PHYSICAL EFFECTS OF LEAF LITTER ON NITROGEN DYNAMICS IN FRESHWATER TIDAL WETLANDS

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Abstract. The role of tidal freshwater marshes as nitrogen sinks for river systems is of particular importance due to recent increases in anthropogenic nitrogen input and subsequent eutrophication of aquatic bodies. Leaf litter, which accumulates on the marsh sediment surface, plays a significant role in nitrogen removal both through immobilization/release during decomposition and through long-term burial. This study examines the possibility that leaf litter also influences nitrogen cycling by acting as a physical barrier to diffusion between surface water and porewater- blocking downward diffusion of nitrate and oxygen and upward diffusion of ammonium. In both mesocosm and field experiments comparing sediment covered with *Phragmites australis* (Common reed) litter, plastic pseudolitter, and no leaf litter, no effect on the diffusion of ions was observed. However, the presence of litter may reduce the diffusion of oxygen into the sediments, reducing nitrification and subsequent denitrification.

INTRODUCTION

Freshwater tidal marshes serve an important ecosystem function as nitrogen sinks. This function is especially significant due to increased run-off of nitrogen from fertilizer and sewage inputs to waterways. This input causes algal blooms and eutrophication in many aquatic systems downstream (Ryther and Dunstan, 1971; Turner and Rabalais, 1994). In the Hudson River specifically, nutrient loading is greatest around the large cities of Albany and New York City. Between the two cities, nitrogen concentration in river water decreases (Lampman et al. 1999). The nitrogen decrease, at least in part, can be attributed to uptake by the many freshwater tidal marshes located along this section of the Hudson. For example, nitrate concentrations are lower in outflowing ebb-tide water from Tivoli North Bay marsh than in incoming tidal water, indicating that the marsh is acting as a net nitrogen sink (Kiviat et al., unpublished).

Uptake of nitrogen by marshes can occur through several different mechanisms. Plant uptake of nitrogen contributes to removal from surface waters, but this effect is seasonal- net uptake of nitrogen occurs in spring and early summer months, while senescence and decomposition in the fall and winter months result in a release of nitrogen. Long-term removal of nitrogen occurs through two mechanisms- burial of plant litter and denitrification of ammonium to nitrogen gas (Howard-Williams, 1985). Plant litter plays an important role in the nitrogen dynamics, actually increasing in nitrogen content during decomposition. Jordan et al. (1989), for example, found that the amount of nitrogen in *Typha angustifolia* litter increased by 230% over a period of 860 days. There is disagreement as to whether the mechanism for this effect is a result of abiotic adsorption or microbial accumulation (Findlay et al. 1990; Bowden 1986). Whichever is the case, burial of plant material accounts for an estimated 5 g N/m^2/yr of nitrogen removal while 2 g N/m^2/yr is removed through denitrification (Merrill 1998).

While its role in burial of nitrogen is well established, Leaf litter may also influence N cycling in tidal marshes by acting as a physical barrier limiting diffusion between tidal surface water and marsh porewater (Odum 1988). Several gradients exist between surface and porewater. Ammonium concentration is higher in porewater, while nitrate is higher in surface water. The presence of a litter layer may limit the diffusion of these ions in and out of the sediments (Nichols 1983). An oxygen gradient also occurs between the well-aerated surface water and the highly anaerobic porewater. Therefore, the litter layer may also reduce the diffusion of oxygen into marsh sediments.

By limiting oxygen diffusion, leaf litter has the potential to alter rates of denitrification in the marsh. Denitrification is a long-term nitrogen removal, however, it may play a relatively small role in overall nitrogen removal in freshwater tidal wetlands (Bowden et al., 1991). Since marsh soils are highly anaerobic, denitrification rates are limited by availability of nitrate, rather than availability of anaerobic habitat. Nitrate in turn is limited by either the rate of nitrification occurring within the sediment or the downward diffusion of nitrate from the surface water. Since nitrification is an aerobic process, increased oxygen availability can increase nitrate concentrations and therefore denitrification rates. Patrick and Reddy (1976) observed increased denitrification rates in flooded soils exposed to higher concentration of oxygen in the overlying air. Leaf litter may reduce oxygen exposure, thus limiting nitrification and subsequent denitrification rates.

