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Nitrate contamination of groundwater: Measurement and prediction

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Abstract

Agriculture makes a significant contribution to the diffuse source contamination of surface and groundwater resources, particularly contributing to the NO_3^- contamination of groundwater. Two approaches were adopted to evaluate management practices (within the context of the whole farming system) for their impacts on the environment : (1) measurement of the quality of groundwater under different farming systems, and (2) comparison of predictions of the impact of farming systems on water quality, obtained using whole farm N budgets, with measured values.

The Ontario Farm Groundwater Quality Survey evaluated the rural groundwater quality in Ontario, with respect to common contaminants including NO_3^-. Approximately 1300 domestic farm wells were sampled, and wells were drilled in some fields of farms involved in the study. NO_3^- was present at concentrations above the maximum acceptable for drinking water (10 mg N l^{-1}) in 14% of wells, including 7% of wells that also had unacceptable concentrations of coliform bacteria. Significant levels of NO_3^- contamination were observed under most agricultural land use practices investigated.

Calculation of N budgets was simplified by assuming that there was no net change in the N content of farm assets. The N inputs to agricultural systems considered were: purchases from off-farm suppliers, N_2 fixation and atmospheric deposition. Symbiotic N_2 fixation was estimated from empirical relationships between crop yield and N_2 fixed. The N outputs were in sales of plant and animal produce, gaseous and leaching losses. Gaseous loss was assumed to result only from volatilization of ammonia, estimated to be 39% of total manure N.

We have identified one cash crop farming system where there was a true balance. The rotation included corn soybeans and wheat, with two years of soybean always being grown before corn. Many livestock farms, including two organic farms, gave large imbalances of N which might indicate that these operations were not in equilibrium.

The relationship between measured and predicted values of NO_3^--N expected in the groundwater under the different management systems showed that the simplified N budget overestimated the NO_3^--N concentration by about one third. However, the budget approach appeared to identify farms where contamination was likely even if the actual amount was over estimated. Simplified budgets could therefore be used to compare the potential of different farming systems for causing environmental contamination.

Introduction

There is increasing awareness that water resources are vulnerable to contamination from point and diffuse sources within agricultural watersheds (Byrnes, 1990; Follett and Walker, 1989). In industrial areas much emphasis has been placed on preventing point source contamination from manufacturing sites. However, diffuse source contamination can be much more difficult to deal with. Agricultural activity is recognised as making a significant contribution to diffuse source contamination of surface and groundwater resources (Addiscott *et al.*, 1991). In particular, agriculture is considered to be the major contributor to the NO_3^- contamination of groundwater (Juergens-Gschwind, 1989; Power and Schepers, 1989).

Much effort has been aimed at optimizing application rates of manures and mineral fertilizers to meet crop yield goals. The current goal is to provide sufficient food and to protect water quality. This requires the evaluation of management practices within the context of the whole farming system, and assessment of impact on the environment. One way to study the effectiveness of current practices is to measure the quality of groundwater under different farming systems. Another approach is to compare predictions of the impact of farming systems on water quality, obtained from empirical or mechanistic stimulation, with measured values. Limitations in our understanding of soil and plant processes can then be identified, and possibilities for extending recommendations on fertilizer practices to other soils and climates can be increased. Where agriculture has resulted in contamination, new practices need to be developed or existing systems modified to improve water quality. A potentially useful method for predicting losses of NO_3^- from agriculture to groundwater is to calculate the N balance for a whole farm, taking account of animals and crops. Excess N in the farming system can be equated with losses to the environment. Causes of excess nutrients can be identified by the sensitivity of the balance to different aspects of management.

This paper considers the use of a groundwater survey and a simplified N budget for estimating the impact of agriculture on the contamination of water resources with NO_3^-, including an assessment for farms where organic manures only were used.

Methods

Measurement of NO_3^- contamination

In 1991–92, the Federal Government of Canada, commissioned a major survey of groundwater quality in Ontario "The Ontario Farm Groundwater Quality Survey" (Rudolph and Goss, 1993). The aim was to evaluate the rural groundwater quality in Ontario at a provincial scale. This was approached through two separate sampling programmes of approximately 1300 domestic farm wells. Wells were tested for NO_3^-, several common herbicides, and for total and faecal coliform bacteria. In addition a limited number of monitoring wells were specially installed in fields, and were sampled for the same contaminants. The participating farm families also completed questionnaires about the practices and activities carried out in the vicinity of the well, and on the land-use management. This multifaceted approach allowed the impact of farming practices on drinking water quality to be studied.

