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PHYTOREMEDIATION OF NITRATE IN THE KARLSRUHE AQUIFER, MCHENRY COUNTY, NORTH DAKOTA

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as a Geological Engineering Design Project

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EXECUTIVE SUMMARY

Nitrate concentrations in the Karlsruhe aquifer (23,070 acres), located in north central McHenry County, North Dakota have been monitored by the North Dakota State Water Commission since 2001. The average nitrate-N concentration in the top ten feet of the aquifer was determined to be about 14.0 mg/L. The objective of this engineering design was to determine the location of shallow areas in the Karlsruhe aquifer where phytoremediation would be most suitable and to evaluate the effect of phytoremediation on attenuating nitrate-N concentrations. The determination of areas in the Karlsruhe aquifer where phytoremediation would be most effective was carried out through analysis of the average depth to water table in the spring and fall, and land use for that region. The potential phytoremediation areas were narrowed down further by accessing the location of primary discharge points in the aquifer. Cross-sections and flownets were utilized to gain a general understanding of groundwater flow beneath these areas. Calculations of nitrate-N loss were based on the hydraulic conductivity, porosity, hydraulic gradient, and the average nitrate-N concentration in the aquifer as well as the hybrid poplar's nitrogen uptake ability. Overall, the influence of phytoremediation on nitrate-N concentrations in aquifer discharge was variable. The 66 ft long buffer was able to decrease the average concentration of 14 mg/L by about 50% to a value below the EPA-MCL when the hydraulic conductivity was 20 ft/day. The 30 ft long buffer decreased the initial nitrate-N concentration by only 20% when the hydraulic conductivity was 20 ft/day. Both riparian buffers had negligible effects on nitrate-N concentrations at maximum hydraulic conductivity. The geologic material comprising the Karlsruhe aquifer appears to have the greatest influence on the hybrid poplar's ability to remove nitrate from the subsurface. The high hydraulic conductivity values for the aquifer create groundwater flow conditions in which the interaction between

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nitrate and the root zone is limited. However, it was recommended that a 66 ft long buffer be implemented along the Wintering River because the average nitrate-N concentration in the upper portion of the aquifer is above the EPA-MCL and a riparian buffer has the potential to decrease the concentrations to a suitable level.

INTRODUCTION AND OBJECTIVE

The application of nitrogen fertilizer on agricultural land has been a growing subject of concern for many years. High nitrate concentrations in drinking water have been linked to health problems such as methemoglobinemia (blue baby syndrome) (Zeman et al., 2002), gastric cancer (Bakan et al., 2002), goiters (enlargement of thyroid) (Chaoui et al., 2004; Gatseva et al., 1998), and birth malformations (Majumdar and Gupta, 2000; Scragg et al., 1982). Additionally, researchers have suggested that "dead zones" produced by the overgrowth and death of algae in the Gulf of Mexico are caused by an increased use of nitrogen fertilizer in the Midwest (Barkdoll et al, 2003).

The remedial use of plants to remove and convert nitrate from agricultural regions has begun to receive attention as it is aesthetically pleasing, environmentally friendly, and requires minimal monitoring and low start-up costs compared to alternative methods (Hinchee et al., 1995).

The objective of this engineering design is to determine the location of shallow areas in the Karlsruhe aquifer where phytoremediation would be most suitable and to evaluate the effect of phytoremediation on attenuating nitrate concentrations.

PROBLEM DEFINITION

Monitoring of the nitrate concentrations in the Karlsruhe aquifer located in McHenry County in north central North Dakota (Figure 1) has been carried out since 2001 by the North Dakota State Water Commission (NDSWC). The Karlsruhe aquifer is a predominantly

unconfined aquifer located beneath a highly active agricultural area, making it susceptible to nitrate leaching and contamination (Schuh et al., 2002).



Figure 1. Location of McHenry County and the Karlsruhe aquifer in north central North Dakota. The Karlsruhe aquifer is depicted by the darker blue area.

Previous research (Schuh et al., 2002) in the spring through fall of 2001 indicated that the total nitrate-N load over the entire aquifer (23,070 acres) was approximately 4 million pounds, producing an average nitrate-N loss of 181 pounds per acre. The economic loss based on \$0.20 per unit nitrogen was calculated to be about \$800,000. Nitrate-N leaching rates were as high as 100 pounds per acre per year in some parts of the aquifer. An index called the "Potential Mixed Concentration Index" (PMCI) was used for comparison between nitrate-N concentrations in the

aquifer and the Maximum Contaminant Level set by the Environmental Protection Agency (EPA-MCL) for nitrate-N of 10 mg/L. It represents the possible nitrate-N concentration over the entire aquifer depth assuming it was thoroughly mixed. Typically, nitrate was stratified with the largest concentrations at or slightly below the water table. 34% of the measured data locations were determined to have nitrate-N concentrations above the EPA-MCL for the entire depth of the aquifer if fully mixed, which equates to approximately 6,000 acres of the Karlsruhe aquifer. The highest measured nitrate-N concentration was 68 mg/L (Schuh et al., 2002).

The amounts (in millions of pounds) of nitrate-N loads from the fall of 2001 to the fall of 2003 over the entire aquifer were as follows: 4.2 (fall 2001), 3.8 (spring 2002), 3.9 (summer 2002), 4.2 (fall 2002), 3.3 (spring 2003), 3.2 (summer 2003), and 3.1 (fall 2003) (Schuh et al. 2003; Schuh et al. 2004). The decreases of nitrate during this time period were attributed to natural denitrification, the possible leaching of nitrate below monitoring well depths, and stream discharge. The PMCI value indicated that the number of acres with nitrate-N concentrations between 4 and 10 mg/L decreased in the fall of 2002 (Schuh et al., 2003) and remained unchanged in the fall of 2003 (Schuh et al., 2004). The number of acres having low levels (<4 mg/L) almost doubled in the fall of 2002 (Schuh et al., 2003) and nearly doubled again in the fall of 2003 (Schuh et al. 2004). The total number of acres with PMCI > 10 increased by approximately 80% in the fall of 2002 (Schuh et al., 2003) and then decreased in the fall of 2003 (Schuh et al., 2004). Table 1 reports the changes in acreage overlaying the aquifer in certain nitrate-N concentration ranges from the fall of 2001 to 2003. Additionally, nitrate-N contamination greater than 5 times the EPA-MCL occurred at depths of 22 feet below the water table. Even at 85 feet below the water table, persistent levels of nitrate-N contamination existed above the EPA-MCL in some areas of the aquifer (Schuh et al., 2004).

