Falls Lake Sediment Study

Prepared for
Upper Neuse River Basin Association

by
Marc Alperin, Ph.D.
Department of Marine Sciences
University of North Carolina at Chapel Hill

November 23, 2018

Acknowledgements

Shoua Yang assisted with sampling and processing of sediment cores and water samples. Dr. Mark River (formerly a graduate student at Nicholas School for the Environment, Duke University) assisted in sampling at the upper arm stations in Falls Lake and conducted the Total Phosphorous Analyses. Dr. Matthew Van De Bogert and Dr. Doug Durbin contributed to an earlier draft of this report. I wish to thank Doug Durbin for providing detailed guidance regarding the content of this report.

INTRODUCTION

In 2015, a Special Study was implemented to evaluate sediments in Falls Lake. Dr. Marc Alperin of the University of North Carolina's Marine Science Department was the Principal Investigator for that study. The Plan of Study developed for this evaluation summarized its purpose:

> *This Special Study will quantify the nutrient and organic carbon content of sediment samples from Falls Lake and use that data to help develop a more precise understanding of the spatial variability of sediment characteristics, bottom water, pore water, and benthic nutrient fluxes in Falls Lake. This evaluation will provide site- specific information which can be used to simulate spatial variability in benthic nutrient flux. The existing version of the Falls Lake Nutrient Response Model assumed uniform nutrient flux conditions throughout the lake and thus used a single set of model calibration factors. Information from this study will help develop a better understanding of the importance of internal nutrient loads to the waters of Falls Lake.*

There are two approaches to quantify the flux of solutes across the sediment-water interface (Zabel et al., 2000):

(1) Benthic flux chambers—sediment and overlying water are contained in a closed or semi-closed (open at the bottom) chamber equipped with a mechanism to mix the overlying water. Solute concentrations in the overlying water are monitored over time, and the benthic flux is calculated from the rate of concentration change, the volume of overlying water, and the surface area of enclosed sediment. A control chamber without sediment is used to correct for concentration changes caused by factors other than benthic flux.

(2) Porewater concentration gradients—solute concentrations are measured in the overlying water and porewater, and the diffusive flux at the sediment-water interface is calculated by Fick's First Law modified for a porous medium (Jørgensen and Boudreau, 2001).

The benthic chamber and concentration gradient approaches have both been employed *in-situ* (benthic chambers and microelectrode profilers deployed directly in sediments) and *ex-situ* (intact sediment cores brought to the laboratory for incubation and analysis). *In-situ* methods are generally more costly, but are necessary for quantifying benthic fluxes in environments where ambient conditions (e.g., extreme temperature and pressure) cannot be maintained during sample retrieval and are difficult to reproduce in the laboratory.

Both of these approaches have their limitations. For the benthic flux chamber method, overlying water in the chamber may become depleted in oxygen during the flux measurement, thereby decreasing the depth that oxygen penetrates into the sediment. This could affect the flux of any solute that is involved in oxygen-dependent processes. For example, shoaling of the oxygen penetration depth could affect ammonium and nitrate benthic fluxes by altering nitrification (conversion of ammonium and nitrate, which requires oxygen) and denitrification (conversion of nitrate to N_2, which occurs in the absence of oxygen), and promoting ammonification (ammonium production from breakdown of organic matter) if obligate aerobic organisms are asphyxiated due to reduced oxygen supply. If sediments are populated by infauna (invertebrates dwelling within the sediment), reduced oxygen could affect benthic fluxes by altering the rate that infauna pump overlying water through their burrows (a process known as bioirrigation). In addition, the benthic chamber itself may alter the natural turbulence structure in the overlying water, which would also affect the oxygen penetration depth, and thus the flux of solutes that are sensitive to oxygen.

For the porewater concentration gradient method, accuracy of the flux estimate depends on depth resolution of the concentration profile. Microelectrodes provide high resolution (<0.01 cm) profiles that accurately define the concentration gradient at the interface. However, micro-sensors for many solutes, including ammonium and nitrate, are not commercially available. The highest depth resolution possible using a conventional method of sediment sectioning and porewater extraction (~0.5 cm) is likely to miss significant changes in the concentration gradient near the sediment-water interface. In addition, the gradient method only measures the diffusive flux, and does not include the contribution to the benthic flux from bioirrigation and other non-local exchange processes.

For this study, the porewater gradient method was modified for application in Falls Lake. This new approach—the porewater concentration profile method—mitigates the limitations of the gradient method by expanding the focus beyond the sediment-water interface and exploiting information contained in the entire porewater profile. As such, benthic fluxes from this approach are less dependent on high resolution concentration data than the gradient method, and include the contribution from irrigation. In addition, the profile method provides information that is not available from either the benthic chamber or the concentration gradient approach. This includes an estimate of the effective “lifetime” of reactive organic matter in the sediments (critical to understanding how long it will take the sediments to respond to a change in nutrient supply to the lake), and activity and location of irrigating organisms within the sediment (critical to understanding the potential for coupled nitrification-denitrification as well as controls on the benthic flux of redox sensitive solutes such as phosphate). However, the porewater profile method is subject to its own limitations. Thus, the benthic chamber and porewater profile approaches are better viewed as complimentary rather than alternative methods, and should be used in tandem whenever possible.

METHODS

A reconnaissance visit to the lake was conducted in May of 2015, with sample collection occurring on June 8 and 10, and July 16, 2015. Data acquisition involved the collection of sediment cores from 27 locations in the lake. Core collection focused on the historic river channel and the adjacent “shelf” (i.e., historic river floodplain). Coring locations were generally associated with DWR’s monthly water quality monitoring locations, and extended from the vicinity of the I-85 causeway in the upper lake to the City of Raleigh intake structure in the lower lake. In addition to the 12 DWR stations, three additional stations above the I-85 causeway were included to extend coverage into the upper portion of Falls Lake.

Figure 1 is a map of the locations from which cores were obtained.

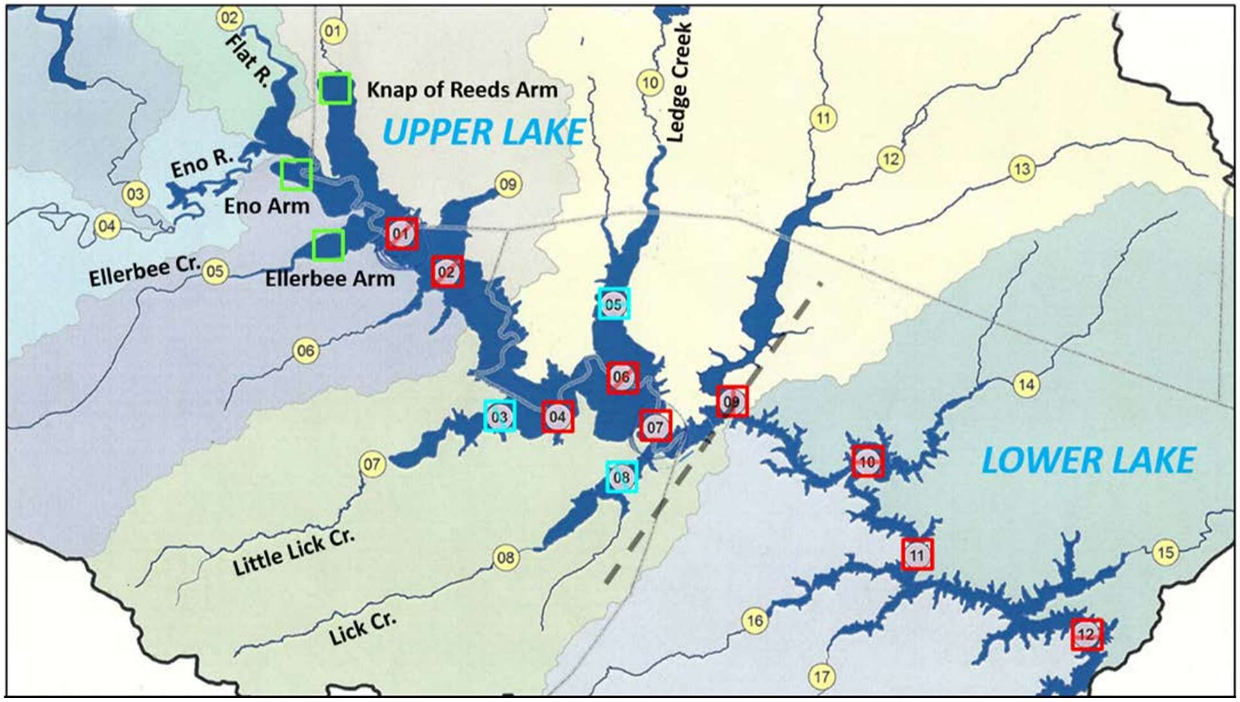

Figure 1. Core locations in Falls Lake Sediment Study. A total of 29 cores were collected at 27 stations (duplicate cores were collected at two stations). The red boxes denote sampling sites centered on the historic channel. Blue boxes are sites that were tributaries to the Neuse River before dam construction. The 12 stations marked by blue and red boxes are at the same locations as the DWR monthly sampling sites. Three additional upper arm stations (green boxes) were added to include the portion of the Falls Lake above I-85, The upper arm sampling effort was done in collaboration with Mark River (formerly at Duke University). The nine stations with diagonals represent transect sites where cores were collected perpendicular to the main lake axis. Replicate cores were also taken at two locations to provide information on small-scale variability.

At each coring location, water samples from ~1 m above the sediment surface (overlying water) were collected to provide concentration boundary conditions needed to quantity fluxes at the sediment-water interface. Overlying water samples were collected using a Van Dorn sampler lowered to ~1 m above the sediment surface. At shallow sites (e.g., < 1 m deep), water samples were collected from just below the water surface. Water samples were stored in Nalgene 500-mL PETG bottles pre-cleaned with dilute detergent and rinsed with tap water followed by distilled-deionized water (DDW). Each Nalgene bottle and cap were rinsed three times with bottom water before taking the sample. Water samples were immediately placed in an ice-filled cooler and then transferred to a cold room (4 °C) on return to the lab (< 6 hours). All water samples were filtered (0.45 µm Millepore-Millex-HN, or equivalent) within one day of collection. Filters were pre-cleaned with 20-mL DDW and flushed with 5-mL of sample. Filtrate (20 mL) was stored in 20-mL plastic scintillation vials or Falcon tubes (pre-cleaned as described above) and stored in the laboratory freezer. Blanks were prepared for each site by filtering and storing 20-mL of DDW.

Cardno staff measured the temperature and dissolved oxygen (DO) concentration of the overlying water.

Sediment cores were collected using a Kajak-Brinkhurst (K-B™) corer (Wildco Supply Company). The K-B corer is a lightweight gravity corer equipped with a 50 cm × 5 cm (o.d.) Plexiglas core liner. Cores were immediately capped on top and bottom with Plexiglas o-ring seal inserts, stored in an ice-filled cooler in the field (< 6 hours), and then placed in a cold room (4°C) until processing. Care was taken to keep the cores vertical from the time of collection to sectioning.

