for Fickian diffusion (Equation 1).

$$F = -D_s \frac{dc}{dz} \quad (g \text{ cm}^{-2} \text{ sec}^{-1}) \quad \text{Equation 1}$$

$$\begin{aligned} -D_s &= \frac{\phi D_m}{\theta} (\text{cm}^2 \text{ sec}^{-1}) \\ \phi &= \text{porosity (unitless)} \\ D_m &= \text{molecular diffusion coefficient (cm}^2 \text{ sec}^{-1}) \\ \theta &= \text{tortuosity (unitless)} \\ \frac{dc}{dz} &= \text{concentration gradient (g cm}^{-4}) \end{aligned}$$

Molecular diffusion coefficients were corrected for temperature and viscosity using Equation 2 (Presley and Trefry, 1980) that was modified for use in sediments by accounting for variations in sediment water content (ϕ) and the increased path length for diffusion around sediment grains (tortuosity, θ).

$$\left(\frac{D_m \eta}{T}\right)_{T1} = \left(\frac{D_m \eta}{T}\right)_{T2} \quad \text{Equation 2}$$

$$\eta = \text{viscosity of seawater (centipoise) at a given temperature and salinity (S)}$$

Identifying the linear portion of concentration gradients is complicated by mixing processes and chemical reactions at the sediment water interface. Adsorption and precipitation reactions in surface sediments can add or remove dissolved species from solution before they diffuse into the overlying water, possibly leading to an over- or under-estimate of diffusive fluxes when only the surface layers of sediments are used.

Previous studies in the IRL and other locations have used varying thicknesses of sediments for diffusion calculations (e.g., Trefry et al., 1992, 2015; Khalil and Rifaat, 2013). During development of the Quick-Flux technique, concentration gradients from a range of sediment depths were used to identify the optimum mini-core length needed to obtain consistently linear concentration gradients for dissolved N and P in IRL sediments. Steep concentration gradients (and therefore higher fluxes) were identified when only the surface 0–0.5 cm were used (Figure 7). More consistent concentration gradients in IRL muck were identified for core lengths of 1.5–4.5 cm. For core lengths greater than ~5 cm, concentration gradients were non-linear and calculated fluxes were lower (Figure 7). Through our validation exercises, a core length of 3 cm was selected for use with the Quick-Flux technique. This value is consistent with sediment thicknesses used in the literature, even when data for 30 cm long sediment cores are available (e.g., Trefry et al., 1992, 2015).

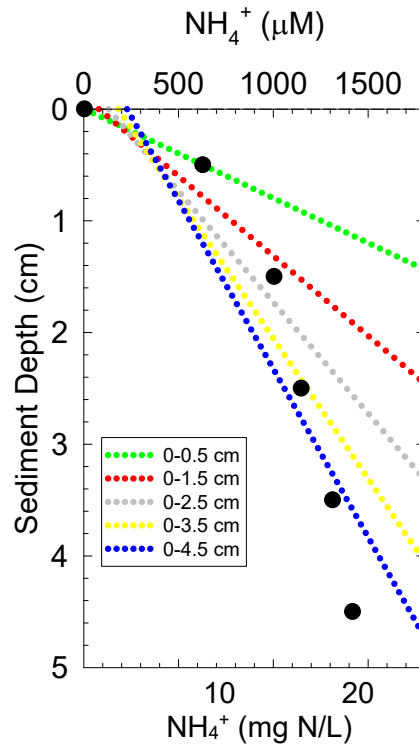


Figure 7. Concentrations of dissolved ammonium (NH_4^+) versus sediment depth. Dotted lines represent concentration gradients calculated for each depth range (0–0.5, 0–1.5, 0–2.5, 0–3.5, 0–4.5).

In contrast with fluxes determined using detailed interstitial water profiles, the Quick-Flux technique relies on a homogenous interstitial water sample that integrates solute concentrations over a 3-cm sediment core. Upward advection of water caused by the increased pressure of newly accumulated sediment leads to a decrease in porosity with increased depth of sediments. Therefore, homogenized Quick-Flux cores may contain a larger volume of water from surface sediments that can lower average N and P concentrations for the whole core and underestimate benthic fluxes. This concern, albeit minor, was addressed by adjusting linear concentration gradients based on an average decrease in porosity of ~5% over 3 cm depth as determined from sediment cores from throughout the IRL (e.g., Figure 8). Overall, a 5% decrease in porosity yielded 1.2% higher fluxes of N and P relative to uncorrected values.

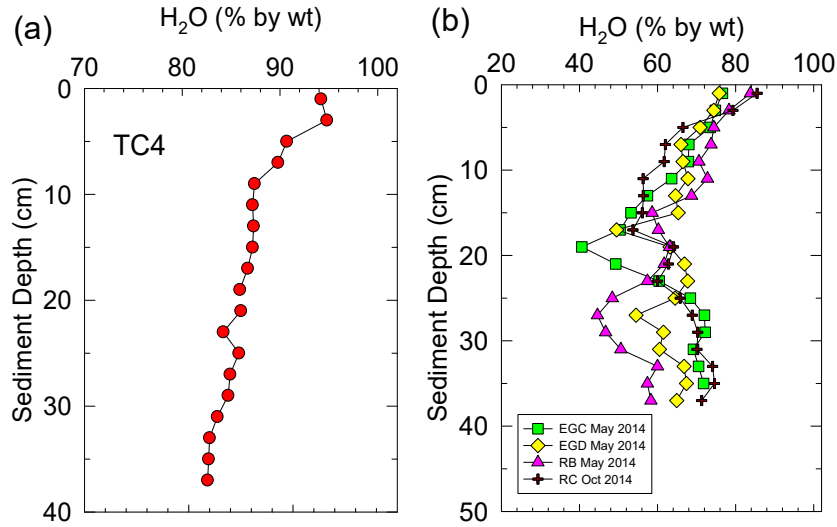


Figure 8. Sample profiles showing a decrease in water content with increasing sediment depth (a) at station TC4 in Turkey Creek and (b) at four stations in the open lagoon (EGC and EGD = Eau Gallie Causeway area; RB and RC = Rockledge area).

Twenty-two sediment cores were collected for direct comparison of the Quick-Flux technique with fluxes determined by us using the following accepted methods: (1) interstitial water profiles (e.g., Sundby et al., 1992; Fox and Trefry, 2018), (2) in-situ flux measurements (e.g., Devol and Christensen, 1993; Forja et al., 1994, 1998; Hammond et al., 2004) and (3) laboratory incubations (e.g., Trefry et al., 1992; Cowen and Boynton, 1996; Hammond et al., 2004). The Quick-Flux technique determines diffusive fluxes in a manner most like the approach used with detailed interstitial water profiles (IW). Overall, diffusive fluxes determined using Quick-Flux and interstitial water profiles agreed well over a wide range of values from 1.2 to 80 tons N/km²/year and from <0.05 to 6.8 tons P/km²/year ($r = 0.92$ and $r = 0.77$ for N and P, respectively; Figure 9).