Although leaf litter's role as a barrier to diffusion has not been directly studied, there is some evidence that it occurs. Jordan et al. (1989) found that sediments took up added phosphorus at a significantly greater rate in treatments with no litter than treatments with litter or pseudolitter. In *Phragmites australis* and *Spartina patens,* observed diffusion rates of ammonium are lower than those predicted from the concentration gradient (Windham 1999). Physical separation by leaf litter may account for this discrepancy. Since diffusion accounts for most nutrient transfer between interstitial and surface waters in an intertidal marsh (Gardener 1975), barriers to diffusion may have an important effect on nitrogen transfer between fresh-tidal marshes and the rivers they border.

There is also some evidence that leaf litter might not affect nitrogen cycling by limiting diffusion in tidal marshes. Jordan et al. (1989) compared plots with litter, pseudolitter, and no litter in a *Typha angustifolia* dominated, freshwater tidal marsh. They were not specifically looking at diffusional effects, but found that sediments not covered by litter or pseudolitter actually accumulated higher levels of ammonium. This is the opposite of what would be predicted if leaf litter limited diffusion of ammonium out of the sediments. However, the effect observed by Jordan et al. is attributable to differences in temperature caused by the shading of sediments.

Leaf litter changes may also be important in the impacts of invasive species since the characteristics of leaf litter vary by species. Of particular current interest is *Phragmites australis*, which is native to North American wetlands, but has recently become invasive in many locations, forming rapidly expanding monotypic stands (Windham, 1999). *Phragmites* produces a thick litter layer that decomposes slowly compared to the narrow leafed cattail (*Typha angustifolia*) stands that they often replace (Findlay et al., 2002a). As a result, *Phragmites* leaf litter may form more of a barrier to diffusion than other marsh species.

The role of leaf litter in freshwater tidal marshes is important for management decisions. The potential costs and benefits of removing invasive species such as *Phragmites* are controversial (Ludwig et al., 2003). Removal of *Phragmites* by herbicide and cutting reduces nitrogen sequestration. It also results in the loss of leaf litter cover in the marsh in the winter months (Findlay et al., 2002b). Understanding the role of leaf litter in diffusion can help inform such management decisions, as well as providing a better understanding of marsh processes.

This study combines field and mesocosm experiments to examine the possibility that leaf litter may affect diffusional processes in freshwater tidal marshes. Comparing the effects of plastic pseudolitter, *Phragmites* plant litter, and absence of litter allows separation of the physical and biological effects of leaf litter on nitrogen processing.

METHODS

Study Site

Tivoli North Bay marsh is a tidal freshwater marsh located along the Hudson River, near Red Hook, NY. It is fed by Stony Creek and separated from the Hudson by a railway line with two bridge openings allowing flow between

the marsh and the river. The dominant plant species is *Typha angustifolia*, however several stands of invasive *Phragmites australis* have become established in the marsh in recent years. This site was the source of sediment cores for the mesocosm experiment and the location of the field experiment.

Mesocosm Experiment

Fifteen sediment cores from Tivoli North Bay marsh were collected in 4-inch diameter PVC pipe on 27 June 2003. The 20 cm deep cores were taken from a patch of the marsh dominated by *Phragmites australis*. Immediately following collection, the bottom ends of the cores were capped and upon return to the laboratory, the cores were placed in a tank of Hudson River water. Throughout the experiment, all cores were subjected to a simulated tidal cycle by pumping water in and out of the tank. Water height varied from the sediment surface level to 6 cm above the sediment surface. Holes drilled in the PVC pipe just above the sediment surface allowed the tidal water to cover and uncover the sediment cores. There were two tidal cycles per day consisting of 3.5 hours of high tide and 9 hours of low tide. This pattern approximates the tidal cycle observed at the Tivoli North site.

