

Does Management Intensive Grazing Protect Groundwater by Denitrification?

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Summary

Groundwater quality and gases were evaluated at four grazing paddocks and one conventionally cropped field. These results support the idea that denitrification actively mitigates groundwater nitrate contamination beneath management intensive grazing paddocks compared to conventional cropping. It is clear from the solute and dissolved gas composition of groundwater beneath the pasture that conditions were highly favorable for denitrification in groundwater under grazing and that a large portion of the nitrate that leached to groundwater was transformed to harmless N₂ gas. Similar patterns were not evident at the corn study site due to the absence of a sufficient supply of dissolved organic carbon (DOC) to fuel the denitrification reaction.

Introduction

By definition, sustainable agricultural practices have positive or very little negative impact on the environment. A lesson learned from "conventional" agriculture is that we cannot assume that all practices are benign. Whenever the natural holding capacity for a parcel of land is exceeded, we create the potential for negative consequences to the natural system. These negative impacts can degrade ecosystem health and function, reducing both the quality of rural lifestyle and the ability of the system to sustain agricultural activities over time. For example, concerns about non-point source water quality problems have been increasing nationwide. Although point sources are largely controlled, groundwater quality in

many areas continues to deteriorate, particularly where aquifers are shallow or underlie sandy soils and conventional, high input agriculture is practiced. This is the case for much of the North Central Region, including Central Wisconsin, an area experiencing agriculture-related degradation of groundwater quality. In Wisconsin, federal drinking water standards for nitrate-N are exceeded in about 10% of the private wells and in more than 40% of the private wells in some areas (Wisconsin Groundwater Coord. Council, 2000; UWSP Groundwater Center Database, Unpub. Data). Studies indicate that 90% of groundwater contaminants in Wisconsin result from agriculture (Shaw, 1994; Mechenich and Kraft, 1997). This contamination of groundwater affects rural private wells and small municipal wells with a cost to human and livestock health, and to the economic health of small communities for construction of replacement wells or nitrate removal facilities.

In an attempt to minimize agricultural impacts on the environment, much effort and money are invested nationally to develop and implement agricultural Best Management Practices (BMPs). Some BMPs successfully achieve environmental goals, whereas others do not. Studies conducted to evaluate BMPs recommended to protect groundwater in Central Wisconsin (e.g., fertilizer rate and timing, tillage management, etc.) indicate that current BMPs are not reducing contaminants in groundwater to levels consistent with federal drinking water standards (Saffigna et al., 1997; Osborn et al., 1990; Shaw and Turyk, 1992; Mechenich and Kraft, 1997; Stites and Kraft, 1997). Close hydrologic connection between surface and groundwater in the area promotes the exchange and movement of contaminants.

The role of Management Intensive Grazing (MIG)

It is desirable to find sustainable and profitable agricultural practices that can reduce impacts to groundwater in environmentally sensitive areas. Our contention is that annual cropping in many of these landscapes has exacerbated leaching, because annual crops cannot capture water or nutrients over as long a period nor in as great a quantity as many perennial crops (Bergstrom, 1987; Peterson and Russelle, 1991; Randall et al., 1997; Kelley and Russelle, 2000). MIG can be an economically viable form of dairy farming (Kriegl, 2000) that uses perennial plants within much of a farming system. One must recognize, however, that the intensity of nitrogen cycling is generally greater in grazed than non-grazed systems, thereby increasing the risk of nitrogen losses.

The concept of using MIG to reduce nutrient impacts to water quality is not a new one. It appears to be an agricultural option which has several components that may protect groundwater. Manure is distributed over the land, which if properly managed is always vegetated, allowing plants to quickly utilize nutrients in the dung and urine during the growing season. Grasses and legumes are the primary food source for the livestock throughout the grazing season (May - October), so fewer annual crops need to be grown as feed (Bobbe, 1994). This reduces nutrient inputs and eliminates pesticide inputs that make their way to groundwater. Many studies have shown that rotational grazing can reduce input costs (feed, fuel, machinery), improve animal health, and if done properly improve forage quality (Jackson-Smith, 1996; Tranel and Frank, 1991; Bender, 1997; Mann, 1997; UW-Madison, 1993). However, in MIG systems, manure is not always distributed evenly, and therefore nutrients contained in the manure and urine can be concentrated in areas within the paddocks (Mathews et al., 1996; Peterson and Gerrish, 1996; Russelle, 1996; Cropper, 1997). These areas of nutrient accumulation typically relate to location of water, lanes, and shade trees. As dairy farmers expand their use of MIG, many are interested in applying fertilizer to improve pasture production, thus creating the potential for similar environmental consequences as from conventional farming practices.

Denitrification

One way that natural or managed land can moderate nitrate accumulation in ground and surface water is through denitrification. Denitrification is the naturally occurring process by which nitrate is reduced by microorganisms to gases, primarily nitrous oxide (N₂O) and dinitrogen (N₂). Of these two gases, nitrous oxide is formed first and is an undesirable end product, because it acts as a 'greenhouse' gas and destroys stratospheric ozone. The final step in denitrification yields dinitrogen gas, which makes up about 78% of our atmosphere and is a benign end product.

The substrates for denitrification are nitrate and available energy compounds [usually carbon, although methane and reduced sulfur and iron compounds can play a role (Pedersen et al., 1991; Korom, 1992)],

and the organisms are active only when oxygen pressures are low. Nitrate disappearance from groundwater may be due to denitrification, but also occurs by immobilization (plant and microbial uptake) and a biotic fixation by condensation reactions (Groffman et al., 1996). Grassed and forested riparian zones are often recommended to reduce nitrate loading to surface water, because both can enhance denitrification. For example, Verchot et al., (1997) measured significant reductions of nitrate concentrations in groundwater as it moved from below a cropped field to below a grass buffer.