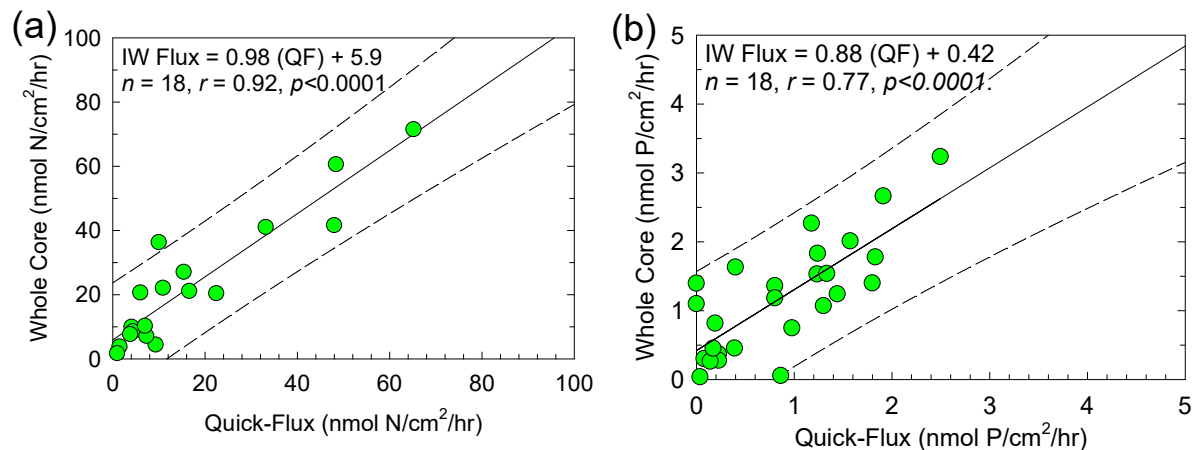


Figure 9. Fluxes determined using Quick-Flux versus data obtained from detailed interstitial water (IW) profiles collected via whole core squeezers for (a) ammonium-N and (b) phosphate-P. Solid lines and equations are from

the best fit line from linear least squares analysis, dashed lines indicate the 95% prediction interval, n is number of samples, r is the correlation coefficient and p is the p statistic.

Differences in flux determined using the Quick-Flux technique versus detailed interstitial water profiles were likely due to small-scale spatial variability within muck deposits over the ~10-m radius that defined each station. However, variability among methods (10–15%) was no greater than that observed for replicate samples calculated using either method independently. These observations are consistent with results for precision of 5–20% from replicate samples in a study comparing in-situ chambers versus laboratory incubations (Hammond et al., 2004). Considering the various sampling, analytical and mathematical actions required to obtain a Quick-Flux value, agreement with other techniques was considered by the authors to be within an acceptable range, generally <20%. Therefore, the technique seemed sufficiently validated to move forward and collect more samples.

Quick-Flux: Explaining Variations in Benthic Fluxes

Benthic fluxes of N and P were determined by Quick-Flux for >400 individual samples from ~50 distinct areas in the BRL and north IRL. This large data set enabled us to better determine how benthic fluxes vary as a function of sediment (1) water and organic matter concentrations, (2) temperature and (3) location.

From our Quick-Flux study, sediment porosity correlated very strongly ($r>0.9$) with log[OM] content (as log[LOI]) following the equation: $\log[\text{LOI}] = 2.6(\text{H}_2\text{O}) - 1.2$ (Figure 10b). The exponential trend for LOI versus porosity results from the non-linear relationship between porosity and the surface area of particles available for sorption of dissolved organic matter (Chilingar et al., 1963).

Within the overall LOI versus porosity relationship, muck with the same OM content had 5–6% higher porosity in tributaries and canals relative to the open lagoon ($p < 0.0001$ two-tailed, t-test assuming equal variance for porosity/log[LOI], as shown by offset of data for canals and tributaries with blue diamonds in Figure 10). This trend is consistent with enhanced flocculation in mixing zones where freshwater first enters the lagoon (e.g., Chandra et al., 2012). A 5–6% higher porosity for muck in tributaries and canals relative to sites in the open lagoon (assuming same OM content) results in a ~5% higher diffusion coefficient (D_m in Equation 1) and N and P fluxes. Data from this study follow salinity-related patterns for N and P fluxes in other estuaries including Chesapeake Bay, estuaries in North Carolina and the Potomac River Estuary (Martens and Goldhaber, 1978; Callender and Hammond, 1982; Bailey 2005). Clearly, porosity and LOI are important variables in the Quick-Flux story as further explained below.

Benthic fluxes of N and P in the BRL and IRL have been shown to be highest in poorly consolidated sediments with high porosity ($\phi > 0.9$; > 90% water by volume) and >10% OM (dry weight) (Trefry et al., 1992, 2015; Fox and Trefry, 2018). Ammonium fluxes ranged from 1.2 to >500 metric tons N/km²/year (0.1 to >60 mg N/m²/hr). Phosphate fluxes ranged from <0.05 to >30

metric tons P/km²/year (<0.5, the MDL to >3.5 mg P/m²/hr). Porewater concentrations of ammonium and phosphorus from the Quick-Flux study were within ranges previously reported for both sandy sediments (Zimmerman and Montgomery, 1984) and fine-grained, organic-rich