On a number of other farms, solution samplers were used to sample the water draining from the rooting zone in fields representative of the rotation. The samplers, were installed at an angle of 45° to a depth of 0.8 m. Each sampler consisted of a porous ceramic cup, 50 mm long × 20 mm OD, attached to a length of PVC pipe. Two pieces of narrow-bore nylon tubing were sealed into the porous cup, one to apply a pressure of −80 kPa and draw water into the cup, the other for collecting the sample using a replaceable evacuated tube sealed with a septum. Attempts were made to collect samples in spring and fall following major rainfall events.

Prediction of NO_3^- contamination

The basic relationships for the N budget of a farm can be summarized as:

N in inputs = N in output + change in the N contents of the soil, livestock and other components

Calculation of an N budget can be simplified by assuming that there is no net change in the N content of farm assets. Thus for an arable farm it is assumed that soil organic matter content, and consequently soil N content, remain constant on a yearly basis for monoculture systems or over the course of a rotation when a sequence of crops are grown (Fried *et al.*, 1976). For a livestock operation it is assumed further that the number of animals and their demography remain constant.

Components of a simplified N budget

The main components of the N inputs to agricultural systems are derived from purchases from off-farm suppliers (e.g. animals, seed, fertilizers and feed), and from natural processes that occur during the growth of crops (e.g. symbiotic N_2 fixation) or from natural processes that are influenced by anthropogenic activity (e.g. atmospheric deposition).

Fertilizer inputs were obtained from farmer records. N contents of animal manures were taken from published tables (Fraser, 1985), as were the N content of seeds used in crop production (McBride, 1987). Feed contents were determined in the same way. The N in animals bought in were estimated from average weights of cattle, pigs or poultry typically purchased for fattening, breeding or milking, and assuming typical values for protein content (Ensminger and Olentine, 1978).

Natural inputs through symbiotic N_2 fixation were estimated from empirical relationships between crop yields and N_2 fixed (Barry *et al.*, 1993).

A single value of 18.4 kg N ha^{-1} was used for atmospheric deposition (Barry *et al.*, 1993).

The main outputs of N from agricultural systems are in the form of direct sales of plant and animal materials, and from gaseous and leaching losses. Sales were calculated from the crude protein content or N concentration of materials, and the weight of the material. Gaseous loss was assumed to result only from volatilization of ammonia, estimated to be 39% of total manure N (Barry *et al.*, 1993).

The excess N on the farm at the end of a crop cycle was assumed to be susceptible to leaching in the total through drainage. This was estimated to average 160 mm in Ontario (Barry *et al.*, 1993). The concentration of NO_3^--N predicted was compared with that in the drinking water well, in the water collected from the well installed during the groundwater quality survey, or in the water collected from the solution samplers.

Field investigations of variables used in the simplified N budgets

A number of the values used in calculating the N budgets have not been validated. They were best estimates based on information obtained from the literature. A full validation of individual values would require considerable investment in resources, but check measurements were carried out on a number of farms.

Atmospheric deposition

Wet deposition of N was calculated using the monthly precipitation and the average concentration of NH_4^+ and NO_3^- in the rainwater. On three farms, rainfall was collected in plastic-wedge-style rain gauges over the period 1st May to 1st October 1992. The rainwater was transferred to 1 l amber, high density polyethylene bottles for storage in a refrigerator until collected for analysis at the end of each month. Determination of the N concentration in precipitation was restricted to the summer months because the rain gauges and collection bottles were unsuitable for winter conditions, or for snow collection.

Bulk deposition of N was collected for the months of August and September for two of the farms, and for September only in the case of the third farm. Samples were collected using Teflon macrofiltration screen material, mesh size 150 μm, secured over the top of a polypropylene funnel of 180 mm diameter that was connected to a glass bottle. The screen was used to trap any deposition of aerosol particles or particulate matter that settled by gravity. It also prevented the entry of insects into the bottle. At the end of each month, the inner sides of the funnel and the teflon mesh were washed with deionised water, and the total volume of water, rainwater and wash water, in the collection bottle was recorded. A subsample of this water was taken back to the laboratory for analysis. Only on one farm did the N measured in bulk deposition exceed that in the rain gauge. On a further eight farms, rainwater was collected for the months of May and August in gauges considered to be large enough to act as bulk deposition samplers.

The ammoniacal and NO_3^- components of all the water samples collected were determined simultaneously using a TRAACS-800 autoanalyzer (Tel and Heseltine, 1990).