Denitrification rates can be quite high in groundwater, but can also be low or nonexistent (see Groffman et al., 1996, for several references). Many studies have found insufficient dissolved organic carbon concentrations to support denitrification (e.g., Hiscock et al., 1991), even when nitrate supply was adequate and oxygen levels were low. Denitrification rates from pastures are often higher than annual cropland (e.g., Bijay-Singh et al., 1989; Sotomeyer and Rice, 1996), but results depend on experimental conditions. Significant losses typically are confined to situations where water filled pore space in the soil is greater than 80% (Rudaz et al., 1999), which is rare in coarse-textured soils. Thus, one would not expect to find high denitrification rates in pastures on sandy soils, except in zones in or near the water table, under temporary wet conditions, and in areas affected by dung or hoof compaction.

Several investigators have found that 'patchiness' in energy substrate is typical under forests and riparian zones, resulting in very low denitrification rates in much of the matrix, but very high rates in small volumes or microsites where labile carbon is present (Parkin, 1987; Parkin et al., 1987; Nelson et al., 1995). These patches support microbial growth, which reduce oxygen concentrations, thereby facilitating anaerobic processes like denitrification. The distribution of fresh plant residues is often positively correlated with denitrification intensity in the field (e.g., Aulakh et al., 1984; de Cantazaro and Beauchamp, 1985; Parkin, 1987). Although denitrification rate and potential typically decline exponentially with depth into the soil (e.g., Weier et al., 1993; Luo et al., 1998), Jarvis and Hatch (1994) found greatly increased denitrification potential in subsoils under pasture compared to annual cropland. Under the conditions of their experiment, potential denitrification rate could be as high as 200 kg nitrogen per hectare, considering the entire 6-m-deep soil profile.

Jacinthe et al. (1998) found that these patches represented less than 1% of the aquifer weight. The most active patches in their study site were comprised of decomposing roots. Unlike pastures in humid environments, where shallow rooted (ca. 45 cm) forages like white clover and perennial ryegrass dominate, pastures in MIG are comprised of more deeply rooted grasses (orchard grass, tall fescue, reed canary grass, timothy, and smooth brome grass), with a small percentage of legumes (red clover, birdsfoot trefoil, alfalfa, and Kura clover). Root systems of these grasses can penetrate to 2.5 m or more, and alfalfa is well known for its extremely deep root system. In preliminary sampling, we found roots to 1 m in paddocks with the shallow groundwater table (Bestul farm) and to 1.8 m at another collaborator's farm (Onan farm). More complete reduction of nitrate to dinitrogen gas may be promoted at depth in the soil, in part because nitrous oxide cannot escape the soil rapidly and can be reduced further, making such losses of nitrogen more environmentally benign (Rolston et al., 1976).

In addition, the patchiness of excreta addition is a factor in pastures. Denitrification rates are typically increased by fertilizer application (Scholefield et al., 1991; Colbourne, 1992). Similarly, urine 'hotspots' [Freifelder et al. (1998)] on 10 to 15% of the pasture can contribute more to total denitrification than the remaining pasture area (Ruz-Jerez et al., 1994). Denitrification rate may also be affected by pasture management as indicated in a watershed study conducted by Valiela et al. (1997), in which they estimated that denitrification rates were 10 times greater in heavily used than in infrequently grazed pastures. Conversion of forests to pastures greatly increased nitrous oxide loss (Matson and Vitousek, 1990), but losses were higher in young pastures (less than 10-years-old) than in older pastures (Keller et al., 1993).

Objectives/Performance Targets

The primary objective is to determine whether denitrification is higher in soil and groundwater under MIG than annual cropping. We are focusing on coarse and medium-textured soils, where nitrate loading

potential is higher than for fine-textured soils.

Materials and Methods

Study Sites

All study sites were located in the Central Sands region of Wisconsin in the counties of Columbia, Portage, and Waupaca. This region is characterized by shallow depths to groundwater and medium to coarse textured soil, a combination that can result in groundwater that is susceptible to contamination. Data evaluated by the UW-Extension Central Wisconsin Groundwater Center in 2002 showed the percent of private wells that exceeded the federal drinking water standards for nitrate were more than 15% in Columbia and Portage Counties and approximately 10% in Waupaca County.

Four rotational grazing paddocks and one conventionally cropped field were evaluated in this study. Three of the paddocks (two at Bestul and one at Onan) were included in soil, groundwater, forage, and economic studies that were conducted between 1997 and 2000.

The Bestul Farm is located in Waupaca Co. There are two paddocks at this site that are included in this study; the west paddock is 2 hectares and the north/east paddock is 3.4 hectares. The soils below the paddocks are Plainfield and Richford medium textured loamy sand. The depth to groundwater below the west paddock is 1.2 to 1.8 m and 1.8 to 2.4 m below the north paddock. The paddocks were in conventional row crops until 1993, when they were seeded and managed as intensive grazing for 35 to 50 dairy cows and 15 to 20 heifers. Animals are grazed between April and November. Forage is supplemented with grain for the cows. Fourteen units of N/acre were applied on each paddock in 2002.

The Onan Farm is located in Portage County in an area of gently sloping topography. The study paddock is comprised of Rosholt coarse sandy loam soil with a depth to groundwater between 6 and 10.6 m. This producer has used managed intensive grazing for 35 to 50 dairy cows and approximately 20 heifers since 1994. The study paddock is 2.3 hectares. Grazing generally occurs from April to November; however, the study paddock had 30 animals over-winter during 2002/03. In addition to forage, the cows are fed approximately 5.4 kg of grain per day. Ten and 12 units of N/hectare were applied to the paddock in 2002 and 2003, respectively.

The Breneman Farm is located in Columbia County in an area of gently sloping topography. Depth to groundwater in the study paddock ranges from 1.2 to 2.4 m, with sandstone at approximately 3.5 m. The study paddock is 3 hectares. Grazing at this site occurs from April through November, and this paddock serves as an out-winter paddock for a portion of the winter. The 75 to 90 dairy cow operation shifted from a freestall conventional dairy to rotational grazing in 1993. Milk cows are fed an additional ration of grain daily. The Breneman Farm is part of Wisconsin's Discovery Farms program. These are farms that are being studied on a system-wide basis.