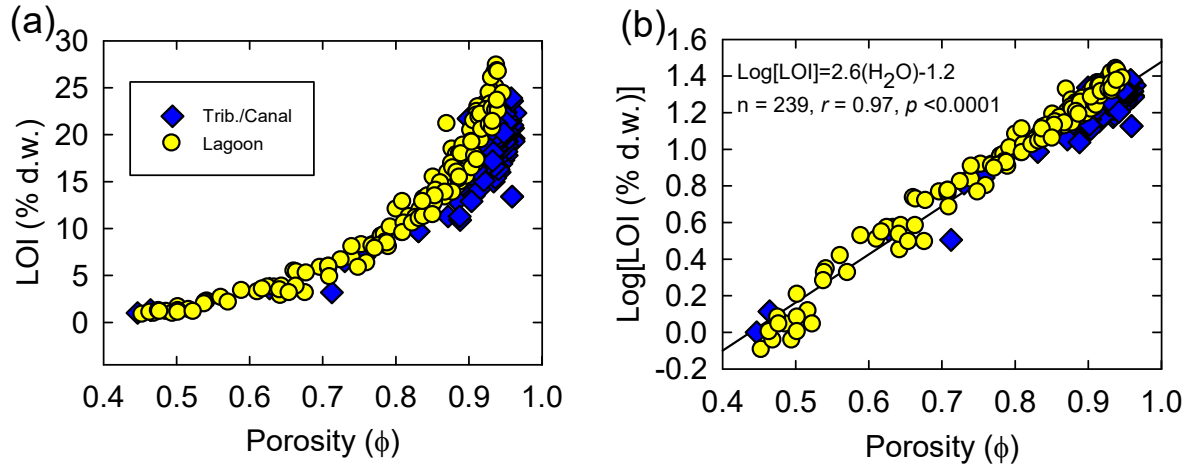


Figure 10. Sediment porosity (ϕ) versus (a) OM content determined using loss on ignition (LOI) from the open lagoon (yellow circles) and tributaries plus canals (blue diamonds), (b) $\log[\text{LOI}]$ for samples from the open lagoon and tributaries plus canals. Lines and equations are from linear least squares regression, r is the correlation coefficient, n is number of data points and p is p statistic.

sediments (Gu et al., 1987; Trefry et al., 1992; Fox and Trefry, 2018) from the IRL and from other estuaries around the globe (e.g., Forja et al., 1994; Bailey, 2005; Sheibley and Paulson, 2014).

The lowest ammonium fluxes, <2 tons N/km²/year, were identified for sandy sediments with low porosity ($\phi < 0.7$, Figure 11a) and low OM content (<5% OM, $\log[\text{LOI}] < 0.7$, Figure 11c). Moderate fluxes were identified for sediments containing a mixture of muck and sand with ϕ of 0.7–0.9 and LOI of 5–9% ($\log[\text{LOI}] = 0.7–0.95$, Figure 11). Fluxes increased sharply in muck ($\phi > 0.9$) reaching values of >100 tons N/km²/year in sediments near the maximum porosity in this study of 0.968. A similar trend was observed for N flux versus OM content with a sharp increase in flux in sediments containing >10% OM ($\log[\text{LOI}] > 1.0$). Linear equations for N flux versus porosity and OM content were obtained by plotting one over the ammonium flux versus porosity or OM content, a method commonly used for asymptotic trends (Figure 11b and d).

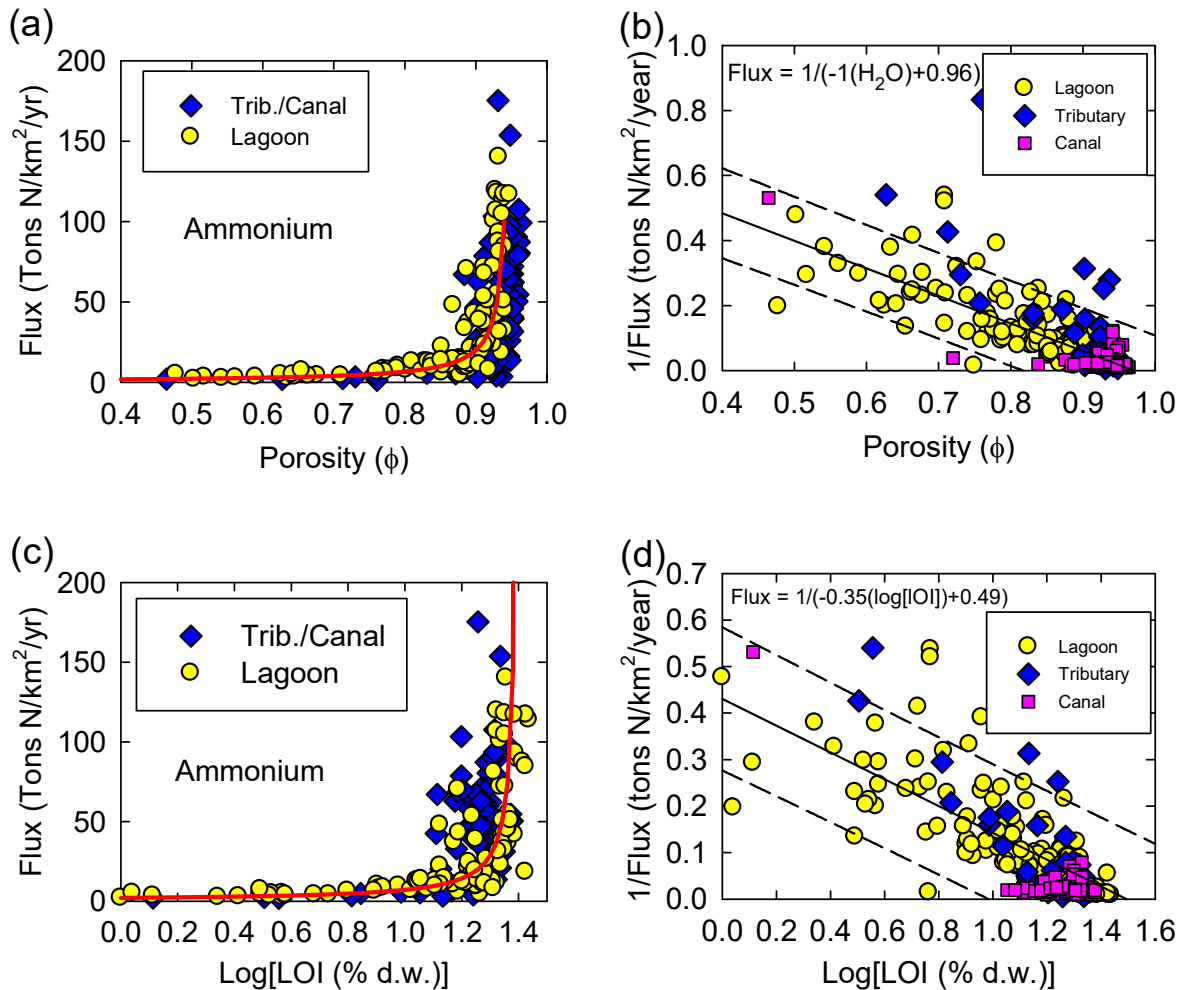


Figure 11. Benthic fluxes of (a) ammonium-N versus porosity (ϕ) (b) 1/flux of ammonium-N versus porosity (ϕ) and (c) ammonium-N versus $\log[\text{LOI}]$ and (d) 1/flux of ammonium-N versus $\log[\text{LOI}]$. Red lines on (a) and (c) are best fit lines from (b) and (d). Solid lines and equations on (b) and (d) are from best fit lines from linear least squares analysis, dashed lines indicate the 95% prediction interval.