| PMCI | | | | | |
|---------------------------------|-----------|-----------|-------------|-------------|-----------|
| [NO3-N] | Fall 2001 | Fall 2002 | Spring 2003 | Summer 2003 | Fall 2003 |
| mg/L | acres | acres | acres | acres | acres |
| 1-3 | 1,818 | 5,241 | 10,096 | 10,366 | 10,171 |
| 4-5 | 2,725 | 2,524 | 2,641 | 2,729 | 2,408 |
| 6-9 | 3,538 | 2,999 | 3,769 | 3,465 | 3,595 |
| 10-19 | 1,280 | 3,342 | 3,321 | 2,851 | 2,923 |
| 20-29 | 788 | 1,615 | 926 | 901 | 855 |
| 30-39 | 788 | 541 | 689 | 596 | 565 |
| 40-49 | 338 | 166 | 245 | 370 | 400 |
| 50-59 | | 77 | 61 | 139 | 202 |
| 60-65 | | 7 | 20 | 1 | 14 |
| Acres with PMCI > 10 mg/L | 3,194 | 5,748 | 5,262 | 4,831 | 4,959 |

Table 1. Estimated acreage overlaying aquifer having PMCI concentrations in certain ranges. (Adapted from Schuh et al., 2004)

Another area of concern is the New Rockford aquifer which is confined at most locations by glacial till from the overlying Karlsruhe aquifer. Some places exist between the New Rockford and Karlsruhe aquifer where sand comprises the interface between the two, making them hydraulically connected. The New Rockford aquifer does not seem to be affected by nitrate leaching from the Karlsruhe aquifer; however, small amounts have been observed ranging from 0.6 to 6 mg/L nitrate-N (Schuh et al., 2002).

Earlier research of the Karlsruhe aquifer revealed that the aquifer does not contain sufficient amounts of electron donors in its sediments in some areas to carry out denitrification. Sulfide and organic carbon electron donors in shallow sediments were measured and found to be much lower than those of the Elk Valley Aquifer in Grand Forks County, which apparently has high capabilities of denitrification (Korom, personal communication). It was concluded that the Karlsruhe aquifer was highly susceptible to nitrate accumulation from surface leaching and that nitrate removal would occur through some form of discharge, either man-made or natural (Durbin and Korom, 2001). However, more recent studies (Spencer, 2005; Warne, 2004) have revealed that significant denitrification does occur in certain portions of the aquifer.

Finally, it has been proposed that the agricultural application of nitrogen fertilizers has been the main contributor to the high concentrations of nitrate in the Karlsruhe aquifer. Nitrate load density maps indicated a strong correlation between agricultural regions and areas of elevated nitrate levels (Schuh, 2002). Spencer (2005) used isotopic tracers to measure denitrification in the Karlsruhe aquifer; he also provided evidence that the most likely source of nitrate was from the oxidation of ammonia-based fertilizers.

DESIGN CONSTRAINTS

Geology and Hydrogeology

The geology of the Karlsruhe and New Rockford area can be described by two separate depositional events. Sand and gravel deposited in a buried valley eroded into the bedrock by an ice marginal river make up the New Rockford aquifer. A later period of erosion took place followed by the deposition of an unconfined surficial deposit of sand and gravel. The surficial deposit is referred to as the Karlsruhe aquifer and it is generally separated in most places from the New Rockford aquifer by low permeable glacial till. Some boundaries between the Karlsruhe and New Rockford aquifer consist of sand creating hydraulic connectivity between the two aquifers (Schuh et al., 2002).

The geology of the Karlsruhe region can have an effect on the overall success of phytoremediation. The majority of nitrate removal from agricultural lands through phytoremediation occurs through riparian buffers. However, a certain geological constraint can inhibit the nitrate removal performance of a riparian buffer. It has been determined that most riparian zones that successfully remove nitrate contain a low permeable layer near the ground surface (about 1-5 m). The layer with low permeability allows for shallow groundwater flow through the riparian zone and increased nitrate residence times in the vicinity of the root zones (Hill, 1996). A low permeable layer within 1 to 5 meters from the ground surface may not be a significant constraint in the Karlsruhe aquifer because most of the nitrate contamination is already within the top 10 feet of the saturated zone (Schuh et al., 2002). Additionally, general cross sections (Wanek, 2002; Wanek, 2003) of the Karlsruhe aquifer illustrate that the depth to a low permeable layer is generally more than the recommended 1 to 5 meters, especially near rivers.

The type of soil present is important, too, as it influences factors such as infiltration and plant growth. A general soil map (U.S. Department of Agriculture and Soil Conservation Service, 1990) for the Karlsruhe aquifer area is presented in Figure 2. The main soil types that cover a majority of the Karlsruhe aquifer are represented by the classes 2 (tan), 3 (orange), 4 (pink), 11 (blue), and 13 (purple). Classes 2 and 3 specify level to hilly land with sandy and loamy soils on delta and outwash plains. They are both coarse to moderately textured, but class 2 soils tend to be well to somewhat poorly drained while class 3 soils are excessively to well drained. Class 4 soils represent level to very steep land with loamy and silty soils on till plains and moraines. The soil is medium textured and well to moderately well drained. Classes 11 and 13 specify clayey, loamy, and silty soils overlying level to undulating land. Class 11 soils tend

to be fine textured and poorly to very poorly drained while class 13 soils are medium to moderately fine textured and well to poorly drained.