The Rambo dairy farm is located two miles east of the Bestul farm. The study site was a cropped 8 hectare field that was in corn in 2001, 2002, and 2003. The depth to groundwater is 2.4 to 5 m. Manure and inorganic fertilizers are applied annually. In 2002, 23,950 kg manure and 238 kg N fertilizer were applied to the field and in 2003 50,180 kg manure along with 57, 45, and 57 kg N fertilizer that were applied in April, May, and June, respectively.

Groundwater Gases

Miniature Groundwater Wells

Grid networks of miniature wells (mini-piezometers) were established in a paddock at the Bestul's MIG farm north/east site (n=91) and at the Rambo's conventionally cropped (corn) site (n=26) in spring of 2002 (Fig. 1). The mini-piezometers were constructed from polyethylene tubing (0.43 cm i.d., 0.63 cm o.d.). Well screens consisted of 8 to 10 lines of perforations 2.5 cm long which were created in four to five passes through a sewing machine. A retractable tempered stainless steel insertion rod was used to place the well screens at a depth 30 to 60 cm below the water table's position at the time of installation (to allow for variation in water table depth). After installation, the wells were recessed 10 to 15 cm,

beneath surface soil plugs, to avoid nuisance by grazing animals or disruption during harvest.

Grid nodes were established at approximately 10.7 m spacings, along 12 east-west transects, distributed at 30.5 m intervals in the Bestul north/east paddock. Grid nodes were established at approximately 15.2 m separations along five north-south transects distributed at approximately 30.5 m intervals at the Rambo site. Mini-piezometers (n=3) were also established in a radial pattern at each of six dung and six urine patches identified within the Bestul north/east paddock in August 2002. Replacement wells were installed as necessary at each experimental site to accommodate attrition due to overwintering and soil cultivation (Rambo's). Vertical and horizontal coordinates of mini-piezometers at each site were incorporated into a GIS.

Soil Gas Wells

Soil gas wells were established in the rooting zone to evaluate the aeration status and confirm the presence of aerobic conditions within the unsaturated zone above the capillary fringe/water table environment. Wells were installed at three depths (10, 20 and 30 cm) at each grid node. Well construction was the same as for mini-piezometers.

Sample Collection and Analysis

Groundwater samples were collected using a peristaltic pump attached directly to the mini-piezometer. Soil gas samples were collected into a syringe via suction after three well volumes had been withdrawn from the well.

Samples for dissolved solids analyses were field filtered (0.45 µm nitrocellulose membrane filter), chemically preserved (sulfuric acid for nutrients, nitric acid for metals), and stored at 4°C for analysis in the laboratory. Field measurements, including water temperature, pH, specific conductance, dissolved oxygen and oxidation reduction potential, were obtained using an YSI 650 DMS sonde (YSI, Yellow Springs, OH). Total dissolved gas pressure (D'Aoust and Clark, 1980) (PT) was measured in the field using a total dissolved gas pressure sensor, calibrated using an air equilibration procedure. A sealed flow-through cell, connected to the outlet of the peristaltic pump, was used to obtain sonde and PT readings from the mini-piezometer samples without exchanging gases with the atmosphere.

Dissolved gas samples were collected in the field directly from groundwater using pumping induced ebullition (PIE) (Browne, 2004). The PIE gas samples were maintained in gas-tight 10-mL syringes (summer 2002) or were kept over-pressurized in pre-evacuated septum sealed 15-mL serum bottles (summer 2003) until dry gas mole fractions (X) could be determined by gas chromatography in the laboratory. Mole fractions of Ar, N₂, and O₂ measurements were performed using high purity helium carrier gas and a pulse discharge detector (PDD) in helium ionization mode (Wentworth et al., 1994). Chromatographic conditions (columns, temperatures, and carrier gas flow rates) for Ar, N₂ and O₂ were similar to those reported in Busenburg and Plummer (1992). Mole fractions of N₂O, CH₄, and CO₂ were measured using a gas chromatograph equipped with electron capture (ECD) and flame ionization (FID) detectors. Instrument configuration and operating conditions were modified from Coolman and Robarge (1995) and Lotfield et al. (1997). Coefficients of variation for detection of the target gases within ambient air are less than 2% (UWSP, Dissolved Gas Laboratory). The gas chromatographs were calibrated with a reference standard air from the National Oceanic and Atmospheric Administration and using commercial N₂O, CH₄, and CO₂ blends.

Dissolved gas concentrations at field water temperature were obtained by Henry's Law calculation: $[1] [C] = KH (X/Fc) * (PT - w)$ where C is the concentration of gas in mol L⁻¹; KH is a gas specific Henry's Law constant (mol L⁻¹ atm⁻¹); PT and w are the total dissolved gas pressure (atm) and water vapor pressure (atm), respectively; and Fc is a unitless gas-specific coefficient that adjusts for fractionation during the PIE sample collection process (values of Fc are reported in Browne, 2004).

Denitrified N in Groundwater

The dissolved concentrations of N₂ and Ar gas in groundwater were used to estimate the excess N₂ produced by denitrification (X_sN₂) (Vogel et al., 1981; Martin et al., 1995). The atmosphere and denitrification were assumed to be the only sources of N₂ in groundwater. The amount of X_sN₂ in each

sample was estimated from the difference between the N₂ concentration in the sample and the N₂ concentration in air-saturated water at the temperature of groundwater recharge (Bolke and Denver, 1995). The apparent temperature of groundwater recharge was determined from the measured concentrations of dissolved Ar (Busenburg et al., 1993). The potential contribution of excess air (supersaturation by dissolution of entrapped air bubbles during recharge; Heaton and Vogel, 1981; Holocher et al., 2003) to dissolved Ar and N₂ was checked by iteratively solving Henry's law expressions for the excess air amount providing the same apparent recharge temperature for both the Ar and air-saturated N₂ concentrations. These calculations revealed excess air to be negligible in our samples; thus, apparent recharge temperatures were based on the measured dissolved Ar concentration (and corresponding corrected N₂ concentration), assuming equilibration with general atmosphere (i.e., air-saturated water).

