

# Considerations for the mitigation of nitrate contamination: stable isotopes and insights into the importance of soil processes

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## ABSTRACT

Nutrient management is widely promoted to minimize the impact of intensive fertilizer use on groundwater quality, however watershed-scale stable isotope studies in eastern North America suggest nitrogen transport to groundwater is dominated by non-growing season fluxes derived principally from the mineralization and nitrification of soil organic matter. In the current field scale study,  $\delta^{15}\text{N}$  ratios of nitrate in tile drain effluents from experimental potato plots treated with 300 kg/ha ammonia nitrate and those with no fertilizer both average +4.7‰, close to the +4.0‰ ratios observed in soils of the same plots, and distinct from values near 0‰ for inorganic fertilizer. A source apportionment model using  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in nitrate suggests that even with heavy fertilizer application, less than 10% of non-growing season N flux is derived from direct leaching of fertilizer, the remainder representing N from various sources, including residual fertilizer that has been assimilated into the broader soil organic matter pool and subsequently released via mineralization and nitrification. Factors controlling these losses could be as closely related to cropping practices as initial N application rates, providing potential opportunities for more efficiently utilizing N available in the soil profile and reducing initial N application rates.

**Key words** | agriculture, groundwater, nitrate, potato, stable isotopes

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## INTRODUCTION

Global efforts to provide a sufficient food supply to meet the needs of a rapidly growing population have depended on the expansion and intensification of agricultural production. These efforts have been accompanied by increases in the widespread and intensive use of inorganic (chemical) fertilizers and manures and have been accompanied by a progressive degradation of groundwater (GW) and surface water (SW) in many regions (Galloway *et al.* 2004; Townsend & Howarth 2010). In response, minimization of N inputs has been widely promoted. Comparatively less attention has been devoted to the complex role that agricultural soils and cropping practices play in the overall cycling of nutrients and their release to GW and SW resources.

Nitrogen isotopes ( $\delta^{15}\text{N}$ ) have been used to shed light on sources of N (Kendall *et al.* 2007), and are used here in combination with oxygen isotopes ( $\delta^{18}\text{O}$ ) of nitrate to draw inferences on the fate of N inputs in the form of inorganic fertilizer, manure and soil organic matter (SOM) sources during the non-growing period following harvest of a potato crop.

For the purposes of this discussion we consider the overall soil organic pool to comprise the sum of humic material, crop residues and associated microbiological community. Previously, we have documented the importance of nitrification of soil organic matter in mediating the transfer of N from agricultural lands to GW in the Wilmot watershed in Prince Edward Island Canada, a region dominated by intensive potato production and fertilizer use. Similar work has also been conducted in the Earncliffe region of the Province (Somers & Savard 2009), characterized by intensive livestock and associated forage crop production, and while representing significantly different production systems, results again highlight the importance of mineralization and nitrification of SOM in mediating N cycling.

Potato production is of particular interest in eastern Canada because of its association with high inorganic fertilizer inputs and poor N use efficiency. Growing season N fluxes were marginally dominated by leaching of inorganic fertilizer, but non-growing season contributions were

derived primarily from the nitrification of soil organic matter (Savard *et al.* 2007, 2009). Non-growing season N fluxes were estimated to account for as much as three quarters of the total annual N load to GW (Somers & Savard 2009), suggesting a significant portion of the annual flux of N to GW is controlled by factors affecting the rate of mineralization and nitrification in the overall SOM pool during the non growing season, rather than on initial N source characteristics or application rates alone.

Data from Agriculture and Agri-Food Canada's Harrington Experimental Farm demonstrate that N losses from typical potato production systems are highest following potato harvest compared with cereal and forage crop portions of the rotation (MacLeod *et al.* 2002). Here results for  $\delta^{15}\text{N}$  in soils and nitrate isotopes ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) in tile drain effluents from experimental plots with varying N sources and application rates are used to shed light on the fate of residual N left in the soil following harvest of a potato crop. Our aim is to provide insight into the processes controlling N losses to GW that will support the on-going development of effective remediation strategies within the Province and for similar settings under temperate climate conditions.