Sediment cores were sectioned at 3-cm intervals over the entire length of the core. An aliquot of wet sediment from each section was collected for porosity and Loss on Ignition analyses. A separate 30-mL aliquot of wet sediment was transferred to a pre-cleaned 50-mL Falcon centrifuge tube and spun using an Eppendorf 5810R centrifuge (5000G for 15 min) to separate porewater and solid matter. The porewater (supernatant) was transferred to a 35-mL plastic syringe, filtered as described above, and stored frozen in 30-mL Falcon tubes. The sediment pellet in the centrifuge tube was frozen and then lyophilized for 72 hours in a Labonco FreezeDryer 8. The freeze-dried sediment was ground to fine powder with mortar and pestle, and stored at room temperature in 15-mL glass vials for organic carbon, total nitrogen, and total phosphorous analyses.

Aliquots of wet sediment from each depth interval were weighed before and after drying (24 hr at 100°C in a Fisher Scientific Isotemp oven) using a Denver Instruments XS-410 balance. Masses were recorded after three consecutive measurements agreed to ±0.01 g. The balance was checked daily for drift using a certified brass weight. Fifteen samples were dried for an additional 48 hours; the difference in mass between 24 and 48 hours was ~±0.01 g.

Lyophilized sediment samples were analyzed for Organic Carbon (OC) and Total Nitrogen (TN) content by Wetland Biogeochemistry Analytical Services (WBAS) using a Costech 1040 CHNOS Elemental Analyzer. Total Phosphorous (TP) was measured by Mark Rivers at Duke University. Lyophilized sediment digested by nitric-perchloric acid and elemental concentrations were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, Teledyne Leeman Lab).

Dried sediment samples were combusted in a ThermoScientific Lindberg Blue M muffle furnace. The temperature was programed to increase from room temperature to 550°C in one hour, hold at 550°C for 2 hours, and then cool back to room temperature (typically overnight). Samples were re-weighed after sample combustion.

Nutrients (ammonium, nitrate plus nitrite, and phosphate) were measured in overlying water and porewater samples by WBAS using an OI Analytical Flow Solutions IV.

All data analysis was conducted under the direction of Dr. Alperin. This analysis included refinement of a mathematical model to estimate nutrient fluxes.

Benthic fluxes of ammonium and nitrate plus nitrite were calculated using a mathematical diagenetic model. A complete description of the model is provided in the Appendix.

RESULTS and DISCUSSION

An interesting observation during collection of the cores was the variability in the thickness of the unconsolidated sediment layer (muck) among the locations. In general, the river and tributary channels had substantial sediment with cores ranging from 13 to 40 cm (the upper limit of the corer). In contrast, areas along the “shelf” typically had much less accumulated sediment, with cores ranging from less than 5 to just over 20 cm. Some shelf areas had little to no sediment, where the corer simply contacted hard clay, sand or gravel.

Table 1 provides a general summary of the laboratory data for the sediment, porewater and overlying water. The full data set was transmitted to the UNRBA’s monitoring contractor. The values in the table above fall in the range expected for lake sediments and waters.

Table 1. Summary of Laboratory Results for Sediment Cores Collected from Falls Lake in June/July 2015.

Parameter	Units	Count (n)	Minimum	Mean	Maximum	Comment
Solid phase						
Porosity	%[1]	185	0.19	0.76	0.93	Decreases with sediment depth
Loss on Ignition	%[2]	185	0.2	8.0	23.4	High value contained wood fragments
Organic Carbon	%[2]	152	0.06	2.08	4.67	High value contained wood fragments
Total Nitrogen	%[2]	152	0.00	0.21	1.08	No pattern with depth
Total Phosphorus	%[2]	152	0.001	0.061	1.24	No pattern with depth
Porewater						
Total Phosphate	µM[3]	119	0.3	1.2	13.6	Porewater contains higher concentrations of Total Phosphate and Total Ammonium, suggesting a flux from sediments to lake
Total Ammonia	µM[4]	119	43.9	1387	4466	
Bottom Water						
Total Phosphate	µM[3]	26	0.2	0.3	0.62	No spatial pattern to Total Phosphate
Total Ammonia	µM[4]	26	0.3	22.8	146	Low DO water has high Total Ammonium
Nitrate+ Nitrite	µM[4]	26	0.1	0.3	0.8	Nitrate + Nitrite is the minor form of Dissolved Inorganic Nitrogen

[1] mL porewater per 100 mL wet sediment.

[2] per cent dry weight.

[3] To convert µM P to µg P/L, multiply by 31.

[4] To convert µM N to µg N/L, multiply by 14.

The decay of organic matter buried in lake sediments transforms organic nutrients into inorganic forms (e.g., NH_3 and PO_4) which may then be released back into the water column. Because decomposition is the source of nutrients, it is important to characterize the organic content within the sediment pool in conjunction with assessments of benthic nutrient flux. The organic content of all cores was assessed through the determination of loss on ignition (LOI) and measurement of total organic carbon (TOC) concentration.

Loss on Ignition (LOI) is a measure of the non-mineral fraction of the sediment that is liberated when dried sediment is heated to 550 °C (> 1000 °F) in an oven. LOI in Falls Lake cores ranged from near 0 to about 15 percent, with cores from the lower portion of the lake having generally higher LOI values than cores from the upper lake.

Total organic carbon (TOC) in Falls Lake cores ranged from near 0 to about 4 percent, with generally the same spatial pattern seen for LOI. This is because TOC and LOI are often highly correlated, since the volatile and combustible organic substances in the sediment comprise much of what is burned off during the LOI process. For the Falls Lake cores overall, the correlation analysis of LOI and TOC yielded an r^2 of 0.72, indicating a high degree of correlation. This relationship can be of value since the cost of measuring TOC is higher than for LOI, so being able to use LOI as a surrogate can save money in future evaluations. Organic carbon was also correlated with porosity (r^2 of 0.62), indicating that organic matter is associated with the finer grained sediments.

Decomposition of sedimentary organic matter produces both inorganic carbon (CO_2) and Dissolved Organic Carbon (DOC). As a result, it is common for sediment porewaters to contain higher DOC concentrations than overlying water. The flux of DOC out of the sediments depends on the diffusion coefficient for the dissolved organic molecules, sediment porosity, the DOC concentration gradient at the sediment-water interface, and DOC oxidation near the sediment surface. DOC was not measured in sediment porewater or overlying bottom water, thus DOC flux was not quantified in the study.

Phytoplankton tend to have a C:N value close to the Redfield ratio (106 mol C:16 mol N = 6.6, whereas terrestrial vascular plants have a C:N ≥ 20 due to the abundance of carbon-rich lignocellulose in the plant’s structural tissue. Hence, C:N ratios in sediment have been used as a tracer of organic matter source. However, elemental ratios are altered by decomposition processes occurring before and after deposition. Preferential remineralization of nitrogen-rich components in fresh algae (e.g., proteins) can increase the C:N ratio in the residual organic matter from 6.6 to 8 to 12. Likewise, colonization of vascular plant material by nitrogen-rich microbes can decrease the C:N ratio from ≥20 to ~11.

C:N ratios from all depths in each core were averaged to highlight differences between stations (Figure 2). At 18 of the 26 sites, depth-averaged C:N values are <12.5 and fall in a narrow range (11.2±0.8) that does not distinguish between altered organic matter derived from fresh algae or vascular plants. C:N values at these 18 locations do not differ systematically between upper arm, upper lake, and lower lake sites. Of the eight sites where average C:N values are >12.5 — suggesting a significant component of vascular plant-derived material — six are “slope” or “shelf” sites from the upper lake stations (1B, 2B, 1C, 1E, 2C, 3C). The two other sites with C:N > 12.5 (Ellerbe arm and 9C) contained plant debris (e.g., leaves, wood fragments, and roots) throughout the 12-cm long cores.

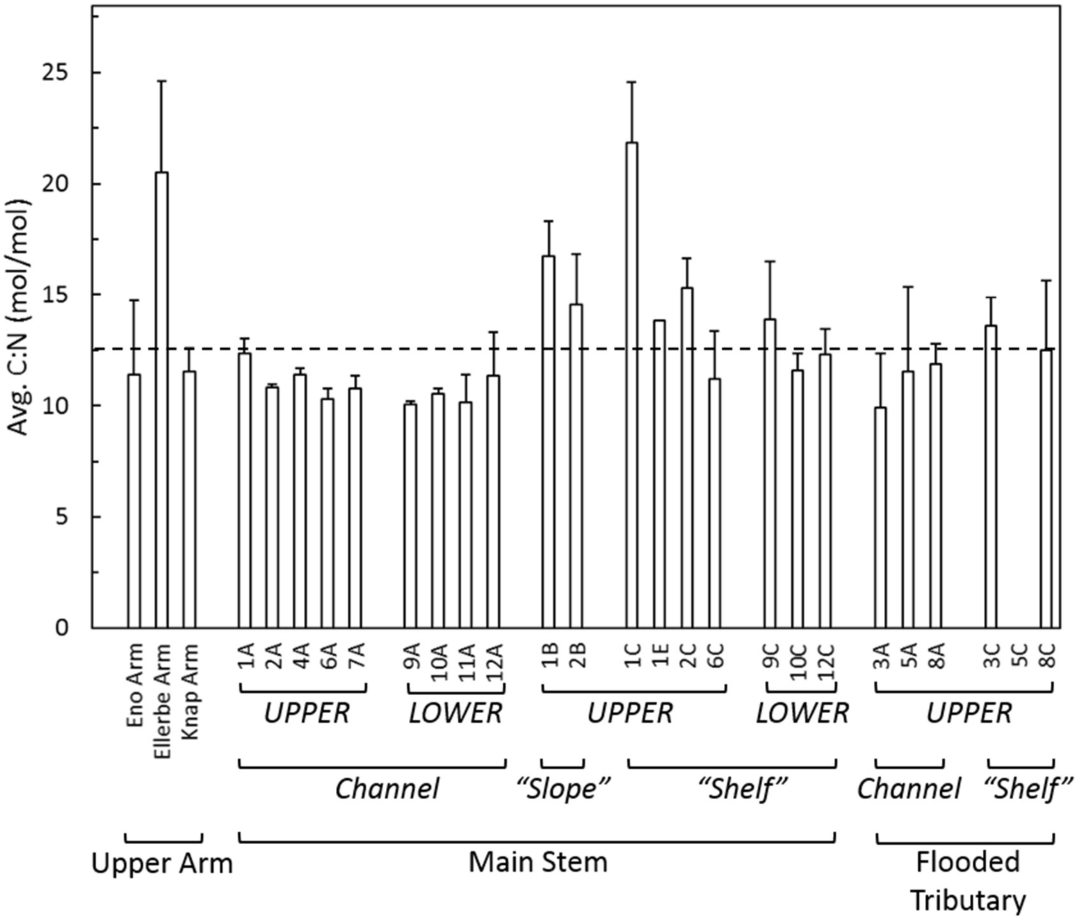

Figure 2. Average C:N (molar) ratios of each core collected in Falls Lake in Summer 2015. The dashed line indicates the value expected for aquatic organic matter (following selective remineralization of nitrogen) or terrestrial-derived organic matter (following microbial colonization).

Given the presence of decaying organic matter, nutrients can move out of the sediment through diffusion across the sediment-water interface as well as through non-local transport caused by physical activity of organisms such as burrowing worms ("irrigation") or eruption of methane bubbles. Diffusion is determined by the concentration gradient between the sediment pore water and the overlying water and therefore the nutrient concentrations of both were measured. NH_3 concentrations in bottom water were low at stations <5 m deep (mean = 0.014 mg/L), but increased dramatically at deeper stations, with Station 12 yielding a NH_3 concentration of 2.0 mg/L. Concentrations of NO_x in the bottom water averaged 0.0042 mg/L and were similar across all stations. PO_4 levels averaged 0.0093 mg/L and were also relatively constant among the stations.