Following the first high tide, the litter treatments were instituted. Each core was covered with *Phragmites* litter, covered with plastic 'pseudolitter', or left bare. For the litter treatment, the leaf litter accumulated on the sediment in the marsh was left undisturbed. In the no litter and pseudolitter treatments, the leaf litter on the cores was removed. Woven plastic shade cloth of equal surface area to the litter removed (ranging from 57-124 cm^2) was added to the pseudolitter treatments and held in place with small stones.

Reservoir water was replaced every four days with water pumped from the Hudson River at Rhinebeck, NY (just downstream of Tivoli Bay). Beginning 28 June 2003, 2.5 mg/l KNO_3 and 0.5 g/l NaCl were added to the reservoir water. These are high but realistic concentrations for tributaries to the Hudson River (Findlay, *unpublished data*). Stony Creek has annual mean NO_3 between 3 and 4 mg NO_3/L (W.C. Nieder, HRNERR, unpublished data). The chloride was added as a tracer to measure the rate of diffusion between surface water and sediment in each of the treatments.

Throughout the experiment, samples of surface water and porewater were collected from each core. Rubber stoppers in tidal ports allowed surface water to be isolated above each sediment core for the duration of high tide. At the end of a high tide, a syringe was used to collect 20 ml of surface water from each core. A syringe and needle were also used to sample sediment porewater at depths of 3 and 13 cm. In order to ensure that porewater was not drawn in from other depths, only 5 mL total was collected at each depth from at least three locations in the core. Surface water samples were collected on the initial cores, following implementation of litter treatments, and twice weekly during the experiment. Samples of the reservoir water were also collected whenever surface water samples were taken. Porewater samples were collected from the initial cores and once weekly during the experiment.

The mesocosms were maintained for 24 days, until 21 July (Day 23). Denitrification Enzyme Analysis (DEA) was carried out on deep (9-13cm) and shallow (0-3 cm) sections of the sediment from each core.

Field Experiment

For the field litter manipulation experiment, litter was removed on 11 July 2003 from 5 circular plots 1 m in diameter in a *Phragmites* stand in Tivoli North Bay marsh. Alternating with the litter removal plots were five plots where the litter was undisturbed. The temperature of the sediment in each plot was measured on a sunny day (August 12th) to determine whether litter removal was affecting temperature. 'Peepers', were inserted into the center of each plot on July 22. These peepers consist of either a 2x7 or 2x8 grid of 10 mL wells at roughly 3 cm depth intervals in a piece of PVC that initially contained deionized and were separated from the sediment by a membrane. The peepers allowed the concentration of nutrients in pore water to be sampled at several sediment

depths. The peepers were left for 7 days to equilibrate. On July 29, the peepers were collected along with two 9 cm deep cores from each plot. The cores were analyzed for DEA immediately upon return to the lab. The peeper samples were also collected and acidified, then refrigerated until analysis for nitrate and ammonium using the Alpkem.

Analysis

All surface and porewater samples were refrigerated until analysis. Beginning Day 10, all samples were filtered and acidified immediately following collection. The conductivity of all samples was measure using a YSI Model 32 Conductance Meter. Nitrate and ammonium concentrations were measured using standard automated wet chemistry (Alpkem 1991).

To assess the denitrification potential of sediments DEA analysis was carried out according to the procedure described in Smith and Tiedje (1979). Soil samples were homogenized and KNO_3, glucose, chloramphenicol acetylene were added, and then samples were incubated in an anaerobic atmosphere for 90 minutes. Gas samples were collected after 30 and 90 minutes and analyzed for N_2O using a gas chromatograph.

Chloride, nitrogen, and ammonium concentrations and denitrification potential, were compared using ANOVA.

