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Biological Remediation of Nitrate (NO_3^-) Pollution at the Land/Water Interface

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Abstract

The Environmental Protection Agency has identified nonpoint source pollution (NPS) as the as the nation's largest water quality problem. NPS pollutants include chemical fertilizers and pesticides, animal effluent leakage and application to agricultural fields and urban runoff. Nitrogen-rich runoff leaches into rivers and lakes, primarily in the form of nitrate (NO_3^-), causing algal and dinoflagellate blooms, fish kills, eutrophication, hypoxia and groundwater contamination. All of these effects threaten human and ecosystem health. The EPA has recommended wetland preservation and restoration, and creation of wetlands and riparian buffer zones as tools for managing nitrate and other agricultural pollutants. Natural and constructed wetlands and riparian buffers are an important interface between pollutant sources and waterways that improve water quality by slowing and filtering runoff, wherein NO_3^- and other pollutants are captured and transformed or removed before entering the waterway. Methods for *in situ* remediation of NO_3^- contamination include: establishment of nitrogen catch-crops capable of rapidly accumulating or transforming the target pollutant; riparian forest buffers; and by enhancing nitrate transformation by microbes. Here, methods for *in situ* NO_3^- remediation at the land/water interface from agricultural runoff are examined. Temporal, hydrologic and ecological considerations are discussed.

Introduction

Environmental contamination results from either point source (PS) or nonpoint source (NPS) pollution. Point source (PS) pollutants are concentrated sources for contaminants such as: municipal and industrial wastewater and runoff, runoff from landfills, runoff from concentrated animal feeding operations, and runoff or spillage from waste-treatment sites (Carpenter *et al.* 1998). PS pollutants, although more easily monitored and regulated than NPS pollutants, may seriously impact water quality. NPS pollution includes: agricultural runoff, pasture and range runoff, urban runoff from sewers or drains, septic leakage, runoff from construction sites or abandoned mines, atmospheric deposition and any land-based activities that generate contaminants (Carpenter *et al.* 1998). The Environmental Protection Agency (EPA) has identified nonpoint source pollution as the nations largest water quality problem. Among NPS pollutants, agricultural runoff has been named as the leading impact on river and lake water quality, groundwater contamination, and wetland degradation (EPA 1997).

Agricultural pollutants impact waterways, lakes and wetland ecosystems by overloading them with nutrients, particularly NO_3^- and phosphorus. Excessive nutrient inputs result in eutrophication where algal overgrowth and dinoflagellate blooms deplete oxygen and/or release toxic substances, ultimately killing or choking out other wildlife (EPA 1997). High concentrations of NO_3^- in drinking water may also impact human health and kill infants (EPA 1997, Carpenter *et al.* 1998). Downstream, severe oxygen depletion (<2 mg/l) results in large-scale hypoxic, or "dead zones" that now occur in the Gulf of Mexico and mid-Atlantic as a direct result of agricultural runoff delivered by the Mississippi and Chesapeake rivers, respectively (Burkart and James 1999).

Nitrogen cycling in the form of NO_3^- is part of normal, global biogeochemical processes, wherein atmospheric nitrogen (N_2) is fixed by soil microbes or plant root *Rhizobia* and taken up by plants in the form of NO_3^-, nitrite (NO_2^-), or ammonium (NH_4^+). Nitrogen in plant material is then consumed and/or decomposed, then recycled, leached or returned to the atmosphere as N_2. However, nitrate pollution results from the effects of human activities on normal biotic fixation, transformation and cycling of nitrogen, such as atmospheric deposition of N from fossil fuel combustion, industry and agricultural activities that results in increased nitrification and transformation by soil microbes (Burkart and James 1999). For this reason, NO_3^- in agricultural runoff of manure and chemical fertilizers, leakage from storage facilities, and storm spills are a serious impact to rivers, wetlands and groundwater quality (EPA 1997, Carpenter *et al.* 1998, Burkart and James 1999). Burkart and James (1999) identified the upper Midwest as a major source of nitrogen causing hypoxia in the Gulf of Mexico due to large-scale corn and soybean agriculture, where manure and fertilizer application accounted for about 40% of the NO_3^- sources in the Mississippi river basin.

Because of the cumulative environmental impacts of NO_3^- pollution on water quality, it needs to be eliminated or reduced near its source where it can be captured on land or from groundwater. Hill (1996) identified subsurface flows as the major NO_3^- pathway in agricultural landscapes. Wetland and riparian areas naturally capture and transform NO_3^- by slowing ground and surface-water flow where it may by accessed by the biota before entering the waterway. Within a riparian ecosystem nitrate may be captured by several mechanisms: bacterial denitrification ; uptake by plant roots; and by immobilization in soil microbes (Pinay *et al.* 1993, Haycock and Pinay 1993). It is at the land/water boundary that these energy and nutrient transformations occur in addition to hydrologic mixing of ground and stream water (Haycock and Pinay 1993). Denitrification has been identified as the most important means of NO_3^- transformation in these systems (Pinay *et al.* 1993).