Higher nutrient concentrations in the sediment porewater are necessary for net diffusive flux to move nutrients from the sediments to the water column. In all cores, Total Phosphate concentrations in the first sediment interval (0-3 cm) are elevated above the overlying water (Figure 3). This indicates an upward diffusive flux of phosphate toward the sediment-water interface. However, the amount of phosphate that escapes from the sediments by diffusion is expected to be minimal if surface sediments are in contact with overlying water that contains dissolved oxygen

(Sundby et al., 1986). Since the *in situ* benthic flux of phosphate depends on the concentration of oxygen in the bottom water, the diffusive phosphate flux from the sediments should be considered a “potential” flux.

The average potential diffusive phosphate flux calculated from the phosphate concentration gradient at the sediment-water interface is 0.004 mmol $P \cdot m^{-2} \cdot d^{-1}$ (range: 0.0003 to 0.016 mmol $P \cdot m^{-2} \cdot d^{-1}$). In contrast, the average diffusive ammonium flux calculated from the ammonium concentration gradient at the sediment-water interface is 1.26 mmol $N \cdot m^{-2} \cdot d^{-1}$ (range: 0.038 to 5.04 mmol $N \cdot m^{-2} \cdot d^{-1}$). On average, the benthic ammonium flux is >300× the potential phosphate flux. Allowing for the 16:1 N:P ratio in phytoplankton, sediments provide a 20-fold excess of available nitrogen compared to phytoplankton requirements for phosphorous. For this reason, nitrogen was the focus of the sediment study. Note that diffusive fluxes do not include the contribution from irrigation.

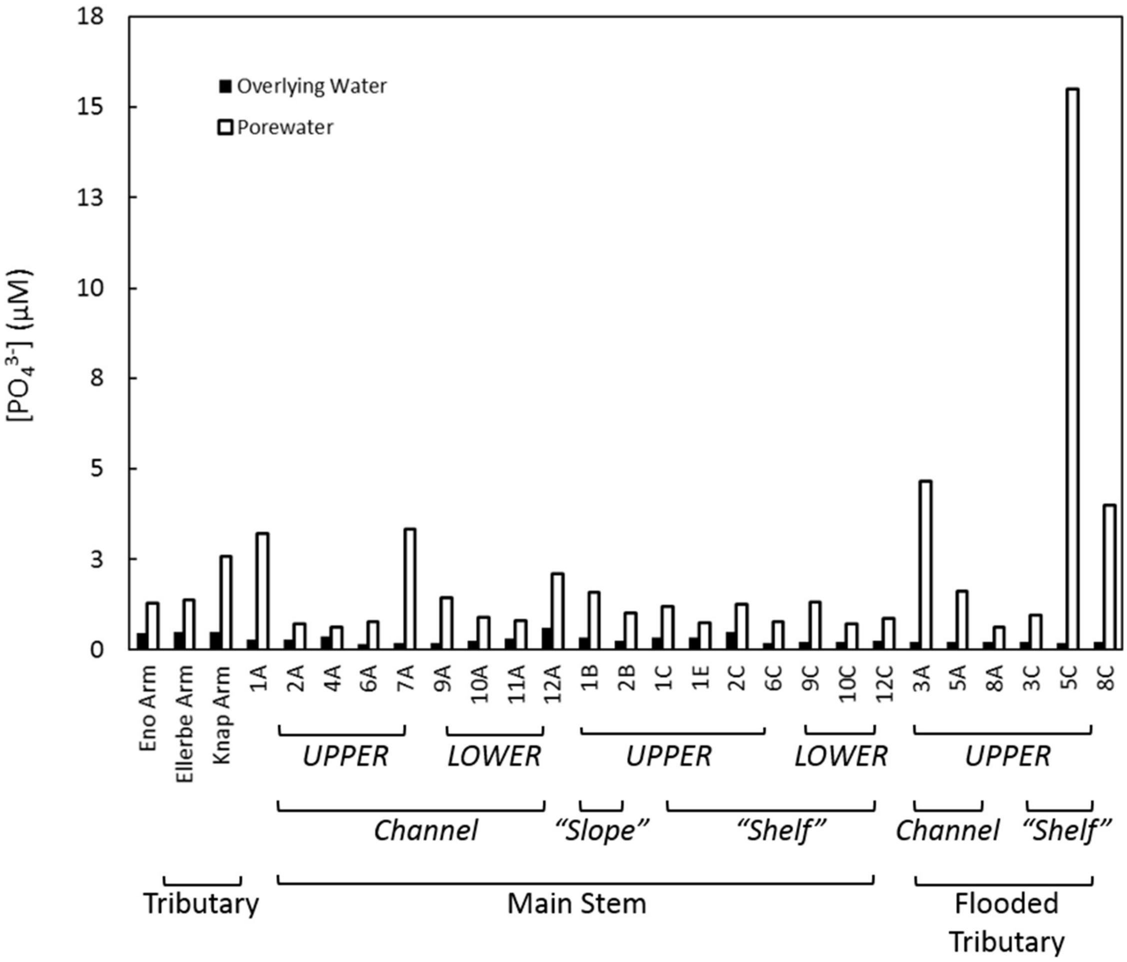

Figure 3. Phosphate concentrations in overlying water and first porewater sample (0-3 cm) for each core collected in Falls Lake in Summer 2015. To convert µM PO_4^{3-} to µg P/L, multiply by 31.

Most ammonium in sediments is produced by ammonification: the hydrolysis and decomposition of organic nitrogen. A portion of the organic nitrogen pool is refractory and resistant to hydrolysis over the timescale reflected by the core. Ammonium may also be produced by dissimilatory nitrate reduction to ammonium (DNRA), in which nitrate is used as an electron acceptor to oxidize reduced substrates such as organic matter or hydrogen sulfide. Ammonium is consumed by nitrification, an aerobic process whereby ammonium is oxidized to nitrate; the process may take place in two steps, mediated by distinct bacteria, with nitrite as intermediate. Ammonium may also be consumed during anaerobic ammonium oxidation (ANAMMOX) whereby ammonium is oxidized to N_2 with nitrite as electron acceptor. Finally, ammonium, being a cation will adsorb onto the negative-charged surfaces of clay minerals.

This study also found conditions suitable for NH_3 movement from the sediment to the water at every location where a core was collected, with the average NH_3 porewater concentration in the upper section of the sediment being some 2.5 mg/L higher than the overlying water. The highest observed difference between the upper sediment section porewater and the overlying water was nearly 10 mg/L. NH_3 concentrations increased with depth in the sediment porewater in all 24 cores, indicating the presence of a gradient to drive a net upward flux.

Concentrations of NO_x were also higher in the upper layer of porewater than in the overlying water but NO_x did not increase with depth in the sediment profile like NH_3, because the anoxic conditions prevented the nitrification of ammonia to an oxidized form. Similarly, PO_4 in the sediment porewater was at higher concentrations than the overlying water at all sampled locations, indicating the potential for an upward flux. When dissolved oxygen is present at the sediment-water interface, the diffusive flux of PO_4 into the water column is generally believed to be minimal. When dissolved oxygen is depleted in the bottom water, the diffusive flux of PO_4 may be high.

As noted above, a mathematical diagenetic model was developed to estimate inorganic nitrogen flux using the bottom water and pore water profiles of NH_3 and NO_x concentrations (see Appendix). The model applies known relationships and sediment processes and provides a method for estimating benthic fluxes that compliments direct measurements using flux chambers. Results are summarized below.

The nitrogen fluxes were typically dominated by NH_3, with NO_x generally making up less than 2% of the total flux. Estimates of NH_3 fluxes were widely variable among cores, ranging from less than 1 to nearly 90 mg/m^2/d (Figure 4). Although no clear pattern is apparent along an upstream to downstream location gradient, clear patterns did emerge when coring sites were organized based on lake morphology and bottom bathymetry. On average, fluxes from cores collected within the historic river channel were more than three times higher than cores collected nearby, but outside of the historic channel (61 and 16 mg N / m^2/d, respectively, $p=1x10^{-4}$).

The average nitrogen flux based on the sediment core analysis is similar to the two values obtained by the North Carolina Division of Water Quality (now DWR) in 2006 using sediment chambers (DWQ 2006), when differences in temperature and bottom bathymetry are takin into account. That study estimated an average flux of 50 mg/m^2/d within the historic channel near this study's station 2A (between I-85 and Cheek Road). Their value is within 20% of the average flux estimated from all channel cores and within 30% of the core-based estimate from the same location. Near station 7 (upstream of Highway 50), DWQ's study estimated a flux of 10 mg/m^2/d. Based on the water depth recorded for their chamber location (4.7m), this estimate was not within the historic Neuse River channel (depth of 8.5m). Although the UNRBA survey does not include a 'shelf' core at this particular location, DWQ's value (10 mg N / m2 /d) is near this study's lake-wide average from all cores collected outside of historic channels (16 mg N /m2/d). The ranges of values observed in both studies overlap and also underscore the large potential for spatial variation within the lake.

Although the flux estimates from the sediment cores are widely variable (Figure 4), the number of cores collected allows for a better understanding of benthic fluxes across the lake and how fluxes might vary with other measurable properties.

