24. In Situ Bioremediation of High Nitrate Concentrations in Shallow Waters caused by Non-point Sources

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Abstract

Since the production of nitrogen fertilizer by the chemical industry, ammonium and nitrate have been applied in large amount to agricultural fields. This has caused a severe nitrate contamination of surface and ground water and has become a major concern in environmental issues (Phipps, 1997).

Although nitrogen is one of the most growth limiting nutrients for plants and its presence is often desired, in high concentrations it may pose many dangers to the ecological environment and human health. High levels of nitrate in drinking water can cause methaglobemia, especially with small children, which causes suffocation. Therefore water purification processes are often required to remove nitrate from dinking water. Excess nitrogen also causes eutrophication in ponds and lakes. Algae bloom, stimulated by the presence of abundant nutrients, blocks light penetration and causes death of many other organisms dependent on this light (Phipps, 1997). In aquatic systems a moderate amount of nutrients is desired. Both shortage and excess will result in a decrease of the biodiversity among living organisms.

Soil particles are negatively charged in nature. This means that the leaching of nitrogen greatly depends on the form it's in. The positively charged ammonium is adsorbed to the soil particles and is less likely to be drained out by runoff water. But ammonium is transformed by nitrifying bacteria to the negatively charged nitrate. In a way this is desirable because fast growing crops prefer to take up nitrogen in this form. Application of nitrate instead of ammonium means that the nitrogen will be readily available to the crops. The problem however is that because of the negative charge nitrate is poorly retained by the soil and when raining it drains out easily with the percolating water.

The amount of nitrate lost is influenced by many factors, such as the time of application, the crops grown, and the nature of the fertilizer. Given the proper soil and fertilizer management nitrate leaching can be minimized.

There this isn't always to control methods to prevent nitrate reaching groundwater and rivers and creeks are examined and compared in this paper. We will study some of the most common methods that can be used to establish an efficient nitrate removal from shallow subsurface flows. The proposed method should be cost effective as decisions made by landowners greatly depend on financial gain or loss. Another consideration is that the benefits of installing the infrastructure will go most likely to the neighbor downstream instead of the own property (Brewer, 2002). In this light some planning must be done from upper hand.

Keywords

groundwater, denitrification, riparian buffers, ecosystem restoration, wetlands, denitrification walls, permeable reactive barriers

Introduction

Development of the problem

The last decades the amount of nitrogen fertilizer used in agricultural applications has increased significantly. Before World War II manure was used as a fertilizer. Manure is characterized as a slow fertilizer. This means that the ammonium contained in it will only slowly be transformed to nitrate by nitrifying bacteria. Thus nitrate is only slowly generated and most of it can be taken up by the plant before it can leach out. After this period chemical nitrogen fertilizers were developed

to make nitrogen more readily available for the crops and improve yields. Usually nitrogen fertilizer is a combination of ammonium and nitrate. In the soil the nitrifying bacteria will transform ammonium to nitrate, a form that is easily taken up by the plant.
Nowadays, 100 to 200 kg of N $ha^{-1}yr^{-1}$ is used (Phipps, 1997).

1. Methods of nitrogen removal

One of the most cost effective methods to remove nitrate from polluted groundwater is biological removal by bacteria. Bacteria can use nitrate for assimilatory reduction or dissimilatory reduction or denitrification.

1.1 Assimilatory nitrate reduction
Assimilatory nitrate reduction transforms nitrate back to ammonia and is subsequently incorporated into the cell.
Assimilatory nitrate reduction:

$$NO_3^- \rightarrow NH_4^+$$

Nitrate can also be taken up directly by bacterial cells or plants. Assimilation doesn't remove the nitrogen from the system permanently however. When the biomass dies and decays nitrogen is recycled back into the system as ammonia. This ammonia can then de transformed back into nitrate by nitrifying bacteria. This mechanism offers a valuable buffering capacity but doesn't provide a permanent removal for the excess nitrate found in polluted areas.

1.2 Dissimilatory nitrate reduction or denitrification
The bacteria most of interest to us are the denitrifying bacteria. In anaerobic circumstances nitrate is the next compound after oxygen to be used as the terminal electron acceptor.
One of the most cost effective measures for nitrogen removal is biological denitrification. The following reaction occurs:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

This is called dissimilatory nitrate reduction or denitrification. This means that nitrogen is released out of the system as nitrogen gas into the atmosphere, the place where it originally came from. Also N2O is released however, which is an important gas in the global warming issue. Therefore the complete transformation into nitrogen gas must be promoted. This entire reaction cannot be performed by a single bacteria species but by different kinds of bacteria. Hence, we must consider not a single bacterium, but rather an entire micro ecosystem of denitrifying bacteria.