Values of the initial total concentration of NO₃⁻ in groundwater were reconstructed from the sum of measured NO₃⁻ and XsN₂ concentrations in each groundwater sample:

$$\text{Total NO}_3^- \text{ (mg-N L}^{-1}\text{)} = \text{NO}_3^- + \text{XsN}_2 \quad [2]$$

Denitrification reaction progress in groundwater was gauged by the following ratio:

$$\text{DenitrifiedN(\%)} = [\text{XsN}_2]/([\text{NO}_3^-]+[\text{XsN}_2]) \times 100 \quad [3]$$

Groundwater Monitoring Wells

Multi-port monitoring wells that allow groundwater sampling at several depths at one field location were used on the Onan, Bestul, Breneman, and Rambo farms. Six multiport monitoring well nests were installed at all study plots with three wells installed in each well nest. The wells were constructed from 2-cm PVC with 0.3-m screens. The shallowest screen was placed with the lower half of the screen just into the water table. This design provided a monitoring network that accommodated fluctuations in the water table that are common to central Wisconsin, allowing us to obtain samples from the top of the saturated zone.

Wells were sampled in February and monthly from May through September. Analyses included NO₂+NO₃-N, NH₄-N, and Cl. Chloride is frequently used as a conservative tracer. Soluble reactive phosphorus was also measured in samples several times per year. Samples were collected using a peristaltic pump, field filtered, acidified and transported on ice to the state-certified Water and Environmental Analysis Lab at the University of Wisconsin-Stevens Point. Samples were analyzed by flow injection method.

Soil In-field Experiments

During 2002, soil cores were obtained from the pastures three times and from the corn field twice. One set of cores was collected from each site in November 2003. Cores were taken to a depth of 1.2 m, except where subsurface conditions (i.e., gravel, dryness, or saturation) caused refusal of the coring device. Two 4.1-cm diam. cores were taken under 4 to 6 replicates of dung pats, in suspected urine spots (based on herbage growth and appearance), and in background areas. Soil was divided into 15- to 30-cm-deep increments, the two cores were bulked by depth, crushed and mixed, and sub-sampled into plastic bags. Sub-samples were stored in coolers until they could be refrigerated. Soil moisture, pH, inorganic N, and dissolved organic carbon (DOC) were determined on all samples. Additional soil cores were taken to determine dry bulk density of the soil at each site.

Larger cores (7.5-cm) were taken in six locations of one grazed field and the corn field after harvest in fall 2002. These were stored in PVC sleeves in a refrigerator and were sampled by horizon for the presence roots, mottling, and other regions where DOC supply may be elevated.

Field-moist samples were analyzed, because air drying causes large increases in water soluble carbon and denitrification potential (e.g., Bijay-Singh et al., 1988). Inorganic N analysis was conducted via flow injection (Sechtig, 1992; Switala, 1993) after extraction with 2 M KCL. Water soluble carbon was extracted (Bijay-Singh et al., 1988) and analyzed on a Dohrmann analyzer. Soil water content was

determined gravimetrically after drying at 105 C. Separate cores were taken for soil bulk density.

Intact Soil Core Experiments

Because we were unable to detect the expected differences in soil N and DOC distribution from soil cores taken in the pastures, we added a new experimental approach to this research. We obtained more than 60 intact, 6-cm diameter soil cores in plastic sleeves from one paddock on the Bestul farm on two occasions, 25 June and 20 November 2003. Cores were stored vertically at room temperature and leached occasionally with tap water over several weeks to reduce variability. Cores were cut to about 58 cm in depth before the bottoms were capped and sealed. The first incubation experiment began 12 January 2004 and the second began 15 March 2004.

Nanopure water was added to the deepest 7 to 12 cm of each core to establish high moisture conditions the week before treatment application to mimic a shallow water table. Complete saturation was not achieved, as evidenced by soil water content measurements and visual presence of air-filled pores. Tubes were taped to exclude light and minimize algae growth. Air temperature was maintained at about 15 C.

Treatments consisted of controls (40 mL deionized water), fresh dairy cow urine (28 mL mixed with 12 mL deionized water), or fresh dairy cow feces (113 g fresh mass mixed with 40 mL deionized water to make a slurry). These application rates roughly mimic in situ deposition rates by dairy cattle.

Immediately after treatment application, a subset of tubes was closed and air was pumped through the headspace (about 100 cm³/min, or 10 to 20 headspace volumes per hour) and then through two phosphoric acid traps to capture volatilized ammonia. The remaining tubes were left open to the atmosphere of the growth chamber.

During the first experiment, we noted that the cores were drying more quickly than anticipated, so we simulated a 2-cm rainfall event on Day 4 by adding water four times in 14-mL increments over 2 h.

Soil cores were destructively sampled on several dates during the incubation. Vegetation and the dung layer (when present) were removed and the soil was divided into three depth increments. Depth intervals were 0 to 15 cm, 15 cm to the depth of the saturated zone, and the saturated zone. Thickness of the nearly saturated zone varied among tubes from 8.5 to 26 cm in the first experiment (mean 16.7 cm) and from 8 to 21 cm in the second (mean 11 cm).

Soil pH, inorganic N, and DOC concentrations were determined on moist subsamples of each depth increment. Inorganic N was determined by flow injection analysis of 2M KCl extracts (Sechtig, 1992; Switala, 1993). Soil DOC was determined on filtered (0.22 µm) water extracts on a Dohrmann analyzer. Soil N data were adjusted to a soil dry mass basis after determining soil water content gravimetrically on separate subsamples. Dry bulk density of each depth increment was determined based on volume, wet mass at sampling, and measured soil water content.

Phosphoric acid traps were analyzed by flow injection analysis for NH₄, mass of NH₄-N was calculated from the volume of acid, and results were summed over the two traps for each core.