Ammonia volatilization from spread manure

The technique of Schjoerring *et al.* (1992) was adapted to estimate the amount of NH_3 volatilized from surface applied composted liquid dairy cattle manure (CLCM). Passive flux samplers were used to measure the concentration of NH_3 in the air flowing from the source to the surroundings, and vice versa. Each sampler consisted of two glass tubes, 100 mm in length and 7 mm ID, connected by a small piece of silicon tubing. The inner surface of the tubes were coated with oxalic acid. A stainless steel disc, 0.5 mm in thickness and with a 1 mm diameter hole drilled in the centre, was glued to the end of one of the two tubes. The stainless steel disc acted to decrease the air speed inside the tubes in order to achieve a low friction resistance and a high NH_3 collection efficiency. The experimental area was a circular plot of radius 15 m (area 707 m^2) in a cultivated field on a dairy farm. CLCM equivalent to 45,000 l ha^{-1} (140 kg total N ha^{-1} and 45 kg NH_4^+-N ha^{-1}) was applied to the plot by broadcasting to one side of a tractor-drawn, top-loading tank spreader. Masts were quickly erected at right angles to each other on the circumference of the plot. Pairs of samplers, one with the steel disc directed towards the centre, the other with the disc away from the plot, were mounted at heights of 0.50, 1.0, 1.5 and 2.0 m on each mast. At the end of 20 hours exposure the flux samplers were taken down from the masts and closed immediately with parafilm.

Samples of the CLCM were taken from the tanker for analysis of total Kjeldahl N, NH_4^+-N, NO_3^--N and dry matter content. The oxalic acid coating was washed from the passive sampler tubes using deionised water, and the NH_4^+-N determined (Tel and Goorahoo, 1993).

N_2 fixation by soybeans

Soybeans (*Glycine max* cv. Maple Donovan) were grown on three fields of one farm in 1992. The seeds were inoculated with *Bradyrhizobium japonicum* strain 532C prior to sowing in rows 18 cm apart at 108 kg ha^{-1}. Microplots 2 × 2 m were sown with the non-nodulating variety 'Evans' at the same density. Yield of the nodulating crop was assessed on two randomly selected plots 1 × 1 m, and yield of the non-nodulating variety was determined in the 2 × 2 m microplots. The above ground portions of the plants were sampled, and the pods were separated and hulled to obtain the grain. In addition, the above-ground portion and the roots of four plants were collected from each plot. The roots were washed under running tap water to remove adhering soil, and then examined for the presence of pink nodules. The plants were dried at 60 °C, ground and analyzed for N content. The grain yield from each plot was calculated at a moisture content of 14%.

The amount of N_2 fixed by soybeans on each field was determined from the difference in the N content between nodulating and non-nodulating soybeans.

Results

The general quality of rural groundwater

A key finding of the Ontario Farm Groundwater Quality Survey (Rudolph and Goss, 1993) was that NO_3^- in excess of the maximum acceptable concentration (10 mg N l^{-1}) was found in 14% of wells (Table 1), including 7% of wells that also had unacceptable concentrations of coliform bacteria.

Water quality and cropping systems

Farms with clearly identifiable cropping or grazing systems were divided into different land use classes. About 20 per cent of wells in each major class contained NO_3^- in excess of 10 mg N l^{-1} (Table 1).

Table 1. Number of water wells that exceeded 10 mg nitrate-N l^{-1} for farms in Ontario using various cropping systems (Rudolph and Goss, 1993)

Land use	Wells tested (no.)	Exceeds Ontario objective (%)
>90% row crop	183	12.8 ± 5.0[a]
30–90% row crop	385	15.7 ± 3.7
>85% small grains	28	5.4 ± 8.4
>50% hay	158	8.3 ± 4.4
>50% pasture	78	12.9 ± 7.6
Berries	6	16.7 ± 15.2
Field vegetables	18	30.6 ± 21.6

[a] ± 95% confidence interval.

There were no significant differences between classes as diverse as row cropping (continuous cropping with row crops such as soybeans and maize), grain cropping (turf and small grain production) and berry cropping (soft fruit production) (Rudolph and Goss, 1993).

Simplified N budgets

Validation of literature values

Atmospheric deposition

The atmospheric deposition of N determined from bulk samplers ranged between 11.1 and 46 kg N ha^{-1}, and the average value was 18.4 kg N ha^{-1}. As nitric oxide deposition was not likely to have been captured, these values were likely to have been about 3 kg N ha^{-1} less than that actually adding to the local N burden (Ro *et al.*, 1988). Nonetheless, given the range of values the results give good support to the average value of 18.4 kg N ha^{-1} estimated from the literature (Barry *et al.*, 1993).