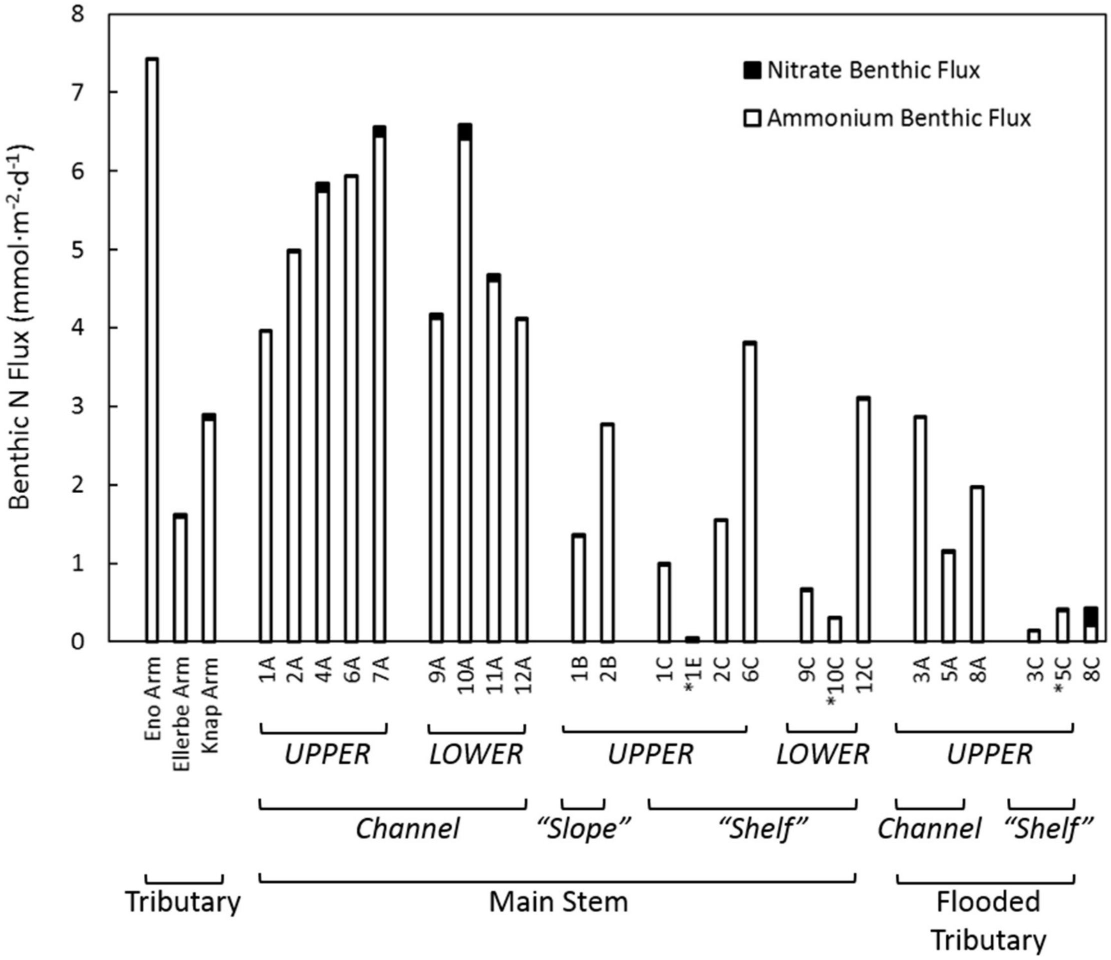

Figure 4. NH_3 and NOx sediment flux rates estimated using data from cores collected in Falls Lake in Summer 2015. To convert units to mg N m^{-2} d^{-1}, multiply the flux by the atomic weight of nitrogen (14 g/mol).

Despite the high spatial variability, there are some clear patterns in the data.

- The ammonium flux from main-stem, channel sediments in the Upper Lake steadily increases between stations 1A and 7A.
- The ammonium flux from main-stem, channel sediments in the Lower Lake is generally uniform.
- The benthic ammonium flux decreases from channel to "slope" to "shelf" sediments at all sites.
- The benthic ammonium flux from channel sediments that were Neuse River tributaries prior to dam construction is lower than main-stem channel sediments, and does not follow a pattern along the lake's longitudinal axis.

These patterns provide insights into how water column and sediment processes are coupled in

Falls Lake.

In the Upper Lake, the steady increase in benthic ammonium flux from main-stem stations 1A to 7A (from 4.0 to 6.5 mmol·m^{-2}·d^{-1}) suggests a downstream increase in deposition of particulate organic nitrogen (PON) in channel sediments. This may be explained as follows. During the growing season, nutrients delivered to the Upper Lake by tributaries are assimilated by phytoplankton. The resulting PON may be remineralized (converted back to DIN, fueling new phytoplankton growth) or may settle out of the water column. PON that reaches the lake bed in a shallow region of the lake is subject to winnowing and may be re-suspended. PON that settles at deeper sites has a greater probability of becoming part of the sediment. Once incorporated into sediments, the reactive PON is converted to ammonium (ammonification), which accumulates in the porewater. The porewater ammonium eventually returns to the water column by diffusion and possibly irrigation, where it is available for re-assimilation by phytoplankton. (A portion of the diffusive ammonium flux may be nitrified, and about half of the nitrate produced may be denitrified.) This ability to “hopscotch” between the water and sediments is one of the reasons why lakes tend to retain nitrogen. Superimposed on these depositional and biogeochemical processes is the flow of water through the lake, which serves as a conveyor that focusses PON deposition in downstream sediments.

In contrast to the Upper Lake, the ammonium flux from main-stem, channel sediments in the Lower Lake is generally uniform (4.1±0.3 mmol·m^{-2}·d^{-1}; average for stations 9A, 11A, and 12A), the exception being station 10A (6.4 mmol·m^{-2}·d^{-1}). The abrupt decline in benthic ammonium flux between the lower Upper Lake (6.5 mmol·m^{-2}·d^{-1} at station 7) and the upper Lower Lake (4.1 mmol·m^{-2}·d^{-1} at station 9) suggests that the conveyor-type transport described above does not continue into the Lower Lake. This may be due to the fact that Upper Falls Lake becomes much wider at station 6 (Fig. 1), thereby increasing the water retention time and promoting sedimentation. Also, the channel depth at station 7A is 8.5 m, sufficiently deep to allow deposition of fine-grain sediments which includes organic matter. The lower portion of Upper Falls Lake may function as a settling pond that traps nitrogen in the Upper Lake and decouples the systems. It is worth noting that number of exceedences of chl standard decreases abruptly between Upper and Lower Lake, consistent with a reduced supply of nutrients.

The importance of bathymetry in controlling benthic ammonium fluxes is clearly illustrated at the nine transect sites. On average, the ammonium flux from channel sediments is 3.4±1.7 (*n*=7) times larger than from “shelf” sediments (the average omits stations 3 and 10 that appear to be outliers in this metric; the “shelf”:channel flux ratio at these two stations is ~20).

The benthic ammonium flux from channel sediments that were Neuse River tributaries prior to dam construction (1.1-2.9 mmol·m^{-2}·d^{-1}) is lower than main-stem channel sediments and does not follow a pattern along the lake’s longitudinal axis. Little Lick Creek (site 3), Ledge Creek (site 5), and Lick Creek (site 8). Sediments at these sites are less important as nitrogen sources to the lake than the main stem.

The benthic flux values shown in Figure 4 will be integrated with the results of the bathymetric and sediment mapping Special Study undertaken by the UNRBA. The synthesis of the two efforts will allow for the development of lake wide estimates of nutrient flux, with far greater resolution of location and sediment thickness than has been possible before.

Once the benthic nutrient flux data are integrated lake wide, this value (internal loading) may be compared to external nutrient loading. If external loading dominates over internal loading, the supply of nutrients available to phytoplankton may be expected to respond quickly to a decrease in nutrient concentrations in the rivers and tributaries that are source waters to Falls Lake. However, if internal loading is a significant nutrient source to Falls Lake waters, the lake response time to a decrease in external nutrient loading will depend to some degree on the lifetime of reactive organic matter in the sediments.

The lifetime of reactive organic matter may be estimated from the depth-attenuation coefficient (α) for ammonification and the sedimentation rate. Values of α are lowest (i.e., reactive organic matter persists to greater depths) in channel vs. “slope” and “shelf” sediments. In general, α values for channel sediments are higher in the upper lake (~0.1 cm^{-1}) compared to lower lake (~0.05 cm^{-1}). Assuming a sedimentation rate of 1 cm/y in the upper lake and 0.5 cm/y in the lower lake, the lifetime of reactive organic matter is on the order of 10-40 years. In contrast, for “slope” and “shelf” sediments, α values are ~0.5 cm^{-1}. Assuming a sedimentation rate <0.1 cm/y, lifetimes of reactive organic matter are >20 years.

CONCLUSIONS

- Sediments are a source of reactive nitrogen to the water column at all 27 Falls Lake stations sampled in this study.
- Sediments are also a source of available phosphate to the water column at all 27 Falls Lake stations sampled in this study. The average potential diffusive flux of phosphate from sediments is <0.3% (mole/mole) of the average diffusive flux of ammonium.
- Patterns in the spatial distribution of benthic ammonium fluxes appear to be related to location and bathymetry within the lake.
- Benthic nitrogen fluxes from this study may be used as boundary conditions for the next generation of the Falls Lake nutrient response model.

RECOMMENDATIONS

- Quantify the effect of bottom water anoxia on the benthic phosphate flux. This can be done using in situ flux chambers with oxygen regulation (Sundby et al., 1986) or using laboratory incubations of intact cores bubbled with air or inert gas. Combined with bottom water oxygen concentration data, a quantitative understanding of the relationship between benthic phosphate flux and bottom water dissolved oxygen will provide a more accurate assessment of the role of sediments in supplying phosphate to the overlying water.
- Spatially integrate benthic fluxes for the whole lake. This can be done easily using the detailed Falls Lake bathymetric maps generated by Brown and Caldwell. This information will be helpful in assessing what fraction of the lake’s nutrient pool is supplied by sediments vs. tributaries.
- Quantify porewater irrigation rates. These rates may be quantified by addition of a passive tracer to overlying water in situ or ex situ flux experiments (Heilskov et al., 2006).
- Quantify rates of coupled nitrification-denitrification. Isotope-pairing (Nielson, 1992) is the preferred method for quantifying rates of both these processes.
- Quantify sedimentation (geochronology) and bioturbation rates using geochronometric tracers such as excess ^{210}Pb and ^{7}Be.

All data and analytical outputs have been provided to the UNRBA via its monitoring program consultant, Brown and Caldwell.

REFERENCES

Berner, R. A., 1980. *Early Diagenesis, A Theoretical Approach*, Princeton University Press.

Boudreau, B. P., 1997. *Diagenetic Models and Their Implementation*, Springer.

Burdige, D. J., 2006. *Geochemistry of Marine Sediments*, Princeton University Press.

Di Toro, D. M. and J. J. Fitzpatrick, 1993. *Chesapeake Bay Sediment Flux Model*, US Army Corps of Engineers, AD-A267 189.

Geider, R. J. and J. La Roche, 2002. Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis, *Eur. J. Phycol.* 37:1-17.

Hecky, R. E. and P. Kilham, 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment, *Limnol. Oceanogr.* 33:796-822.

Hedges, J. I. and J. M. Oades, 1997. Comparative organic geochemistries of soils and marine sediments, *Geochim. et Cosmochim. Acta* 27:319-361.

Hedges, J. I., J. A. Baldock, Y. Gélinas, C. Lee, M. L. Peterson, and S. G. Wakeham, 2002. The biochemical and elemental compositions of marine plankton: A NMR perspective, *Marine Chemistry* 78:47-63.

Heilskov, A. C., M. Alperin, and M. Holmer, 2006. Benthic fauna bio-irrigation effects on nutrient regeneration in fish farm sediments. *J. Exp. Mar. Biol. Ecol.* 339:204-225.

Jørgensen, B. B. and B. P. Boudreau, 2001. Diagenesis and Sediment-Water Exchange, in *The Benthic Boundary Layer*, B. P. Boudreau and B. B. Jørgensen (eds), Oxford, p. 211-244.

Martin, W. R. and G. T. Banta, 1992. The measurement of sediment irrigation rates: a comparison of Br- tracer and ^{222}Rn/^{226}Ra disequilibrium techniques. *J. Mar. Res.* 50:125-154.

Miele, C., C. M. Koretsky, and P. Van Cappellen, 2001. Quantifying bioirrigation in aquatic sediments: an inverse modeling approach, *Limnol. Oceanogr.* 46:164-177.

Nielsen, L. P., 1992. Denitrification in sediments determined from nitrogen isotope pairing. FEMS Microbiol. Ecol. 86:357-362.

NC Department of Water Quality, 2006. Falls of the Neuse Reservoir Sediment Oxygen Demand and Nutrient Flux Tests, April 2006.

Sundby, B., L. G. Anderson, P. O. J. Hall, A. Iverfeldt, M. M. Rutgers van der Loeff, and S. F. G. Westerlund, 1986. The effect of oxygen on release and uptake of cobalt, manganese, iron and phosphate at the sediment-water interface, *Geochim. et Cosmochim. Acta* 50:1281-1288.