The Ideal Gas Law was used to convert measured volume concentrations of trace gases to mass units and to correct to standard conditions (Holland et al., 1999), and then corrected for dissolution of the gases in soil water (Groffman et al., 1999).

The number of replicates varied from 2 to 6 for each of 12 to 13 NH₃ sampling times, 6 to 7 trace gas sampling times, and 6 to 8 whole core sampling times. Standard analysis of variance techniques were used to detect differences among treatments, soil depths, and sampling times.

Results and Discussion/Milestones

Surface Soil Aeration

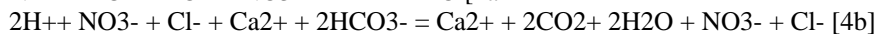
Soil gas samples collected from the rooting zone during dry periods showed that aerobic conditions were generally present in the surface soil at both experimental sites under field capacity moisture conditions. The partial pressure of oxygen generally remained above 0.20 atm at all locations sampled and CO₂ concentrations were generally less than 0.01 atm. Thus, low oxygen status conducive to denitrification was not detectable within the soil atmosphere samples collected from the macropores of the rooting zone at either study area. The fairly open architecture of soil pores in the coarse sandy soil, at both the pasture and corn study sites, appeared to allow rapid gas exchanges between the rooting zone and the general atmosphere levels. This suggests that the air-filled pore space may also provide an important mechanism for exchange of atmospheric gases to and from the water table environment.

The apparent absence of reducing conditions within the rooting zone based on the biogenic gas composition of the soil atmosphere suggested that denitrified N gases (N₂, N₂O) encountered within groundwater generally would not be generated first within the rooting zone and then leached to groundwater. Thus, the occurrence of denitrified N gases in groundwater most likely primarily reflects the reduction of NO₃⁻ after leaching to groundwater.

However, the possibilities of leaching dissolved denitrified N gases from the unsaturated zone due to (1) sustained or transient denitrification progress within micropores of soil aggregates [Tiedje, 1988] or the poorly ventilated capillary fringe or (2) transient denitrification pulses associated with the infiltration of water within and beneath dung and urine patches can not be fully eliminated based on the existing soil gas data. These distinctions would require installation of soil moisture access tubes at selected locations for soil moisture depth profiles, collection of soil gas samples from the rooting zone during rainfall or snowmelt events, and installation of deeper soil gas wells for monitoring of biogenic gases within the unsaturated zone immediately within and above the capillary fringe.

Groundwater Chemistry

The dissolved solids in groundwater beneath both the pasture and corn study areas ranged from very dilute to moderately concentrated. The results for specific conductance, acid neutralizing capacity, dissolved inorganic carbon and pH suggest a comparable inorganic ionic composition between the sites. However, the slightly higher specific conductance and lower ANC (acid neutralizing capacity aka alkalinity) and DIC (dissolved inorganic carbon) concentrations at the corn study area are consistent with the idea the bicarbonate anions generated naturally by dissolution of carbonates (dolomite) have been partially depleted by strong acids associated with fertilizer salts (e.g., eq. [4], nitric acid generated by nitrification reactions).



Despite apparent similarities in inorganic chemical composition, dissolved organic carbon (DOC) and O₂ concentrations in shallow groundwater revealed a strong biogeochemical contrast between the two study areas. DOC concentrations were significantly higher and ranged more broadly at the pasture site than at the corn site due to the leaching of dissolved organic matter from dung and urine patches. Consistent with greater availability of DOC as a potential electron donor and microbial food source, groundwater O₂ concentrations were significantly lower beneath the pasture study area than the corn site. The percent O₂ saturation (relative to air equilibration at field temperature) levels show that the differences were attributable to oxygen consumption rather than the temperature dependence of O₂ solubility. The absence of more complete depletion of O₂ may reflect an exchange of gases to and from the general atmosphere through the air-filled pore space of the unsaturated zone.

Fueled by leaching of soluble organic matter, heterotrophic respiration in the water table environment will cause an increase in the concentration of dissolved carbon dioxide in groundwater. Accordingly, comparison of the dissolved CO₂ concentrations beneath pasture and corn revealed somewhat higher concentrations of CO₂ in groundwater beneath the pasture consistent with its higher DOC level. However, CO₂ concentrations were apparently too high at many locations within both study areas to be explained solely by aerobic heterotrophic activity. Under strictly aerobic respiration, the depression of dissolved oxygen should have been accompanied by a roughly 1:1 stoichiometric increase in dissolved

CO₂ (i.e., if one mole of O₂ consumed produces roughly one mole of CO₂). Yet at both locations, the dissolved CO₂ concentrations were substantially in excess of the apparent O₂ deficit in groundwater.

Under anaerobic conditions, the upper limit of CO₂ production is no longer bounded by the solubility of dissolved O₂ but is controlled by the availability of other electron acceptors (NO₃⁻, Fe³⁺, Mn⁴⁺, SO₄²⁻, CO₂). Thus, CO₂ has the potential to accumulate to concentrations well above the saturation CO₂ concentration corresponding to the consumption of O₂ in air-equilibrated water. Despite the presence of measurable O₂ at most locations, evidence of anaerobic conditions beneath the pasture (1) included an accumulation of CH₄ produced by methanogens to concentrations well above its solubility under air-equilibration, elevated concentrations of dissolved (2) Fe²⁺ and (3) Mn²⁺ reflecting the reduction of Fe and Mn oxides in the solids (data not shown), (4) an accumulation of N₂O gas (an intermediate in denitrification) greatly above its solubility under air-equilibration, and (5) total concentrations of N₂ gas above the N₂ concentration in air-saturated water at the apparent recharge temperature of the sample. Evidence of anaerobic conditions beneath the corn was limited to elevated N₂O and total N₂ concentrations and was therefore less striking. It is important to note, however, that the accumulation of N₂O is an ambiguous indicator of anaerobic conditions because N₂O can be produced by both nitrification (an O₂ requiring reaction) and denitrification reactions (Davidson et al. 2000).