2. Factors influencing denitrification

One could ask why there are excessive concentrations of nitrate in the groundwater if bacteria can remove it so easily. The truth is that these denitrifying bacteria are among the most sensitive bacteria present in the soil. Circumstances must be ideal to achieve optimal biological denitrification.

2.1 Carbon source
The main part of denitrifying bacteria has a heterotrophic metabolism. They receive their energy required for growth and maintenance from the oxidation of various organic carbonaceous compounds such as cellulose, sugar, ethanol, and others. The oxidation half-reaction is:

$$CH_2O + H_2O \leftrightarrow CO_2(g) + 4H^+ + 4e^-$$

This gives the following reaction for denitrification:

$$5CH_2O + 4NO_3^- + 4H^+ \leftrightarrow 2N_2(g) + 5CO_2(g) + 7H_2O$$

This means that the removal of nitrogen will always need a carbon source to let the reaction continue to the right.
When designing a system for bacterial nitrogen removal an easy degradable carbonaceous substance will have to be provided to maintain a decent denitrification rate.

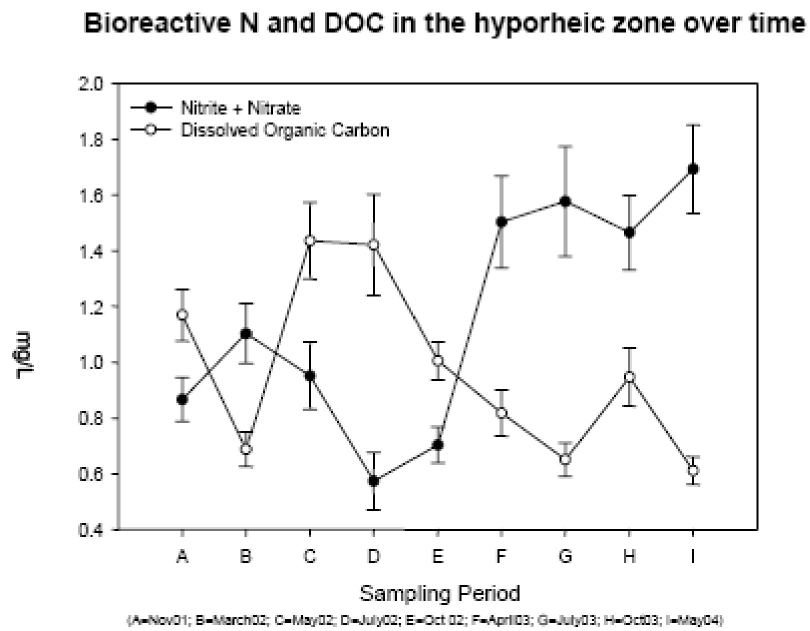

Figure 1 Mayer and Striz, Environmental Protection Agency

2.2 Oxygen
Another concern involving denitrifying bacteria is the oxygen present as denitrification will only occur when all oxygen is depleted. Only a small concentration of oxygen present inhibits denitrification significantly (Fahrner, 2002).
Oxygen is the primary terminal electron acceptor. When all oxygen is used nitrate is the next candidate to be used as a terminal electron acceptor.
Oxygen in the soil doesn’t pose a problem if there is sufficient organic carbon present in the soil. For the degradation of this carbon, oxygen is respired and when diffusion is slow it creates an anaerobic micro-environment, which allows nitrate to be use as the terminal electron acceptor, and nitrogen is removed from the system as nitrogen gas.
It is recognized that denitrification kinetics are mainly dependent on the concentration of oxygen, the concentration of carbonaceous substrate and the concentration of nitrate itself (Fahrner, 2002).

2.3 pH and temperature
Denitrification rates are correlated with pH. Optimal pH is found between 6 and 8. Below pH 6 there is no denitrification occurring anymore. Another factor is temperature. At low temperatures denitrification is low, but measurable. Denitrification is observed up to temperatures as high as 75degrees Celsius. Significant nitrogen removal is said to be between 15 and 60 degrees Celsius (Fahrner, 2002).

Of all these factors it is often the lack of an organic carbon source that inhibits denitrification in natural soils.
This means that this will be the main concern when using microbial denitrification as a

bioremediation method to remove nitrate from groundwater.