Figure 2. General soil map for the Karlsruhe area, McHenry County, North Dakota. (Adapted from Soil Survey of McHenry County)

Overall, a majority of the aquifer appears to underlie moderately to well drained soil, which could be contributing to nitrate leaching into the aquifer. Certain portions of the aquifer, particularly near the Souris River where the soil tends to be poorly drained, may have greater nitrate attenuation and could be more suitable locations for phytoremediation. Simmons et al. (1992) demonstrated that poorly drained soils tend to have greater nitrate attenuation than moderately to well drained soils. Poorly drained soils create anaerobic conditions which enhances the occurrence of natural denitrification. Since most of the soil overlying the Karlsruhe aquifer is moderately to well drained, it may not possess high denitrification capabilities in those areas. The hydrogeology of the Karlsruhe aquifer has considerable control on the spread of nitrate within the region. Figure 3 displays equipotential lines and a southwest – northeast trending groundwater divide located through T 154 N, R77 W, (Sections 20, 29, and 31) and T 153 R 78 W, (Sections 1 and 12). Groundwater flowing northwest of the divide flows beneath a complex stratigraphy of glacial till towards the Souris River. Southeast of the divide water flows towards the northeastward-flowing Wintering River, which is a tributary of the Souris River. Groundwater on the southeast side of the Wintering River also flows in a northeastward direction towards the Wintering River (Schuh et al., 2002). Currently, nitrate concentrations in wells near the Wintering River are not high and do not threaten to surpass the EPA-MCL. This could be a result of denitrification near the river where electron donors, that are required for denitrification, may be in greater supply (Korom, 2005). Nevertheless, nitrate from high loading areas in the aquifer may eventually spread and reach the river.

It is generally believed that the presence of the root zone below the water table, or immediately above it, during the growing season is necessary for riparian zones to effectively remove nitrate (Simmons et al., 1992; Hill, 1996). Water table elevations varying spatially and seasonally seem to have a strong influence on the fate of groundwater nitrate in riparian buffers. The depth to water table over the entire aquifer during the spring and fall was analyzed to determine suitable areas for phytoremediation. Generally, phytoremediation is most suited for sites with shallow contamination (< 5 m) (Schnoor et al., 1995). The groundwater velocity, which is dependent upon the hydraulic conductivity, also influences the effectiveness of phytoremediation. The retention time, or amount of time that nitrate is in contact with the root zone, relies on the flow rate of the groundwater. When groundwater is flowing at a low rate, the



Figure 3. Water table surface of the Karlsruhe aquifer on December 11, 2001 (Adapted from Schuh et al., 2002).

chances of removing a greater amount of nitrate from the subsurface increases. On the contrary, phytoremediation can have minimal effects on the nitrate concentrations in groundwater if the groundwater is flowing too fast (Hill, 1996). In addition to groundwater velocity and depth to water table, the flow direction and nature of groundwater flow within the aquifer was utilized in order to estimate the fate of nitrate in the presence of roots. Due to insufficient geological and hydrogeological data on the Souris River, this area was not considered in the final phytoremediation design. The remaining portion of the aquifer, primarily the Wintering River, was analyzed in more detail to determine the effect of phytoremediation on nitrate-N concentrations.

The majority of nitrate-N load in the Karlsruhe aquifer lies within approximately ten feet of the water table. Nitrate-N concentrations generally diminish to trace amounts below ten feet from the water table (Schuh et al. 2002). Similar stratification of nitrate has been noted in previous research where higher concentrations tend to remain near the water table surface (Trudell et al., 1986; Hallberg, 1989). However, elevated nitrate-N concentrations have been measured in deeper portions of the Karlsruhe aquifer (Schuh et al., 2002). The average nitrate-N concentration in the top ten feet of the aquifer was calculated from 88 monitoring wells (Wanek, 2003) and was determined to be approximately 14.0 mg/L.

Vegetation Selection

The loss of nitrate in a riparian zone is influenced by the type of vegetation present. In turn vegetation is sensitive to the environment it inhabits. Inherent limitations to the use of phytoremediation are that (1) root depths are finite and they usually only grow as deeply as they need to find water and nutrients. This depth could range from 1 to 10 meters depending on the pollutant, stratigraphy, water table depth, and climate; (2) roots are living and have environmental requirements for pH, temperature, moisture, and oxygen; (3) roots produce an imperfect barrier to leaching; (4) the contaminant must be biologically available; and (5) the level of contamination may be toxic to the plant itself and prior decontamination of the area in question may have to occur (Hinchee et al., 1995).

Most plants need nitrogen for everyday survival. In fact nitrogen compounds such as nitrate and ammonium account for more than 70% of the total cations and anions taken up by plants (Zhang et al., 2002). Most plants are able to take up nitrate and reduce it into usable forms by the action of the enzyme nitrate reductase. Nitrate reductase uses several electron-transfer mediators, including riboflavin, molybdenum, and NADH (Nicotinamide Adenine Dinucleotide)/NADPH (Nicotinamide Adenine Dinucleotide Phosphate) to reduce nitrate. The synthesis of nitrate reductase in a plant is triggered by the presence of nitrate in the environment, and its activity appears to be greatest under high-light and high-temperature conditions. The enzyme is also found in other organisms such as soil fungi. Denitrification activity tends to be highest in the rhizosphere of a plant, and that activity promotes microbial growth that is capable of degrading other organic compounds (Larson et al., unpublished). Based on research, a toxic level of nitrate for plants has not been determined. The determination of a fatal level of nitrate would be very difficult to conclude since it would most likely vary among species.