Sutherland, R. A., 1998. Loss-on-ignition estimates of organic matter relationships to organic carbon in fluvial bed sediments, *Hydrobiologia* 389:153-167.

Ullman, W. J. and R. C. Aller, 1982. Diffusion coefficients in near-shore marine sediments. *Limnol. Oceanogr.* 27:552-556.

Wetzel, R. G. 2001. *Limnology: Lake and River Ecosystems*, Academic Press.

Zabel, M., C. Hensen, and M. Schlüter, 2000. Back to the Ocean Cycles: Benthic Fluxes and Their Distribution Patterns, in *Marine Geochemistry*, H. D. Schulz and M. Zabel (eds), Springer, p. 373-395.

APPENDIX: BENTHIC FLUXES FROM POREWATER CONCENTRATION PROFILES

General Approach

This approach is based on conservation of mass: the solute flux at the sediment-water interface must equal the sum of all reactions that occur throughout the sediment column minus the change in solute inventory in the sediment (with a small correction for solute burial). The mathematical basis is provided by the diagenetic equation (Berner, 1980), a general mathematical description of all transport (diffusion, advection, and non-local) and reaction processes that occur in unconsolidated aquatic sediments. The following diagenetic equation describes the concentration profile of any porewater constituent:

$$\underbrace{\frac{\partial(\varphi c)}{\partial t}}_{\substack{\text{Change in}\\ \text{Concentration}}} = \underbrace{\frac{\partial}{\partial x}\left(\frac{\varphi D_o}{\theta^2}\frac{\partial c}{\partial x}\right)}_{\text{Molecular Diffusion}} \underbrace{-\varphi_\infty \omega_\infty \frac{\partial c}{\partial x}}_{\text{Advection}} \underbrace{-\varphi\beta\left(c - c_{\mathrm{OW}}\right)}_{\text{Non-local}} + \underbrace{\varphi \sum R}_{\text{Reaction}} . \qquad [1]$$

The notes under the brackets explain the meaning of each term in the equation; all symbols are defined in the table at the end of the Appendix. This equation assumes (1) there is no forced advection (porewater flow caused by external pressure gradients), (2) vertical concentration gradients are $\gg$ lateral gradients, and (3) irrigation may be parameterized as a non-local exchange process.

The depth-dependence of porosity may be described by the following equation:

$$\varphi = \left(\varphi_0 - \varphi_\infty\right) e^{-\gamma x} + \varphi_\infty ,$$

where φ_0, φ_∞, and γ are determined by non-linear regression (least-squares fit) to measured porosity data. For most Falls Lake cores analyzed in this study, this equation provides a reasonable fit to the data.

The most common mechanism for non-local transport of porewater constituents is bioirrigation (i.e., bottom-dwelling organisms flushing their burrows with overlying water). The depth-dependence of the bioirigation coefficient (β) depends on the density, size, and shape of macrofaunal burrows (Martin and Banta, 1992). Miele et al. (2001) used an inverse model to determine the depth-dependence of bioirrigation coefficients from a variety of aquatic sediments known to harbor irrigating macrofauna. They report that bioirrigation coefficients generally decrease rapidly with depth below the sediment surface, reflecting a decrease in infauna abundance. However, some sites have a pronounced sub-surface maximum in irrigation coefficient (centered 10-20 cm below the sediment surface) in addition to, or instead of the near-surface irrigation. They attribute the sub-surface peak to an increase in the cross-sectional area of the burrow at the depth corresponding to a chamber or the base of a U-tube. A bioirrigation coefficient that decreases rapidly with sediment depth and/or peaks below the sediment surface may be simulated by adding exponential and Gaussian functions:

$$\beta = \beta_0 e^{-\lambda x} + \beta_{\max} e^{-(4(x - z_{\max})/\sigma)^2} .$$

Ebullition provides another mechanism for “irrigating” sediments. When a gas bubble bursts out of the sediment, it creates a channel and pushes out a column of porewater that is replaced by infiltration of overlying water.

Infaunal populations in Falls Lake were not surveyed during this study, and rates of non-local porewater transport were not directly measured. However, there is clear evidence for non-local transport in the many of the NH_4^+ concentration profiles (see below), and circumstantial evidence suggests that macrofauna and/or ebullition may be responsible. Burrow-like structures were visible through the transparent core liner in many of the collected cores, a small (~1.5 cm) worm (see if Matt can identify species) was observed at the sediment surface in core 2A, and a majority of cores had visible gas bubbles in the sediment (presumably methane) at the time of sectioning. Hereafter, the general term “irrigation” is used to account for the fact that non-local transport in Falls Lake sediment may be caused by macrofauna and/or ebullition.

The parameters λ, $z_{\max}$, and σ define the shape of the irrigation zone and their values are determined by *a priori* analysis of the NH_4^+ concentration profile (since active irrigation results in predictable concavity). The parameters β_0 and $\beta_{\max}$ control the magnitude of the irrigation rate and are estimated using an iterative approach (described below). This approach is designed to yield a minimum (i.e., lower-limit) estimate of the *in-situ* irrigation flux. The magnitude of the error is assessed.

The diagenetic equation is a second-order differential equation and thus requires two boundary conditions. As a matter of convenience, the upper boundary is set at the sediment-water interface, where the solute concentration is assumed to equal that in the overlying water ($_{\mathrm{OW}}$). The lower boundary ($_{\mathrm{LB}}$) is set sufficiently deep in the sediment (100 cm for Falls Lake) that reaction and bioirrigation rates approach zero ($R \approx \beta \approx 0 \text{ for } x \geq x_{\mathrm{LB}}$). This implies zero concentration gradient at the lower boundary:

$$\begin{aligned} &c = c_{\mathrm{OW}} \ \text{ at } x = 0 \\ &\frac{\partial c}{\partial x} = 0 \ \text{ at } x = x_{\mathrm{LB}} \end{aligned}.$$

The benthic flux (F_0, or flux at x = 0) is the sum of diffusive, advective, and irrigation fluxes at the sediment-water interface:

$$F_0 = \underbrace{-\left(\frac{\varphi D_o}{\theta^2}\frac{\partial c}{\partial x}\right)_{x=0}}_{\textit{Molecular Diffusion}} + \underbrace{\varphi_\infty \omega_\infty c_{\mathrm{OW}}}_{\textit{Advection}} - \underbrace{\int_0^{x_{LB}} \varphi\beta\left(c - c_{\mathrm{OW}}\right)dx}_{\textit{Irrigation}}.$$

Upon integrating the diagenetic equation over the interval $0 \leq x \leq x_{\mathrm{LB}}$, the benthic flux is shown to equal the integral of all rates of reaction that affect the solute, adjusted for solute burial (advection at the lower boundary) and temporal changes in inventory:

$$F_0 = \underbrace{-\int_0^{x_{LB}} \varphi \sum R \; dx}_{\textit{Reaction}} + \underbrace{\varphi_\infty \omega_\infty c_{\mathrm{LB}}}_{\textit{Burial}} + \underbrace{\frac{\partial}{\partial t}\int_0^{x_{LB}} \varphi c \; dx}_{\textit{Change in Inventory}}.$$

Given the following three assumptions,

(1) steady-state ($\frac{\partial c}{\partial t} = \frac{\partial \varphi}{\partial t} = 0$),

(2) advective transport (sedimentation) is negligible relative to diffusion over the model length-scale (i.e., $Pe = \omega_{\infty} x_{\mathrm{LB}} \theta^2 / D_o \ll 1$, where *Pe* is the Peclet number), and

(3) the relationship between tortuosity and porosity is described by Archie's Law: $\theta^2 = \varphi^{1-m}$ or $\theta^{-2} = \varphi^{m-1}$ where *m* = 2 if average $\varphi \leq 0.7$ and *m* = 3 if average $\varphi > 0.7$ (Ullman and Aller, 1982),

the general diagenetic equation reduces to:

$$\underbrace{\frac{d}{dx}\left(\varphi^m D_o \frac{\partial c}{\partial x}\right)}_{\textit{Molecular Diffusion}} + \underbrace{\varphi \sum R}_{\textit{Reaction}} - \underbrace{\varphi \beta \left(c - c_{\mathrm{BW}}\right)}_{\textit{Irrigation}} = 0 \ ,$$

and the benthic flux is given by:

$$F_0 = \underbrace{-\varphi_0^m D_{\mathrm{o}} \left(\frac{dc}{dx}\right)_0}_{\textit{Molecular Diffusion}} - \underbrace{\int_0^{x_{LB}} \varphi \beta \left(c - c_{\mathrm{BW}}\right) dx}_{\textit{Irrigation}} = \underbrace{-\int_0^{x_{LB}} \varphi \sum R dx}_{\textit{Reaction}} .$$

Thus, the solute flux (diffusive plus irrigation) across the sediment-water interface may be calculated by integrating reaction rates in the sediment. Reaction rates, in turn, may be quantified by solving the diagenetic equation and tuning the adjustable model parameters to simulate the measured concentration profiles. To solve the diagenetic equation for a specific solute, the mathematical forms of the rate laws must be specified.

b. Rate laws for ammonium and nitrate

Most $\mathrm{NH_4^+}$ in sediments is produced by *ammonification*: the hydrolysis and decomposition of organic nitrogen. Ammonium may also be produced by *dissimilatory nitrate reduction to ammonium* (*DNRA*), in which $\mathrm{NO_3^-}$ is used as an electron acceptor to oxidize reduced substrates such as organic matter or hydrogen sulfide. Ammonium is consumed by *nitrification*, an aerobic process whereby $\mathrm{NH_4^+}$ is oxidized to $\mathrm{NO_3^-}$; the process may take place in two steps, mediated by distinct bacteria, with $\mathrm{NO_2^-}$ as intermediate. Ammonium may also be consumed during *anaerobic ammonium oxidation* (*ANAMMOX*) whereby $\mathrm{NH_4^+}$ is oxidized to N_2 with $\mathrm{NO_2^-}$ as electron acceptor. Finally, $\mathrm{NH_4^+}$, being a cation will *adsorb* onto the negative-charged surfaces of clay minerals.

Nitrate is produced from $\mathrm{NH_4^+}$ during *nitrification*. Nitrate is consumed during *denitrification*, an anaerobic process whereby $\mathrm{NO_3^-}$ is used as an alternative to O_2 for the oxidation of organic matter; the end-product of denitrification is N_2. *Denitrification* and *nitrification* may be coupled; the net reaction in terms of nitrogen is oxidation of $\mathrm{NH_4^+}$ to N_2. Nitrate is also converted to $\mathrm{NH_4^+}$ during *DNRA*, and $\mathrm{NO_2^-}$ is reduced to N_2 during *ANAMMOX*.

Nitrite, being produced as an intermediate in nitrification, is usually present at much lower concentrations than $\mathrm{NO_3^-}$ (i.e., $[\mathrm{NO_3^-}] + [\mathrm{NO_2^-}] \cong [\mathrm{NO_3^-}]$). Thus, the rate laws for the $\mathrm{NO_3^-}$ and $\mathrm{NO_2^-}$ will be aggregated and the two species will be a combined, resulting in a single diagenetic equation for $\mathrm{NO_3^-}$.