In this paper some different methods to stimulate nitrogen assimilation and dissimilation in the environment are discussed.

Riparian Buffers

1. What is a riparian buffer area?

A riparian area is the vegetation area surrounding rivers and creeks. It is not a well-defined area but more the transition zone between aquatic and upland vegetation (Schultz et al., 2000).
The installation or restoration of these areas is an effective way to reduce nitrate pollution of the rivers and creeks surrounded by the riparian buffer (Lyons et al., 2000).
They do this by reducing nitrate levels of runoff water from agricultural areas that flows into the river.
The riparian area is usually made up out of different kinds of vegetation. From water towards the upland we first find trees, then bushes, and eventually grasses. This combination of woody vegetation and and warm-season grasses offers many benefits in maintaining a healthy environment.

2. Working

As runoff water from agricultural areas is slowed down by the vegetation, erosion sediment is trapped and is prevented from getting into the river what would lead to an increased turbidity and thus killing of life that is dependent on sunlight for its survival. An excess of nutrients and pesticides are transformed within the riparian buffer.
An extra accomplishment is its aesthetic value and the shelter it provides for wildlife surrounding the river (Daniels and Gilliam, 1996; Lee et al., 1999).

Figure 2 Effect of ecosystem restoration in rural areas (Environmental Protection Agency)

As much as 68-92 % of nitrogen present in runoff water is filtered by the riparian buffering system (Lee et al., 2000). This means that a healthy riparian ecosystem is a necessity to ensure good drinking water quality for men and wildlife.
Nitrogen is removed from the water flow in different ways. The vegetation slows down the runoff water and facilitates infiltration into the soil. Nitrate is taken up by the plants and bacteria present and assimilated into the growing biomass.
A great part however is permanently removed from the system through denitrification.
The higher the amount of organic carbon in the soil, the higher the rate of nitrogen removal through biological denitrification. This is one of the reasons why it is important to maintain proper carbon levels in the soil. This can be obtained by good soil management and a suitable vegetation choice. One can also decide to add an artificial organic carbon source such as ethanol or methanol. The problem with this however is that it must be dosed correctly or the substance itself can become toxic for the environment.
Denitrification in riparian buffer systems could be encouraged by altering the characteristics of the buffer strip. One can adjust width, length, vegetation, and soil characteristics (Pyper, 2004).
Soil carbon reserves should be protected by minimizing vegetation removal and cultivation, and

by building up soil organic carbon levels with deep-rooted plant species.

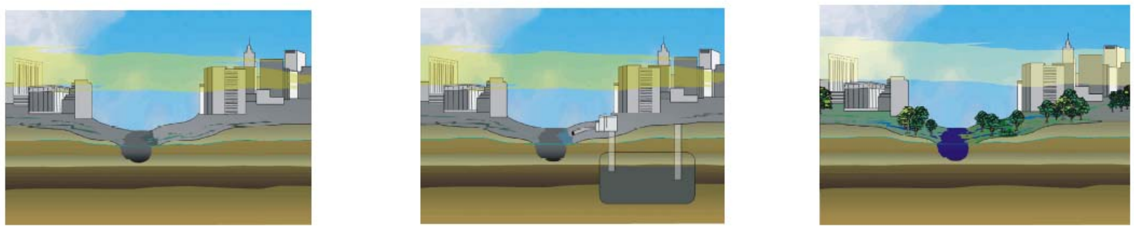

Figure 3 the effect of ecosystem restoration in urban streams (Environmental Protection Agency)

As can be expected, efficiency of riparian buffers can be increased widening the planted strip along the river sides (Lee et al., 2000).
A limitation of the system is that the depth until which nitrate removal is stimulated is limited by the root depth of the concerning vegetation. Also, when nitrate levels are excessively high they can become toxic to the vegetation and thus inhibit nitrate removal from the system (Fahrner, 2002).