## BACKGROUND

The study takes place in the Province of Prince Edward Island, situated at latitude 46°N/longitude 63°W in the Gulf of St. Lawrence, eastern Canada. The Province relies entirely on GW supplied from a series of unconfined, fractured sandstone aquifers as a source of potable water. The Province has gently rolling topography, a humid-continental climate, and 46% of its overall land mass of 5,656 km<sup>2</sup> is devoted to agriculture. Elevated GW nitrate levels are a growing concern for drinking water, and also with respect to the role the discharge of nitrate-rich GW plays in nutrient loading to small but ecologically and economically important estuaries. It has been suggested that a reduction in N losses of as much as 50% may be required to reduce groundwater nitrate concentrations to acceptable levels in some areas of the Province (Paradis *et al.* 2007; Jiang & Somers 2009).

## METHODS

Stable isotope characteristics ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in soil water, and  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in soil-water nitrate,) were determined for samples of agricultural tile drain effluents collected from three experimental plots following a potato crop at the

Harrington Experimental Farm of Agriculture Canada, located 11 km north of the capital city of Charlottetown. The plots are equipped with tile drains and have been in consistent rotations of potatoes-barley-red clover since 1995. The specific design and set-up of these experimental tile-drain plots have been described in detail by Milburn & MacLeod (1991). In the current work, we focus on the non-growing season period of 2007–2008, following harvest of a potato crop. Potatoes were harvested on October 23, 2007 and the succeeding barley crop was planted and fertilized (51 kg/ha N) on June 9, 2008. Treatments include fertilizer application of 300 kg/ha N as ammonium nitrate, liquid hog manure at a rate of 200 kg/ha N and a check plot with no added N. In addition,  $\delta^{15}\text{N}$  in soils from each plot were determined to characterize the isotopic characteristics of the local soil organic matter pool. Relative N source proportions for each plot were estimated using the same approach described by Savard *et al.* (2010) for previous watershed scale studies.

Fifteen grab samples of drainage water were collected directly from tile drain outlets during five sampling events over the period of November 20, 2007 to June 23, 2008. Samples were kept cool until delivery to the laboratory, filtered, and aliquots for nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  analyses immediately frozen. Soil samples were collected on January 17, 2008 at three points in each plot (total of 18 samples) at depths of 10–15 cm and 20–25 cm, mid-way and at the bottom of the ploughing depth respectively. Samples were collected directly from auger flights and placed in zip-lock bags, and immediately frozen prior to transport to the laboratory for analysis.

Nitrate concentrations in tile drain samples were determined at the PEI Analytic Laboratories by quantitatively reducing nitrate to nitrite by passage of the sample through a copper cadmium column and reduced nitrate plus original nitrite then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride (NED). The resulting water soluble dye was measured by colorimetry at 520 nm, using a Quickchem 8000 Flow Injection Analyzer. Precision for nitrate concentration is 7%.

Isotopic analyses included  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in water,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in nitrate dissolved in water and  $\delta^{15}\text{N}$  in soil samples. Analyses were performed by the Delta-Lab of the Geological Survey of Canada (Québec). The preparation for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  analyses of  $\text{NO}_3^-$  is performed following ion-exchange resin extraction and silver-nitrate precipitation as described in Savard *et al.* (2007). Silver nitrate sub-samples are placed in silver capsules then processed using an Elemental Analyzer on-line with a gas-source Isotope Ratio Mass Spectrometer (GS-IRMS) for the analyses of  $\delta^{15}\text{N}$  values,

and a pyrolysis system connected to a GS-IRMS for the  $\delta^{18}\text{O}$  analysis. Average precisions obtained on sample replicates are 0.1‰ for  $\delta^{15}\text{N}$ , and 0.2‰ for  $\delta^{18}\text{O}$  values.

## RESULTS AND INTERPRETATION

The current focus is on results of stable isotope analyses, but it is noted that nitrate concentrations for the fertilizer and check plot samples were very similar throughout the sampling period, while manure plot results showed generally higher concentrations. The significance of the relationship between N application rates and N leaching losses is examined briefly in the discussion.

