

Report for 2001NC1461B: Role of Sediment Processes in Regulating Water Quality in the Cape Fear River

There are no reported publications resulting from this project.

Report Follows:

Problem and Research Objectives:

We selected the Cape Fear River system, the largest river system in North Carolina, since during the recent decades it has experienced a proliferation of agriculturally related industries including large-scale agricultural operations, agrochemical manufacturing, and intensive livestock operations. This has resulted in dramatic increases in anthropogenic imports of nitrogen and phosphorus into the river basin. Between 1985 and 1995 hog production in North Carolina increased by 248% and turkey production increased by 92%. North Carolina is now the second largest producer of hogs in the nation. The majority of these intensive livestock operations are located within the Cape Fear and Neuse River watersheds. Given the magnitude of increased phosphorus and nitrogen import into the watershed, even relatively effective water quality management practices will still allow considerable nitrogen and phosphorus loading to the river, thus increasing the potential for eutrophication. While the Neuse River basin has been the focus of numerous water quality related investigations, the Cape Fear River basin has been accorded relatively little attention. However, there is a clear trend in water quality degradation on the Cape Fear River.

Although, surface waters in North Carolina rivers have been the focus of intense monitoring and research, the role of the sediment chemical environment (SCE) in regulating surface water quality has been essentially ignored. The reciprocal interaction between surface water quality and the processes occurring within the SCE underscores the need to better understand this (SCE) important but least understood class of conditions that dictate the nutrient status and quality of adjoining water bodies.

Our primary objectives for this study were:

- 1) *To identify the chemical forms in which nutrients are input into the Cape Fear River basin, and*
- 2) *To address the previously overlooked role of sediments in buffering water quality in order to facilitate its incorporation in future water quality management programs.*

These objectives were achieved with a focus on Phosphorus (P) fractions.

Methodology:

Site Selection: Water quality data were collected from three Lock and Dam locations within the middle Cape Fear River basin. Lock and Dam #1 (which is located furthest downstream) was completed 1915, Lock and Dam #2 was complete in 1917, and Lock and Dam #3 (the furthest upstream) was completed in 1935. Additionally, sediment samples were also collected from the Barra Farms site for NMR analyses. The Barra Farms Cape Fear River Mitigation Bank is located at the headwaters of Harrison Creek, a tributary of the Cape Fear River that drains just downstream of Lock and Dam # 3 and upstream of Lock and Dam # 2. The Barra Farms site was originally part of a Carolina Bay wetland, large areas of which were ditched and converted to agricultural production. In 1997 about 600 acres of this converted agricultural land was restored to wetland, while adjacent agricultural areas remained in production.

Surface water monitoring: The surface water quality at the selected sites were monitored monthly. Surface water at these sites were monitored for nutrient parameters such as ammonium, nitrate+nitrite, total Kjeldahl nitrogen, soluble reactive phosphorus, total phosphorus, dissolved organic carbon, and major cations and anions. Three replicate samples were collected at each site during each sampling event to ensure sufficient statistical replication.

Sediment Characterization: Bulk densities of riverbank sediments were determined after drying intact sediment cores to a constant weight. The organic matter content of the sediments was calculated as weight loss upon ignition at 550 °C overnight. Total Carbon and nitrogen were measured on a CHN analyzer, while total P and elemental composition of the sediments was determined using an Atomic Absorption Spectrometer after acid digestion of the sediment samples.

Nutrient buffering capacity of sediments: Surface sediments (0 – 10 cm depth) from the selected sites were used to estimate their nutrient buffering capacity. Sediment samples were incubated with solutions of increasing phosphorus concentration. The sorption coefficients were estimated by fitting the data to sorption models such as Freundlich adsorption model. The zero equilibrium phosphate-P concentration (ZEPC) (a concentration at which no net adsorption or desorption occurs) was also estimated from the above data set. Phosphorus binding capacities of sub-surface sediments (10-20 cm depth) from our sites were also estimated

³¹P NMR Studies: To identify various phosphorus species in the riverbank (from the three lock and dam structures) and Barra Farms sediments (from agricultural lands, restored wetlands and a natural wetland), triplicate surface sediment cores (0-10 cm depth) from each site were pooled and extracted overnight at room temperature (using a soil:solution ratio of approximately 10 g dry sediment : 100 ml 0.5 M NaOH + 0.1 M EDTA). Extraction efficiencies were calculated as the difference in total phosphorus concentrations between un-extracted sediment samples and the total phosphorus in the NaOH+EDTA extract. Extracts were centrifuged at 3200 rpm after adjusting the pH to 12.5, and 3ml of the supernatant was used for NMR analyses after adding 0.3 ml of D₂O. All spectra were collected over 24 hrs with a 100 ppm window centered at 0 ppm on a Varian 500 spectrometer. Chemical shifts (relative to 85 % phosphoric acid) were assigned based on external standards and literature. ³¹P NMR analysis was also run on surface water from lock and Dam # 3 that was concentrated approximately 140 fold using a rotary evaporator.