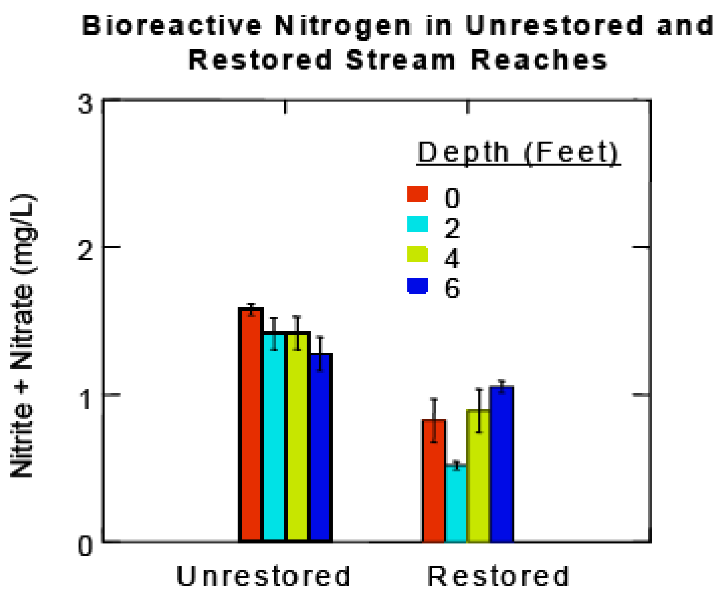

Figure 4 Nitrate levels are lower when riparian ecosystem is restored (Mayer et al., 2005).

Riparian buffer systems have been recognized nationwide as an effective method to restore aquatic systems and improve water quality. Much research however is still needed to model the riparian buffer in function of width, length, vegetation composition, root depth, soil type, and other influencing factors (Jorgensen et al., 2002). Hence, restoring riparian ecosystems provides many benfits and secures a more beautiful and healthy environment.

Restoring riparian vegetation increases the amount of carbon available to denitrifying bacteria. However, adding an artificial source of carbon may prove useful to increase denitrification rates (Mayer et al., 2004)

Reshaping the channel bank may influence stream hydrology in such a way that the region of saturation is increased, which makes a larger anaerobic environment available for the denitrifiers and thus increases denitrification as well.

Restoring river ecosystems will improve water quality and is as such not just an aesthetical project.

Another application could be the use of switchgrass in these riparian buffers. Switchgrass is a warm-season perennial grass that is of great interest as an energy crop. When grown it needs less nitrogen fertilizer because of its perennial nature. It can be used as a biorenewable crop because of its high yields and specific composition.
If switchgrass would be planted between feed crops such as corn and the riparian area, it probably will take up a lot of the excess nitrate present in the agricultural field runoff water. Research in this area still needs to be performed.

“Restoration appears to be a potentially sustainable means of improving water quality by reducing bioreactive nitrogen concentration in the surface water and groundwater of urban streams.” (Mayer and Striz, 2004)

Constructed Wetlands

Another promising treatment strategy to reduce nitrate contamination from non-point sources in shallow waters is the use of natural or constructed wetlands (Brewer, 2002).

During the nineteenth century the policy has been to drain wetlands to make them suitable for all kinds of purposes such as agriculture (Heimlich et al., 1997). This policy, however greatly diminished, is still going on. This situation has increased the problem of an excessive amount of nitrogen present in the environment. Reconstructing wetlands and preserving those that are left may have great benefits towards water quality improvement (Boudreau et al., 2004).

How do wetlands reduce nitrate levels?
Wetlands can be used to reduce pollution by runoff water into rivers and creeks in the sense that they allow the suspended sediment in the runoff water to settle and nutrients, among which nitrogen, are taken to the bottom. Nitrogen is also taken up by plants and microorganisms, and a significant part is removed permanently through denitrification (Phipps, 1997).
As for riparian buffers the capacity of wetlands, constructed or natural, is dependent on many factors. The vegetation, benthic life, and aquatic life is of importance as it influences the gas fluxes in the water, and more important in the anoxic sediment, which is the main region where denitrification takes place. Besides this, also fluctuating factors such as temperature, pH, nitrate concentrations, oxygen concentration have a great impact on the nitrogen removal. The sink capacity is even influenced in such a way that at certain times of the year the wetland doesn’t act as a sink, but as a source of nitrogen. The overall effect remains a loss of nitrogen however (Phipps, 1997). For effective nitrogen removal the wetland has to be periodically flooded and dry so that nitrification and denitrification can occur alternately (Boudreau et al., 2004).
In wetlands adjacent to the Des Plaines River 78-95 % of the nitrate and 54-75 % of the total amount of nitrogen received was removed on an annual basis (Phipps and Crumpton, 1997).
When integrated into a riparian area, the benefits of using wetlands as a bioremediation method increase even more.
Questions remain however what the long term effects are of using these wetlands as sinks for different kinds of pollutants. Research in this direction is being performed by Canfield and Burden (2003).