Ammonia volatilization from spread manure

The horizontal net flux of NH_3 from the plot treated with composted liquid cattle manure, decreased with height (Fig. 1), and could be represented by the following quadratic equation:

$$\sum F_h = 0.019z^2 - 9.22z - 105.4$$

where F_h is the horizontal flux and z is height in metres.

The vertical net flux of NH_3 from the experimental plot was calculated as 29.10 μg NH_3-N $m^{-2}s^{-1}$ or

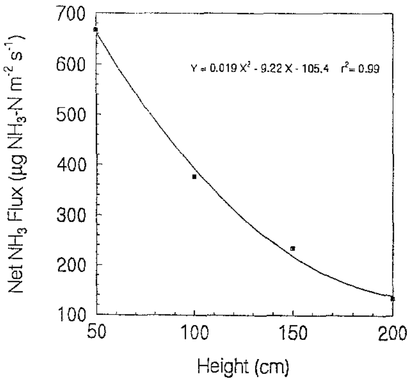

Fig. 1. Relation between net horizontal flux of NH_4 from composted liquid cattle manure and height above the soil surface.

1.05 kg NH_3-N $ha^{-1}h^{-1}$. The NH_3 volatilized was therefore 21 kg NH_3-N ha^{-1} over the 20 hour period. This amount would represent 15% of the total N and 46% of the ammoniacal N applied.

The vertical net flux of 1.05 kg NH_3-N $ha^{-1}h^{-1}$ is comparable to maximum fluxes during a general diurnal pattern observed by Beauchamp *et al.* (1982). In that study, the maximum ammonia volatilization from liquid dairy cattle manure occurred after midday at times corresponding to maximum daily temperatures.

The 46% loss of applied ammoniacal N determined in this study lies within the wide range of volatilization losses reported for various manures (Gordon *et al.*, 1988; Lauer *et al.*, 1976; Thompson *et al.*, 1990). This loss over 20 hours after application is higher than the 24–33% reported by Beauchamp et al. (1982), and the 44–60% reported by Thompson *et al.* (1990), for losses that occurred within six days of application. However, losses as high as 62% of NH_4^+-N in pig or cattle slurry have been observed, in which 24–39% of the total NH_4^+-N loss occurred during the first hour following application and up to 85% within 12 hours (Pain *et al.*, 1989).

Losses of N from manure in animal housing and during storage appear to be less influenced by management practices than losses during application. For farms in Ontario, the loss from manure during collection and storage (liquid or solid) was about 28% of total N excreted (Beauchamp and Burton, 1985). Similar losses have been measured when manure was composted (Kirchmann, 1985). The loss measured in the field was therefore consistent with an average loss of N from manure, totalling 39% of excreted N over the period of excretion to plant utilization.

N_2 fixation by soybeans

The average soybean yields obtained for the three fields were 0.85, 1.33 and 1.55 t ha^{-1} were appreciably less than the 1987–1990 average of 2.3 t ha^{-1} for the farm because adverse weather conditions, particularly the cool temperature, delayed crop maturation. The cumulative crop heat units (an index based on day and night air temperatures, and the relationship between development rate and temperature for warm season crops Brown, 1985) recorded between May and October, 1992 were 93511-350 less than average (K. Reid, 1993, Ontario Ministry Agric Food, pers. comm.).

The average N_2 fixed was 94 kg N ha^{-1}, and ranged from 53 to 108 kg N ha^{-1}. These values could be underestimations of the actual amount of N_2 fixed because fallen leaves were not collected. The values obtained might also have been less than average because of the weather in 1992.

This value of N_2 fixation by soybeans was somewhat less than the 108 to 151 kg N ha^{-1} reported from other field experiments with the same variety conducted in Ontario from 1988 to 1989 (Ravuri, 1992). The amount of N_2 fixed by soybean showed no correlation with grain yield (Fig. 2). The soybeans had not reached physiological maturity when the plants were harvested in December 1992, and the harvest index was likely to be considerably smaller than normal. As N_2 fixation in soybean is virtually completed by the pod filling stage (Deibert *et al.*, 1979), this would account for the measured values being much greater than expected from those predicted by the equation derived by Barry et al. (1993). The proposed method of prediction of N_2- fixation still requires validation. Nonetheless, for typical grain yields of soybeans in Ontario of about 2.5 t ha^{-1}, the predicted N_2-fixation is close to 100 kg N ha^{-1}, a value close to the mean reported here.