Trends for P flux versus sediment porosity and OM content were similar to those observed for N (Figure 12). For example, the lowest P fluxes of < 0.2 tons/ km^2 /year, were identified for sandy sediments ($\phi < 0.7$, $\log[\text{LOI}] < 0.7$). In contrast with N, sharper, but less predictable increases in flux were identified for sediment with high porosity ($\phi > 0.9$) and OM content ($\text{OM} > 10\%$) (Figure 12a and c). This trend is likely related to an inverse relationship for both sediment porosity and OM content versus the redox state of the sediments. Sediments with high porosity and OM content have a higher propensity for anoxia and observed releases of inorganic P. Best fit equations were obtained by plotting one over the phosphate flux squared (Figure 12b and d) and were unreliable for porosity and OM contents above 0.99 and 27%, respectively. These data and trends are consistent with very high P fluxes from anoxic sediments from other studies. For example, Cowan

and Boynton (1996) reported P releases as high as 40 tons/km²/year (148 μmoles/m²/hr) in Chesapeake Bay during summertime anoxic events.

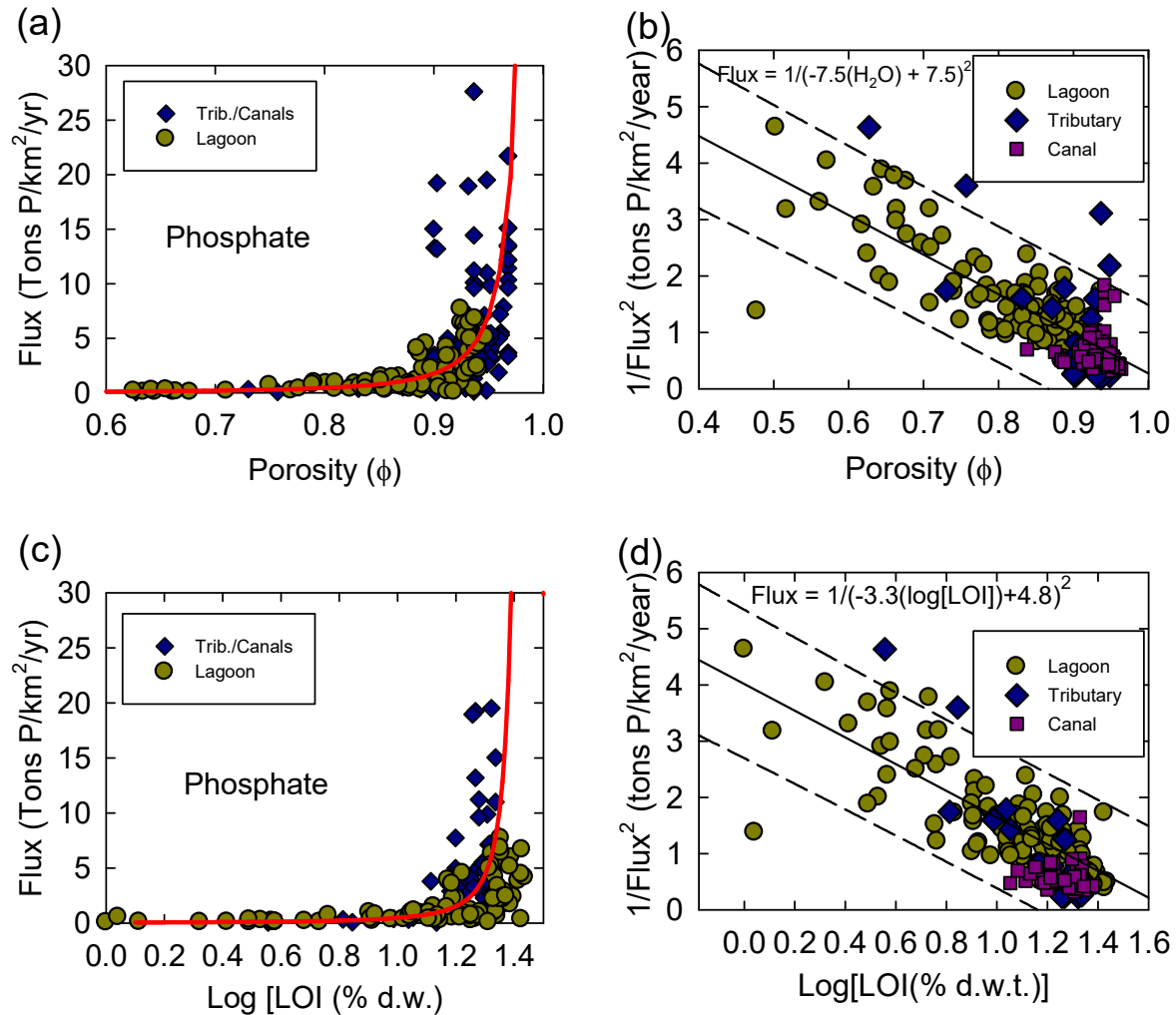


Figure 12. Fluxes of (a) phosphate-P versus porosity and (b) 1/(flux)² of phosphate-P versus porosity and (c) phosphate-P versus log[LOI] and (d) 1/(flux)² of phosphate-P versus log[LOI]. Red lines on (a) and (c) are best fit lines from (b) and (d). Solid lines and equations on (b) and (d) are from best fit lines from linear least squares analysis, dashed lines indicate the 95% prediction interval.

Our earlier efforts to study the role of temperature on benthic fluxes of N and P (Trefry et al., 2015, 2016; Fox and Trefry, 2018, Figure 13a) have been greatly augmented by our large Quick-Flux data set. Previous investigators reported that benthic fluxes of N and P increased by factors of 2- to 25-fold with increasing temperature in response to temperature-related increases in microbial activity (e.g., Klump and Martens, 1989). Increases in diffusion coefficients as a function of temperature alone are small relative to biological effects. For example, an increase in temperature from 15–32°C, yields only a 5% increase in diffusion coefficients (D_m in Equation 1; Figure 13).

Microbial metabolism also can be influenced by temporal variations in the supply of labile organic matter (Cowan and Boynton, 1996; Boynton and Bailey, 2008; Brady et al., 2013). In estuaries with an annual spring bloom, benthic fluxes were reported to increase following patterns for increasing temperature and the availability of labile organic matter (e.g., Boynton and Bailey, 2008). Following algal blooms, organic matter limitation has been shown to reduce benthic fluxes during late summer despite increasing sediment temperatures (Brady et al., 2013; Boynton and Bailey, 2008). Where organic matter is abundant throughout the year, such as in the IRL, benthic fluxes were more closely aligned with variations in sediment temperature (Brady et al., 2013; Fox and Trefry, 2018). Many of the past studies have identified a lag between changes to sediment temperature and benthic fluxes, likely related to the time required to accumulate ammonium and phosphate in sediments during spring and then release large amounts of ammonium and phosphate produced during summer.