Denitrification Walls and Trenches

1. What are denitrification walls and trenches?

As discussed above the insufficient availability of a carbon source is often the most inhibitory towards denitrification. The presence of a carbon source is important for two reasons. At first all

oxygen s used for the oxidation of the organic carbon, thus creating an anaerobic environment in which denitrification can take place. The carbon source is than needed as an energy source for the metabolism to continue when nitrate is used as the terminal electron acceptor.
This means that the placement of organic walls in the soil should increase the denitrification rate. Greenan (2004) says: “A denitrification wall is a trench that is dug perpendicular to the flow path of water, and backfilled with an organic C-source such as wood chips or sawdust”. Water flows through the wall of carbon-rich material where denitrification is now stimulated since the carbon source is no longer a limiting factor.

2. Types of denitrification, efficiency, and working

Many different types of denitrification walls have been described, using different carbonaceous materials such as wood chips, sawdust, coconut fiber, tree bark, and compost. All of them proved to have a beneficial effect on denitrification. Nitrate removal went from 74 to 80 % for removal in septic sites. Up to 91 % removal was achieved for nitrate removal of septic plumes (Greenan, 2004). This is a very good result that can be obtained with relatively low costs.
An important issue in the choice of the carbon source to be used is the lifetime, the length of time that the denitrifying bacteria can use the provided carbon. It is not desirable to replace a denitrification wall every year. If we want to cover large areas to capture runoff water a denitrification wall should have a lifetime that is at least ten years would you want to keep it cost-effective. The main cost is the installation of the wall, not maintenance.
Understanding how rapidly organic materials decompose under anaerobic conditions will help to establish criteria in choosing carbon sources for denitrification walls, bioreactors, biofilters, and treatment barriers.

Also a better understanding is needed about the fate of the removed nitrate. It is assumed that it is removed through denitrification because of the presence of denitrification enzymes. However, certainty about this subject must be obtained. When nitrogen is assimilated it can be recycled back into the system and this is not desirable.

Zero-Valent Iron Permeable Barriers and Autotrophic denitrification

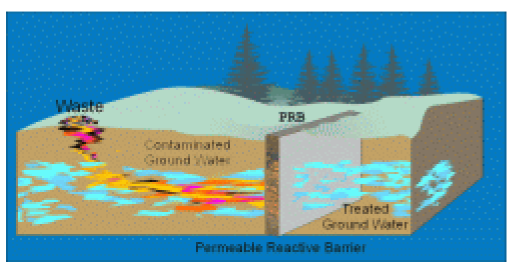

Figure 5 working mechanism of a permeable barrier (Environmental Protection Agency)

Zero-valent iron as been used to treat toxins like chlorinated solvents and hexavalent chromium. However, it can also be used as an inexpensive method to treat nitrate contaminated groundwater (Till et al., 1998).

1. Working

Zero-valent ion reduces nitrate stoichiometrically to ammonium. The following reaction occurs:

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow NH_4^+ + 4Fe^{2+} + 3H_2O$$

In the meanwhile hydrogen is produced at the cathode trough anaerobic corrosion by water. This hydrogen can then be used by denitrifying bacteria as an energy source and denitrification is stimulated. There can be concluded that it is beneficial to the nitrate removal process to combine zero-valent iron and hydrogenotrophic denitrifying bacteria. However, the knowledge is this field is so small that on this point it is still impossible to fully exploit the advantages of this system. The questions that must be answered concern both the biological side (how to augment the hydrogenotrophic bacteria) and the physical side (proportions of barrier) (Till et al., 1998). Especially attractive is the ease at which the zero-valent iron can be applied in situ. It can be placed in the path of a contaminant plume, either as a trench, buried as a broad continuous curtain, or injected a colloids.
Effects of groundwater chemistry on barrier longetivity:
When the groundwater is more highly buffered, that is, when alkalinity and sulfate are high, the pH change within the iron is moderated, and both precipitation and microbial activity are enhanced.