Terrestrial plants considered for implementation in the riparian buffer, because of their ability to take up nitrogen and survive in North Dakota, included hybrid poplars (Populas balsamifera x Populas deltoides, Populas trichocarpa x Populas deltoides) (Larson et al., 2002; Licht and Schnoor, 1993; Johnson, 2006), cottonwoods (Populas deltoides), switchgrass (Pancium virgatum L.) (Larson et al., 2002), alfalfa (Medicago sativa L.) (Blumenthal et al., 1999), and perennial ryegrass (Lolium perenne L.) (Lowrance and Sheridan, 2005). A singlespecies riparian buffer containing trees was chosen primarily because trees have the ability to remove more subsoil nitrate than grass alone (Hill, 1996). A multi-species riparian buffer with three zones (trees, shrubs, grass) could be more effective and accurately portrays a natural riparian buffer. The major function of the tree zone, however, is to quickly develop deep roots and filter out nitrate from the groundwater. The shrub zone is usually the smallest zone (about 2 rows) and is mainly established to add diversity to the riparian buffer and assist in adding slope stability. The grass zone primarily acts as a means of controlling surface runoff (Schultz et al., 1997). Grasses could have an effect on groundwater nitrate, but they tend to be limited by root length. Therefore, the decision to use a single-species riparian buffer containing trees in the analysis was made because trees are mostly responsible for removing nitrate from groundwater compared to shrubs and grasses. If a single-species riparian buffer of trees was implemented, grasses and shrubs would most likely establish themselves naturally and the riparian buffer could eventually gain all of the additional benefits provided by a multi-species buffer.

Tree species such as hybrid poplars and cottonwoods arise naturally along stream and river environments (Johnson, 1994, Braatne et al., 1996, Scott et al., 1997). Natural hybrids between native cottonwoods commonly occur within riparian zones throughout North America (U.S. Environmental Protection Agency, 1999). Species of cottonwoods and other poplars can

ordinarily be found in McHenry County and are recommended for environmental and windbreak plantings (U.S. Department of Agriculture and Soil Conservation Service, 1990), for that reason they were both considered in the final selection. Both hybrid poplars and cottonwoods have advantages and disadvantages, but the hybrid poplar was chosen as the plant species for the riparian buffer for the following reasons: 1) high nitrogen requirement; 2) high transpiration rates to minimize groundwater leaching; 3) a deep root system (6 – 16 feet); 4) minimal maintenance costs (Johnson, 2006); 5) rapid growth; and 6) high biomass production (Schultz et al., 1997). On the negative side, hybrid poplars tend to be slightly less drought tolerant and disease resistant than cottonwoods (Herman et al., 2006). Hybrid poplars and other poplar species have been estimated to take up approximately 57 mg-N/tree/day (Licht and Schnoor, 1993). It was assumed for this analysis that hybrid poplars would both be able to remove 57 mg-N/tree/day from the saturated zone.

Climate

It is already known that vegetative uptake of nitrate is possible during the summer season where most plant growth takes place under the condition that the plant roots come into contact with the water table. In temperate regions, it is also important to understand the efficiency of a riparian buffer during the winter months since almost 80% of nitrate leaching from agricultural soil occurs during this time (Haycock and Pinay, 1993). This may be a limitation in North Dakota due to the long winters.

Social and Political Concerns

The requirements and needs of farmers and land owners in the Karlsruhe area are currently unknown. It is assumed that substantial support from farmers and land owners for

phytoremediation experimentation is unlikely especially if they have to fund the project. Area support may increase if outside sources provided funding for at least a majority of the project. During a situation where a groundwater drinking source was in serious danger of being contaminated, the public would probably be more supportive of remediation. In that case, however, phytoremediation would not be recommended because the problem would require a faster solution.

Another social disadvantage of implementing riparian vegetation is the possible lowering of water levels in the associated waterways. The extent to which this may happen is unknown, but the possibility of it occurring may be viewed by many North Dakotans as a disadvantage of phytoremediation. However, the addition of riparian forest in North Dakota may be seen as advantageous since the state only contains natural forests on 1% of its land area (North Dakota Forest Service, 2006).

The availability of land for phytoremediation was assessed by determining where cropland and developed land intersected areas in the aquifer where phytoremediation was suitable. All other land use types (i.e. prairie, shrubland, woodland, etc) were considered as possible locations for phytoremediation implementation. On the other hand, it is unlikely that officials from the U.S. Fish and Wildlife Service and other government agencies would support the destruction of natural habitat so that new vegetation could be planted in its place. Ultimately the most acceptable location for phytoremediation, if it was implemented, would probably be along river sections already lacking riparian vegetation.

DESIGN APPROACH

The determination of areas in the Karlsruhe aquifer where phytoremediation would be most effective was carried out through analysis of the average depth to water table in the spring and fall, and land use for that region. The potential phytoremediation areas were narrowed down further by assessing the location of primary discharge points in the aquifer. Cross-sections and flownets were utilized to gain a general understanding of groundwater flow beneath these areas. Calculations of nitrate loss were based on the hydraulic conductivity, porosity, hydraulic gradient, and the average nitrate-N concentration in the aquifer as well as the plant's nitrogen uptake ability.

DATA AND METHODS

Water table elevation and surface elevation measurements were obtained from the North Dakota State Water Commission (NDSWC) website (www.swc.state.nd.us). 96 observation wells located in the Karlsruhe aquifer were used to obtain water table elevation readings for the spring and fall from the year 2000 to the present and 202 wells were used for surface elevations. The depths to water table were calculated by subtracting the water table elevations from the surface elevations. Contour maps representing the depth to water table were generated using an inverse distance weighted interpolation method in ArcGIS (ESRI). A GAP Analysis land use map was obtained from the North Dakota GIS Hub website (http://www.nd.gov/gis/) along with surficial aquifer, water body, river, and city shapefiles.

The variation in thickness of the aquifer underneath the Wintering River was determined from general cross-sections provided by the NDSWC. Potentiometric maps representing the

groundwater surface during the summer and winter supplied by the NDSWC were utilized to calculate the hydraulic gradient of the water table near the river. The distribution of hydraulic head values next to the Wintering River was calculated from the following equation (Fetter, 2001):

$$h = \sqrt{\left(h_1^2 - \frac{\left(h_1^2 - h_2^2\right)x}{L}\right)}$$
(1)

where h = head at x, $h_1 =$ head upgradient from river, $h_2 =$ head at river stage, L = distance between h_1 and h_2 , and x = distance from h_1 . MODFLOW (Harbaugh et al., 2000) was utilized to create equipotential contours of head values underneath the Wintering River based on the calculated hydraulic head values and varying aquifer thickness measurements. Flow lines, the water table surface, and the land surface were hand drawn with the equipotential contours to create a flownet which approximated the nature of groundwater flow beneath the Wintering River.