The following rate laws are assumed to describe the processes involving NH_4^+ and NO_3^- (all symbols are defined in Table 2):

(1) The *ammonification* rate decreases exponentially with sediment depth: $R^{Amm} = R_0 e^{-\alpha x}$.

(2) The *nitrification* rate is first-order with respect to NH_4^+ concentration $-R^{Nit} = k_{Nit}[\mathrm{NH}_4^+]-$ in the oxic zone (*x* < *L*, where *L* is the oxygen penetration depth); *nitrification* does not occur below the oxic zone (*x* > *L*).

(3) The *denitrification* rate is first-order with respect to NO_3^- concentration below the oxic zone: $R^{Den} = k_{Den}[\mathrm{NO}_3^-]$ (*x* > *L*); *denitrification* does not occur in the oxic zone (*x* < *L*) or if the nitrate concentration falls below a threshold concentration ($[\mathrm{NO}_3^-]^*$), equal to minimum nitrate concentration in each profile.

(4) *ANAMMOX* is aggregated with coupled *nitrification-denitrification*, and occurs at a rate that is negligible compared to *ammonification*.

(5) The rate of *DNRA* is much slower than *ammonification* and may be neglected from the equation for NH_4^+. *DNRA* in the diagenetic equation for NO_3^- is aggregated with *denitrification*.

(6) *Adsorption* of NH_4^+ onto clay particles (ion exchange) may be neglected (valid at steady-state if advective transport is negligible relative to diffusive transport).

With these rate laws, the general digenetic equations for NH_4^+ and NO_3^- are:

$$\underbrace{\frac{d}{dx}\left(\varphi^m D_o^{\mathrm{NH}_4^+} \frac{d[\mathrm{NH}_4^+]}{dx}\right)}_{Molecular\ Diffusion} + \underbrace{\varphi R_0 e^{-\alpha x}}_{Ammonification} - \underbrace{\chi_1 \varphi k_{Nit}[\mathrm{NH}_4^+]}_{Nitrification} - \underbrace{\varphi\beta\left([\mathrm{NH}_4^+]-[\mathrm{NH}_4^+]_{\mathrm{BW}}\right)}_{Irrigation} = 0$$

$$\underbrace{\frac{d}{dx}\left(\varphi^m D_o^{\mathrm{NO}_3^-} \frac{d[\mathrm{NO}_3^-]}{dx}\right)}_{Molecular\ Diffusion} + \underbrace{\chi_1 \varphi k_{Nit}[\mathrm{NH}_4^+]}_{Nitrification} - \underbrace{\chi_2 \chi_3 \varphi k_{Den}[\mathrm{NO}_3^-]}_{Denitrification} - \underbrace{\varphi\beta\left([\mathrm{NO}_3^-]-[\mathrm{NO}_3^-]_{\mathrm{BW}}\right)}_{Irrigation} = 0 \quad , [2]$$

where

$$\chi_1 = 0.5\left[1 - erf\left(\frac{x-L}{0.05}\right)\right] \cong \begin{cases} 1 & \text{if } x < L \\ 0 & \text{if } x > L \end{cases}$$

$$\chi_2 = 0.5\left[1 + erf\left(\frac{x-L}{0.05}\right)\right] \cong \begin{cases} 0 & \text{if } x < L \\ 1 & \text{if } x > L \end{cases}.$$

$$\chi_3 = 0.5\left[1 + erf\left(\frac{[\mathrm{NO}_3^-]-[\mathrm{NO}_3^-]^*}{0.01[\mathrm{NO}_3^-]^*}\right)\right] \cong \begin{cases} 0 & \text{if } [\mathrm{NO}_3^-] < [\mathrm{NO}_3^-]^* \\ 1 & \text{if } [\mathrm{NO}_3^-] > [\mathrm{NO}_3^-]^* \end{cases}$$

The error functions (χ_i) serve as toggles that “turn on” aerobic processes and “turn off” anaerobic processes in oxic sediments (and vice-versa in anoxic sediments), and “turn-off” *denitrification* if NO_3^- concentrations fall below the threshold value. (The real numbers in the denominator control the slope of χ_i in the vicinity of $x = L$ and $[\mathrm{NO}_3^-] = [\mathrm{NO}_3^-]^*$. The values were chosen to minimize numerical stiffness; changing them by a factor of two does not noticeably affect the solution).

Since *nitrification* (NO_3^- production) only occurs in the presence of oxygen, and *denitrification* (NO_3^- consumption) only occurs in the absence of oxygen, the oxygen penetration depth (L) is taken to be the depth of the near-surface NO_x^- maximum. Based on this criterion, the base of the oxic zone in Falls Lake sediment is 1.5 cm at all sites where benthic fluxes were calculated by the porewater concentration profile method except stations 3C and 9C where the NO_x^- peaks are at a depth of 4.5 cm.

c. Constraining adjustable model parameters

The two diagenetic equations have ten fixed parameters that are determined empirically (φ_0, φ_∞, γ, m, $[\mathrm{NH}_4^+]_{\mathrm{OW}}$, $[\mathrm{NO}_3^-]_{\mathrm{OW}}$, L and $[\mathrm{NO}_3^-]^*$) or from the literature ($D_o^{\mathrm{NH}_4^+}$ and $D_o^{\mathrm{NO}_3^-}$), up to five adjustable parameters that define the irrigation coefficient (β_0, λ, β_{max}, z_{max}, and σ), and four adjustable rate parameters (R_0, α, k_{Nit} and k_{Den}). As a general rule of thumb, each concentration-depth distribution may constrain up to two unknown parameters (analogous to a linear regression constraining the slope and intercept of two correlated variables). Thus, NH_4^+ and NO_3^- profiles in tandem may be used to constrain the four adjustable rate parameters in sediments where irrigation is negligible. However, if irrigation is an important transport process, the number of "unknowns" exceeds the number of "knowns" and the system is underdetermined.

The shape of the NH_4^+ profile provides information as to whether irrigation is an important transport process, and if so, the location(s) in the sediment column where irrigation is a dominant process. This can be seen from diagenetic equation for NH_4^+ below the oxygen penetration depth (i.e., $x > L$) where the nitrification rate is zero (i.e., $\chi_1 = 0$). After rearranging:

$$\frac{d^2[\mathrm{NH}_4^+]}{dx^2} = \left[\underbrace{\beta\left([\mathrm{NH}_4^+]-[\mathrm{NH}_4^+]_{\mathrm{BW}}\right)}_{Irrigation} - \left(\underbrace{R_o e^{-\alpha x}}_{Ammonification} + \underbrace{m\varphi^{m-2} D_o^{\mathrm{NH}_4^+} \frac{d\varphi}{dx}\frac{d[\mathrm{NH}_4^+]}{dx}}_{Compaction}\right)\right]\left(\varphi^{m-1} D_o^{\mathrm{NH}_4^+}\right)^{-1}$$

.

The ammonification and compaction terms are opposite in sign, but mass conservation requires the sum of these two terms to be ≥ 0. Thus, in sediments where irrigation is minor compared to ammonification, $d^2[\mathrm{NH}_4^+]/dx^2 < 0$ and the NH_4^+ profile will be concave-down. Conversely, if the irrigation term exceeds the ammonification/compaction term, $d^2[\mathrm{NH}_4^+]/dx^2 > 0$ and the NH_4^+ profile will be concave-up. Hence, the protocol for constraining the adjustable model parameters will depend on the shape of the NH_4^+ concentration profile.

Type 1 profiles (no inflection points)

The NH_4^+ profiles from the majority of cores in this study (13 of 24 sites) are concave-down. For these cores, irrigation is assumed to be negligible (i.e., $\beta = 0$) and the four adjustable rate parameters are constrained as follows:

(1) R_0 and α are determined by tuning the model solution to the observed NH_4^+ depth-profile.
(2) k_{Nit} and k_{Den} are determined by tuning the model solution to the observed NO_3^- depth-profile.
Model tuning is guided by the "goodness-of-fit" coefficient, r^2:

$$r^2 = 1 - \frac{\Sigma\left(c_i - \hat{c}_i\right)^2}{\Sigma\left(c_i - \overline{c}_i\right)^2},$$

where c_i and $\hat{c}_i$ are measured and model-derived $\mathrm{NH_4^+}$ or $\mathrm{NO_3^-}$ concentrations, respectively, at each sampled depth, and $\overline{c}_i$ is the mean of all measured concentrations. In cases where the concentrations are nearly constant with depth (most $\mathrm{NO_3^-}$ and a few $\mathrm{NH_4^+}$ profiles), $\left(c_i - \overline{c}_i\right) \approx 0$ and r^2 is not useful.

Note that a concave-down $\mathrm{NH_4^+}$ profile does not necessarily indicate that irrigation is absent. Rather, $d^2[\mathrm{NH_4^+}]/dx^2 < 0$ indicates that the rate of $\mathrm{NH_4^+}$ production by ammonification exceeds the rate of $\mathrm{NH_4^+}$ removal by non-local transport. Thus, the benthic $\mathrm{NH_4^+}$ flux based on the assumption that irrigation is negligible should be considered a lower-limit.

Type 2 profiles (one inflection point)

The $\mathrm{NH_4^+}$ profiles from eight sites are concave-up near the core top and concave-down deeper in the sediment. The zone of upward concavity in these cores (3-9 cm) extends below the oxygen penetration depth (1.5 cm), and is assumed to result from near-surface irrigation in which the exchange coefficient decreases exponentially with depth ($\beta = \beta_0 e^{-\lambda x}$). In this case, the diagenetic equations for $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ have six adjustable irrigation and rate parameters (R_0, α, k_{Nit}, k_{Den}, β_0, and λ). The following protocol is adopted to yield a minimum (i.e., lower-limit) estimate of the *in-situ* irrigation flux:

(1) Depth-attenuation coefficients for irrigation (λ) are estimated using the depth of the inflection point in the $\mathrm{NH_4^+}$ concentration profile (Fig. 19N-U). Defining the base of the irrigation zone (z_{Irr}) as the depth where $\beta = \left(0.1\%\right)\beta_0$, then

$$\lambda = \frac{-\ln(0.001)}{z_{Irr}} = \frac{6.9}{z_{Irr}}.$$

As explained above, upward concavity in the $\mathrm{NH_4^+}$ profile below the oxic zone is evidence for net removal by irrigation. Below the inflection point (z^*) in the $\mathrm{NH_4^+}$ profile denotes the onset of net $\mathrm{NH_4^+}$ production, and that depth marks the uppermost boundary of the irrigation zone. That is, irrigation must extend at least to the depth of the inflection point but may continue below (albeit at a rate slower than ammonification). Since $z^* \le z_{Irr}$, $\lambda \ge 6.9/z^*$; that is, λ calculated this way tends to overestimate the true value. Hence the depth-integrated irrigation exchange coefficient,

$$\int_0^\infty \beta_0 e^{-\lambda x} dx = \beta_0/\lambda$$

("irrigation velocity") and the benthic flux due to irrigation represent a lower-limit.