The  $\delta^{15}\text{N}$  values for dissolved nitrate in soil water from the fertilizer plot and check plot are essentially the same throughout the entire period of sampling in spite of significant differences in initial N source characteristics and application rates, averaging +4.7‰ (Figure 1(a)) and generally falling close to values for soil samples from the same plots (mean of +4.0‰, range of +3.5 to +4.5). We interpret this to imply that by the time of harvest, most N remaining in the soil profile associated with the fertilizer application has been immobilized in the SOM pool, to be subsequently released by mineralization and nitrification of this organically bound N, explaining the similarity of tile drain effluent and soil  $\delta^{15}\text{N}$  signatures. In contrast  $\delta^{15}\text{N}$  results for the manure plot are more enriched throughout most of

the sampling period, and are consistent with a slower rate of break-down and N release from the original manure source. Although the last round of sampling was conducted 14 days after planting and fertilization of the succeeding barley crop,  $\delta^{15}\text{N}$  characteristics of nitrate from all plots still fall in the range expected from an SOM source, and do not yet appear to reflect the influence of inorganic fertilizer applied to the succeeding barley crop (Figure 1).

Oxygen isotopes of nitrate in effluents from all the plots display somewhat distinctive characteristics until late spring (Figure 1(b)), when they converge to values near  $-1.0$ ‰. The  $\delta^{18}\text{O}$  value in nitrate is determined in part by original source characteristics, and in part by its subsequent history. For nitrate produced by the nitrification of soil organic matter,  $\delta^{18}\text{O}$  ratios reflect O contributions of approximately 1/3 and 2/3 from the atmosphere and soil water, respectively (Kendall & Aravena 2000; Snider *et al.* 2010). For ammonium nitrate fertilizer, both the original signature inherited from the manufacturing process and nitrification of the ammonium component will determine  $\delta^{18}\text{O}$  characteristics, whereas manure  $\delta^{18}\text{O}$  ratios can be expected to reflect initial values characteristic of manure, modified by nitrification of ammonium and volatilization (Kendall & Aravena 2000). We suggest that the lower  $\delta^{18}\text{O}$  ratios observed in the fertilizer plot relative to the check plot represent remnants of residual fertilizer that has incorporated relatively depleted  $\delta^{18}\text{O}$  from soil water during nitrification of the ammonium component in late spring, shortly after

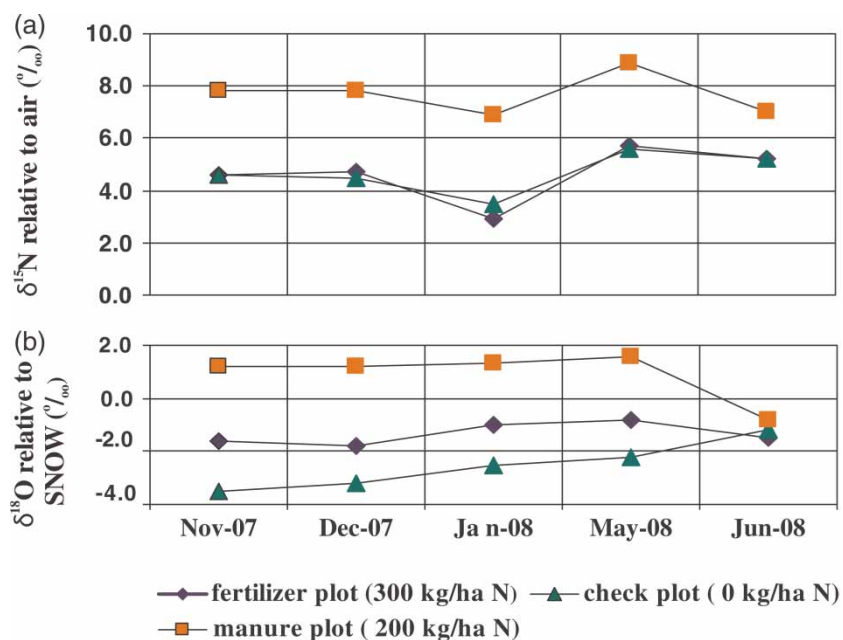


Figure 1 | Nitrate  $\delta^{15}\text{N}$  (a), and  $\delta^{18}\text{O}$  values (b) for tile-drain effluents (soil water) following potato harvest from the Harrington Experimental Farm.

application. The enriched  $\delta^{18}\text{O}$  values for the manure plot relative to the check plot are interpreted to reflect the initially high  $\delta^{18}\text{O}$  values characteristic of organic sources, modified by the gradual nitrification of the ammonia and more refractory components over the growing season, with incorporation during the summer of soil water O relatively enriched  $^{18}\text{O}$ .