Calculation of the average linear groundwater velocity was carried out by the following equation (Fetter, 2001):

$$v_x = \frac{K}{n_e} \frac{dh}{dl} \tag{2}$$

where v_x = average linear velocity, K = hydraulic conductivity, n_e = effective porosity, and dh/dl = hydraulic gradient. The hydraulic conductivity and effective porosity values were obtained from NDSWC reports (Schuh et al., 2002). The following equation determined the retention time or the length of time that nitrate and water would remain within the root zone:

$$t_r = \frac{L}{v_x} \tag{3}$$

where t_r = retention time of nitrate, L = flow distance, and v_x = average linear velocity calculated

by Eq. (2). Average linear groundwater velocity and retention time calculations are reported in Appendix A.

A more simplified approach was taken to gain an estimate of the overall effect of phytoremediation on nitrate-N concentrations. Two orthogonal riparian sections were "cut" out of the aquifer and mass balance calculations of nitrate-N were performed on each. In other words, the initial nitrate-N mass was compared to the final nitrate-N mass in each riparian section to determine the percent decrease of nitrate-N as a result of plant uptake. Each riparian section was subdivided based on the number of tree rows in each buffer. Each subdivision represented the volume of aquifer acted upon by one tree. An initial nitrate-N mass was calculated for the first subdivision. As the initial mass migrated through the riparian section the sequential decrease in nitrate-N was calculated for each subdivision. The final nitrate-N mass and concentration was determined for each riparian section along with the percent decrease in nitrate-N. The following assumptions were made for the loss of nitrate-N calculations in each riparian section.

- 1) Tree uptake is the only reduction of nitrate-N concentrations.
- 2) There is no flow in or out of the riparian section (except through tree uptake).
- 3) All trees are physiologically identical. 6 and 16 foot long tree roots both take up 57 mg-N/tree/day from the saturated zone only; therefore, the length of the tree root does not affect the amount of nitrate-N taken out of the closed section.
- Nitrate-N and water remain in a subdivision of the riparian section for the calculated retention time.
- 5) The average nitrate-N concentration is evenly distributed throughout the saturated zone of the riparian section.

The dimensions of both riparian sections were determined from the scientific literature and flownets and represent the flow path of nitrate within the riparian zone. The lengths of the riparian sections were 30 ft and 66 ft (Schultz, 1997). The suggested spacing between tree rows varied from 6 to 10 ft with a 4 to 8 ft spacing between trees within rows (Schultz et al., 1997). In order to obtain maximum nitrate-N uptake, a minimum row spacing of 6 ft and a minimum spacing between trees within rows of 4 ft was utilized. Therefore, the 30 ft and 66 ft long riparian sections contained 5 and 11 tree rows, respectively. The average depth to water table near the Wintering River was obtained from Figure 4 and was estimated to be about 2 feet. The saturated thickness of the riparian section was chosen to be 10 feet, which represents the top portion of the aquifer that contains most of the nitrate contamination. Figures 5 and 6 display the 30 ft and 66 ft long buffers as riparian sections with their corresponding water volumes.



Figure 4. Cross section of the Karlsruhe aquifer near the Wintering River.



Figure 5. 30 ft buffer as a riparian section. The width of the riparian section is 4 ft.



Figure 6. 66 ft buffer as a riparian section. The width of the riparian section is 4 ft.

RESULTS

Determining Suitable Areas

Figures 7 and 8 illustrate the approximate depth to water table over the Karlsruhe aquifer during the spring and fall, respectively. The lighter green contours depict areas where the water



Figure 7. The variation in depth to water table for the Karlsruhe aquifer during the spring from 2000 to the present.



Figure 8. The variation in depth to water table for the Karlsruhe aquifer during the fall from 2000 to the present.

table is shallow. Due to little variation between the spring and fall depth to water table maps, an average depth to water table map was created for the entire aquifer. Regions where the average depth to water table was ten feet or less were extracted for further analysis. Figure 9 represents areas in the aquifer where the use of phytoremediation would be the most effective. Shallow areas tend to be located in close proximity to rivers, ponds, lakes, and wetlands.

Land use for the Karlsruhe area (Figure 10) was divided into the following seven categories: cropland, developed, woodland, shrubland, prairie, planted perennials, and wetlands. Developed and cropland regions were determined to be unsuitable for phytoremediation; all other categories were considered further. Cropland and developed regions that intersected the shallow areas of the aquifer (Figure 9) were selected and extracted to produce a final map (Figure 11) of suitable regions for phytoremediation. The suitable areas in the Karlsruhe aquifer are near the Souris and Wintering rivers and other water bodies.



Figure 9. Shallow areas in the Karlsruhe aquifer where the average depth to water table is 10 feet or less.



Figure 10. Land use in the Karlruhe area.



Figure 11. Suitable shallow areas of the Karlsruhe aquifer.

Direction of Groundwater Flow

The approximate direction of groundwater flow is illustrated by Figure 12 (Wanek, 2005). The groundwater generally flows towards two primary discharge points in the aquifer: the Souris River in the northwest and the Wintering River in the southeast. The remaining wetlands, ponds, and lakes appear to have insignificant influence on groundwater discharge in comparison to the Souris and Wintering Rivers. Due to insufficient information on the Souris River, the focus of the project was directed towards phytoremediation in the form of a riparian buffer of the portion of the Wintering River flowing through the Karlsruhe aquifer (Figure 13).



Figure 12. General groundwater flow direction in the Karlsruhe aquifer. (Adapted from Wanek, 2005)



Figure 13. Portion of the Wintering River that will be the main focus for phytoremediation.

Construction of Flownets

Flownets were constructed to gain a better understanding of the groundwater flow beneath the Wintering River. The aquifer thickness beneath the Wintering River ranged from approximately 30 feet (Wanek 2002) to 60 feet (Wanek 2003). The estimated hydraulic gradient near the Wintering River was calculated from potentiometric maps for the summer (Wanek 2005) and the winter (Wanek 2003) and were determined to be about 0.0044 ft/ft and 0.0053 ft/ft, respectively. An average value for the hydraulic gradient from the summer and winter values was determined to be about 0.0048 ft/ft and used in further calculations. The distribution of hydraulic head values near the Wintering River was estimated with Eq. (1) and is reported in Table 2.