(2) Depth-attenuation coefficients for ammonification (α) are estimated from the $\mathrm{NH_4^+}$ concentration profile. Assuming steady-state, constant porosity > 0.7, and no irrigation/nitrification/advection, the diagenetic equation for $\mathrm{NH_4^+}$ reduces to a differential equation with a closed-form solution:

$$\varphi^2 D_o^{\mathrm{NH}_4^+} \frac{d^2[\mathrm{NH}_4^+]}{dx^2} + R_o e^{-\alpha x} = 0 . \quad [3]$$

For the boundary conditions

$$[\mathrm{NH}_4^+] = [\mathrm{NH}_4^+]_{\mathrm{OW}} \text{ at } x = 0$$

$$\frac{d[\mathrm{NH}_4^+]}{dx} = 0 \text{ at } x = \infty \qquad ,$$

integration yields:

$$\left([\mathrm{NH}_4^+] - [\mathrm{NH}_4^+]_{\mathrm{OW}}\right) = \left([\mathrm{NH}_4^+]_\infty - [\mathrm{NH}_4^+]_{\mathrm{OW}}\right)\left(1 - e^{-\alpha x}\right).$$

If porewater $[\mathrm{NH}_4^+]$ □ $[\mathrm{NH}_4^+]_{\mathrm{OW}}$, the NH_4^+ concentration at any depth *x* in the sediment ($[\mathrm{NH}_4^+]_x$) is simply a function of the asymptotic concentration and *α*:

$$[\mathrm{NH}_4^+]_x \approx [\mathrm{NH}_4^+]_\infty \left(1 - e^{-\alpha x}\right).$$

Thus, at steady-state and in the absence of irrigation, compaction, nitrification and advection, *α* may be estimated from the measured NH_4^+ concentration at one depth in the profile and at the asymptote:

$$\alpha \approx \frac{-1}{x} \ln\left(1 - \frac{[\mathrm{NH}_4^+]_x}{[\mathrm{NH}_4^+]_\infty}\right).$$

Since these assumptions (steady-state, no irrigation, no compaction, no nitrification) do not hold in Falls Lake sediment, and NH_4^+ concentration profiles do not extend to the asymptote at most sites with Type 2 profiles, *α* calculated this way provides only a first-order approximation. The error in *α* may be minimized by selecting the depth *x* near the bottom of the profile where concentrations are most steady and least affected by irrigation, compaction, and nitrification.

(3) R_0 and β_0 have opposing effects on the NH_4^+ profile (i.e., increasing R_0 increases NH_4^+ production due to ammonification while increasing β_0 increases NH_4^+ removal by irrigation). Thus, there are no unique values of R_0 and β_0 that yield a best-fit to the data. Instead, values of R_0 and β_0 resulting in the minimum NH_4^+ benthic flux consistent with the concentration profile are constrained using an iterative approach:

- (i) The initial value for R_0 is selected such that the predicted NH_4^+ profile matches observed values below the irrigation zone (this represents a minimum value);
- (ii) β_0 is then selected to reproduce the observed concentration gradient near the sediment-water interface (this represents a minimum value);
- (iii) The final R_0 value is determined by tuning the model solution to the observed NH_4^+ depth-profile: R_0 is gradually increased until the predicted NH_4^+ profile yields the maximum value for the "goodness-of-fit" coefficient (r^2). This procedure provides a lower-limit estimate of ammonification and bioirrigation rates and benthic NH_4^+ flux.

(4) k_{Nit} and k_{Den} are determined by tuning the model solution for NO_3^- to the observed NO_3^- depth-profile.

Type 3 profiles (two inflection points)

The NH_4^+ profile from one site (station 7A) shows upward concavity at mid-depth in the sediment column (~4.5-13.5 cm) indicating a sub-surface peak in the irrigation coefficient. Here, the irrigation coefficient is assumed to follow a Gaussian distribution:

$$\beta = \beta_{\max} e^{-(4(x-z_{\max})/\sigma)^2},$$

where $z_{\max}$ is the depth marking the midpoint (9.0 cm) and σ is the vertical extent (thickness) of the irrigation zone (9.0 cm). Because of the deep irrigation, α may not be constrained by the procedure described for Type 2 profiles. Rather, the four adjustable rate parameters (R_0, α, k_{Nit}, k_{Den}) and maximum irrigation coefficient ($\beta_{\max}$) are constrained by the following iterative approach:

(1) The initial value for α is selected as described in "Type-2 profiles (2)" above.

(2) R_0 is selected such that the predicted NH_4^+ profile matches observed values above and below the irrigation zone.

(3) The initial value for $\beta_{\max}$ is selected to reproduce the concentration profile in the irrigation zone. This weakens the fit to the data above and below the irrigation zone.

(4) α and $\beta_{\max}$ are then iteratively adjusted until the simulated NH_4^+ profile captures the major features in the data. The maximum α and minimum $\beta_{\max}$ that reproduce the data are selected; this will yield a lower-limit estimate of the NH_4^+ benthic flux.

(5) k_{Nit} and k_{Den} are determined as described in "Type-2 profiles (4)" above.

Type 4 profiles (three inflection points)

The NH_4^+ profiles from two sites (stations 10A and 11A) have two zones of upward concavity: one near the sediment surface and one at mid-depth (Fig. 16W and X). Here, the irrigation rate constants are assumed to be the sum of exponential and Gaussian functions:

$$\beta = \beta_0 e^{-\lambda x} + \beta_{\max} e^{-(4(x-z_{\max})/\sigma)^2}.$$

The nine adjustable parameters are constrained by combining the approaches used for Type 2 and Type 3 profiles:

(1) λ, α, β_0 and R_0 are constrained as described for Type 2 profiles.

(2) z_{MAX}, σ and $\beta_{\max}$ are constrained as described for Type 3 profiles.

(3) k_{Nit} and k_{Den} are determined by tuning the model solution for NO_3^- to the observed NO_3^- depth-profile as described above.

d. Solving the diagenetic equations

The diagenetic equations for NH_4^+ and NO_3^- were solved using a finite difference method (subroutine *BVPFD* from the IMSL Math Library). The grid resolution was usually 0.005 cm for NH_4^+ and 0.0005 cm for NO_3^-. The convergence parameter was set so that solutions conserve mass to better than 99.99%. Model output includes simulated NH_4^+ and NO_3^- concentration profiles, predicted rate profiles of ammonification (NH_4^+ production), nitrification and denitrification (NO_3^- reaction), and irrigation rates for NH_4^+ and NO_3^-.

Benthic fluxes are calculated by depth-integrating reaction rates based on the best-fit model parameters and simulated concentration profiles:

$$\begin{aligned} F_0^{\mathrm{NH}_4^+} &= -\left[\underbrace{\int_0^{x_{LB}} \varphi R_0 e^{-\alpha x}\,dx}_{\mathit{Ammonification}} - \underbrace{\int_0^{x_{LB}} \chi_1 \varphi k_{Nit} [\mathrm{NH}_4^+]\, dx}_{\mathit{Nitrification}}\right] \\ F_0^{\mathrm{NO}_3^-} &= -\left[\underbrace{\int_0^{x_{LB}} \chi_1 \varphi k_{Nit} [\mathrm{NH}_4^+]}_{\mathit{Nitrification}} - \underbrace{\int_0^{x_{LB}} \chi_2 \chi_3 \varphi k_{Den} [\mathrm{NO}_3^-]\, dx}_{\mathit{Denitrification}}\right] \end{aligned} . \qquad [4]$$

Likewise, the diffusion and irrigation portions of the benthic flux may be calculated:

$$\begin{aligned} F_0^{\mathit{Diffuion}} &= -\varphi_0^m D_{\mathrm{o}} \left(\frac{dc}{dx}\right)_0 \\ F_0^{\mathit{Irrigation}} &= -\int_0^{x_{LB}} \varphi \beta \left(c - c_{\mathrm{BW}}\right) dx \end{aligned} .$$

The sign on the flux denotes direction: $F_0 < 0$ indicates an upward flux (i.e., out of the sediment), $F_0 > 0$ indicates a downward flux (i.e., into the sediment).

3. Porewater Profile Method Evaluation

a. Assumptions

The following twelve assumptions are incorporated into the porewater concentration profile method (see equation [2]) used to estimate NH_4^+ and NO_3^- benthic fluxes (italicized processes are described in Section IV.2b):

(1) porewater profiles are at steady-state;

(2) vertical porewater concentration gradients are □ lateral gradients;

(3) no forced advection in the sediment;

(4) sediment advection is negligible relative to diffusion;

(5) *adsorption* of NH_4^+ onto clay particles may be neglected;

(6) irrigation may be parameterized as a non-local exchange process;

(7) tortuosity and porosity are related according to Archie's Law;

(8) *ammonification* decreases exponentially with sediment depth;

(9) *nitrification* is pseudo first-order with respect to NH_4^+ concentration and requires oxygen;

(10) *denitrification* is pseudo first-order with respect to $\mathrm{NO_3^-}$ concentration and is restricted to anoxic sediments;

(11) *ANAMMOX* and *DNRA* and are negligible compared to *ammonification*;

(12) oxygen penetrates to the depth of the near-surface NO_x^- maximum.

Most of these assumptions are justified for Falls Lake sediment based on porewater data (assumption 2), scaling analyses (assumptions 4-5), and literature (assumptions 6-11). This discussion will focus on two assumptions that are not justified: steady-state (assumption 1) and nitrate maximum as indicator of the oxygen penetration depth (assumption 12).

A porewater concentration profile will be at steady-state if input and output fluxes are equal and constant over time. In the case of porewater $\mathrm{NH_4^+}$, the process that dominates the input flux—ammonification—is ultimately controlled by the supply of reactive particulate nitrogen to the sediment surface. The quantity and quality of particulate organic nitrogen reaching the bottom of Falls Lake must have changed dramatically in 1982 when the Neuse River was dammed to create a reservoir, and has likely been variable ever since. However, the response time of the $\mathrm{NH_4^+}$ profile (0-20 cm) to a perturbation (i.e., the diffusion time-scale) is only ~4 months.[1] This means that $\mathrm{NH_4^+}$ profiles measured in 2015 are only minimally influenced by any temporal variations in ammonification rates that occurred before 2014.

Porewater concentration profiles are subject to non-steady variability when input and/or output fluxes change over periods shorter than the diffusion time-scale. Since ammonification rates are affected by temperature, porewater $\mathrm{NH_4^+}$ concentration profiles in Falls Lake will vary seasonally. A simple numerical simulation provides insight into how the benthic $\mathrm{NH_4^+}$ flux responds to seasonal changes in ammonification rate. Assuming constant porosity and diffusivity, and no irrigation, nitrification, and advection (these simplifications do not affect the overall conclusions related to seasonal variations in benthic flux), the general diagenetic equation [1] for $\mathrm{NH_4^+}$ reduces to a time- (i.e., temperature) dependent form of equation [3]:

$$\frac{d[\mathrm{NH_4^+}]}{dt} = \varphi^2 D_o^{\mathrm{NH_4^+}} \frac{d^2[\mathrm{NH_4^+}]}{dx^2} + R_o^T e^{-\alpha x}, \quad [5]$$

where $R_o^T = R_o^{20^\circ\mathrm{C}} \Phi^{T-20^\circ\mathrm{C}}$ is the temperature-dependent ammonification rate at $x = 0$ (Φ is the temperature coefficient and the equation is a parameterization of the Arrhenius expression), T is temperature (°C). Sediment temperature is assumed to follow a sinusoidal function over the course of a year:

---

[1] The diffusion time-scale (τ) for a porewater profile of length (Δx) is given by the Einstein-Smoluchowski equation: $\tau = \Delta x^2 / (2D_s)$, where D_s is the sediment diffusion coefficient ($= D_o/\theta^2 = D_o/\varphi^{1-m}$). D_o, φ, and m values at each Falls Lake station are in Table 3.

$$T = -\frac{A}{2}\sin\left[\frac{2\pi}{365}\left(t + t_{shift}\right)\right] + \overline{T},$$

where A is the annual temperature range, t_{shift} sets the timing of the temperature maximum to Julian Day 210 (July 29), and $\overline{T}$ is the average annual temperature. Boundary conditions are $[\mathrm{NH}_4^+] = 1.07\ \mu\mathrm{M}$ at $x = 0$ and $d[\mathrm{NH}_4^+]/dx = 0$ at $x = 100\ \mathrm{cm}$. The initial condition was an arbitrary concentration profile. The equation was solved using Matlab solver *pdepe* and “spun-up” for 35 years until the solution was independent of the initial condition.