RESULTS

Mesocosm experiment

A chloride gradient existed with surface water conductivity significantly higher than porewater conductivity ($p<0.001$). Over the course of the experiment, chloride concentrations in the shallow porewater increased from 173 ± 18 mg/L (mean$\pm$standard deviation) on day 0 to 981 ± 27 mg/L on day 23. Likewise, the deep porewater samples had a concentration of 201 ± 53 mg/L on day 0 and 800 ± 93 mg/L on day 23. However, there was no significant difference in chloride concentration among litter treatments at any depth.

The nitrate concentration in the surface water of the litter treatment was significantly lower than in the no litter or pseudolitter treatments ($p<0.001$, figure 1). There was no treatment effect on nitrate at either depth of porewater however (figure 2). The reservoir nitrate concentration was significantly higher than surface water concentrations ($p=0.002$). Surface water nitrate concentrations were significantly higher than porewater concentrations ($p<0.001$).

Ammonium concentrations were significantly lower in surface water than in porewater ($p<0.001$). Reservoir ammonium concentration was significantly lower than surface water ammonium concentrations ($p<0.05$). There was no difference in surface water ammonium concentrations between treatments (figure 3). At 3 cm depth the no litter treatment had significantly lower ammonium concentrations than either litter or pseudolitter treatments ($p<0.05$, figure 4). There was no effect at 13 cm depth.

Denitrification potential was highly variable between cores. The DEA was significantly higher in shallow than in deep sediments ($p<0.001$). In both shallow and deep sediments, the average DEA of the no litter treatment was greater than the other two treatments, but not significantly so ($p=0.69$ at 3 cm, $p=0.29$ at 9cm, figure 5).

Field experiment

The removal of litter had no effect on sediment temperature ($p=1$). There was no significant treatment effect on nitrate or ammonium concentration at any depth. Neither nitrate nor ammonium concentrations varied significantly with depth. The removal of litter also did not significantly affect denitrification potential.

DISCUSSION

Throughout the experiment, chloride concentrations in the porewater increased across all treatments, indicating that downward diffusion was occurring along the chloride gradient. Surface water samples, which had been isolated over the sediment core for several hours, showed significantly lower chloride concentrations than the reservoir water, also indicating that diffusion of chloride into the sediments was occurring. However, the presence or absence of leaf litter did not affect the rate of diffusion of chloride, indicating that leaf litter does not appear to act as a barrier to ion diffusion.

The results of nitrate analysis were also consistent with the conclusion that leaf litter does not affect ion diffusion. As with chloride, lower surface water than reservoir concentrations of nitrate indicate that nitrate was diffusing into the sediment. Nitrate concentrations were lower in the surface water of litter cores than in no litter or pseudolitter cores, but there were no differences in nitrate concentration in the shallow porewater. This indicates that the leaf litter absorbed the nitrate from the surface water, which is consistent with previous observations of nitrogen uptake by leaf litter during decomposition (Findlay et al. 1990).

The significantly lower ammonium concentrations in the shallow sediment porewater of treatments with no litter could be caused either by increased diffusion of ammonium into the surface water or by the increased nitrification of ammonium to nitrate. The lack of differences among treatments in ammonium concentrations in surface water and absence of a treatment effect on the diffusion of chloride and nitrate indicate that diffusion of nitrate into the surface water did not cause the lower ammonium concentrations in the no litter treatment. Alternatively, oxygen diffusion into the uncovered sediments could have resulted in accelerated rates of nitrification. In such anaerobic sediments, accelerated nitrification would also be expected to cause accelerated denitrification. The denitrification potential of the sediments did not differ significantly with treatment, due to a high degree of variability in the measurements. However, the difference in denitrification potential, though not significant, is sufficient, over the period of the experiment to account for the significant differences in ammonium concentrations. (The difference between the mean nitrification potentials of no litter and pseudolitter treatments, for example, was 1250 ng-N/g dry soil/hour or 5.98 mg-N/L/day. On day 23, the difference in mean ammonium concentrations between these treatments was 0.55 mg-NH_4-N/L.) This indicates that the presence of leaf litter can influence the diffusion of oxygen and therefore, the cycling of nitrogen in freshwater tidal marshes.