Flownets with 60 ft and 30 ft aquifer thicknesses are shown in Figures 14 and 15, respectively. Groundwater flow does not change significantly with varying aquifer thickness according to the flownets especially near the water table where the root zone would be interacting with the groundwater. Previous research indicated that a shallow low permeable layer near the ground surface enhances the effectiveness of phytoremediation (Hill, 1996). However, the monitoring of nitrate in the Karlsruhe aquifer revealed that a majority of the contamination appears within the top ten feet of the saturated zone (Schuh et al., 2002). Therefore, the aquifer thickness beneath the Wintering River would not appear to inhibit the uptake of nitrate by plants.

| | x (m) | x (ft) | h (m) | h (ft) |
|-----------------------------------------|---------|---------|----------|----------|
| Center of Wintering River | 40 | 131.24 | 463.273 | 1519.999 |
| | 36 | 118.116 | 464.6377 | 1524.476 |
| | 32 | 104.992 | 464.6554 | 1524.534 |
| | 28 | 91.868 | 464.6731 | 1524.592 |
| | 24 | 78.744 | 464.6908 | 1524.651 |
| | 20 | 65.62 | 464.7085 | 1524.709 |
| | 16 | 52.496 | 464.7262 | 1524.767 |
| | 12 | 39.372 | 464.7439 | 1524.825 |
| | 8 | 26.248 | 464.7616 | 1524.883 |
| 118 feet from center of Wintering River | 4 | 13.124 | 464.7793 | 1524.941 |
| | | | | |
| $h_1 =$ | 1525 | ft | 464.797 | m |
| $h_2 =$ | 1520 | ft | 463.273 | m |
| L = | 1127.19 | ft | 344 | m |

Table 2. Distribution of hydraulic head near the Wintering River. Note: Values reported in meters were used to create equipotential contours in MODFLOW.



Figure 14. Flownet with an aquifer thickness of 60 ft beneath the Wintering River.



Figure 15. Flownet with an aquifer thickness 30 ft beneath the Wintering River.

Determining Effect of Riparian Buffer on Nitrate-N Concentrations

Retention Time Calculation

The retention time, or the length of time that nitrate and water would remain within one tree cell of the riparian section, was calculated with Eq. (3). Eq. (2) was used to determine the average linear velocity of the groundwater where the hydraulic conductivity (*K*) ranged from 20 to 200 ft/day (Schuh et al., 2002), the effective porosity (n_e) was approximated as 0.2 (Schuh et al., 2002), and the average hydraulic gradient (dh/dl) was calculated to be 0.0048 ft/ft. The resulting average linear groundwater velocity values and retention times are reported in Table 3 and sample calculations are reported in Appendix A.

Table 3. Calculated average linear groundwater velocity and retention times at different hydraulic conductivity values for one subdivision of the closed section. The subdivision is 6 ft long.

| Hydraulic Gradient, K (ft/day) | 20 | 200 |
|-----------------------------------------|------|------|
| Average Linear Velocity, v_x (ft/day) | 0.48 | 4.8 |
| Retention Time, t_r (days) | 12.5 | 1.25 |

The hydraulic conductivity appears to have a substantial affect on the velocity and retention time values and is the most variable parameter. The hydraulic conductivity field of an aquifer in a natural setting can normally vary over two orders of magnitude or more while the values for porosity and hydraulic gradient tend to fluctuate less (Fetter, 2001; Fetter, 1999). The amount of time that nitrate is within the root zone affects uptake by trees because as the retention time increases the chances of removing nitrate from the subsoil also increases (Hill, 1996).

Geologic and hydrogeologic properties may influence the fate of contaminants as they affect the direction, speed, and chemical or biological fate of constituents in an aquifer. Consequently, the hydraulic conductivity may be the most important parameter and have the greatest influence on the tree's ability to uptake nitrate.

Nitrate-N Loss Calculations

Nitrate-N loss calculations for the 30 ft and 66 ft closed sections were performed with Microsoft Excel using the calculated retention times reported in Table 3, nitrogen tree uptake of 57 mg-N/tree/day, and an average nitrate-N concentration of 14.0 mg/L. Table 4 and 5 summarize the nitrate-N loss calculations in the riparian sections. Appendix B illustrates the nitrate-N loss calculations in more detail.

Table 4. Final results from nitrate-N loss calculations for a 30 ft long buffer with 5 tree rows.

| F | Retention Time, t_r (days) | 12.5 | 1.25 |
|---|---------------------------------------|---------|---------|
| Ι | nitial Nitrate-N Concentration (mg/L) | 14.0 | 14.0 |
| Ι | nitial Nitrate-N Mass (mg) | 15214.1 | 15214.1 |
|] | Гree Uptake (mg-N/tree) | 712.5 | 71.3 |
| F | Final Nitrate-N Mass (mg) | 11651.6 | 14857.8 |
| F | Final Nitrate-N Concentration (mg/L) | 10.7 | 13.7 |
| F | Percent Change (%) | 23.4 | 2.3 |

Table 5. Final results from nitrate-N loss calculations for a 66 ft long buffer with 11 tree rows.

| Retention Time, t_r (days) | 12.5 | 1.25 |
|----------------------------------------|---------|---------|
| Initial Nitrate-N Concentration (mg/L) | 14.0 | 14.0 |
| Initial Nitrate-N Mass (mg) | 15214.1 | 15214.1 |
| Tree Uptake (mg-N/tree) | 712.5 | 71.3 |
| Final Nitrate-N Mass (mg) | 7376.6 | 14430.3 |
| Final Nitrate-N Concentration (mg/L) | 6.8 | 13.3 |
| Percent Change (%) | 51.5 | 5.2 |