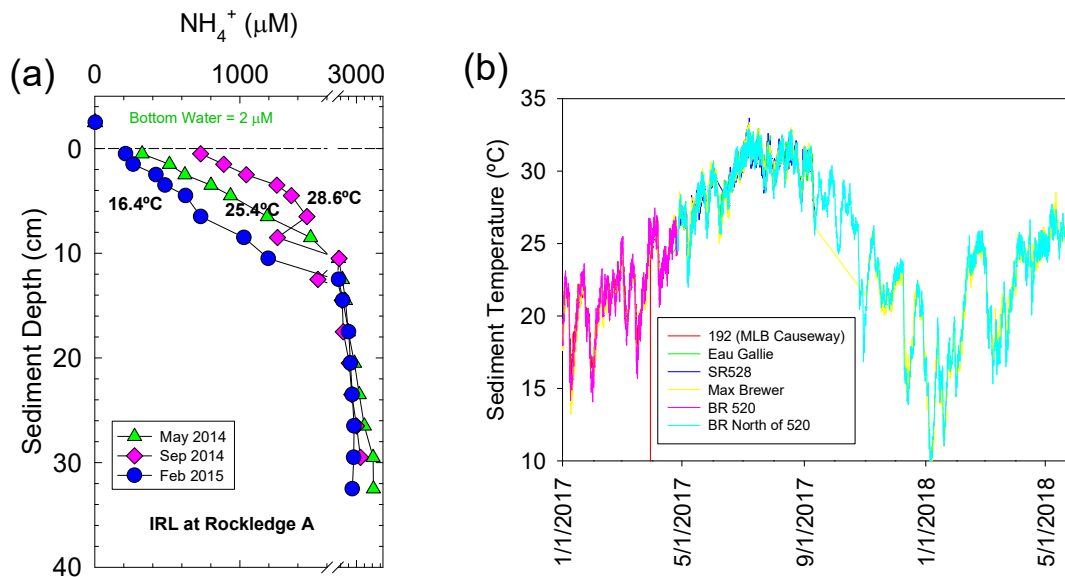


Figure 13. (a) Vertical profiles for ammonium in sediment interstitial water for cores collected from the IRL near Rockledge during three different months with different sediment temperatures, and (b) lagoon temperature record for the IRL between January 2017 and June 2018 at 6 sites throughout the study area (Data from SJRWMD).

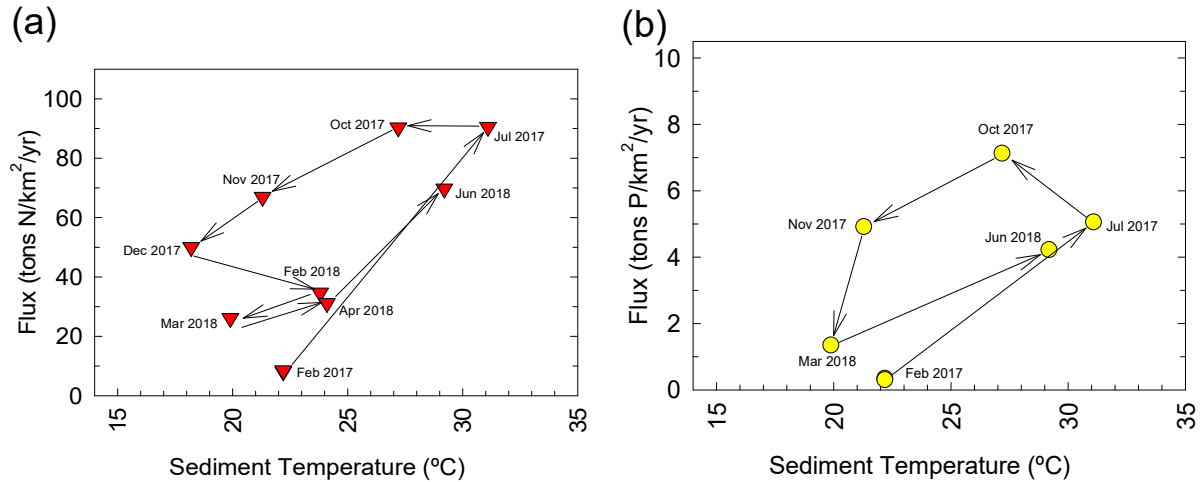


Figure 14. Fluxes of (a) nitrogen and (b) phosphorus from a residential canal in Satellite Beach versus sediment temperature over time from February 2017 to June 2018.

Our Quick-Flux time series data show that a large fraction of the temporal variability in nitrogen (as ammonium) and phosphorus (as phosphate) fluxes can be attributed to variations in sediment temperature coupled with a lag between the production and flux of ammonium and phosphate. These lags are observed as counterclockwise patterns on plots of flux versus temperature (Brady et al., 2013; Fox and Trefry, 2018; Figure 14). At sites in residential canals, benthic fluxes of N and P were lowest in February 2017 at 8.2 tons N/km²/yr and 0.3 tons P/km²/yr when the temperature was 22°C (Figure 14). As temperatures increased to >30°C in July 2017, fluxes of N and P increased to 90 tons N/km²/yr and 5.0 tons P/km²/yr. Following Hurricane Irma in September 2017, fluxes remained high or increased during October in the relatively protected canal system despite a lower sediment temperature. This trend reflected the lag between ammonium and phosphate production and flux during the summer. During winter and spring 2018, a warm February yielded higher N and P fluxes than March. These observations demonstrate both an annual cycle for N and P flux as well as month-to-month variability within the annual trend.