The lack of significant results in the field experiment may be a result of increased variability in field conditions. Another possibility is that nitrogen uptake by plants in summertime may overwhelm the effects of leaf litter. Repeating the experiment in winter or fall might reveal an effect of leaf litter on sediment ammonium concentrations as was observed in the mesocosm experiment. Unlike Jordan et al. (1989), this study found that the removal of leaf litter did not affect sediment temperatures. This is likely due to a higher degree of shading by standing *Phragmites* than the cattail studied by Jordan et al. These results indicate that the mechanisms by which leaf litter affects nitrogen cycling depends on the plant species being studied and perhaps seasonal effects.

Overall, the results of this experiment indicate that leaf litter does not act as a physical barrier to diffusion in freshwater tidal marshes, contrary to the suggestions of Nichols (1983) and Odum (1988). However, there is some indication that the leaf litter does alter diffusion of oxygen into marsh sediments. Whether this effect has any significant effect on nitrogen cycling in marshes is unclear. Study of the effect of leaf litter in marshes during the fall and winter as well as direct measurements of oxygen in sediments are needed.

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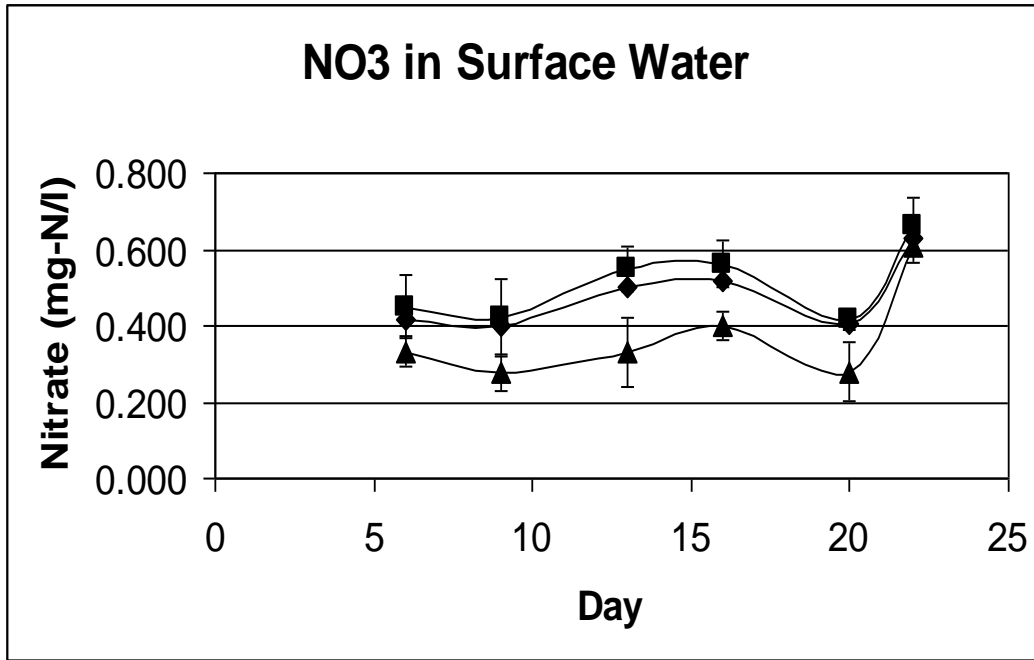
APPENDIX