DISCUSSION

According to the results in Tables 4 and 5, both riparian buffers had variable effects on nitrate-N concentrations. The 66 ft long buffer was able to decrease the average concentration of 14 mg/L by about 50% to a value below the EPA-MCL when the hydraulic conductivity was 20 ft/day. The 30 ft long buffer decreased the initial nitrate-N concentration by only 20% when the hydraulic conductivity was 20 ft/day. Both riparian buffers had negligible effects on nitrate-N concentrations at maximum hydraulic conductivity. Nitrate-N removal appears to be greatly influenced by the hydraulic conductivity, which in turn is dependent upon the aquifer medium. Geologic well logs (www.swc.state.nd.us) from the Karlsruhe aquifer reveal that it is mainly comprised of gravel and sand with some silt and clay. Geologic material such as gravel and sand tend to have larger pore spaces which would increase the hydraulic conductivity of an aquifer making it more permeable (Fetter, 2001). Therefore, due to inherent properties, nitrate in the Karlsruhe aquifer may not be as affected by phytoremediation when compared to other locations where the geologic material is finer. However, a riparian buffer along the Souris River, where the soil is more poorly drained, may be even more successful at removing subsoil nitrate.

COST ANALYSIS

A general economic analysis for the implementation of a riparian buffer includes costs for site preparation, planting, and maintenance. Schultz et al. (1997) provides a basic outline for riparian buffer design, establishment, and maintenance. In preparation for planting, the site should be tilled and cleared to eliminate competing vegetation through mechanical or chemical methods. Chemicals should be used with caution in a riparian zone because they may leach

directly into water supplies. One- to two- year-old tree seedlings should be used and they can be machine or hand planted. 10 to 15 percent more plants should be ordered than what may be needed. Weed control may be carried out for the first two to three years through shallow cultivation, weed fabrics or herbicides. Mowing also helps control weeds and aids in marking the plant rows. It is recommended that the riparian buffer be monitored at least once a year to be inspected for erosion and vegetation replacement. After 8 - 12 years trees may be harvested to remove nutrients and chemicals stored in their biomass. Table 6 provides a cost estimate for the completion of a riparian buffer. Price information was provided by cost tables from the Natural Resources Conservation Service (NRCS) for November 2005 and Iowa's State Forest Nursery website (www.iowadnr.com/forestry/). Each cost listed in Table 6 was applied to a 4ft x 6ft area, which represents the area acted upon by one tree. Buffer widths of 30 and 66 feet were recommended by the scientific literature (Schultz et al., 1997), so these prices were converted to cost per square-foot and total costs were estimated for one-sided 30 and 66 foot wide buffers depending on certain conditions (i.e. no chemical application). According to Table 7, costs double when everything is carried out compared to doing the bare minimum of tilling, buying trees and planting them.

Table 6. Itemized riparian buffer cost estimate. The price per 4ft x 6ft area estimates the cost per tree area.

| SITE PREPARATION | | | Price per |
|--------------------------------------------------------|----------|----------------|-----------|
| | | | 4ft x 6ft |
| Chemical Site Preparation | Cost | | area |
| Chemicals | \$20.00 | per acre | \$0.01 |
| Chemical Application (limited to 2 applications) | \$4.00 | per acre | \$0.002 |
| | | | |
| Mechanical Site Preparation | \$20.00 | per acre | \$0.01 |
| Heavy Site Preparation (dozed, sheared, clipped, etc.) | \$106.00 | per acre | \$0.06 |
| PLANTING COSTS (includes planting and materials) | | | |
| Hybrid Poplars | \$37.00 | per 100 trees | \$0.37 |
| Machine Planting | \$19.00 | per 100-ft row | \$0.76 |
| PLANT MAINTENANCE / MANAGEMENT | | | |
| Mechanical (tilling/mowing weeds) | \$2.40 | per 100-ft row | \$0.10 |
| Chemical | \$4.60 | per 100-ft row | \$0.18 |
| Thinning (long term) | \$7.50 | per 100-ft row | \$0.30 |

Table 7. Estimated total costs for riparian buffer completion depending on certain conditions. The cost for a one-sided buffer corresponds to the estimated cost of implementing a riparian buffer along the portion of the Wintering River shown in Figure 13. The length of the Wintering River was approximated from Figure 10 and determined to be about 35,300 feet long. Note: These costs take into account two years of mechanical and/or chemical maintenance and one year of thinning.

| | Price per | | Cost for | Cost for |
|----------------------------------------------------|-----------|-----------|-------------|--------------|
| | 4ft x 6ft | Price per | one-sided | one-sided |
| | area | sq. foot | 30' buffer | 66' buffer |
| Everything | \$2.07 | \$0.09 | \$91,509.08 | \$201,319.98 |
| No chemicals | \$1.70 | \$0.07 | \$75,032.03 | \$165,070.46 |
| No chemicals and heavy site preparation | \$1.64 | \$0.07 | \$72,417.13 | \$159,317.68 |
| No chemicals, heavy site preparation, or thinning | \$1.34 | \$0.06 | \$59,179.63 | \$130,195.18 |
| No chemical, heavy site preparation or maintenance | \$1.14 | \$0.05 | \$50,354.63 | \$110,780.18 |

LAND AVAILABILITY

According to an ArcGIS buffer analysis, the recommended buffer widths of 30 and 66 feet (Schultz et al., 1997) would intersect with a minor proportion of agricultural land (Figure 16). Generally, the majority of the Wintering River could have a buffer of 66 feet in width and still not interfere with much cropland. In the areas where cropland is close to the river, the buffer could be decreased. This is unfortunate, however, since these areas probably possess greater needs for controlling nitrate runoff and discharge into the Wintering River.



Figure 16. Areas along the Wintering River where a 30 and 66 foot wide buffer would interfere with cropland.

RECOMMEDATIONS AND CONCLUSIONS

Overall, the implementation of a riparian buffer would have a substantial effect on nitrate concentrations in aquifer discharge. At the minimum hydraulic conductivity value the 66 ft long buffer was able to decrease the initial nitrate-N concentration by approximately 50% while the 30 ft long buffer decreased it by about 20%. The nitrate-N loss calculations offer a primitive estimation for the overall effect of phytoremediation when certain conditions are assumed and parameters are given. These estimates could be improved through further research, field work, and analysis. More accurate nitrate removal estimations in the riparian buffer could be obtained by actually comparing the chemistry of water samples in wells before and after the riparian zone.