At neither study area, was the accumulation of the products or consumption of reactants by anaerobic processes fully sufficient to explain the excess of CO₂ in groundwater. Thus, it is probable that some of the apparent excess of CO₂ was derived by the reaction of strong acids with bicarbonate salts in groundwater (e.g., reaction with nitric acid from nitrification reactions, see eq. [4], above).

The apparent co-occurrence of both aerobic and anaerobic indicators (albeit weakly at the corn study area) within groundwater at both locations deserves some consideration. One explanation is that the anaerobic processing of DOC in groundwater proceeds more rapidly at times than CO₂ and O₂ can be exchanged to and from the soil atmosphere within the aerobic unsaturated zone. In the pasture study area, pulses of soluble organic matter from dung and urine patches could periodically produce short term anaerobic responses which subside after fresh substrate has been consumed. Diffusive and advective pumping of O₂ from the air-filled pore space of the unsaturated zone could then later resupply O₂ and reset aerobic conditions. In the absence of apparent sources of pulses of soluble organic matter, the subtle combination of aerobic/anaerobic indicators is more difficult to explain at the corn study site. Further, study is needed to clarify the transient anaerobic/aerobic conditions and processes in the water table environment beneath pasture environments and to elucidate whether such conditions/processes are also happening beneath conventional crops.

The distributions of dissolved N and P provide an additional line of evidence supporting the importance of soluble organic matter from dung and urine patches in nutrient cycling beneath the pasture study area. At the corn study site high concentrations of dissolved N in groundwater were comprised almost exclusively of inorganic N as NO₃-N, reflecting an excess of N from fertilizer salts in the N cycle. However, beneath the pasture, concentrations of NO₃-N were much lower, dissolved organic nitrogen (DON) comprised a much greater share of dissolved N, and there was a greater accumulation of NH₄⁺. (The presence of high DOC and lower O₂ concentrations at the pasture study area may inhibit the formation of NO₃⁻ from NH₄⁺ by nitrification, allowing it to accumulate to higher levels in groundwater at the pasture site.) These patterns are consistent with a greater role of organic matter in the N cycle at the pasture site. Similarly, although the total dissolved concentrations of P in groundwater were somewhat similar at the two study areas, the distribution of P was dominated to a greater degree by dissolved organic P (DOP) at the pasture study area than at the corn study area.

Groundwater Denitrification

Concentrations of N₂ (X_sN₂) in excess of the amount contributed by equilibration with the general atmosphere during groundwater recharge can be calculated as follows:

$$X_s N_2 = \text{Total } N_2 - \text{Recharge } N_2 \quad [6]$$

Here “Recharge N₂” represents the N₂ concentration in air-saturated water at the apparent temperature of recharge (Tr) based on the measured Ar concentration and “Total N₂” represents the total N₂

concentration measured in the groundwater sample. To obtain “Recharge N₂”, the Henry’s Law constant for N₂ at Tr was used to compute the concentration of dissolved N₂ contributed by the partial pressure of N₂ in air (~0.2095 x 0.965 atm):

$$\text{Recharge N}_2 = K_{\text{Tr}_H, \text{N}_2} * P_{\text{N}_2} \quad [7]$$

Based on the XsN₂ measurements, results suggest (1) that the dissolved concentration of denitrified N as N₂ ranged from 0 to roughly 5 mg-N L⁻¹ across both study areas and (2) that concentrations of denitrified N based on XsN₂ were similar in groundwater at both study areas. However, at the pasture study area, concentrations of XsN₂ were similar in magnitude to the measured NO₃⁻ concentrations. Thus, total NO₃⁻ concentrations reconstructed by eq. [2] were generally more than double the measured NO₃⁻ concentrations in groundwater beneath the pasture. In contrast, at the corn study area, concentrations of XsN₂ were much smaller than measured NO₃⁻ concentrations and were a small contributor to total NO₃⁻.

Only a small percentage of the NO₃⁻ leached to groundwater at the corn site was converted to N₂ gas in the near water table environment. Three factors potentially inhibit an efficient conversion of NO₃⁻ to N₂ gas at the corn study site. First, the electron donation capacity of DOC is limited due to the relatively low concentration of DOC in groundwater. Second, the electron accepting capacity of the available NO₃⁻ may greatly exceed the electron donating capacity of the DOC present in groundwater. For example, assuming as an upper bound that each mole of DOC can potentially donate 4 moles of electrons, approximately 0.8 moles of NO₃⁻ could be reduced per mole of DOC in groundwater. On this basis, 1 mg L⁻¹ of DOC could potentially reduce only 0.93 mg L⁻¹ of NO₃⁻ to N₂ gas; thus, comparison of the NO₃⁻ and DOC concentrations shows that the available NO₃⁻ probably greatly exceeded the reducing power of DOC at the corn study site. Under such conditions, Chapin et al. (2002) suggest that N₂O, an intermediate product of denitrification, will potentially accumulate to high levels, a condition which is consistent with the high N₂O concentrations observed for the corn study. (However, an alternate plausible explanation for the high N₂O may be its accumulation as a byproduct of nitrification [Davidson et al. [2000]). Third, the oxygen levels in groundwater at the corn study site may inhibit denitrification.

In contrast, a much larger percentage of the NO₃⁻ leached to groundwater was converted to harmless N₂ gas in the near water table environment at the Bestul’s north/east pasture study area. Based on the same calculus used for the corn study area, the high concentrations of DOC present in groundwater beneath the pasture likely represent a sufficient supply of available electrons to reduce all NO₃⁻ to N₂ gas. However, complete conversion of all NO₃⁻ is probably still somewhat inhibited by the residual dissolved O₂ present in groundwater beneath the pasture.

Groundwater denitrification was readily quantified at two contrasting study areas based on the accumulation of excess N₂ in groundwater. It is clear from the solute composition and dissolved gas composition of groundwater beneath the Bestul north/east pasture that conditions were highly favorable for denitrification in groundwater under management intensive grazing and that a large portion of nitrate that leached to groundwater was transformed to harmless N₂ gas. Similar patterns were not evident at the corn study site due to the absence of a sufficient supply of DOC to fuel the denitrification reaction. Further, it’s clear from comparing total NO₃⁻ concentrations (XsN₂ + NO₃⁻) at the two study areas that leaching to groundwater is much lower under managed intensive grazing than conventional cropping with corn. These results support the idea that denitrification actively mitigates groundwater nitrate contamination beneath management intensive grazing areas compared to conventional cropping.