Where large quantities of NO_3^- threaten the health of rivers, streams and groundwater structural, biological and chemical NO_3^- remediation methods may be employed at the land/water interface that may maintain the long-term integrity of both the waterway and the wetland ecosystem. The structure and functioning of riparian forests were first evaluated as NPS pollution buffers in the early to mid-1980s by Lowrance *et al.* (1984, 1985). This early work points out the characteristics of riparian areas make them particularly well-suited for NO_3^- remediation: 1) riparian soils generally possess strong water-holding capacity (WHC) due to high clay and organic matter content (Lowrance *et al.* 1984, 1985); 2) seasonal fluctuations in the water table causes groundwater to come into prolonged contact with plant roots and soil microbes (Lowrance *et al.* 1984, 1985, Nelson *et al.* 1995); and 3) high rates of aboveground productivity provide carbon for microbial denitrification (Lowrance *et al.* 1984, 1985, Pinay *et al.* 1993, Nelson *et al.* 1995). In addition, the linear shape of riparian areas gives them a high degree of contact with surrounding ecosystems, a quality that further underlines their importance to landscape-scale ecosystem health (Lowrance *et al.* 1985). Methods and considerations for the design and management of riparian buffers for remediation of NPS NO_3^- pollution are examined here.

Considerations for Riparian Buffers

Soil Type & Hydrology

Riparian zone hydrology must be considered in context of climate and geology (Hill 1996). Soil type should therefore be considered as both climate and geology effect soil drainage, water-holding capacity, biological activity and thereby, rates of biogeochemical cycling (Haycock and Pinay 1993). Past research has shown that riparian zones are most effective in assimilating or removing NO_3^- from shallow groundwater (Hubbard and Lowrance 1997), so riparian/wetland buffer methods are most effective in poorly drained soils where shallow groundwater can be accessed by plant roots. Sites where NO_3^- remediation is most effective possess similar hydrology: an impermeable layer occurring 1-4 meters below the soil surface that allows shallow flow of groundwater near plant roots Hill 1996). Lack of an impermeable layer or sandy soils that drain directly to deep groundwater may limit the effectiveness of a riparian buffer.

Structural & Temporal Considerations

Seasonality should be considered in the structural design of a riparian buffer, wherein reduced above-ground biological activity in the winter months may be compensated for by maintain a standing crop of trees or by otherwise ensuring that sufficient carbon is available t o maintain microbial N transformation below-ground (Groffman et al. 1992). Haycock and Pinay (1993) found that above-ground biomass effects the uptake, retention and loss of nutrients during different seasons. Nelson et al. (1995) found no significant influence of temperature on NO_3^- removal from groundwater in a North American riparian forest.

In temperate zones NO_3^- runoff is greatest in the winter months (up to 80%), when removal and die-back of vegetation limits nutrient use. In the autumn, crop removal and/or field preparation increases rates of NO_3^- inputs, while aboveground biological activity declines along with temperature and evapo-transpiration (Nelson *et al.* 1995). For this reason, the timing of agricultural activities may significantly alter the rates of nitrate inputs into the buffer system. In winter and spring snow-melt may also cause pulses in NO_3^- levels which requires an active microbial community for buffering effects. Haycock and Pinay (1993) found that buffer zones containing higher percentages of woody species, which retain above-ground biomass during the winter and larger root biomass year-round, were more effective in assimilating NO_3^- during winter months. The concentration of NO_3^-, width of the buffer and soil type also determined NO_3^- reduction.

Riparian Nitrate Remediation Methods

Wetland Preservation & Restoration

Shoreline and riverbank vegetation can significantly reduce NO_3^- inputs into waterways (Lowrance *et al.* 1994, Carpenter *et al.* 1998). Managed wetlands similarly intercept pollutants, sediments and nutrients (EPA 1997). For this reason, protection and restoration of existing wetland ecosystems represents the most efficient and cost effective remediation technique. The EPA (1997) recommends use of existing state and federal wetland preservation programs and restoration of degraded/fragmented wetlands and riparian areas. In most intensive agricultural areas this is not feasible, however, and installation of vegetated filter strips of catchcrops, grasses and trees or constructed wetland systems have been recommended to intercept nutrient runoff and sediments (EPA 1997).