Excess N on farms in Ontario

The main assumption made in the simplified budgetary approach was that the farming practices had reached a state of equilibrium. An established orchard would be expected to be close to equilibrium, and hence be a good. test of the budgetary approach. Close agreement was found between the concentration of NO_3^- predicted to be in the groundwater under an apple orchard farm (13.5 mg N l^{-1}), and the value measured in the drinking water well (13. 6 mg N l^{-1}). (Goss *et al.*, 1993).

In many parts of southern Ontario the most common rotation is based on corn, soybeans and wheat.

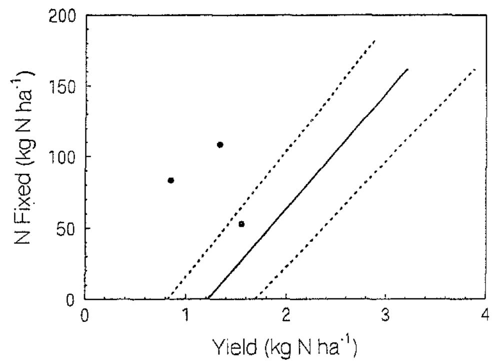

Fig. 2. Relationship between grain yield and the mass of the atmospheric nitrogen fixed by soybeans. The solid line is the regression used for predicting N fixation in the simplified N budget calculation, and the dotted lines indicate the associated 95% confidence intervals. The points are the values determined for three fields in 1992.

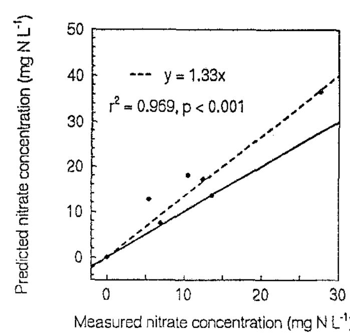

Fig. 3. Relationship between measured values of nitrate-N in or moving to groundwater, and values predicted using the simplified N budget for the farms in this study. The solid line is the 1:1 relationship, and the dotted line is the fitted regression.

The simplified N budget approach for farm 1 having this rotation indicated NO_3^- contamination would be approximately 7.5 mg N l^{-1} (Table 2). The concentration of NO_3^- in water from the solution samplers averaged over all the fields was 6.9 mg N l^{-1}.

A modification of this rotation was the introduction of a second year of soybeans immediately after the first. The N budget for a farm (farm 2) with this rotation showed almost a balance between inputs and outputs of N (Table 2). Under these conditions the simplified N budget approach indicated no measurable NO_3^- in the drainage water. The NO_3^- content of the farm well water was below the 0.2 mg N l^{-1} limit of detection (Table 2).

Even where mineral fertilizers constitute the main input of N, the predicted value is not always close to the measured value. On a tobacco farm (farm 3) the concentration of NO_3 predicted to be in the groundwater was 18.1 mg N l^{-1}, whereas the value measured in the well water was only 7.4 mg N l^{-1} (Table 2). However, rye was used as a cover crop to minimize soil erosion, and it is possible that this would affect the quality of the soil organic matter. If so this could influence the rate and timing of mineralization of organic matter.

Many livestock farms appear to give large imbalances of N which could be due to the fact that these operations were not in equilibrium. For example under a dairy farm (farm 4), the predicted concentration of NO_3^- in the groundwater was 36.6, whereas the value in the farm well was 10.1 mg N l^{-1}, but that in the monitoring well was 27.6 mg N l^{-1} (Table 2). In this case the farm well was probably sampling groundwater not connected to that under the worked land.

Inorganic N fertilizers were not used on any of the three farms where components of the simplified budget were tested. One was a cash crop farm (farm 5, Table 2). The prediction from the simplified budget was that there was an excess of N that would lead to NO_3^- moving to groundwater at a concentration of 13.7 mg N l^{-1} (Table 2). No solution samples could be extracted from the soil during the period of the study in 1992. The predicted excess of N for the dairy farm (farm 6) would have resulted in a concentration of 17.2 mg N l^{-1} in the groundwater. The measured value was 12.4 mg N l^{-1} (Table 2). The third farm was a hog farm (farm 7). Again an excess of N was predicted and this was expected to result in 12.7 mg N l^{-1} of soil solution, whereas the measured value was only 4.9 mg N l^{-1} (Table 2). Potential denitrification measured for the different fields on the hog farm averaged 14.5 kg N ha^{-1} y^{-1} (Goorahoo, 1993). When this value was included as an additional output in the budget (farm 7a, Table 2), the predicted value of NO_3^- moving to the groundwater was 3.6 mg N l^{-1} (Table 2).