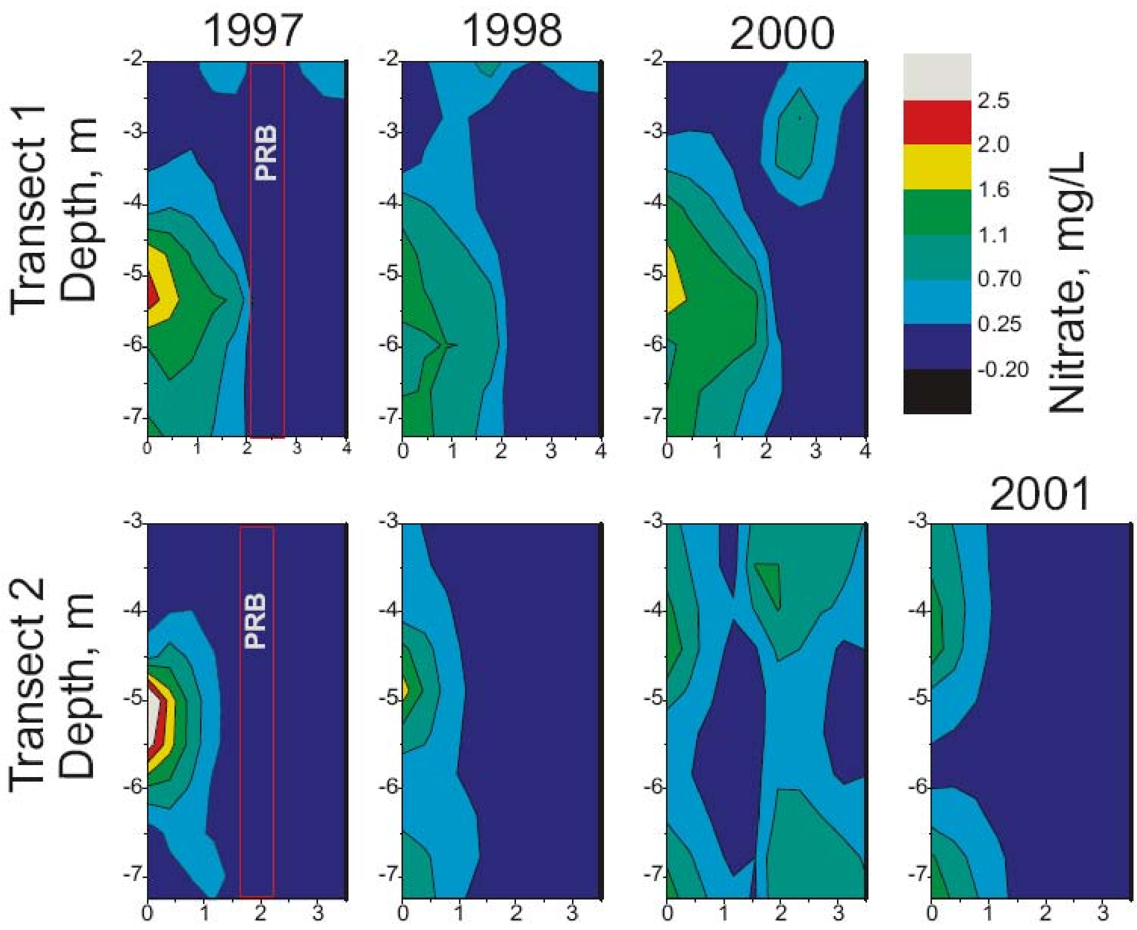

Figure 3.17 Cross-sectional profiles showing nitrate concentrations (mg/L) in transects 1, 2, and 3, Elizabeth City PRB. (Environmental Protection Agency)

However much of the promises maid by this new technology, haven't been answered. This is due to much factors dependent on construction process and soil type.

Sufficient attention must be paid to the groundwater geochemistry. Sites with high levels of dissolved oxygen and/or high levels of carbonates and sulfate are much more susceptible to

clogging and buildup of microbial biomass than are systems that are poorly buffered and have low levels of suspended solids. (An iron barrier might have a role at highly buffered sites, but expectations regarding performance and longevity have to be consistent with the groundwater geochemistry.) (Gavaskar et al., 1998)
A consistent approach (field tools, analyte lists, modeling, etc.) for monitoring performance is required. The success or failure of barriers with similar operating characteristics may be differently perceived because of differences in expectations rather than differences in there technical performance (Korte, 2001).

Conclusion

To maintain good water quality in rivers and creeks it is important to restore riparian buffer areas. Integrated wetlands can increase the efficiency of these buffer strips at some places. Surrounding intensive agricultural areas where there is a significant nitrate concentration present in shallow waters it is a good idea to install denitrification walls to prevent the contaminants from reaching deeper ground water layers. At certain places (a leaking septic tank for example) a zero valent iron barrier can be used to treat the contaminated plume.
It is clear that not one option is the solution to everything. An integrated approach of both on-field and off-field treatment is necessary to solve the nitrate contamination in large areas.

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