Grass & Catch Crop Buffers

For any NO_3^- remediation effort, carbon-supplementation may be advisable to enhance denitrification by microbes. Benham and Mote (1999) suggest that addition of carbon increased microbial denitrification efficiency from 25% to 95%. These authors used carbon additions in a constructed wetland system with bulrush (Scirpus acutus), common reed (Phragmites communis) and cattail (Typha spp.), wherein bulrush was most effective at NO_3^- uptake presumably due to deep root penetration and oxygen transfer to the rhizosphere. The supplemental carbon source was not named in this study. However, turning over the catch-crop or another annual crop in the fall may provide adequate carbon for microbial activity during the winter. It should also be considered that while many agricultural species may be utilized as NO_3^- catch-crops, leguminous species could be counter-productive due to the nitrogen-fixing rhizobia associated with their roots.

Riparian Forest Buffers

Where land use and ecological conditions allow, a riparian forest buffer may be the most efficient and inexpensive method for remediating nitrate. Since the mid-1980s numerous North American researchers have examined the effectiveness of riparian forest buffers (Lowrance 1992, Lowrance et al. 1984, 1985, Jacobs and Gilliam 1985, Haycock and Pinay 1993, Pinay et al. 1993, Nelson et al. 1995, Hill 1996, Hubbard and Lowrance 1996, 1997, Addy et al. 1999). Hubbard and Lowrance (1997) found no difference in the effectiveness of forested vs. non-forested riparian buffers. Three forest management techniques were examined for their effectiveness in assimilating NO_3^- from agricultural runoff in coastal plain riparian forest system. A 3-zone buffer system was created immediately downslope from agricultural fields. The area adjacent to the agricultural field, Zone 3, consisted of a 10 meter-wide strip of bermudagrass (*Cynodon dactylon* L. Pers.) interplanted with abruzzi rye (*Secale cereale* L.) and overseeded with several other grass species during the first winter of buffer establishment. During the study, vegetation was harvested from Zone 3 twice a year to maintain a productive standing crop. Zone 2 consisted of 40-50 meter-wide belt of mixed hardwood-evergreen forest (*Pinus elliottii* Engelm., *Pinus palustris* Mill., *Liriodendron tuilipifera* L. and *Nyssa sylvatica* Marsh.) downslope from the grass buffer and received three different management treatments: clear-cutting, selective cutting and a mature forest control. A 10 meter-wide strip of unmanaged forest next to the stream comprised Zone 1. Nitrate (NO_3^-), ammonia (NH_4^+) and Chloride (Cl) in shallow groundwater was monitored along well transects, perpendicular to the stream interface, for four years (1992-1995). Chloride, from KCl in fertilizer, was used as an indicator of dilution, as it is not used by plants or microbes in large quantities, whereby reduction in NO_3^- but not Cl indicated biological removal.

All three treatments were effective in reducing NO_3^- in shallow groundwater, resulting in a nearly 10-fold decline in NO_3^- levels between the field/buffer interface and the forest/stream interface. The forest buffer was demonstrably more effective in assimilating NO_3^- than the grass buffer. The authors suggest that their results were consistent with previous studies on riparian forest assimilation of NO_3^- (Jacobs and Gilliam 1985, Lowrance *et al.* 1984, 1985, Hubbard and Lowrance 1996).

Slope of the study area was not directly addressed in any of the studies cited here, however overall, they suggest that a moderate slope of 10% may be required for a buffer of this size. The results of other riparian buffer studies (Hill 1996, Schmitt *et al.* 1999, Machate *et al.* 1999, Addy *et al.* 1999) suggest that, to some degree, a greater slope or pollutant load might be compensated for by increasing the width of the buffer strip. Overall, it appears that the greater the overall root surface area and groundwater residence time the more effective the riparian buffer in remediating nitrate pollution.

Conclusion

Several recent studies have demonstrated the effectiveness of riparian buffers and constructed wetlands in reducing NO_3^- pollution from agricultural systems (Haycock and Pinay 1993, Hill 1996, Machate *et al.* 1999, Addy *et al.* 1999, Benham and Mote 1999, Schmitt *et al.* 1999). Although these studies vary in the structure and species composition utilized for NO_3^- remediation, they all identified the land/water interface as an important area of biological activity for nitrogen transformation. These studies identified the following factors as the most important to successful nitrate remediation: presence of poorly-drained or somewhat-poorly-drained soils or an impermeable layer; plant species that are deep rooting and grow quickly, including tree species where feasible; maintenance of a standing crop or available carbon source during winter months to allow microbial transformation and immobilization of NO_3^- (Haycock and Pinay 1993, Nelson *et al.* 1995, Hubbard and Lowrance 1997). Species assemblages, vegetation structure and width of riparian buffers should be determined based upon nutrient loads, slope, soil type and any other factors that may affect water levels and thereby the pollutants residence time in the buffer zone.

Nitrate pollution is a serious threat to the health of rivers, streams, wetlands and groundwater quality. Where point and/or nonpoint sources of NO_3^- pollutants cannot be eliminated at their source, remediation methods may be employed immediately below the source to the land/water interface, where natural or constructed riparian buffers and wetland ecosystems are demonstrably effective in reducing nitrate pollution in waterways.

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