FIGURE 1. Concentrations of nitrate in surface water samples across the course of the experiment. Error bars are ± 1 standard deviation. (Diamonds- No litter, Squares- Pseudolitter, Triangles-Litter)
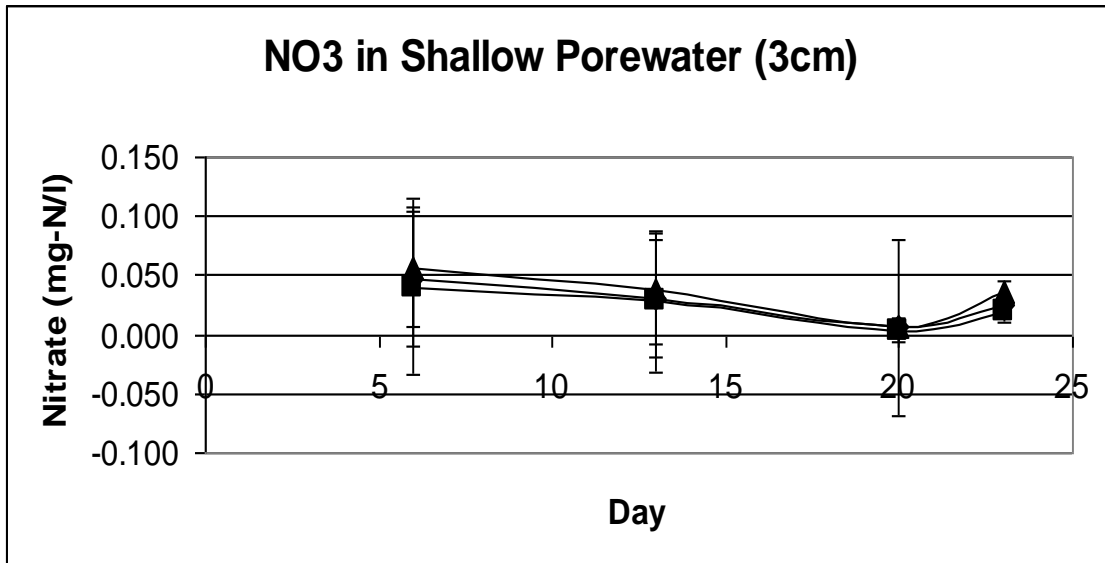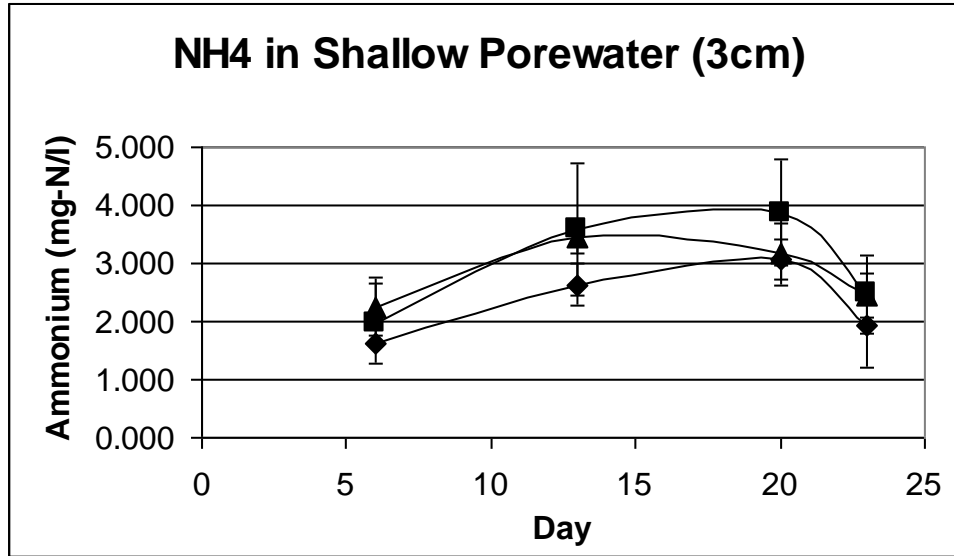