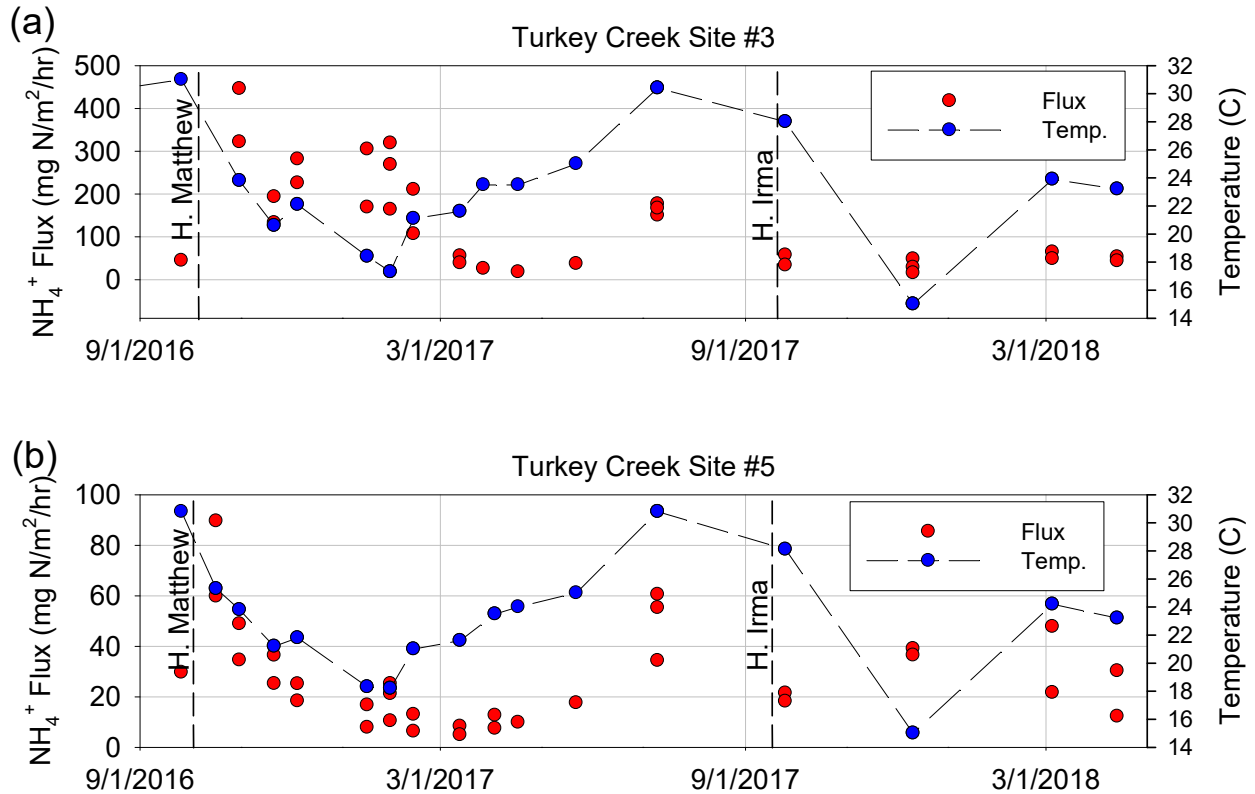


Figure 15. Time series data for N and P fluxes at stations (a) 3 and (5) in Turkey Creek from September 2016 to May 2018.

A time series for temperature and fluxes of NH_4^+ from sediments in Turkey Creek showed the lag effect described previously plus the impacts of dredging and Hurricanes Matthew and Irma in October 2016 and September 2017, respectively (Figure 15). Muck sediments were resuspended and redistributed during hurricane Matthew. Post-hurricane nutrient fluxes peaked in muck that remained after dredging at >400 tons $\text{N}/\text{km}^2/\text{yr}$ and >25 tons $\text{P}/\text{km}^2/\text{yr}$ at station TC3 and >60 tons $\text{N}/\text{km}^2/\text{yr}$ and >3 tons $\text{P}/\text{km}^2/\text{yr}$ at station TC5, respectively. Following Hurricane Matthew, fluxes decreased over the winter to 24 tons $\text{N}/\text{km}^2/\text{yr}$ and 0.2 tons $\text{P}/\text{km}^2/\text{yr}$ at station TC3 with similar reductions in flux at station TC5 (Figure 15). Within six months after completion of dredging, fluxes of N and P seemed to follow more predictable temperature related trends. The several month recovery period following dredging was consistent with results from previous studies where sediment interstitial water profiles were investigated or simulated before and after dredging (Forja et al., 1994; Klump and Martens, 1989; Cornwell and Owens, 2011).

Previous studies have used various equations to relate fluxes to enhanced bacterial metabolism at higher temperatures (e.g., Forja et al., 1994). One common exponential equation uses temperature coefficients (Q_{10}) from bacterial literature (Bailey 2005; Equation 5). Other studies have shown that ammonium fluxes were overestimated during spring and underestimated during fall, likely

due to the seasonal lag for increases (spring to summer) and decreases (fall to winter) in production of ammonium within the sediments (Cowan and Boynton, 1996; Brady et al., 2013; Fox and Trefry, 2018). To address this lag effect, the average sediment temperatures for the month prior to sample collection was used in this study to develop our flux versus temperature equations (temperatures from Figure 14).

$$Q_{10} = \frac{F_2(T_2 - T_1)^{10}}{F_1} \quad (\text{Equation 5})$$

Q_{10} : temperature coefficient

F_1 : Flux at in-situ sediment temperature

T_1 : In-situ sediment temperature ($^{\circ}\text{C}$)

F_2 : Flux at standardized temperature

T_2 : Standard temperature (e.g., 25°C)

Based on all our data and Equation 5, we calculated mean (\pm SD) Q_{10} values of 1.8 ± 0.8 and 2.0 ± 2.5 for N and P, respectively, for sediment temperatures of $16\text{--}32^{\circ}\text{C}$. Values for Q_{10} from our study correspond to $\sim 6\%$ and $\sim 7\%$ increases in benthic N and P fluxes, respectively, per 1°C increase in sediment temperature. These values are at the low end of ranges of values from other estuaries around the world likely because of a lower range of annual sediment temperatures in the IRL. For example, a review of 48 estuaries identified temperature coefficients (Q_{10}) of 2.9 and 3.0 for N and P, respectively (Bailey 2005; Boynton and Bailey, 2008).

The Quick-Flux data set also provided an opportunity to better track temporal variations in the N:P flux ratio. Our data for the IRL followed a seasonal pattern with higher N:P molar ratios (>50) during winter and lower N:P ratios (<10) during late spring and summer (Figure 16). Similar trends have been identified in other estuaries. For example, Boynton and Bailey (2008) reported that N:P molar ratios in Chesapeake Bay decreased from ~ 60 during May to ~ 16 during August-September. Similar patterns also have also been observed in other estuaries from around the world (e.g., Elderfield et al., 1981; Forja et al., 1994). Increased phosphorus fluxes during summer have been linked to the spread of hypoxic or anoxic regions (Boynton and Kemp, 1985; Krom and Berner 1980; Sundby et al., 1992; Cowan and Boynton, 1996). During cooler months, P may be trapped in oxic sediments due to sorption to iron oxides. During warmer months, when sediments are more reduced, N:P ratios were closer to and sometime lower than Redfield values of 16:1 (Boynton and Bailey, 2008; Cowan and Boynton, 1996; Figure 16). Molar N:P ratios less than Redfield values were likely related to desorption of inorganic phosphate when iron oxides underwent reductive

dissolution mediated by anaerobic bacteria. These processes led to a temporal trend for the molar N:P flux ratio that was related to the temperature dependence of hypoxia and anoxia in the IRL. Overall, sediments in the IRL supply N and P at a relatively predictable rates following seasonal patterns for sediment temperature; however, P is also supplied in pulses in regions experiencing hypoxia or anoxia.