The results of the simulation show that as sediments warm from 6-30°C, the benthic NH_4^+ flux increases by a factor of only ~2.5 (2 to 5 mmol·m^{-2}·d^{-1}) while the depth-integrated ammonium production rate increases ten-fold (0.7 to 7 mmol·m^{-2}·d^{-1}). Also, note that the NH_4^+ inventory roughly tracks ammonification. These results illustrate that sediments function as a capacitor, dampening seasonal variations in benthic flux by storing NH_4^+ when the sediment warms and gradually releasing NH_4^+ to the overlying water when the sediment cools. Since temporal variations in benthic flux are periodic, there are two times within a year when the flux is equal to the annual average flux: June 5 and Nov 11. By coincidence, cores for this study were collected from Falls Lake on June 8 and June10. Hence, we expect benthic fluxes based on these cores to approximate the annual average.

The error in benthic flux introduced by assuming steady-state depends on the magnitude of the temporal term (left-hand side of equation [1]) relative to transport and reaction terms (right-hand side of [1]). This error was assessed by applying the porewater concentration profile model (assuming steady-state) to the NH_4^+ profile predicted for June 9 by the time-dependent numerical simulation. The diffusive flux of NH_4^+ at the sediment surface predicted by the steady-state model (2.8 mmol·m^{-2}·d^{-1}) underestimates the flux from the time-dependent model (3.2 mmol·m^{-2}·d^{-1}) by 13%.

In order to model nitrification and denitrification, oxygen was assumed to penetrate to the depth of the nitrate maximum, which in most cores was the first sample interval (1.5 cm midpoint; Fig. 20, Table 3). This may overestimate the oxygen penetration depth in Falls Lake sediments. Di Toro and Fitzpatrick (1993) note that sediment oxygen profiles are approximately linear, implying that for non-irrigated sediments, the oxygen penetration depth (*L*) can be estimated from sediment oxygen demand (*SOD*). Using this approach with *SOD* values for Falls Lake (1.5 and 0.8 g·m^{-2}·d^{-1} at stations 2 and 7, respectively; NC Department of Water Quality, 2006), and assuming 100% O_2 saturation for overlying water, the estimated oxygen penetration depth at these sites in Falls Lake sediments is $\leq$0.2 cm.[2]

---

[2] $L \cong \left(\varphi_0^3 D_o^{\mathrm{O}_2}[\mathrm{O}_2]_{\mathrm{ow}}\right)/SOD$, where $\varphi_0 = 0.9$, $D_o^{\mathrm{O}_2} = 2\times10^{-5}\ \mathrm{cm}^2\cdot\mathrm{s}^{-1}$ at 20°C, $[\mathrm{O}_2]_{\mathrm{ow}} = 285\ \mu\mathrm{M}$ (100% saturation at 20°C). Symbols are defined in Table 2.

This highlights a potential limitation to the approach used here to estimate $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ benthic fluxes: the depth-resolution of the porewater $\mathrm{NO_3^-}$ data is too coarse to accurately characterize coupled nitrification-denitrification at the oxic-anoxic interface. For example, an average $\mathrm{NO_3^-}$ concentration of 0.5 μM above background in the 0-3 cm interval could result from a sharp 7 μM peak in an oxic zone that is only 0.2 cm deep.

The sensitivity of $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ benthic fluxes from the porewater profile method to oxygen penetration depth was tested for profiles from station 1A. The value for L was reduced from 1.5 cm to 0.2 cm, while R_o, α, β_o, and λ were held at constant values. To simulate the maximum effect of coupled nitrification-denitrification on benthic fluxes, the nitrification rate constant (k_{Nit}) was increased (from 5 $\mathrm{y^{-1}}$ to 9.5×10^5 $\mathrm{y^{-1}}$) until the benthic $\mathrm{NH_4^+}$ flux was zero (i.e., $\mathrm{NH_4^+}$ produced by ammonification was quantitatively nitrified), and the denitrification rate constant (k_{Den}) was increased (from 100 $\mathrm{y^{-1}}$ to 3.5×10^5 $\mathrm{y^{-1}}$) until the average [$\mathrm{NO_3^-}$] in the 0-3 cm interval of the simulated profile matched the measured value (1.09 μM).

Coupled nitrification-denitrification in a 0.2 cm oxic layer (at maximum rates consistent with observed $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ concentration profiles) eliminates the diffusive $\mathrm{NH_4^+}$ flux, but has little effect on the $\mathrm{NH_4^+}$ profile below 0.2 cm. Since irrigation enables $\mathrm{NH_4^+}$ to bypass the nitrification filter, the $\mathrm{NH_4^+}$ irrigation flux is unaffected by high nitrification rates. In contrast, rapid nitrification generates a sharp $\mathrm{NO_3^-}$ peak near the sediment-water interface that enhances the diffusive $\mathrm{NO_3^-}$ flux by an amount equivalent to about half of the diffusive $\mathrm{NH_4^+}$ flux for L = 1.5 cm. Since the phytoplankton community may assimilate $\mathrm{NH_4^+}$ or $\mathrm{NO_3^-}$, high rates of coupled nitrification-denitrification in station 1A sediments would reduce the benthic flux of available nitrogen ~20%.

There are a number of arguments suggesting that the upper-limit rates used in this simulation overestimate coupled nitrification-denitrification in Falls Lake sediment. First, $\mathrm{NO_3^-}$ concentrations did not increase significantly in the overlying water in *in-situ* flux chambers deployed at stations 2 and 7 in April 2006 (NC Department of Water Quality, 2006). The initial $\mathrm{NO_3^-}$ concentration and analytical detection limit are not included in the report, but assuming that [$\mathrm{NO_3^-}$] in overlying water was similar to that measured in this study (0.33±0.16 μM), a benthic $\mathrm{NO_3^-}$ flux of 0.2 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$ (~30% of upper-limit simulated flux) would have increased [$\mathrm{NO_3^-}$] in the chamber water by a factor of four (easily detectable) during the 24 hour deployment. Second, $\mathrm{NO_3^-}$ concentrations in overlying water in Falls Lake are low, even at the deeper stations (> 6 m water column depth) where the lake bottom is below the euphotic zone, suggesting that sediments are not supplying $\mathrm{NO_3^-}$ to the overlying water. In contrast, $\mathrm{NH_4^+}$ concentrations are elevated in overlying water at stations deeper than 6 m, consistent with a sediment source. Third, nitrification is limited by low DO in the overlying water, which is likely for deeper sections of the Falls Lake (> 4 m deep) during the summer.

b. Constraining Adjustable Parameters for Underdetermined Systems

About half of the porewater $\mathrm{NH_4^+}$ profiles in Falls Lake have sections that are concave-up below the oxygen penetration depth, suggesting $\mathrm{NH_4^+}$ removal by non-local transport (i.e., irrigation). For these profiles, non-local transport introduces additional unknowns such that the number of adjustable parameters exceeds the number of "knowns". The protocol for constraining adjustable parameters for underdetermined systems was designed to be objective, yield a unique solution, and provide a lower-limit value for the total $\mathrm{NH_4^+}$ benthic flux. The error introduced by this protocol was assessed using synthetic porewater concentration profiles: $\mathrm{NH_4^+}$ (Type 2) and $\mathrm{NO_3^-}$ profiles (concentrations from 1.5 to 19.5 cm at 3 cm intervals) were generated using equation [2] with arbitrary input values for R_0, α, k_{Nit}, k_{Den}, β_0, and λ (. The six adjustable parameters were then constrained using the protocol for Type 2 $\mathrm{NH_4^+}$ profiles, and the benthic fluxes predicted by the porewater concentration profile method compared to "true" (input) values. The porewater concentration profile method accurately predicted the diffusion fluxes of $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$, but underestimated the irrigation fluxes (Fig. 24). In summary, this sensitivity analysis suggests that the porewater concentration profile method when applied to irrigated sediments underestimates the total benthic $\mathrm{NH_4^+}$ flux by ~35%.

c. Method Validation

The porewater concentration profile method may be validated by comparing it to the benthic flux chamber method. (These two approaches are subject to independent sources of error.) In April 2006, the Intensive Survey Unit at the North Carolina Department of Water Quality deployed *in-situ* benthic flux chambers at two sites in Falls Lake: NEU013B (near station 2) and NEU018E (near station 7). For station 2, the benthic $\mathrm{NH_4^+}$ flux from the porewater concentration profile method (5.0 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$) exceeds that measured by the *in-situ* chamber method (3.6±0.5 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$; NC Department of Water Quality, 2006) by nearly 40%; for station 7, the profile method (6.5 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$; Table 3) exceeds the chamber method (0.7±0.2 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$, NC Department of Water Quality, 2006) by nearly a factor of 10.

However, the conditions for comparing the two methods were not ideal. First, the flux of reactive particulate nitrogen to Falls Lake sediment (hence, ammonification rate and benthic $\mathrm{NH_4^+}$ flux) may have changed during the nine years that elapsed between the two sets of measurements. Second, benthic $\mathrm{NH_4^+}$ fluxes were measured at different sediment temperatures: ~23 °C (profile method) vs. ~20 °C (chamber method). Third, at station 7, the benthic flux chambers were deployed at a water depth of 5.0 m (NC Department of Water Quality, 2006), whereas the sediment cores were collected at 8.5 m.

Some of the differences between these two studies may be compensated. The temperature-dependent model (equation [5]) suggests that the diffusive NH_4^+ flux increases by 15% between 20-23 °C. Decreasing NH_4^+ fluxes from the porewater profile method by this factor reduces the difference at station 2 to <20% and at station 7 to a factor of seven. Unfortunately, cores from "shelf" sediments were not collected at station 7. At the closest main-stem transect site (station 6), the depth difference between the channel and the "shelf" is 3.4 m, and the benthic NH_4^+ flux from the channel (station 6A) exceeds that from "shelf" (station 6C) by a factor of 1.6. Decreasing the NH_4^+ flux from the profile method at station 7 by this factor reduces the difference between the two methods to a factor of five. It's important to note that this attempt to correct the two studies to common conditions is approximate. For example, the ratio of NH_4^+ flux from main-stem channel:"shelf" sediments ranges from 1.3 (station 12) to 6.2 (station 9).[3]

---

[3] A side-by-side comparison of benthic nutrient fluxes from Falls Lake measured by *in-situ* and *ex-situ* benthic flux chambers and the porewater concentration profile method was conducted in June 2018.