FIGURE 2. Concentrations of nitrate in shallow porewater samples across the course of the experiment. Error bars are ± 1 standard deviation. (Diamonds- No litter, Squares- Pseudolitter, Triangles-Litter)
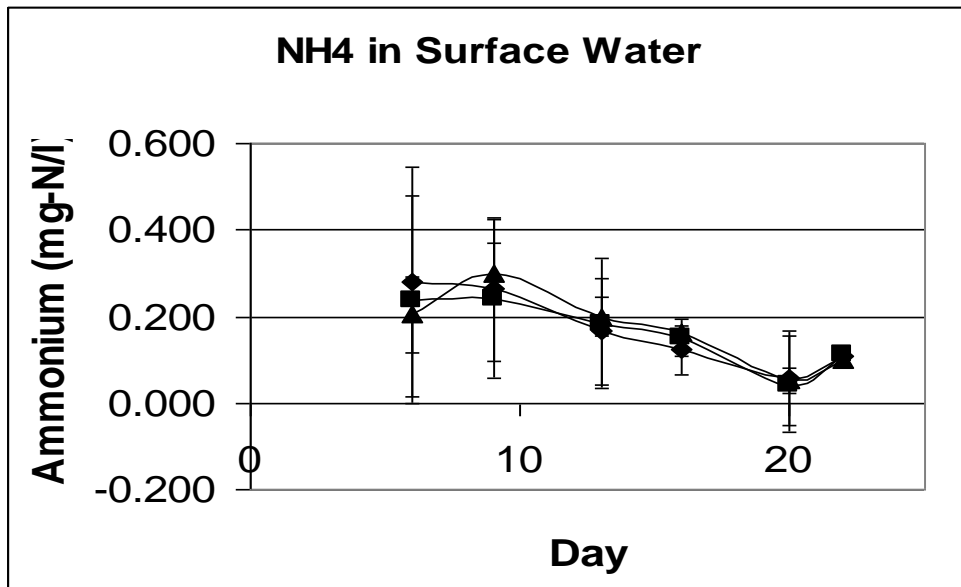
FIGURE 3. Concentrations of ammonium in surface water samples across the course of the experiment. Error bars are ± 1 standard deviation. (Diamonds- No litter, Squares- Pseudolitter, Triangles-Litter)

FIGURE 4. Concentrations of ammonium in surface water sample across the course of the experiment. Error bars are ± 1 standard deviation. (Diamonds- No litter, Squares- Pseudolitter, Triangles-Litter)
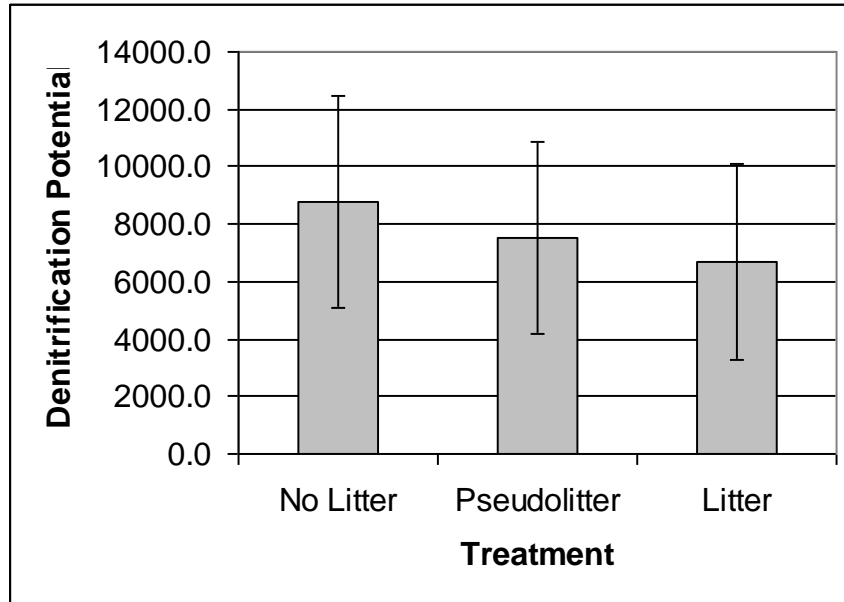
FIGURE 5. Denitrification potential of the top three cm of sediment on day 23. Error bars are ± 1 standard deviation.