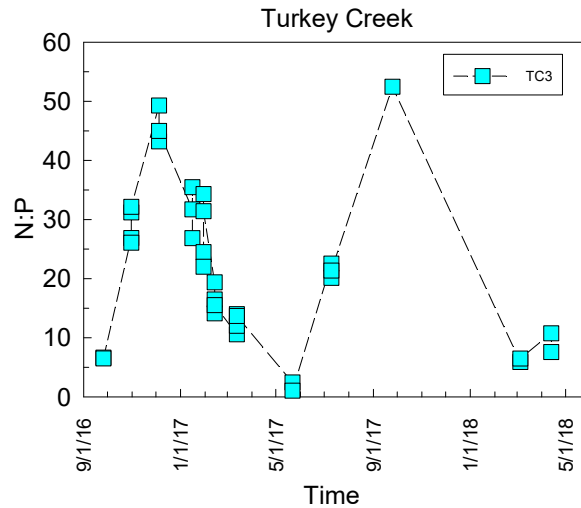


Figure 16. Molar N:P ratio for benthic fluxes versus time at station TC3 in Turkey Creek.

Quick-Flux: Increasing Spatial Distribution of Benthic Flux Data for the IRL

One goal of the Save Our Lagoon Project Plan (SOLPP) is to decrease internal loading of N and P by 25% (Tetra Tech, 2016). To assess the success of restoration efforts in achieving this goal, data are needed to (1) establish a baseline point of reference for future reductions and (2) guide restoration efforts that choose the best locations for use of available resources. The new and expanded data set made possible via Quick-Flux has greatly enhanced the spatial resolution for N and P flux data in the IRL as shown below and in Johnson et al. (2019) and Trefry et al. (2019).

Fluxes from >400 muck sites in the IRL were first normalized to a temperature of 25°C, a reasonable median value for IRL sediments and a common value used in low-temperature geochemistry. Equation 6, rearranged from Equation 5, was used to normalize fluxes of N and P to 25°C (R_2) using Q_{10} values of 1.8 and 2.0 for N and P, respectively. When temperature-adjusted fluxes were used, correlation coefficients (r) for 1/N flux from lagoon samples increased from 0.81 to 0.84 for porosity and from 0.76 to 0.81 for log[LOI] (from Figure 11b and d). These data support use of temperature-adjusted fluxes for comparing sites in the IRL.

$$F_2 = 10^{\left(\frac{\log_{10} 10}{T_2 - T_1}\right) + \log F_1} \quad \text{or} \quad F_2 = F_1 Q_{10}^{\frac{(T_2 - T_1)}{10}} \quad (\text{Equation 6})$$

The spatial distribution of benthic fluxes in this study focused on the 20 largest muck deposits in the Northern IRL and BRL, excluding the northern BRL and NASA property (Table 2). Temperature-adjusted fluxes of N and P varied throughout the IRL and BRL system with no consistent north-south trends (Figure 17). The observation is not surprising because the IRL, unlike many estuaries, is shallow (mean depth 2 m) and virtually unaffected by tides. In addition to a unique physical environment 12 of the 20 major sites were in anthropogenic borrow pits (Table 2).

Results from the Quick-Flux study show the wide range of N and P fluxes throughout the lagoon and identify some key differences among muck deposits. Higher porosity for sediments in tributaries and canals led to higher fluxes of N and P relative to sites with the same OM content from the open lagoon. In some cases, large differences in flux were identified between adjacent pits. For example, at sites 3 and 4, both located just north of Eau Gallie Causeway had quite different fluxes. With the background on Quick-Flux presented here, results are discussed in much more detail in Johnson et al. (2019) and Trefry et al. (2019).

Table 2. Area number, surface area, N flux, P flux, porosity (ϕ), OM content as LOI, and description for each of the 20 largest muck sites identified during this study. Supporting information and locations in Table 1 and Figure 5.

Area	Surface Area (m²)	N flux (tons/km²/yr) @25°C	P flux (tons/km²/yr) @25°C	ϕ	OM (% LOI)	Water Depth (m)	Description
1	100,000	28 ± 42	3.7 ± 5.1	0.91 ± 0.05	15 ± 5	4.2 ± 1.0	Tributary
2	301,000	9.0 ± 4.5	1.7 ± 0.5	0.89 ± 0.01	17 ± 0.6	-	Open Lagoon
3	235,000	8.8 ± 5.0	0.7 ± 0.6	-	-	-	Borrow Pit
4	294,000	23 ± 6	3.2 ± 0.2	0.9 ± 0.0	15 ± 1	3.7 ± 0.2	Borrow Pit
5	149,000	20 ± 18	2.1 ± 1.6	0.87 ± 0.05	15 ± 4	3.0 ± 0.4	Open Lagoon
6	152,000	32 ± 12	3.5 ± 1.5	0.93	18.2	-	Open Lagoon
7	572,000	9.2 ± 3.9	1.4 ± 0.7	0.91	16.3	-	Open Lagoon
8	106,000	12 ± 9	1.1 ± 1.1	0.80 ± 0.13	14 ± 7	3.4 ± 0.9	Open Lagoon
9	460,000	10 ± 2	0.2 ± 0.1	0.85 ± 0.06	16 ± 6	2.1 ± 0.2	Open Lagoon
10	78,000	5.0 ± 1.3	0.3 ± 0.1	0.88 ± 0.01	18 ± 0	3.3 ± 0.1	Open Lagoon
11	101,000	25 ± 10	1.2 ± 0.6	0.91 ± 0.02	20 ± 3	3.2 ± 0.5	Borrow Pit
12	138,000	103 ± 18	4.9 ± 1.3	0.94 ± 0.00	27 ± 1	2.5 ± 0	Borrow Pit
13	147,000	24 ± 10	1.0 ± 0.5	0.85 ± 0.13	17 ± 8	2.4 ± 0.3	Borrow Pit
14	283,000	33	1.3	0.93	24	2.10	Borrow Pit
15	26,000	53 ± 33	2.4 ± 2.1	0.80 ± 0.19	16 ± 10	1.1 ± 0.2	Borrow Pit
16	99,000	32 ± 9	1.6 ± 0.5	0.91 ± 0.02	20 ± 4	3.0 ± 0.1	Borrow Pit
17	223,000	103 ± 25	5.6 ± 1.2	0.92 ± 0.02	20 ± 3	3.9 ± 0.5	Borrow Pit
18	566,000	34 ± 16	2.3 ± 1.5	0.90 ± 0.03	-	3.9 ± 0.4	Borrow Pit
19	103,000	40 ± 7	2.3 ± 0.1	0.94 ± 0.00	22 ± 1	3.5 ± 0.1	Borrow Pit
20	113,000	86 ± 34	3.9 ± 1.4	0.94 ± 0.00	24 ± 0.4	2.7 ± 1.4	Borrow Pit