Pyrophosphate analysis in water samples: We used a new technique to specifically measure pyrophosphate (Ppi) in water samples. This technique relies on a cascade of enzymatic reactions, of which the first enzyme is Ppi dependent. Thus the reaction will only occur in the presence of Ppi (e.g. in water sample from our sites).

Principle Findings and Significance:

Our results indicate that there are differences in water quality parameters among the three Lock and Dam (LD) structures. In comparison to the upstream site, LD 3, downstream sites LD 2 and LD1 generally had higher concentration of nutrient parameters such as dissolved reactive phosphorus (DRP) and total phosphorus (TP) in surface waters. However, the relative contributions of organic and particulate fractions of phosphorus were generally higher at LD 3 site than those measured at downstream sites LD 2 and LD 1. While trends in DRP concentrations may partly be due to the difference in number of permitted discharge locations just upstream of these sites, accumulation of phosphorus in the riverbank sediments is most certainly controlled by sediment loading from the sub-watersheds and in situ sediment processes. Results from our previous study indicate that the sedimentation rates vary from 0.5 cm/yr at Lock and Dam 3 to 1.5 cm/yr and 1.3 cm/yr at Lock and Dam 2 and 1, respectively. The sedimentation rates correspond well to the total sediment phosphorus concentrations, which indicate that sediment deposition during the recent decades (\approx 40 years) has caused an increase in nutrient loading to the CFR. The present study reveals that the total phosphorus in sediments at these sites, in general, was positively correlated with the sum of total Fe, Al, Ca and Mg. This positive relationship was observed for surface and sub-surface sediments at all sites except in surface sediments at LD 2. At this site, while sub-surface sediments exhibited a positive relationship, the surface sediments site did not. This suggests that recent input of phosphorus and mineral elements from external sources may have altered this relationship. Among the three lock and dam sites, the floodplain sediments at LD 2 had the greatest phosphorus binding capacity, while the most downstream site LD 1 had the lowest. This trend in P-sorption capacity of the riverbank sediments persisted for the sub-surface sediments, although the P-binding capacity of the sub-surface sediments was lower than the binding capacity of corresponding surface sediments. Importantly, the intra-site variability in P-sorption capacity and mineral element composition increases downstream, most likely due to differential sorting of the riverine sediment load. Despite the higher sorption capacity of LD 2 sediments, the surface water concentrations of dissolved phosphorus were

highest at this site. ^{31}P Nuclear Magnetic Resonance (NMR) analyses of concentrated river water and floodplain sediments reveal that phosphorus loading in this river occurs in diverse chemical forms. NMR analyses of riverbank sediments reveal the presence of P-forms such as Glyphosate (a commonly used weedkiller), Aminomethylphosphonic Acid (a degradation product of Glyphosate) and pyrophosphate (the smallest chemical form of polyphosphate with wide industrial applications), in addition to more commonly observed P-forms. The concentration of pyrophosphate in surface waters was below detection, however, ^{31}P NMR analysis of surface water that was concentrated 140 fold showed a peak that corresponded to pyrophosphate. Although the surface water concentration of these forms of phosphorus may be very low, overtime, the phosphorus binding properties of the deposited sediments may concentrate these forms of phosphorus in the floodplain of the CFR. Our NMR analyses of sediment samples from the areas under varying landuse within the Barra Farms site, demonstrates that converting natural wetlands to agricultural land results in the loss of natural ‘diversity’ in the chemical forms of phosphorus – analogous to the loss of ‘biodiversity’ in impacted ecosystems. Results from the restored site indicate that restoration of impacted sites may result in re-establishment of the lost diversity in chemical speciation of nutrients. This also provides a valuable tool to track the progress of a restored site relative to a corresponding undisturbed and natural wetland. Together, these finding suggest that sediments play a key role in regulating the water quality of the Cape Fear River. The diversity in the chemical forms of phosphorus in the riverbank sediments helps identify the types and sources of nutrient loading in the CFR. It is conceivable that, after few years of sustained nutrient loading (e.g. phosphorus), floodplain sediments of the Cape Fear River system will eventually become saturated with nutrients and thus will be unable to ameliorate nutrient driven surface water quality degradation. Importantly, increasing variability downstream in the mineral element composition and the P-binding capacity of riverbank sediments suggests that moving seaward, sediment sorting will lead to creation of ‘hot spots’ for efficient P-sorption and release along the riverbank of the CFR, and this could pose a considerable challenge with regard to water quality management. This implies that sources for sediment load to the CFR need to be identified and effective BMPs implemented to restrict the sediment loading in the upper reaches of the watershed. These findings have important implications for water quality management in this largest river system in North Carolina.