Nitrogen Budgets and Groundwater Monitoring Wells

Nitrogen budgets were calculated for each study paddock and the cropped field. Calculations for inputs to the grazing paddocks included the number, duration, types of animal (adjusted for size, supplemental feed and loss in milk), addition of N (inorganic fertilizer and land spread manure), precipitation, and dry deposition. Grazing paddock nitrogen budget outputs included estimated N removal in forage by animals during grazing, and N losses to the atmosphere (ammonia and denitrification loss at 25% and 6% of the total N inputs, respectively). The amount of forage removal was based on the results of a previous study at the Bestul and Onan paddocks. That study estimated forage quantities before and after the paddocks were grazed and analyzed the N (crude protein) content in forage samples. The cropped field inputs

included the addition of fertilizer, land spread manure, precipitation, and dry deposition and outputs from silage removal and N losses to the atmosphere.

Variability occurred between the sites with stocking densities, particularly when out-wintering animals was practiced in the study paddock. Predictably, the out-wintered paddocks also had the greatest residual nitrogen. In 2003, the amount of nitrogen added to and removed from the Bestul paddocks was nearly balanced. At the Rambo field, in 2002 there was less N added to the land than was removed in the harvest, but in 2003 there were more than 112 kg/ha of N added than was removed by the crop. This was primarily due to a larger application of manure in 2003.

Average N concentrations in the groundwater monitoring wells showed a good relationship to the amount of residual N calculated in the N budget in 2002, with an r value of 0.74 in 2002. However, in 2003 the relationship between the residual N and groundwater concentrations was minimal. This difference may be due to the inconsistent movement of N to groundwater depending upon the amount of precipitation in a given year. During drier years with less groundwater recharge, residual N builds up in the soil, moving to groundwater during subsequent recharge events.

In central Wisconsin, groundwater background concentrations are considered to be less than 1 mg L⁻¹ for NO₃ and 2 mg L⁻¹ for Cl. Concentrations of NO₃ in groundwater ranged from 0.5 to 47.8 mg L⁻¹ from all of the wells at all of the sites. Concentrations of NO₃ were below the drinking water standard (10 mg L⁻¹) in most of the samples collected from the Bestul north/east, Bestul west, and Breneman paddocks. However, the Breneman site had several outlier elevated concentrations. Greatest concentrations were measured in groundwater below the Rambo and Onan sites. A similar pattern was observed with Cl concentrations below the grazing paddocks. These concentrations ranged from 0.5 to 45 mg L⁻¹. Background groundwater chloride concentrations in this region are generally near 2 mg L⁻¹, demonstrating that there are impacts to groundwater from management intensive grazing. However, this large range also reveals the non-uniform nature of the contamination below these systems.

Soil In-field Experiments

High variability was evident in data from field cores. There were few statistical differences among sampling locations and sampling dates that were consistent. In each pasture, higher NO₃ concentrations were present under putative urine spots than other treatments on at least one sampling date. Differences among sampling dates were present under corn (Rambo field) and NO₃ concentrations tended to be smaller under corn than under pasture, at least on some dates. Results of DOC concentrations were more variable, with no differences among sampling times at any site and minor differences among treatments in two pastures.

In the large-diameter soil cores, root mass was greater under pasture than under corn for the uppermost sampled horizon, but no differences were noted at deeper depths. We had hypothesized that soil DOC would be related to visible horizon differences (mottling, old animal burrows, etc.), but we found no relationship. There was no difference in the depth distribution of soil DOC under corn and pasture.

Intact Soil Core Experiments

Soil water content varied during each experiment, but averaged 40 to 45%, 50%, and 60 to 65% water-filled pore space for the 0 to 15, 15 to ~40, and >~40 cm depth increments. Denitrification is increasingly likely when water-filled pore space exceeds 60%, as long as both NO₃ and DOC are present. Although all soil samples were analyzed for DOC, the results showed no effect of treatment, sampling time, or depth in either experiment. This was unexpected, as others had noted rapid increases in DOC after urine application (Shand et al., 2000). A later report by the same group indicated that synthetic sheep urine caused much larger changes in soil solution nutrient composition, including DOC, than natural sheep urine (Shand et al., 2002).

The control cores showed no appreciable changes in soil pH, inorganic N content, or gas evolution during either experimental run. The same was true for the dung application, except that trace gas evolution was twice or more than from the control cores. Methane evolution, in particular, was evident immediately after dung application. This can be expected, because dung contains high amounts of

microbially available C substrates, and because oxygen levels are low due to high moisture content. Dung pats in Denmark released CH₄ for 10 to 18 days in the field, but CH₄ production from dung in pastures was estimated to be less than 4% that of stored manure (Holter, 1997). Yamulki et al. (1999) found that net release of CH₄ from pastures was small relative to sources such as enteric fermentation in cattle. Greater CO₂ evolution from dung was likely due to microbial respiration, whereas the initial release of CO₂ with urine application was likely due to bicarbonates contained in urine.

Application of urine caused a rapid increase in soil pH in both the 0 to 15 and 15 to ~40cm depth increments. This is due to rapid hydrolysis of urea to ammonia. As ammonium was oxidized to nitrate, soil pH declined because two moles of protons are produced per mole of NH₄ oxidized. Thus, by the end of the month-long incubation, soil pH was 0.5 to 1 unit lower in the top two horizons than the control cores. This has been seen in field experiments (Vallis et al., 1982) and the changes that occur are related to the amount of urea + NH₄ applied in urine and the pH buffering capacity of the soil. Increased soil pH enhances NH₃ volatilization from urine spots. Total NH₃-N loss averaged 0.1, 2.5, and 18.8 mg N in the control, dung, and urine treatments in the second experiment, respectively. Ammonia loss from urine represented 13% of the maximum NH₃ content of the 0 to 15 cm soil layer. Lower NH₃ losses in the first experiment may be attributable to deeper infiltration of urine in the soil, as evidenced by higher NH₄ contents below 15 cm in the first than the second experiment.