To shed further light on the relative contribution of different sources to the non-growing season flux of nitrate observed for each of the test plots, we use the same source apportionment model described by Savard *et al.* (2010). Using the isotopic characteristics of key N sources (inorganic fertilizer, manure and SOM), and isotopic values for nitrate from tile drain effluents in a system of 3 unknown variables and 3 equations (Equations (1–3)), we estimate the proportions of nitrate derived from these discrete N sources. A constant contribution of 5% from atmospheric deposition of N is assumed, based on Environment Canada data and mass balance calculations (Somers *et al.* 2007), thus N proportions from the three main sources are calculated to total 95%.

$$1 = F_{\text{pr}} + F_{\text{m}} + F_{\text{cf}} \quad (1)$$

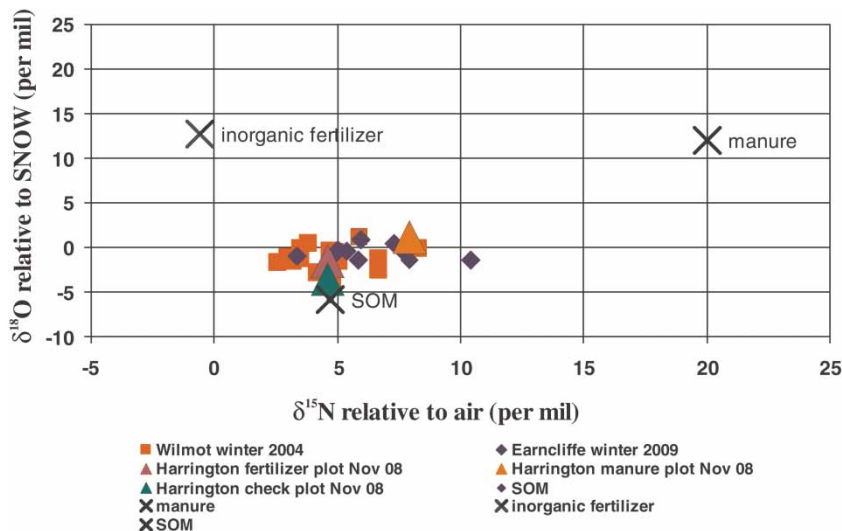
$$\delta^{18}\text{O}_{\text{mea}} = F_{\text{som}} \times \delta^{18}\text{O}_{\text{pr}} + F_{\text{m}} \times \delta^{18}\text{O}_{\text{m}} + F_{\text{cf}} \times \delta^{18}\text{O}_{\text{cf}} \quad (2)$$

$$\delta^{15}\text{N}_{\text{mea}} = F_{\text{som}} \times \delta^{15}\text{N}_{\text{pr}} + F_{\text{m}} \times \delta^{15}\text{N}_{\text{m}} + F_{\text{cf}} \times \delta^{15}\text{N}_{\text{cf}} \quad (3)$$

where F stands for fractions of nitrate from the 3 sources identified with the subscripts som, m and cf for soil organic

matter, manures and chemical fertilizers, respectively. To represent conditions immediately after harvest we use observed  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values in nitrate from the first sampling event in November of 2008. In assigning isotopic characteristics for the source end-members, we use measured values for liquid-hog manure and chemical fertilizer (ammonium nitrate) modified according to the considerations noted above regarding nitrification of the ammonium component and soil organic matter characteristics are based on GW sample results for a watershed essentially devoid of agricultural or development activity (see Figure 2). The results of the calculations suggest that only 7% of the observed non-growing season flux of nitrate observed in tile drain water from the fertilizer plot can be attributed to leaching of unmodified chemical fertilizers, with 85% being derived from nitrification of N mineralized from the SOM pool and 3% from organic sources. For the manure plot, organic sources constitute 25% of the N load, compared with 69% from SOM sources, and for the check plot, 93% of N is from SOM sources, the remainder being attributed to atmospheric deposition and trace amounts of chemical fertilizers.