The relationship between the measured and predicted values of NO_3^--N expected in the groundwater under these different management systems (Fig, 3) showed that on average the simplified N budget over-estimated the NO_3^- concentration by about one third.

Conclusions

The conclusion from the comparisons so far made suggests that the budgetary approach can predict contamination of groundwater with NO_3^- for farming systems that are close to equilibrium. Even in systems where there was poor agreement between the predict-

Table 2. Whole-farm nitrogen budgets for 7 farming systems in Ontario, Canada

	Farm							
	1	2	3	4	5	6	7	7a
Crop rotation (–) or Livestock system (.)	C-Sb-W[a]	W-Sb-Sb-C-Sb-Sb-C	Tb-R	Dairy C,O,Sb, Af	Organic cash-crop. C-O-Ws-Sb-O-B-H-H	Organic dairy H-H-H-Ws-C-mix grn-R for, H	Organic swine. Sb-W-mix grn-H-H-P	Organic swine Sb -Denit induded
N-inputs (kg N $ha^{-1}y^{-1}$)								
Seed	2.7	5.4	0.6	0.7	0.9	1.6	3.5	3.5
Feed	0	0	0	32.5	0	0.1	140.8	140.8
Fertilizer	66.3	50.2	37.4	79.0	0	0	0	0
Manure	0	0	0	22.0	0	0	0	0
Animals	0	0	0	0	0	0	1.4	1.4
N_2-fixation								
Non-symbiotic*	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Symbiotic	51.7	83.7	0	20.9	66.9	35.5	0	0
Atmosphere	18.4*	18.4*	18.4*	18.4*	17.0	45.3	26.0	26.0
TOTAL INPUTS (I_T)	**144.1**	**162.7**	**61.4**	**178.5**	**105.5**	**87.5**	**243.6**	**243.6**
N-outputs (kg N $ha^{-1}y^{-1}$)								
Plant produce	132.2	163.0	32.4	54.5	83.6	18.2	56.0	56.0
Animal produce	0	0	0	32.1	0	22.9	37.5	37.5
Manure	0	0	0	0	0	0	84.3	84.3
Volatilization	0	0	0	33.3	0	18.9	45.5	45.5
Denitrification	–	–	–	–	–	–	–	14.5
TOTAL OUTPUTS (O_T)	**132.2**	**163.0**	**32.4**	**119.9**	**83.6**	**60.0**	**223.3**	**237.8**
$I_T - O_T$(kg N $ha^{-1}y^{-1}$)	11.9	−0.3	29.0	58.6	21.9	27.5	20.3	5.8
Groundwater recharge (mm y^{-1})	160	160	160	160	160	160	160	160
N in leachate								
Predicted	7.4	0	10.1	36.6	13.7	17.2	12.7	3.6
Measured in well	–	<0.2	7.4	10.1	–	–	–	–
Measured in soil soln	6.9	–	–	27.6	–	12.4	4.9	4.9

[a]Af-alfalfa, B-barley, C-maize, H - alfafa and grass hay, mix grn - mixed grains (barley, oats and peas), O- oats, P - pasture, R - rye, Sb- soybeans, W-wheat, Ws - spelt.
*Values generally applicable in Southern Ontario as determined by Barry *et al.* (1993).

ed and measured concentration in the farm well, the approach has indicated that there will be contamination of groundwater even if the actual amount is over estimated. They can therefore be used to compare the potential of different farming systems to cause contamination of the environment. The survey approach did not serve to discriminate between different farming systems.

This simplified N-budget approach has been used to estimate the potential for N leaching from individual fields, whole farms or from small regions, primarily under intensive management. Many soils in the tropics receive little N-fertilizer, and this might be one reason why appropriate measurements are largely unavailable. Some of the farms investigated in this study had received no mineral-N fertilizer, and the approach was satisfactory for assessing these farming practices. For some regions in India and in Central and South America, fertilizer use is similar to that in some temperate regions, and leaching can be significant during the rainy season. Thus, there are good reasons for investigating the impact of the farming practices on the potability of groundwater. It is hoped that this paper will provide a stimulus for those working in the tropics to have regards for the quality of groundwater, and provide a guide for the study of agricultural practices in this regard.

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