Soil nitrate contents increased beginning 7 to 10 days after urine application. This response is also typical of what has been observed in the field (Shand et al., 2002). There were no appreciable changes in NO₃ contents in the dung or control cores, nor in the deepest depth of the urine cores. Even where NH₄ was present in the deepest increment under urine in the first experiment, little NO₃ accumulated. The low gas-filled pore space in this zone would have inhibited NH₄ oxidation and enhanced conversion to N₂O and other products during partial NH₄ oxidation and reduction of NO₃.

Nitrous oxide-N losses over 4 weeks were 0.5 mg N in the control, 1.8 mg N in the dung treatment, and 5.4 mg N with urine in the second experiment. Nitrous oxide loss comprised about 3% of the total accumulated NO₃ at the end of the experiment, well within the ranges reported in the literature. However, incubations were not sufficiently long to determine total N loss as N₂O, nor do we know how much NO or N₂ was lost during denitrification. It is possible that these compounds comprised a significant proportion of total gaseous N loss.

No leaching of NO₃ out of these cores occurred, because the base was sealed to permit a water table to be maintained. Under field conditions, NO₃ formed in the upper part of the soil profile would be subject to uptake by plants and leaching to the water table in these permeable soils. Given the evidence in these experiments and in the literature for high denitrification rates under urine spots, we suspect that leaching of NO₃ and DOC to the water table would result in rapid denitrification.

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Impact of Results/Outcomes

Groundwater denitrification was readily quantified at two contrasting study areas based on the accumulation of excess N₂ in groundwater. It is clear from the solute composition and dissolved gas composition of groundwater beneath the Bestul north/east pasture that conditions were highly favorable for denitrification in groundwater under management intensive grazing and that a large portion of nitrate that leached to groundwater was transformed to harmless N₂ gas. Similar patterns were not evident at the corn study site due to the absence of a sufficient supply of DOC to fuel the denitrification reaction. Further it's clear from comparing total NO₃⁻ concentrations (XsN₂ + NO₃⁻) at the two study areas that leaching to groundwater is much lower under managed intensive grazing than conventional cropping with corn. These results support the idea that denitrification actively mitigates ground water nitrate pollution beneath management intensive grazing areas compared to conventional cropping.

Residual N calculated from N budgets for the study areas and groundwater nitrate concentrations showed a fairly strong relationship to one another. Although management intensive grazing generally results in less nitrate contamination of underlying groundwater than some conventional agricultural practices, it is

possible to overload the capacity for mitigation and/or denitrification of N by over-application of fertilizer or overloading the system with manure from practices such as out-wintering animals. These results substantiate the importance of creating and following nutrient management plans with management intensive grazing systems as well as other agricultural practices.

It is clear from the soil sampling and intact soil core experiments that soil inorganic N concentrations can be substantial in a pasture after urine is applied, but that little accumulation occurs under dung pats. Both ammonia and nitrous oxide losses were large after urine application to the intact cores. The intact cores allowed more precision, while maintaining some of the inherent soil variability present in the field. Patterns of inorganic N content were readily traceable over time with this method. These results support the field observations of active denitrification activity in shallow ground water under pasture.

Economic Analysis

The economic impact of management intensive grazing systems is enhanced compared to conventional cropping. Groundwater is protected by the transformation of nitrate into harmless N₂ gases when MIG practices are employed. This protection of groundwater is a vital component to the long term economic viability of the environment. Without the denitrification process that results from MIG systems, conventional cropping cannot provide the same safeguards to the ecosystem.

Publications/Outreach

This denitrification study was discussed at the Onan and Bestul farms at pasture walks in June and July 2003. Participants included farmers and agency personnel, and a group of 25 individuals from around the world that were participating in an International Watershed Management Seminar through UWSP. Presentations have been made to professional audiences at the Wisconsin Chapter of the American Water Resource Association Annual Meeting, American Society of Agronomy meetings, Denver, CO., and the Minnesota-Wisconsin Nutrient Management Research and Planning Workshop for Grazing Systems, River Falls, WI.

Farmer Adoption

No study was conducted for this grant regarding Farmer Adoption.

Areas Needing Additional Study

Conditions prevalent at the Bestul's north/east grazing study area may not be representative of conditions at other management intensive grazing farms. This study should be expanded to include a larger population of sites under different geophysical environments and pasture management regimes. The transient conditions and processes promoting denitrification in the water table environment should be examined in more detail by tracking denitrification over time at selected locations. The importance of the exchange of soil gases from the unsaturated zone with the gases in the water table environment should be evaluated by performing detailed depth profiles of soil gas composition and water chemistry at selected sites. Attempts should be made to explore, characterize and explain the spatial variation and scale of conditions affecting groundwater denitrification within paddocks

Given the losses of N₂O found in the intact core experiment, there is a need to determine all products of denitrification (N₂O, NO, N₂) after urine application. This will require application of ¹⁵N labeled urine to differentiate between atmospheric N₂ and N₂ from denitrification. Using tracer methods, one could determine the effect of soil pH buffering capacity, dissolved organic carbon (DOC), water filled pore space, and other factors on total denitrification of urinary N.

The DOC measurements were highly variable and appeared to be affected by the day of analysis, so we

do not have confidence in them. Urine-induced DOC release from soil organic matter has been reported in the literature, but it is quite sensitive to urine composition (Shand et al., 2002). This is an area of research that will require better methodology.

The practice of out-wintering animals on management intensive grazing paddocks may impact groundwater and surface water quality by the significant inputs of urine and dung over a relatively long time period during a phase when the ground is not vegetated. This practice should be further assessed to obtain recommendations that may have lesser environmental impacts.