These estimated source contributions clearly demonstrate the importance of nitrification of soil organic material as the dominant process contributing to non-growing season fluxes of N to GW following harvest of a potato crop, regardless of initial N source or application rate. While the results of the fertilizer plot suggest some residual fertilizer is left in the soil profile after harvest, the majority, even from this heavily fertilized plot appears to have been assimilated into the overall SOM pool, and subsequently released through nitrification from this temporary N reservoir. Similar conclusions are



**Figure 2** | Non-growing season nitrate isotopes for Wilmot and Earncliffe GW samples and Harrington Farm soil water (tile drain effluent). Shown for reference are the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values used in the source apportionment calculations for the tile drain effluents.

drawn for the manure plot, however it is evident that the rate of degradation of this source is somewhat slower than that of inorganic fertilizers, and a higher proportion of residual manure N is left in the soil profile after harvest.

## DISCUSSION

The results of the current study suggest that the principle contribution of nitrate leaching to GW during the non-growing season following a potato harvest under typical production practices in PEI can be attributed to the nitrification of SOM. This interpretation is consistent with previous observations from watershed-scale stable isotope studies conducted in the Wilmot intensive row-crop setting with extensive inorganic fertilizer application associated primarily with potato production systems (Savard *et al.* 2007, 2010) and for the Earncliffe Peninsula characterized by intensive livestock and associated forage crop production (Somers & Savard 2009). The  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  results for nitrate in GW in non-growing season samples from each watershed, and for the Harrington Farm tile drain effluents show similar average values (Figure 2). In the Wilmot row-crop setting, while growing season N fluxes are marginally dominated by direct leaching of inorganic fertilizers (Savard *et al.* 2010), on average, non growing seasons fluxes are dominated by nitrate derived from the nitrification of SOM (76%) with direct leaching of inorganic fertilizers accounting for only 13% of the observed N load (Figure 2). In the current work on an experimental field plot scale, we again observe small remnant portions of nitrate attributable to leaching of unmodified inorganic fertilizer during the non-growing season for the fertilizer plot, but the majority of N losses again appear to reflect the process of nitrification of SOM. In the Earncliffe-livestock setting with extensive manure use, only slight seasonal variations in isotopic values of nitrate are observed, and on average N fluxes were dominated year round by the products of nitrification of SOM (74 to 76%), with only 15% attributed to the direct influence of organic sources. Comparison between the experimental tile-drain manure plot and the Earncliffe livestock setting is more difficult because the crops and cropping practices are considerably different, but nonetheless, we infer that in either case, the magnitude of leaching of unmodified manures is limited, and the dominant process responsible for the loss of N to GW again is nitrification of SOM.

Collectively, these observations support the premise that regardless of the initial source, the majority of N not taken up by crops, or leached from the soil profile during the growing

season is incorporated into the broader SOM pool, to be subsequently released during the non-growing season by mineralization and nitrification of N temporarily 'stored' in this reservoir, either as crop residual material or the associated microbial biomass. These conclusions are consistent with those of other researchers. Maly *et al.* (2002) for instance attribute increased N mineralization rates in spring and late summer and fall (relative to main growing season) among other factors, to the availability of post-harvest residues, and suggest only a short-term response of mineralization to N application rates after fertilization. Given these considerations, it is important to think about the factors that control the rate of nitrification during this period, in developing strategies to reduce these non-growing season N losses.

We have previously estimated that non-growing season N losses in Wilmot watershed represent as much as three quarters of overall annual N losses (Somers & Savard 2009). Here, by combining mean nitrate concentrations in tile drain effluents, GW recharge estimated following the approach of Healy & Cook (2002), and the proportions derived from our source apportionment model, we estimate that non-growing season N losses following a potato crop related to mineralization and nitrification of SOM to be approximately 13 and 15 kg/ha for the fertilizer and check plots, respectively. The same considerations applied to the Wilmot watershed where all crops in the rotation are represented, suggest that non-growing season N losses of approximately 10 kg/ha can be attributed to the same processes. Putting this in perspective, this flux represent roughly a third of independent estimates for total annual N losses for the Wilmot watershed, which range from 30.2 kg/ha (van Bochove *et al.* 2007) to 34.6 kg/ha (Jiang & Somers 2007). Thus it is apparent that under temperate climatic conditions, especially during periods where there is little plant uptake and weather conditions are favourable for significant GW recharge, nitrification of SOM may represent a highly significant proportion of total annual N leaching losses. Furthermore, climate change is expected to result in warmer winter-soil temperatures and potentially more frequent winter recharge events, thus consideration of these processes might play an increasingly critical role in the mitigation of N losses to GW.