The implementation of a 66 ft long riparian buffer along the Wintering River is recommended as it has the ability to decrease nitrate-N concentrations in the top ten feet of the aquifer below the EPA-MCL. The cost of preparing, planting, and maintaining a riparian buffer is moderate and a majority of the land adjacent to the Wintering River is available. The fact that the average nitrate-N concentration in the top ten feet of the aquifer is above the EPA-MCL suggests that some form of remediation should be utilized in the near future because even higher concentrations may be migrating away from agricultural regions towards the Wintering and Souris Rivers.

APPENDIX A

Average Linear Groundwater Velocity and Retention Time Calculations

$$\max K = 20 \text{ ft/day}$$
$$\min K = 200 \text{ ft/day}$$
$$n_e = 0.2$$
$$\max \frac{dh}{dl} = 0.0053 \text{ ft / ft}$$
$$\min \frac{dh}{dl} = 0.004 \text{ ft / ft}$$

average
$$\frac{dh}{dl} = \frac{(0.0053 + 0.0044)}{2} = 0.0048 \, ft/ft$$

$$\max v_x = \frac{K_{\max}}{n_e} \frac{dh}{dl} = \left(\frac{200 \, ft \, / \, day}{0.2}\right) 0.0048 \, ft \, / \, ft = 4.8 \, ft / day$$

$$\min v_x = \frac{K_{\min}}{n_e} \frac{dh}{dl} = \left(\frac{20 \, ft \, / \, day}{0.2}\right) 0.0048 \, ft \, / \, ft = 0.48 \, ft \, / \, day$$

$$\max t_r = \frac{L}{v_{x,\min}} = \frac{6ft}{0.48ft/day} = 12.5 \, days$$

$$\min t_r = \frac{L}{v_{x,\max}} = \frac{6\,ft}{4.8\,ft/day} = 1.25\,days$$

APPENDIX B

Nitrate-N Loss Calculations

30 ft Buffer and Maximum Retention Time

Length = 6 ft

Width = 4 ft

Saturated Thickness = 8 ft

Porosity = 0.2

Water Volume = $6 ft \times 4 ft \times 8 ft \times 0.2 = 38.4 ft^3$

$$38.4 ft^3 \left(\frac{28.3L}{1 ft^3}\right) = 1086.72 L$$

Initial Nitrate-N Mass = $14.0 mg/L \times 1086.72 L = 15214.08 mg$

Tree Uptake = 57 *mg-N/tree/day* × 12.5 *days* = 712.5 *mg-N/tree*

Final Nitrate-N Mass = 15214.08 mg - (712.5 mg-N/tree)×(5 tree rows) = 11651.58 mg

Final Nitrate-N Concentration = $\frac{11651.58mg}{1086.72L} = 10.7 mg/L$

Percent Change =
$$\frac{(14.0 - 10.7)}{14.0} \times 100 = 23.4\%$$

30 ft Buffer and Minimum Retention Time

Length = 6 ft

Width = 4 ft

Saturated Thickness = 8 ft

Porosity = 0.2

Water Volume = $6 ft \times 4 ft \times 8 ft \times 0.2 = 38.4 ft^3$

$$38.4 ft^3 \left(\frac{28.3L}{1 ft^3}\right) = 1086.72 L$$

Initial Nitrate-N Mass = $14.0 mg/L \times 1086.72 L = 15214.08 mg$

Tree Uptake = 57 mg-*N/tree/day* × 1.25 *days* = 71.25 mg-*N/tree*

Final Nitrate-N Mass = 15214.08 mg - (71.25 mg-N/tree)×(5 tree rows) = 14857.83 mg

Final Nitrate-N Concentration = $\frac{14857.83mg}{1086.72L}$ = 13.7 mg/L

Percent Change = $\frac{(14.0 - 13.7)}{14.0} \times 100 = 2.3\%$

66 ft Buffer and Maximum Retention Time

Length = 6 ft

Width = 4 ft

Saturated Thickness = 8 ft

Porosity = 0.2

Water Volume = $6 ft \times 4 ft \times 8 ft \times 0.2 = 38.4 ft^3$

$$38.4 ft^3 \left(\frac{28.3L}{1 ft^3}\right) = 1086.72 L$$

Initial Nitrate-N Mass = $14.0 mg/L \times 1086.72 L = 15214.08 mg$

Tree Uptake = 57 *mg-N/tree/day* × 12.5 *days* = 712.5 *mg-N/tree*

Final Nitrate-N Mass = 15214.08 mg - (712.5 mg-N/tree)×(11 tree rows) = 7376.58 mg

Final Nitrate-N Concentration = $\frac{7376.58mg}{1086.72L} = 6.8 mg/L$

Percent Change =
$$\frac{(14.0 - 6.8)}{14.0} \times 100 = 51.5\%$$

66 ft Buffer and Minimum Retention Time

Length = 6 ft

Width = 4 ft

Saturated Thickness = 8 ft

Porosity = 0.2

Water Volume = $6 ft \times 4 ft \times 8 ft \times 0.2 = 38.4 ft^3$

$$38.4 ft^3 \left(\frac{28.3L}{1 ft^3}\right) = 1086.72 L$$

Initial Nitrate-N Mass = $14.0 mg/L \times 1086.72 L = 15214.08 mg$

Tree Uptake = 57 mg-*N/tree/day* × 1.25 *days* = 71.25 mg-*N/tree*

Final Nitrate-N Mass = 15214.08 mg - (71.25 mg-N/tree)×(11 tree rows) = 14430.33 mg

Final Nitrate-N Concentration = $\frac{14430.33mg}{1086.72L}$ = 13.3 mg/L

Percent Change = $\frac{(14.0 - 13.3)}{14.0} \times 100 = 5.2\%$

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