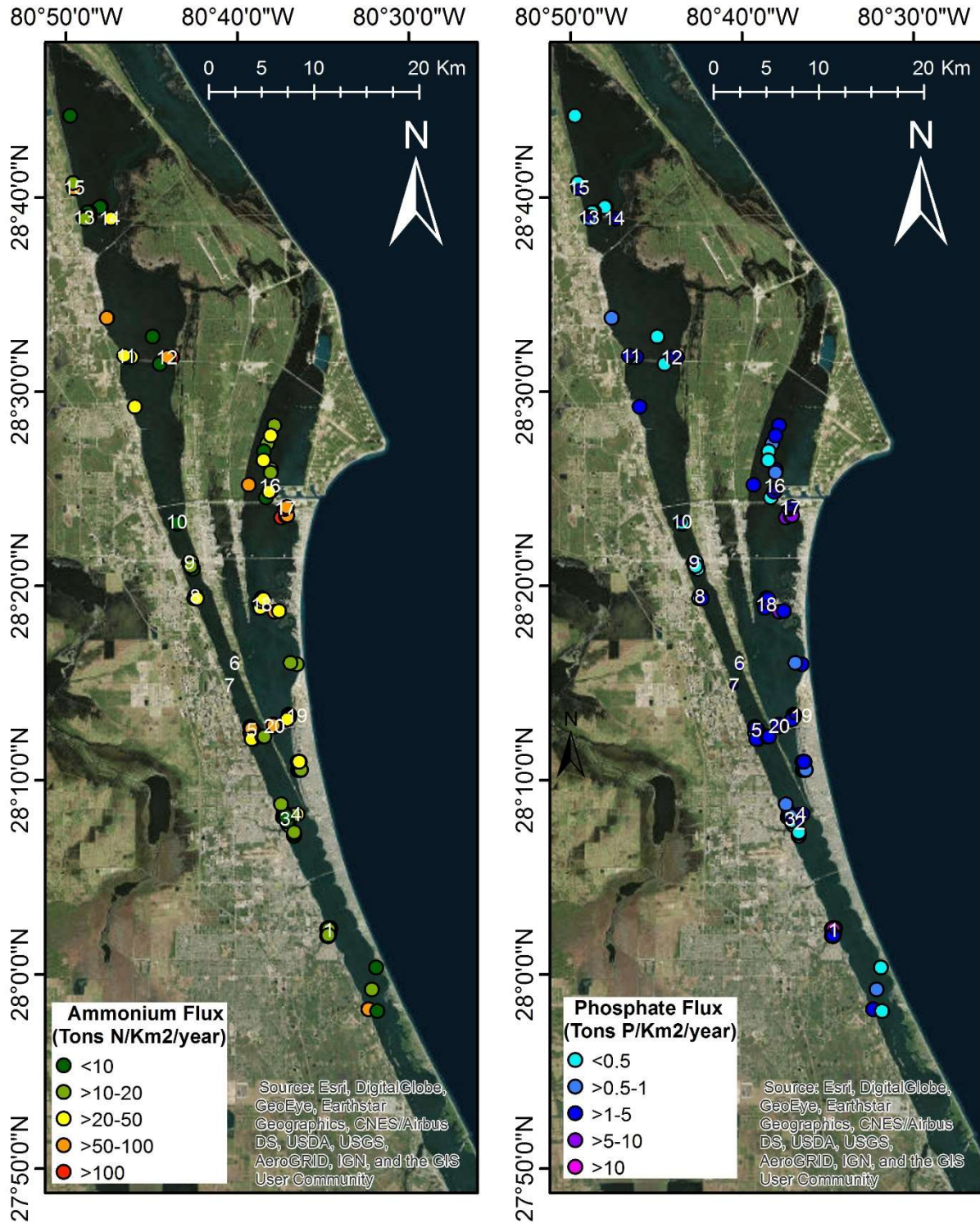


Figure 17. Map of the study area from Sebastian Inlet to the northern Indian River Lagoon (IRL) plus the adjacent Banana River Lagoon (BRL) with color coded (a) ammonium-N fluxes and (b) phosphate-P fluxes. Extensive overlap of points in many areas obscure the detail available in GIS versions. Station numbers are shown for sites 1–20 (Tables 1 and 2).

Conclusions

The goals of our Quick-Flux research were as follows:

- Substantiate existing data for muck distribution in the IRL.
- Improve and validate the Quick-Flux method.
- Increase the temporal and spatial resolution of benthic flux data throughout the IRL and support the requirements of Johnson et al. (2019) and Trefry et al. (2019).

In the process of meeting these goals, we reached the following conclusions:

- All major and many minor muck deposits in the IRL and BRL most likely have been identified, excluding the northern BRL near NASA property, where access is limited.

To reach this conclusion, we have visited nearly all muck deposits previously identified by acoustics or probing. Several of the sites identified via acoustics contained high-water content shell deposits or excess benthic algae, but not muck. All muck sites previously identified by probing were confirmed. Numerous new sites were discovered using NOAA LIDAR data that identified deeper pockets of water throughout the lagoon system.

- The Quick-Flux technique is a viable technique for determining benthic fluxes of N and P from IRL muck based on our statistical validation against an accepted method that uses detailed interstitial water profiles.

During the period of improvement and validation of Quick-flux, we achieved the following: (1) demonstrated that N and P fluxes determined using the Quick-Flux technique strongly correlated with values determined from detailed interstitial water profiles ($r = 0.92$ and 0.77 , respectively), (2) showed that porosity and log LOI were strongly correlated ($r = 0.99$) and that equations could be written to calculate benthic fluxes of N and P from porosity and LOI, (3) fluxes of nitrogen and phosphorus followed seasonal temperature fluctuations with 2 to 25-fold ranges; equations were developed to standardize benthic fluxes to a sediment temperature of 25°C and (4) molar (atomic) N:P ratios for interstitial water varied from <10 to >50 temporally and spatially, likely related to variations in the redox environment of sediments and overlying water.

- The Quick-Flux study yielded >400 benthic flux determinations for N and P and thereby provided a robust data set to more effectively meet the goals of Johnson et al. (2019) and Trefry et al. (2019).

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