As the dominant controls on the rate of nitrification of SOM depend on a broad range of factors, it follows that there is a need to expand the scope of efforts to control N leaching to include those elements of natural soil processes where we can effectively intervene to reduce these losses. Nutrient management has been widely promoted as a strategy to reduce leaching losses to GW, and typically focuses on matching N delivery to crop needs with the



general premise that reducing fertilizer application rates will result in reduced nitrate leaching. Non-growing season nitrate concentrations observed in this study display little difference between fertilized and unfertilized plots. Unpublished daily data from the full suite of 12 plots at the research facility display significant variation in nitrate concentrations over short periods of time and between replicates, however on average support a positive correlation between initial N input rates and non-growing season nitrate concentrations in tile drain effluents (Yefang Jiang, personal communication 2011). Given the isotopic evidence implying that most of the non-growing season N flux is derived from nitrification of SOM, it is suggested that the response in non-growing season nitrate leaching concentrations to initial N application rates during this period is largely a function of increased plant bio-mass and the resulting increased availability of plant residues in the post harvest soil profile.

Important elements in controlling N losses from the SOM pool during the vulnerable period of limited plant uptake could include such measures as avoiding application of N close to the end of the growing season, maintaining as much N as possible in living plant tissue, or reducing activities that promote mineralization and nitrification during this period. Thus for slow-release N sources, such as manures, it may be important to ensure that application is limited to periods where there is sufficient time for significant plant uptake. Similarly, the planting of cover crops at an early enough stage to sequester a significant portion of residual soil N in living plant tissue may reduce over winter N leaching losses. Tillage practices and their role in the nitrogen cycling including stimulation of mineralization and nitrification are noted by a number of authors (Martens 2001; Sharifi *et al.* 2008). Sanderson & MacLeod (2002) have demonstrated reductions in N-leaching losses by delaying the timing of tillage of forage crops within typical potato rotations from early to late fall. Given the evidence for active nitrification throughout the winter and spring (Savard *et al.* 2007), we suggest that where possible, delaying of the timing of tillage until spring, immediately prior to the growing season would further reduce non-growing season losses, as well as reducing fertilizer requirements during the subsequent growing season.

## CONCLUSIONS

Our stable isotope data suggest that regardless of initial N sources, the nitrification of crop residues plays a critical

role in the cycling of N in various agricultural settings. While nitrogen applied in excess of crop requirements may result in undesirable leaching of nitrate to GW during the growing season, a significant proportion of this excess nitrogen appears to be rapidly incorporated into plant residual material or other components of SOM, where its subsequent rate of release during the non-growing season is controlled by a variety of factors including cropping practices, and weather and hydrologic conditions.

Assessing the quantitative impact of possible changes to current agricultural practices on a reduction of N losses holds significant uncertainties. Nonetheless, from a qualitative perspective, it is clear that both the timing of N inputs and the agricultural practices which influence nitrification of SOM, especially during the vulnerable non-growing season are worthy of further exploration. We suggested that measures such as delaying ploughing from fall until spring, with the aim of leaving more N from crop residues immobilized in the winter SOM pool, would result in its release at an optimum time to meet subsequent crop needs and reduce pre-planting fertilizer requirements. Similarly, the application of manures early enough in the fall to allow for uptake by cover crops, or delaying application until spring when N can be more effectively used by subsequent crops could also be expected to reduce non-growing season losses. Thus while traditional management of N inputs on agricultural lands are an important part element in controlling N losses to GW, we believe significant benefits can be obtained by including broader considerations related to the overall role of natural soil processes in minimizing adverse impacts associated with agricultural activity on GW and SW resources.

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